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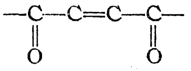
Bromonitrothiophene

BY V. S. BABASINIAN

Although iodonitrothiophene has been prepared by the earliest workers in the thiophene series,[1] the corresponding bromine compound has scarcely been mentioned in the literature.[2] After describing the nitration of iodothiophene, Kreis[1] (pp. 2073–2075) stated that due to difficulties encountered in the preparation of bromothiophene its nitration was not attempted.

At the present time the preparation of bromothiophene does not present insurmountable difficulties. Although the yield of the costly product is under the most favorable conditions barely over one-half of that required by theory, a number of convenient methods are available for its preparation.[3] The bromothiophene used in this investigation was prepared from thiophene and acetbromamide, the method of Steinkopf and Otto[3b] (p. 69) being employed with certain modifications.

The Nitration of Bromothiophene.—The nitration of negatively substituted thiophene derivatives has been possible in a number of instances with the usually employed nitric–sulfuric acid mixture.[4] Contrary to expectation, the presence of the strongly negative bromine atom in bromothiophene does not inhibit undesirable side reactions when the compound is treated with this nitrating mixture. Töhl and Schultz[5] have shown that concentrated sulfuric acid reacts very readily with bromothiophene at the ordinary temperature, converting it into dibromothiophene, dithienyl derivatives, and two isomeric sulfonic acids. Moreover, observations made in this Laboratory support the conclusion that the nitric acid in the nitrating mixture oxidizes a part of the bromothiophene into open chain decomposition products. With pure nitric acid the reaction proceeds with almost explosive violence, yielding a dark oil in which sulfuric acid may be identified. It may also be added that by the action of fuming nitric acid Angeli and Ciamician[6] have almost completely converted the more stable tetrabromothiophene into dibromomaleic anhydride and sulfuric acid; and the study of other brominated compounds in the thiophene series has led the authors to the conclusion that these halogen derivatives oxidize into products in which the atomic grouping  $-\underset{\underset{\displaystyle O}{\|}}{C}-C{=}C-\underset{\underset{\displaystyle O}{\|}}{C}-$ may in general be recognized[6b] (p. 1347).

It is clear that while the presence of bromine tends to make the thiophene ring more resistant to oxidation, the formation of by-products in

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[1] (a) Kreis, *Ber.*, **17**, 2073 (1884); (b) Meyer, "Die Thiophengruppe," Braunschweig, 1888, p. 104.

[2] The experimental work outlined in this paper had almost been completed when a brief paragraph on bromonitrothiophene appeared in *Ann.*, **512**, 161 (1934). The conditions under which the compound was produced are not stated, and there is no reference to the yield of the product or its properties. Its melting point is given as 48–49°.

[3] (a) Töhl and Schultz, *Ber.*, **27**, 2835 (1894); (b) Steinkopf and Otto, *Ann.*, **424**, 69 (1921); (c) Steinkopf and co-workers, *ibid.*, **430**, 98 (1922); (d) Krause and Renwanz, *Ber.*, **62B**, 1710 (1929).

[4] (a) Kreis, *ibid.*, **17**, 2074 (1884); (b) Rosenberg, *ibid.*, **18**, 3028 (1885); (c) Rosenberg, *ibid.*, **19**, 652 (1886); (d) Babasinian, THIS JOURNAL, **50**, 2751 (1928).

[5] Töhl and Schultz, *Ber.*, **27**, 2835 (1894).

[6] (a) Angeli and Ciamician, *ibid.*, **24**, 75 (1891); (b) Ciamician and Angeli, *ibid.*, **24**, 1347 (1891).

large quantities can hardly be prevented if an attempt is made to nitrate bromothiophene with pure nitric acid or a mixture of nitric and sulfuric acids.

Nitration in Acetic Anhydride and Glacial Acetic Acid.—Side reactions are checked to a great extent when bromothiophene dissolved in acetic anhydride is nitrated with a solution of nitric acid in the same solvent. Under these conditions there is a decided increase in the yield of bromonitrothiophene if a reaction temperature of -5 to 0° is maintained during nitration.

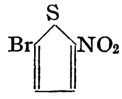
An acetic anhydride solution of bromothiophene may also be nitrated at 5° with a solution of nitric acid in glacial acetic acid. Moreover, nitration takes place at 50° when acetic acid alone is employed as a solvent. However, the yield of bromonitrothiophene is always poor when the anhydride is either diluted with glacial acetic acid or is entirely replaced by it. The use of pure acetic anhydride is therefore suggested for the nitration of bromothiophene.

Experimental

Twenty-five grams of bromothiophene (b. p. 149.5–150.5°) dissolved in 50 cc. of acetic anhydride was introduced into a half-liter round flask, provided with a stirrer and a cooling device. At -5° the liquid was treated, during rapid stirring, with a solution of 25 g. of nitric acid (sp. gr. 1.51) dissolved in 50 cc. of ice-cold acetic anhydride. The acid was added dropwise within a period of forty-five minutes and the temperature was not permitted to rise above 0°. In the earlier phases of the reaction a faint yellow color developed in the mixture. This was followed by the formation of a lemon-yellow precipitate weighing less than a gram. The color of the precipitate and its quantity remained practically unchanged during the nitration. At the end of the forty-five-minute period the stirring was continued for half an hour. The nitrating flask was then surrounded with ice and kept in a refrigerator for twenty-four hours. It was poured, with stirring, into finely crushed ice. The yellow-brown crystalline solid formed in this way was dried in a brown desiccator over sulfuric acid. It was dissolved in a large volume of hot ligroin, decolorized with darco and concentrated to crystallization at the room temperature. The first fraction of crystals consisted of long faint-yellow prisms. From the mother liquor three additional fractions were obtained, the last and smallest fraction being darker in color. The acid filtrate was found to contain a very small quantity of the product upon neutralization with sodium carbonate and distillation with steam. The total yield of the crude product was 21.3 g., or 66% of that required by theory. This was purified by distillation with steam; weight of the pure product 19.5 g., or 61% of the theoretical quantity.

Anal. Calcd. for $C_4H_2S(NO_2)Br$: S, 15.41; Br, 38.42. Found: S, 15.39; Br, 38.37.

Properties.—Bromonitrothiophene is a pale yellow solid, usually crystallizing in fine prisms. It melts at 45–46° and distils at 235–237° (750 mm.) with only slight decomposition. It has a sweetish taste, developing an extremely astringent after-taste. The compound is very volatile with steam. The steam distillate forms snow-white fine prisms. In a very short time the product assumes a yellow color. The same changes in color are noticed upon crystallization from solvents. It is very soluble in ether, methanol, chloroform, carbon tetrachloride, methyl formate, ethyl alcohol and benzene. It dissolves sparingly in petroleum ether. By slow crystallization it separates out from this solvent in beautiful transparent needles.

Bromonitrothiophene is assumed to be the 2,5-derivative of thiophene. Its provisional formula  remains to be established.

Summary

1. Bromothiophene may be nitrated into bromonitrothiophene in pure acetic anhydride. The yield of the product is over 60% when a reaction temperature of -5 to 0° is maintained.

2. The yield is not satisfactory when nitration is carried out in a mixture of acetic anhydride and glacial acetic acid at 5°, or in pure acetic acid at 50°.

3. The properties of bromonitrothiophene are described. The compound is assumed to be the 2,5-derivative of thiophene.

BETHLEHEM, PENNSYLVANIA RECEIVED JUNE 21, 1935

[CONTRIBUTION FROM THE LABORATORY FOR ENDOCRINE RESEARCH, THE JOHNS HOPKINS UNIVERSITY, SCHOOL OF MEDICINE]

Chemical Studies on Toad Poisons. VII. Bufo arenarum, Bufo regularis and Xenopus laevis[1]

BY H. JENSEN

As further chemical evidence for the correctness of the formulas assigned to arenobufagin ($C_{25}H_{34}O_6$) and arenobufotoxin ($C_{39}H_{60}O_{11}N_4$), which were isolated by Chen, Jensen and Chen from the secretion of Bufo arenarum,[2] several derivatives of arenobufagin have been prepared and analyzed. From the secretion of the South African toad, *Bufo regularis,* which has been studied pharmacologically by Epstein and Gunn,[3] two analogous physiologically active compounds, regularobufagin and regularobufotoxin were isolated by Chen and Chen, in amounts sufficient only for pharmacological study.[4] It seemed desirable therefore to prepare these principles in somewhat larger amounts for chemical identification. On the basis of several analyses of these principles as well as certain of their derivatives, the following empirical formulas have been assigned to regularobufagin, $C_{25}H_{34}O_6$, and to regularobufotoxin, $C_{39}H_{60}O_{11}N_4$.

The isomeric arenobufagin and regularobufagin are both lactones, forming hydroxy acids by the action of alcoholic sodium hydroxide. Simultaneously with the hydrolysis of the lactone ring, one molecule of acetic acid (identified as the silver salt) is liberated, presumably from an acetoxy group. Oxidation with chromic acid gives the corresponding monoketones, indicating the presence of a secondary hydroxy group. On treatment of arenobufagin with acetic anhydride, acetylarenobufagin, $C_{27}H_{36}O_7$, is formed. On treatment of regularobufagin under the same conditions, it was found that one molecule of acetic acid is split off (probably from a tertiary acetoxy group) giving a product $C_{25}H_{32}O_5$. There are certain known examples of an intramolecular loss of water by similar treatment, notably the dehydration of ouabain to anhydroouabainheptaacetate,[5] and of ergostadienetriol to dehydroergosteryl acetate[6] by acetic anhydride. Neither the acetyl derivative of arenobufagin nor the compound $C_{25}H_{32}O_5$ obtained from regularobufagin gives a ketone on oxidation with chromic acid, which indicates that acetylation of the secondary hydroxy groups has taken place. Arenobufagin and regularobufagin are C_{23}-derivatives (after splitting off the acetyl radical which is attached to a tertiary hydroxy group), and can be considered as acetyl derivatives of a doubly unsaturated trihydroxy lactone $C_{23}H_{32}O_5$. It is of interest to note that the analytical data for arenobufagin and regularobufagin closely agree with those reported for bufotalin (the bufagin of *Bufo vulgaris*) by Wieland and co-workers,[7] and to which they assigned the empirical formula $C_{26}H_{36}O_6$. The bufagins probably possess a ring structure identical with that of the aglucones of certain plant glucosides. They likewise are C_{23}-derivatives and recently have been shown to contain a ring structure identical with that of the sterols.[8] Further investigation is required to confirm these possibilities.

Pharmacological investigation has indicated the presence of epinephrine in the secretion of *Bufo arenarum* and *Bufo regularis*[2,3,4,9] and this has been substantiated by the isolation and identification of the base from both secretions. Bufothionine, a sulfur-containing compound which has been obtained by Wieland and co-workers from the secretion of the Japanese toad,[10] and from an alcoholic extract of the dried skin secretion of *Bufo arenarum,*[11] was found to be present in small quantities in the secretion of *Bufo arenarum.* From the secretion of *Bufo regularis,* there has been isolated as a flavianate, a basic constituent which is identical with that obtained by Jensen and Chen from the secretion of *Bufo valliceps.*[12]

From the skin secretion of the South African clawed toad, *Xenopus laevis,* which is biologically more closely related to *Rana* than to *Bufo,*

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[1] Presented before the Division of Biological Chemistry at the 88th Meeting of the American Chemical Society, New York City, April 22–26, 1935.

[2] Chen, Jensen and Chen, *J. Pharmacol.,* **49,** 1 (1933).

[3] Epstein and Gunn, *ibid.,* **39,** 1 (1930).

[4] Chen and Chen, *ibid.,* **49,** 503 (1933).

[5] Jacobs and Bigelow, *J. Biol. Chem.,* **96,** 647 (1932).

[6] Dunn, Heilbron, Phipers, Samant and Spring, *J. Chem. Soc.,* 1580 (1934).

[7] Wieland and Hesse, *Ann.,* **517,** 22 (1935).

[8] Jacobs and Elderfield, *J. Biol. Chem.,* **108,** 497 (1935); Tschesche, *Ber.,* **68,** 7 (1935).

[9] Novaro, *Compt. rend. soc. biol.,* **87,** 824 (1922); **88,** 371 (1923).

[10] Wieland and Vocke, *Ann.,* **481,** 215 (1930).

[11] Wieland, Konz and Mittasch, *ibid.,* **513,** 1 (1934).

[12] Jensen and Chen, *Ber.,* **65,** 1310 (1932).

the following constituents have been isolated: cholesterol, fatty acids, and a basic compound as the flavianate. The base was found to be identical with bufotenidine, which is present in Ch'an Su and in the secretion of certain other toads, and the constitution of which has recently been determined.[11,12] No evidence of the presence of any bufagin-like substance in this secretion has been thus far obtained. The chemical findings are in agreement with the results of the pharmacological study of this secretion by Gunn.[13]

Most of the analyses reported in this paper were carried out by Dr. Ing. A. Schoeller, Berlin-Schmargendorf, Germany.

Experimental

Secretion of Bufo arenarum

The usual methods were employed for the isolation of arenobufagin.[2,14]

Acetylarenobufagin, $C_{27}H_{36}O_7$.—Fifty milligrams of arenobufagin was heated with 1 cc. of acetic anhydride for two hours in a boiling water-bath. The acetyl compound was isolated in the usual manner, and crystallized from alcohol. The fine white needles melted at 162–163°.

Anal. Calcd. for $C_{27}H_{36}O_7$: C, 68.64; H, 7.63. Found: C, 68.51, 68.46; H, 7.85, 7.77.

Arenobufagone, $C_{25}H_{32}O_6$.—Eighty milligrams of arenobufagin was dissolved in 2 cc. of glacial acetic acid, and 0.15 cc. of chromic acid solution (40 g. of water, 8 g. of sulfuric acid, and 5.3 g. of chromium trioxide) was added with thorough stirring. The solution was allowed to stand for fifteen minutes and then diluted with water. After standing overnight the precipitate was filtered off and recrystallized from dilute ethyl alcohol. The ketone consisted of faintly yellow rhombohedric leaflets, melting at 219–220°.

Anal. Calcd. for $C_{25}H_{32}O_6$: C, 70.09; H, 7.41. Found: C, 69.82, 69.84; H, 7.25, 7.22.

Arenobufaginic Acid, $C_{23}H_{34}O_6$.—Three-tenths gram of arenobufagin was refluxed with 25 cc. of 1 *N* alcoholic sodium hydroxide for three hours. After cooling, the solution was diluted with water and allowed to stand overnight. The small amount of flocculent precipitate which might have formed was filtered off, and the filtrate made slightly acid with hydrochloric acid. After standing for several days, the precipitate was filtered off and dried at room temperature. The acid, however, could not be obtained in crystalline form. For further purification it was dissolved in ethyl alcohol and water added until a permanent turbidity resulted. The next day a pale yellow amorphous precipitate had settled out. This was filtered off and the filtrate further diluted with water. The precipitate thus obtained was filtered off, washed with water, and dried at room temperature. The product was an amorphous white powder; the analytical data indicated a considerable degree of purity. The acid began to decompose at 220°, and became progressively darker until it was completely melted at 235°. Water is probably eliminated at the higher temperature.

Anal. Calcd. for $C_{23}H_{34}O_6$: C, 67.98; H, 8.37. Found: C, 67.70, 67.68; H, 7.92, 7.98.

Detection of an Acetyl Group in Arenobufagin.—The filtrate from the bufaginic acid was distilled from an oil-bath. The distillate (acid toward litmus) was shaken with silver oxide and allowed to stand for one day. The silver oxide was then filtered off and the filtrate evaporated *in vacuo* over sulfuric acid. The silver acetate was recrystallized from dilute alcohol.

Anal. Calcd. for CH_3COOAg: Ag, 64.61. Found: Ag, 64.31, 64.29.

Bufothionine, $C_{12}H_{14}O_4N_2S$.—In working up the alcoholic extract of the secretion of *Bufo arenarum*, the cholesterol fraction, which crystallizes out on evaporation, was found to be accompanied by a foreign crystalline substance. After filtration, the cholesterol was removed by extraction with petroleum ether, and the insoluble residue purified from 96% ethyl alcohol. The compound crystallized as prisms, darkening at 240°, and melting at 250° with decomposition. The properties of this substance were identical with those described for bufothionine by Wieland and his co-workers.[10,11]

Anal. Calcd. for $C_{12}H_{14}O_4N_2S$: C, 51.06; H, 5.00; N, 9.93; S, 11.34. Found (average of several analyses): C, 50.93; H, 4.97; N, 8.80; S, 11.10.

Epinephrine, $C_9H_{13}O_3N$.—Epinephrine was isolated from about 10 g. of the dried secretion, which had been extracted twice with alcohol in accordance with the procedure of Jensen and Chen.[15] Approximately 40 mg. of the substance was obtained. It melted at 211° with decomposition and showed no depression of the melting point when mixed with epinephrine.

Anal. Calcd. for $C_9H_{13}O_3N$: C, 59.01; H, 7.18; N, 7.65. Found: C, 58.73; H, 7.42; N, 7.97.

Secretion of Bufo Regularis.—Regularobufagin and regularobufotoxin were obtained from the secretion according to methods previously described.[4,14] The derivatives of regularobufagin were prepared similarly to those of arenobufagin.

Regularobufotoxin, $C_{39}H_{60}O_{11}N_4$.—The principle was repeatedly crystallized from 96% ethyl alcohol and finally from acetone. It crystallized in colorless spheroids, which soften at 190° and melt at 205°. Like the bufotoxins of other species of toads, it gives a positive Sakaguchi reaction indicating the presence of arginine.

Anal. Calcd. for $C_{39}H_{60}O_{11}N_4$: C, 61.69; H, 7.97; N, 7.39. Found: C, 61.82, 61.88; H, 8.28, 8.37; N, 7.58, 7.50.

Regularobufagin, $C_{25}H_{34}O_6$.—The compound was purified from either dilute alcohol, or from a chloroform–ether–petroleum ether solution. It crystallizes in prisms melting at 235–236°. Its color reactions are similar to those of the other bufagins.[16]

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(13) Gunn, *Quart. J. Expt. Physiol.*, **20**, 1 (1930).

(14) Jensen and Chen, *J. Biol. Chem.*, **87**, 741 and 755 (1930).

(15) Jensen and Chen, *ibid.*, **82**, 397 (1929).

(16) The melting point and the analytical data for regularobufagin agree closely with the results given by Chen and Chen for this principle. However, they assigned a different empirical formula to it.[4]

Anal. Calcd. for $C_{25}H_{34}O_6$: C, 69.71; H, 7.94. Found: C, 69.88, 69.95; H, 8.18, 8.20.

Acetylation of Regularobufagin, $C_{25}H_{32}O_5$.—White needles crystallized from dilute methyl alcohol, melting at 224–225°.

Anal. Calcd. for $C_{25}H_{32}O_5$: C, 72.81; H, 7.77. Found: C, 72.95, 73.00; H, 8.02, 7.92.

Regularobufagone, $C_{25}H_{32}O_6$.—Recrystallizes from dilute methyl alcohol in rhombohedric leaflets, faintly yellow, melting at 210–211°.

Anal. Calcd. for $C_{25}H_{32}O_6$: C, 70.09; H, 7.41. Found: C, 69.72, 69.80; H, 7.21, 7.51.

Regularobufaginic Acid, $C_{23}H_{34}O_6$.—The acid begins to decompose at 125°, and becomes more and more colored until it is completely melted. Water is probably split off at the higher temperatures. For analysis, the substance was dried *in vacuo* over calcium chloride.

Anal. Calcd. for $C_{23}H_{34}O_6$: C, 67.98; H, 8.37. Found: C, 67.62, 67.58; H, 7.91, 7.90.

Detection of the Acetyl Group in Regularobufagin.—*Anal.* Calcd. for CH_3COOAg: Ag, 64.61. Found: Ag, 64.28, 64.25.

Epinephrine, $C_9H_{13}O_3N$.—The base was isolated from about 10 g. of the dried secretion, after it had been extracted twice with alcohol. Approximately 30 mg. of the compound was obtained, which melted at 210° with decomposition and showed no depression of the melting point when mixed with epinephrine.

Anal. Calcd. for $C_9H_{13}O_3N$: C, 58.01; H, 7.18; N, 7.65. Found: C, 58.71; H, 7.46; N, 7.90.

Regularobufotenine.—This compound was isolated as the flavianate from an aqueous solution of the material, obtained by evaporation of the alcoholic extract of the secretion. The procedure was similar to that employed by Jensen and Chen in the preparation of the flavianates of the different basic constituents present in the secretions of the various species of toads.[12] The flavianate was recrystallized several times from water, and it then melted at 264° with decomposition. It showed no depression of the melting point when mixed with the flavianate of *Bufo valliceps*.

Anal. Calcd. for $C_{11}H_{12}O_2N_2 \cdot C_{10}H_6O_8N_2S$: C, 48.65; H, 3.48; N, 10.81; S, 6.18. Found: C, 48.82, 48.91; H, 3.82, 3.77; N, 11.11, 11.15; S, 6.48.

The flavianate was converted into the picrate by decomposing the salt with barium acetate according to the procedure of Wieland and co-workers.[11] The picrate crystallized from water as red clusters of needles melting at 203–204°. The picrate contains one molecule of water of crystallization, and showed no depression of the melting point when mixed with the picrate of *Bufo valliceps*.

Anal. Calcd. for $C_{11}H_{12}O_2N_2 \cdot C_6H_3O_7N_3 \cdot H_2O$: C, 45.23; H, 3.77; N, 15.52. Found: C, 45.20, 45.32; H, 4.11, 3.92; N, 16.2, 15.92.

Secretion of Xenopus laevis

The procedure was similar to that for the secretions of other species of toads. Fifty grams of the dried skin secretion was extracted twice with 300 cc. of 96% ethyl alcohol. The crystalline matter which separated out on concentration of the alcoholic solution was identified as cholesterol. The filtrate from the cholesterol fraction was evaporated to dryness *in vacuo*, and extracted twice with 100 cc. of water. Most of the material went into solution, the insoluble part consisting mostly of protein material and higher fatty acids. The aqueous solution was shaken out twice with chloroform, flavianic acid was added and the precipitate recrystallized several times from water. The flavianate crystallized in long needles melting at 200°, and showed no depression in melting point when mixed with the flavianate of bufotenidine obtained from Ch'an Su and certain other species of toads.[11,12]

Anal. Calcd. for $C_{13}H_{18}ON_2 \cdot C_{10}H_6O_8N_2S \cdot H_2O$: C, 50.18; H, 4.73; S, 5.82. Found: C, 49.88, 49.94; H, 5.12, 4.99; S, 5.74.

The flavianate was converted into the picrate and also into the hydriodide salt following the method of Wieland and his co-workers.[12] The derivatives showed the same melting points as the corresponding salts of bufotenidine, and mixed melting points showed no depression. The chemical analysis of these salts also supports the view that the base is identical with bufotenidine. The picrate crystallized from ethyl alcohol in red needles melting at 197°.

Anal. Calcd. for $C_{13}H_{18}ON_2 \cdot C_6H_3O_7N_3$: C, 51.01; H, 4.70; N, 15.67. Found: C, 51.21, 51.11; H, 5.10, 4.94; N, 16.01, 15.92.

The hydroiodide salt crystallized from methyl alcohol in prisms, melting at 208–209°.

Anal. Calcd. for $C_{13}H_{18}ON_2 \cdot HI$: C, 45.09; H, 5.50; N, 8.08. Found: C, 45.21, 45.06; H, 5.82, 5.71; N, 7.8.

The author is greatly indebted to Professor J. W. C. Gunn of the University of Cape Town, South Africa, for the supply of the secretions of *Bufo regularis* and *Xenopus laevis*, and to Professor B. A. Houssay, University of Buenos Aires, Argentina, for the supply of the secretion of *Bufo arenarum*.

Summary

Various derivatives of arenobufagin and regularobufagin have been prepared. The analytical data obtained for these compounds substantiate the empirical formula $C_{25}H_{36}O_6$ assigned to these principles. The two compounds are isomers and are C_{23}-derivatives after removing the acetyl radical which is attached to a hydroxy group. Regularobufotoxin has been isolated in pure form from the secretion of *Bufo regularis*. Epinephrine has been isolated and identified as such from the secretions of both *Bufo arenarum* and *Bufo regularis*.

Cholesterol, fatty acids and a basic principle have been obtained from the secretion of the South African clawed toad. The base was obtained as the flavianate, which was found to be

identical with that of bufotenidine. No evidence for the presence of any bufagin-like substance in this secretion has been obtained.

BALTIMORE, MARYLAND RECEIVED JULY 1, 1935

The Action of Perthiocyanic Acid on Amines

BY H. G. UNDERWOOD AND F. B. DAINS

In preparing dithiobiurets for another investigation, the action of perthiocyanic acid on various substances containing the amino group has been investigated. Glutz[1] has shown that perthiocyanic acid unites with aniline to form phenyldithiobiuret and Fromm[2] has pointed out that in the formation of phenyldithiobiuret an excess of aniline tends to increase the amount of thiocarbanilide formed along with the dithiobiuret. The reactions for the formation of dithiobiurets and dithioureas occur as follows

$$RNH_2 + C_2H_2N_2S_3 \longrightarrow RNHCSNHCSNH_2 + S \quad (I)$$
$$4RNH_2 + C_2H_2N_2S_3 \longrightarrow 2(RNH)_2CS + 2NH_3 + S \quad (II)$$

In this work fusions were carried out first at water-bath temperature and if no reaction was evident higher temperatures were employed. The ratio of the amine to perthiocyanic acid was usually 2:1. The results indicate that the nature of the reaction product depends upon the amine employed; thus there were formed (a) normal dithiobiurets, (b) thioureas, (c) fused side rings with certain substituted amines or (d) no reaction occurred.

Experimental

Synthesis of Dithiobiurets (I–VIII).—The new dithiobiurets listed in Table I (I–VIII) were prepared by fusing the amine (2 moles) with perthiocyanic acid (1 mole) on the water-bath. Di-*p*-bromophenylthiourea (IV) was obtained as a by-product in the preparation of *p*-bromophenyldithiobiuret. It is probable that dithioureas are also formed along with the other dithiobiurets but the small amounts formed did not warrant their separation.

TABLE I

Text no.	Compound	Formula	M. p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found
I	*m*-Tolyldithiobiuret	$C_9H_{11}N_3S_2$	159	18.66	18.63
II	*m*-Chlorophenyldithiobiuret	$C_8H_8ClN_3S_2$	164	17.11	16.96
III	*p*-Bromophenyldithiobiuret	$C_8H_8BrN_3S_2$	169	14.48	14.30
IV	α,β-Di-*p*-bromophenylthiourea	$C_{13}H_{10}BrN_2S$	184		
V	*p*-Iodophenyldithiobiuret	$C_8H_8IN_3S_2$	240	12.49	12.22
VI	α-Naphthyldithiobiuret	$C_{12}H_{11}N_3S_2$	235–236	16.09	15.93
VII	*m*-Aminophenyldithiobiuret[a]	$C_8H_{10}N_4S_2$	226	24.77	24.40
VIII	1-Methyl-1-*p*-tolyldithiobiuret	$C_{10}H_{13}N_3S_2$	236	17.55	17.51
IX	α,β-Di-*p*-xenylthiourea	$C_{25}H_{20}N_2S$	228	7.37	7.45
X	α,β-Dibenzylthiourea	$C_{15}H_{16}N_2S$	147–148	10.93	10.73
XI	4-Keto-2-thiotetrahydroquinazoline	$C_8H_6N_2OS$	285	15.72	15.61
XII	*o*-Phenylenethiourea	$C_7H_6N_2S$	298–299	18.66	18.84
XIII	Benzoxazole thiourea	$C_8H_7N_3OS$	205	21.74	21.57

[a] Only one amino group of *m*-diaminobenzene reacted.

Synthesis of Thioureas

α,β-Di-*p*-xenylthiourea (IX).—*p*-Xenylamine (0.1 mole) and perthiocyanic acid (0.05 mole) were heated for one hour at 150°. Only a small quantity of the reaction product was soluble in base. The main product insoluble in alkali was the thiourea which on recrystallization from hot water formed plate-like crystals melting at 228°,[3,4] yield 13 g.

α,β-Dibenzylthiourea (X).—The reaction was spontaneous on mixing benzylamine (0.05 mole) and perthiocyanic acid (0.05 mole), ammonia being evolved. The reaction mixture almost completely liquefied and then resolidified. To ensure complete reaction the product was warmed on the water-bath for one hour. Large plate-like crystals of dibenzylthiourea melting at 147–148°[5,6] were obtained from alcohol.

Reaction of Secondary Butylamine with Perthiocyanic Acid.—Secondary butylamine at room temperature gave an oily product which on distillation yielded secondary butyl thiourea and secondary butyl isothiocyanate.

Fused Ring Compounds

$\overline{C_6H_4NHCSNHCO}$, **4-Keto-2-thiotetrahydroquinazoline (XI).**—This product resulted when anthranilic acid or methyl anthranilate was heated at 180° for two hours. The reaction product was extracted with sodium hy-

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(1) Glutz, *Ann.*, **154**, 44 (1870).

(2) Fromm, *ibid.*, **275**, 20 (1893).

(3) Friebel and Rassow, *J. prakt. Chem.*, [2] **63**, 457 (1901).

(4) Zimmermann, *Ber.*, **13**, 1963 (1880).

(5) Werner, *J. Chem. Soc.*, **59**, 406 (1891).

(6) Salkowski, *Ber.*, **24**, 2724 (1891).

droxide solution (10%) and filtered. Neutralization gave the quinazoline which was recrystallized from glacial acetic acid (m. p. 285°).[7]

***o*-Phenylenethiourea (XII).**—*o*-Phenylenediamine and perthiocyanic acid were heated for two hours at 180° with evolution of ammonia. An extraction was made of the fusion mixture with dilute sodium hydroxide solution. The basic product, obtained on acidifying the alkaline filtrate, gave light yellow, almost colorless leaflets from alcohol melting at 298–299°.[8,9]

Fusion of *o*-Aminophenol with Perthiocyanic Acid (XIII).—*o*-Aminophenol was fused with perthiocyanic acid at 180° for one hour with evolution of hydrogen sulfide. Light orange colored leaflets, melting at 205°, were obtained on acidifying the sodium hydroxide extraction solution of the fusion product. The analyses and properties correspond to a benzoxazole thiourea, $\underline{C_6H_4—N=C}O$-$(NHCSNH_2.)$[10]

No Reaction.—Perthiocyanic acid failed to react to form dithiobiurets or dithioureas with *p*-nitroaniline, 2,6-dibromo-3-methylaniline, 2,5-dichloroaniline, glycine, phenylglycine, benzanilide and glutamic acid.

Summary

Perthiocyanic acid reacted with amines to form (a) normal dithiobiurets, (b) thioureas, (c) fused rings or (d) no reaction occurred, depending upon the nature of the amine employed.

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[7] Rupe, *Ber.*, **30**, 1098 (1897).

[8] Lellmann, *Ann.*, **221**, 9 (1893).

[9] Billeter and Steiner, *Ber.*, **20**, 231 (1887).

[10] Deck and Dains, THIS JOURNAL, **55**, 4986 (1933).

Some Dithiazane Rings

BY H. G. UNDERWOOD AND F. B. DAINS

The formation of thiazolidines and of *m*-thiazanes from thioureas and ethylene dibromide or trimethylene dibromide has been fully investigated. With the methylene dihalides and thioureas the only ring compound listed is one described by Foerster[1] as the methylene ether of thiocarbanilide, $\underline{SCNH_2NC_6H_5C}=NC_6H_5$ (from methylene iodide and diphenyl thiourea). Further examples of such ethers are described later in our paper. It has been shown in our work, however, that six-membered rings of the type 1,3,5-dithiazanes, $\underline{\overset{1}{S}\overset{2}{C}HR\overset{3}{S}\overset{4}{C}(NR)\overset{5}{N}H\overset{6}{C}}(NR)$ can be formed by the action of methylene halides on thiourea, monoaryl thiourea or 1,5-diaryldithiobiurets. To date derivatives of the dithiazanes have been confined to the thialdine, $\underline{SCHRSCHRNHC}HR$, the 2,4,6-trimethyldithiazane formed by the action of hydrogen sulfide on aldehyde ammonia, or an N-methyl derivative from methylamine and thioacetic aldehyde.[2,3,4] The structure of these thialdins has not been confirmed by direct experiment.

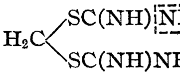
The following work shows that such rings can be synthesized by methods that give some definite proof of their constitution.

Experimental

4,6-Diimino-1,3,5-dithiazane Hydroiodide.—Dixon and Taylor[5] had heated methylene diiodide in alcohol solution with thiourea. The free base (m. p. 198°) from the salt was assumed to be the methylene ether of dithiourea, $CH_2(SC=NHNH_2)_2$, on the basis of a sulfur determination. In repeating this work the methylene iodide (1 mole) was heated in alcohol solution with thiourea (2 moles) for two hours and filtered hot; the salt that separated was purified by crystallization from hot water. Since the free base (m. p. 202–209°) failed to give concordant results on analysis for nitrogen, due seemingly to hydrolysis and loss of ammonia, the stable hydriodide salt was examined.

Anal. Calcd. for $C_3H_5N_3S_2·HI$: N, 15.27. Found: N, 15.08, 15.22, 15.16.

The results correspond to the dithiazane structure and not to the monohydriodide salt of methylene dithiourea (N, 19.16) or the dihydroiodide salt (N, 13.37). The mechanism of this reaction is evidently as follows; a mol of ammonia is lost from the methylene thiourea,



, thus closing the ring which in the form of a salt is stable.

Benzal Chloride and Thiourea, 4,6-Imino-2-phenyl-1,3,5-dithiazane.—Abel[6] heated benzal chloride with thiourea and obtained a compound $C_9H_{10}ClN_3S_2$ for which he gives no structural formula or melting point. In this work thiourea and benzal chloride in excess were heated in an oil-bath, the temperature not being allowed to rise above 150°. Unless care is used the temperature goes to 190° and a resin results. The solid residue was difficultly soluble in hot water and was further purified by solution in alcohol and precipitation with ether. The salt melted at 236° and was formed as follows

$$C_6H_5CHCl_2 + 2CS(NH_2)_2 \longrightarrow C_9H_9N_3S_2·HCl + NH_4Cl$$

Anal. Calcd. for $C_9H_{10}ClN_3S_2$: N, 16.15; S, 24.69; Cl, 13.65. Found: N, 16.23, 15.95; S, 24.45, 24.25; Cl, 13.11, 13.22.

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[1] Foerster, *Ber.*, **21**, 1872 (1888).

[2] Marckwald, *ibid.*, **19**, 1826 (1886).

[3] Nord, *ibid.*, **52**, 1208 (1919).

[4] Delépine, *Bull. soc. chim.*, [3] **15**, 889 (1896).

[5] Dixon and Taylor, *J. Chem. Soc.*, **109**, 1255 (1916).

[6] Abel, *Am. Chem. J.*, **13**, 118 (1891).

The free base was not isolated in a pure condition. Excess alkali decomposes the salt yielding benzaldehyde, hydrogen sulfide and ammonia, while neutralization with 0.1 *N* alkali gave mixtures in which part of the nitrogen had been lost. The imino group was easily hydrolyzed to ammonia.

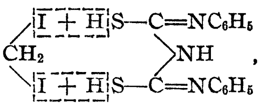
Phenylthiourea Derivative, 4,6-Diphenylimino-1,3,5-dithiazane.—The stability of the dithiazane ring is greatly increased by the presence of phenylimino rather than imino groupings. Phenylthiourea and methylene iodide were refluxed in alcoholic solution for four hours. The difficultly soluble hydroiodide salt when crystallized from hot water melted at 263°.

Anal. Calcd. for $C_{15}H_{14}IN_3S_2$: N, 9.83; S, 14.98. Found: N, 9.90; S, 15.04.

The Hydrobromide Salt.—A mixture of methylene bromide and phenyl thiourea was heated in an oil-bath at 120–130° for one-half hour. The mixture was treated with alcohol and the precipitated salt crystallized from hot water (m. p. 268°). The free base was obtained on neutralizing hot dilute solutions of the bromide or iodide salts with alkali. It crystallized from alcohol in the form of a light yellow powder of m. p. 107°.

Anal. Calcd. for $C_{15}H_{13}N_3S_2$: N, 14.04; S, 21.46; mol. wt., 299. Found: N, 13.98; S, 21.92; mol. wt., 297.

The dithiazane was decomposed by boiling with 15% potassium hydroxide, yielding hydrogen sulfide, phenyl isothiocyanate and aniline.

Thiazanes from Dithiobiurets.—Final proof of the dithiazane structure was shown as follows. 1,5-Diphenyldithiobiuret and methylene bromide were heated at 120°, giving a hydrobromide salt that melted at 263°. The free base was insoluble in alkali, melted at 109° and was shown by analysis and mixed melting point to be identical with the compound from phenylthiourea. Ring closure evidently occurred as follows, , thus confirming the structure.

Benzoyl Derivative (5- or 6-Benzoyl).—The diphenyliminodithiazane was readily benzoylated in pyridine solution, yielding a product of m. p. 120–121°.

Anal. Calcd. for $C_{28}H_{22}N_3OS_2$: N, 8.77. Found: N, 8.71.

4,6-Di-*p*-tolylimino-1,3,5-dithiazane Hydrobromide.—*p*-Tolyl thiourea was heated with methylene dibromide at 130° for one-half hour. From the melt on crystallization from hot water was isolated a yellow salt, m. p. 283°.

Anal. Calcd. for $C_{17}H_{18}BrN_3S_2$: N, 10.29. Found: N, 10.18, 10.98.

The free base melted at 175°.

Anal. Calcd. for $C_{17}H_{17}N_3S_2$: N, 12.83. Found: N, 12.47, 12.58.

4,6-Di-*o*-tolylimino-1,3,5-dithiazane Hydrobromide.—The yellow hydrobromide salt melted at 236°.

Anal. Calcd. for $C_{17}H_{18}BrN_3S_2$: N, 10.29. Found: N, 10.29, 10.04.

The free base melted at 174°.

Anal. Calcd. for $C_{17}H_{17}N_3S_2$: N, 12.83. Found: N, 12.31, 12.35.

Ethylidene Dibromide and Monophenyl Thiourea: 2-Methyl-4,6-diphenylimino-1,3,5-dithiazane Hydrobromide.—Molar quantities of ethylidene dibromide and monophenyl thiourea were heated at 160° for four hours. From the reaction product was isolated and purified by crystallization from hot water the hydrobromide salt of 2-methyl-4,6-diphenylimino-1,3,5-dithiazane melting at 248°.

Anal. Calcd. for $C_{16}H_{16}BrN_3S_2$: N, 10.66. Found: N, 10.60, 10.52.

The free base melted at 181°.

Anal. Calcd. for $C_{16}H_{15}N_3S_2$: N, 13.48. Found: N, 13.37, 13.30.

2-Phenyl-4,6-phenylimino-1,3,5-dithiazane.—Monophenyl thiourea (35 g.) and benzal chloride (30 g.) were heated on a paraffin bath. The reaction began at 100° and the flask was removed from the bath, the temperature rising to 150°. The solid residue was crystallized from water–alcohol and melted at 232°.

Anal. Calcd. for $C_{21}H_{18}ClN_3S_2$: N, 10.21; S, 15.57; Cl, 8.61. Found: N, 10.22; S, 15.60; Cl, 8.52.

The free base melted at 145°.

Anal. Calcd. for $C_{21}H_{17}N_3S_2$: N, 11.19; mol. wt., 375. Found: N, 10.69; mol. wt., 368.

Further evidence as to the dithiazane structure was shown by its synthesis from 1,5-diphenyldithiobiuret which was heated with benzal chloride at 150° until evolution of hydrogen chloride ceased. A hydrochloride was obtained melting at 232°, which by mixed melting point and analysis proved to be identical with the product from benzal chloride and monophenyl thiourea.

Anal. Calcd. for $C_{21}H_{18}ClN_3S_2$: N, 10.21. Found: N, 9.91, 10.02.

2-Phenyl-4,6-di-*p*-tolylimino-1,3,5-dithiazane Hydrochloride.—Benzal chloride and *p*-tolyl thiourea gave the corresponding 2-phenyl-4,6-di-*p*-tolylimino-1,3,5-dithiazane hydrochloride which was obtained as a light yellow powder melting at 222°.

Anal. Calcd. for $C_{23}H_{22}ClN_3S_2$: N, 9.55. Found: N, 9.46.

The Action of Methylene Iodide on Disubstituted Thioureas.—This was tried in order to see whether a dithiazane ring could be made with the loss of a RNH_2. The results show that not to be the case, but instead evidence was obtained of the formation of the methylene ethers of the thioureas. Foerster[1] heated methylene iodide with thiocarbanilide in alcoholic solution and obtained a base (m. p. 68°). It was analyzed as the platinum salt which gave figures corresponding to the methylene ether of diphenylthiourea. On repeating his work a gummy base was obtained which gave an impure platinum salt and a product melting at 68–69°, which proved to be phenyl thiourethan.

Methylene Ether of Di-*p*-tolyl Thiourea.—Molar quantities of di-*p*-tolyl thiourea and methylene iodide were heated in acetone solution for a period of four hours. The reaction product was found to contain unchanged thiourea, tolyl mustard oil, toluidine and a basic compound that melted at 151° when crystallized from alcohol.

Anal. Calcd. for $C_{16}H_{16}N_2S$: N, 10.41; mol. wt., 268. Found: N, 10.77, 10.83; mol. wt., 271.

These results point to a methylene ether and not a dithiazane derivative or a methylene dithio ether, $CH_2(SC{=}NC_6H_5NHC_6H_5)_2$, which has nearly the same percentage composition but a molar weight of 468.

1,5 - Diphenyl - 2 - thiolmethyl - 4 - thiolmethylenedipseudodithiobiuret Hydroiodide and Base.—A corresponding methylene ether was obtained from 1,5-diphenyl-2-thiolmethylpseudodithiobiuret ($C_6H_5N{=}C(SCH_3)NHCSNHC_6H_5$) when heated with methylene iodide alone at 120° or in alcoholic solution. This was obtained as the difficultly soluble hydroiodide salt (m. p. 275°) together with phenyl mustard oil.

Anal. Calcd. for $C_{16}H_{16}IN_3S_2$: N, 9.52. Found: N, 9.53, 9.58.

The light yellow base melted at 125°.

Anal. Calcd. for $C_{16}H_{15}N_3S_2$: N, 13.48. Found: N, 13.44.

Benzal chloride failed to give ethers of this type. Heated with thiocarbanilide or di-*p*-tolyl thiourea at 160° it gave only the triphenyl or tritolyl guanidine.

2 - Phenylimino - 3 - thioformanil - tetrahydrothiazole.—While 1,5-diphenyldithiobiuret with methylene iodide gave a dithiazane ring, with ethylene dibromide, a thiazole is formed. An alcoholic solution of the thiobiuret and ethylene dibromide with an excess of ammonium hydroxide was allowed to stand for several days, when light yellow crystals of the thiazole separated (m. p. 165°).

Anal. Calcd. for $C_{16}H_{15}N_3S_2$: N, 13.41. Found: N, 13.39.

Hydrolysis with alcoholic potassium hydroxide gave phenyl mustard oil and 2-phenylaminothiazolidine.

Thiazolidone Synthesis.—The action of chloroethyl acetate on 1,5-diphenyl-2-thiolmethylpseudodithiobiuret was studied in order to note the influence of the two groups upon the constitution of the possible thiazolidone. Heating the two components in alcoholic solution gave a thiazolidone $\underline{SC(NCSCH_3NC_6H_5)NC_6H_5COCH_2}$, melting at 127° with the structure phenyl-4-thiazolidone-thiolmethylpseudothiourea. This was shown by the fact that the 5-benzal derivative melting at 157° (N, calcd. 9.79; found, 9.86) on hydrolysis yielded the known 5-benzal-3-phenyl thiazoledione identified by melting point and analysis.

Anal. Calcd. for $C_{17}H_{15}N_3OS_2$: N, 12.26. Found: N, 12.17.

α,α-Phenylmethyl-β-thiazolidone Thiourea.—This compound was readily formed by heating the phenylmethyldithiobiuret with chloroethyl acetate or chloroacetyl chloride with one mol of pyridine in acetone solution for four hours (m. p. 222°).

Anal. Calcd. for $C_{11}H_{11}N_3OS_2$: N, 15.85. Found: N, 15.92, 15.95.

Hydrolysis of the 5-benzal derivative (m. p. 274°) with 50% sulfuric acid gave 5-benzal-2,4-thiazoledione, thus proving that the thiourea grouping was at position 2.

Anal. Calcd. for $C_{18}H_{16}N_3OS_2$: N, 11.86. Found: N, 11.37, 11.38.

Summary

Methylene dihalides reacted with thiourea, monoaryl thioureas and 1,5-diaryldithiobiurets to form dithiazanes while α,β-diaryl thioureas formed methylene ethers or products of hydrolysis.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Densities of Adsorbed Gases. I. Carbon Dioxide on Charcoal[1]

BY THOS. DE VRIES

It is possible, by the use of Polanyi's theory,[2] to calculate from an adsorption isotherm the isotherms for other temperatures. It is also possible to calculate the average density of the adsorbed layer. An experimental method was developed to determine the density of adsorbed carbon dioxide, and the agreement between observed and calculated densities lends confirmation to the reasonableness of the underlying assumptions. The density of water on silica gel at 25° has been determined by Ewing and Spurway.[3] No other densities of adsorbed vapors have been recorded in the literature. In this paper an apparatus and technique are described which gave results with a precision of 3 to 5% for the density of carbon dioxide adsorbed on activated coconut charcoal. In brief the method consisted in using helium as the displaced fluid to determine, before and after carbon dioxide adsorption, the unoccupied volume in a tube containing charcoal. A temperature of 30.00° was chosen which is just under the critical temperature of carbon dioxide.

Experimental

Carbon dioxide was prepared according to the method of Lowe and Guthmann,[4] and thoroughly dried by passing over anhydrous magnesium perchlorate. Helium was

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[1] Presented before the Division of Physical and Inorganic Chemistry at the New York Meeting of the American Chemical Society, April 22–26, 1935.

[2] Polanyi, *Verh. d. Deutsch. Phys. Ges.*, **18**, 55 (1916); Berényi, *Z. physik. Chem.*, **94**, 628 (1920).

[3] Ewing and Spurway, THIS JOURNAL, **52**, 4635 (1930).

[4] Lowe and Guthmann, *Ind. Eng. Chem.*, *Anal. Ed.*, **4**, 440 (1932).

purified by passing over hot copper oxide and over activated charcoal cooled with liquid air. It was stored in glass flasks sealed to the apparatus. When used the helium was again passed over charcoal cooled with liquid air. No rubber connections were used, and all possible precautions were taken to prevent contamination of the gases with stopcock grease, moisture or traces of air. For the experiments, ash-free coconut charcoal was used.

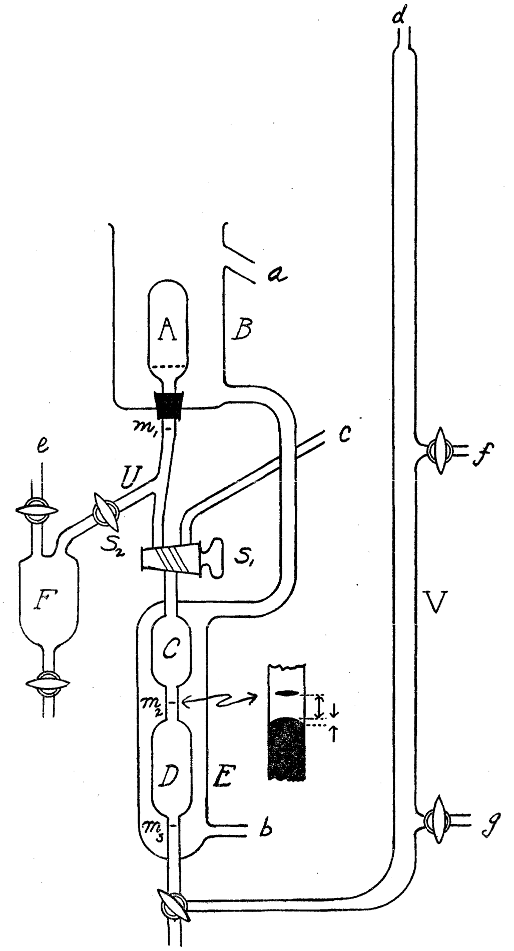

Fig. 1.—a, Return to thermostat; b, from thermostat via pump; c, to carbon dioxide and helium supply, and vacuum; d, e, to vacuum; f, g, to leveling bulbs; other symbols described in the text.

A diagrammatic sketch of the apparatus is given in Fig. 1. Water from a thermostat was circulated by pump around bulbs C and D (55.158 and 78.024 ml., respectively) in which the gases were measured and into the can surrounding the charcoal bulb, A. The temperature was read at this point and was kept constant to within 0.01°. The charcoal was supported by an iron washer covered with iron gauze. This made it possible to fill the tube with charcoal and move the washer in position with a magnet before inverting the tube and sealing it on to the apparatus.

The successive steps for a typical determination were as follows. The charcoal was degassed at 375° by slipping an electric heater over the charcoal tube. The time varied from twelve to forty-eight hours. A high-capacity double-stage mercury vapor pump of special design was used, backed by a Cenco Hyvac. There was a slow change in the volume of the bulb when a higher temperature was used for degassing. Bore 1 of stopcock S_1 was filled with mercury before the volume of carbon dioxide was measured in bulb C. The pressure on the gas was measured with a Gaertner cathetometer reading to 0.005 cm. By the use of an auxiliary lens the cathetometer could be brought close to the menisci and thus a more precise setting was obtainable. A thermometer, reading to 0.1°, was used to determine the temperature of the mercury columns and the appropriate corrections were made to 30° as standard. Corrections were also made for capillary depression in the tubes m_1, m_2, m_3 and V. These corrections were taken from "International Critical Tables,"[5] for mercury menisci of different heights and were checked experimentally to eliminate any error arising from the refraction of light as it passed through the outer glass wall and the intervening water. The optimum size for tubes m and V was 6 and 12 mm., respectively. A third important factor which added materially to the precision of the results was to bring the mercury meniscus up to but not opposite the reference mark (see Fig. 1), and then from the cathetometer readings and with the aid of an alignment chart, the volume was determined of the space between the mark and the curved mercury surface. The variability in the curvature of the mercury surface introduced errors of sufficient magnitude to make this correction necessary when volumes of gas must be measured with precision. The pressure on the gas was given directly from the difference in height of the two mercury menisci since the tube F was evacuated.

When the carbon dioxide was admitted into the charcoal bulb, mercury floating over into tube U would completely prevent leakage of air into the apparatus or loss of helium when it was used. When the pressure of the carbon dioxide in equilibrium with the charcoal became steady or changed very slowly at a constant rate, a known amount of helium was admitted to the charcoal bulb. The mercury between the mark m_1 and stopcock S_2 was first drawn down into the reservoir F, and the helium was admitted slowly so that the mercury might not be carried up into the bulb above the mark m_1. After about an hour, when the helium had diffused through the carbon dioxide, the pressure was constant and was measured. The same kind of corrections were applied as when the gases were measured in bulb C. After subtracting the partial pressure of the carbon dioxide from the total pressure, the volume of space occupied by the helium was easily calculated by using the gas law (V in Table II). Several determinations at different times with the carbon dioxide omitted gave values for the volume when no carbon dioxide was adsorbed. These values are recorded in Table I as V_0. The difference was the volume of the adsorbed layer into which the helium could not penetrate. The calculations with Polanyi's theory showed that the helium did not penetrate very far into the adsorbed layer. The weight of adsorbed gas was calculated from the amount measured in the bulb C, allowing for the amount left unadsorbed in the charcoal

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[5] "International Critical Tables," Vol. I, p. 72.

bulb. In the calculations PV values were used with the pressure in cm. of mercury and the volume in ml. The acceptable results of the experiments are tabulated in Tables I and II.

TABLE I

VOLUME OF BULBS CONTAINING CHARCOAL

PV of helium used		2817	2857	2719
Volume of bulb, cc.		36.214	36.213	36.214
PV of helium used	1900	2014	1974	1918
Volume of bulb, cc.	33.219	33.200	33.200	33.200

TABLE II

DENSITY OF ADSORBED CARBON DIOXIDE

PV of CO_2(p. in cm.; V in ml.)	PV of helium	Eq. press. CO_2, cm.	Obsd. vol. change	Density adsorbed CO_2
2925	2329	1.856	0.073	0.91
2983	2741	1.945	.075	.90
4884	1913	2.230	.124	.90
10003	1852	5.119	.263	.860
10572	1918	5.584	.278	.866
9887	1907	5.956	.263	.854
14612	1914	8.367	.377	.882
15434	1765	8.628	.407	.865
30666	1545	21.100	.822	.845
30532	1520	21.252	.814	.850

Lowry and Olmstead's[6] method of calculation was followed in applying Polanyi's condensed film theory to the experimental data. Their notation is also used in this paper. These authors showed that the work of compressing carbon dioxide at 303.1°K. from a molal volume,[7] $V = 1$ to a molal volume V_{δ_i}, is given by

$$\epsilon_i = 4.5767T\left[\frac{0.4343(b_g)_T}{V\delta_i - (b_0)_T} - \frac{237.213\ a_T}{TV\delta_i} - \log V\delta_i - \frac{(b_g)_T}{(b_0)_T}\log\left(1 - \frac{(b_0)T}{V\delta_i}\right)\right]$$

If the original pressure is such that V is not equal to 1, then a $\Delta\epsilon$ is calculated by $\Delta\epsilon = 4.5767\ T \log V_{\delta_x}$. The values given by this equation (see Table III) are needed to calculate the curve. The values given in Table IV and calculated from the experimental results are also needed. The resulting ϵ–φ curve (see Table V and Fig. 2) was used to calculate the milligrams of carbon dioxide adsorbed per gram of charcoal (see last column in Table IV). The calculations for one of the experimental values are given in Table VI, which shows how the average density can vary with the adsorption volume, φ.

TABLE III

VALUES OF ϵ_i FOR DIFFERENT DENSITIES δ_i

δ_i	$V\delta_i \times 10^3$	ϵ_i (calc.)	ϵ_i (used)
0.01	195.23	958	958
.05	39.05	1825	1825
.10	19.52	2113	2113
.20	9.762	2300	2300
.30	6.507	2325	2325
.334	5.857	2321	2321
.4	4.881	2303	
.5	3.905	2269	
.6	3.254	2246	2321
.7	2.789	2251	2326
.8	2.440	2302	2377
.9	2.169	2424	2499
1.0	1.952	2652	2727
1.1	1.775	3039	3114
1.2	1.627	3693	3768
1.3	1.502	4818	4893
1.4	1.394	6945	7020
1.5	1.302	11669	11744

$a = 0.007312 \quad b_g = 0.002381 \quad b_0 = 0.001171$

Density of vapor (30°) 0.334.

Density of liquid[a] 0.598.

[a] Lowry and Erickson, THIS JOURNAL, **49,** 2729 (1927).

TABLE IV

MILLIGRAMS OF CARBON DIOXIDE ADSORBED PER GRAM OF CHARCOAL

CO_2 pressure	x (obsd.)	$\Delta\epsilon$	x (calcd.)
1.856	3.78	2299	3.77
1.945	3.87	2271	3.87
2.230	4.30	2189	4.45
5.119	8.80	1688	8.89
5.584	9.70	1636	9.57
5.956	8.68	1597	10.11
8.367	12.83	1392	12.92
8.628	13.56	1374	13.19
21.100	26.84	835	26.69
21.252	26.72	830	26.83

$V_{\delta_i} = 84.337/P$(cm. of Hg): $\epsilon_s = \Delta\epsilon + 2321$.

TABLE V

ADSORPTION POTENTIAL, ϵ, AND VOLUME OF ADSORPTION, φ

ϵ, cal.	7250	6000	5000	4606	3982	3702
φ, cu. mm.	0	0.50	1.80	2.84	7.50	10.90
ϵ, cal.	3153	2500	2000	1500	1000	500
φ, cu. mm.	22.90	50.0	85.0	120	139	149

It is also possible to calculate how far the helium penetrated into the layer of adsorbed carbon dioxide by using the ϵ–φ curve. The experiments gave the volume of the adsorbed layer (see Table II). The boundary of this layer is characterized by an "adsorption potential" which corresponds to the work required to compress the gas from the density at the equilibrium pressure to the density at the boundary of the adsorbed layer. Hence when $\Delta\epsilon$ is subtracted from ϵ, values of ϵ_i are obtained from which densities of carbon dioxide can be determined with the use of the data in Table III. The results of the calculation are given in

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[6] Lowry and Olmstead, *J. Phys. Chem.*, **31,** 1601 (1927).

[7] In Lowry and Olmstead's notation, $V = 1$ represents a volume of 22,416 ml. and $V\delta_i$ a molal volume corresponding to the density δ_i g. per ml.

Table VII. It is evident that the helium did not penetrate appreciably into the layer of adsorbed carbon dioxide when the density was larger than 0.09 g. per ml.

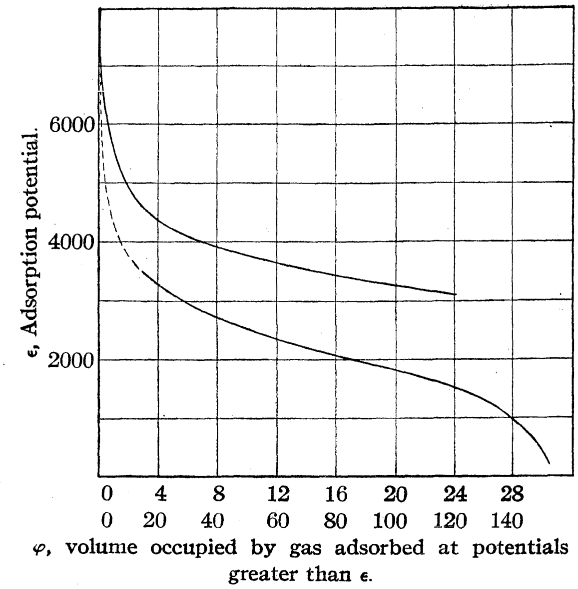

Fig. 2.—Upper curve is a five-fold extension of the dotted section. See Table V for values of the complete lower graph.

TABLE VI

CALCULATION OF AMOUNT OF CARBON DIOXIDE ADSORBED

δ_i	ϵ_i	ϵ	φ	$\Delta\varphi$	$\bar{\delta}$	x
	0	830	143			
0.01	958	1788	100	43	0.005	0.215
.05	1825	2655	43	57	.03	1.710
.10	2113	2943	30.5	12.5	.075	0.937
.334	2321	3151	23.0	7.5	.067	.488
.6	2321	3151	23.0			
.9	2499	3329	18.8	4.2	.750	3.150
1.0	2727	3557	13.5	5.3	.950	5.040
1.1	3114	3944	7.3	6.2	1.050	6.510
1.2	3768	4598	2.9	4.4	1.150	5.070
1.3	4893	5723	0.7	2.2	1.250	2.750
1.372		7250	0.0	0.7	1.336	0.960
1.4	7020	7850				

x (calcd.) = 26.83. x (obsd.) = 26.72. x_s = 23.48

TABLE VII

LIMIT OF PENETRATION OF HELIUM INTO CARBON DIOXIDE

x, mg.	φ (obsd.)	ϵ	$\Delta\epsilon$	ϵ_i	δ_i
3.78	4.20	4360	2299	2061	0.087
3.87	4.30	4340	2271	2069	.089
4.30	4.80	4270	2189	2081	.091
8.80	10.23	3760	1688	2072	.090
9.70	11.20	3690	1636	2054	.086
8.68	10.16	3770	1597	2173	(.115)
12.83	14.54	3520	1392	2128	.105
13.53	15.68	3460	1374	2086	.092
26.84	31.76	2900	835	2065	.088
26.72	31.44	2910	830	2080	.091
				Average	0.091

When the application of Polanyi's theory to the experimental data is considered from the viewpoint of how much of the adsorption volume, φ, must be included to obtain an average density equal to that observed experimentally, then it is evident, as can be seen from one of the calculations given in Table VI, that the experimental values agree well with the densities which can be calculated with the aid of Polanyi's theory, and that less than 10% of the carbon dioxide, which can still be considered as under the attractive influence of the charcoal, mixes with the helium.

The author acknowledges with gratitude a Grant-in-Aid from the National Research Council for this research project which is being continued.

Summary

1. By using helium as an inert gas the density of adsorbed carbon dioxide on charcoal was determined at 30°.

2. By using Lowry and Olmstead's modification of Polanyi's theory, an ϵ–φ curve was calculated. From the experimental results and this curve, it was shown that helium did not penetrate the carbon dioxide layer when its density was more than 0.09 g. per ml.

3. Polanyi's theory gives densities for the adsorbed layer equal to those observed if the assumption is made that the helium penetrates the outer portion of the adsorbed layer.

LAFAYETTE, IND. RECEIVED JUNE 24, 1935

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

The Photo-oxidation of Hydrogen and Deuterium Iodides[1]

BY G. A. COOK AND J. R. BATES

Many investigations[2] have been made of the reaction of hydrogen atoms with oxygen molecules. One such study was that of Bates and Lavin,[3] who obtained the hydrogen atoms for the reaction by the photo-dissociation of hydrogen iodide. It was pointed out by Bodenstein and Schenk[4] that the results of Bates and Lavin might be equally well explained on the assumption that the reaction $H+O_2$ occurred as either a two-body or a three-body process. The present work represents an attempt to differentiate between these two alternatives by studying the same reaction with improved experimental accuracy and under much more widely varied conditions. The problem is of theoretical importance in connection with the interpretation of a number of different reactions[2] such as the explosion limits of hydrogen and oxygen,[5] the effect of oxygen on the photochemical hydrogen–chlorine reaction,[4] etc. The general theoretical implications of the problem have been discussed by Kassel.[6]

A similar study was also made on the reaction of deuterium iodide with oxygen. A comparison of the results for hydrogen and deuterium iodides is of interest in connection with the effect of mass and zero point energy on chemical reactions.[7]

Method and Apparatus

The method used was similar to that of Bates and Lavin.[3] A mixture of hydrogen (or deuterium) iodide with oxygen (and also in a few cases with nitrogen) in a quartz reaction vessel of 277.1 cc. effective volume, was illuminated, the pressure change was noted and the products analyzed for hydrogen and iodine. The reaction vessel was kept at 0° except in two 20° runs. The source of light was a low-voltage mercury–argon quartz lamp designed by Duffendack and Owens.[8] It used a nickel cathode activated by a coating of barium and strontium oxides.

The hydrogen iodide was synthesized by passing a mixture of hydrogen and iodine vapor through a tube containing two glowing platinum spirals, the first spiral being kept hotter than the second. Deuterium iodide was made in a similar way, using deuterium obtained by electrolysis of 99.9% D_2O.

No stopcocks were employed in connection with the reaction vessel or the storage tube for hydrogen iodide; instead, two greaseless valves were employed. These made use of a glass bellows similar to that of Bodenstein,[9] but substituting for his glass-in-glass seat a fused silver chloride seat as described by Ramsperger.[10]

The hydrogen was analyzed by a method suggested by Professor H. N. Alyea of Princeton. It made use of a sensitive slanting mercury manometer, calibrated for the purpose, to measure the decrease in both pressure and volume resulting from the combustion of hydrogen in a sample of known volume.

The rest of the apparatus was essentially the same as that described by Bates and Lavin.[3]

Experimental Results

Results of the runs are incorporated in the tables.

TABLE I

RUNS MADE WITH HYDROGEN IODIDE AND OXYGEN

HI_0	Initial oxygen	HI decomposed	H_2 formed	k_2/k_1[a]	$k_5/k_1 \times 10^4$
200.6	506.4	36.57	14.84	0.084	1.20
200.5	449.9	37.15	15.20	.090	1.53
199.9	400.7	41.92	17.39	.092	1.56
150.8	551.1	41.56	15.22	.086	1.25
150.6	550.0	44.44	16.99	.072	1.05
151.3	449.2	32.38	13.57	.058	0.98
150.2	450.0	35.19	13.88	.079	1.34
151.4	350.6	35.23	14.89	.070	1.42
150.9	352.5	32.96	14.15	.063	1.27
100.6	601.3	35.41	11.64	.072	1.04
99.9	608.8	40.48	13.19	.069	1.00
99.3	499.5	27.86	9.64	.076	1.28
101.0	451.1	37.95	14.40	.057	1.06
50.0	699.4	41.07	7.07	.077	1.05
49.8	700.7	34.34	6.19	.081	1.10
50.2	600.3	30.01	6.83	.068	1.07
50.0	602.1	30.42	6.94	.067	1.06
50.2	499.7	30.24	7.47	.070	1.31
50.1	500.3	32.82	7.89	.070	1.32
50.0	398.6	25.38	6.89	.077	1.76
50.2	400.0	37.77	10.36	.060	1.39
38.5	362.1	10.82	3.39	.054	1.37
25.5	702.4	21.44	2.75	.059	0.82
25.7	507.1	20.55	3.21	.063	1.22
24.8	499.9	21.95	3.24	.062	1.20
25.1	300.3	20.57	5.32	.042	1.32
26.1	300.3	21.95	5.37	.048	1.51

[a] Assuming that $k_4/k_3 = 0$.

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[1] (a) The material in this paper comprises a portion of a thesis presented by Gerhard Albert Cook to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1935. (b) Presented before the Division of Physical and Inorganic Chemistry at the New York Meeting of the American Chemical Society, April 22–26, 1935.

[2] (a) For references see Bates, *J. Chem. Phys.*, **1**, 457 (1933); (b) Farkas and Sachsse, *Z. physik. Chem.*, **B27**, 111 (1934).

[3] Bates and Lavin, THIS JOURNAL, **55**, 81 (1933).

[4] Bodenstein and Schenk, *Z. physik. Chem.*, **B20**, 420 (1933).

[5] Kassel and Storch, paper presented before the Division of Physical and Inorganic Chemistry at the New York Meeting of the American Chemical Society, April 22–26, 1935.

[6] Kassel, in "Annual Survey of American Chemistry," Chemical Catalog Company, New York, 1934, Vol. VIII, pp. 27–30.

[7] Eyring, *J. Chem. Phys.*, **3**, 107 (1935).

[8] Unpublished paper.

[9] Bodenstein, *Z. physik. Chem.*, **B7**, 387 (1930).

[10] Ramsperger, *Rev. Sci. Instruments*, **2**, 738 (1931).

TABLE II

RUNS MADE WITH DEUTERIUM IODIDE AND OXYGEN

DI_0	Initial O_2	DI_0-HI_F	D_2 formed	k_2/k_1[b]	$k_5/k_1 \times 10^4$
198.7	516.6	51.59	17.22	0.166	2.39
200.8	513.5	29.91	10.19	.169	2.39
201.4	301.0	29.20	11.62	.158	3.21
151.2	543.0	33.95	10.65	.147	2.16
150.0	399.7	44.26	15.44	.138	2.58
150.3	297.6	28.31	10.70	.148	3.38
99.3	605.0	53.37	11.73	.152	2.24
100.4	599.0	28.31	7.45	.129	1.88
100.6	499.9	25.64	7.67	.118	1.99
100.1	397.7	26.31	8.96	.102	2.09
50.7	649.3	25.55	4.98	.090	1.31
52.2	300.8	26.62	7.59	.096	2.83
26.1	688.1	20.35	1.68	.115	1.64
25.1	297.3	18.35	3.45	.085	2.73
101.3[a]	497.6	47.64	13.18	.124	2.15
100.5[a]	498.5	26.95	8.31	.108	1.85

[a] 20.0°, all other runs at 0°. [b] Assuming that $k_4/k_3 = 0$.

TABLE III

SPECIAL PAIRS OF RUNS MADE WITH AND WITHOUT NITROGEN

HI_0	Initial O_2	Initial N_2	$HI_0 - HI_F$	H_2 formed	k_2/k_1[a]	$k_5/k_1 \times 10^4$
50.3	299.0	...	23.51	8.99	0.039	1.14
51.3	301.7	388.4	24.26	6.75	.102	1.39
50.9	198.4	...	30.93	12.73	.036	1.52
50.5	205.1	474.2	34.66	10.65	.096	1.34
25.6	150.3	...	18.97	7.58	.024	1.43
24.7	150.2	473.7	21.11	5.02	.094	1.46
DI_0				D_2		
50.5	101.7	...	19.69	8.77	0.048	3.31
51.8	104.2	391.8	16.35	5.99	.149	2.75
24.3	100.4	...	14.75	6.15	.032	2.67
24.5	98.2	369.3	17.69	4.42	.152	3.14

[a] Assuming that $k_4/k_3 = 0$.

In general these data confirm the experimental results of Bates and Lavin, and in addition it is immediately evident that the following qualitative statements are true: (1) in any two runs, if all conditions are the same except that hydrogen iodide is used in one and deuterium iodide in the other, more of the deuterium is always oxidized than of the hydrogen; and (2) in any two runs, if all conditions are the same except that nitrogen is added in one case and not in the other, a great deal more of the hydrogen is oxidized when the nitrogen is added than when it is absent. In other words, the presence of an inert gas greatly speeds up the reaction of hydrogen atoms with oxygen molecules. This is true whether hydrogen or deuterium is used.

Products of the Oxidation

No experimental test was made for hydrogen peroxide in the presence of the hydrogen iodide; instead, the pressure of hydrogen that should have been formed was calculated from the observed decrease in pressure[3] (page 86) under two assumptions: (1) that only hydrogen peroxide formed; (2) that only water formed. These calculated results were then compared with the actual pressure of hydrogen formed as determined by the gas analysis. Results showed that assumption (1) gave about twice as good results as (2), the two hydrogen pressures always lying between the values calculated on each of the two assumptions. Thus apparently about one-third of the hydrogen peroxide formed[11] decomposed to water during the run. Most of the runs lasted ten minutes; a few of them fifteen minutes.

Theoretical Discussion

The two mechanisms to be compared were as follows.

MECHANISM I

(A)	$HI + E \longrightarrow H + I$	A
(1)	$H + HI \longrightarrow H_2 + I$	k_1
(2)	$H + O_2 \longrightarrow HO_2$	k_2
(3)	$HO_2 + HI \longrightarrow H_2O_2 + I$	k_3
(4)	$HO_2 \longrightarrow H + O_2$	k_4

leading to the integrated expression

$$[H_2] = -\frac{1}{2}\left[HI_F - HI_0 + ([O_2]k_2/k_1) \ln \frac{HI_0 + [O_2]k_2/k_1 + k_4/k_3}{HI_F + [O_2]k_2/k_1 + k_4/k_3}\right] \qquad (I)$$

in which $[H_2]$ = the pressure of hydrogen formed during the reaction; HI_0 = the initial pressure of hydrogen iodide; HI_F = the final pressure of hydrogen iodide; $[O_2]$ = the average pressure of oxygen; all pressures being measured in millimeters.

MECHANISM II

(A)	$HI + E \longrightarrow H + I$	A
(1)	$H + HI \longrightarrow H_2 + I$	k_1
(5)	$H + O_2 + M \longrightarrow HO_2 + M'$	k_5
(3)	$HO_2 + HI \longrightarrow H_2O_2 + I$	k_3

leading to the integrated expression

$$[H_2] = -\frac{1}{2}\left[HI_F - HI_0 + ([O_2][M]\,k_5/k_1) \ln \frac{HI_0 + [O_2]\,[M]\,k_5/k_1}{HI_F + [O_2]\,[M]\,k_5/k_1}\right] \qquad (II)$$

in which $[M]$ = the average total pressure.

From equation (I) values of k_2/k_1 may be calculated for any assumed value of k_4/k_3. From equation II values of k_5/k_1 may be calculated directly. Results of these calculations are given in Tables I, II and III.

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[11] Bates and Salley, THIS JOURNAL, **55**, 110 (1933).

It is seen that for pairs of runs in which the only difference is the presence or absence of nitrogen (Table III) the value of k_5/k_1 remains fairly constant, whereas the value of k_2/k_1 (assuming $k_4 = 0$) is not constant. k_2/k_1 values were calculated also for values of k_4/k_3 up to 10^6, but the values of k_2/k_1 did not stay constant under any conditions. The evidence seems to show, therefore, that Mechanism II is much to be preferred to Mechanism I, and hence that the action of hydrogen atoms on oxygen molecules is a trimolecular process.

The values of k_5/k_1 show a slight variation with the O_2:HI ratio employed. This particular variation can be eliminated by using a more complicated mechanism, replacing the step $H + O_2 + M$ with the steps:

$$\begin{array}{lll} (6) & H + O_2 + O_2 \longrightarrow HO_2 + O_2' & k_6 \\ (7) & H + O_2 + N_2 \longrightarrow HO_2 + N_2' & k_7 \\ (8) & H + O_2 + HI \longrightarrow H_2O_2 + I & k_8 \end{array}$$

For this the integrated expression is found to be

$$\frac{1}{K} = \frac{1}{(HI_0 - HI_F - 2[H_2])\,(1 + [O_2]k_8/k_1)} \ln \frac{HI_0 + K}{HI_F + K}$$

$$\text{Where } K = \frac{[O_2]\,k_6/k_1 + [O_2]\,[N_2]\,k_7/k_1}{1 + [O_2]\,k_8/k_1}$$

To simplify the calculations, it was assumed that $k_6 = k_7$. Various values of k_6/k_1 were assumed and the corresponding values of k_8/k_1 calculated. For both hydrogen and deuterium it was found that $k_8/k_1 \cong 2k_6/k_1$; hence $k_8 \cong 2k_6$.

The mean values found experimentally were as follows, the errors indicated being mean deviations.

(1) From Table I, hydrogen iodide plus oxygen
$k_5/k_1 = (1.24 \pm 0.17) \times 10^{-4}\,\text{mm.}^{-1} = (2.11 \pm 0.29) \times 10^3\,\text{cc. mol.}^{-1}$

(2) From Table II, deuterium iodide plus oxygen,
$k_5/k_1 = (2.34 \pm 0.44) \times 10^{-4}\,\text{mm.}^{-1} = (3.98 \pm 0.75) \times 10^3\,\text{cc. mol.}^{-1}$

The rate k_5 of the reaction $H + O_2 + M$ varies somewhat with the nature of the third body.[12] In the present work, the third body was chiefly either oxygen or hydrogen iodide.

Moreover, the value to be assigned to k_5 depends on the value assumed for k_1, since experiment gave only the ratio of k_5 to k_1. It is known from the work of Bonhoeffer and Farkas[13] that $(k_{H + I_2})/(k_{H + HI}) \cong 100$. The reaction $H + I_2$ should go on every collision since the reaction has zero activation energy and there is no reason to ascribe to it a steric factor which would materially differ from unity.[14] However, the value 100 is only approximate and can be trusted only to an order of magnitude.

The constant $k_{H + HI}$ may be calculated, using the usual equation given for the number of collisions per cubic centimeter per second between the molecules of two different gases. The result is $k_{H + I_2} = 2.699 \times 10^{14}$ cc.^{2} moles^{-1} sec.$^{-1}$. Then $k_{H + HI} = 2.699 \times 10^{12}$, and $k_{H + O_2 + M} = 5.7 \times 10^{15}$. That k_5 is probably smaller than this value may be seen from the following considerations. It was shown above that $k_{H + O_2 + HI} \cong 2k_{H + O_2 + O_2}$. If the reaction $H + O_2 + HI$ goes on every collision, then its specific reaction rate as calculated by the method outlined by Bates[2a] (p. 460) using $\tilde{\nu} = 3804$ cm.$^{-1}$, is $k_8 = 2.4 \times 10^{14}$ cc.^{3} moles^{-2} sec.$^{-1}$. This would give $k_6 \cong k_8/2 \cong 1.2 \times 10^{14}$. There are two other reasons for choosing this value rather than the maximum value of 5.7×10^{15} calculated above for $H + O_2 + M$.

(1) Calculation shows that if the reaction $H + O_2 + O$ goes on every trimolecular collision, k_6 would be only 3.0×10^{14}. This makes the high value ot 5.7×10^{15} seem improbable.

(2) In a study of the rate of recombination of hydrogen atoms and of the reaction $H + O_2$, Farkas and Sachsse[2b] found that $k_{H + H + H_2} \cong 3.4 \times 10^{16}$ cc.^{3} moles^{-2} sec.$^{-1}$, and that $k_{H + H + H_2}/k_{H + O_2 + H_2} \cong 500$. If their value for $k_{H + H + H_2}$ is used together with the value of 1.2×10^{14} for $k_{H + O_2 + O_2}$, it is seen that $k_{H + H + H_2}/k_{H + O_2 + O_2} = 283$, which is in remarkably good agreement with their ratio of 500 mentioned above. If Steiner's best value[15] for $k_{H + H + H_2} = 1.1 \times 10^{16}$ is used, $1.1 \times 10^{16}/1.2 \times 10^{14} = 91$, which is still in fair agreement with the ratio found by Farkas and Sachsse. But if Smallwood's value[16] of $k_{H + H + H_2} = 3.4 \times 10^{14}$ is used, the ratio is 3, in disagreement by a factor of over 150 with the findings of Farkas and Sachsse. Extremely poor agreement is found if the maximum value of 5.7×10^{15} for $k_{H + O_2 + M}$ is used, the ratios with the same three values of $k_{H + H + H_2}$ mentioned above being 6, 2 and 0.06, respectively.

If the value of $k_{H + O_2 + O_2}$ is taken, therefore, as 1.2×10^{14}, and compared with the calculated value for the same reaction if it went on every collision, namely, 3.0×10^{14}, it is seen that the reaction goes on at least one out of every two or

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(12) Senftleben and Hein, *Ann. Physik*, **22**, 1 (1935).

(13) Bonhoeffer and Farkas, *Z. physik. Chem.*, **132**, 235 (1928).

(14) Bates, *ibid.*, **B22**, 469 (1933).

(15) Steiner, *Trans. Faraday Soc.*, **31**, 623 (1935).

(16) Smallwood, THIS JOURNAL, **56**, 1542 (1934).

three trimolecular collisions, a result that is not at all in bad agreement with the conclusion of Bodenstein and Schenk[4] that $H + O_2 + M$ goes on every trimolecular collision. Their third body was in part oxygen, but also largely hydrogen and chlorine.

The results of the present study together with that of Farkas and Sachsse[2b] may be taken as evidence that Steiner's value[15] for the rate of recombination of hydrogen atoms is much to be preferred to Smallwood's latest value.[16] In this connection it is interesting to note that Senftleben in his most recent work[12] completely reverses his previous stand[17] with regard to the relative efficiencies of hydrogen atoms and molecules as the third body in the recombination of hydrogen atoms, bringing his latest findings in this regard into line with those of Steiner[15] and Farkas and Sachsse.[2b] This is doubly confusing in that Smallwood's method, of all those used, seems to offer the least possibility of experimental difficulty. In addition, Amdur[18] in a recent publication claims to have as yet unpublished data which confirm the results of Smallwood.

It may also be shown in this connection that if the trimolecular recombination of hydrogen atoms takes place almost wholly with hydrogen *atoms* as third body, as Smallwood[16] believes, the thermal decomposition of the molecules must proceed through activation by collision with atoms: $H + H_2 \longrightarrow 3H$. This would mean that activation by an atomic collision must be about 100 times more effective than a similar collision involving molecules. Why this should be is not at present immediately evident.

There are several reasons why an exact agreement between the values of $k_{H + O_2 + M}$ as determined by Farkas and Sachsse and ourselves should not be obtained. The third bodies (M) are different, and in addition, the re-formation of hydrogen atoms by the reaction $HO_2 + H_2$ might take place to a large extent at low oxygen pressures[2a] (p. 461). It is apparent that for a better comparison between our work and that of Farkas and Sachsse the large discrepancy between the results of Smallwood and Steiner's work on the rate of recombination of hydrogen atoms should be cleared up, and an investigation of the inhibiting effect of iodine on the reaction $H + HI$ should be included in our program of photoreaction studies.

Deuterium Atoms

The experimental results yield the relationship $\frac{k_{D + O_2 + M}}{k_{H + O_2 + M}} \times \frac{k_{H + HI}}{k_{D + DI}} = 1.89$. Kinetic theory leads to the conclusion that the rates of the two trimolecular reactions should not be a function of the masses of the hydrogen and deuterium atoms, since the increased number of collisions between the H and O_2 would be just compensated by the smaller lifetime of HO_2. On the other hand, if the full zero point energy difference (936 calories) were operative, the reaction $H + HI$ should be 7.8 times as fast as the reaction $D + DI$. Thus we are led to the belief that the zero point energies of the respective activated complexes[7] are of the same magnitude as those of the halide molecules. If this is so, the frequencies of the complex must be fairly high, calling for a dependence of the reaction rates upon mass lying between $(\mu_1/\mu_2)^{1/2}$ and $(\mu_1/\mu_2)^{3/2}$, where the μ's are reduced masses. This is in agreement with the results found.

Summary

1. Definite evidence has been given to show that the reaction between hydrogen atoms and oxygen molecules is a three-body process.

2. The experimental data yielded the following mean values (with mean errors). $k_{H + O_2 + M}/k_{H + HI} = (2.11 \pm 0.29) \times 10^3$ cc. × mole^{-1}, and $k_{D + O_2 + M}/k_{D + DI} = (3.98 \pm 0.75) \times 10^3$ cc. × mole^{-1}.

3. Evidence has been given to show that Steiner's value[15] for $k_{H + H + H_2}$ is to be preferred to the very different one given by Smallwood.[16]

4. Calculation shows that $k_{H + O_2 + O_2} \cong k_{D + O_2 + O_2} \cong 1.2 \times 10^{14}$ cm.^{2} moles^{-2} sec.$^{-1}$.

ANN ARBOR, MICHIGAN

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(17) Senftleben and Riechemeier, *Physik. Z.*, **30**, 745 (1929).

(18) Amdur, THIS JOURNAL, **57**, 856 (1935).

[CONTRIBUTION FROM THE FRUIT PRODUCTS LABORATORY AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

The Kinetics of Absorption of Oxygen by Catechol

BY M. A. JOSLYN AND G. E. K. BRANCH

The absorption of oxygen by polyhydric phenols and its catalysis by ferric and manganous ions, by alkali, and by plant phenolases is well known. However, the kinetics of the reaction in absence of any other catalyst but alkali have not been systematically investigated, except in the case of hydroquinone for which the results as to order of the reaction with respect to OH^- have been rather contradictory.[1,2,3,4,5,6,7]

In this paper we are reporting a study of the kinetics of the auto-oxidation of catechol in absence of any catalyst but alkali and in the absence of light.

A fairly stable *p*-quinone is formed in the oxidation of hydroquinone so that the kinetics of its auto-oxidation may be studied either by determining the rate of absorption of oxygen or the rate of formation of quinone. However, the *o*-quinone is much more unstable[8] and the auto-oxidation of catechol is more complex, yielding intensely dark brown products which are evidently compounds of considerable complexity.

Auto-oxidations in general involve a preliminary absorption of oxygen with the formation of peroxides, followed by secondary reactions. The initial rate of absorption of oxygen is a measure of the rate of the primary reaction. When the subsequent reactions do not involve oxygen gas, or are slow with respect to the primary reaction, and when no catalyst or inhibitor is produced during the reaction, the initial rate of absorption of oxygen remains constant over a measurable time during which absorption of appreciable quantities of gas occurs, and the rate of the primary reaction can be measured. It is evident that the primary reaction as defined above is not necessarily the first step in the reaction. For instance, it cannot be the formation of active chain continuing molecules, for the time taken to reach a steady state of such active molecules is too short to be measured. It is probably the formation of peroxides no longer capable of continuing a chain leading to the absorption of oxygen.

In the auto-oxidation of catechol in buffered alkaline solution, easily measured quantities of oxygen are absorbed at a constant rate (see Fig. 2). Further evidence that this constant rate of absorption of oxygen is a measure of the rate of the primary reaction was given by the fact that the rate was unaltered in the presence of about 10% of freshly oxidized catechol. It was found also that the rate of the primary reaction could be measured in alkaline solutions even in absence of buffer.

The dependence of the primary reaction on such variables as H^+-ion concentration, catechol concentration, partial pressure of oxygen, temperature and surface was studied, both in buffered and unbuffered solutions.

Experimental Part

Reagents.—A fresh stock of Eastman catechol was used without further purification. The crystals were perfectly colorless, gave a colorless solution, and melted sharply at 105°. The other chemicals used were of the purest commercial grade obtainable, either Eastman or analytical reagent grade.

Apparatus.—The rate of oxygen absorption was followed by measuring the rate of decrease in pressure, at practically constant volume, occurring when definite quantities of catechol dissolved in water, phosphate buffers or sodium hydroxide solutions, were rapidly shaken in an atmosphere of oxygen. The apparatus consisted essentially of two flasks, each connected to one arm of a manometer, to each other, and to an oxygen supply and a vacuum pump so that they could be at will flushed out and filled with oxygen at the desired pressure. Both flasks were connected to a metal swing and immersed in a darkened thermostat at 25 ± 0.03°. The manometer liquid was Brodies' solution[9] and the volume of the manometer was small, less than 0.1% of the volume of the flasks. During each individual experiment the concentration of catechol and the pressure of oxygen were practically constant as the total amount of oxygen absorbed was small with respect to both the oxygen and the catechol in the reaction vessel.

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(1) Hans v. Euler and Ivan Bolin, *Z. phyisol. Chem.*, **57**, 80 (1908).

(2) Victor K. La Mer and Eric K. Rideal, THIS JOURNAL, **46**, 223 (1924).

(3) Hans v. Euler and Edvard Brunius, *Z. physik. Chem.*, **139**, 615 (1928).

(4) Victor K. La Mer and J. W. Temple, *Proc. Nat. Acad. Sci.*, **15**, 191 (1929).

(5) René Dubrisay and Albert Saint-Maxen, *Compt. rend.*, **189**, 694 (1929).

(6) Albert Saint-Maxen, *ibid.*, **191**, 212 (1930).

(7) W. Reinders and P. Dingemans, *Rec. trav. chim.*, **53**, 209–230 (1934).

(8) For example see J. B. Conant and L. F. Fieser, THIS JOURNAL, **46**, 1858 (1924).

(9) R. Siebeck in Emil Abderhalden, "Handbuch der biochemischen Arbeitsmethoden," 1915, Vol. VIII, p. 25.

The rates are expressed in cc. of oxygen at 25° and 1 atmosphere absorbed by 125 cc. of solution.

The experiments were performed by introducing 100 cc. of the buffer solution or other substrate into one of the flasks, and 25 cc. of freshly prepared aqueous catechol solution (usually 0.5 *M*) into a small tube supported in the flask by a glass rod. Both flasks were evacuated and filled with oxygen. The system was then cut off from the oxygen supply and allowed to stand until temperature equilibrium was reached, usually one hour. The stopcocks connecting the two flasks were turned, the glass rod lifted to precipitate the catechol into the buffer solution and the shaker started. The shaking was sufficiently violent to shatter the tube, to cause practically immediate mixing, and to keep the solution in a state of froth. The empty thermostated flask attached to one arm of the manometer was found to effectively prevent movements of the manometer liquid other than those caused by the reaction.[10]

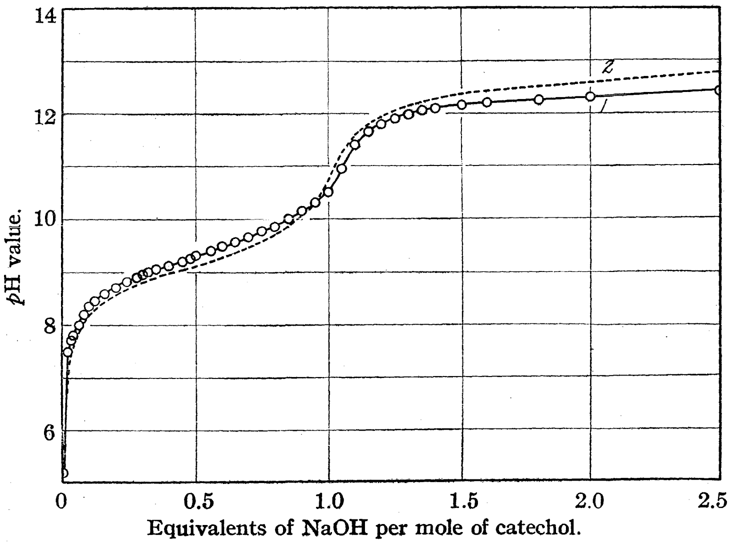

Fig. 1.—Titration curve: 1, pure catechol; 2, in presence 0.8 *M* KCl.

Measurement of pH.—The actual hydrogen-ion concentrations of the alkaline solutions of catechol used were measured by means of a Leeds and Northrup large bulb type glass electrode No. 7685 using an L and N saturated calomel electrode No. 7724, a type K potentiometer, and a 2500-f type R galvanometer. The glass electrode was used in preference to the hydrogen electrode, because of the difficulty of determining the *p*H of the alkaline catechol solutions by the latter, particularly in presence of the products of oxidation. However, by saturating the catechol solution with hydrogen and making the measurements in an atmosphere of hydrogen, it was found possible to measure *p*H values of unoxidized catechol solutions. The glass electrode was calibrated from *p*H 4 to 9 against buffers whose *p*H value was measured by a hydrogen electrode. The *p*H values above 9 were taken from an electrometric titration curve for unoxidized catechol determined in an atmosphere of hydrogen.

Accuracy.—Except in the most acid or most alkaline regions studied, the rates were readily reproducible to well within an error of 5%, particularly in buffered solutions. The results for the rates lower than 0.02 or higher than 20 cc. per minute were less accurate. The *p*H values were reproducible to less than ±0.05 unit except in the most alkaline range, where the limit of error is probably 0.1 unit. The internal evidence of the accuracy of the measurements indicates an average error of 7%, most of which is due to error in *p*H measurement.

Data and Discussion

Titration Curve.—Catechol is capable of existing in alkaline solutions in three forms—undissociated molecule, monovalent ion, and divalent ion—and it is necessary to know the proportions in which these various substances are present in a given solution. The dissociation constant of 3.2×10^{-10} given in the "International Critical Tables" (Vol. VI, p. 259) is corrected for salt effect and it was desirable to determine this value under our conditions in sodium hydroxide solutions and in the presence of added potassium chloride. The electrometric titration curve (at t = 23°) constructed in part from data obtained by glass electrode and in part by hydrogen electrode, both in absence and presence of 0.8 *M* potassium chloride for 0.1 *M* catechol is shown in Fig. 1. The pK value of the first dissociation is 9.3 without added salt and 9.1 in presence of 0.8 *M* potassium chloride. These values neglecting the slight temperature correction[11] are in fair agreement with the value given in the literature ($pK = 9.5$). The difference of these results from each other and from the accepted pK value of 9.5 is evidently due largely to a salt effect. The titration curve does not show a break for the second dissociation. This is in agreement with the results obtained by Kolthoff, who found that the conductivity curve for catechol shows only one break.[12] The lack of a second break indicates a pK value greater than 12.5 for the second dissociation. Sheppard[13] gives 1.75×10^{-10} and 3.97×10^{-12} as the two dissociation constants for hydroquinone.

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[10] The necessity for a thermobarometer to serve as a control is clearly pointed out by R. Siebeck, see reference 9, page 30.

[11] Following the procedure of Euler and Brunius[3] the temperature correction was made by comparison with Lundén's values for phenol at various temperatures [*Z. physik. Chem.*, **70**, 249 (1910)]. The values for k decrease with decrease in temperature but the pK values increase. The correction in our case amounts to about −0.03 pK units which is within the limits of experimental error.

[12] I. M. Kolthoff, *Z. anorg. allgem. Chem.*, **112**, 187–195 (1920).

[13] S. E. Sheppard, *Trans. Am. Electrochem. Soc.*, **39**, 429–440 (1922).

Homogeneity of the Reaction.—The addition of large amounts of powdered Pyrex or soft glass had no appreciable effect on the rate of oxygen absorption; the reaction is thus homogeneous and free of wall effects.

Difference between Buffered and Unbuffered Solutions.—When the reaction is carried out in a well buffered solution, whether an external buffer is used or the concentration of sodium hydroxide is sufficient to nearly half neutralize the catechol present, more than 10 cc. of oxygen can be absorbed without any noticeable change in the rate. But when no external buffer and only a small amount of sodium hydroxide is used the rate decreases after the absorption of but little oxygen, and the initial rates must be obtained by extrapolation. Typical runs obtained in phosphate buffers prepared by mixing 1 *M* dipotassium phosphate and 1 *M* monopotassium phosphate and in sodium hydroxide solutions, shown in Fig. 2, illustrate this behavior. This is nothing but the usual phenomenon that is shown by any reaction whose rate depends on the concentration of hydrogen ion and in which the hydrogen-ion concentration changes. That it occurs in this reaction shows that the products of the auto-oxidation of catechol include an acid or acids stronger than catechol.

We have tested for other factors causing a reduction in rate in unbuffered solutions. No gas was formed in the reaction for the residual oxygen was found to contain no impurity.[14] No inhibitor was formed during the reaction. This was shown by oxidizing an alkaline solution 0.01 *N* with respect to catechol and then using the resulting solution as a substrate for a new experiment. Both in unbuffered and buffered solutions these new experiments gave the same rate of oxygen absorption as in experiments with clean substrate and pure catechol at the same *p*H value. These experiments also show that no catalyst is formed in the reaction.

Confirmation of the production of an acid or acids in the auto-oxidation was obtained by measuring the *p*H values present after reactions in which the rate had changed considerably. In these cases the observed decrease in *p*H was more than sufficient to account for the change in rate.[15]

A similar decrease in rate was observed in the auto-oxidation of hydroquinone in unbuffered or slightly buffered solutions.[1,2,5] Dubrisay and Saint-Maxen[5] found that in presence of small amounts of sodium hydroxide the rate of oxygen absorption by hydroquinone rapidly decreases and finally tends to be practically zero, while the solution changes from alkaline to slightly acid.

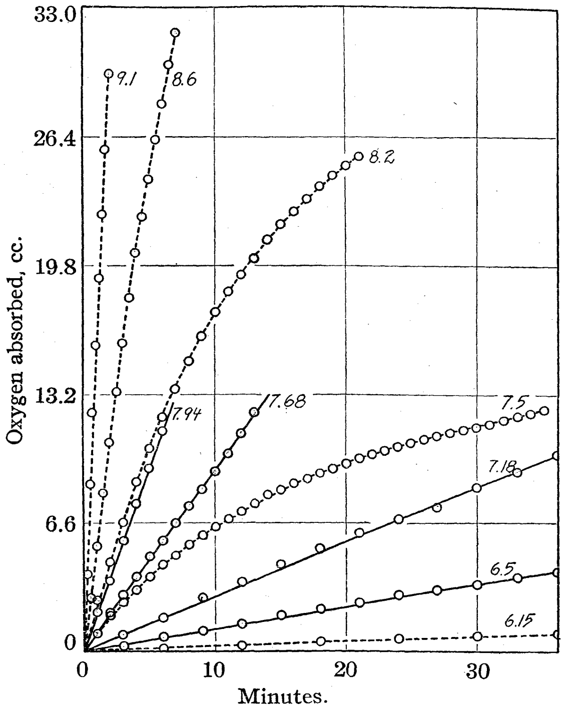

Fig. 2.—Rate of oxygen absorption at the *p*H values indicated on the curves: ——, in buffered solutions; ----, in NaOH solutions.

Variation of Rate with *p*H.—The results obtained for rates of oxygen absorption by a 0.1 *M* catechol solution in buffered solutions, and in sodium hydroxide solutions with and without added potassium chloride, at 1 atmosphere pressure of oxygen are shown in Tables I to V. The values of *K* were calculated on the assumption that the rate was directly proportional to the concentration of hydroxyl ions. It is seen that in all cases *K* is sensibly constant over a wide range of concentration. The average value of *K* in 0.8 *M* phosphate buffer solution is 1.46×10^6 in the range *p*H 6.5 to 8.25; in sodium hydroxide solutions it is 1.07×10^6 in the range *p*H 6.6 to 8.2; in sodium hydroxide solutions containing 0.8 *M* potassium chloride it is 1.89×10^6 in the range, *p*H 6.68 to 8.74; in sodium hydroxide solutions containing 1.6 *M* potassium chloride it

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[14] Carbon monoxide has been reported to be formed in the auto-oxidation of alkaline pyrogallol solutions.

[15] Alkaline solutions of catechol absorb oxygen so rapidly that an appreciable amount of reaction occurs between the cessation of rate measurements and measurement of *p*H values.

is 1.95×10^6 in the range *p*H 6.54 to 8.74; and in solutions containing 2.4 *M* potassium chloride it is 2.54×10^6 in the range *p*H 6.12 to 8.55.

TABLE I

RATE OF OXYGEN ABSORPTION IN PHOSPHATE BUFFERS

*p*H	K = rate in cm.^{3}/min./ (OH$^-$) $\times 10^{-6}$	*p*H	K = rate in cm.^{3}/min./ (OH$^-$) $\times 10^{-6}$
4.0	8.8	7.43	1.39
4.1	13.1	7.65	1.37
5.9	2.01	7.83	1.38
6.2	2.27	7.98	1.34
6.5	1.59	8.08	1.50
6.72	1.51	8.15	1.47
6.90	1.48	8.20	1.59
7.15	1.36	8.25	1.56

Av. k in range *p*H 6.5–8.25 = 1.46×10^6.

TABLE II

RATE OF OXYGEN ABSORPTION IN SODIUM HYDROXIDE SOLUTIONS

*p*H	K = rate (cc./min.)/ (OH) $\times 10^{-6}$	K' = rate/ (Cat.$^-$)	*p*H	K = rate (cc./min.)/ (OH) $\times 10^{-6}$	K' = rate/ (Cat.$^-$)
5.23	4.65	932	8.45	0.937	214
5.30	5.00	1000	8.60	.852	204
5.40	4.54	907	8.80	.802	210
5.53	1.98	395	8.88	.783	217
6.15	1.56	312	9.00	.704	211
6.60	1.00	199	9.10	.702	228
6.91	1.03	206	9.26	.588	225
7.10	1.045	211	9.39	.517	230
7.22	1.06	214	9.53	.435	235
7.65	1.04	213	9.69	.337	232
7.80	1.01	208	9.85	.262	237
7.85	1.20	248	10.25	.121	240
7.96	1.10	230	11.1	.199	255
8.05	1.14	239	11.9	.0408	324
8.10	1.08	229	12.3	.01785	357
8.20	1.075	231	12.5	.01195	378
8.35	0.906	202	12.7	.0089	445

Average K in *p*H region 6.60 to 8.2 is 1.07×10^6.
Average K' in *p*H region 6.60 to 10.25 is 221.

TABLE III

RATE IN SODIUM HYDROXIDE SOLUTIONS IN PRESENCE OF 0.8 *M* POTASSIUM CHLORIDE

*p*H	K = rate (cc./min.)/ (OH$^-$) $\times 10^{-6}$	K' = rate/ (Cat.$^-$)	*p*H	K = rate (cc./min.)/ (OH$^-$) $\times 10^{-6}$	K' = rate/ (Cat.$^-$)
5.22	3.97	501	8.95	1.345	288
5.31	3.92	493	9.07	1.305	315
5.54	4.24	532	9.20	1.088	308
5.80	3.25	292	9.36	0.825	293
6.68	1.93	243	9.52	.598	273
7.02	1.97	245	9.69	.418	258
7.40	2.11	270	10.03	.232	241
7.75	1.80	236	11.90	.302	240
7.85	2.30	303	12.11	.189	244
8.05	1.89	257	12.22	1.55	257
8.18	1.78	250	12.29	.147	287
8.28	1.61	234	12.32	.135	281
8.38	1.80	270	12.40	.122	306
8.53	1.755	280	12.60	.0800	318
8.58	1.87	306	12.8	.0513	323
8.74	1.82	327			

Average K in *p*H region 6.68 to 8.74 is 1.89×10^6.
Average K' in *p*H region 6.68 to 12.2 is 270.

TABLE IV

RATE IN SODIUM HYDROXIDE SOLUTIONS IN PRESENCE OF 1.6 *M* POTASSIUM CHLORIDE

*p*H	K = rate (cc./min.)/ (OH$^-$) $\times 10^{-6}$	*p*H	K = rate (cc./min.)/ (OH$^-$) $\times 10^{-6}$
4.8	6.66	7.93	1.97
5.30	2.60	8.07	1.88
5.88	2.39	8.30	1.84
5.73	3.07	8.40	1.96
6.54	1.90	8.48	2.08
6.91	1.90	8.58	1.97
7.35	1.88	8.74	1.81
7.45	1.90	8.91	1.57
7.68	2.21		

Av. k in range *p*H 6.54–8.74 = 1.95×10^6.

TABLE V

RATE IN SODIUM HYDROXIDE SOLUTIONS IN PRESENCE OF 2.4 *M* POTASSIUM CHLORIDE

*p*H	K = rate (cc./min.)/ OH$^-$ $\times 10^{-6}$	*p*H	K = rate (cc./min.)/ OH$^-$ $\times 10^{-6}$
4.84	6.35	8.0	2.64
5.72	5.45	8.1	2.67
6.12	2.67	8.2	2.75
6.63	2.00	8.34	2.69
6.95	2.17	8.44	2.69
7.22	2.77	8.55	2.54
7.65	2.36	8.81	1.91
7.85	2.53	8.95	1.73

Average K in *p*H range 6.12–8.55 = 2.54×10^6..

At the higher *p*H values, particularly in the two cases carried into the strongly alkaline range, K rapidly decreases with increase in *p*H. But this decrease in K is to be expected in the reaction of an acid in the range where the alkali concentration is sufficiently large to neutralize an appreciable fraction of the acid. If we assume that the rate of oxygen absorption, V, is proportional to the concentration of the monovalent catechol ion (cat.$^-$), the rate law can be expressed as

$$V = K' \frac{k_a C}{k_a + (\mathrm{H}+)}$$

where K' is the specific rate constant for the oxidation of cat.$^-$, k_a the first dissociation constant of catechol, and C the concentration of total catechol (= 0.1 *M*). The values of K' calculated from the above expression are shown in column 3 of Tables II and III. It can be seen that these values are practically constant almost throughout the entire range from slightly acid to strongly alkaline solutions. The average value of K' in absence of added salt is 221 and in presence of 0.8 M potassium chloride it is 270.

The constancy of K and K' suggests that the monovalent ion of catechol is the oxygen absorbing species. This is not strictly warranted because the product of (cat.) by (OH^-) is proportional to the concentration of (cat.$^-$) and the reaction may be one in which the OH ion acts as a basic catalyst for the oxidation of undissociated catechol.

In this case the negative ions of the phosphate buffer are also basic catalysts and the rate in buffered solution should be faster than in solutions in which the same pH values and ionic strength are obtained with sodium hydroxide and potassium chloride. This is contrary to the facts. It is, therefore, best to attribute the effect of alkali to the formation of the more reactive catechol ion from the less reactive undissociated catechol.

The constancy of K' from pH 6 to 10, shows that in this range absorption by the second ion of catechol is negligible, but in more alkaline solution there is a definite upward trend of the values of K' indicating that absorption of oxygen by the second ion has a greater specific rate than that by the first. If we assume that the absorption of oxygen by the second ion is first order with respect to its concentration, the rate in strongly alkaline solution ($p\text{H} > 10$) is given by the expression $V = K'(\text{cat.}^-) + K''(\text{cat.}^{--})$. On this assumption the rates in strongly alkaline solutions in the absence of potassium chloride correspond to values for K'' and the second dissociation constant of catechol having the orders of magnitude of 10^3 and 10^{-13}, respectively.

At low pH values, particularly below pH 6, K (and also K') is considerably higher than the average. This indicates that not only the ions but the undissociated catechol itself must be able to absorb oxygen. However, the rate of absorption of oxygen by the undissociated catechol molecule is very much less than that by the monovalent ion, since it only interferes with the constancy of K on the acid side of neutrality, that is, when the concentration of the monovalent ion is exceedingly small compared to that of catechol.

Salt Effect.—In the range pH 6 to 10, the rate of absorption of oxygen increases with added salts. The salt effect is not entirely determined by the ionic strength. for the rate in phosphate buffers is less than that in potassium chloride solutions of similar ionic strength. A large part of this salt effect is due to the influence of salt on the acidic strength of catechol. Thus K in 0.8 M potassium chloride is 77% greater than K in absence of extraneous salt, but K' which is independent of the strength of catechol is only 22% greater in 0.8 M potassium chloride than in 0.0 M potassium chloride.

Potassium chloride decreases the rate of absorption of oxygen by the second ion of catechol. This is shown by the fact that in strongly alkaline solutions the rate in the presence of potassium chloride falls below that in its absence.

Variation of Rate with Concentration of Oxygen.—Measurements of the rate of oxygen absorption by 0.1 M catechol solution in phosphate buffers at pH 8.40 were made at varying partial pressures of oxygen. These were produced both by making the runs in partially evacuated system and in presence of air at atmospheric pressure. The results obtained are shown in Table VI.

TABLE VI

RATE OF OXYGEN ABSORPTION AT VARYING PARTIAL PRESSURES OF OXYGEN

Partial press. of O_2, atm.[a]	Rate	$K = \text{rate}/(P_{O_2})$
0.082	0.220	2.78
.097	.260	2.68
.206[b]	.53	2.57
.206[b]	.56	2.72
.272	.790	2.90
.423	1.15	2.72
.439	1.38	3.14
.627	1.63	2.60
.792	2.07	2.61
.969	2.55	2.63
	Average K =	2.72

[a] Corrected for vapor pressure of water. [b] In air.

The constancy of the values of K calculated on the assumption that the rate of oxidation is proportional to the partial pressure of oxygen shows that over a more than tenfold range of oxygen pressure the reaction is directly proportional to the pressure of oxygen.

Variation of Rate with Concentration of Catechol.—To determine the effect of varying the catechol concentration at constant pH, the rate of oxygen absorption was measured at varying concentrations of catechol in a strongly buffered phosphate solution at pH 6.5 and in sodium hydroxide solutions in which the equivalence of sodium hydroxide added per mole of catechol was maintained at 0.08 mole of sodium hydroxide per mole of catechol. The *p*H value of the sodium hydroxide solutions was practically constant at 8.20. The results obtained are shown in Table VII.

TABLE VII

RATE OF OXYGEN ABSORPTION AT VARYING CONCENTRATIONS OF CATECHOL

Concn. of catechol, M	Rate in phosphate buffer	Rate in NaOH	K_1 Buffer	K_1 NaOH	K_2 Buffer	K_2 NaOH
0.025	..	0.345	..	13.8	..	24.8
.05	0.0253	.782	0.506	15.6	7.08	21.9
.075	.041	..	.547	..	6.92	..
.10	.051	1.885	.510	18.9	6.12	22.7
.125	.071	..	.568	..	6.60	..
.15	.098	2.91	.652	19.4	7.42	22.1
.175	.107	..	.610	..	6.80	..
.20	.123	3.75	.614	18.8	6.77	20.7
.30	.202	..	.673	..	7.20	..
.40	..	8.00	..	20.0	..	28.7
				Average K_2 =	6.86	23.5

K_1 = rate/(concentration).
K_2 = rate × (concn. + 0.02)/(concn.)^2.

The rate is approximately first order with respect to catechol but it is slower than would be expected from this law at low concentrations of catechol. Thus, the values of K_1 calculated on the assumption that the reaction is first order with respect to catechol are over 30% lower at concentrations of catechol below 0.1 M. The rate obeys more exactly the law: rate = $K_2 (C)^2/(C + A)$, where C is concentration of catechol and A some constant. The K_2 values shown in Table VII were calculated using the same value of A, namely, 0.02 for both solutions.

By combining the results obtained by separately varying the *p*H value, the pressure of oxygen, and the total concentration of catechol, the rate of oxygen absorption in the range *p*H 6 to 10 is given by the expression

$$V\alpha(\text{Cat.}^-)(\text{O}_2) \times C/(C + A)$$

In view of the facts that A is approximately the same at two very different concentrations of hydroxide ion, and that the values of K' given in Tables II and III are constant over wide degrees of neutralization of the catechol, the concentration represented by C is to be taken as that of the sum of the concentrations of the undissociated catechol and of its first ion. The proportionality constant in the above expression is $K' \times (0.1 + 0.02)/0.1$. This is 266 expressed in the units cc. of oxygen × atm.$^{-1}$ × mole^{-1} × liter × min.$^{-1}$, for solutions containing no extraneous salts.

Variation of Rate with Temperature.—The rates of oxygen absorption by 0.1 M catechol solution in phosphate buffers at *p*H 8.35 and in sodium hydroxide at *p*H 8.20 were measured at 20, 25, 30 and 35°. The results are shown in Table VIII. It is seen that the values for the phosphate buffer are somewhat more consistent. The average heat of activation is 12,900 calories for the phosphate solutions and 9400 calories for the sodium hydroxide solution. The temperature coefficient V_{35}/V_{25} is 2.16 for the phosphate solutions and 1.68 (corr.) for the sodium hydroxide solutions. These heats of activation include not only the heat of activation of the oxygen absorbing species but also the heats of neutralization of catechol by $HPO_4^=$ and OH^-, respectively. The difference in these heats of neutralization largely accounts for the higher heat of activation in the buffered solution.

TABLE VIII

EFFECT OF TEMPERATURE ON RATE OF OXYGEN ABSORPTION

Temp., °C.	Rate Phosphate	Rate NaOH
20.0	1.76	1.35
25.0	2.51	1.70
30.0	3.74	2.22
35.0	5.22	3.00

Acknowledgment.—Leo A. Joslyn is to be thanked for his aid in making the runs, and Professor J. P. Bennett for making available to us the thermostat and other equipment.

Summary and Conclusions

The rate of oxygen absorption by catechol solutions has been studied under various conditions.

1. In the range of *p*H value 6.5 to 10, $V\alpha \times (\text{Cat.}^-) \times O_2 \times C/C + A$.

2. In more acid solutions absorption of oxygen by the undissociated molecule is appreciable; and in more alkaline solutions, the divalent ions also absorb oxygen.

3. In moderately alkaline solutions potassium chloride increases the rate of absorption, chiefly through a positive salt effect on the dissociation constant of catechol. In strongly alkaline solutions salt retards the reaction.

4. The heats of activation in sodium hydroxide solutions and in phosphate buffers were measured over the range 20 to 35°. The apparent heat of activation is higher in the phosphate buffer.

This difference can be accounted for by the difference between the heats of neutralization of catechol by $HPO_4^=$ and OH^-, respectively.

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[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL SCIENCES OF WEST VIRGINIA UNIVERSITY]

The Adsorption of Methane by Coal[1]

BY J. BARTLETT SUTTON AND EARL C. H. DAVIES

Introduction

To determine the adsorption equilibrium between a highly adsorptive coal and methane, we have recently used an apparatus which contains a variable volume unit, by means of which the total system volume can be varied through four stages, enabling one to obtain adsorption values for four pressures with each gas sample and to check such values on both the adsorption and desorption side of the equilibrium point. The fact that approximately twenty-four hours were required for equilibrium conditions to be attained led us to enclose, in an electric refrigerator at constant temperature (± 0.1°), not only the adsorption bulb but the entire apparatus.

Materials and Apparatus

The coal was obtained from the Carreta, West Virginia, mine of the Carter Coal Company, which is the most gassy mine in the world. It was of semibituminous rank and from the Pocahontas No. 4 seam. A ton sample, collected from all over the mine, was passed through a jaw crusher and then quartered several times to obtain a representative sample of fifty pounds. A portion of this was then ground in a "coffee mill" to approximately 100-mesh average size.

The analysis of this coal[2] as given by the Bureau of Mines was H, 4.4; C, 88.7; N, 1.3; O, 2.2; S, 0.5; H_2O, 0.4 and ash, 2.9. After refluxing with water for two weeks, we found the average density (nine determinations) to be 1.3521. The range of particle sizes, in the coal sample, as determined by the application of Stokes' equation to sedimentation data, was: 63.0%, 0.132 mm.; 10.0%, 0.045 mm.; 10.8%, 0.030 mm.; 10.2%, 0.021 mm.; 1.7%, 0.016 mm. and 4.3%, 0.007 mm. The coal received no preliminary heat treatment but was evacuated to 10^{-4} mm. for a period of seventy-two hours.

The methane was obtained from the Bureau of Mines at Pittsburgh, Pennsylvania. The higher hydrocarbons[3] had been removed from natural gas by passing it through 117 cm. of activated coconut charcoal.

The analysis of the methane[4] supplied by the Bureau of Mines was: CH_4, 97.8–98.0%; C_2H_6, 0.05%; O, 0.10% and N, 1.85%. The density found by the Regnault method was 0.7196. Traces of moisture were removed from the methane, before it was admitted to the system, by passing through a coil submerged in an ether–solid carbon dioxide mixture.

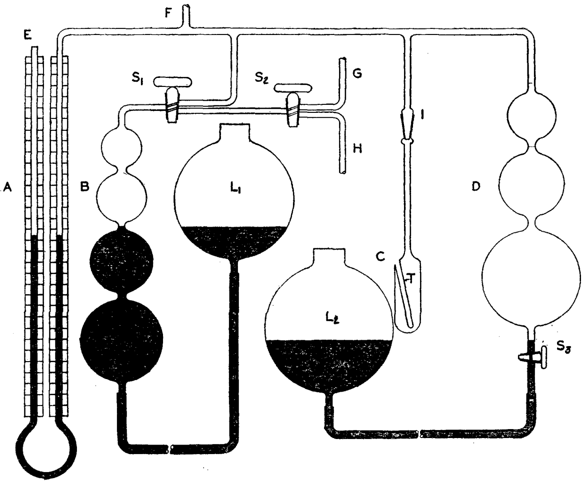

Fig. 1.—Adsorption apparatus with variable volume unit.

The apparatus (Fig. 1), designed and constructed in this Laboratory, consists essentially of the four units, A, B, C and D. A is the manometer, B the gasometer, C the adsorption bulb and D the variable volume unit. The volumes, between constricted portions, of both the gasometer and variable volume unit, as well as the total system volume, were accurately measured by the use of mercury. The temperature was determined by means of two ten-junction copper–constantan thermocouples, the hot junctions of which were en-

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[1] This paper is from a dissertation submitted in June, 1935, by J. Bartlett Sutton to the Faculty of the Graduate School of West Virginia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] R. S. Selden. R. I–3233; U. S. B. M., June, 1934.

[3] H. H. Storch and P. L. Golden, THIS JOURNAL, **54**, 4662 (1932).

[4] H. H. Storch, Bureau of Mines, personal communication.

closed in a paraffin-filled glass tube, embedded in the adsorbing material, while the cold junctions were enclosed in a glass tube immersed in a water–ice mixture, contained in a Dewar flask.

Experimental Procedure

By means of blank determinations, we found that the glass and mercury surfaces within the apparatus did not adsorb a measurable amount of methane. The procedure followed was similar to that used in other investigations of the same nature except for the use of the variable volume unit, by means of which the pressure was varied through four stages by changing the mercury level within the unit.

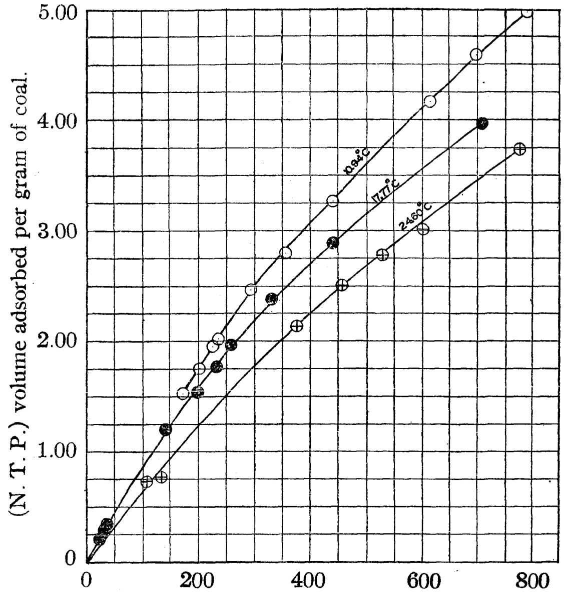


Fig. 2.—Adsorption isotherms.

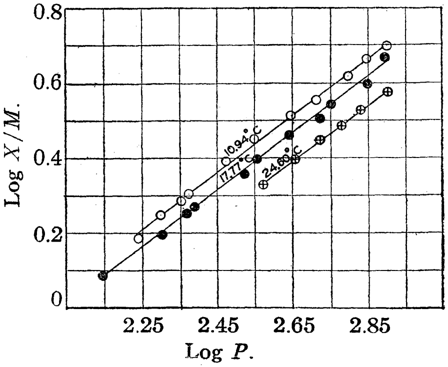


Fig. 3.—Log isotherms.

A weighed sample of coal was then placed in C and the manipulations carried out as before. After adsorption values had been determined and checked at four different pressures, more gas was then added and the above procedure repeated. The volume of gas adsorbed is $V_a = (273/760\ T_1)(P_1V_1 - P_2V_2)$, where T_1 is the temperature of the system, V_1 the volume of gas introduced, P_1 the atmospheric pressure, V_2 the volume of the system and P_2 the pressure produced by the gas introduced into the system.

Data and Graphical Interpretations

The relationships between adsorption and pressure for temperatures of 10.94, 17.77 and 24.60° are represented graphically in Fig. 2.

The Freundlich equation has been found to be applicable to the data, as shown by the straight line curves in Fig. 3. Here the log of x/m has been plotted against the log of P. A straight line is obtained, because the Freundlich equation in the form $\log x/m = \log k + 1/n \log P$ yields a straight line if it is applicable to the data. The slope of this line is equal to $1/n$ and its intercept with the $\log x/m$ axis is equal to $\log k$.

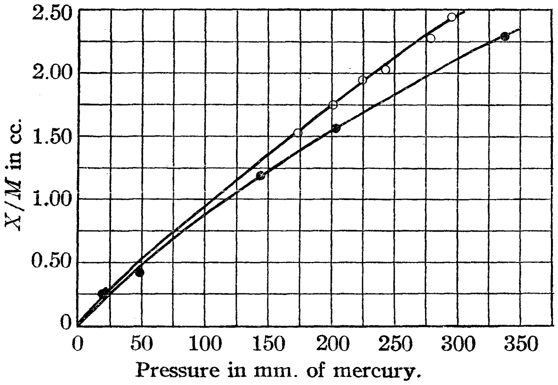


Fig. 4.—Effect of moisture in decreasing adsorption.

The effect of traces of moisture in lowering the adsorption of methane is shown in Fig. 4. The data for these curves were obtained at 10.94°.

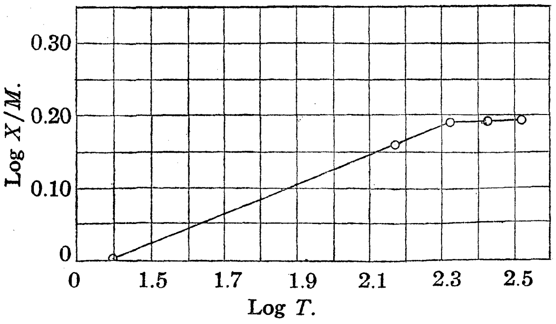


Fig. 5.—Log rate curve.

Figure 5 gives a log rate curve, the values for which were obtained at 17.77°.

The heats evolved per mole of gas adsorbed, as obtained by the application of the Clausius–Clapeyron equation to pressure and temperature readings taken from adsorption isosteres (Fig. 6), are plotted against amounts of gas adsorbed in Fig. 7.

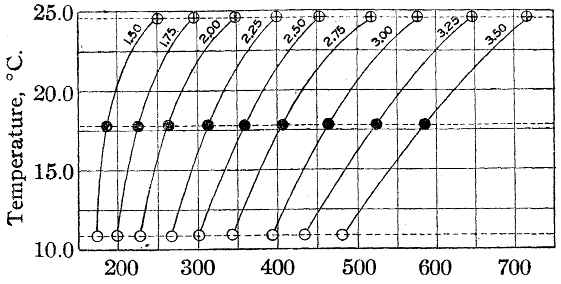


Fig. 6.—Adsorption isosteres.

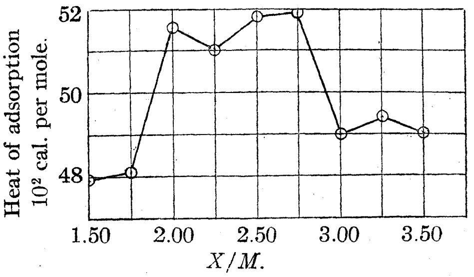


Fig. 7.—Heats of adsorption of methane on coal at 17.77°.

Summary

1. It has been shown that an apparatus equipped with a variable volume unit offers an accurate means of checking adsorption equilibrium on both the adsorption and desorption side of the equilibrium point.

2. The maintenance of the total adsorption system at constant temperature has been found to offer advantages of accuracy of measurement and simplicity of calculation.

3. A successful application of the Freundlich equation, to data found for the adsorption of methane by coal, has been made.

4. The calculated heats of adsorption of methane on coal have been found to be between 4700 and 5200 calories per mole for *x/m* values between 1.5 and 3.5.

MORGANTOWN, W. VA. RECEIVED JUNE 8, 1935

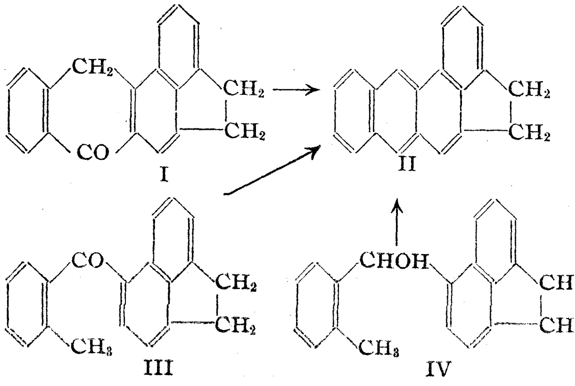
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHEASTERN UNIVERSITY]

A Pyrolytic Synthesis of 2,3-(Naphtho-2',3')-acenaphthene[1]

BY BRADFORD P. GEYER AND SAVERIO ZUFFANTI

2,3-(Naphtho-2',3')-acenaphthene (II) has been synthesized by Cook[2] by reduction of the anthrone (I), and, according to the statements in some patents,[3] the hydrocarbon also can be obtained by the pyrolysis of 3-*o*-toluylacenaphthene (III) or 3-acenaphthyl-*o*-tolylcarbinol (IV) in the presence of a dehydrating catalyst. These intermediates have not been described in the literature, however, and there is no evidence to indicate that a catalyst is required in their pyrolysis. It appeared a matter of interest, therefore, to synthesize 3-*o*-toluylacenaphthene and then, by subjecting this ketone to the conditions ordinarily employed for effecting the Elbs reaction, to prepare the hydrocarbon II.

The ketone III was obtained from *o*-toluyl chloride and acenaphthene by the Friedel–Crafts reaction. When pyrolyzed at 400–410°, it was converted smoothly into a hydrocarbon having the composition and the properties of the substance described by Cook.[2]



The authors are greatly indebted to Professor Louis F. Fieser of Harvard University for much helpful advice.

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[1] A thesis submitted in June, 1935, by Bradford P. Geyer in partial fulfilment of the requirements for the degree of Bachelor of Science at Northeastern University.

[2] Cook, *J. Chem. Soc.*, 1087 (1930).

[3] O. Nicodemus, German Patent 481,819 (1929); O. Nicodemus and W. Berndt, U. S. Patent 1,776,925 (1930).

Experimental Part[4]

The *o*-toluyl chloride used in this work was made from the acid by the use of thionyl chloride; yield, 89%; b. p. 212°, corr.

3-*o*-Toluylacenaphthene (III).—Anhydrous aluminum chloride (30 g.) was added slowly, a little at a time, to an ice-cold mixture of 30 g. of pure acenaphthene and 30 g. of *o*-toluyl chloride in 75 cc. of carbon disulfide. After six hours at 0–5° the mixture was allowed to warm gradually to room temperature and then carefully treated with water and cracked ice. The solvent and some unchanged acenaphthene were removed from the crude, dark brown ketone by steam distillation, first in the presence of dilute hydrochloric acid, and then dilute sodium hydroxide, and the product was extracted with ethyl alcohol from a considerable amount of tarry residue. After three crystallizations from ethyl alcohol and a final recrystallization from methyl ethyl ketone, 3-*o*-toluylacenaphthene was obtained in the form of glistening, pale yellow, rhombic plates, m. p. 139–140°; yield, 12 g. (23%). The solution of the ketone in concentrated sulfuric acid is of a deep yellow-orange color.

Anal. Calcd. for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found: C, 88.11; H, 5.89.

2,3-(Naphtho-2′,3′)-acenaphthene (II) was prepared by the pyrolysis of 0.7 g. of 3-*o*-toluylacenaphthene under an atmosphere of carbon dioxide in a two-bulb distilling flask at a bath temperature of 400–410° for forty minutes. At the conclusion of this time the elimination of water seemed to be complete. The crude product was then submitted to distillation in vacuum at a pressure of 2 mm., whereupon a golden-yellow crystalline solid was obtained. This material, when treated with an equal quantity of picric acid in benzene, formed a picrate which crystallized in clusters of slender, short, dark red-brown needles, m. p. 182.5–183.0°, corr. Decomposition of this picrate with ammonia and recrystallization of the regenerated hydrocarbon from ligroin (b. p. 90–120°) gave 2,3-(naphtho-2′,3′)-acenaphthene, very pale yellow leaflets, m. p. 192.5–193.5°, corr.; yield, 0.15 g. (23%). A benzene solution of this hydrocarbon possesses a yellow-green fluorescence, and the concentrated sulfuric acid solution has a red-violet color with an exceedingly strong, deep red fluorescence.

Anal. Calcd. for $C_{20}H_{14}$: C, 94.50; H, 5.50. Found: C, 94.37; H, 5.80. Calcd. for $C_{26}H_{17}O_7N_3$: N, 8.70. Found: N, 9.00.

Summary

2,3-(Naphtho-2′,3′)-acenaphthene has been synthesized by the Elbs condensation of 3-*o*-toluylacenaphthene.

BOSTON, MASSACHUSETTS RECEIVED JULY 25, 1935

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[4] Microanalyses by Mrs. G. M. Wellwood.

[CONTRIBUTION FROM THE ORGANIC CHEMICAL LABORATORY OF THE UNIVERSITY OF FLORIDA]

Derivatives of Piperazine. VI. Alkylation by Means of Aldehydes

BY W. T. FORSEE, JR., AND C. B. POLLARD

Some secondary amines have been alkylated by using aldehydes in the presence of a reducing agent.[1–5] However, the possibilities of the reaction seem to have attracted little attention.

Piperazine and N-monophenylpiperazine were quite readily alkylated by this method. In most cases products were obtained in better yields and were more easily purified than when prepared by other methods. N,N′-Dimethylpiperazine and N,N′-diethylpiperazine were prepared by the action of formaldehyde and acetaldehyde, respectively, on piperazine in the presence of powdered zinc and hydrochloric acid. N-Phenyl-N′-methylpiperazine and N-phenyl-N′-ethylpiperazine were prepared by the respective action of formaldehyde and acetaldehyde on N-monophenylpiperazine in the presence of zinc and hydrochloric acid. With one exception, good yields were obtained and in some cases one distillation served to give a pure product. This method was not satisfactory for aldehydes which are insoluble in hydrochloric acid even when sufficient alcohol was added to keep them in solution.

Formic acid was used as the reducing agent for those aldehydes which are insoluble in hydrochloric acid. Where aliphatic aldehydes were involved the reaction required from one to three hours. With aromatic aldehydes the reaction velocities were very slow, requiring as much as five days of refluxing. All products were easily purified. The solid derivatives were crystallized from 60% alcohol.

The yields, properties and analyses of these compounds are shown in Table I.

Experimental

Using Zinc and Hydrochloric Acid as Reducing Agent.—To a water solution of the amine hydrochloride were added, for each equivalent of secondary nitrogen, one

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[1] Wallach, *Ann.*, **343**, 54 (1905).

[2] Clarke, Gillespie and Weisshaus, THIS JOURNAL, **55**, 4571 (1933).

[3] Wagner, *ibid.*, p. 724.

[4] Skita and others, *Ber.*, **66B**, 1400 (1933).

[5] German Patents, 376,013 (1923), 491,856 and 503,113 (1930).

TABLE I

YIELDS, PROPERTIES AND COMPOSITION OF ALKYLPIPERAZINES PREPARED

	Compound	Yield, %	B. p., °C.	Mm.	M. p., °C.	N analyses, % Found	Calcd.
1	N-Phenyl-N′-methylpiperazine[b]	42	109–110	5		15.95	15.91
2	N-Phenyl-N′-ethylpiperazine[b]	98	144–145	10		14.81	14.74
3	N,N′-Dimethylpiperazine[b]	88	130–135			24.51	24.56
4	N,N′-Dimethylpiperazine dihydrochloride[a]	74			263 (dec.)	14.83	14.97
5	N,N′-Diethylpiperazine[b]	92	174–177			19.69	19.70
6	N,N′-Dibutylpiperazine[c]	62	195–195.5	12		14.15	14.14
7	N,N′-Dibenzylpiperazine[c]	84			91.5–92.5	10.60	10.53
7	(From benzyl chloride)	75			92–93	10.83	10.53
8	N,N′-Di-(*p*-methylbenzyl)-piperazine[c]	31			101–102	9.54	9.53

[a] Prepared from N,N′-dimethylpiperazine by passing dry hydrogen chloride into the anhydrous ether solution of the free base. [b] Prepared by using zinc and hydrochloric acid as the reducing agent. [c] Prepared by using formic acid as the reducing agent.

mole of the aldehyde and two moles (twice the calculated amount) of powdered zinc. A quantity of concentrated hydrochloric acid sufficient to react with the zinc was added gradually with stirring and cooling. After the zinc had all reacted, the mixture was made alkaline and the free base was extracted with ether. The ether solution was dried over anhydrous sodium carbonate, filtered and the ether evaporated. The free base was purified by distillation.

Using Formic Acid as Reducing Agent.—A mixture of 0.1 equivalent of the secondary amine and 0.1 mole of the aldehyde was refluxed with 40 cc. of formic acid (90%) until the evolution of carbon dioxide had ceased. The excess formic acid was evaporated on a water-bath and the residue made alkaline. The free base was extracted with ether, dried, filtered and the ether evaporated. The derivative was purified by recrystallization or distillation.

Summary

Satisfactory methods are described for the preparation of alkyl piperazines by the condensation of piperazine or N-monophenylpiperazine with aldehydes in the presence of a reducing agent.

GAINESVILLE, FLORIDA RECEIVED JULY 8, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF VERMONT]

The Free Energy Change that Accompanies Hydrogenation of Pyridine to Piperidine[1]

BY GEORGE H. BURROWS AND LOUIS A. KING, JR.

That pyridine is readily hydrogenated to piperidine, and that the reaction is reversible, has been shown by Zelinski and Borisov.[2] The purpose of the present investigation is to determine the free energy change of the reaction, through direct determination in the vapor phase of the equilibrium involved at each of several temperatures.

Attempts to achieve this equilibrium through initial use of hydrogen and pure pyridine or of hydrogen and pure piperidine did not lead to the desired results, and substantiated the conclusion of Sadikov and Mikhailow[3] that side products are extensively formed. It was also our experience that the active life of the platinum or nickel catalyst was short.

On these accounts experiments were devised to apply the use of trial mixtures of the several components, that mixture being deemed of equilibrium composition which underwent no appreciable change on being passed over the active catalyst at the selected temperature.

Materials and Experimental Details

Pyridine and piperidine of high quality were obtained from the Eastman Kodak Company. The pyridine was refluxed over solid potassium hydroxide and distilled. Its boiling point was 115.2–115.4°, its index of refraction $n^{25}\text{D}$ was 1.50682. In some instances the piperidine was given this same treatment, in others no treatment was necessary, as shown by its refractive index. This had the value $n^{25}\text{D}$ 1.45036.

The hydrogen, a commercial electrolytic product of high purity, was freed from possible oxygen contamination by palladinized asbestos and thoroughly dried before use.

The compositions of pyridine–piperidine mixtures were determined through their refractive

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[1] Grateful acknowledgment is made to the Elizabeth Thompson Science Fund for aid in financing this research.

[2] Zelinski and Borisov, *Ber.*, **57**, 150 (1924).

[3] Sadikov and Mikhailow, *J. Russ. Phys.-Chem. Soc.*, **58**, 527 (1927).

indices. The data for synthetic mixtures of known composition are shown in Table I.

TABLE I

% pyridine	% piperidine	n^{25}_D
0.00	100.00	1.45036
26.92	73.08	1.46394
53.03	46.97	1.47840
74.79	25.21	1.49134
100.00	00.00	1.50682

The composition–refractive index curve is almost linear, but is slightly concave toward the composition axis. The data of Table I may be expressed by the equation, $n_D = 1.45036 + 0.0_349$ (% pyridine) $+ 0.0_673$ (% pyridine),^{2} with an average deviation of 0.0001. Precision of analysis is favored by the wide difference between the indices of the pure components.

The nickel used as catalyst in the final experiments was prepared from oxide reduced in place by hydrogen and on an unglazed porcelain support. Complete reduction and removal of moisture is necessary and was indicated by ultimate constancy in weight of a drying tube through which the effluent gas was passed.

The experimental procedure was as follows. A bubbler system immersed in a constant temperature bath contained a mixture of pyridine and piperidine. It was provided with tubes through which this mixture could be withdrawn and replaced for the purpose of change of composition. Hydrogen entering the bubbler at constant rate of flow passed with the vapors of pyridine and piperidine in constant ratio either through the catalyst chamber or through the by-pass. Both catalyst chamber and by-pass were supported in a furnace that maintained the temperature constant within 0.5°. The catalyst chamber or the by-pass, as the case might be, led to a weighed condensing tube immersed in a freezing mixture; beyond this the hydrogen was collected and measured. The condensed mixture of pyridine and piperidine was weighed and analyzed.

Through systematic change in composition of the bubbler mixture and alternate use of catalyst chamber and by-pass, it proved not difficult to fix upon a mixture that remained essentially unchanged by the catalyst.

Sadikov and Mikhailow[3] noted that use of nickel as catalyst led to opening of the pyridine ring, with formation of amylamine. Under the conditions of the present work, this side product could not have been present in other than relatively small amounts, for the condensate from the catalyst chamber gave negative results when subjected to the Van Slyke method of analysis for amines. Absence of significant amounts of this side product was deemed sufficient evidence that other side products were not formed in sufficient quantities to necessitate consideration, under the existing condition of brief contact with the catalyst, and at the temperatures of the experiments used in our calculations.

The indices of refraction and compositions of the final equilibrium mixtures at the several furnace temperatures used, and the partial pressures and equilibrium constants calculated from these are shown in Tables II and III.

TABLE II

Furnace temp., °C.	n_D catalyst condensate	n_D by-pass condensate	Wt. of catalyst condensate, g.	Vol. H_2, cc. (reduced)
150	1.45627	1.45627	1.3586	257.3
170	1.47948	1.47967	0.9924	250.5
180	1.48113	1.48142	.6848	255.3
180	1.48500	1.48568	.5984	258.7

TABLE III

Temp., °C.	Composition catalyst condensate		Partial pressures (atm.)			K_p
	% pyridine	% piperidine	H_2	C_5H_5N	$C_5H_{11}N$	
150	11.75	88.25	0.415	0.073	0.509	97.4
170	54.88	45.12	.486	.288	.220	7.45
180	57.70	42.30	.573	.251	.171	3.6
180	64.20	35.80	.607	.256	.132	2.3

Greater difficulty was experienced at 180° in gaining close agreement between the compositions of mixtures that passed over the catalyst and through the by-pass, than at the lower temperatures. This is thought to be due to increased formation of side products at the higher temperature. The results at this temperature, therefore, are not used in the free energy calculations. The equilibrium constant at 180° calculated from the values at 150 and 170° is 2.25.

From the constants at 150 and 170°, the free energy changes at these temperatures are $F^\circ_{423} = -3835$ cal. and $F^\circ_{443} = -1760$ cal., respectively, corresponding in each case to the reaction

$$C_5H_5N(g) + 3H_2 = C_5H_{11}N(g)$$

Heat capacity data for pyridine and for piperidine in the gaseous state are not available and cannot be estimated reliably; consequently reduction of the free energy change to that at 25° is not attempted.

The equilibrium constants at 150 and 170° give as the heat of reaction between these temperatures, $H = -47{,}680$ cal. Approximate reduction to 25° and pyridine and piperidine in liquid state gives for these conditions $H = -45{,}000$ cal. The corresponding value calculated from thermochemical data ("International Critical Tables") is −38,600 cal.

Summary

The equilibrium between pyridine, hydrogen and piperidine has been measured at 150 and at 170°, and more approximately at 180°. The heat of reaction and the accompanying free energy changes have been calculated.

BURLINGTON, VERMONT RECEIVED JULY 15, 1935

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

Diffusion Coefficients in Alcohol–Water Mixtures

BY H. MOUQUIN AND W. H. CATHCART

The diffusion coefficients of a number of organic dyes dissolved in water–ethyl alcohol mixtures of varying composition were studied by Ostwald and Quast.[1] Their method, which essentially involves a continuously varying diffusion layer, seemed to contain some experimental difficulties. In view of this fact and the rather unusual nature of their results, the present authors attempted to repeat the original experiments with the intention of extending the work in this field. In spite of every effort to duplicate the conditions described in the original paper, the method proved too unreliable to permit verification of the previous findings.

The Ostwald method contained two obvious limitations: first, the solutions were placed in an unsealed vessel and were thus very sensitive to any disturbances capable of bringing about mass flow; second, the arrangement of the apparatus was such that it necessarily involved the tacit assumption that the density of the solution was greater than that of the solvent.

Testing the relative densities of crystal violet solutions and corresponding solvents at varying alcohol concentrations by means of the "schlieren" method, it was soon discovered that at least in the region between 25 to 50% (by weight) of alcohol the density of the 0.1% dye solution was actually less than that of the corresponding solvents. This no doubt is the major difficulty involved in the Ostwald method.

In recent years, a method first used for the measurement of diffusion coefficients by Northrup and Anson,[2] and greatly extended by McBain and co-workers, has become available. We refer to the so-called fritted glass membrane method, involving a constant diffusion-layer thickness. In two recent papers, McBain and Dawson[3] have pointed out the advantage of using a closed system. In a previous paper,[4] the disadvantages of stirring had been mentioned, but this was attempted only in an open cell.

The major requirements in the membrane cells not only include the existence of an undisturbed diffusion gradient in the membrane, but also adequate stirring in the bulk of the solutions right up to the surface of the fritted glass disk. If this last condition is not fulfilled, secondary diffusion layers build up beyond the strict confines of the membrane and this introduces a variable and unknown factor.

In the original technique, density difference between solvent and solution must be depended upon entirely for adequate mixing. Variations in viscosity must certainly affect the efficiency of this gravitational streaming, but, besides this, the density differences can vary over a wide range from case to case.

In the case at hand where the density differences may become vanishingly small, it is obvious that the traditional technique is impossible. In fact the formation of vague secondary diffusion layers beyond the physical boundaries of the membrane could easily be seen in the case of the more highly colored solutions.

The cell shown in Fig. 1 was designed to overcome the above difficulties and has been in use in this Laboratory for more than a year. First, it is entirely enclosed;[3] this effectively prevents any mass flow, outside of the most violent agitation. Second, the entire cell is slowly rotated at a speed somewhat under one r. p. m. by means of a wheel and belt drive placed in the thermostat. This motion coupled with the rise and fall of the en-

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(1) Ostwald and Quast, *Kolloid-Z.*, **48**, 83–95 (1929); **51**, 273 (1930).

(2) Northrup and Anson, *J. Gen. Physiol.*, **12**, 543 (1929).

(3) McBain and Dawson, THIS JOURNAL, **56**, 52 (1934); also *Proc. Roy. Soc.* (London), **A148**, 32 (1935).

(4) McBain and Liu, THIS JOURNAL, **53**, 59 (1931).

closed glass balls brings about gentle but sufficient mechanical stirring right up to the membrane surface.

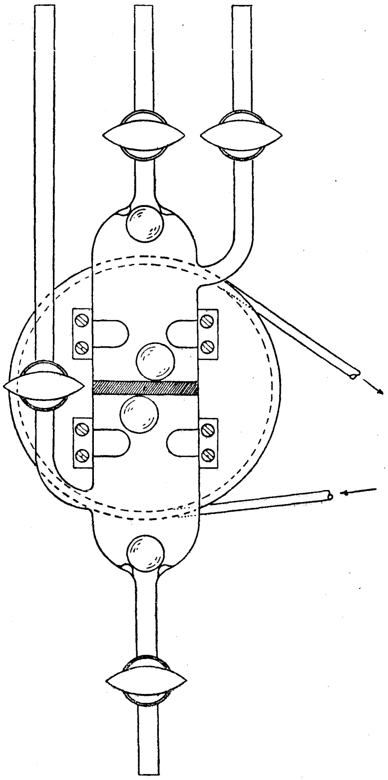

Fig. 1.

A few more practical details may be useful to other workers. One of each pair of glass balls is light enough to float, while the other sinks. The relative buoyancy of these, as well as the rate of rotation, should not be exaggerated, since the resultant excessive wear and tear tends to form a groove on the friable glass disk. Attempts to substitute mercury globules for the glass spheres have yielded unsatisfactory results. Indentations in the cell walls, near the ends, prevent the balls from blocking the end-tubes while the solutions are being removed. If sufficiently large stopcocks are used (6 mm. or more) and the solutions are of ordinary viscosity, the side tubes shown may be dispensed with. As in former methods, one end of the cell and the membrane are first filled by suction and the usual routine of refilling, etc., carried out before starting the rotation.

The effect of the stirring is at once evident when the cell constant of the rotating cell is compared with the same cell in a stationary position. As determined according to McBain, with 0.1 N hydrochloric acid, the constant in the cell used here showed an increase of nearly 5% when adequate stirring was maintained.

The data given in Table I show the diffusion coefficients of crystal violet taken over the whole range of water–alcohol mixtures, as obtained by this method. Curve II on Fig. 2 shows the data plotted graphically. Curve I is taken from Ostwald's data for comparison. The crystal violet was a very pure sample obtained from Grübler which has proved satisfactory in other research carried out in this Laboratory. The original solutions contained 0.1 g. of the monohydrate dye in 100 cc. of the solvent mixtures; the changes in concentration were measured by known dilution of the original solution until a close match was obtained in the colorimeter. The thermostat was kept at 25° and the viscosity corrections were made relative to water at that temperature. In verifying the fact that there is no appreciable difference in the viscosities of solvent and corresponding solution, the results seemed to be in bet-

Table I

Data with Present Cell

Rotating cell constant = 0.066/day

Wt. % alcohol	$D \times 10^6$ (diffusion coefficient/sec.)			Av. value (corr. for viscosity)
0.00	7.48	7.68	7.48	7.55
15.48	4.41	4.44		8.18
26.76	3.62	3.68		8.54
40.58	3.36			8.90
49.62	3.49	3.54		9.28
55.31	3.68	3.62		9.43
61.84	3.98	3.92		9.71
67.51	3.69	3.69		8.58
71.16	3.30	3.20		7.25
80.62	3.63			6.90
94.75	4.26	4.31	4.35	6.11

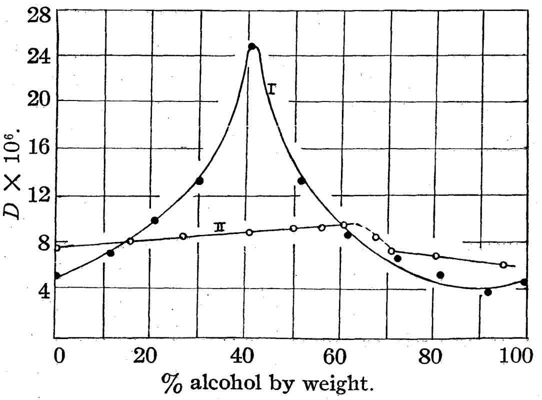

Fig. 2.

ter agreement with those published by Butler[5] than with the data given in the "International Critical Tables;" accordingly, the former were used to make the corrections.

Compositions of the water–alcohol mixtures were checked by determining the density by means of a pycnometer and tables given in "I. C. T."

The most interesting region of the curve consists of a definite "break" observable in the vicinity of 65 wt. % alcohol. Robinson and co-workers[6] have shown that it is seldom justifiable to interpret data for electrolytes such as given above, in terms of particle sizes. In any case some primary cause for the sharp break would have to be accounted for.

Since the days of Mendeléjeff attempts to furnish evidence of compound formation in alcohol–water mixtures have not been very successful. If we now take the break at 65 wt. % of ethyl alcohol as such evidence we are immediately confronted with the fact that this composition does not correspond to a one-to-one or any other whole number ratio of the traditional molecular weights. This criticism becomes less destructive when it is realized that the ratio of the two molecular weights in the liquid state of such compounds is not definitely known. If we assume the molecular weight of the alcohol to be normal, and that 65% corresponds to a one-to-one compound tendency it is necessary to assume an average molecular weight for water of about 25. A fairly reliable and independent substantiation of this value is to be found in the calculations made by Murray[7] based on the vapor pressure data obtained by Makowiecki for acetone–water mixtures.

Further search revealed a considerable quantity of evidence suggestive of the peculiar significance of the 65% region. If we restrict ourselves to the mixtures (neglect values for pure water and 100% alcohol), plotting various sorts of physical properties against the weight percentage very frequently demonstrates an abrupt change in the character of the solvents at this particular composition. In some cases, this is best revealed by a logarithm plot.

TABLE II

A. C. RESISTANCES OF THE ORIGINAL SOLUTIONS (CELL CONSTANT 1.3943)

% alcohol by wt.	$R \times 10^{-3}$ resistance (ohms)	$\eta^{25°}$ compared to H_2O	$R/\eta^{25°} \times 10^{-3}$
15.48	11.30	1.75	6.47
30.50	14.36	2.45	5.86
40.58	18.20	2.66	6.84
49.61	19.17	2.64	7.25
55.30	19.00	2.57	7.39
61.84	19.77	2.47	8.00
67.50	19.37	2.33	8.31
71.16	19.57	2.22	8.82
80.62	20.00	1.92	10.41
94.75	19.76	1.43	13.80

Figure 3 shows the plot of Table II, which is the electrical resistances, corrected for viscosity, of the crystal violet solutions used in the diffusion experiments. (The dye contains less than 0.5% sodium chloride.) A "break" around 65% is noticeable. A similar effect can be seen by making a log plot of the conductivity data (viscosity correction) published[5] for zinc chloride and potassium iodide solutions.

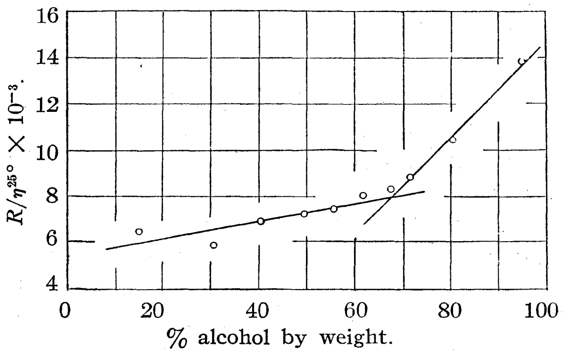

Fig. 3.

Other data which show irregularities in the 65% region are (1) log plot of the solubilities of zinc valerate, phenyl salicylate, ammonium benzoate, lithium benzoate and others (data from "I. C. T."); (2) log plot of % deviation of kinematic viscosity from a linear additivity rule (data from "I. C. T."); (3) dielectric constant for water–ethyl alcohol mixtures (plot on large scale).[8]

From the above evidence it seems fairly clear that the observed break in the diffusion coefficient must be caused by a peculiar condition characteristic of this solvent mixture.

Summary

1. The inadequacies of some former diffusion measurements are pointed out.

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[5] Connell, Hamilton and Butler, *Proc. Roy. Soc.* (London), **A147**, 418–423 (1934).

[6] Hartley and Robinson, *ibid.*, **A134**, 20 (1931); Robinson, *Soc. Dyers and Colourists*, p. 161 (June, 1934); Robinson, *Proc. Roy. Soc.* (London), **A148**, 881 (1935).

[7] Murray, *J. Phys. Chem.*, **33**, 904 (1929).

[8] Åkerlöf, THIS JOURNAL, **54**, 4130 (1932).

2. A new technique is developed and described.
3. The diffusion coefficients of crystal violet in alcohol–water mixtures are determined.
4. A possible explanation for an observed break in the regularity of the experimental curve is suggested.

NEW YORK, N. Y. RECEIVED AUGUST 1, 1935

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

Studies in the Physical Chemistry of Amino Acids, Peptides and Related Substances. V. Influence of Amino Acids, Urea and Alcohol upon the Velocity Constants of Chemical Reactions[1]

BY DANELLA STRAUP AND EDWIN J. COHN

The velocity constants of most chemical reactions are not independent of changes in the medium but vary with the ionic strength and the dielectric constant. The variation with change in salt concentration appears to be explained adequately by Brönsted's[2] theory of reaction rates, which considers the rate proportional to the activity coefficients of the reactants and inversely proportional to the activity coefficient of the critical complex. In the present communication we are concerned with the influence of alcohol, urea and amino acids upon reaction rates. All of these substances profoundly influence the dielectric constant of the medium and their activity coefficients vary in a very different manner from those of electrolytes.

In dilute electrolyte solution activity coefficients, and therefore changes in reaction rate, may be estimated by means of the Debye limiting law. The effect of more concentrated electrolytes or of non-electrolytes may be calculated by the method of Christiansen.[3] This method has been recently discussed by Harned and Samaras,[4] La Mer[5] and Scatchard.[6] The Brönsted–Christiansen and Debye–Hückel theories yield[6]

$$\log \frac{k}{k_0} = \frac{\epsilon^2 Z_A Z_B}{2.303\ DKT} \frac{\kappa}{1 + \kappa a} \tag{1}$$

in which k is the velocity constant in the salt solution, k_0 that in the absence of salt, K is the Boltzmann constant, κ the reciprocal distance proportional to the square root of the ionic strength, and a the distance of closest approach of the ions. The velocity constant should vary, according to equation (1), not only with the valence, Z, and ionic strength, μ, of the electrolytes, but with any change in the dielectric constant[7] of the solution, D, from its value in the standard state, D_0. Signifying by k' the velocity constant at zero ionic strength in a medium having a dielectric constant other than that of the standard state, equation (1) may be written

$$\log \frac{k}{k'} = \frac{Z_A Z_B\ (D_0/D)\ \sqrt{(D_0/D)\mu}}{1 + (a/3)\ \sqrt{(D_0/D)\mu}} \tag{2}$$

When D is equal to D_0, k' is equal to k_0.

The effect of changing dielectric constant on reactions between ions at zero ionic strength has been calculated[6] as

$$\log \frac{k'}{k_0} = \frac{\epsilon^2 Z_A Z_B}{2.303\ KTa}\left(\frac{1}{D} - \frac{1}{D_0}\right) = \frac{242.3\ Z_A Z_B}{a}\left(\frac{1}{D} - \frac{1}{D_0}\right) \tag{3}$$

This equation is analogous to the Born–Fajans equation for equilibrium relations.

Amino acids, due to their zwitterionic structure, exert electrostatic forces in solution. Since they do not contribute to the ionic strength, Debye's equation does not apply even in dilute solution. Solutions of amino acids have high dielectric constants and attempts have been made to describe the effect of amino acids on activity coefficients[8] in terms of the Born–Fajans equation. Another treatment of the effect of amino acids is described later on in this paper.

Two types of reactions have been studied: (1) a reaction between a non-electrolyte and an ion, and (2) a reaction between two ions. The thio-

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(1) A preliminary account of this investigation was read to the Society of Biological Chemists [*J. Biol. Chem.*, **105**, Proc. 87 (1934)].

(2) Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); **115**, 337 (1925); Brönsted and Livingston, THIS JOURNAL, **49**, 435 (1927).

(3) Christiansen, *Z. physik. Chem.*, **113**, 35 (1924).

(4) Harned and Samaras, THIS JOURNAL, **54**, 9 (1932).

(5) La Mer, *Chem. Rev.*, **10**, 179 (1932).

(6) Scatchard, *ibid.*, **10**, 229 (1932).

(7) The dielectric constants of the solvents employed have been determined by Wyman [THIS JOURNAL, **53**, 3292 (1931); *ibid*, **55**, 4116 (1933)]. In dilute solution they have been estimated by the equation: $D = D_0 + \delta C$, where D_0 is 78.54 at 25°, δ is 2.8 for urea, 22.7 for α-, and 36 for β-amino acids [Wyman and McMeekin, *ibid.*, p. 908].

(8) Failey, *ibid.*, **54**, 576 (1932).

sulfate ion was employed in both reactions; in the one type in the reaction with uncharged alkyl iodide molecules, in the other with bromoacetate ions, for which there is a positive salt catalysis. Both types of reactions have previously been shown to be bimolecular.

Materials and Methods.—All solutions were made up immediately before starting each experimental run.

Thiosulfate solutions were made from a stock solution of 0.1 *N* sodium thiosulfate which was standardized with weighed samples of resublimed iodine, dried over calcium chloride. A tenth dilution of this solution was titrated against standard iodine. These two standardizations agreed within 0.1%. 0.01 *N* iodine solutions were standardized with arsenic trioxide obtained from the U. S. Bureau of Standards, according to the method of Washburn.[9]

The glycine used was three times recrystallized from water. The urea obtained from the Eastman Kodak Co. was once recrystallized. Methyl iodide of Eastman Kodak and also of Kahlbaum, and ethyl iodide of Kahlbaum were used without further purification. Both preparations of methyl iodide gave the same results.

Reactions were carried out at 25 ± 0.03°. In the reaction with alkyl iodide and thiosulfate, the methyl iodide or ethyl iodide was added to the thiosulfate solutions containing the additional component at 25° from a weight buret. The reaction was carried out in special flasks to allow of pipetting without loss of alkyl halide by volatilization. Some of the experiments with these reactions were repeated using a separate flask for each determination. In these cases a saturated solution of ethyl iodide or a half saturated solution of methyl iodide was added to the thiosulfate solution, taking precaution to avoid loss by volatilization during the transfer of the solutions.

Bromoacetate solutions were made from weighed samples of bromoacetic acid, obtained from Eastman Kodak Co., and dried over sulfuric acid, and titrated with standard sodium hydroxide using phenolphthalein as indicator. The concentration of the sodium bromoacetate was checked by allowing it to react with a three-fold excess of thiosulfate and determining the concentration of thiosulfate remaining when the reaction was completed. The concentration of the sodium bromoacetate solution as determined by weighing, titration with sodium hydroxide and reaction with thiosulfate agreed within 0.5%.

Reaction between Thiosulfate and Alkyl Iodides.—Both salts and amino acids increase the rate of reaction between the bromoacetate and thiosulfate ions, and diminish that between the latter and uncharged alkyl iodides. The experimental error in determining the velocity constant of the latter reaction is greater, due to the tendency toward volatilization of the non-electrolyte.[10] The values of *k* for this reaction, given in Table I, are the averages of at least three determinations during the run. They are accurate only to two significant figures.

TABLE I

INFLUENCE OF ADDITIONAL COMPONENTS UPON THE VELOCITY CONSTANT OF THE REACTION

$$RI + S_2O_3^{=} \longrightarrow RS_2O_5^{-} + I^{-}$$

	Concn. of additional component, moles per liter	*k*	Log *k*/*k*$_0$
	Ethyl alcohol		
CH_3I	0.00	1.98	0.000
	1.72	2.52	.104
	3.44	3.45	.241
	5.11	4.92	.395
C_2H_5I	0.00	0.11	.000
	3.44	.18	.214
	5.11	.21	.281
	Urea		
CH_3I	0.00	1.95	0.000
	1.00	2.06	.024
	5.00	2.05	.022
	Glycine		
CH_3I	0.00	1.98	0.000
	.40	1.75	− .054
	.62	1.67	− .074
	1.00	1.50	− .121
C_2H_5I	0.00	0.11	.000
	.40	.10	− .041
	.62	.09	− .087
	Sodium chloride		
CH_3I	1.00	1.32	−0.176
	Potassium chloride		
C_2H_5I	0.00	0.11	0.000
	.10	.10	− .041
	.40	.09	− .087
	1.00	.08	− .138

The addition of glycine to the solution brings about a decrease in the velocity constant for both the reaction of methyl iodide and of ethyl iodide with thiosulfate ion (Fig. 1). The effect of amino acids is less than that of electrolytes, but is of the same order of magnitude, whereas urea has only a slight effect on these reactions. Ethyl alcohol on the other hand brings about a large increase in the velocity constant for both reactions.

In order to test the influence of the dielectric constant upon reaction rates, solutions have been prepared, having the same dielectric constant as water, but different compositions. The values of the velocity constant for the alkyl iodide–thiosulfate reaction in solutions isodielectric with water are given in Table II. The addition of glycine or urea to alcoholic solutions yields lower

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[9] Washburn, THIS JOURNAL, **30**, 31 (1908).

[10] The initial concentration of thiosulfate in these experiments was 0.01 *N*, the initial concentration of alkyl iodide varied from 0.005 to 0.010 *N*.

velocity constants than in the alcohol solutions alone, but the decrease is far smaller than that expected on the basis of proportionality between change in velocity constant and change in dielectric constant.

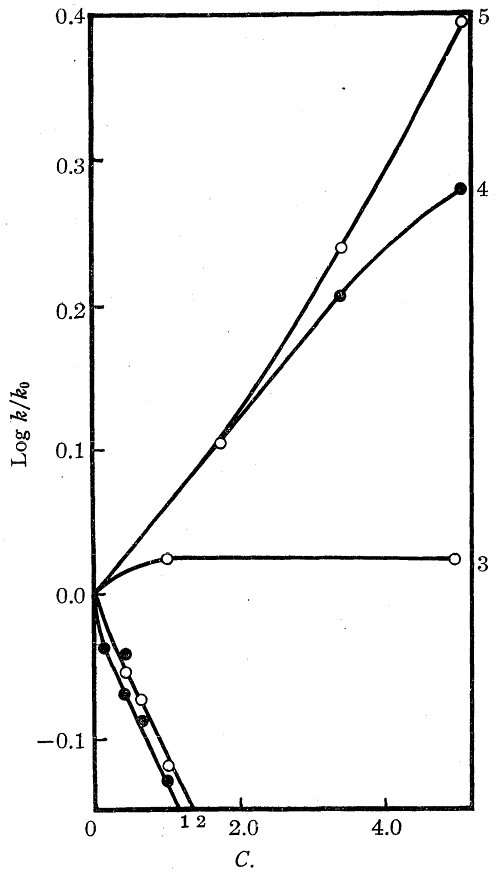

Fig. 1.—Hollow circles represent methyl iodide, solid circles ethyl iodide, in media containing (1) potassium chloride; (2) glycine; (3) urea; (4) and (5) ethanol.

Indeed the effect of glycine or of urea in diminishing the velocity constant is not very different in 20 or 30% alcohol from that in water. The rate of reaction in mixtures of glycine or urea and alcohol appears to depend rather upon specific properties of solute molecules than upon the dielectric constant of the solution.

TABLE II

VELOCITY CONSTANT OF THE REACTION

$RI + S_2O_3^{=} \longrightarrow RS_2O_3^{-} + I^{-}$

IN MIXTURES OF KNOWN DIELECTRIC CONSTANT

Medium	D	$1/D-1/D_0$	Log k/k_0
	CH_3I		
20% Alcohol	69.47	+0.0017	+0.241
0.40*m* glycine in 20% alcohol	78.55	.0000	+ .204
0.40*m* glycine in water	87.62	− .0013	− .054
30% Alcohol	64.45	+ .0028	+ .395
0.62*m* glycine in 30% alcohol	78.52	.0000	+ .241
0.62*m* glycine in water	92.61	− .0019	− .074
5.00*m* urea in 30% alcohol	78.55[a]	.0000	+ .353
5.00*m* urea in water	91.07[a]	− .0018	+ .022
	C_2H_5I		
20% Alcohol	69.47	+0.0017	+0.214
0.40*m* glycine in 20% alcohol	78.55	.0000	+ .113
0.40*m* glycine in water	87.62	− .0013	− .041
30% alcohol	64.45	+ .0028	+ .281
0.62*m* glycine in 30% alcohol	78.52	.0000	+ .154
0.62*m* glycine in water	92.61	− .0019	− .087

[a] The urea concentrations were calculated on the basis of $\delta = 2.82$.

Reaction between Thiosulfate and Bromoacetate Ions.—The reaction between bromoacetate and thiosulfate ions has repeatedly been studied. Recently La Mer,[11] La Mer and Fessenden,[12] and Kappanna[13] have shown that the velocity constant of this reaction is influenced by the ionic strength according to the expectation from the theory of Debye and Hückel. On the basis of linear extrapolation in the presence of monovalent cations, La Mer and Fessenden[12] estimate log k_0 to be $\bar{1}.396$. Kilpatrick[14] has employed equation (1) to describe several reaction rates, putting a, for convenience, equal to 3 Å. Accepting La Mer and Fessenden's value for k_0 for the bromoacetate reaction, our measurements yield values of a of 5.30, 5.19, 5.89, 5.67. The intermediate value of 5.6 Å. is employed in subsequent calculations.[15]

Effect of Alcohol.—In striking contrast to its effect upon the reaction between the alkyl iodides and thiosulfate, ethyl alcohol has very little influence on the reaction between thiosulfate and bromoacetate ions. Alcohol produces a very marked change in the dielectric constant of the solution, however, and one might therefore anticipate a large change in velocity constant of the basis of equation (3). The change in the logarithm of the velocity constant of these solu-

[11] La Mer, THIS JOURNAL, **51**, 3341 (1929).

[12] La Mer and Fessenden, *ibid.*, **54**, 2351 (1932).

[13] Kappanna, *J. Ind. Chem. Soc.*, **6**, 419 (1929).

[14] Kilpatrick, THIS JOURNAL, **56**, 2326 (1934).

[15] La Mer and Fessenden's measurements as well as ours are better described by a still higher value of a, 6.2 Å., and of log k_0, $\bar{1}.398$. On the other hand, Kappanna's measurements in dilute solutions yield $\bar{1}.376$ for log k_0. It is probable that an equation more complicated than (1) should be employed in concentrated salt solutions.

tions with change in the dielectric constant is calculated in Table III, where k^* is the velocity constant of a solution of the same ionic strength, but with no additional component. So considered, the result bears no relation to the expectation.

TABLE III

INFLUENCE OF ADDITIONAL COMPONENTS UPON THE VELOCITY CONSTANT OF THE REACTION

$BrCH_2COO^- + S_2O_3^= \longrightarrow S_2O_3CH_2COO^= + Br^-$

Concn. of additional component[a] C	Velocity constant k	$\frac{\text{Log } k/k^*}{\left(\frac{1}{D} - \frac{1}{D_0}\right)}$	$\frac{\text{Log } k'/k_0}{\left(\frac{1}{D} - \frac{1}{D_0}\right)}$	$\frac{\text{Log } k/k^*}{C}$
Ethyl alcohol, $\sqrt{\mu} = 0.204$				
0.00	0.485			
1.70	.468	−19	− 53	−0.0088
3.41	.473	− 7	− 39	− .0032
5.11	.483	− 1	− 34	− .00039
6.81	.475	− 2	− 35	− .00132
8.52	.476	− 1	− 35	− .00094
Urea, $\sqrt{\mu} = 0.204$				
0.00	0.485			
1.00	.517	−65	− 95	0.028
2.00	.551	−68	− 96	.028
3.22	.596	−72	−102	.028
4.00	.630	−77	−106	.028
5.00	.660	−77	−109	.028
Glycine, $\sqrt{\mu} = 0.204$				
0.00	0.486			
.10	.516	−74	−100	0.26
.20	.539	−65	− 93	.23
.26	.553	−63	− 91	.22
.30	.565	−65	− 92	.22
.40	.588	−63	− 92	.21
.62	.640	−62	− 91	.19
1.00	.744	−65	− 94	.19
Glycine, $\sqrt{\mu} = 0.228$				
0.00	0.516			
.11	.548	−65	− 98	0.24
.21	.580	−70	−101	.24
.42	.635	−65	− 99	.21
Glycine, $\sqrt{\mu} = 0.270$				
0.00	0.548			
.10	.577	−64	−103	0.23
.20	.608	−65	−101	.23
.40	.662	−62	− 99	.21
Glycine, $\sqrt{\mu} = 0.289$				
0.00	0.576			
.10	.599	−47	− 86	0.17
.20	.632	−59	− 97	.21
.40	.685	−58	− 96	.19
α-Alanine, $\sqrt{\mu} = 0.204$				
0.00	0.483			
.11	.513	−65	− 97	0.25
.22	.538	−62	− 93	.21
.44	.600	−66	− 97	.22
α-Alanine, $\sqrt{\mu} = 0.228$				
0.00	0.513			
.22	.570	−61	− 93	0.21
.44	.627	−61	− 93	.20
α-Alanine, $\sqrt{\mu} = 0.289$				
0.00	0.570			
.22	.627	−54	− 87	0.19
.44	.683	−55	− 88	.18
β-Alanine, $\sqrt{\mu} = 0.228$				
0.00	0.517			
.10	.555	−56	− 89	0.31
.20	.586	−51	− 85	.27
.40	.660	−54	− 87	.27

[a] Equal concentrations of the materials were employed in the experiments of $\sqrt{\mu} = 0.204$ and 0.289. In those of $\sqrt{\mu} = 0.228$ the concentration of thiosulfate was double and that of $\sqrt{\mu} = 0.270$ half that of the bromoacetate.

Both our measurements and conclusions regarding the influence of alcohol in this reaction are consistent with those of Kappanna,[13] whose measurements extend up to 80% alcohol and over a wide range of ionic strengths. We have attempted to correct both his measurements and ours for the increased electrostatic forces in media of low dielectric constant by means of equation (2). The estimated values of k' substituted in equation (3) yield values which vary from 53 to approximately 35 in our measurements and to 22 in Kappanna's measurements in 80% alcohol.[16] The expectation, according to equation (3), is 86.6 if a is equal to 5.6 Å. It is perhaps not surprising that the agreement is no better, for other effects than those due to electrostatic forces should unquestionably be considered.

Effect of Urea.—Whereas urea has no appreciable effect upon the velocity constant of the reaction between thiosulfate and an uncharged molecule, it greatly increases the rate of reaction with the bromoacetate ions.[17] Values of log k/k^* for the bromoacetate reaction are negative

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(16) Kappanna's measurements are most satisfactorily studied by plotting D/D_0 log k against $\sqrt{(D_0/D)\mu}$. The curve for 80% alcohol is superimposable throughout its length with that for water, but the other curves, especially that for 20% alcohol, are very different.

(17) The dissertation of Mildred Elsie Kamner, Columbia University 1934, has been received since this was written. Miss Kamner has also studied urea, as well as sucrose, glycerol and dioxane. She reports that all of these increase the rate of this reaction, and concludes that "there is no simple relation between the dielectric constant of the solvent and the velocity constant." The ratio log k/k^* calculated from her result with urea at approximately the ionic strengths studied by us, is in excellent agreement with those in Table III. The velocity constant in the presence of dioxane, 0.567, is very close to that reported by Kappanna for the same ionic strength in 80% alcohol, 0.589, and the solutions are approximately isodielectric. The influence of the other substances studied is far smaller even than that of urea, and of a different order than that of the amino acids.

in ethyl alcohol and positive in urea. Since $(1/D - 1/D_0)$ is positive in alcohol, but negative in urea, the ratios have the same sign (Table III). Moreover, the ratios in the case of urea are approximately those predicted by equation (3). Substituting values of k/k^* in this equation yields estimates of a from 6.3 to 7.5 Å., whereas correcting for diminished electrostatic forces at higher dielectric constants by means of equation (2) (k'/k_0) yields values of a from 4.4 to 5.1 Å. The influence of urea upon this reaction is in the direction and of the order to be expected from its effect on the dielectric constant.

Effect of Amino Acids.—The effects of glycine and α-alanine upon the dielectric constant of solutions, and upon the velocity constant of the bromoacetate–thiosulfate reaction are almost identical. Where they have been studied at the same concentration and ionic strength, the influence of α-alanine appears to be slightly smaller than that of glycine, but the effect of β-alanine with its higher dipole moment is very much greater. The changes in velocity constant with changes in dielectric constant are, moreover, of the same order for urea and the amino acids (Table III), though there is a tendency for them to increase with concentration in the presence of urea and generally to decrease in the presence of glycine. The greater influence of β-alanine on the dielectric constant is reflected in a somewhat smaller value of the ratio in the calculations in the third, though not those in the fourth column, which are corrected for the diminished electrostatic forces at higher dielectric constants. The influence of amino acids and urea upon the velocity constant of this ionic reaction thus appears, as a first approximation, to depend upon their influence on the dielectric constant of the solution.

Isodielectric Solutions.—If the rate of the thiosulfate bromoacetate reaction depended only upon change in ionic strength and dielectric constant, k should be the same in mixtures however constituted, having the same dielectric constant as water. The experiments reported in Table IV demonstrate that this is too simple a postulate in reactions between ions, as well as in reactions between ions and uncharged molecules (Table II).

A slight difference in the effect of urea and glycine on the bromoacetate reactions may be mentioned. The velocity constants are smaller in alcoholic than in aqueous solutions containing the same concentration of urea, but are greater for glycine in alcohol than in water, an effect interpretable in terms of increased electrostatic forces in alcoholic solutions.

TABLE IV

VELOCITY CONSTANT OF THE REACTION $BrCH_2COO^- + S_2O_3^{=} \longrightarrow S_2O_3CH_2COO^- + Br^-$ IN MIXTURES OF KNOWN DIELECTRIC CONSTANT

Medium	k	D	Log k/k^*	Log k'/k_0
0.4m Glycine at $\sqrt{\mu}$ = 0.289				
Water	0.685	87.62	0.076	0.126
20% Alcohol	.724	78.55	.100	.100
0.4m Glycine at $\sqrt{\mu}$ = 0.204				
Water	0.588	87.62	0.083	0.121
20% Alcohol	.604	78.55	.095	.092
0.62m Glycine at $\sqrt{\mu}$ = 0.204				
Water	0.640	92.61	0.120	0.176
30% Alcohol	.702	78.52	.160	.157
3.22m Urea at $\sqrt{\mu}$ = 0.204				
Water	0.596	87.62	0.089	0.128
20% Alcohol	.574	78.55[a]	.073	.073
5.00m Urea at $\sqrt{\mu}$ = 0.204				
Water	0.666	92.64	0.138	0.191
30% Alcohol	.588	78.55[a]	.083	.083

[a] These solutions may have had slightly lower dielectric constants. Urea concentrations were calculated on the basis of δ = 2.82.

The effect of amino acids on the velocity constant of this reaction is less than that of electrolytes, but is of the same order of magnitude. In order to facilitate comparison the values of k in the presence of electrolytes estimated by La Mer and Fessenden[12] and by Kiss[18] have been plotted in Fig. 2 against the concentration beyond $\sqrt{\mu}$ equal to 0.2, at which k^* equals 0.486.[19] Although the influence of amino acids and of salts is of the same order of magnitude, the influence of electrolytes varies as the square root of the ionic strength, whereas that of urea and of amino acids varies as the first power of the concentration. The influence of amino acids is therefore described by the ratio (log k/k^*)/C. All our measurements are so calculated in Table III and show that the change in velocity constant with change in amino acid concentration increases (1) with decreasing values of C, (2) of μ, and (3) with increasing values of the dipole moment of the amino acid.

The Kirkwood Equation.—The lack of agreement between change in velocity constant and

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[18] Kiss, *Z. anorg. allgem. Chem.*, **209**, 236 (1932).

[19] The data of Kiss (18) on the effect of electrolytes of high concentrations do not give the actual concentration of the reactants, and the ionic strength due to the reactants is not taken into account here.

change in dielectric constant is not limited to rates of reactions but occurs in any consideration of activity coefficients. Kirkwood has recently developed a theoretical equation for the activity coefficients of amino acids[20] in terms of the distance, R, separating the positive and negative charges of the zwitterion, the mean distance of closest approach of zwitterion and ion, a, the concentration of the former, C, and the ionic strength of the latter, μ. Assuming that the relative distributions of the ions of valence Z_A and Z_B is determined by electrostatic forces, both in the presence and absence of zwitterions, Kirkwood has developed equations[21] relating change in velocity constant to amino acid concentration. Ignoring multipole moments of higher order than the dipole, his equation valid only at low zwitterion concentration becomes

$$\frac{\log k/k^*}{C} = \frac{3\pi N\epsilon^4 Z_A Z_B}{2303\ (DKT)^2}\,\frac{R^2}{a}\,\frac{1 + \kappa a/2}{(1 + \kappa a + \kappa^2 a^2/3)^2} \qquad (4)$$

Substituting numerical values at 25° yields

$$\frac{D/D_0 \log k/k^*}{(D_0/D)\ C} = 0.125 Z_A Z_B\,\frac{R^2}{a} \times$$
$$\frac{1 + 0.165a\sqrt{(D_0/D)\mu}}{(1 + 0.329a\sqrt{(D_0/D)\mu} + 0.036a^2\,(D_0/D)\mu)^2} \qquad (5)$$

Glycine.—The value of R for glycine has been estimated to be 3.17 Å. by Kirkwood[20] on the basis of our measurements upon the solvent action of lithium chloride on glycine in alcohol–water mixtures[22] and to be 3.1 Å. by Scatchard and Prentiss[23] on the basis of freezing point measurements. The distance of closest approach, a, may be taken as the sum of the radius of the glycine, 2.82, estimated from its molal volume[24] and one-half the value of a for the ions estimated by equation (1). The valence of the reacting ions being two and one, the expression $0.125\ Z_A Z_B R^2/a$ becomes 0.44 if a for the ions be taken as 5.6 Å. and the influence of amino acids on the rate of reaction at the ionic strengths becomes

$\sqrt{\mu}$	$\left(\frac{\text{Log } k/k^*}{C}\right)$ Obs.	$\left(\frac{0.44\ (1 + 0.93\sqrt{\mu})}{(1 + 1.85\sqrt{\mu} + 1.14\ \mu)^2}\right)$ Calcd.
0.204	0.26	0.26
.228	.24	.24
.270	.23	.22
.289	.21	.21

The agreement with the highest results recorded in Table III is considerably greater than is warranted by the simplifying assumptions on which the theory and calculations are based. A larger value for a, or a smaller value of R, would render the agreement less satisfactory.

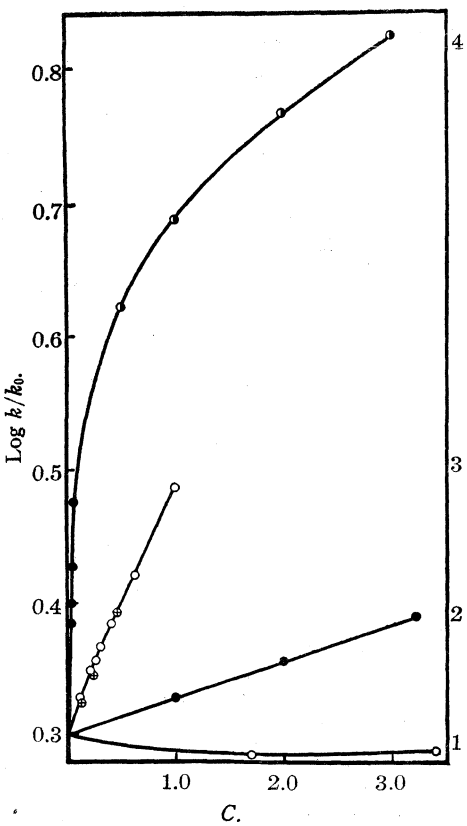

Fig. 2.—Concentration of reactants, $a = b = 0.010$: (1) ethanol, ○; (2) urea, ●; (3) glycine, ○ and α-alanine, ⊕; (4) sodium salts, La Mer and Fessenden, ●; and Kiss, ◑.

Alanine.—The radius of both α- and β-alanine is somewhat greater than that of glycine, 3.08 Å.[24] and so is the dipole moment of the β-alanine. Assuming the amino acids to be rods leads to a value of R of 4.4 Å., whereas the assumption that the increment in dielectric constant, δ, increases as the square of R[25] leads to 3.9 Å. for this constant when the amino group is in the β-position.

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(20) Kirkwood, *J. Chem. Physics*, **2**, 351 (1934).

(21) We are indebted to Dr. Kirkwood for developing this very interesting consequence of his theory. On the basis of the Brönsted–Christiansen theory (with the assumption that the distance of closest approach of the ions in the so-called critical complex is the same as the mean distance of closest approach of the zwitterion to the ions) he obtains for low amino acid concentrations

$$\log_{10}\frac{k}{k^*} = \frac{2\pi N Z_A Z_B \epsilon^2}{2303\ (DKT)^2}\, C \sum_{n=1}^{\infty}$$
$$\frac{(2n+1)\ Q_n}{(2n-1)(n+1)^2\, a^{2n-1}}\,\frac{(2n+1)K_{n-1}\,K_{n+1} - (2n-1)K_n{}^2}{K_{n+1}{}^2}$$

the symbols having the same significance as in his paper (20).

(22) Cohn, *Naturwissenschaften*, **20**, 663 (1932).

(23) Scatchard and Prentiss, THIS JOURNAL, **54**, 2696 (1932).

(24) Cohn, McMeekin, Edsall and Blanchard, *ibid.*, **56**, 784 (1934).

(25) Wyman, *ibid.*, **56**, 536 (1934).

$$\left(\frac{0.0425\ R^2\ (1 + 0.97\ \sqrt{\mu})}{(1 + 1.93\ \sqrt{\mu} + 1.25\ \mu)^2}\right)$$

	α-Alanine	β-Alanine	
$\sqrt{\mu}$	$R = 3.1$	$R = 3.9$	$R = 4.4$
0.228	0.22	0.35	0.44

The observed values for α-alanine (Table III) are 0.21 and for β-alanine 0.31 at this ionic strength and the lowest amino acid concentration.

Kirkwood's equation should hold only for very dilute solutions, whereas the concentrations of the glycine studied in alcohol–water mixtures were appreciable (Table IV). None the less the following comparison can be made with aqueous solution containing the same glycine concentration, and having the same ionic strength (Table III).

Volume fraction alcohol, v_2	$\sqrt{\mu}$	Amino acid concn., C	$\left(\frac{\text{Log}\ k/k^*}{C}\right)$	$\left(\frac{D/D_0 \log k/k^*}{(D_0/D)C}\right)$
0.0	0.204	0.40	0.21	0.26
.2	.204	.40	.24	.24
.0	.289	.40	.19	.24
.2	.289	.40	.25	.25
.0	.204	.62	.19	.27
.3	.204	.62	.26	.26

The right-hand expression of equation (2) changes very little with change in dielectric constant. Thus the calculated value at infinite dilution of glycine at $\sqrt{\mu} = 0.204$ is 0.25 for 20% alcohol as compared with 0.26 for water.

Urea.—Whether or not urea is a zwitterion remains a controversial question and is considered elsewhere.[26] On the assumption[25] that the increment in dielectric constant, δ, increases as the square of the dipole distance, and that the radius of urea is 2.6 Å.[24] a becomes 5.4 Å. and the right-hand side of equation (5) yields 0.033 at the ionic strength at which urea has been studied. The observed ratio was 0.028 (Table III). The calculated effect of urea in 20 and 30% alcohol is 0.031. The observed values are 0.023 and 0.015.

Kirkwood's equation was developed on the assumption that the dipole moment is large relative to that of a solvent molecule, and this condition does not obtain for urea. In the cases for which it was intended the Kirkwood equation appears to describe the effect of zwitterions as satisfactorily as does the Debye equation that of ions.

Summary

1. The rates of reaction of thiosulfate with uncharged alkyl iodide molecules and with bromoacetate ions have been studied.

2. The rates of reaction with the uncharged molecule are increased with alcohol and to a small extent by urea, and decreased by ions and by amino acids.

3. The rate of reaction with ions is increased by salts, amino acids and urea and but slightly influenced by alcohol.

4. Whereas salts increase the logarithms of the velocity constant proportionately with the square root of the concentration, the effect of amino acids and urea varies with the concentration.

5. Both urea and the amino acids increase the dielectric constant of water proportionately with the concentration. That the influence upon the rate of reaction is not due merely to change in dielectric constant is indicated by the effect of alcohol, and of urea and glycine in alcoholic solutions isodielectric with water.

6. Kirkwood's equation for the activity coefficients of the amino acids extended to apply to rates of reaction satisfactorily describes the observed results in terms of the valence of the reactants, the dimensions of ions and amino acids and the dipole moments of the amino acids.

BOSTON, MASSACHUSETTS RECEIVED MAY 15, 1935

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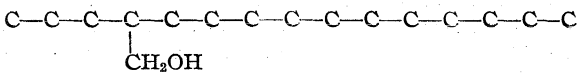
[26] Cohn, "Annual Review of Biochemistry," 1935, Vol. IV, p. 93.

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

Some Isomeric Branched Hexadecanols

BY WARREN M. COX, JR., AND E. EMMET REID

In a previous paper[1] we were led to the provisional view that certain aliphatic alcohols, such as cetyl alcohol, might possess mild purgative properties. On the basis of this hypothesis we have prepared all the eight primary hexadecanols which are theoretically possible when a —CH_2OH group is successively attached to each carbon in pentadecane.



$$\underset{\substack{|\\ CH_2OH}}{\text{C—C—C—C}}\text{—C—C—C—C—C—C—C—C—C—C—C}$$

Only the first member of this series, cetyl alcohol had been previously prepared.

Preparation

The correct conditions for the simplest method of preparation, *i. e.*, reduction of the branched chain aldehyde obtained by heating the glycidic ester condensation product of the corresponding ketone and chloroethyl acetate,[2] could not be found. Consequently, the branched chain acid[3] corresponding to the alcohol was prepared by means of the malonic ester synthesis, and the ethyl ester of this substituted acetic acid reduced by the method of Bouveault and Blanc.[4]

The required thirteen normal halides, from methyl to tridecyl, were prepared in the usual way[5] from the corresponding alcohols. The alcohols above butyl, with the exception of heptyl, were made from ethyl esters of the corresponding acids by reduction with metallic sodium in butyl alcohol.[4] Heptanol was prepared according to the method of Clarke and Dreger.[6] With the exception of undecylic acid the odd acids were prepared by the malonic ester synthesis or the nitrile reaction. *Ethyl Undecylate.* The crude undecylenic acid was distilled, esterified, and the ethyl ester cut 185–190° (100 mm.),[7] iodine no. 113. The ester was hydrogenated with a nickel catalyst, and reduced to the alcohol in the usual way.[4] The resultant undecyl alcohol, iodine no. 5.1, was dissolved in absolute ethyl alcohol and hydrogenated (Adams platinum oxide) to an iodine no. of 1.0.

Substitution of the Halides in Malonic Ester

One of the most annoying factors involved in the use of the malonic ester synthesis is the large volumes of anhydrous ethyl alcohol required. This difficulty has been overcome by the use of butyl alcohol, which is obtained anhydrous by mere distillation. The ethyl malonate should first be converted to the butyl ester[8] but in the present work ethyl malonate was used in butyl alcohol solution, with a resultant formation of ethyl butyl, diethyl and dibutyl esters of the mono-substituted malonic ester. Fortunately, the dibutyl ester predominated. Substitution of halides was in the usual way.

Saponification.—The disubstituted ester was refluxed for three hours with 25% alcoholic potassium hydroxide (with occasional addition of a little water to prevent separation of potassium malonate). The ethyl and butyl alcohols were steam distilled.[9] The remaining dipotassium-disubstituted-malonate was refluxed with concentrated hydrochloric acid in 100% excess until the fatty acid layer was clear. The disubstituted acid was separated, and heated to 190° in an oil-bath.

Esterification of α,α' Dialkyl Acetic Acids.—The branched chain acids are more difficult to esterify than are normal acids. The usual procedure (refluxing with 95% ethyl alcohol containing 3% hydrochloric acid), was modified by the addition of anhydrous calcium chloride, 1.5 mols for 4 mols of water. After refluxing for twenty-four hrs., the aqueous layer was removed, and the procedure repeated. This procedure applied to a straight chain acid (as palmitic) gives 98–99% esterification, but

TABLE I

YIELDS OF INTERMEDIATES AND HEXADECANOLS

$RR_1CHCOOH$		$RR_1CHCOOC_2H_5$			RR_1CHCH_2OH		
R =	R_1 =	Yield, %	B. p. °C.	Mm.	Yield, %	B. p., °C.	Mm.
CH_3-	$C_{13}H_{27}$-	70	185–187	12	66	185–187	15
C_2H_5-	$C_{12}H_{25}$-	67	191–199	15	53	186–188	15
C_3H_7-	$C_{11}H_{23}$-	60	181–183	14	32	181–184	15
C_4H_9-	$C_{10}H_{21}$-	57	180–185	15	30	181–183	15
C_5H_{11}-	C_9H_{19}-	57	180–182	14	33	181–182	15
C_6H_{13}-	C_8H_{17}-	49	181–183	14	27	181–183	15
C_7H_{15}-	C_7H_{15}-	40	182–183	14	28	181–182	15

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(1) W. M. Cox and E. E. Reid, THIS JOURNAL, **54**, 220 (1932).

(2) G. Darzens, *Compt. rend.*, **139**, 1214 (1905); *Frdl.*, **8**, 1257; M. A. Verley, *Bull. soc. chim.*, **35**, 487 (1924).

(3) This series of hexadecanoic acids was prepared by W. M. Stanley, M. S. Jay and R. Adams, THIS JOURNAL, **51**, 1261 (1929), who did not, however, make the corresponding esters and alcohols.

(4) Bouveault and Blanc, *Compt. rend.*, **136**, 1676 (1903); **137**, 60 (1903).

(5) "Organic Syntheses," John Wiley and Sons, Inc., 440 Fourth Ave., New York City, 1921, Vol. I, p. 1.

(6) H. T. Clarke and E. E. Dreger, Ref. 5, 1926, Vol. VI, p. 52.

(7) G. R. Yohe and R. Adams, THIS JOURNAL, **50**, 1503 (1928), reduced undecenyl alcohol with hydrogen and platinum.

(8) J. D. Meyer and E. E. Reid, *ibid.*, **55**, 1574 (1933); Ref. 5, 1935, Vol. XV, p. 51.

(9) This procedure was found more satisfactory than that employed by R. Adams, W. M. Stanley, S. G. Ford and W. R. Peterson, THIS JOURNAL, **49**, 2934 (1927). Alcoholic potassium hydroxide saponification was used by R. Adams, W. M. Stanley and H. A. Stearns, *ibid.*, **50**, 1475 (1928).

TABLE II

PROPERTIES OF BRANCHED CHAIN HEXADECANOLS AND THEIR ACETATES

RR_1CHCH_2OH R =	R_1 =	$n^{25}D$	d^{25}_4	M. p., °C.	Analysis[b] C	H	Acetates[a] d^{25}_4	$n^{25}D$	Sapon. no.[e]
H	$C_{14}H_{29}$	1.4283[d]	0.798[d]	49.3[d]	79.41	13.58	0.8574	1.4390	197.2
CH_3	$C_{13}H_{27}$	1.4453	.8320	12–13	79.23	13.91	.8527	1.4378	184.2[f]
C_2H_5	$C_{12}H_{25}$	1.4484	.8366	− 0.2	79.25	13.94	.8584	1.4391	193.7
C_3H_7	$C_{11}H_{23}$	1.4478	.8349	5.5	79.20	13.90	.8567	1.4385	191.6
C_4H_9	$C_{10}H_{21}$	1.4476	.8345	−14.5–14	79.05	13.96	.8567	1.4381	194.3
C_5H_{11}	C_9H_{19}	1.4476	.8341	− 9–8[c]	78.78	14.09	.8563	1.4380	195.5
C_6H_{13}	C_8H_{17}	1.4470	.8336	−30–26[c]	79.24	13.90	.8560	1.4379	195.4
C_7H_{15}	C_7H_{15}	1.4470	.8342	−25–18[c]	78.79	13.69	.8565	1.4380	194.7

[a] Prepared by refluxing with acetic anhydride and sodium acetate, and distilling directly under reduced pressure. [b] Analyzed by Dr. Ing. A Schoeller, Berlin, Germany. Calculated for $C_{16}H_{34}O$: C, 79.26; H, 14.14. [c] Readings approximate. Alcohols supercool to glassy solids. [d] "I. C. T." $n^{78.9}D$ $d^{78.9}_4$. [e] Calculated saponification no. 197.5. [f] This was reacetylated and the product redistilled but without essential change. The densities of the other acetates are 0.0222 greater than those of the alcohols according to which the density of this acetate is 0.0015 low which indicates 6.8% of unchanged alcohol. The saponification number found indicates 93.2% ester. According to this the true density is 0.8542.

with the substituted acids, much poorer yields were obtained (see Table I).

Reduction.—Reduction of the distilled esters was accomplished by the Bouveault–Blanc reaction. With the exception of the α-methylpentadecylate, the reaction was very sluggish, and instead of cooling the reaction flask, it had to be heated. The yields were poor (Table I). Separation of unreduced acid from the alcohol formed by the reaction could not be accomplished in the usual way, *i. e.*, by taking advantage of the insolubility of the calcium soaps in toluene. This method of separation was effective only in the case of the α-methylpentadecylate. The calcium salts of the other branched chain acids are soluble in toluene. To effect this separation it was necessary to convert the unreduced acid into the zinc salt, during steam distillation of the solvent butyl alcohol, and then to distil the branched chain alcohol, directly, under reduced pressure. The zinc salt remains liquid, and apparently undergoes no decomposition at moderately high temperatures. It may be removed from the still, after distillation of the alcohol, and converted to the ester by refluxing with ethyl alcohol containing hydrochloric acid.

The properties of the seven branched chain hexadecanols and their acetates are compiled in Table II. The purgative qualities of the alcohols and acetates was not marked. 2-Ethyl-2-dodecylethanol-1 and 2-hexyl-2-octylethanol-1 were reported by Macht and Barba-Gosè[10] as stimulating intestinal peristalsis in rats.

Acknowledgment.—The authors wish to express their appreciation to Dr. Marie Josefa Barba-Gosè for assistance in the preparation of these materials.

Summary

Substituted ethanols of the type  $\begin{matrix}R\\R_1\end{matrix}\!\!>\!CHCH_2OH$, where R and R_1 are straight chain aliphatic residues and total 14 carbon atoms, have been synthesized and their physical properties studied.

BALTIMORE, MARYLAND RECEIVED JUNE 17, 1935

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[10] D. I. Macht and J. Barba-Gosè, *Proc. Soc. Exptl. Biol. Med.*, **28**, 772 (1931).

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

A New Synthesis of Benzoins. 2′,4′,6′-Trimethylbenzoin

BY REYNOLD C. FUSON, H. H. WEINSTOCK, JR., AND G. E. ULLYOT

The great reactivity of the aldehyde group in α-ketoaldehydes suggested that, in the presence of aluminum chloride, these compounds might condense with aromatic hydrocarbons to give benzoins, according to the equation

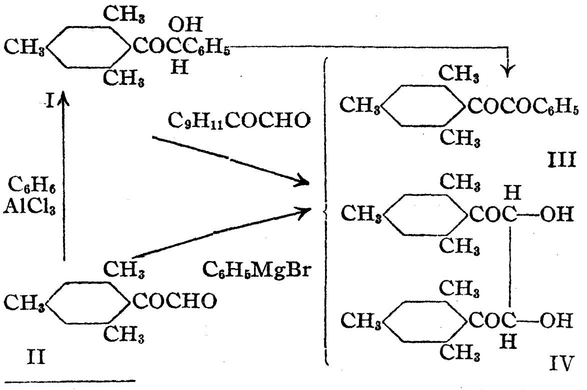
$$RCOCHO + ArH \xrightarrow{AlCl_3} RCOCH(OH)Ar$$

We have been able to show that this is a general method for the synthesis of benzoins of the type indicated. In view of the fact that the selenium dioxide oxidation method[1] has made α-keto aldehydes readily available, it is felt that the new method of preparing benzoins will prove in many instances to be superior to older methods. A detailed report of the work on this method will be published separately. The work presently reported makes use of the new synthesis in a study of the benzoin, 2′,4′,6′-trimethylbenzoin (I).

2′,4′,6′-Trimethylbenzoin (I) was not obtained when mesitylglyoxal (II) was condensed with phenylmagnesium bromide; instead, there resulted a mixture of mesityl phenyl diketone (III) and 1,2-di-(2,4,6-trimethylbenzoyl)-ethylene glycol (IV).[2] To account for this result it was suggested that the bromomagnesium alkoxide may have been oxidized to the diketone by the keto aldehyde, the latter being reduced to the bromomagnesium derivative of the glycol.

$$C_9H_{11}COCH(OMgBr)C_6H_5 + 2C_9H_{11}COCHO \longrightarrow C_9H_{11}COCOC_6H_5 + C_9H_{11}COCH(OMgBr)CH(OH)COC_9H_{11}$$

The present work has been carried out in an effort to test this hypothesis.



The benzoin is easily prepared by condensing mesitylglyoxal with benzene in the presence of aluminum chloride. It is very readily converted to the diketone by the action of oxidizing agents. In particular, it is rapidly oxidized in solution by the oxygen of the air. This ease of oxidation seems to offer a satisfactory explanation for the fact that in many attempts to synthesize the benzoin the product was the oxidation product.

Of especial interest, of course, was the action of mesitylglyoxal on the benzoin. It was found that when the benzoin is treated with mesitylglyoxal in benzene solution, reaction occurs and the diketone and the glycol are formed. This result provides an explanation of the fact that the benzoin could not be obtained from mesitylglyoxal and phenylmagnesium bromide.

Another method which was tried in the early attempts to prepare the benzoin was the action of alkali on mesityl phenyl triketone (V). De Neufville and von Pechmann[3] had found that diphenyl triketone was decomposed by alkali to give benzoin, together with benzoic acid, mandelic acid and carbon dioxide. Since we happened to have some mesityl phenyl triketone, it occurred to us that it might react with alkali to give the desired benzoin. As a matter of fact, the products which were isloated were the diketone (VI), 2,4,6-trimethylbenzoic acid (VII) and carbon dioxide.

$$\underset{V}{C_9H_{11}COCOCOC_6H_5} \xrightarrow{NaOH}$$

$$\underset{VI}{C_9H_{11}COCOC_6H_5} + CO_2 + \underset{VII}{C_9H_{11}COOH}$$

Experimental

Phenyl Mesityl Triketone.—The triketone was made by oxidation of 2,4,6-trimethyldibenzoylmethane, which was prepared by the method of Kohler and Barnes.[4] Ten grams of the diketone was dissolved in 200 cc. of commercial dioxane, and 8.2 g. of selenium dioxide was added. After eight hours of refluxing, the mixture was allowed to cool to room temperature. Hydrogen sulfide was bubbled through the reaction mixture for three hours, and then it was allowed to stand for two hours. The precipitated selenium and sulfur were removed by filtration, and a clear orange-colored solution was obtained. The dioxane was

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(1) Riley, Morley and Friend, *J. Chem. Soc.*, 1875 (1932); "Organic Syntheses," John Wiley and Sons, Inc., 440 Fourth Ave., New York City, 1935, Vol. XV, p. 67.

(2) Gray and Fuson, THIS JOURNAL, **56**, 739 (1934).

(3) De Neufville and von Pechmann, *Ber.*, **23**, 3375 (1890).

(4) Kohler and Barnes, THIS JOURNAL, **55**, 690 (1933).

removed by distillation under diminished pressure; the red oil which remained underwent partial crystallization when treated with a small amount of ligroin. Fractional crystallization (from ligroin) of this material gave 2.6 g. of mesityl phenyl triketone, which is a yellow solid, melting at 90–91°.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.1; H, 5.71. Found: C, 76.73, 77.04; H, 5.7, 5.96.

In addition to the triketone and a large amount of the red oil (which did not solidify and which could not be distilled) there was obtained 1 g. of an orange-yellow solid, melting at 169–170°. It contained selenium. *Anal.* Found: C, 70.84, 70.87; H, 5.39, 5.77. This compound has not yet been identified.

The Action of Alkali on Mesityl Phenyl Triketone.—Two grams of the triketone was added to 10 cc. of a 10% solution of sodium hydroxide; a reaction occurred and the solution became opaque. The triketone disintegrated, and a new solid formed which melted at 134.5–135.5°, and proved to be mesityl phenyl diketone. The alkaline filtrate was allowed to stand overnight; during this time additional small amounts of the diketone separated. These were removed by filtration, and the solution was acidified by hydrochloric acid. Carbon dioxide was identified by passing the evolved gas into a solution of calcium hydroxide. The acidification of the solution caused the precipitation of an acid which melted at 151–152°, and proved to be 2,4,6-trimethylbenzoic acid.

2 - Phenyl - 3 - (2,4,6 - trimethylbenzoyl) - quinazoline.—Five-tenths of a gram of mesityl phenyl triketone and 0.21 g. of *o*-phenylenediamine were dissolved in 4.5 cc. of hot alcohol. The orange color of the solution faded to a pale yellow, and a colorless crystalline compound separated. The product, after recrystallization from alcohol, was light yellow in color, and melted at 134–134.5°.

Anal. Calcd. for $C_{24}H_{20}ON_2$: N, 7.95. Found: N, 8.07.

2′,4′,6′-Trimethylbenzoin.—To a mixture of 26.6 g. of anhydrous aluminum chloride and 100 cc. of dry benzene contained in a 500-cc., three-necked flask immersed in water at a temperature of 10° was added 17.6 g. of mesitylglyoxal[5] dissolved in 100 cc. of dry benzene. The addition was carried out, with stirring, over a period of two hours. Stirring was continued an additional five hours at room temperature. The mixture was poured slowly into ice and concentrated hydrochloric acid. The benzene layer, containing the benzoin, was removed. The aqueous layer was extracted once with a small amount of benzene. The benzene solution was added to the main portion of the solution. The benzene was removed at 50° by evaporation at diminished pressure. Because of the ease of oxidation of the benzoin, nitrogen instead of air was admitted through the ebulliator tube. The residual yellow liquid was crystallized from 100 cc. of ethyl alcohol. There was obtained 16.1 g. of a colorless substance, melting at 97–99°. The pure compound melted sharply at 102°.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.3; H, 7.08. Found: C, 79.9; H, 7.10.

Urethan Derivative.—One cubic centimeter of phenyl isocyanate was added to 0.5 g. of 2′,4′,6′-trimethylbenzoin dissolved in 20 cc. of high-boiling petroleum ether. The solution was refluxed for four hours, cooled, and filtered. There was obtained a good yield of a white crystalline substance, which, after recrystallization from petroleum ether, melted at 158.5–159°.

Anal. Calcd. for $C_{24}H_{23}O_3N$: C, 77.62; H, 6.20. Found: C, 77.33; H, 6.20.

Oxidation.—One gram of 2′,4′,6′-trimethylbenzoin was added to 40 cc. of glacial acetic acid. Dry air was bubbled through the solution for eight hours at a temperature of 50°. The solution was reduced by evaporation under diminished pressure to a volume of 5 cc., cooled, and the bright yellow solid which crystallized was collected on a filter. The yield of mesityl phenyl diketone (m. p. 133–134.5°) was 0.72 g. A mixed melting point with a known sample of mesityl phenyl diketone showed no depression.

The Action of 2′,4′,6′-Trimethylbenzoin on Mesitylglyoxal.—Five grams of 2′,4′,6′-trimethylbenzoin and 5.6 g. of mesitylglyoxal in 150 cc. of dry benzene were refluxed for four hours. The benzene was removed at 50° under diminished pressure, no ebulliator tube being used. The yellow oil remaining was dissolved in 50 cc. of ethyl alcohol, cooled, and filtered. The crude product melted at 122–127°. Treatment of this with hot, high-boiling petroleum ether left 0.35 g. of a white, insoluble substance, melting at 155–157°. Cooling of the petroleum ether solution yielded 3.6 g. of a bright yellow substance (m. p. 129–132°) which, on purification, was shown (by the mixed melting point method) to be mesityl phenyl diketone. By the same method, the white solid was found to be identical with 1,2-di-(2,4,6-trimethylbenzoyl)-ethylene glycol.

Summary

2′,4′,6′-Trimethylbenzoin was prepared by condensing mesitylglyoxal with benzene in the presence of aluminum chloride. This is a general method for making benzoins.

Attempts to prepare the benzoin by condensing mesitylglyoxal with phenylmagnesium bromide, and by decomposition of mesityl phenyl triketone with alkali, failed; in each case the product was mesityl phenyl diketone.

2′,4′,6′-Trimethylbenzoin is readily converted to the diketone by oxidizing agents.

Mesitylglyoxal oxidizes the benzoin to the benzil, being itself reduced to the pinacol.

URBANA, ILLINOIS RECEIVED JULY 29, 1935

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(5) The mesitylglyoxal was prepared by the method of Gray and Fuson [THIS JOURNAL, **56**, 739 (1934)], who report it to be a liquid boiling at 118–119° at 12 mm. It has now been found to have a melting point of 45°.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 353]

The Application of Equations for the Chemical Potentials to Partially Miscible Solutions

BY GEORGE SCATCHARD AND WALTER J. HAMER

It has been shown[1] that an analytical expression for the thermodynamic functions is extremely valuable for the treatment of solutions containing more than two components. The method is equally valuable when the temperature varies with the composition, and is essential when one equilibrium relation is calculated from a quite different one. In the present paper this method is applied to the equilibrium between the two liquid or two solid phases of partially miscible solutions, and the results are used to calculate the liquid–vapor equilibrium when there are experimental measurements of the latter to serve as a check.

The liquid solutions which we discuss have at least one polar component, and should not be expected to obey the simple expression derived for non-polar mixtures,[2] that the free energy of mixing per mole, F_x^M, of a binary mixture is

$$F_x^M = RT\,(x_1 \ln x_1 + x_2 \ln x_2) + \beta V z_1 z_2 \qquad (1)$$

in which x_1 and x_2 are the mole fractions of the two components, V is the volume of one mole of the mixture or $x_1V_1 + x_2V_2$, the z's are the volume fractions, $z_1 = x_1V_1/V$, and β is a parameter expressing the deviations from ideality, with the further relation that βV is independent of the temperature. However, the concentrations of the two phases in equilibrium, or the fact that the chemical potential of each component must have a horizontal inflection at the critical mixing point, permit the calculation of two parameters at each temperature. We have calculated them for equations of the form

$$F_x^M - RT(x_1 \ln x_1 + x_2 \ln x_2) = F_x^E = \beta V z_1 z_2 + \gamma z_1^2 z_2 = V z_1 z_2[(\beta + \gamma/2) + \gamma(z - 1/2)] \qquad (2)$$

and also of the form to which equation 2 reduces for components of equal molal volumes

$$F_x^E = Bx_1x_2 + Cx_1^2x_2 = x_1x_2[(B + C/2) + C(x - 1/2)] \qquad (3)$$

F_x^E may be termed the excess free energy of mixing per mole.

The equations for the changes in chemical potential on mixing, μ_1^M and μ_2^M, and the excess chemical potentials, μ_1^E and μ_2^E, corresponding to equation 2 are

$$\mu_1^E = \mu_1^M - RT \ln x_1 = V_1(\beta + 2\gamma)z_2^2 - 2V_1\gamma z_2^3 \qquad (4)$$

$$\mu_2^E = \mu_2^M - RT \ln x_2 = V_2(\beta - \gamma)z_1^2 + 2V_2\gamma z_1^3 \qquad (5)$$

Those corresponding to equation 3 are

$$\mu_1^E = (B + 2C)x_2^2 - 2Cx_2^3 \qquad (6)$$

$$\mu_2^E = (B - C)x_1^2 + 2Cx_1^3 \qquad (7)$$

It will be noted that μ_1^M is RT times the natural logarithm of the activity of the first component, and μ_1^E is RT times the natural logarithm of the activity coefficient of that component.

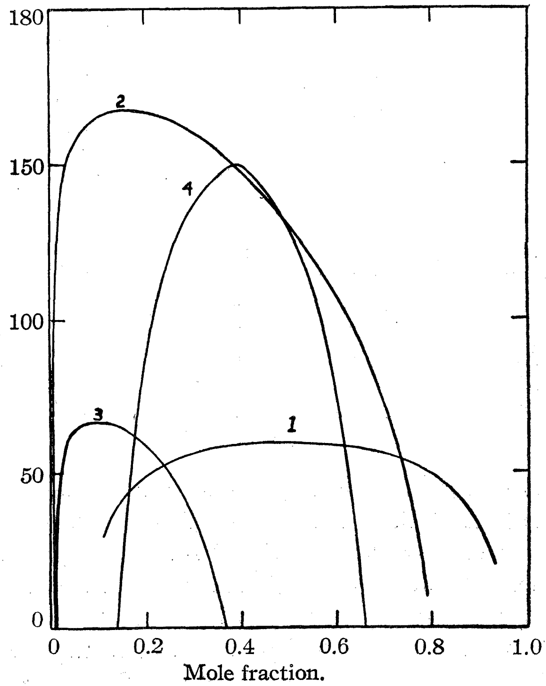

Fig. 1.—Equilibrium compositions: 1, aniline–hexane; 2, water–aniline; 3, water–phenol; 4, platinum–gold (add 1000° to t).

The magnitude of γ relative to $(\beta + \gamma/2)$ indicates the extent of the failure of equation 1 to represent the dependence on the concentration; and the change of $(\beta + \gamma/2)$ with the temperature

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[1] G. Scatchard and S. S. Prentiss, THIS JOURNAL, **56**, 1486, 2314, 2320 (1934).

[2] G. Scatchard, *Chem. Reviews*, **8**, 321 (1931); *Kemisk Maanedsblad* (*Copenhagen*), **13**, 77 (1932); THIS JOURNAL, **56**, 995 (1934). See also J. J. van Laar, *Z. physik. Chem.*, **72**, 723 (1910); **83**, 599 (1913); J. H. Hildebrand and S. E. Wood, *J. Chem. Phys.*, **1**, 817 (1933).

TABLE I

COMPOSITION OF EQUILIBRIUM SOLUTIONS AND PARAMETERS

t	x_2'	x_2''	z_2'	z_2''	$\frac{\beta + \gamma/2}{2.3R}$	$\frac{\gamma}{2.3R}$	$\frac{B + C/2}{2.3R}$	$\frac{C}{2.3R}$
				Aniline (91.06)–Hexane (130.47)				
59.6	0.4994	0.4994	0.5884	0.5884	2.511	−1.017	289.0	0.5
58	.3371	.6420	.4215	.7199	2.621	−0.943	292.5	17.9
55	.2669	.7257	.3428	.7913	2.726	−1.033	308.0	3.7
50	.2064	.7825	.2715	.8375	2.859	−1.000	320.4	6.7
40	.1412	.8691	.1906	.9049	3.113	−1.278	345.4	− 9.0
30	.1115	.9068	.1524	.9330	3.258	−1.440	359.5	−20.7
				Water (18.07)–Aniline (91.06)				
167.5	0.1424	0.1424	0.4555	0.4555	6.942	−2.010	− 858.7	1503.8
165	.0786	.2385	.3008	.6122	7.226	−2.149	− 714.3	1452.7
160	.0573	.3021	.2345	.6857	7.568	−2.422	− 525.0	1331.4
140	.0296	.4458	.1331	.8021	8.453	−3.085	− 147.5	1083.9
120	.0191	.5432	.0895	.8570	9.089	−3.691	+ 59.7	929.0
100	.0148	.6277	.0702	.8947	9.585	−4.629	+ 213.6	766.0
80	.0113	.6886	.0546	.9177	9.906	−5.214	+ 290.8	677.9
60	.0088	.7326	.0430	.9325	10.048	−5.543	+ 331.8	620.9
40	.0077	.7617	.0374	.9416	9.919	−5.733	+ 347.8	565.9
20	.0070	.7838	.0341	.9481	9.646	−5.820	+ 350.8	514.1
				Water (18.07)–Phenol (87.78)				
68.5	0.0880	0.0880	0.3192	0.3192	4.645	1.043	−2985	3163
66	.0898	.0898	.3241	.3241	4.670	0.923	−2807	3013
65	.0568	.1393	.2262	.4402	4.831	.837	−2523	2822
60	.0372	.1903	.1582	.5332	5.047	.839	−2152	2593
50	.0250	.2428	.1107	.6090	5.270	.827	−1737	2322
40	.0199	.2782	.0899	.6519	5.392	.748	−1430	2094
30	.0180	.3079	.0819	.6837	5.474	.513	−1130	1834
20	.0168	.3311	.0767	.7063	5.482	.326	− 925	1642
10	.0157	.3511	.0720	.7244	5.450	.190	− 775	1496
0	.0146	.3699	.0673	.7404	5.400	.081	− 655	1374
				Platinum (91.9)–Gold (101.2)				
1150	0.395	0.395					1174	379
1100	.218	.567					1177	449
1050	.170	.622					1175	479
1000	.138	.660					1167	509
950	.116	.686					1153	532
900	.098	.706					1133	560
850	.082	.722					1109	596
800	.066	.738					1088	646

shows how far the solution is from regular in the sense of Hildebrand.[3] Figure 1 shows the equilibrium compositions for liquid solutions of aniline–hexane,[4] water–aniline[4] and water–phenol,[4] and for solid solutions of platinum–gold[5] (for which 1000° must be added to the temperature scale). Table I gives the mole fractions and volume fractions of the larger component in the two equilibrium solutions, and the parameters computed from them. The figures in parentheses after the names of the substances are the molal volumes in cubic centimeters at 20 or at 25°, the values used in equations 2, 4 and 5.

For aniline–hexane, equation 3 gives a much smaller asymmetry term than equation 2, but for the solutions containing water, equation 3 leads to so great asymmetry that the excess free energy of mixing is negative over a large part of the range even though the solutions are not completely miscible. Equation 2 gives about the same degree of asymmetry for each of the three liquid solutions, and the constants decrease with increasing temperature as should be expected with polar components. For platinum–gold solid solutions, the volumes are so nearly equal and are

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[3] J. H. Hildebrand, THIS JOURNAL, **51**, 66 (1929).

[4] "I. C. T.," Vol. III, pp. 397, 389.

[5] C. H. Johansson and J. O. Linde, *Ann. Physik*, [5], **5**, 762 (1930).

measured at a temperature so far from those of the equilibrium measurements that no attempt was made to use equation 2. We note that its use would reduce the asymmetry, but by only a small amount. For this system $(B + C/2)$ is independent of the temperature over a large range, and the change at lower temperatures may well be within the experimental error. The simple theory would predict this behavior for non-polar components. Equation 3 might be expected to give the variation with composition for two isomorphous solids. The asymmetry may arise from the fact that a foreign molecule which is too large distorts a crystal lattice more than one which is too small.

Keyes and Hildebrand[6] obtain 290 mm. for the vapor pressure of hexane and 277 mm. for the vapor pressure of the two-liquid system at 40°. Using the former figure and 1 mm. for the vapor pressure of aniline, we obtain 262 mm. for the two-liquid system by equation 2, and 263 mm. by equation 3, assuming the vapors to be perfect gases. Since the vapor pressure of hexane is 15 mm. higher than that accepted for the "International Critical Tables," it is not certain that the discrepancy should be attributed to our calculations.

For water–aniline, the "International Critical Tables" give values for the composition of the vapor in equilibrium with two liquid phases from 40 to 90°, and the vapor composition and pressure for several compositions of the water-rich phase at 75°. Figure 2 shows the comparison of the first (circles) with calculations from equation 2 (full line) and from equation 3 (broken line), using the parameters determined from the liquid–liquid equilibrium. For equation 2 the discrepancy varies from 50% at 41.5° to 7% at 90°; for equation 3 the discrepancies are somewhat larger.

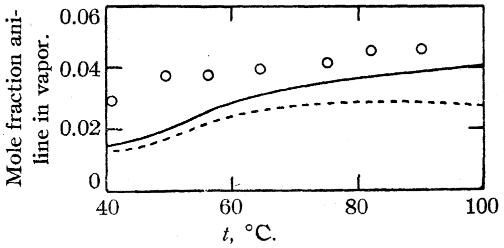

Fig. 2.—Water–aniline, two liquids: full line, equation 2; broken line, equation 3; circles, observed.

Figure 3 shows the vapor pressure and the vapor composition at 75° as a function of the liquid composition, with calculations from equation 2 only. The agreement of the vapor compositions is excellent, except for the saturated solution. The calculated pressures are consistently 2% lower than the measured values. It should be noted that the condensate is two-phase in almost all these measurements, and that the experimenter (Schreinemakers) claimed no great accuracy.

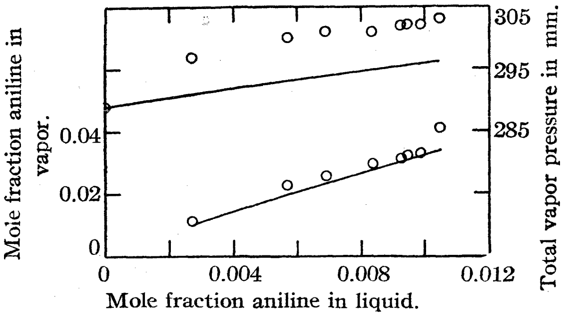

Fig. 3.—Water–aniline, 75°: above, total vapor pressure; below, mole fraction aniline in vapor.

For water–phenol there are measurements of the composition and pressure of the vapor in equilibrium with two liquid phases from 15 to 68.5°, and measurements over the whole composition range at 56.3[7] and at 58.4°.[8] The calculations require the vapor pressure of liquid phenol (supercooled through much of the range) and no measurements were found. The values found were obtained by extrapolating the "I. C. T." equation valid from 116 to 180°. Figure 4 shows the vapor composition and pressure of the two-liquid system as a function of the temperature. The agreement of equation 2 is apparently well within the uncertainty in the vapor pressure of phenol. Equation 3 leads, however, to absurd results for this system, as might be expected from the large values of the parameters.

The vapor compositions and pressures were calculated at 57.5°, and compared with the measured values at the two neighboring temperatures. For this comparison the measured pressures were multiplied by the ratio of the vapor pressure of water at 57.5° to its vapor pressure at the temperature of the measurements. The vapor composition is shown as the logarithm of the "relative volatility," α.

$$\log \alpha = \log (y_2x_1/y_1x_2) = \frac{(\mu_2^E - \mu_1^E)}{2.3RT} + \log (P_2/P_1) \quad (8)$$

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[6] D. B. Keyes and J. H. Hildebrand, THIS JOURNAL, **39**, 2126 (1917).

[7] F. A. H. Schreinemakers, *Z. physik. Chem.*, **35**, 459 (1900).

[8] H. D. Sims, Chem. Eng. Thesis, M.I.T., 1933.

in which y_1 and y_2 are the mole fractions in the vapor, and P_1 and P_2 the vapor pressures of the pure components. The comparison is shown in Fig. 5, with the liquid composition expressed as weight fraction, rather than mole fraction, to give a better distribution of the points. The broken line for log α is that obtained by increasing log P_2 by 0.1. The agreement with the experiments appears to be within this range, which is probably smaller than the experimental error.

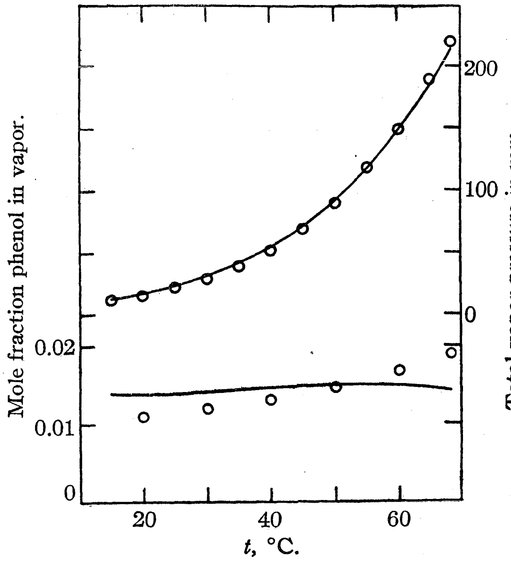

Fig. 4.—Water–phenol, two liquids: above, total vapor pressure; below, vapor composition.

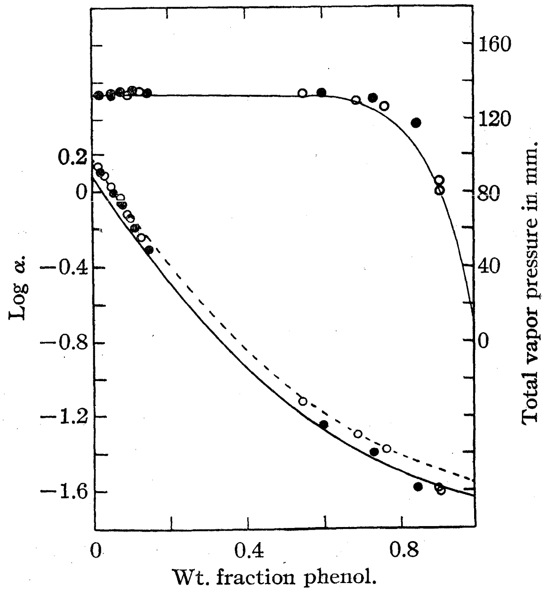

Fig. 5.—Water–phenol, 57.5°: above, total vapor pressure; below, log α; ●, Schreinemakers; ○, Sims.

Recently Guggenheim[9] has criticized the use of such equations, particularly that to which equation 1 reduces when the molal volumes are equal

$$F_x^E = Bx_1x_2 \tag{9}$$

for solutions which deviate so widely from ideality as to be only partially miscible on the ground that these equations neglect the deviations from random distribution. There is no doubt about the basis of his criticism, but there is reason to believe that the equations used in this paper agree better with the behavior of actual systems than the approximate treatment offered by Guggenheim (equation 21). We may compare this equation with equation 9 if we assume that each molecule is in contact with twelve others, as in closely packed crystals. The upper curves in Fig. 6 show the equilibrium temperature divided by the critical mixing temperature as a function of the composition for a regular solution obeying equation 9 (B independent of the temperature) as a full line, and for Guggenheim's equation 21 as a broken line. The lower curves in this figure show, as functions of the composition, $-[x_1 \ln x_1 + x_2 \ln x_2]$; $F_x^E = H_x^M$ for the critical mixing isotherm according to equation 9; F_x^E according to Guggenheim; and H_x^M according to Guggenheim.

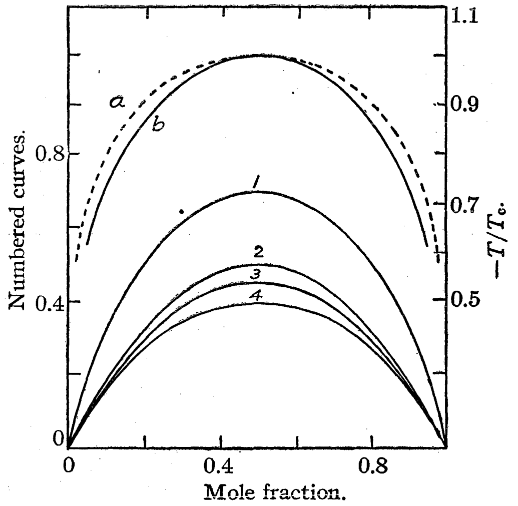

Fig. 6.—Comparison with Guggenheim's equation: a, equilibrium compositions by Guggenheim's Equation 21; b, equilibrium compositions by Equation 9; (1) $-[x_1 \ln x_1 + x_2 \ln x_2]$; (2) $F_x^E = H_x^M$ at T_c, Equation 9; (3) F_x^E at T_c, Guggenheim's Equation 21; (4) H_x^M at T_c, Guggenheim's Equation 21.

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[9] E. A. Guggenheim, *Proc. Roy. Soc.*, (London), **A148**, 304 (1935).

F_x^M is given by the difference between the second, or third, curve and the first.

From the upper curves we see that Guggenheim's equation fits most partially miscible liquids better than equation 9 in that it is somewhat flatter, but there is no assurance that this is not a coincidence and that B should not actually decrease with increasing temperature because of polarity, giving rise to a flatter curve than that corresponding to equation 9. The platinum–gold system, which should correspond closely to the model used by Guggenheim, shows little or no flattening. In any case most systems deviate from equation 9 much more seriously through their lack of symmetry than through their flatter maxima.

The lower curves show that the difference between the two treatments is not very great, and that the modification introduced by Guggenheim is probably in the wrong direction, for the second curve is independent of the temperature but the third and fourth increase with increasing temperature with the second curve as limit at infinite temperature. Experimentally it is found, even with non-polar mixtures, that when any variation of F_x^E with temperature can be detected it is a decrease and not an increase, and that whenever F_x^E and H_x^M have both been measured the second is larger than the first. We believe that Guggenheim's approximation, in addition to its failure to represent the asymmetry of most real systems, gives much too large an effect of the deviation from random distribution.

Summary

Equations for the free energy of mixing are computed from the mutual solubilities of partially miscible substances, and the vapor compositions and pressures computed from these equations are compared with the experimental measurements with good agreement.

Guggenheim's treatment is discussed and found less satisfactory than the simpler one given here.

CAMBRIDGE, MASS. RECEIVED JUNE 29, 1935

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 354]

The Application of Equations for the Chemical Potentials to Equilibria between Solid Solution and Liquid Solution

BY GEORGE SCATCHARD AND WALTER J. HAMER

The method of determining the composition of liquid and solid phases in equilibrium at each temperature from the melting points and heats of fusion of the components when both solutions are ideal, or when the activity coefficients are known, has been developed by Seltz.[1] His treatment of the activity coefficients is, however, completely qualitative. Analytical expressions for the chemical potentials[2] permit a consistent treatment of such equilibria. From the compositions of the two phases at equilibrium it is possible to calculate two parameters, one of which may be attributed to each solution. The accuracy of the experimental measurements, which are carried out at constant composition and not at constant temperature, does not warrant the calculation of these constants at each temperature, but the solutions may be treated as regular and the parameters calculated at one temperature may be used to compute the equilibrium compositions at other temperatures. Since the molal volumes of the metals at the equilibrium temperatures are not well known and are not very different, we have expressed the excess free energies of mixing in terms of mole fractions rather than volume fractions.

For the liquid solution the changes on mixing of the free energy per mole and of the molal chemical potentials are

$$F_x^M = RT(x_1 \ln x_1 + x_2 \ln x_2) + Bx_1x_2 \quad (1)$$

$$\mu_1^M = RT \ln x_1 + Bx_2^2 \quad (2)$$

$$\mu_2^M = RT \ln x_2 + Bx_1^2 \quad (3)$$

Similar equations would apply to the solid solutions, but we need the change in these functions in going from the two liquid components to the solid solutions, which functions we shall designate with primes.

$$F_x^{M'} = x_1L_1(T/T_1 - 1) + x_2L_2(T/T_2 - 1) + RT(x_1 \ln x_1 + x_2 \ln x_2) + B'x_1x_2 \quad (4)$$

$$\mu_1^{M'} = L_1(T/T_1 - 1) + RT \ln x_1 + B'x_2^2 \quad (5)$$

$$\mu_2^{M'} = L_2(T/T_2 - 1) + RT \ln x_2 + B'x_1^2 \quad (6)$$

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(1) H. Seltz, THIS JOURNAL, **56**, 307 (1934); *ibid.*, **57**, 391 (1935).

(2) G. Scatchard and W. J. Hamer, *ibid.*, **57**, 1805 (1935).

For approximate work we have found the method of Gibbs[3] more convenient than that of Seltz, although the latter would be preferable for exact calculations. Gibbs' method is to plot F_x^M and $F_x^{M'}$ against x_2 at each temperature, draw the common tangent and read the points of tangency as the composition of the respective phases. It is necessary to determine the two parameters by trial and error, so that some general conclusions may be noted. If $B = B'$ the liquidus and solidus will each approach asymptotically at each end the corresponding curve for ideal solutions, but they will deviate from the ideal curves in the middle unless B and B' are zero: if the parameters are positive the curves will spread outside (liquidus above, solidus below) the ideal curves; if the parameters are negative both curves will lie between the two ideal curves. If the parameters are unequal both curves will be displaced from the ideal toward the region which has the more positive parameter: if B' is more positive than B, the curves will be lowered and may give a minimum if the difference is great enough; if B' is more negative both curves will be raised and may give a maximum. The separation of the two curves will increase as the average of B and B' becomes more positive. The application of the method is illustrated for two systems.

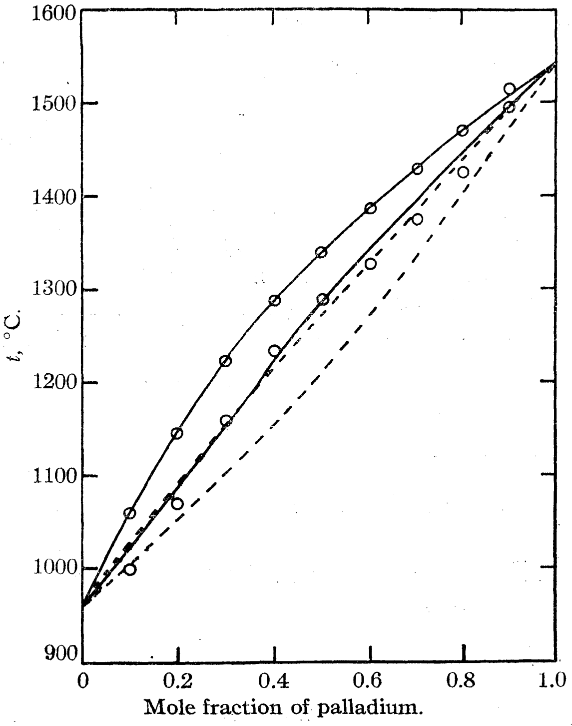

Fig. 1.—Silver–palladium equilibrium compositions: broken line, ideal; full line, equations 1 and 4; circles, observed.

Figure 1 shows the silver–palladium system, calculated with 2628 and 3822 cal. per mole for the heats of fusion of silver and palladium, respectively, and $B/2.3R = +83.93$; $B'/2.3R = -52.85$. The agreement with the liquidus is excellent. The parameters were chosen to fit the solidus near the middle of the temperature range, and miss some of the points as much as 25°. They obviously could have been chosen to give a better average fit over the whole curve, but it is not at all certain that the solidus curve is determined experimentally any more accurately than the present agreement. The figure shows definitely that a much more complicated equation would be required to give as pronounced a hump in the solidus curve as the experimental results indicate. The broken lines are the ideal curves.

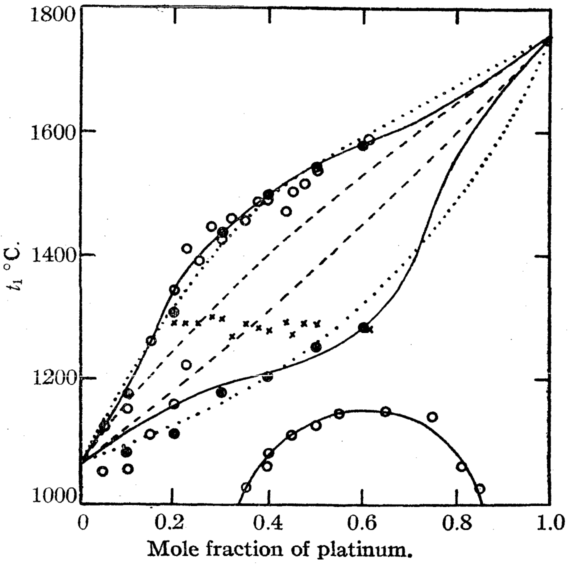

Fig. 2.—Gold–platinum equilibrium compositions: – – –, ideal; . . . . , customary curves ——, equations 1 and 4; ●, Doerinckel; ○, Grigorjew (liquidus and solidus); ×, Grigorjew (three phase); lower curve and circles, solid–solid equilibrium.

Figure 2 shows the gold–platinum system, calculated with 3130 and 5250 cal. per mole for the latent heats of fusion of gold and platinum, respectively, and $B/2.3R = +1155.5$; $B'/2.3R = +1164.6$. The top of the solid–solid equilibrium curve is also shown. The broken lines are those calculated for ideal solutions, and the dotted lines are the lens shaped pair usually drawn

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(3) J. W. Gibbs, "Collected Works," Longmans, Green, and Co., New York, 1906, p. 118.

from the measurements of Doerinckel,[4] which are represented by the black circles. The open circles represent the measurements of Grigorjew[5] of the liquidus and solidus, and the crosses represent his supposed equilibrium between two solids and a liquid. Our curves (full line) fit the liquidus and solidus at least as well as the usual curves. (Failure to obtain equilibrium should give too low a solidus.) They probably explain also the observations of Grigorjew, whose own explanation is certainly wrong.[6] The solidus curve is so flat from 1300 to 1200° that most of the remaining liquid solidifies in so small a temperature range that he interpreted it as an isothermal transition.

Since $B'/2R = 1340$, it indicates partial miscibility below 1340°A. or 1067°C., with the critical mixing composition fixed at the equimolal mixture by the nature of the equation. The experimentally observed critical mixing point is at 1150° and 60 mole per cent. platinum. Those forces, neglected in our equations, which displace this point from 50 to 60 mole per cent., might well raise the temperature 5 or 6%. The agreement may be considered a very good confirmation of the approximate accuracy of our treatment.

We attempted to apply the same method to the manganese–cobalt system, which shows a minimum melting point. In equilibria between two different states of aggregation, the temperature of a minimum or maximum gives only the difference between B and B', and the composition at the minimum or maximum is determined from the transition temperatures and heats of the components. Unless the heats of fusion in the literature are in error by more than their rather wide scattering, B–B' for this system decreases rapidly with increasing temperature, or with increasing cobalt concentration, and our equations are quite inadequate.

Seltz believed that "A phase diagram with liquidus curve displaced above the ideal and with solidus displaced below is shown to require the existence of very unusual activity curves," but we have reproduced such a diagram for the gold–platinum system accurately with equations corresponding to the simplest form of non-ideal curves. The discrepancy arises because Seltz makes the comparison between the deviations of the two components in each solution rather than between the deviations of each component in the two solutions. Such a phase diagram may result if the deviation of the higher melting component is more positive in the liquid than in the solid, and the deviation of the lower melting component is more positive in the solid than in the liquid. Since the solid solution is at every temperature richer in the higher melting component and poorer in the lower melting component than the liquid, this criterion is not hard to satisfy if the deviations are all positive.

Summary

Simple equations for the change in chemical potentials on mixing are applied to the equilibria between solid and liquid solutions of the silver–palladium and the gold–platinum systems, and some general conclusions are noted.

CAMBRIDGE, MASSACHUSETTS RECEIVED JUNE 29, 1935

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[4] Fr. Doerinckel, *Z. anorg. Chem.*, **54**, 345 (1907).

[5] A. T. Grigorjew, *ibid.*, **178**, 97 (1929).

[6] C. H. Johansson and J. O. Linde, *Ann. Physik*, [5] **5**, 762 (1930); W. Stengel and J. Weerts, *Siebert Festschr.*, 300–308 (1931).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Catalytic Decomposition of Nitramide in Acid and Salt Solutions[1]

BY CHARLES A. MARLIES AND VICTOR K. LA MER

Introduction

Brönsted developed his important theory of generalized basic catalysis from his kinetic studies of the reaction

$$NH_2NO_2 \text{ (nitramide)} \longrightarrow H_2O + N_2O^2$$

The reaction proceeds to completion without the complications of side reactions or any change in environment in aqueous systems[2b,3,4,5,6,7,8] and may be followed by physical means. The simplicity of the products and the sensitivity of the reaction to catalytic influence renders it particularly valuable for elucidating the theory of chemical kinetics in its various aspects, especially protolytic reactions. However, the difficulties of preparation and storage of nitramide have prevented the exhaustive investigation which the reaction deserves. A study of the preparation and the measurement of the decomposition of nitramide was accordingly undertaken to render this desirable reaction more conveniently available for kinetic investigations.

When this study was begun in 1929, the published work of Brönsted and his students[2b,4,5] showed that the decomposition of nitramide exhibited only generalized base catalysis, without appreciable primary salt effect. On the other hand, the other two well-established examples of generalized base catalysis, namely, the mutarotation of glucose[9] and the acetone–iodine reaction,[10] exhibited generalized acid catalysis as well. Other objectives were consequently the search for and the exact investigation of an acid catalysis and a salt effect for the nitramide reaction.

Using ordinary technique and methods of purification, an acid catalysis was quickly discovered, but the velocity constants obtained in duplicate experiments showed wide variations (5–10%). This same range of values was obtained by Brönsted and his students in their work on nitramide, but was by no means precise enough for the purpose, due to the small magnitudes of the acid and salt constants. By refining the technique the deviation from the mean was reduced to less than 1%. The first group of experiments (42 in number) in which the precision technique was not used and for which the variation in results was considerable are not reported.

Surprisingly few reactions even in solution have been measured within 1%. Furthermore, in practically all these cases a chemical method of following the reaction was used, which is surprising in view of the many advantages of physical methods.

A few experiments were made in low concentration of deuterium oxide (heavy water) and a marked decrease in rate was found (February, 1934). Further investigation in heavy water should throw light on the mechanism of the decomposition, which is still not certain, and the catalytic action of deuterium.

Materials

Nitramide.—Several modifications were made of the synthesis described by the discoverers, Thiele and Lachman.[3] The most important involves the manner of extraction of the nitramide from the aqueous solution in which it is made.[11] Other attempted methods of preparation, such as addition of silver nitrite to chloramine (explosion occurred) or addition of hydrogen chloride to an ether suspension of potassium nitrocarbamate, resulted in little or no yield of nitramide.

Further purification[5] of the nitramide produced no change in the velocity constants. The nitramide was stored in an open vessel in a desiccator over phosphorus pentoxide in the refrigerator. The desiccator was always brought to room temperature before opening to prevent condensation of moisture on the inside. The nitramide was handled exclusively in glass or bright platinum, as it attacks brass and other base metals.

Water.—Conductance water, prepared so as to ensure the absence as far as possible of all bases, *e. g.*, carbonates, silicates, etc., was used. In the last two distillations scrap platinum was used to prevent bumping, and the distillate was collected hot, a large proportion being allowed to escape as steam. The final distillation was from a quartz still.

Hydrochloric Acid.—Constant boiling hydrochloric acid was prepared from specially purified reagents. The con-

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(1) This paper was presented at the New York Meeting of the American Chemical Society, April, 1935.

(2) (a) Brönsted, *Rec. trav. chim.*, **42**, 718 (1923); (b) Brönsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924).

(3) Thiele and Lachman, *Ann.*, **288**, 267 (1895).

(4) Brönsted and Duus, *Z. physik. Chem.*, **117**, 299 (1925).

(5) Brönsted and King, THIS JOURNAL, **49**, 193 (1927).

(6) Brönsted and Volqvartz, *Z. physik. Chem.*, **A155**, 211 (1931).

(7) Brönsted and Vance, *ibid.*, **A163**, 240 (1933).

(8) Brönsted, Nicholson and Delbanco, *ibid.*, **A169**, 379 (1934).

(9) Brönsted and Guggenheim, THIS JOURNAL, **49**, 2554 (1927).

(10) Dawson and Lowson, *J. Chem. Soc.*, 1217 (1929).

(11) Marlies and La Mer, THIS JOURNAL, **57**, 2008 (1935). The modified method will be described in full in "Inorganic Syntheses."

centrations of acid were calculated from Bonner and Wallace's tables.[12]

Potassium and sodium chlorides were recrystallized from laboratory distilled water, constant boiling hydrochloric acid and conductance water. The dried salt was fused in a platinum crucible, the melt poured onto a wide platinum dish, broken up and bottled while hot.

Nitrous oxide, stated by the manufacturers[13] to contain 2% nitrogen as the only significant impurity, was passed in succession through sodium hydroxide solution, ferrous sulfate–sulfuric acid solution, water and a dense cotton plug.

Solutions.—Solutions were made up by weight to avoid contact with soft glass (ordinary calibrated) volumetric containers, using such precautions that the error in the concentration of the solutions was probably less than 0.01%. In most cases, at least one dilution of each solution was made. Analyses of the diluted solutions showed a maximum error of 0.1%, always in the direction of greater concentration, which is ascribed to evaporation during handling. Purified nitrous oxide was passed into the solutions through a quartz delivery tube.

Solutions more acid than 0.05 *M* were stored in quartz, and the more dilute in non-sol bottles, which were proved satisfactory for the purpose.

Apparatus and Experimental Procedure

The apparatus and method were similar to those used by Brönsted and his students[4,14] with some changes in design and procedure. The solution was shaken in a flask of about 200 ml. capacity and the rate of shaking was adjusted to the resonance period to give maximum agitation; for the same reason the flask was half filled with solution. The flask was closed by a ground glass stopper with a mercury seal. By regrinding the surfaces with levigated alumina and rubbing with Acheson graphite (99.9%), the ungreased joint held a vacuum of less than 1 mm. for several weeks.

The spiral connecting the flask to the manometer system was 3-mm. o. d. Pyrex tubing bent to permit a 2–3 cm. horizontal displacement of the flask. The manometer capillary, made of 1 mm. i. d. tubing, was not graduated itself, since Pyrex cannot be etched accurately, but was surrounded by a soft glass jacket, graduated from 0 to 18 cm. in 0.1 with a maximum error of 0.01 cm. The space between the jacket and the manometer tube was filled with very dilute hydrochloric acid to magnify the meniscus, the acid keeping the glass bright. The mercury reservoir was 5 cm. in diameter so that the maximum movement of the mercury in the manometer produced a fall in level in the reservoir of 0.01 cm. A mercury lubricant composed of dibutyl phthalate saturated with mercury-*p*-ditolyl[15] prevented sticking of the mercury column. The manometer and a very small part of the adjacent gas space were the only portions of the apparatus not immersed. No distillation into this space was observed at any time.

The space over the mercury column was evacuated to the lowest pressure possible with a Hy-Vac pump, because an appreciable pressure in this space would have necessitated a correction for change of room temperature during the run. No leakage into this space occurred over a period of months.

After introduction of the solution, the system was evacuated for two minutes while shaking, then carbon dioxide-free air admitted through a soda lime tower to the flask, the charge of nitramide (approximately 130 mg. = 0.002 mol.) added and the evacuation repeated. The procedure of double evacuation was followed, so that the entire system could be checked before the nitramide was introduced, and to ensure complete removal of the carbon dioxide. After five minutes of the second evacuation, the stopcock to the pump was closed and readings of pressure taken at ten-minute intervals.

In the absence of pretreatment with nitrous oxide, it was found that one to two hours were necessary before the readings could be used, probably due to the expulsion of dissolved air and traces of carbon dioxide by the nitrous oxide being formed. Using solutions containing nitrous oxide reduced this period to twenty or thirty minutes.

Occasionally the manometer temperature during the end-point reading or during the second set of readings (Guggenheim method) was sufficiently different to necessitate a correction for the expansion of the mercury, which never exceeded 0.01 cm. The Beckmann thermometer was compared with a platinum resistance thermometer calibrated by the Bureau of Standards, and with a *verre dur* thermometer calibrated by the International Bureau of Weights and Measures. The temperature of the thermostat[16] was controlled to within 0.01°. During the summer months artificial cooling was obtained by an electric fan directed on the surface of the bath and thrown into circuit on the cooling cycle, by means of a four pole Mercoid switch mounted on the relay of the regulator.

Calculations and Precision

The decomposition follows accurately the unimolecular law

$$k = (1/t) \ln (C_0/C) \qquad (1)$$

The final pressure measures the initial concentration of nitramide C_0. Since

$$C \sim (p_\infty - p);\ \ln (p_\infty - p) = \text{Const.} - kt \qquad (2)$$

or

$$\log (p_\infty - p) = \text{Const.}^* - k^*t \qquad (3)$$
$$\text{where } k^* = 0.4343k$$

Duplicate experiments under various conditions showed that this equation applies accurately. They also indicate that large indeterminate errors, such as effect of dissolved glass, etc., were absent.

Methods of Calculation.—In equation (3) the error in p_∞ exerts a greater influence than do the errors in the various p's. Guggenheim[17] avoids this source of error by taking two complete series of readings, separated by a constant time. However, the Guggenheim method need only be

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[12] Bonner and Wallace, THIS JOURNAL, **52,** 1747 (1930).

[13] S. S. White Dental Manufacturing Company.

[14] Brönsted and King, THIS JOURNAL, **47,** 2523 (1925).

[15] Hickman, *J. Opt. Soc. Am.*, **19,** 190 (1929).

[16] Beaver and Beaver, *Ind. Eng. Chem.*, **15,** 359 (1923).

[17] Guggenheim, *Phil. Mag.*, [7] **2,** 538 (1926).

used when the end-point reading is known with no more, or even less, accuracy than the other readings. In the present experiments, the end-point reading was observed over a long period of time (two to three hours), the reading being sometimes repeated on successive days; consequently it was more precise than any other observation. In check experiments the two methods gave the same results and the same deviation in k; consequently the one chosen for any particular experiment was dictated by convenience.

Guggenheim[17] suggests plotting log $(p'-p)$ against t, where p' refers to the reading in the second set corresponding to the reading p in the first set of observations. However, as Birge[18] has pointed out, graphical methods "give no objective criterion for the error. . . .They are never as accurate as an analytic method, and have no unique solution. . . .One of the most fundamental rules of computing is that the error introduced by the calculation itself shall be negligibly small, compared to the probable experimental error. A graphical solution obviously fails to satisfy this criterion." Although a direct plot and deviation line may be used as directed by Goodwin,[19] this involves considerable work with no certainty that the best solution has been obtained, unless several deviation plots are made.

An especially simple analytic method, if the observations are separated by equal time intervals, has been suggested by Roeser.[20] Applying this method to equation (3)

Let r = log $(p_\infty - p)$
m = number of values of r
i = interval between successive values of r (10 min.)

$$\text{Therefore } k^* = \frac{6}{im(m+1)\,(m-1)}\Sigma \qquad (4)$$

where $\Sigma = (m-1)\,(r_m - r_1) + (m-3)\,(r_{m-1} - r_2) + \ldots$

This method is based on the principles of least squares, where all the values r are of equal weight. It is of striking mathematical simplicity in contrast to other schemes.[21]

Errors.—In the construction of the apparatus and calculation of results, the following sources of errors received consideration: (1) assumptions in equation (2) leading to non-linearity of relationship between pressure change and concentration—(a) deviations from Henry's law; (b) deviation from Boyle's law; (c) change in volume of the gas space due to movement of mercury into manometer; (2) errors of apparatus and measurement—(a) non-uniformity of manometer bore; (b) temperature of manometer; (c) error in reading pressure; (d) supersaturation; (e) timing; (f) temperature of thermostat; (3) concentration of the solutions; (4) equality of the weights of the different points r.

Nitrous oxide[22] follows Henry's law in aqueous solution within the error of measurement, which was 0.25%. The assumption that this is the maximum deviation from Henry's law leads to only 0.07% error in equation (2) for the present apparatus. The error increases with increasing ratio of liquid to gas space and equals $(3.9 + 6.7\ V_g/V_1)^{-1}\%$. In the present case this ratio was 1.5. Nitrous oxide deviates from Boyle's law but in the low pressure range pV is a linear function of the pressure. This corrects equation (2) to

$$C \sim (p_\infty - p)/[1 - A(p_\infty + p)] \qquad (5)$$

where A = 0.0055/atm. at 25°.[23] The maximum correction amounted to 0.07% $(r_m - r_1)$ and was smaller for the succeeding terms of the series Σ.

On correction for error 1 c, eq. (2) becomes

$$C \sim (p_\infty - p)\ [1 + (p_\infty + p - p_1)\pi D^2/4V_g] \quad (6)$$

where p_1 is first reading used in the calculation and D is diameter of manometer capillary. The maximum correction was 0.04% $(r_m - r_1)$ and was smaller for the succeeding terms of the series Σ

Errors 2a, b and c produced a probable effect of 0.02 cm. This resulted in an error of about 0.5% $(r_m - r_1)$ which was about the same for all the terms of the series Σ. The error changed but slightly with the individual values of r, ranging from *ca.* 0.2% for r_1, to *ca.* 0.3% for r_m.

Pedersen[24] has shown that supersaturation merely invalidates the early readings; after a sufficient induction period, the usual graph of log $(p_\infty - p)$ has the same slope as though supersaturation were absent, provided the rate of stirring is kept constant. Experiments showed the maximum induction period to be four minutes. Error 2d is not present.

Error 2e was 0.02%, the maximum deviation of the watch from a frequency controlled standard. Error 2f amounted to 0.12% of k, based on E_{act} equal to 190 × 10^2 cal. Even at the highest concentration of salt used (2.9 M sodium chloride), error 3 was less than 0.1% k.

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[18] Birge, *Phys. Rev. Suppl.*, **1**, 1 (1929).

[19] Goodwin, "Precision of Measurements and Graphical Methods," McGraw-Hill Book Co., Inc., New York City, 1920.

[20] Roeser, *Bur. Standards Bull.*, **16**, 363 (1920), (Sci. paper 388).

[21] Reed and Theriault, *J. Phys. Chem.*, **35**, 673, 950 (1931).

[22] Findlay and Howell, *J. Chem. Soc.*, **105**, 291 (1914).

[23] Cawood and Patterson, *ibid.*, 619 (1933).

[24] Pedersen, THIS JOURNAL, **49**, 2681 (1927).

The various errors discussed above have different effects on the weights of the various r's. However, the only significant error is in the measurement of pressure and it has about the same effect on the various r's, the range being 0.2–0.3%. Therefore, all the points have about the same weight, justifying the above application of the method of least squares (*cf.* Roseveare[25] and Luten[26]).

Precision of the Data.—Since the various errors are present to the same extent in all experiments the deviation from the mean can be obtained by an analysis of the results of a large set of duplicate experiments. The results are given in Table I for 0.01 M hydrochloric acid (k^* is given in min.$^{-1}$, M in mole/kg. and C in mole/liter).

TABLE I

Expt.	$k^*_{obs.}$	Wt.	d
95	0.001187	16	0.000051
97	1243	13	5
144	1239	10	1
148	1234	14	4
189	1249	14	11
191	1235	11	3
220	1233	20	5
222	1236	18	2

Discarding the first value, the weighted mean is 0.001238, the weighted a. d. is 0.000005 and the % d. is 0.4; the maximum variation of the individual values is 1.3%. In 0.5 M hydrochloric acid a greater variation (2.2%) was obtained: $k^* = 0.001251$; a. d. = 0.000009; % d. = 0.7; $n = 7$ (number of duplicate experiments). Since this a. d. was the largest observed, the diameters of the circles in Figs. 1 and 2 were chosen equal to $0.000009/\sqrt{n}$. In averaging experiments the rate constants were given weights equal to the number of observations used for their calculation.

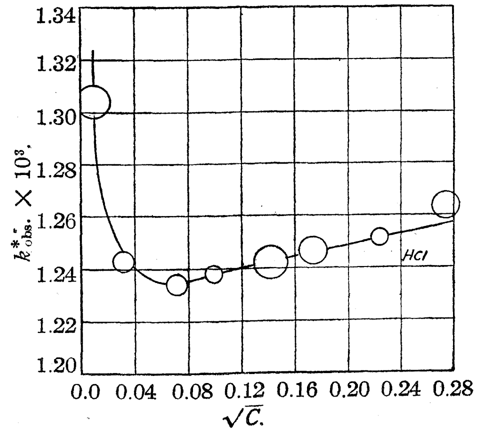

Fig. 1.

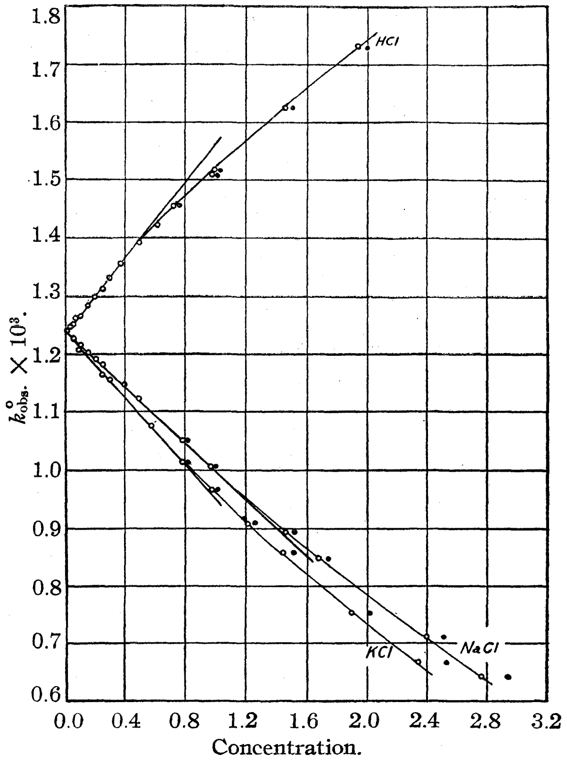

Fig. 2.—Above 0.7 molar: ○, molarity; ●, molality.

After adoption of the precision technique, only 9 values of k in some 180 were rejected and in *all* cases the rejected k's were *lower* than the means of their duplicates, which would be the case if there were a slight leak into the apparatus during the experiment. Since two stopcocks had to be turned to start any experiment and since the apparatus was under vacuum during the entire time (six days in some cases) the occasional occurrence of slight leaks is not surprising. The value of k is sensitive to leaks, as the deviation from the mean of the rejected experiment (No. 95) on 0.01 molal hydrochloric acid can be accounted for by the admission of sufficient air to increase p_∞ by 0.15 cm.

Suggested Improvements in Design.—1. Lengthened manometer tube. This will decrease the effect of the most important error—measurement of pressure. 2. Elimination of all stopcocks in the gas phase. 3. Immersion of the manometer into the thermostat to obviate correction for its temperature change. 4. Decrease of the gas to liquid ratio to enable the use of

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(25) Roseveare, THIS JOURNAL, **53**, 1651 (1931).

(26) Luten, *J. Phys. Chem.*, **39**, 199 (1935).

smaller charges of nitramide, thus compensating for the lengthened manometer tube, which would require larger charges of nitramide.

Data

A typical experiment is given in Table II.

TABLE II

EXPT. NO. 191, HCl 0.01000 M, $p_\infty = 15.47$

t	p	$p_\infty - p$	Log $(p_\infty - p)$	k^*
10	4.59	11.18	1.0484	0.00122
20	4.60	10.87	1.0362	121
30	4.90	10.57	1.0241	121
40	5.19	10.28	1.0120	124
50	5.48	9.99	0.9996	124
60	5.76	9.71	.9872	122
70	6.03	9.44	.9750	122
80	6.29	9.18	.9628	124
90	6.55	8.92	.9504	124
100	6.80	8.67	.9380	122
110	7.04	8.43	.9258	125
120	7.28	8.19	.9133	124
130	7.51	7.96	.9009	122
140	7.73	7.74	.8887	125
150	7.95	7.52	.8762	123
160	8.16	7.31	.8639	126
170	8.37	7.10	.8513	

The graph of $\log(p_\infty - p)$ *vs.* t is a straight line after the forty minutes reading with slope 0.001239.

Using readings 40 to 170: $m = 14$, $i = 10$, $\Sigma = 5.6179$, $k^*_{\text{obs.}} = 0.001235$ min.$^{-1}$.

TABLE III

HYDROCHLORIC ACID SOLUTIONS

n	M	C	$k^*_{\text{obs.}}$	C_W	$k^*_{\text{corr.}} = k^*_{\text{obs.}} - k^*_W C_W$
2	0.0000100	0.0000100	Drift	55.35	...
2	.0001000	.0000997	1.304×10^{-3}	55.35	...
5	.001000	.000997	1.243	55.34	...
5	.00500	.00499	1.234	55.34	...
7	.01000	.00997	1.238	55.33	0.004×10^{-3}
2	.01999	.01993	1.242	55.31	.008
3	.03000	.02990	1.246	55.29	.012
7	.05000	.04981	1.251	55.24	.018
3	.07499	.07467	1.263	55.20	.031
2	.1000	.09953	1.267	55.14	.037
2	.1500	.1492	1.285	55.04	.057
4	.2000	.1987	1.298	54.94	.072
2	.2500	.2481	1.314	54.84	.090
2	.2997	.2972	1.331	54.75	.109
2	.3750	.3713	1.356	54.59	.138
3	.5000	.4940	1.391	54.34	.178
2	.6248	.6158	1.422	54.09	.215
1	.7449	.7325	1.455	53.85	.253
2	.7493	.7368	1.456	53.84	.254
2	1.0000	.9787	1.510	53.34	.320
3	1.0202	.9981	1.517	53.30	.328
5	1.5000	1.4542	1.625	52.36	.457
3	2.0000	1.9294	1.730	51.35	.584

The results of sets of experiments at various concentrations are given in Tables III, IV, V and VI. The densities required for the conversion from molality to molarity were taken from "International Critical Tables"[27] or calculated by the rule of mixtures which has been shown to hold for aqueous solutions of hydrochloric acid, sodium chloride and potassium chloride.[28]

In the hydrochloric acid solutions (Fig. 1) the velocity constant reaches a minimum between 0.001 and 0.005 M. The square root of the concentration has been used to magnify the scale at very low concentrations. The values for the extremely dilute acid solution (10^{-5} M hydrochloric acid) drifted continuously during the course of the experiments from an initial value of 0.0013 to 0.0015 when half completed, the average value being about 10% greater than that for 0.01 M hydrochloric acid, which is identical with the 10% increase found by Brönsted and King[5] for the velocity of decomposition in "pure water" over that in "acid" solution at 15°. However, their claim that the deviations from the unimolecular course were not measurable if the observations were confined to the first two-thirds of the reaction was not confirmed, due we believe to the greater precision of our measurements.

The observed k^*'s of Tables III, IV, and V at concentrations greater than 0.005 M are plotted in Fig. 2 against both molarity and molality, the differences being greater than the experimental error above 0.7 molar. For simplicity the curves connecting the molality values have not been drawn. Similarly, to avoid confusion, points and curves of $k^*_{\text{obs.}}$ *vs.* mole fraction have not been added; they lie between the molarity and molality points but nearer the molarity values. It appears that for this reaction a linear relation holds to a slightly higher concentration for the molarity scale.

The velocity constant may be considered as composite: $k = k_0 + k_s C_s$ (7) where k_0 = spontaneous velocity constant (water reaction), k_s = velocity constant for S (acid or salt), and C_s = concentration of S. Extrapolating the hydrochloric acid curve to zero concentration

$$k^*_0 = 1.235 \times 10^{-3}$$

The limiting slopes in Fig. 2 and the concentrations over which they are valid

$k^*_{\text{HCl, obs.}} = + 0.328 \times 10^{-3}$ from 0 to 0.4 molar

$k^*_{\text{NaCl, obs.}} = - 0.245 \times 10^{-3}$ from 0 to 1.0 molar

$k^*_{\text{KCl, obs.}} = - 0.291 \times 10^{-3}$ from 0 to 0.8 molar

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(27) "International Critical Tables," Vol. III, pp. 54, 79, 87.

(28) Ruby and Kawai, THIS JOURNAL, **48**, 1119 (1926).

TABLE IV

SODIUM CHLORIDE SOLUTIONS, $M_{\text{HCl}} = 0.01000$

n	M_{NaCl}	C_{NaCl}	$C_{\text{H}_3\text{OCl}}$	$k^*_{\text{obs.}}$	C_W	$k^*_{\text{corr.}} = k^*_{\text{obs.}} - k^*_W C_W - k^*_{\text{H}_3\text{OCl}} C_{\text{H}_3\text{OCl}}$
2	0.05035	0.05015	0.00996	1.227×10^{-3}	55.28	-0.010×10^{-3}
1	.1005	.0999	.00995	1.216	55.23	− .020
2	.1512	.1503	.00994	1.204	55.18	− .031
2	.2005	.1991	.00994	1.193	55.13	− .041
2	.2471	.2452	.00993	1.183	55.08	− .050
1	.4010	.3969	.00991	1.148	54.93	− .081
2	.4947	.4889	.00988	1.124	54.84	− .103
2	.8020	.7880	.00983	1.050	54.53	− .170
2	.9887	.9680	.00979	1.005	54.23	− .209
2	1.504	1.458	.00969	0.892	53.80	− .312
2	1.733	1.672	.00965	.848	53.56	− .350
3	2.506	2.381	.00950	.711	52.74	− .469
3	2.927	2.758	.00942	.643	52.28	− .527

TABLE V

POTASSIUM CHLORIDE SOLUTIONS, $M_{\text{HCl}} = 0.01000$

n	M_{KCl}	C_{KCl}	$C_{\text{H}_3\text{OCl}}$	$k^*_{\text{obs.}}$	C_w	$k^*_{\text{corr.}} = k^*_{\text{obs.}} - k^*_w C_w - k^*_{\text{H}_3\text{OCl}} C_{\text{H}_3\text{OCl}}$
3	0.04006	0.03989	0.00996	1.228×10^{-3}	55.27	-0.009×10^{-3}
3	.09004	.08955	.00995	1.210	55.19	− .025
3	.1502	.1491	.00993	1.200	55.10	− .033
3	.2455	.2431	.00990	1.166	54.95	− .064
2	.3000	.2966	.00989	1.156	54.87	− .072
2	.5881	.5768	.00981	1.076	54.42	− .142
3	.8024	.7821	.00975	1.012	54.09	− .199
3	1.0031	.9721	.00969	0.966	53.78	− .238
3	1.252	1.205	.00962	.907	53.39	− .288
3	1.502	1.435	.00955	.857	53.00	− .329
2	2.009	1.890	.00941	.752	52.21	− .417
2	2.521	2.337	.00927	.668	51.44	− .483

TABLE VI

HYDROCHLORIC ACID–POTASSIUM CHLORIDE SOLUTIONS

n	M_{HCl}	M_{KCl}	C_{HCl}	C_{KCl}	$k^*_{\text{obs.}}$
2	0.0000100	0.0000101	0.0000100	0.0000101	Drift
2	.0001000	.0001008	.0000997	.0001005	1.283×10^{-3}
2	.001000	.001008	.000997	.001005	1.239
2	.004961	.004963	.004946	.004948	1.230
2	.05000	.05002	.04974	.04976	1.237
2	.1250	.3752	.1231	.3694	1.160
2	.1500	.1501	.1485	.1486	1.240
2	.2999	.1000	.2966	.09889	1.281
2	.3750	.3761	.3674	.3685	1.232
2	.5000	.2501	.4905	.2453	1.299
1	.5000	.5005	.4870	.4874	1.228
2	.7449	.2556	.7272	.2495	1.346
2	1.0000	.5040	.9646	.4861	1.316
3	0.9999	1.0003	.9590	.9594	1.176
5	1.4997	0.5001	1.4347	.4784	1.436

Water Correction

k_0 is the velocity constant due to the catalysis by water and equals $k_w C_w$. At 24.84° the molar catalytic constant for water is $k^*_w = 0.02231 \times 10^{-3}$. For high concentrations of acid and salt it cannot be assumed that C_w has a constant value of 55.51 m./l. Accordingly, equation (7) is more properly written $k = k_w C_w + k_s C_s$ and correction should be made for the reduced concentration of water as acid and salt are added. Furthermore, in the hydrochloric acid solutions, the proton exists as H_3O^+, still further decreasing the water concentration. Accordingly

$k_{\text{corr.}} = k_{\text{obs.}} - k_w C_w$ for the HCl solutions

$k_{\text{corr.}} = k_{\text{obs.}} - k_w C_w - k_{\text{H}_3\text{OCl}} C_{\text{H}_3\text{OCl}}$ for the NaCl and KCl in 0.01 M HCl solutions

The recalculated results are given in the last columns of Tables III, IV and V; the corrected k's have been plotted against the molarities. The limiting slopes and the concentrations over which they are valid

$k^*_{\text{H}_3\text{OCl, corr.}} = +0.367 \times 10^{-3}$ from 0 to 0.4 molar

$k^*_{\text{NaCl, corr.}} = -0.213 \times 10^{-3}$ from 0 to 1.4 molar

$k^*_{\text{KCl, corr.}} = -0.251 \times 10^{-3}$ from 0 to 0.8 molar

Miscellaneous Experiments

Heavy Water.—Some experiments were conducted with a solution of heavy water containing 4.72 mole per cent. of D_2O (d_{25} 1.00213 g./ml.). To ensure proper purification, a specimen of ordinary water purposely contaminated with potassium hydroxide, rubber and laboratory sweepings was purified at the same time and concurrent experiments carried out with both specimens. In the distillations the liquids were heated to dryness in the stills and the sprayhead and condenser flamed to remove the last traces of water, which was necessary to avoid waste and isotopic separation during the purification. The receivers were kept in freezing mixtures during the distillations. The samples were redistilled five times at atmospheric pressure from various purifying agents and finally in a special two-flask apparatus by vaporization *in vacuo*. The vacuum was broken with purified nitrous oxide and the distillates poured into tared non-sol bottles. By means of a micro weighing buret, a few drops of constant boiling hydrochloric acid was added to make the solutions 0.01 *M* in hydrochloric acid. After one experiment, without withdrawing the solution, an additional charge of nitramide was added and a second experiment carried out. Then the proper amount of potassium chloride was added to make the solutions 1 *M* in potassium chloride and two more experiments performed. The results are given in Table VII.

TABLE VII

Solution	Expt.	$k^*_{\text{obs.}}$	Wt.	Mean
0.00982 *M* HCl in 4.72% D_2O	181	1.174×10^{-3}	35	1.176×10^{-3}
	183	1.178	29	
0.00976 *M* HCl in H_2O	182	1.246	35	1.249
	184	1.252	29	
0.00982 *M* HCl + 1.000 *M* KCl in 4.72% D_2O	185	0.923	29	0.919
	187	.915	26	
0.00976 *M* HCl + 1.000 *M* KCl in H_2O	186	.976	29	0.971
	188	.966	26	

It is evident that the method of purification was adequate. The mean for the 0.01 *M* HCl in H_2O is 0.9% higher, and the mean for the 0.01 *M* HCl + 1 *M* KCl in H_2O is but 0.4% higher than those for the corresponding solutions made up by the usual method.

The velocity constant for 0.01 *M* HCl in 4.7% D_2O is 5.8% lower, and the velocity constant for 0.01 *M* HCl + 1 *M* KCl in 4.7% D_2O is 5.2% lower than those for the corresponding H_2O solutions. An investigation of this striking result is in progress.

Mercuric Chloride.—While studying the effect on the reaction velocity of all possible substances in the system, mercury, mercurous chloride and mercuric chloride were tried. The first two had no effect, but the last showed a marked positive catalysis. In 0.01 *M* HCl + *ca.* 10^{-5} *M* $HgCl_2$, k^* was 2×10^{-3}, an increase of 75% over that in the same solution without the mercuric chloride. This effect is probably related to the molecular rather than ionic nature of mercuric chloride in solution and merits further investigation.

Discussion

Comparison with Previous Work.—Contrary to the earlier published findings from Brönsted's laboratory, a marked primary salt effect and an appreciable acid catalysis were found. On communication of these results, Professor Brönsted disclosed the following values of the velocity constant[29] obtained at 15° in potassium chloride solutions containing a little hydrochloric acid.

C_{KCl}, m./l.	1.00	1.50	2.00
k^*	31.85	27.90	24.50×10^{-5}

They show the same negative salt effects reported here.

After this study was initiated in 1929, Brönsted and Vance[7] reported an acid catalysis in isoamyl alcohol. The molar catalytic constant found was approximately the same for both hydrochloric and hydrobromic acids, which they ascribe to the ion $C_5H_{11}OH_2^+$. For 0.1 *M* this acid effect was about 100 times larger than the spontaneous reaction. Brönsted and his students have not found an acid catalysis in aqueous solution due to the restricted acid range in which they worked, the lower precision of their measurements and the relatively small magnitude of the effect.

Salt Effect.—The action of added salt on the decomposition of nitramide is undoubtedly a primary salt effect upon the catalysis by water. The effect is large amounting to an 18% decrease for 1 molar sodium chloride and 22% for 1 molar potassium chloride.

Of the reactions subject to generalized base catalysis, only one other, the enolization of acetoacetic ethyl ester, has been studied in concentrated salt solutions. For the spontaneous reaction in water Pedersen[30] has found a large linear negative salt effect amounting to 18% in 1 molar sodium chloride and 22% in 1 molar potassium chloride at 18°. This exact agreement with the nitramide results, which can hardly be fortuitous since the temperature effect is very small, points to the same cause operating in the two cases, which is the effect of the salts on the basic proper-

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[29] Brönsted, private communication; experiments made in 1926–27.

[30] Pedersen, *J. Phys. Chem.*, **37**, 751 (1933).

ties of water. (The acid catalysis by water of both reactions must be vanishingly small compared to the base catalysis.) This salt effect is probably due to hydration, since thereby water is removed. Indeed, it is even possible to calculate the average hydration of the ions required to produce the decrease, the values obtained being similar to those given by other methods.

Using Brönsted's results at 15° and the corresponding values at 24.84° interpolated from the curve in Fig. 2, the constants in the integrated form of the Arrhenius equation, $\log k^* = B - E/2.3026RT$ are

C_{KCl}, m./l.	1.00	1.50	2.00
B	10.90	10.71	10.72
E	189.8	187.6	188.9 × 10^2 cal.

The minor variation is within the precision of the data.

Acid Effect.—The positive effect of hydrochloric acid on the decomposition of nitramide is small, being of the same order of magnitude as the salt effects. The increase in reaction velocity is only 2.6% in 0.1 molar hydrochloric acid. Pedersen found a similar increase (3.8%) for the enolization of acetoacetic ethyl ester and was uncertain as to whether it represented primary salt effect or hydrogen ion catalysis. For the nitramide reaction there is little doubt that the effect is acid catalysis, because of the existence of acid catalysis in isoamyl alcohol.[7] The much smaller value of the acid catalysis in water is to be expected from the leveling effect of the base water on strong acids.

Another and better proof of acid catalysis is given by Fig. 3, in which $\log k^*_{\text{corr.}}$ for the hydrochloric acid effect is plotted against the acidity function, $H_0 = -\log a_{H^+}(f_B/f_{BH^+})$, using for the latter the values of Hammett and Paul.[31] With the exception of the value in 2 M hydrochloric acid, all the points agree with the straight line within the experimental error. (The error is large for the first two points because $k^*_{\text{corr.}}$ is obtained as the difference of two quantities which are almost equal.)

Although there may also be a primary salt effect of the hydrochloric acid on the water catalysis, it must be quite small because it is extremely unlikely, as Fig. 3 shows, that this salt effect would follow the same mathematical relationship as the acid catalysis.

Mechanism of the Decomposition.—Pedersen[32] has suggested a plausible mechanism for the decomposition by bases. He assumes that the following equilibria are attained practically instantaneously

$$H_2N\cdot NO_2 \rightleftarrows HN{=}NO_2^- + H^+ \rightleftarrows HN{=}NOOH$$

and that there is present at all times a constant, but very small, fraction of the undissociated nitramide in the form HN=NOOH. He explains the decomposition as taking place when bases remove the last proton bound to the nitrogen. Since HN=NOOH is a neutral molecule, this explanation is in conformity with the absence of appreciable salt effect in dilute solution, as found by Brönsted and his students for all their experiments no matter what the charge type of the base. It should be pointed out that the assumption of a very small fraction of the undissociated nitramide present as HN=NOOH is not necessary, since the decomposition can just as well be explained by assuming that *all* the undissociated nitramide is present in this form and that a very *small* percentage of the collisions by bases is fruitful. Indeed Hantzsch[33] maintains that the nitramide ordinarily exists in the form HN=NOOH rather than $H_2N\cdot NO_2$.

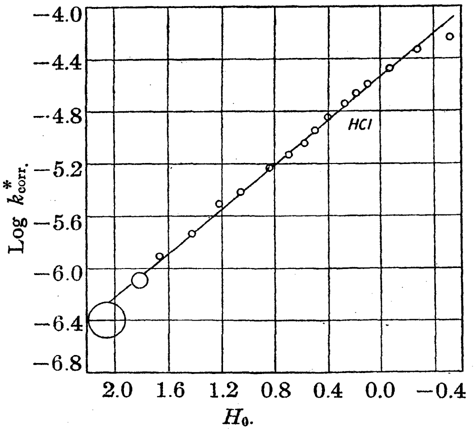

Fig. 3.

It is difficult to see why Pedersen accepts the mechanism proposed by Brönsted to explain the rise in reaction velocity in solutions of very low acidity (pure water). Brönsted postulated[6] that the nitramide ion decomposes about twenty times more rapidly than the undissociated nitramide, so that the increased dissociation as the acidity is decreased causes a more rapid decom-

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(31) Hammett and Paul, THIS JOURNAL, **56**, 827 (1934).

(32) Pedersen, *J. Phys. Chem.*, **38**, 581 (1934). *Vide*, p. 589.

(33) Hantzsch, *Ber.*, **66B**, 1566 (1933).

position. However, the results are just as well explained by assuming catalysis of the undissociated nitramide by OH^-, which increases in concentration as the acidity is decreased. Brönsted mentioned this possibility in an earlier paper.[5] Indeed, because of the equilibrium

$$H_2N_2O_2 + OH^- \rightleftarrows HN_2O_2^- + H_2O$$

it is impossible to differentiate kinetically between the two such conceptions. However, equivalence of the interpretation is not a sufficient reason for a departure from the first mechanism of the nitramide decomposition as a basic catalysis of the molecule.

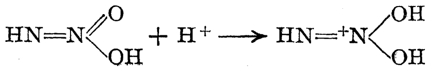
Assuming catalysis of the molecule by OH^-, the molar velocity constant was calculated from the measurements made below 0.005 *M* HCl, in which range the velocity constant increases (see Fig. 1). In calculating the OH^- concentration, correction was made for the influence of the nitramide present for which the dissociation constant of nitramide was taken to be 2.55×10^{-7}, the value for 15°.[5] The results are given in Table VIII.

TABLE VIII

C_{HCl}	C_{OH^-}	$k^*_{obs.}$	$(k^*_{obs.} - k^*_{0,\ corr.})/C_{OH^-}$
0.001000	1×10^{-11}	1.243×10^{-3}	$0.8 \times 10^{+6}$
.0001000	0.8×10^{-10}	1.304	$0.9 \times 10^{+5}$
.0000100	0.2×10^{-9}	*ca.* 1.45	*ca.* $1.1 \times 10^{+6}$

The agreement is within the precision of the data. This molar velocity constant is about 2000 times the most rapid hitherto measured for the nitramide decomposition. A very long and probably unjustified extrapolation of the Brönsted and Pedersen formula[2b] indicates about 10^9 for k_{OH^-} at 15°.

We advance the following mechanism to explain the acid catalysis



$$HN{=}N\begin{smallmatrix}{\nearrow}O\\ {\searrow}OH\end{smallmatrix} + H^+ \longrightarrow HN{=}{}^+N\begin{smallmatrix}{\nearrow}OH\\ {\searrow}OH\end{smallmatrix}$$

The substance formed should be unstable, since two OH groups have never been known to be bound to one nitrogen atom, and therefore the compound should decompose into nitrous oxide and oxonium ion.

Acknowledgment is made to the College of the City of New York for the use of some of the apparatus for this investigation.

Summary and Conclusions

1. The preparation and the measurement of the decomposition of nitramide was studied to render this desirable reaction more conveniently available for kinetic investigations.

2. An improved method of preparation of nitramide is outlined.

3. The rate of decomposition of nitramide has been measured in aqueous acid and salt solutions over a wide range of concentrations with an error of about 1%.

4. A detailed analysis of the errors has been presented.

5. Suggestions have been advanced for an improved apparatus, so as to make the measurement of the velocity of a chemical reaction proceeding by gas evolution more precise.

6. A negative primary salt effect has been found which is ascribed to the effect of salt on the catalytic properties of the base water. The constants of the Arrhenius equation have been calculated.

7. An acid catalysis has been found which is closely correlated with the acidity function H_0.

8. Pedersen's mechanism for the basic catalysis has been discussed and simplified. The catalytic constant for hydroxyl ion is about 2000 times greater than that of any other base measured previously.

9. A mechanism for the acid catalysis has been advanced.

10. Heavy water decreases the velocity of the decomposition as compared to ordinary water.

11. Mercuric chloride has a marked positive effect on the reaction velocity.

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Hydrous Thoria Hydrosols Considered as Polynuclear Basic Thorium Complexes

BY ARTHUR W. THOMAS AND CHESTER B. KREMER

The purpose of this paper is to submit evidence in support of the view that hydrous thoria hydrosols (more accurately, thorium oxychloride or basic thorium chloride hydrosols) may be regarded as polyolated and/or oxolated complexes, differing from thorium chloride crystalloidal solutions of low basicity in degree rather than in kind. This chemical point of view of the so-called metallic oxide hydrosols has been previously proposed for aluminum[1] and chromium oxysalt hydrosols.[2] In the present investigation, twelve basic thorium chloride hydrosols were studied, the results obtained with three of them ("C," "E," "F") being submitted here as typical.

Preparation and Description of Hydrosols.—Hydrosol "C" was prepared as follows. Portions of 3 *N* ammonium hydroxide (redistilled) were added to an aqueous solution of pure thorium chloride at room temperature with mechanical stirring. The addition of ammonium hydroxide was continued until the liquid became decidedly turbid, whereupon the stirring was continued for twenty-four hours. Then the liquid was dialyzed at room temperature against a highly permeable nitrocellulose membrane for five days using running distilled water.

Hydrosols "E" and "F" were prepared by the action of hydrochloric acid ("E") and of thorium chloride ("F") upon hydrous thoria at room temperature as follows. Hydrous thoria was precipitated from a thorium chloride solution by addition of ammonium hydroxide. Centrifugal washings and decantations were then applied until chloride ion had been removed. The hydrous oxide was then suspended in a small amount of distilled water and the desired amount of hydrochloric acid or thorium chloride dissolved in about 1500 cc. of water, was slowly added accompanied by vigorous stirring. After standing for twenty-four hours, the systems were dialyzed for six days as described above.

In all cases, at the conclusion of dialysis the hydrosols were centrifuged for one hour (1200 r. p. m., 42 cm. radius) and the supernatant liquid was siphoned into water-resistant glass bottles.

These three hydrosols which were turbid in appearance are described quantitatively in Table I. The micelles were positively charged.

TABLE I

COMPOSITION OF HYDROSOLS

Sol	Thorium milliequiv. per liter	Chloride milliequiv. per liter	Eq. Th/Eq. Cl	*p*H[a]
C	81.3	12.4	6.6	3.95
E	63.9	5.7	11	3.97
F	100.9	13.1	8	4.16

[a] The *p*H values are those measured immediately at the completion of dialysis.

Action of Neutral Salts.—The hydrosols were titrated with various potassium salts in the following manner. To 10-cc. portions of hydrosol in 30 cc. volume glass-stoppered bottles were added 10 cc. portions of salt solution. The bottles were rotated (7 r. p. m.) for 12 ± 3 hours at 25 ± 0.2° and the *p*H values were then measured. The quinhydrone electrode was used in cases where the *p*H value was below 8, the platinized-platinum hydrogen gas electrode being employed for systems with *p*H values near to or greater than 8.

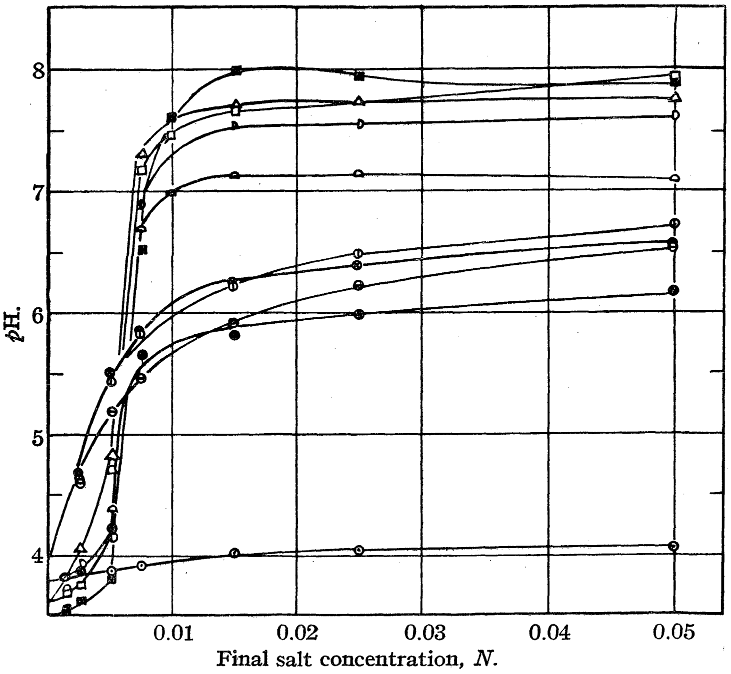

Fig. 1.—Effect of potassium salts on the *p*H value of Sol C: ⦶, acetate; ⊙, chloride (also nitrate); ■, citrate; ⊖, formate; △, malate; ⌓, malonate; □, oxalate; ⊗, propionate; ●, sulfate; D, tartrate.

In the case of the hydrogen electrode, the mixture was filtered to remove precipitate when oxalate was the added salt. No other salt caused precipitation when the *p*H value exceeded 8.

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(1) (a) A. W. Thomas and T. H. Whitehead, *J. Phys. Chem.*, **35**, 27 (1931); (b) A. W. Thomas and A. P. Tai, THIS JOURNAL, **54**, 841 (1932); (c) T. H. Whitehead and J. P. Clay, *ibid.*, **56**, 1844 (1934); (d) A. W. Thomas and R. D. Vartanian, *ibid.*, **57**, 4 (1935).

(2) A. W. Thomas and F. C. von Wicklen, *ibid.*, **56**, 794 (1934).

The *p*H values of the 0.1 *N* potassium salt solutions were adjusted to *p*H = 6.4 ± 0.3[3] by the addition of potassium hydroxide in the case of the chloride, nitrate and sulfate and by addition of the proper 0.1 *N* acid to the other solutions. These values are given in Table II.

TABLE II

*p*H VALUES OF 0.1 *N* POTASSIUM SALT SOLUTIONS

Acetate	6.6	Nitrate	6.3
Chloride	6.2	Oxalate	6.4
Citrate	6.8	Propionate	6.4
Formate	6.4	Succinate	6.4
Malate	6.3	Sulfate	6.3
Malonate	6.4	Tartrate	6.5

The reaction time of twelve hours was well beyond that required for a "practical equilibrium" to be established.

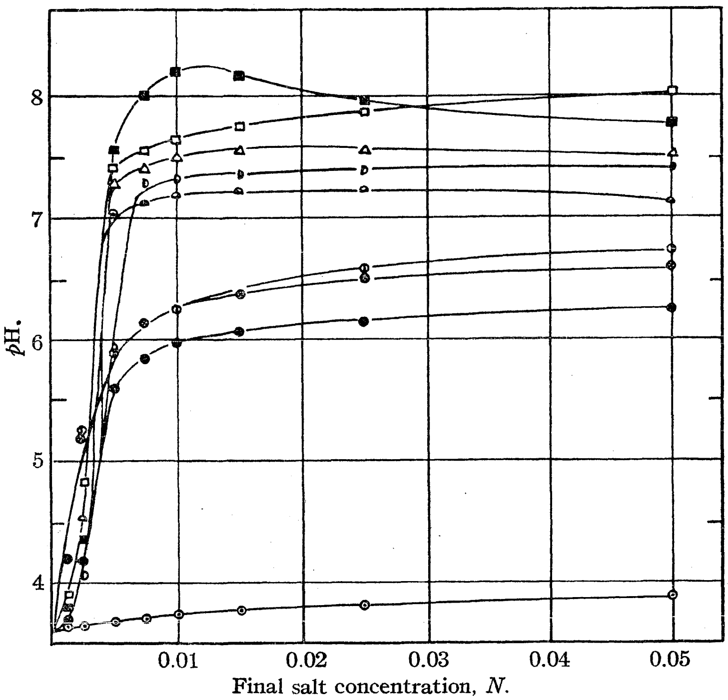

Fig. 2.—Effect of potassium salts on the *p*H value of Sol E: ⦶, acetate; ⊙, chloride (also nitrate); ■, citrate; △, malate; ⌓, malonate; □, oxalate; ⊗, propionate; ●, sulfate; D, tartrate.

The results of the *p*H-salt titrations are shown in Figs. 1, 2 and 3.[4] It is seen that the *p*H raising order is in general: citrate > oxalate > malate > tartrate > malonate > succinate > acetate > propionate > formate > sulfate > chloride = nitrate. This series is similar to those obtained with basic aluminum[1] and chromic[2] salt hydrosols in so far as the above salts were studied with the latter named sols.

As pointed out in previous publications from this Laboratory, these increases in *p*H values are ascribed to the displacement of the coördinatively bound hydroxo (and possibly ol) groups from the thorium atom by the anions of the added salt. Salts producing a marked increase in *p*H value contain anions which have a stronger coördinative binding tendency than those producing smaller *p*H increases. This occurs whether the central metallic atom is part of a colloidal micelle or is a simple crystalloid ion.

Aquo and chlorido groups should likewise be displaced by the added anions. That the latter takes place is evidenced by increased chloride ion activity caused by the addition of salts to other oxide hydrosols.[5] The displacement of aquo groups by the added anions should lead to reversal of the sign of charge of the micelles. In certain instances this happens and the subject will be discussed in a subsequent paper.

Effect of Age.—Basic thorium chloride hydrosols stored at room temperature rapidly become more acid in reaction (to about *p*H 3) as shown in Fig. 4. This may be accounted for by three mechanisms: (1) aquo groups are converted to hydroxo groups and free hydrogen ion, (2) olation removing a product of reaction (1) favors (1) and, (3) oxolation of ol groups liberates hydrogen ion. At room temperature (3) would not be expected to proceed to any great extent. All of these reactions are favored by rise in temperature. Portions of the hydrosols which were boiled in a ground glass joined Pyrex glass reflux apparatus decreased in *p*H to the range of 2.1–2.5 depending upon the concentration of the sol. A typical example of the rate of change is shown in Fig. 5. When these heated sols were allowed to stand at room temperature, partial reversal of the reactions was noted as shown in Fig. 4. Conflicting statements are found in the literature concerning

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(3) With the exception of citrate where the *p*H value was adjusted only to 6.80.

(4) Basic thorium chloride hydrosols "age" rapidly, *i. e.*, they olate and/or oxolate rapidly at room temperature. For example, when dialysis of sol "E" was concluded it had a *p*H value of 3.97; three days later its *p*H value was 3.65 and in five days it was 3.45. This behavior accounts for the *p*H values at zero salt concentration not being identical inasmuch as one could not perform all the salt titrations in one day. The decrease in *p*H on "aging" is, of course, reflected also in the *p*H values attained upon addition of neutral salts.

(5) (a) H. B. Weiser, *J. Phys. Chem.*, **35**, 1, 1368 (1931); (b) S. Roychoudhury, A. Sen and A. Chatterjee, *J. Indian Chem. Soc.*, **11**, 23 (1934).

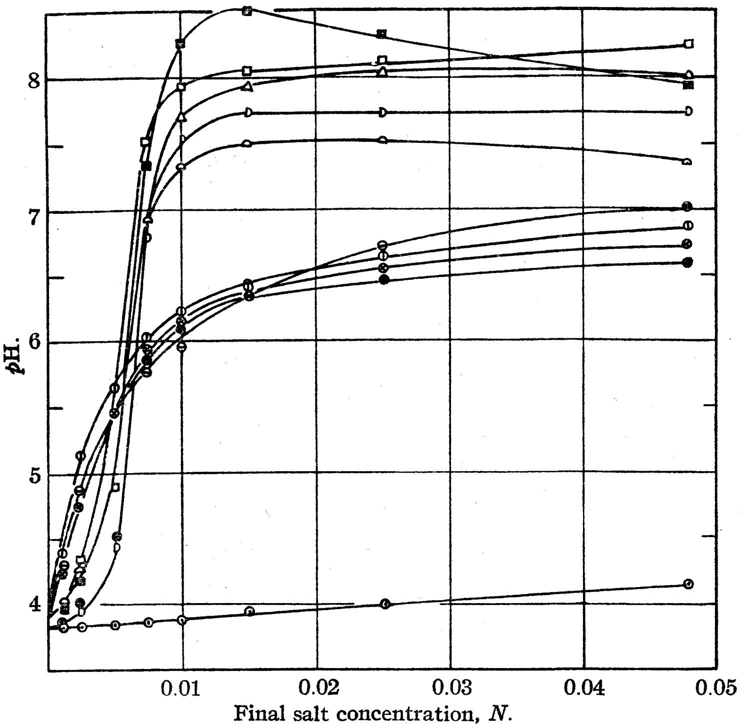

Fig. 3.—Effect of potassium salts on the pH value of Sol F: ⦶, acetate; ⊙, chloride; ■, citrate; ⊖, formate; △, malate; ◓, malonate; □, oxalate; ⊗, propionate; ●, sulfate; D, tartrate.

pH changes in "oxide" hydrosols. That the pH may increase or decrease is explained by the present theory. A metallic "oxide" hydrosol which has been boiled, or which has not been sufficiently dialyzed, becomes less acid on standing due to hydrogen ion reacting with OH groups in the complex and also to partial deolation. A well dialyzed sol, on the other hand, becomes more acid upon aging due to conversion of aquo to hydroxo groups, to olation and to oxolation.

The conversion of hydroxo to ol groups should render a sol less responsive to the pH increasing action of added neutral salts since one would suspect ol groups to be more firmly held by the thorium atoms than hydroxo groups. Oxo groups would, of course, be unaffected by neutral salt additions.

The effect of previous heating on the pH raising effect of neutral salt additions is shown in Fig. 6. This behavior is the same as that noted in the case of basic aluminum[1b] and basic chromium[2] salt hydrosols.

Conductance Titrations.—Conductivity titrations of basic aluminum and basic chromium salt hydrosols with silver salts have revealed that the drop in conductivity is the greater, the stronger the tendency is for the anion to become coördinatively bound to the central metallic atom.[1b,2] Employing a technique essentially the same as that previously described, the data plotted in Fig. 7 were obtained.[6] The relatively effective coördinative binding ions, sulfate and acetate, produce steep drops in the conductivity. To be sure, part of the conductivity drop is due to combination between the chloride ions in the sol and the added silver ions, but the steep drop cannot be attributed entirely to this reaction, as previously stated.

The coördinative binding of the anion results in its being without effect upon the conductivity of the system and, further, if it is bound by replacement of aquo groups, it thereby lowers the positive charge upon the micelle and thus another conductivity lowering factor enters the picture. Silver nitrate produced a slight fall in conductivity in the case of sol "C" while in sol "F" it produced a slight increase in conductivity. Thus nitrate, known in general as a weak coördinative binding ion and in particular as regards thorium,

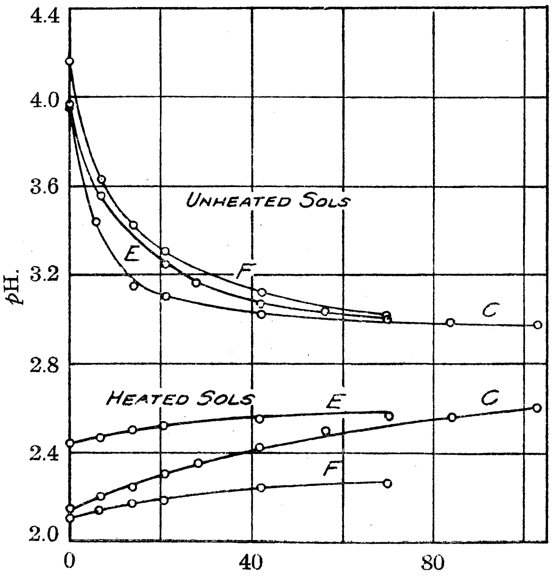

Fig. 4.—Change in the pH values of unheated and of boiled sols upon standing at room temperature.

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[6] The abscissas represent milliequivalents of solid silver salt added to 50 cc. of hydrosol.

shows some coördinative tendency in the case of sol "C" but not with sol "F."

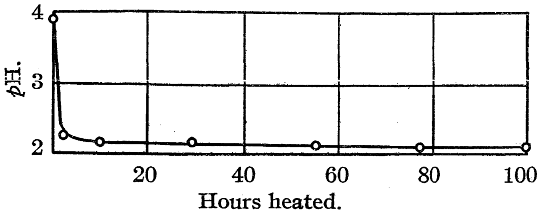

Fig. 5.—Change in *p*H value produced by boiling sol F.

Inasmuch as sols "C" and "F" had approximately the same ratio of Th:Cl, then the difference might be ascribed to the fact that they were prepared by different methods, inasmuch as one would hardly expect the 25% difference in concentration between the two sols to produce the divergence in nitrate penetration.

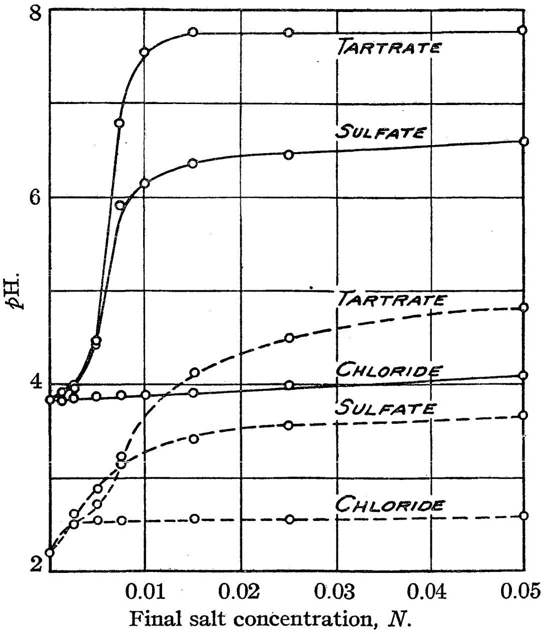

Fig. 6.—Effect of potassium salts on the *p*H value of sol F before and after boiling: ———— unheated sol; – – – – – boiled sol.

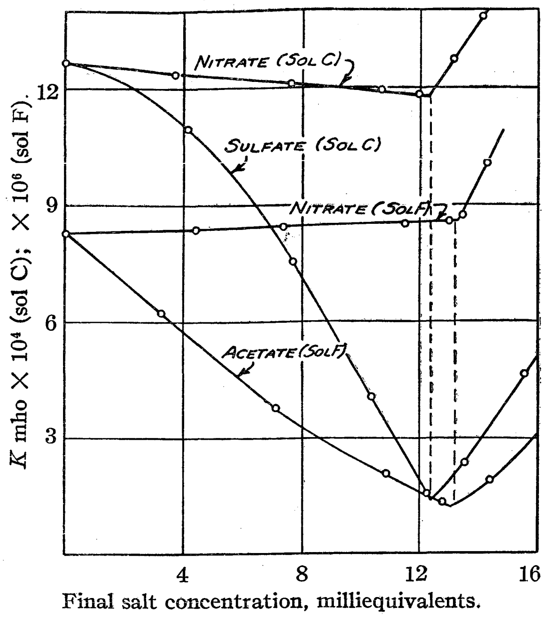

Fig. 7.—Effect of silver salts upon the specific conductivities of sols C and F.

Summary

The *p*H values of basic thorium chloride (so-called "thorium oxide") hydrosols are raised by the addition of potassium salts. The order of effectiveness in general, similar to that found with certain other "oxide" hydrosols, is: citrate > oxalate > malate > tartrate > malonate > succinate > acetate > propionate > formate > sulfate > chloride = nitrate, the first named markedly increasing the *p*H value while the last named exerted very slight effect. The effect is ascribed to displacement of coördinatively bound OH groups by the anion of the added salt, the anion then becoming coördinatively bound. Dialyzed basic thorium chloride hydrosols rapidly become more acid on standing at room temperature; the rate increases upon heating and the reactions producing this effect show partial (or extremely slow) reversal. Heated basic thorium chloride hydrosols are less responsive to the *p*H increasing effect of added neutral salts. The interpretation of these behaviors can be made on the assumption of a polyolated and/or oxolated structure of the micelle, an extension to colloidal dispersions of the postulates which Werner and Pfeiffer applied to crystalloid basic salts.

NEW YORK, N. Y. RECEIVED JUNE 12, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Basic Zirconium Chloride Hydrosols

BY ARTHUR W. THOMAS AND HARRY S. OWENS

Studies upon metallic "oxide" hydrosols previously reported from this Laboratory[1,2,3] have been extended to include basic zirconium chloride hydrosols (generally known as "zirconium oxide" hydrosols).

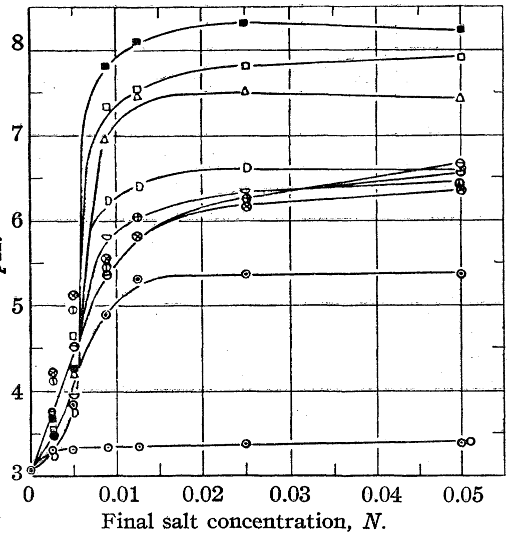

Fig. 1.—Effect of potassium salts on the *p*H value of Sol B; sol one day old: ⦶, acetate; ⊙, chloride; ■, citrate; ⊖, formate; ▽, glycolate; △, malate; ○, nitrate; □, oxalate; ⊗, propionate; ●, sulfate; D, tartrate.

The behavior of fifteen different basic zirconium chloride hydrosols was investigated, the results obtained with three which were typical of all being submitted here.

Preparation and Description of Hydrosols.—Hydrosols "B" and "F" were prepared in the following manner. Hydrous zirconium oxide precipitated from an aqueous solution of pure zirconyl chloride by redistilled ammonium hydroxide was washed by centrifugal decantations to the absence of a test for chloride ion. Portions of this oxide were rotated in contact with a 0.4 *M* zirconyl chloride solution at 25° for twenty-four hours in water-resistant glass-stoppered bottles. They were then dialyzed as previously described,[3] "B" for twenty hours and "F" for one hundred hours. Hydrosol "D" was prepared by boiling a 0.6 *M* aqueous zirconyl chloride solution in a glass-joined Pyrex reflux apparatus for twenty-four hours when it was dialyzed for one hundred and four hours. All sols were then centrifuged for one hour at 120 r. p. m. and a 42-cm. rotating diameter.

These hydrosols were turbid in reflected light, "D" exhibiting a bluish cast. To transmitted light "B" and "F" were colorless and clear while "D" was clear but orange-red in color. The micelles were positively charged in each case. Quantitative data are given in Table I.

TABLE I

COMPOSITION OF HYDROSOLS

The *p*H values are those obtained immediately at the completion of dialysis.

Sol	Zirconium milliequiv. per liter	Chloride milliequiv. per liter	Eq. Zr/Eq. Cl	*p*H
B	89.1	11.2	8.1	3.22
D	136.7	9.0	15	3.50
F	38.5	2.3	17	3.92

Action of Neutral Salts.—The effect of additions of potassium salts upon the *p*H values of the hydrosols was measured as previously described.[3] All of the potassium salt solutions were adjusted to *p*H 6.5 ± 0.3 as listed in Table II. The results obtained are plotted in Figs. 1, 2 and 3. It is seen that the *p*H values were raised in every case, alkaline solutions resulting with citrate, oxalate, malate and tartrate. The order of effectiveness of the anions is, citrate > oxalate > malate > tartrate > glycolate > succinate = malonate = maleinate > propionate = acetate = fumarate = formate > sulfate > chloride = nitrate.

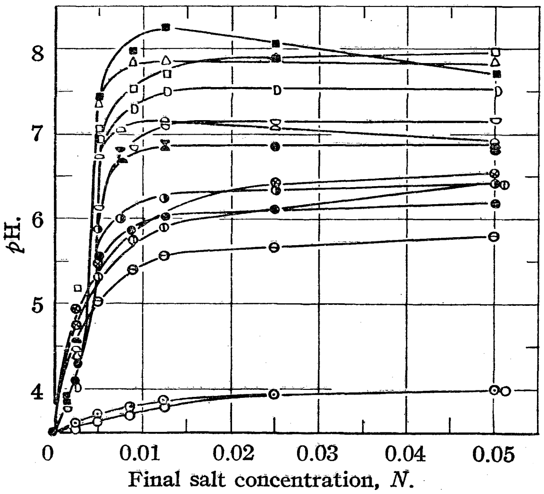

Fig. 2.—Effect of potassium salts on the *p*H value of Sol D; sol four days old: ⦶, acetate; ⊙, chloride; ■, citrate; ⊖, formate; ◑, fumarate; ▽, glycolate; △, malate; ▾, maleinate; ⌓, malonate; ○, nitrate; □, oxalate; ⊗, propionate; ▴, succinate; ●, sulfate; D, tartrate.

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[1] (a) A. W. Thomas and T. H. Whitehead, *J. Phys. Chem.*, **35**, 27 (1931); (b) A. W. Thomas and A. P. Tai, THIS JOURNAL, **54**, 841 (1932); (c) A. W. Thomas and R. D. Vartanian, *ibid.*, **57**, 4 (1935).

[2] A. W. Thomas and F. C. von Wicklen, *ibid.*, **56**, 794 (1934).

[3] A. W. Thomas and C. B. Kremer, *ibid.*, **57**, 1821 (1935).

TABLE II

*p*H VALUES OF 0.1 *N* POTASSIUM SALT SOLUTIONS

Salt	*p*H	Salt	*p*H
Acetate	6.6	Maleinate	6.8
Chloride	6.6	Nitrate	6.4
Citrate	6.8	Oxalate	6.6
Formate	6.5	Propionate	6.6
Fumarate	6.3	Sulfate	6.5
Glycolate	6.5	Tartrate	6.6
Malate	6.3		

In general this is similar to the order found with the other basic metalli-salt hydrosols studied in this Laboratory.[1,2,3] Such an order might be expected from the present incomplete knowledge of the crystalloidal chemistry of zirconium.[4] De Boer,[5] for example, has found the following order for the tendency of anions to become coördinatively bound to zirconium: $OH > F > PO_4 > C_2O_4 > SO_4 > NO_3 > Cl$. Although the OH group seems to be one of the most strongly coördinatively bound (which would indicate difficultly in displacing it), conditions in the experiments performed favored its displacement because the hydroxyl ion concentration in the body of the solution was low while the concentration of the added anion was comparatively high. However, as the hydroxyl ion concentration of the solution increases owing to the displacement of hydroxo groups by the added anion, much greater amounts of salt are required for the reaction to proceed. The equilibria among hydroxo (and ol), hydroxy, aniono, and anion groups accounts for the shape of the curves in Figs. 1–3.

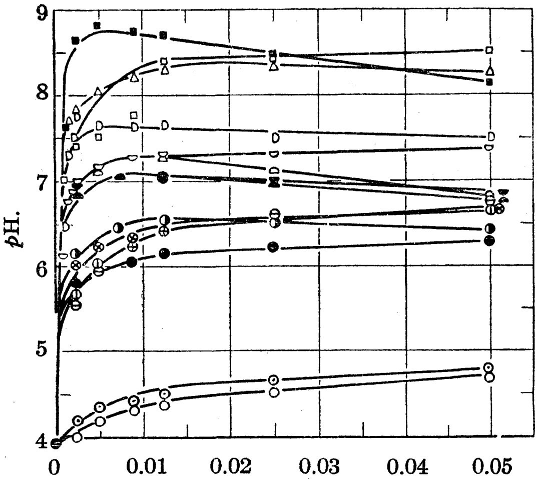

Fig. 3.—Effect of potassium salts on the *p*H value of Sol F; sol four days old: ⦶, acetate; ⊙, chloride; ■, citrate; ⊖, formate; ◑, fumarate; ▽, glycolate; △, malate; ▾, maleinate; ⌓, malonate; ○, nitrate; □, oxalate; ⊗, propionate; ▴, succinate; ●, sulfate; D, tartrate.

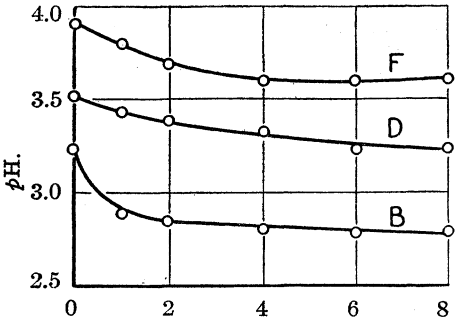

Fig. 4.—Change in *p*H of sols upon standing at room temperature.

Effect of Aging and Heating.—Representative results of the change in the *p*H values of basic zirconium chloride hydrosols stored in water-resistant glass bottles at room temperature are given in Fig. 4. It will be noted that the *p*H values decrease on aging in every case although not so rapidly as reported for basic thorium chloride sols.[3] This decrease is believed to be due to olation, and to a smaller extent oxolation. Olation though not changing the hydrogen ion activity itself, removes the primary hydrolytic

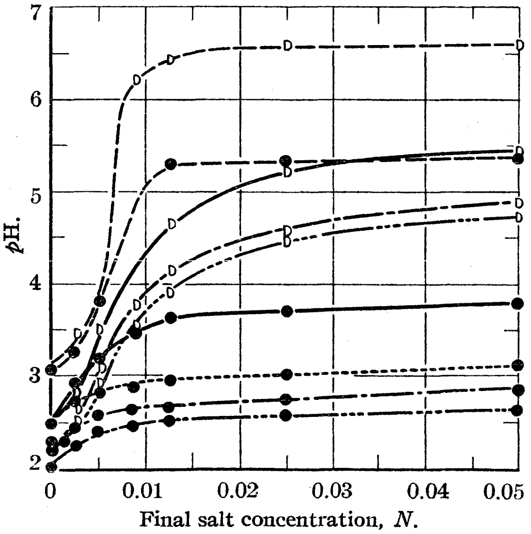

Fig. 5.—The effect of boiling of Sol B upon its reaction to the addition of potassium salts: D, tartrate; ●, sulfate; — — —, not heated; ———, boiled 8 hr.; - - - - - - - -, boiled 96 hr.; — - —, boiled 192 hr.; — - - - —, boiled 240 hr.

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(4) F. P. Venable, "Zirconium," A. C. S. Monograph, Chemical Catalog Co., New York, 1922.

(5) J. H. de Boer, *Z. anorg. allgem. Chem.*, **165**, 1 (1927).

products favoring further hydrolysis and production of hydrogen ions.

Upon boiling, the *p*H of basic zirconium chloride sols decreases as in the case of other "oxide" sols reported from this Laboratory but, upon standing at room temperature after being boiled, the reaction showed no tendency to reverse. In this respect basic zirconium chloride sols differ from those of aluminum, chromium and thorium. Typical results are given in Table III. Among the group of elements named, zirconium is unique in that the normal ion in crystalloidal solution is a basic one. The stability of the zirconyl radical is well known, powerful coördinators being required to decompose it. The inertness of ignited zirconium oxide to nearly all ordinary reagents also typifies the stability of oxygen bridges between zirconium atoms. For these reasons it is believed that boiling a basic zirconium chloride hydrosol produces a high degree of oxolation.[6] The oxygen bridges thus formed are stable to the acid produced during the boiling and consequently little change in the *p*H values of the sols standing at room temperature would be expected.

In view of the shift of the reactions, hydroxo compounds $\rightleftarrows$ ol complexes $\rightleftarrows$ oxo complexes to the right upon heating, one would expect added neutral salts to exert less *p*H raising effects. A typical series of measurements is plotted in Fig. 5.

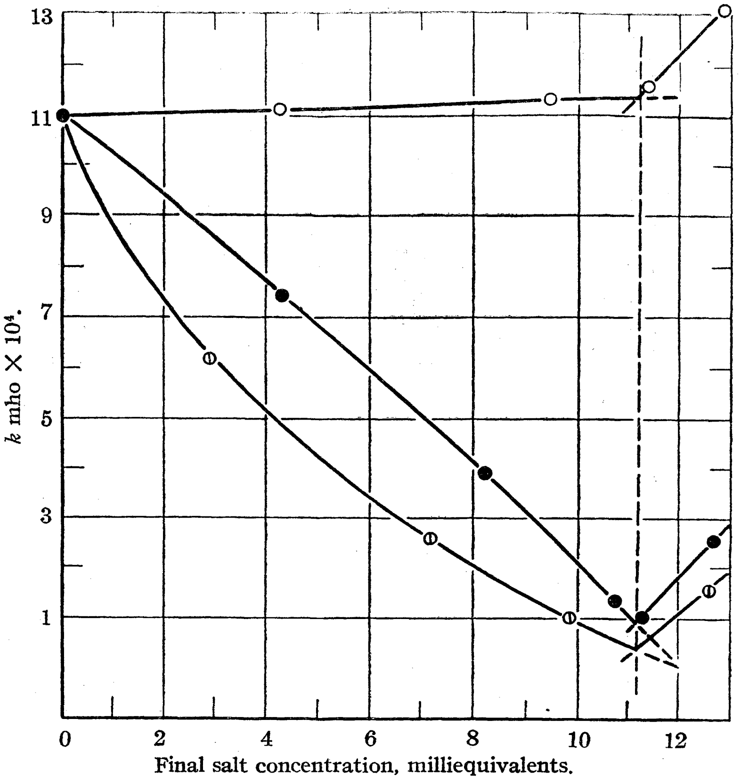

Fig. 6.—The effect of silver salts upon the specific conductivity of Sol B: ◐, silver acetate; ○, silver nitrate; ●, silver sulfate.

TABLE III

DECREASE OF *p*H OF HYDROSOLS UPON BOILING

Sol	*p*H before boiling	Hours boiled	*p*H after boiling	*p*H 6 months later[a]
B	3.11	8	2.50	2.45
	2.80	96	2.40	
	2.80	192	2.22	2.22
	2.80	240	2.04	2.09
D	3.50	72	2.50	2.44
F	3.90	72	3.19	3.12
	3.90	120	3.12	
	3.90	190	2.91	
	3.90	240	2.84	
	3.90	288	2.72	

[a] Kept at 25° for six months after cessation of boiling.

Conductance Titrations.—Conductance titrations with silver salts performed by means of a technique previously described[1b,2,3] produced the values plotted in Fig. 6. Here again the silver salt containing the more strongly coördinative binding anion was the more effective in lowering the conductivity. Nitrate shows little or no such tendency and as a result silver nitrate produced an increase in conductivity just as in the case of a basic chromium[2] and of a basic thorium[3] chloride hydrosol. Interpretations of these behaviors have been published.[1b,2,3] Similar curves for "thorium oxide" and "aluminum oxide" hydrosols have been obtained by Pauli.[7]

Summary

The *p*H values of basic zirconium chloride (so-called "zirconium oxide") hydrosols are raised by the addition of potassium salts. The order of effectiveness in general similar to that found with

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(6) x-Ray investigations made by Böhm and Niclassen [*Z. anorg. allgem. Chem.*, **132**, 1 (1924)] upon the gel obtained by ultrafiltration of a freshly prepared basic zirconium nitrate hydrosol showed it to be amorphous. The gel ultrafiltered from such a hydrosol which had been boiled for many hours showed a few bright rings which, considering their location, were probably those of zirconium oxide. After heating the precipitate from an evaporated sol at a higher temperature, the x-ray diagram for zirconium oxide was obtained.

(7) Wo. Pauli and E. Valkó, "Elektrochemie der Kolloide," Verlag Julius Springer, Vienna, 1929, pp. 552, 554.

other hydrosols is citrate > oxalate > malate > tartrate > glycolate > succinate = malonate = maleinate > propionate = acetate = fumarate = formate > sulfate > chloride = nitrate, the first named markedly increasing the *p*H value while the last named exerted very slight effect. This effect is ascribed to displacement of coördinatively bound OH groups by the anion of the added salt, the anion then becoming coördinatively bound to zirconium atoms in the micelle. Dialyzed basic zirconium chloride sols become more acid upon standing at room temperature although not so rapidly as basic thorium chloride sols. The decrease in *p*H is hastened by heating and the reactions show no sign of reversal after six months of storage at 25°. In the latter respect, basic zirconium hydrosols differ from those of thorium. As in the cases of other basic metalli-salt hydrosols, the heated sols are less responsive, in so far as *p*H changes, to the action of added neutral salts.

It may be said that "zirconium oxide" hydrosols show a very strong tendency to oxolate.

By application of the ideas which Werner and Pfeiffer suggested for crystalloid basic salts, and assuming that the micelles in basic zirconium chloride hydrosols are polyolated and/or oxolated structures, their behaviors can be readily interpreted.

NEW YORK, N. Y. RECEIVED JUNE 12, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

The Extraction of Germanium and Gallium from Germanite. I. The Removal of Germanium by the Distillation of Germanous Sulfide

BY WARREN C. JOHNSON,[1] LAURENCE S. FOSTER AND CHARLES A. KRAUS

Germanite is a sulfide ore containing chiefly copper, iron, arsenic, germanium, zinc, lead, gallium, and aluminum as well as minute amounts of several other elements. It was discovered in 1920 at Tsumeb, South West Africa, by Schneiderhöhn.[2] An analysis by Pufahl[3] showed the presence of germanium, and further analyses by Kriesel,[4] Lunt,[5] and Thomas and Pugh[6] not only verified the germanium but, in addition, showed gallium to be present in appreciable quantities.

Several methods of extraction of germanium from germanite have been reported[7] in which the ore is either roasted or subjected to oxidation with a mixture of nitric and sulfuric acids, leading eventually to the separation of the germanium from aqueous solutions containing the other elements of the ore. The procedures are tedious and require the handling of relatively large quantities of solutions. Patnode and Work[8] chlorinated the ore at 350° and then fractionally distilled the anhydrous chlorides produced. The fraction containing the germanium was hydrolyzed to precipitate the dioxide. After this product had been dissolved in hydrochloric acid, germanium tetrachloride was distilled from the solution in the presence of chlorine, according to the very useful method of Buchanan.[9]

In the present paper, a process is reported for the complete removal of germanium from germanite as germanous sulfide in the vapor phase. The method eliminates the handling of large volumes of solutions, the distillation of liquids, and leaves a residue from which the gallium can be removed very readily. The simplicity of the process will be evident from a description of the operations required for the removal of germanous sulfide.

Operation I.—Finely ground germanite is heated in a stream of dry, oxygen-free, nitrogen gas at 800° with the removal of arsenious sulfide and sulfur.

Operation II.—Ammonia gas is passed over the residue from (I) at 825° whereby the germanic sulfide of the ore is reduced to germanous sulfide, which, in turn, distils from the ore mass to collect in cooler regions of the apparatus. If the arsenious sulfide is completely removed in (I), germanous sulfide is the only substance to leave the ore in (II).

For the preliminary experiments, we are greatly indebted to the late Professor Charles James of

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(1) Present address: University of Chicago, Chicago, Illinois.

(2) Schneiderhöhn, *Metall u. Erz*, **17**, 364 (1920).

(3) Pufahl, *ibid.*, **19**, 324 (1922).

(4) Kriesel, *ibid.*, **20**, 257 (1923); *Chem. Ztg.* **48**, 961 (1923).

(5) Lunt, *S. African J. Sci.*, **20**, 157 (1923).

(6) Thomas and Pugh, *J. Chem. Soc.*, **125**, 816 (1924).

(7) Keil, *Z. anorg. allgem. Chem.*, **152**, 101 (1926); Dede and Russ, *Ber.*, **61**, 2451 (1928); and Pugh, *J. Chem. Soc.*, 2540 (1929).

(8) Patnode and Work, *Ind. Eng. Chem.*, **23**, 204 (1931).

(9) Buchanan, *ibid.*, **8**, 585 (1916); *cf.* Müller, THIS JOURNAL, **43**, 1088 (1921); Dennis and Papish, *ibid.*, **43**, 2131 (1921); Dennis and Johnson, *ibid.*, **45**, 1380 (1923).

the University of New Hampshire for a 50-g. sample of germanite. In addition, ore was purchased during the course of the work from the Otavi Minen und Eisenbahn Gesellschaft, Berlin, Germany. Analyses showed the germanium content of the several lots to range from 4.5 to 7%.

Apparatus

A diagram of the apparatus used in the two stages of the process is shown in Fig. 1. A large furnace A was constructed to take care of considerable quantities of the ore, 600–700 g. in *Operation I* and about twice this quantity in *Operation II*. For this furnace, a threaded Vitreosil tube, 56 cm. in length and 7.6 cm. in diameter, wound with number 14 Chromel A wire in two coils of equal length, was placed in a sheet iron container 20 cm. in diameter. The furnace was insulated with Sil-o-Cel. This arrangement permitted use of the coils either in series or in parallel and provided a satisfactory means for controlling the rate of heating and the temperature. The furnace was arranged so that it could be moved horizontally on two steel rods about 1.5 meters in length which were supported at the ends by steel plates. The furnace and carrier were mounted on a bench (not shown in figure).

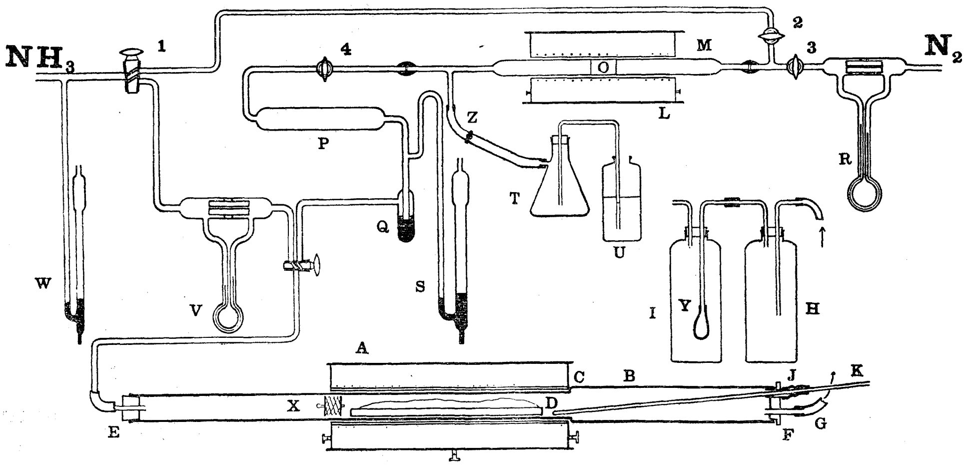

Fig. 1.

The germanite was placed in a cylindrical Alundum boat D, 50 cm. long, 4.5 cm. in diameter and 0.5 cm. thick. The Vitreosil furnace tube B (shown in the figure for *Operation II*) was constructed by fusing a tube, 100 × 5 cm., to a second section, 50 × 10 cm. in dimensions. The joint of the seal at C was made as nearly a right angle as possible. The ends of B were closed with rubber stoppers, E and F; the former being fitted with a glass tube 6 mm. in diameter to permit the entrance of nitrogen or ammonia, while the latter was equipped with a tube G, 15 mm. in diameter, leading to the dust bottles, H and I. A cheesecloth bag, tied at Y, served to remove finely divided material suspended in the gas stream. A large rubber tube led from I to the hood. Through a glass tube J was slipped a loosely fitting Vitreosil tube K, sealed at the inner end and fastened in position with rubber tubing. With this tube it was possible to scrape germanous sulfide crystals from the wall of the large Vitreosil tube B near C to prevent plugging of the apparatus.

For *Operation I*, tube B was replaced by a second Vitreosil tube (not shown in the figure) about 75 mm. long to which was attached by means of an asbestos packed, brass gland an iron tube of the same dimensions. This joint was placed immediately beyond the end of the furnace so that the greater part of the arsenious sulfide condensed in the iron section.

In order to obtain nitrogen free from oxygen, ordinary tank nitrogen was passed over copper wire in the Vitreosil tube M, which was heated to about 600° by an electric furnace L. This tube was provided with a transparent section at O through which one might observe the condition of the copper. After *Operation I*, it was found necessary to reduce the copper oxide in M; ammonia gas was used for this purpose. By proper adjustment of stopcocks 1, 2, 3 and 4, and the screw clamp at Z, the gas stream, which also contained water from the reduction of the copper oxide, was allowed to pass through the trap T and into the bottle U where the excess ammonia was absorbed. A tube P, filled with phosphorus pentoxide, was placed beyond the furnace to dry the nitrogen. The rate of flow of the gas was indicated and regulated by a mercury bubbler Q and a flowmeter R. The apparatus was provided with a mercury safety-trap S which served as an outlet in case of plugging.

The ammonia used in *Operation II* was transferred from commercial cylinders into steel tanks of approximately 10 kg. capacity. The latter contained metallic sodium as drying agent. The ammonia was allowed to escape from these tanks as a gas and to enter the apparatus at a point indicated in the diagram. Its rate of flow was determined by the flowmeter V. A safety-trap W was connected ahead of the furnace tubes. A plug X, made from shredded asbestos held between Chromel wire gauze, was inserted in the furnace tube to prevent heating of the exposed length of quartz tube and circulation of the gases in a direction opposed to the main gas stream. Without this plug considerable material was found to deposit in the cooler regions of the tube in the direction toward E.

Procedure and Results

Operation I.—Between 600 and 700 g. of the ore ground so as to pass through a 100-mesh, but not a 180-mesh, screen was placed in the Alundum boat which was then inserted in the Vitreosil tube. After the air in the apparatus had been expelled by the passage of approximately 50 liters of dry, oxygen-free nitrogen, the furnace was heated to 800° as rapidly as possible, and maintained at this temperature for four and one-half hours with a nitrogen flow of 30 liters per hour. The furnace was allowed to cool and the boat was removed and weighed. After the arsenious sulfide had been scraped from the Vitreosil and iron tubes, another sample was prepared and the above procedure repeated. The resulting slugs were removed from the boat, labeled, and set aside for *Operation II.* The loss in weight for the different lots of ore is recorded in Table I.

TABLE I

LOSS IN WEIGHT OF GERMANITE IN THE TWO OPERATIONS

Ore (lot no.)	Ore, kg.	% loss Operation I	Operation II	Total loss, %
1	8.19	13.6	12.9	26.5
2	17.44	13.6	12.6	26.2
3	24.69	11.9	16.4	28.3
4	19.10	13.2	12.1	25.3
4	4.05	12.6	13.6	26.2
5	16.56	14.0		
5	26.56	15.3	11.1	26.4

Operation II.—Two slugs from (I), equivalent to 1200–1400 g. of the original ore, were placed in the Alundum boat for the second stage of the process. After the plug X was in position, pure nitrogen was passed through the apparatus for fifteen minutes at a rate approaching 60 liters per hour. The furnace was then heated rapidly to a temperature of 825° and kept at this point. Ammonia gas was then admitted at a rate of 50 liters per hour. After a short time, germanous sulfide began to collect at C. Twelve hours of heating was found sufficient to remove all of the germanium. The furnace was allowed to cool, the boat was removed and weighed, and the ore residue was set aside and saved for its gallium content.[10] Tube B was removed from the furnace, the germanous sulfide and metallic germanium were scraped from the walls and separated by hand-picking and screening, and then another charge of the product of *Operation I* was carried through the same procedure.

The loss in weight during *Operation II* is given in Table I. All slugs of ore residue from (I) were numbered and followed through (II) so that the total loss in weight might be known. The loss given in the table for (II) is calculated on the basis of the weight of the original ore.

A complete account of the germanium-containing residues and products and the total amount of germanium found is given in Table II for one lot of ore.

The germanium-containing products were divided into six lots; (1) germanous sulfide crystals, (2) impure germanous sulfide (the chief impurity being metallic germanium), (3) very impure germanous sulfide, (4) germanium-containing dusts, and (5) germanium metal (containing some germanous sulfide as an impurity). All of these products were analyzed for germanium by the usual methods. The impure germanium sulfide shows a higher germanium content than the pure product; this is due to the presence of finely divided metallic germanium, which could not be separated. Analyses of the ore residues (after completion of II) showed the germanium content to range from only 0.04 to 0.05%. On the other hand, the arsenious sulfide distillate, usually amounting to about 10% of the ore, was found to contain between 4 and 5% of germanium. Thus, about 10% of the germanium content of the ore must be recovered from that product.[11]

In the run reported here, product (3) is the largest, but this is accidental; the crystals of pure germanous sulfide were not so coherent and went through the screen in larger percentage. In some runs nearly one-half of the germanium was collected as well crystallized germanous sulfide (1), containing a small amount of metallic germanium, only, as an impurity.

TABLE II

THE AMOUNT OF GERMANIUM OBTAINED FROM GERMANITE (ORE NO. 4, 4.05 KG.)

Type of product	Weight, g.	% Ge	Ge, g.
GeS crystals	68.1	68.1	44.6
Impure GeS	61.2	71.3	43.6
Very impure GeS	157.9	48.8	77.1
GeS in dust bottles	18.3	42.3	7.7
Ge metal	12.8	91.9	11.8
Ge from the tube walls	1.8	69.4	1.3
Ge in As_2S_3 residues	428	4.15	17.8
Ge left in ore	2988.4	0.04	1.2
Total germanium			206.9
% Ge in germanite (based on Ge recovered)		5.11	
% Ge in germanite (based on analysis of 25 g.)		5.13	

Discussion

Attention is called to the fact that the total loss in weight for the combined operations is approximately the same for the different lots of ore, and, in general, it appears that the sum of the germanium and arsenic contents of germanite is very nearly constant. When insufficient time is allotted for (I) more arsenic appears in the products of (II) than would otherwise be the case. With the apparatus described herein, for *Operation I* a nitrogen gas flow of 30 liters per hour, operating for four and one-half hours, was found to be uniformly satisfactory. It is necessary, however, to determine these conditions empirically when working with different lots of ore, since the ratio of the germanium to arsenic varies considerably from lot to lot.

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(10) The recovery of gallium from this residue is described in the following article.

(11) For methods of separating arsenic and germanium, refer to Abrahams and Müller, THIS JOURNAL, **54**, 86 (1932).

In *Operation I* it is essential that the oxygen be removed from the nitrogen. At the temperature of the process, oxygen reacts with germanic sulfide to give germanic oxide. In *Operation II* any germanic oxide in the ore mass would be reduced by the ammonia to metallic germanium which would not be carried out with the gas stream, since its vapor pressure at 825° is exceedingly low. Another precaution which must be observed in (I) is that the temperature should not be permitted to rise much above 800°, as at temperatures ranging from 850–900°, the major portion of germanic sulfide would distil directly from the ore[12] and would be carried along with the arsenious sulfide. Undoubtedly, the germanium found in the arsenious sulfide residues (Table II), even when the temperature is maintained in the neighborhood of 800°, is the result of some distillation of germanic sulfide.

It is apparent that in *Operation II* the germanium leaves the ore mass as germanous sulfide. The presence of a small amount of metallic germanium in the cooler regions of the quartz tube may be attributed to the reduction of germanous sulfide with ammonia in the region of C.

When the furnace has reached the desired temperature, the flow of ammonia gas must be very rapid. If it is too slow, reduction of the sulfide to metallic germanium takes place within the ore before it has an opportunity to get out into the cooler regions. Once the germanium is left in the ore in this condition, its removal can be accomplished only through dissolution with strong oxidizing acids and subsequent distillation of germanium tetrachloride. An ammonia gas flow of 50 liters per hour was found sufficient for the success of (II) with the apparatus described herein.

The only impurity found with the different products of distillation is arsenic, provided all particles of germanite are kept within the region occupied by the furnace. The amount of germanium left in the ore, after the completion of (II), is surprisingly small, approximately 0.5% of the total germanium content. When all of the germanium products and residues are taken into account, the total amount of germanium recovered agrees well with that found by direct analysis.

The procedure described in this article has been used for the extraction of germanium from more than 100 kg. of germanite. The method ensures the removal of at least 99% of the total germanium content. Since only germanium and arsenic in combination with sulfur are removed in the two stages of the process, the ore residues contain all of the gallium.

An advantage of the process is its production of large amounts of nearly pure germanous sulfide, a starting material for the preparation of many compounds of germanium in the lower valence state.[13]

In addition, germanous sulfide is easily oxidized to germanic oxide, which serves as a source for the preparation of germanic compounds. The less pure products are readily converted to pure germanic oxide by the usual methods.

Summary

A method is described which removes at least 99% of the germanium in germanite ore. The procedure is carried out entirely in the dry condition, whereby most of the objectionable features of the usual methods of extraction are eliminated.

PROVIDENCE, R. I. RECEIVED JULY 5, 1935

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[12] Johnson and Wheatley, *Z. anorg. allgem. Chem.*, **216**, 274 (1934).

[13] Johnson, Morey and Kott, THIS JOURNAL, **54**, 4278 (1932); E. A. Flood, *ibid.*, **55**, 4935 (1933).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

The Extraction of Germanium and Gallium from Germanite. II. The Acid Extraction of Gallium

BY LAURENCE S. FOSTER, WARREN C. JOHNSON[1] AND CHARLES A. KRAUS

The methods of recovery of germanium from germanite developed by Thomas and Pugh[2] and Keil[3] involve the complete dissolution of the ore and the subsequent volatilization of germanium tetrachloride. The extraction of gallium from the residual germanium-free solution requires the handling of large volumes of liquids and the carrying out of numerous tedious separations of the remaining elements of the ore. A superior method was introduced by Berg and Keil,[4] who recover the gallium by extracting gallium trichloride from an acid solution by means of ether, but when this method is applied to kilogram lots of the ore, it has the disadvantage of being costly both in time and materials.

The pyrogenetic method of removal of germanium from germanite, described in the preceding article, leaves a black, partially-sintered residue, consisting chiefly of copper sulfide and amounting to about 75% by weight of the original ore. If these residues are boiled with hydrochloric acid, the gallium is removed completely, although only about 25% of the material is dissolved. The removal of the gallium from the extract is accomplished in six further operations involving neither special apparatus nor expensive chemicals. This method has the following advantages: (1) the necessity of completely dissolving the ore residue is eliminated; (2) the volumes of the solutions to be handled are markedly reduced; (3) the number of operations required to reach the final separation of metallic gallium is decreased; (4) loss of gallium through adsorption is minimized, eliminating reprecipitations; (5) the methods used in carrying out the precipitations lead to the formation of granular rather than flocculent and gelatinous masses, making it possible to use suction filtration in each step; and (6) all the gallium present is precipitated in one lot, making it unnecessary to recover traces of the element from many types of residues.

The Extraction Procedures

The Boiling Process.—The partially sintered residue, resulting from the removal of arsenic and germanium from germanite, is broken up and ground to pass a 100-mesh screen. One kilogram of the powder is placed in a 5-liter round-bottomed Pyrex flask, fitted with a rubber stopper carrying a small still-head. A water-cooled condenser and a large filter flask for the distillate are attached. One liter of 6 *N* hydrochloric acid is added to the flask and the mixture is refluxed for a total of twenty-two hours. Twice during this period, 150 cc. of concentrated hydrochloric acid is added to restore the acid concentration to approximately its original value. After heating for twenty-two hours, the rate of boiling is increased until distillation occurs and about 800 cc. of the acid is removed.[5] If during this process caking occurs, 500 cc. of water is added to the residue, the cake is loosened mechanically, and distillation continued until the amount of liquid left in the flask has again been reduced to a small volume.

The removal of hydrochloric acid by distillation minimizes the amount of alkali required for the subsequent neutralization, yet leaves the solution sufficiently acid to prevent hydrolysis of the dissolved salts. The cooled mixture, which contains some crystallized lead chloride, is suction-filtered. The sludge collected is washed by decantation at least five times with 200-cc. lots of 1% hydrochloric acid. The final volume of the filtrate, combined with the wash solution, need not be over 1500 cc.

The insoluble portion of the ore residue is returned to the boiling flask with 750 cc. of 6 *N* hydrochloric acid and refluxed again for five hours. After distilling off part of the acid, the mixture is filtered, the sludge is washed with a small amount of dilute acid, and the filtrate is added to the first extract. Besides gallium, the solution contains relatively large quantities of copper, lead, iron, aluminum and zinc, together with traces of many other elements.

The Efficiency of the Extraction.—The second hydrochloric acid extracts from two different lots of germanite were analyzed for gallium by a determination of the x-ray emission spectra, which gave $K\alpha_1$, $K\alpha_2$ and $K\beta_1$ lines.[6] A semi-quantitative check on the concentration of gallium was obtained by comparison with a known sample prepared to contain 0.5% of gallium oxide thoroughly mixed with ferric oxide. The intensities of the lines from the known and unknown samples showed the latter to contain about 1% of gallium in each case. Calculations made from these results indicate that the first hydrochloric acid extract contains between 99.0 and 99.8% of the total extractable gallium. Taking into account the amounts of

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[1] Department of Chemistry, University of Chicago, Chicago, Illinois.

[2] Thomas and Pugh, *J. Chem. Soc.*, **125**, 816 (1924).

[3] Keil, *Z. anorg. allgem. Chem.*, **152**, 101 (1926).

[4] Berg and Keil, *ibid.*, **209**, 383 (1932).

[5] In case the germanium has not been removed completely in the earlier operations, much of the residuum will be found in the distillate.

[6] We are greatly indebted to Mr. C. M. Olson and Professor W. C. Pierce, of the University of Chicago, for these results. They carried out the experiments with an x-ray spectrograph constructed by them.

gallium reported in the ore by various workers,[7] which average around 0.5%, we may conclude further that the extraction process removes the gallium practically quantitatively. Since such a high percentage of the gallium does appear in the first extract, this conclusion appears reasonable, and certainly indicates that no more than two extractions are profitable.

Treatment of the Extract with Hydrogen Sulfide.—The combined extracts are first treated with strong sodium hydroxide solution until a small amount of a permanent green precipitate is observed (not to be confused with the crystals of lead chloride which appear as neutralization proceeds). Then enough hydrochloric acid is added to dissolve the green precipitate and to render the solution at least 0.2 N in excess acid. Hydrogen sulfide is introduced, the black precipitate which forms is allowed to settle and the mixture is suction-filtered. Finally, the precipitate is pressed dry with a spatula and then washed several times with small amounts of acidified water.

After the removal of the sulfides, the filtrate is tested for complete precipitation of the lead and copper. If shown necessary, the treatment with hydrogen sulfide is repeated, after the acidity of the solution has again been reduced to only 0.2 N in excess acid by the method outlined above.

If the acid concentration is kept at the recommended value, very little gallium is adsorbed on the sulfide precipitate, and, in general, reprecipitation is unnecessary.

The weight of the oven-dried sulfide is about 25 g. If the wash solution is concentrated by boiling before being mixed with the original filtrate, the volume of the combined solutions is kept below 2500 cc.

The Precipitation of Crude Hydrated Gallium Oxide.—As major components, the solution now contains between 4 and 8 g. of gallium, about 40 g. of iron, 30 g. of zinc, and 3–4 g. of aluminum. It is not feasible to precipitate the iron as hydroxide and the zinc as sulfide from an alkaline solution because in these processes a large percentage of the gallium is carried down by adsorption,[8] necessitating many reprecipitations. The extraction of gallium chloride by means of ether, as described by Berg and Keil,[4,9] is very convenient on a small scale, but when kilogram lots of ore residues are used, the method becomes very laborious and wasteful. A method was sought whereby gallium could be precipitated from solutions containing large quantities of iron and zinc. Thomas and Pugh[2] accomplished a similar separation by boiling the solution (containing gallium iron, copper and zinc) with a limited amount of ammonium hydroxide until a permanent precipitate was formed which contained the gallium, a small amount of iron and, in their case, all of the copper. The disadvantage of using ammonium hydroxide is that the precipitate formed is flocculent, making rapid filtration impossible. Dennis and Bridgman[10] found that a granular precipitate of hydrated gallium oxide is formed by boiling the gallium solution in the presence of sodium sulfite, sodium hydrogen sulfite or ammonium hydrogen sulfite. Porter and Browning[11] precipitated gallium quantitatively in the presence of zinc by this method. Following these suggestions it was found possible to separate the gallium and the aluminum from the iron as well as the zinc. The precipitate produced is readily filtered and washed. The small amount of iron present as impurity is subsequently removed without danger of adsorption.

Procedure.—The filtrate resulting from the removal of sulfides is boiled to expel hydrogen sulfide and treated while still warm with ammonium hydroxide until a small amount of permanent precipitate appears. The precipitate is redissolved by the addition of a few drops of hydrochloric acid. The solution is then brought to a boil and ammonium hydrogen sulfite solution, prepared by saturating 5 N ammonium hydroxide with sulfur dioxide, is slowly added. The amount of reagent must be determined by trial; if too large a quantity is used, the precipitate is contaminated with large quantities of basic ferrous sulfite. After the addition of the sulfite reagent, boiling is continued until sulfur dioxide is no longer being rapidly expelled. The granular precipitate settles rapidly and is removed by suction filtration and washed with hot water.

The process must be repeated to guard against incomplete precipitation. Before this is done, the film of gallium oxide, adhering to the walls of the beaker, is dissolved in a few drops of concentrated hydrochloric acid. The filtrate is returned to the beaker, 5 cc. of a 0.1% aqueous solution of sodium alizarin sulfonate added to serve as an indicator, and hydrochloric acid is added until the solution becomes distinctly yellow. The acidified solution is heated to boiling and a limited quantity of ammonium hydrogen sulfite solution is again introduced. During the evolution of sulfur dioxide which ensues, the color of the indicator turns from yellow to pink and, when the pH has become sufficiently high, the remaining traces of gallium and aluminum hydroxides are slowly precipitated. It may be necessary to repeat this process once more before only negligible quantities of precipitate are obtained. Gallium hydroxide is concentrated largely in the first two precipitations, since it is more acidic than aluminum hydroxide.[12]

Analyses.—In two instances, the combined precipitates prepared as described above from equal volumes of solution were analyzed. The results, reproduced in Table I,

TABLE I

ANALYSIS OF CRUDE GALLIUM OXIDE SEPARATED FROM GERMANITE

No.[a]	Vol. of soln., cc.	Ga_2O_3, g.	Al_2O_3, g.	Fe_2O_3, g.
A-1	1365	2.01	1.70	0.103
A-2	1365	2.02	1.60	.206
B-1	400	0.436	0.562	.021
B-2	400	.438	.590	.055

[a] The two solutions, A and B, do not contain comparable amounts of gallium. In case of solution A, the separation of gallium and aluminum was made by precipitating $AlCl_3 \cdot 6H_2O$; in case of solution B, by the extraction of $GaCl_3$ with ether.

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(7) Kriesel, *Metall u. Erz.*, **20**, 357 (1923); *Chem.-Ztg.*, **48**, 961 (1924); Thomas and Pugh, *J. Chem. Soc.*, **125**, 816 (1924); Abrahams and Müller, THIS JOURNAL, **54**, 93 (1932).

(8) Wainer, *ibid.*, **56**, 348 (1934).

(9) It may be pointed out that if the oxidation of the iron, as recommended by Berg and Keil, is omitted, very little iron is dissolved by the ether and the subsequent purification of the gallium is facilitated.

(10) Dennis and Bridgman, THIS JOURNAL, **40**, 1531 (1918).

(11) Porter and Browning, *ibid.*, **41**, 1491 (1919).

(12) Fricke and Blencke, *Z. anorg. allgem. Chem.*, **143**, 183 (1925); Schwarz von Bergkampf, *Z. anal. Chem.*, **90**, 333 (1932).

show that the procedure outlined is capable of yielding quantities of gallium oxide in good agreement, while the amount of aluminum varies. The table shows, in addition, that the precipitate is contaminated with only a small amount of iron.

The Separation of Gallium and Aluminum.—Of the various methods proposed to separate gallium and aluminum, the most satisfactory is that used by Dennis and Bridgman[10] and Ato[13] in which aluminum chloride hexahydrate, $AlCl_3 \cdot 6H_2O$, is precipitated from an ether–water mixture saturated with hydrogen chloride. In adapting it to the large scale extraction of gallium, the procedure described below was followed.

Procedure.—The precipitates containing the hydrated oxides of gallium, aluminum and iron are dissolved in concentrated hydrochloric acid. To the strongly acid solution produced, an equal volume of ether is added slowly with cooling and agitation. The resulting mixture, in two layers, is saturated with hydrogen chloride, care being exercised to keep the contents of the flask thoroughly mixed and cooled. During this process, the ether layer disappears and fine, white crystals of aluminum chloride hexahydrate settle out. The precipitate is filtered off, using a sintered glass Büchner type funnel (Jena 17, G-3), and is washed with a 50–50 mixture of ether and water saturated with hydrogen chloride. The filtrate is transferred to a large beaker and, after the addition of some dilute sulfuric acid, the ether and excess acid are removed by evaporation of the solution to a small volume. The residue is diluted with distilled water to make about 300 cc. of solution in preparation for the removal of traces of iron.

The aluminum precipitate is tested for gallium before being discarded. The separation is usually found to be very satisfactory.

The Separation of Gallium and Iron.—The gallium solution, containing a small amount of iron, but no aluminum, is brought to the boiling point and hydrogen peroxide is added to oxidize the iron. Sodium hydroxide solution, 6 *N*, is then added slowly to the boiling solution until the gallium hydroxide, which at first precipitates, is redissolved, leaving the brick-red hydrated ferric oxide suspended in a clear, colorless solution. Continuing the boiling, for a few minutes, dehydrates the ferric oxide more thoroughly and makes filtration easier. The hot solution is filtered on a suction filter, with only a slight difference in pressure, and the precipitate is washed thoroughly with hot water. The amount of iron oxide precipitated is usually so small that reprecipitation is unnecessary. The filtrate contains all the gallium but only traces of other metallic elements.

The Precipitation of Pure Gallium Hydroxide.—The alkaline filtrate from which the iron has been removed is neutralized and made slightly acid with hydrochloric acid; excess ammonium hydrogen sulfite is added and the solution is boiled vigorously to expel sulfur dioxide. A copious pure white precipitate of hydrated gallium oxide appears. When the evolution of sulfur dioxide is no longer rapid, boiling is discontinued, the precipitate is allowed to settle and is removed by suction filtration. The precipitate is washed with hot water until free from chloride ion. The filtrate may be reboiled to test for completeness of precipitation, but usually there is so little gallium left in solution that it may be collected conveniently by means of tannin, following the directions of Moser and Brukl.[14] The presence of sulfite does not interfere with this procedure.

To indicate the quantities of material that can be handled at one time, we cite an instance in which 10 g. of gallium oxide, dissolved in 1500 cc. of solution, contained in a 2-liter Pyrex beaker, was precipitated by this method so completely that only a few hundredths of a gram of gallium oxide was recovered through the treatment with tannin.

The Preparation of Pure Gallium.—To prepare pure gallium from the hydrated oxide obtained in the above procedure, the latter is dissolved, while still moist, in a slight excess of potassium hydroxide solution and then electrolyzed. The metal may be converted to the volatile chloride, $GaCl_3$, which is readily sublimed *in vacuo*.[15]

Gallium Content of Germanite.—Published analyses[7] of different lots of germanite show the gallium content to range from 0.3 to 0.8%. Table II summarizes the results of the extraction of germanium and gallium from several kilograms of germanite.

TABLE II

RECOVERY OF GERMANIUM AND GALLIUM FROM GERMANITE

Ore lot no.	3	4
Ge recovered, %	6.88	5.13
Ga recovered, %	0.59	0.34

Observations on a large number of different samples of germanite have shown that when the germanium content is high, the gallium content is likewise high. The amount of gallium found is in substantial agreement with the value given by previous workers,[7] but we have observed that the ore contains a much higher percentage of aluminum than is given in their analyses. (Table I shows that with our ores, the gallium and aluminum contents are approximately the same.) It is possible that some of the very high values for gallium which have been published were the result of the failure to effect a complete separation of these elements. The ore is, nevertheless, the richest source of gallium yet discovered.

Summary

Gallium, occurring in germanite, is extracted after the removal of arsenic and germanium, by boiling the residues with hydrochloric acid.

After the precipitation of the sulfides of the heavy metals, the gallium and aluminum are separated from large quantities of iron and zinc by boiling the solution containing them with am-

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[13] Ato, *Sci. Papers, Inst. Phys. Chem. Research* (Tokyo), **14**, 35 (1930); *C. A.*, **24**, 4729 (1930).

[14] Moser and Brukl, *Monatsh.*, **50**, 181 (1928).

[15] Craig and Drake, THIS JOURNAL, **56**, 584 (1934); J. I. Hoffman *Bur. of Stand. Jour. of Research*, **13**, 665 (1934).

monium hydrogen sulfite, leaving the iron and zinc in solution.

Aluminum is separated as $AlCl_3 \cdot 6H_2O$ from a hydrogen chloride saturated ether–water mixture in which gallium and traces of iron remain dissolved.

After the remaining iron has been removed, the gallium is precipitated as the hydrated oxide. The metal is obtained by electrolysis from a solution of the oxide in potassium hydroxide solution.

PROVIDENCE, R. I. RECEIVED JULY 5, 1935

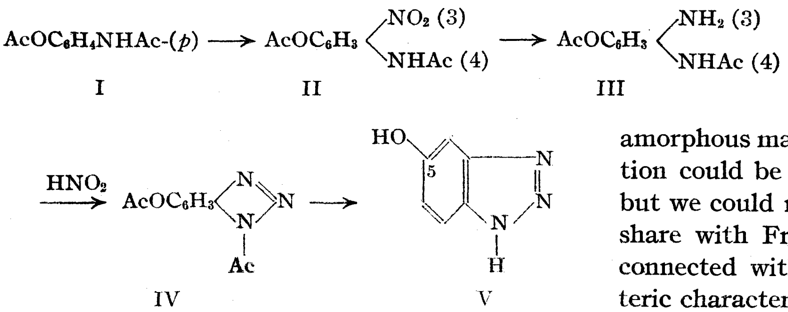
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A Comparison of Heterocyclic Systems with Benzene. V. The Benzotriazole (Azimidobenzene) Series

BY LOUIS F. FIESER AND ELMORE L. MARTIN

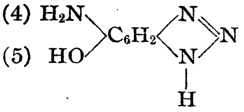
Since only one, rather unfavorable, example of a quinone containing the 1,2,3-triazole nucleus has been studied potentiometrically,[1] the synthesis of simple ortho or para quinones derived from benzotriazole was undertaken in order that a direct comparison might be made with the naphthoquinones. Although it was found that the benzotriazole quinones are unusually elusive substances, we were able to produce one member of the series in solution and to obtain from it the pure, crystalline hydroquinone. This was well suited to the purpose at hand.

The starting point for the preparation was 5-hydroxybenzotriazole, V, a compound which was unknown at the beginning of our investigation, but which has been described by Fries, Güterbock and Kühn[2] in a paper published since the completion of this part of our work. The Fries group prepared the hydroxy compound from the amine, the starting point for the preparation of which is 2,4-dinitroaniline. From the statements in the literature, supplemented by observations of our own, it is estimated that the over-all yield by this method is about 18%. We selected for the synthesis the series of transformations I → V.

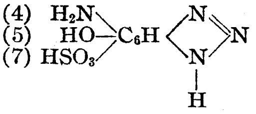


Reduction of the nitro compound II could not be accomplished with stannous chloride or sodium hydrosulfite without hydrolysis, but catalytic hydrogenation to the amine III proceeded smoothly, with a small amount of the hydrazo compound as the only by-product. The remaining steps were nearly quantitative, and the yield from p-aminophenol was 53%.

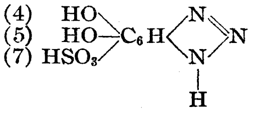
As a means of introducing an amino group in the 4-position, the reduction of the arylazo, nitro, and nitroso derivatives of 5-hydroxybenzotriazole was studied under various conditions. All of these substances gave the same reduction product, VI, but the only satisfactory preparative method consisted in the reduction of the nitroso compound with sodium hydrosulfite in a neutral, aqueous suspension. Like Fries and collaborators, who were the first to prepare 4-amino-5-hydroxybenzotriazole, we were unable to isolate a quinone on oxidation of the substance. Under ordinary conditions only black, amorphous material was obtained. A red coloration could be produced in very dilute solutions, but we could not isolate the red substance. We share with Fries the view that the difficulty is connected with the water solubility and amphoteric character of the unknown quinone.



VI



VII



VIII

From the 4-nitroso derivative we obtained with bisulfite 4-amino-5-hydroxy-7-sulfonic acid,

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[1] Fieser and Ames, THIS JOURNAL, **49**, 2604 (1927).

[2] Fries, Güterbock and Kühn, *Ann.*, **511**, 213 (1934).

VII, and the oxidation of this substance was somewhat more successful. Clear orange-red solutions could be obtained which responded to the usual tests (with aniline, alkali, etc.) for an ortho quinone sulfonate, but the substance appears to be extremely soluble in water and rather sensitive, and we were unable to isolate it. To prepare the hydroquinone, VIII, the sulfonate VII was oxidized with bromine water and the red solution was decolorized with sulfur dioxide. 4,5-Dihydroxybenzotriazole-7-sulfonic acid (VIII) was obtained as colorless crystals of the potassium salt.

As a possible route to a quinone of the para series, we investigated Gattermann's method of preparing *p*-aminophenols by the electrolytic reduction of nitro compounds in concentrated sulfuric acid solution. Benzotriazole, the required starting material, usually is prepared by the action of nitrous acid on *o*-phenylenediamine. A more economical method, which has advantages with respect both to the yield and the quality of the product, consists in diazotizing *o*-aminoacetanilide and hydrolyzing the resulting acetate. To obtain *o*-aminoacetanilide, *o*-nitroaniline was acetylated in benzene solution by a method similar to that of Kaufmann,[3] and the nitro compound was reduced catalytically. In each of the five operations involved in the new synthesis of benzotriazole the yield was 90% or better, and pure products were easily obtained at each step. In the hydrogenation of *o*-nitroacetanilide, small amounts of the hydrazo compound and of 2-methylbenzimidazole were formed, but these substances are easily eliminated. Fries and collaborators[2] showed that the nitration of benzotriazole yields the 4-nitro compound. We were able to transform this substance into 4-amino-7-hydroxybenzotriazole, but all attempts to isolate a quinone by the oxidation of the compound were unsuccessful. No better results were obtained with the known methylated nitrobenzotriazoles. With 1-methyl-4-nitrobenzotriazole the Gattermann reaction was successful, but no quinone could be obtained on oxidation. No pure product was isolated from the electrolytic reduction of 1-methyl-7-nitrobenzotriazole.

Potential Measurements

Solutions of benzotriazole-4,5-quinone-7-sulfonate (XI) prepared by the oxidation of the pure hydroquinone VIII in dilute aqueous solution were found to be quite stable at 25° except in strongly alkaline solutions. The results of a series of electrometric titrations of the reductant, carried out by the method previously described,[4] and under the same conditions, are summarized in Table I. Bromine water proved to be an excellent titrating agent for the acid and neutral range, electrode equilibrium being attained very rapidly.

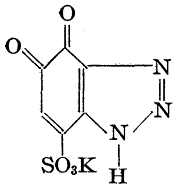
TABLE I

POTENTIALS OF THE SYSTEM FROM POTASSIUM BENZOTRIAZOLE-4,5-QUINONE-7-SULFONATE (25°)

$E_0 = 0.6721$ v. $K_o^b = 1.04 \times 10^{-5}$. $K_r^b = 1.57 \times 10^{-6}$. $E_n = E_0 + E_h + 0.02956 \log [1 + [H^+]/K_r^b] - 0.02956 \log [1 + [H^+]/K_o^b]$.

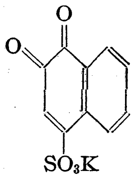
*p*H	Hydrogen elec. potential, E_h, v.	Potential when Ox. = Red., E_n, v.	Titrating agent	E_n (found − calcd.), mv.
0.50	−0.0296	0.6667	Br_2-H_2O	−0.1
1.15	.0680	.6284	Br_2-H_2O	.0
3.27	.1933	.5037	Br_2-H_2O	+ .6
4.31	.2548	.4415	Br_2-H_2O	− .1
4.31	.2548	.4420	$K_3Mo(CN)_8$	+ .4
4.95	.2926	.3962	Br_2-H_2O	− .8
5.34	.3157	.3691	Br_2-H_2O	− .1
5.68	.3358	.3469	Br_2-H_2O	+1.9
6.13	.3624	.3136	Br_2-H_2O	−0.2
6.65	.3931	.2784	Br_2-H_2O	− .6
6.99	.4132	.2587	Br_2-H_2O	− .2
7.62	.4505	.2223	Br_2-H_2O	+ .7
7.78	.4599	.2128	Br_2-H_2O	+ .6
8.35	.4937	.1778	$K_3Mo(CN)_6$	− .6
8.89	.5256	.1588	$K_3Mo(CN)_6$	...

The normal potential (E_0) for the system of which the heterocyclic quinone XI is the oxidant is 42 mv. higher than that for the carbocyclic quinone XII. This comparison is regarded as more accurate than that between α,β-naphthotriazole-4,5-quinone and phenanthrenequinone (difference of 23 mv.),[1] for the factor of dissociation could not be taken into account in the earlier work. According to the present results there is a difference of nearly one *p*K unit in the constants for the basic ionization of the triazole nucleus in the quinone and in the hydroquinone, the latter



$E_0 = 0.672$ v.

XI



$E_0 = 0.630$ v.

XII

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(3) Kaufmann, *Ber.*, **42**, 3481 (1909).

(4) Fieser and Fieser, THIS JOURNAL, **56**, 1565 (1934).

substance being the more strongly basic. The normal potential (E_0) reported refers to conditions under which there is no basic ionization of either the oxidant or the reductant. The value is intermediate between those for the quinones containing a benzene ring and a thiophene ring[5] in place of the triazole nucleus. If the comparison is strictly valid, this would indicate an intermediate degree of aromaticity for the triazole system, this ring being less aromatic than benzene.

Experimental Part

1. Synthesis of 5-Hydroxybenzotriazole (V)

1 - Acetylamino - 2 - nitro - 4 - acetoxybenzene.[6]—1 - Acetylamino-4-acetoxybenzene, m. p. 150–151°, was obtained from *p*-aminophenol hydrochloride in 90% yield. For the nitration, 100 g. of the diacetate was added in small portions to 200 cc. of fuming nitric acid (sp. gr. 1.5) which was mechanically stirred in a freezing mixture. The temperature was kept at 0–5° throughout the addition which, with efficient cooling, required fifteen to twenty minutes. The temperature was allowed to rise to 12–15° and maintained there for twenty to twenty-five minutes, when the solution was poured onto ice. The yellow product was washed entirely free from acid and crystallized from alcohol, when it formed stout yellow needles, m. p. 144–145°; yield, 110 g. (89%).

1-Acetylamino-2-amino-4-acetoxybenzene (III).—The hydrogenation was carried out in the low pressure apparatus, using 30 g. of the nitro compound dissolved in 300 cc. of hot alcohol and 0.1 g. of Adams catalyst. With a good catalyst the temperature rose and the reduction was complete in ten to fifteen minutes. The colorless solution was filtered and the solvent was distilled in vacuum, giving a slightly yellow crude product melting at 172–174°; yield from a total of 120 g., 98 g. (93%). This contained as a by-product the orange azo compound, which was left as a residue on dissolving the crude amine in hot water. On decolorizing the solution and cooling, the amine was obtained as colorless plates, m. p. 175–177°; yield 79 g. (75%). The pure compound crystallizes from water in fine needles, from alcohol as square plates, m. p. 178–179° (Analysis No. 1, Table II).

The following derivatives were obtained in somewhat purer form than by previous methods. 1,2-Di-(acetylamino)-4-acetoxybenzene was prepared by acetylating III in aqueous solution and crystallized from water (No. 2): fine needles, m. p. 187–188° (lit., 184–185°).[7] 3,4-Di-(acetylamino)-phenol was obtained by treatment of the triacetate with cold, dilute alkali for one hour and acidifying the resulting solution (No. 3): stout needles from water, m. p. 214–215° (lit., 205–207°).[7]

2,2′ - Di - (acetylamino) - 5,5′ - diacetoxyazobenzene (No. 4) appeared in amounts of 0.1–1.0 g. in each hydrogenation of 30 g. of the nitro compound, the quantity being greatest when the catalyst was poor and the reduction slow. The substance is not present as such at the end of the hydrogenation but as the hydrazo compound, which becomes oxidized after exposure to the air. The azo compound is insoluble in acids or alkalies and it crystallizes from glacial acetic acid (sparingly soluble) as fine orange needles decomposing at 280–285°.

1-Acetyl-5-acetoxybenzotriazole, IV (No. 5).—To a solution at 0° of 62.4 g. of the pure amine III in 53 cc. of concentrated hydrochloric acid and 750 cc. of water, a solution of 20.7 g. of sodium nitrite in 200 cc. of water was slowly added. The triazole separated at once to give a crystalline paste and it was collected and washed; m. p. 125°; yield, 64 g. (98%). The substance was obtained from benzene–ligroin or from dilute acetone as fine, colorless needles, m. p. 125–126°. From 5-hydroxybenzotriazole and acetyl chloride in pyridine Fries, *et al.*[2] obtained a diacetate which sintered at 115° and melted at 127°. With acetic anhydride and sodium acetate we obtained a sample identical with the above. Unlike the case of 5-methylbenzotriazole[8] the acetylation gives only one of the two possible isomers.

5-Hydroxybenzotriazole Hydrochloride (No. 6).—The moist diacetate obtained as above (64 g., dry) was warmed with 200 cc. of concentrated hydrochloric acid until solution was complete (a slight yellow color was discharged if necessary by the addition of a trace of stannous chloride). On cooling to 0° 43 g. of colorless crystals separated, and 4 g. more was obtained by concentrating the mother liquor; yield, 90%. For analysis the compound was recrystallized from dilute acid, when it formed stout, colorless needles decomposing at about 225°.

5-Hydroxybenzotriazole, V (No. 7).—On mixing aqueous solutions of 5.15 g. of the above hydrochloride and of 2.6 g. of sodium bicarbonate a white, crystalline precipitate began to form after a few minutes; m. p. 232–234°; yield, 3.6 g. (90%). The compound crystallized from water as colorless micro-needles, m. p. 234–235°, with some decomposition. Fries, *et al.*,[2] obtained a slightly yellow product, m. p. 228° dec.

2. Derivatives of 5-Hydroxybenzotriazole

The **4-benzeneazo** derivative (No. 8), orange needles from alcohol, m. p. 230–232°, dec., the **4-*p*-tolueneazo** compound (No. 9), reddish-orange needles from alcohol, m. p. 224–225°, and the **4-*o*-tolueneazo** compound (No. 10), bright red needles from alcohol, m. p. 243–244° dec., were prepared in the usual way. The dyes are insoluble in dilute hydrochloric acid but soluble in alkali (probably because of the acidic character of the triazole nucleus).

4-Nitro-5-hydroxybenzotriazole (No. 11).—To a solution of 10.8 g. of III in 40 cc. of concentrated sulfuric acid at 15–20° 4 cc. of nitric acid (sp. gr. 1.4) was added by drops. After one-half hour at 15–20° and one hour at 50°, the solution was poured onto ice, and the product was crystallized from dilute acetic acid; m. p. 262–263°; yield, 9 g. (63%). Fries, *et al.*,[2] prepared the compound by another method and give the melting point as 236° dec. This probably is a typographical error.

4-Nitroso-5-hydroxybenzotriazole (No. 12) was prepared by a method similar to that of Fries, *et al.*:[2] sodium nitrite solution was added to a solution of 5-hydroxybenzotriazole hydrochloride in water; yield, 97%.

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[5] Fieser and Kennelly, This Journal, **57**, 1611 (1935).

[6] Hähle, *J. prakt. Chem.*, **43**, 63 (1891), prepared this compound but recorded few details of the procedure.

[7] Kehrmann and Gauhe, *Ber.*, **31**, 2404 (1898).

[8] Morgan and Micklethwait, *J. Chem. Soc.*, **103**, 1396 (1913).

4 - Amino - 5 - hydroxybenzotriazole - 7 - sulfonic Acid (VII).—The moist nitroso compound from 5.16 g. of 5-hydroxybenzotriazole was stirred for one hour with a solution of 8.8 g. of sodium bisulfite in 200 cc. of water, when it all dissolved. The filtered, yellow solution was treated with 10 cc. of concentrated sulfuric acid and maintained at 40° for three and a half hours. The solution had become red and a yellow, crystalline product had separated. This was dissolved in a hot solution of 10 g. of sodium bisulfite in 50 cc. of water, the solution was decolorized with Norite and acidified while still hot. The product was pale yellow and weighed 4.8 g. (70%). The color was removed completely by crystallization from water, in which the substance is only sparingly soluble. The compound separates slowly in long, colorless needles; it dissolves in alkali or soda with a green coloration.

Anal. Calcd. for $C_6H_6O_4NS$: S, 13.92. Found: S, 13.94, 14.01.

Potassium Benzotriazole-4,5-hydroquinone-7-sulfonate (VIII).—Of various oxidizing agents tried for the preparation from VII of solutions of the triazolequinone sulfonate, bromine water was the most satisfactory. In the presence of an excess of bromine the orange solution is fairly stable. Treated with alkali, the solution becomes dark and then clear red. With aniline a red anilino quinone is precipitated, but the compound was not obtained in a crystalline condition. The hydroquinone was obtained as follows. A small part of 3.3 g. of VII was suspended in 10 cc. of water and shaken with a small part of 1 cc. of bromine. The material soon dissolved to give an orange solution, and further small quantities of the aminohydroxy compound and of bromine were added with shaking until all had been used. To the filtered quinone solution 10 cc. of saturated potassium chloride solution was added, and the solution was decolorized with sulfur dioxide. The potassium salt VIII began to separate at once as colorless crystals. When crystallized from water containing a little sulfur dioxide the substance formed stout, glistening needles of the tetrahydrate; yield, 2.6 g. (55%).

Anal. Calcd. for $C_6H_4O_5N_3SK \cdot 4H_2O$: S, 9.67. Found: S, 9.62, 9.65.

4-Amino-5-hydroxybenzotriazole.—(a) To a saturated aqueous solution of 10.5 g. of sodium hydrosulfite 3.28 g. of 4-nitroso-5-hydroxybenzotriazole was added slowly with stirring. The mixture became warm and the yellow solid soon was transformed to the colorless, crystalline reduction product. Crystallized from hot water containing a trace of hydrosulfite, this gave 2.5 g. (83%) of the free amine, m. p. 210–214° dec., and from it 3 g. of the pure, colorless dihydrochloride was obtained.

(b) The 4-benzeneazo compound was reduced with stannous chloride and the tin double compound was decomposed with hydrogen sulfide. The dihydrochloride was obtained by evaporation in vacuum; yield, 22%.

(c) Electrolytic reduction of the 4-nitro compound (7 g.) in concentrated sulfuric acid gave 10 g. of the aminohydroxybenzotriazole as the sparingly soluble sulfate.

That these three methods give the same product was shown by a comparison of samples of the free base, which is best prepared from the pure dihydrochloride by the addition of sodium bicarbonate, followed at once by a trace of hydrosulfite, to the aqueous solution of the salt. 4-Amino-5-hydroxybenzotriazole (No. 13) crystallizes from water as long, colorless needles, m. p. 216–217° dec. Fries, *et al.*,[2] report the m. p. 217°. The substance soon darkens when exposed to the air in a moist condition. The **dihydrochloride (No. 14)** was obtained as completely colorless, stout needles, decomposing at about 225°; it does not deteriorate on storage.

3. Preparation of Benzotriazole

2-Nitroacetanilide.—To a solution of 69 g. of *o*-nitroaniline in 75 cc. of warm benzene 75 cc. of acetic anhydride was added, along with 3–5 drops of concentrated sulfuric acid. The latter reagent initiated a vigorous reaction and a part of the benzene distilled. After heating on the steam-bath for thirty minutes, the solvent was removed by evaporation in a dish on the steam-bath, and on cooling the light yellow melt solidified. One crystallization from dilute alcohol gave 84 g. (93%) of yellow needles, m. p. 92–93°.

2-Aminoacetanilide.—Hydrogenation of the nitro compound (30 g. in 200 cc. of hot alcohol, with 0.1 g. of Adams catalyst) proceeded smoothly (ten to fifteen minutes), and on evaporation of the filtered, initially colorless solution in vacuum the crude amine was obtained as a slightly yellow product, m. p. 130–132°. From 120 g. of nitro compound the yield was 97 g. (97%). The main portion dissolved readily in hot water, leaving a yellow residue which, when crystallized from glacial acetic acid, formed orange needles, m. p. 270–271°, having the properties of 2,2′-di-[acetylamino]-azobenzene.[9] On clarifying and cooling the aqueous solution, 2-aminoacetanilide (75 g.) separated as colorless plates, m. p. 132–133°, and an additional crop was obtained by concentrating the mother liquor under reduced pressure; yield, 90 g. (90%). A second concentration of the mother liquor gave 3 g. of another substance which, when recrystallized from water, melted at 174–175°, corresponding with the description of 2-methylbenzimidazole.[10]

1-Acetylbenzotriazole.—A solution at 0° of 100 g. of pure 2-aminoacetanilide in 500 cc. of water and 120 cc. of concentrated hydrochloric acid was treated with a solution of 46 g. of sodium nitrite in 200 cc. of water, added dropwise with stirring. A colorless precipitate separated at once; washed and dried it weighed 102 g. (95%) and melted at 49–51° (recrystallized, 50–51°).

Benzotriazole.—The crude acetate (100 g.) was dissolved by warming in 150 cc. of concentrated hydrochloric acid, a small crystal of stannous chloride being added to remove a slight yellow coloration. On cooling, colorless needles of the hydrochloride separated (82 g.), and a further crop was obtained by concentration of the mother liquor; yield, 89 g. (92%). A solution of 46.7 g. of the pure salt in 200 cc. of water was carefully neutralized with a solution of 26 g. of sodium bicarbonate. Benzotriazole separated as colorless crystals, m. p. 97–98°; yield, 33 g. (92%). Recrystallization from benzene gave long, colorless needles, m. p. 98–99°.

The preparation of benzotriazole by the action of nitrous acid on *o*-phenylenediamine was found to be quite tedious in comparison with the above method. After three treat-

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[9] Willstätter and Pfannenstiel, *Ber.*, **38**, 2351 (1905).

[10] Hübner, *Ann.*, **209**, 353 (1881).

ments with Norite we obtained a light gray product, m. p. 94–96°, in 67% yield.

4. Electrolytic Reduction of the Nitro Compounds

4-Amino-7-hydroxybenzotriazole (No. 15).—4-Nitrobenzotriazole was prepared by nitration essentially as described by Fries, *et al.*,[2] the yield of recrystallized material, m. p. 229–230°, being 68%. A solution of 10 g. of the nitro compound in 100 g. of concentrated sulfuric acid was subjected to electrolytic reduction according to Gattermann,[11] using a 5 × 9 cm. porous clay cell resting in a beaker of 80–90% of sulfuric acid. The current, taken from a 6-v. line, increased from 1–1.5 amp. to about 3 amp. as the temperature rose to the maximum value of 70–80°. The reaction was complete in about twenty hours and a part of the amine sulfate separated during this period and the remainder was obtained by diluting the acid liquor with an equal volume of water and allowing the solution to stand at 0° for two days; yield, 10 g.

The sulfate is sparingly soluble in water and it does not crystallize well. The free base was liberated from the salt with sodium bicarbonate and crystallized from water in the presence of a trace of sodium hydrosulfite. The colorless needles were collected, washed with alcohol and ether, and quickly dried in vacuum. The substance decomposes at about 225–230°, and it is sensitive to air oxidation. It is moderately soluble in water, sparingly soluble in ether. Oxidizing agents added to a solution of the hydrochloride produce a red coloration, but no quinone could be isolated.

1-Methyl-4-nitrobenzotriazole.—Following the method of Fries, *et al.*,[2] 4-nitrobenzotriazole was methylated with dimethyl sulfate. Like their material, our product softened at 163° and melted at 173° even after several crystallizations from alcohol, but after a single crystallization from dilute acetic acid the substance melted sharply at 181–182° and this value remained unchanged on further crystallization. The yield of the pure isomer was 30%.

1-Methyl-4-amino-7-hydroxybenzotriazole was obtained in good yield by reduction of the 4-nitro compound by the Gattermann method. The sulfate forms colorless micro crystals and is moderately soluble in water. The free base is very sensitive to oxidation and was not obtained entirely pure. The **dibenzoate** (No. 16) forms colorless needles from alcohol, m. p. 262–263°.

1-Methyl-7-nitrobenzotriazole.—The **methylation** of benzotriazole by Reissert's[12] method gave the 1-methyl derivative in less than 10% yield. The nitro compound[2] gave no clean products when submitted to electrolytic reduction in sulfuric acid solution.

TABLE II

ANALYSES[13]

No.	Formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H
1	$C_{10}H_{12}O_3N_2$	57.67	5.81	57.64	6.06
2	$C_{12}H_{14}O_4N_2$	57.58	5.64	57.29	5.40
3	$C_{10}H_{12}O_3N_2$	57.67	5.81	57.88	5.97
4	$C_{20}H_{20}O_6N_4$	58.23	4.89	58.00	5.24
5	$C_{10}H_9O_3N_3$	54.78	4.14	54.72	4.50
6	$C_6H_6ON_3Cl$	41.68	3.52	41.91	3.83
7	$C_6H_5ON_3$	53.31	3.73	53.37	4.04
8	$C_{12}H_9ON_5$	60.23	3.79	60.23	3.86
9	$C_{13}H_{11}ON_5$	61.64	4.38	61.51	4.38
10	$C_{13}H_{11}ON_5$	61.64	4.38	61.64	4.44
11	$C_6H_4O_3N_4$	39.98	2.24	40.37	2.12
12	$C_6H_4O_2N_4$	43.89	2.46	44.05	2.74
13	$C_6H_6ON_4$	47.97	4.03	48.09	4.42
14	$C_6H_8ON_4Cl_2$	32.29	3.62	32.35	3.73
15	$C_6H_6ON_4$	47.97	4.03	48.12	4.27
16	$C_{21}H_{16}O_3N_4$	67.71	4.33	67.79	4.73

Summary

Methods of obtaining ortho and para quinones or hydroquinones of the benzotriazole series have been investigated and one compound of the type desired has been prepared and studied potentiometrically. The oxido-reduction potential of a bicyclic quinone containing the triazole nucleus is appreciably higher than that of the corresponding naphthoquinone.

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[11] Gattermann, *Ber.*, **26**, 1846 (1893).

[12] Reissert, *ibid.*, **47**, 677 (1914).

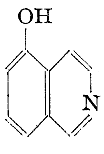
[13] The semimicrocombustion of some of these compounds, particularly those containing the stable triazole nucleus and having a high nitrogen content, presented considerable difficulty. The method found most satisfactory was to mix the sample with fine copper oxide and to conduct the combustion with air in a very hot tube.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

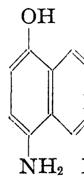
A Comparison of Heterocyclic Systems with Benzene. VI. Quinones of the Quinoline and Isoquinoline Series

BY LOUIS F. FIESER AND ELMORE L. MARTIN

It was desired to obtain for potentiometric study quinones or hydroquinones derived from quinoline and isoquinoline. In the case of the former heterocycle no preparative problem was involved, for 5,8-quinolinequinone is a known compound[1] and Matsumura and Sone[2] have developed a very convenient method for the preparation of the corresponding hydroquinone. In the isoquinoline series, however, compounds of the desired type do not appear to have been described. The three known Bz-hydroxyisoquinolines were first considered as possible starting materials. The only isomer whose structure is fully established, 7-hydroxyisoquinoline, has been prepared by a rather tedious synthesis.[3] The other two compounds have been obtained from the products of high-temperature and low-temperature sulfonation.[4] In analogy with naphthalene, the first of these probably is a β-derivative, and since it differs from the 7-isomer, it probably is 6-hydroxyisoquinoline. The hydroxy compound derived from the other sulfonate has been obtained also from nitroisoquinoline, and since both the sulfonate and the nitro compound are known to be Bz-alpha derivatives[5] the substance is either 5- or 8-hydroxyisoquinoline. The former structure perhaps is the more probable, and we shall refer to the compound as the 5(8)-derivative and formulate it as the 5-isomer, I. Although this compound is not easily obtained, it appeared to be more readily available than the other isomers and a small quantity was prepared and investigated. It was found possible to convert the substance through the benzeneazo derivative into the 5,8 (or 8,5)-hydroxyamino compound II, but the entire process was so unsatisfactory with respect to yields that a better method was sought.

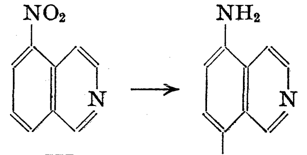


I



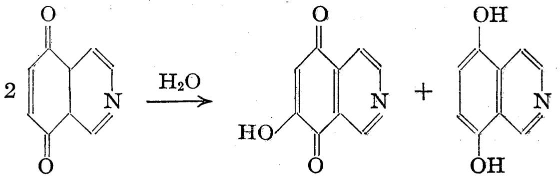
II

Such a method was found in the electrolytic reduction by Gattermann's method of the readily available 5(8)-nitroisoquinoline, III, for this gave in good yield the isomeric 8,5(5,8)-hydroxyamino compound IV. It was expected that the two *p*-hydroxyamino compounds II and IV would yield on oxidation the same *p*-isoquinolinequinone.



III IV

The same yellow product was indeed obtained in each reaction, but instead of being the expected quinone it had the properties of the corresponding hydroquinone. It was observed that the yield was less than half of the expected amount, that mother liquor was deep red whereas solutions of the pure hydroquinone (salt) are yellow, and that the yield decreased as the amount of oxidizing agent was increased. From these facts it appears very probable that the hydroquinone (VI) results from a disproportionation of the quinone first formed.



V (or isomer) VI

Such a reaction has been well established in the *o*-quinone series.[6] The red mother liquor probably contained a mixture of hydroxyquinones, but no pure product could be isolated. The quinone V could be produced in solution from pure VI, but we were unable to isolate it. The two methods of preparing the hydroquinone establish the structure of 5,8-dihydroxyisoquinoline, VI, and the substance was also obtained by the action of iron and hydrochloric acid on the nitroso

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[1] Mathëus, *Ber.*, **21**, 1886 (1888).

[2] Matsumura and Sone, THIS JOURNAL, **53**, 1406 (1931).

[3] Fritsch, *Ann.*, **286**, 12 (1895).

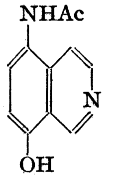
[4] Hoogewerff and van Dorp, *Rec. trav. chim.*, **5**, 308 (1886); Claus and Raps, *J. prakt. Chem.*, **45**, 241 (1892).

[5] Jeiteles, *Monatsh.*, **15**, 814 (1894); Fortner, *ibid.*, **14**, 155 (1893).

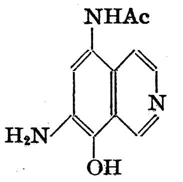
[6] Fieser and Fieser, THIS JOURNAL, **57**, 492 (1935).

derivative of the 5(8)-hydroxy compound (method of Matsumura and Sone[2]).

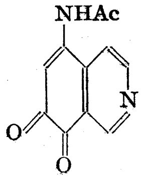
An ortho quinone of the series was obtained starting with the readily available IV, which was converted through the monoacetate VII and its *p*-sulfobenzeneazo compound into the amine VIII. Oxidation yielded an ortho quinone which may have either of the alternate structures: 5-acetylamino-7,8-isoquinolinequinone (IX) or 8-acetylamino-5,6-isoquinolinequinone.



VII



VIII



IX

Potential Measurements

Titrations of the reductants were carried out as indicated in the fifth paper.[7] Both the quinoline- and isoquinoline-quinone were too sparingly soluble in solutions more alkaline than about *p*H 7 to permit an extension of the data of Tables I and II. The normal potentials for the two systems under such conditions that there is no ionization (E_0) are very nearly identical. The difference in the basic dissociation constants of the oxidant and of the reductant is in each case about four *pK* units, the quinone being the weaker base. Quinolinequinone is so weakly basic that the value reported for K^b_0 is in this case only a rough approximation. The isoquinoline compounds are distinctly more basic (one *pK* unit) than the corresponding quinoline derivatives.

TABLE I

POTENTIALS OF THE SYSTEM FROM 5,8-QUINOLINEQUINONE (25°)[8]

Titrations of the reductant with $K_3Mo(CN)_8$. E_0 = 0.5570 v. $K^b_r = 1.76 \times 10^{-5}$. $K^b_0 = 1.10 \times 10^{-1}$. $E_n = E_0 + E_h + 0.0295 \log [1 + [H^+]/K^b_r] - 0.0295 \log [1 + [H^+]/K^b_0]$.

*p*H	Hydrogen elec. potential, E_h, v.	Potential when [Ox.] = [Red.], E_n, v.	E_n (found − calcd.), mv.	
0.10	−0.0059	0.6631	+1.3	0.09 slope
1.05	.0621	.5979	−0.7	
1.24	.0733	.5802	−2.0	
1.64	.0970	.5460	−3.7	
3.49	.2064	.3942	+5.4	
3.71	.2193	.3697	+0.3	
3.89	.2300	.3532	−1.0	
4.45	.2631	.3101	+1.8	
4.80	.2838	.2877	+6.3	
5.70	.3370	.2233	+2.9	0.06 slope
6.32	.3736	.1833	−0.1	
6.80	.4020	.1542	− .8	

TABLE II

POTENTIALS OF THE SYSTEM FROM 5,8-ISOQUINOLINEQUINONE (25°)

Titrations of the reductant with bromine water or (above *p*H 7) $K_3Mo(CN)_8$. For equation see Table I. E_0 = 0.5642 v. $K^b_r = 1.93 \times 10^{-6}$. $K^b_0 = 7.01 \times 10^{-3}$.

*p*H	Hydrogen elec. potential E_h, v.	Potential when [Ox.] = [Red.], E_n, v.	E_n (found − calcd.), mv.	
0.50	−0.0296	0.6397	+0.2	0.06 slope
1.15	.0680	.6015	+1.3	
1.27	.0751	.5941	+1.3	
1.80	.1064	.5592	+0.8	
2.18	.1289	.5298	−1.5	0.09 slope
3.27	.1933	.4445	+2.0	
4.31	.2548	.3500	−1.3	
4.95	.2926	.2934	−1.9	
5.34	.3157	.2639	−0.2	
6.13	.3624	.2018	.0	0.06 slope
6.99	.4132	.1504	− .6	
7.62	.4505	.1137	.0	

5-Acetylaminoisoquinoline-7,8-quinone, IX (or 8,6,5), is so sparingly soluble in water that satisfactory results were obtained only in the strongly acid region. In titrations of the hydroquinone with potassium dichromate at *p*H 0.40–0.50, the difference between the oxido-reduction electrode at half-oxidation and a hydrogen electrode in the same buffer was found to be 0.7573 v. (av.). As nearly as can be judged from available data, this substituted ortho quinone bears the normal relationship in potential to the para quinone of the isoquinoline series.

Discussion

A sufficient number of heterocyclic systems have been studied in this series of investigations to warrant a brief analysis of the main results. In initiating the work it was pointed out[9] that the lowering in the potential of a benzoquinone resulting from the fusing on of a benzene ring to produce a naphthoquinone probably gives a measure of the inertness or aromaticity of the benzene nucleus. The reactivity of one of the quinonoid ethylenic linkages is dampened when it becomes at the same time an integral part of an aromatic ring. If this premise is correct, the lowering in potential produced by a heterocycle, in comparison with the effect of a benzene ring, might give a measure of the relative degree of aromaticity of the heterocyclic ring. The ring systems for

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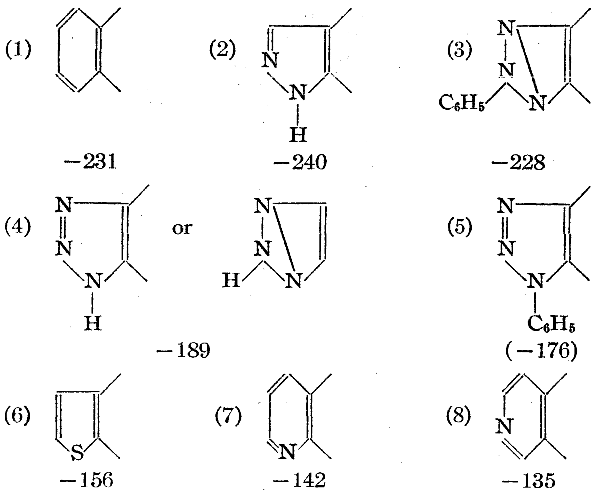
(7) Fieser and Martin, THIS JOURNAL, **57**, 1835 (1935).

(8) Results of W. H. Thalheimer, who prepared 5,8-quinolinehydroquinone by the method of Ref. 2.

(9) Fieser, THIS JOURNAL, **48**, 1097 (1926).

which reliable data are now available are indicated in the accompanying chart.



EFFECT OF AROMATIC RINGS ON THE POTENTIAL OF A QUINONE (IN MV.).

The question of prime importance is whether or not the diminished degree of unsaturation characteristic of the aromatic state is the only factor involved in determining the effect of the different heterocyclic rings. Were this the case the results would indicate that the pyrazole ring (2) is strongly aromatic, that the pyridine ring in the condition of either (7) or (8) is weakly so, and that the thiophene ring occupies a somewhat intermediate position. It is not easy to decide on the basis of other data if this is a reasonable relationship. The ease of substitution is hardly a valid criterion, because it is so likely to be determined, in part at least, by the character of the hetero atom. The ease of substitution of thiophene and furan may be connected with the presence in the ring of a key atom which when joined to a benzene ring facilitates substitution. The reluctance of the pyridine ring to react with many substituting reagents may be because the reaction is conducted in an acidic medium where the hetero atom forms an ionic, positive pole, so that it functions as a meta-directing group and retards substitution. The fact that Py-hydroxyquinolines and isoquinolines, unlike the naphthols, exist to a large extent in the ketonized forms points to a weakened condition of aromaticity of the pyridine ring, for the tendency to retain the completely aromatic type is an important characteristic of the benzene ring. On the other hand, the pyridine ring is remarkably resistant to attack by oxidizing agents, even under conditions such that there is no stabilization of the ring by salt-formation, and indeed it surpasses benzene in this respect. The thiophene ring is much more susceptible to oxidation. Although the different lines of evidence are conflicting, the relative positions of thiophene and pyridine indicated by the electrochemical results appear dubious. On the whole pyridine seems to possess more of the attributes of the truly aromatic type.

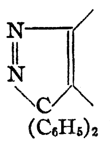
That some factor other than the aromaticity may be of influence in determining the potentials of the heterocyclic quinones has been recognized from the outset,[9] and it has been suggested[9,10] that the hetero atom may function as a part of a substituent group, independently of the stability of the ring. A group containing bivalent sulfur would shift the potential of a quinone to a more negative level, while a substituent containing the —N=C or the —C=N linkage of quinoline or isoquinoline probably would have the opposite effect. If the figures given above could be corrected for these possible effects, the value representing the aromaticity of the thiophene ring would become less negative and that for the pyridine rings would become more negative. These changes would be such as to bring the results into better accord with the general inferences from chemical observations, and we are inclined to believe that until such corrections can be made, or until they can be proved to be negligible, the results of the electrochemical comparisons should be viewed with caution.

While a revision may be required along the lines indicated, it is also possible that the results are essentially valid as they stand. It may be noted that the results of different comparisons of the same heterocycle have been remarkably concordant, and that the influence of a pyridine ring is practically the same whether the nitrogen atom is in the α- or the β-position with respect to the quinonoid nucleus. One other observation may be made which strongly indicates that the potential-lowering effects defined above reflect in some measure a property fundamentally connected with the aromatic character of the heterocycles. As judged by the general criteria of stability and lack of chemical reactivity, the 1-phenyltriazole ring system (5) certainly is to be classed as aromatic, and, like the benzene ring, it produces a decided lowering in the potential of a quinonoid nucleus to which it is joined. While formally

[10] Fieser and Kennelly, THIS JOURNAL, **57**, 1611 (1935).

similar to (5), the diphenyl pseudopyrazole ring (9) has entirely different properties.[11] The azo linkage is very reactive, the ring can be cleaved with great ease, and the system is distinctly unstable and in no sense aromatic. The difference is adequately reflected in the potentials, for the effect of fusing this truly unsaturated ring to *p*-benzoquinone is to raise the potential by the substantial amount of 110 mv. From the potentials above it would be concluded that (5) and (9) are fundamentally different, and that the azo group of (5), if indeed it exists as such, has a modified or dampened character quite distinct from an ordinary center of unsaturation, for in the latter case the effect upon the potential would be in the positive direction.

(9)



Experimental Part

5(8)-Hydroxyisoquinoline.—Isoquinoline sulfate (0.2 mole) was sulfonated essentially according to Weissgerber[12] (with 110 g. of fuming acid, 50% sulfur trioxide, at 20–25° for forty-eight hours), the solution was poured onto 500 g. of a mixture of ice and water and the solution was allowed to stand undisturbed. Long, colorless needles soon separated, and the pure α-sulfonic acid was easily obtained by recrystallization of this material from water; yield, 30 g. (72%). We consider the tedious separation through the barium salt unnecessary. No improvement could be made in the alkali fusion and the best yield was 17% (m. p. 228–230°).

5(8)-Hydroxy-8(5)-aminoisoquinoline (II).—The hydroxy compound (1.45 g.) was coupled with diazotized aniline in alkaline solution and the azo compound was reduced with sodium hydrosulfite. The yellow amine which separated was dissolved with a trace of stannous chloride in 3 cc. of concentrated hydrochloric acid and 5 cc. of water. After clarification, 20 cc. of concentrated acid was added to the hot, yellow filtrate. On cooling, the product separated as stout, bright yellow needles of the dihydrochloride; yield, 1 g. (43%).

Anal. Calcd. for $C_9H_{10}ON_2Cl_2$: C, 46.35; H, 4.33. Found: C, 46.07; H, 4.47.

5(8)-Amino-8(5)-hydroxyisoquinoline (IV).—5(8)-Nitroisoquinoline was prepared as described by Claus and Hoffmann,[13] the yield of crude material, m. p. 104–108°, being 74%. The electrolytic reduction of the nitro compound (12 g.) in sulfuric acid solution (120 cc.) was carried out as described in the fifth paper.[7] After twenty-four hours the yellow solution was filtered from calcium sulfate through asbestos, diluted with an equal volume of water, and allowed to stand for several days in the ice box. Fine yellow needles of the amine sulfate separated and were collected on an asbestos filter; yield, 20 g. This salt probably contains two molecules of sulfuric acid; it dissolves readily in water and presently the solution deposits fine yellow needles of the **monosulfate**, which is very sparingly soluble in water.

Anal. Calcd. for $C_9H_8ON_2 \cdot H_2SO_4$: C, 41.83; H, 3.90; S, 12.42. Found: C, 41.89; H, 4.30; S, 12.57.

The dihydrochloride, which is considerably more soluble in water, was prepared as follows. The crude sulfate from 12 g. of the nitro compound was suspended in 100 cc. of water, covered with a layer of ether to prevent oxidation, and the acid was neutralized with solid sodium bicarbonate. The solid became bright red and then yellow, as the neutral point was reached. The yellow amine was collected, washed with water and quickly dissolved with a trace of stannous chloride in 18 cc. of concentrated hydrochloric acid and 50 cc. of water. After heating the solution and filtering it through charcoal, 200 cc. of concentrated hydrochloric acid was added. The stout yellow needles which separated on cooling were washed with dilute acid, alcohol and ether; yield, 13.3 g. (83%). The salt is readily soluble in water and it dissolves in alkali with a green coloration.

Anal. Calcd. for $C_9H_8ON_2 \cdot 2HCl$: C, 46.35; H, 4.33; Cl, 30.44. Found: C, 46.25; H, 4.34; Cl, 30.61.

The dibenzoyl derivative was prepared by shaking an aqueous suspension of the sulfate with benzoyl chloride and alkali. An oil formed and soon solidified. The substance crystallized from alcohol as fine, colorless needles, m. p. 223–224°.

Anal. Calcd. for $C_{23}H_{16}O_3N_2$: C, 74.98; H, 4.38. Found: C, 74.96; H, 4.42.

Isoquinoline-5,8-hydroquinone Hydrochloride (VI).—(a) A suspension of 5.16 g. of crude 5(8)-amino-8(5)-hydroxyisoquinoline sulfate in 25 cc. of water was treated at 5° with 24 cc. of cold 20% ferric chloride solution. The solid material soon dissolved to give a deep red solution and after standing for a time a fine, yellow precipitate began to separate. After cooling in ice for one hour, this was collected and washed free of red mother liquor with ice water. The crude product was dissolved in 40 cc. of hot water and 10 cc. of concentrated hydrochloric acid and brought down with 75 cc. of concentrated acid, when it gave no test for sulfate ion. After a further crystallization from dilute acid the hydrochloride was obtained as fine, yellow leaflets; yield, 0.73 g. It darkens at about 260° and has no melting point. The substance gives no coloration with ferric chloride, it rapidly darkens in alkali and it gives a very sparingly soluble sulfate.

Anal. Calcd. for $C_9H_7O_2N \cdot HCl$: C, 54.71; H, 4.09; Cl, 17.95; N, 7.18. Found: C, 54.76; H, 4.20; Cl, 18.05; N, 7.16.

(b) The preparation from 5(8)-hydroxy-8(5)-aminoisoquinoline was similar and gave an identical product.

(c) 5(8)-Hydroxyisoquinoline (1.45 g.) was converted into the nitroso derivative by slowly acidifying an alkaline solution of the substance containing sodium nitrite. The crude, moist nitroso compound was dissolved quickly in 400 cc. of hot water containing 12 cc. of concentrated hydrochloric acid and the filtered solution was treated at 95° with 3 g. of iron powder, added in one hour with stirring. The solution was filtered, concentrated in vacuum, and treated with 10 cc. of concentrated hydrochloric acid.

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[11] Fieser and Peters, THIS JOURNAL, **53**, 4080 (1931).

[12] Weissgerber, *Ber.*, **47**, 3179 (1914).

[13] Claus and Hoffmann, *J. prakt. Chem.*, **47**, 253 (1893).

Yellow crystals of the hydroquinone hydrochloride separated on cooling; yield, 0.2 g. (10%).

Dibenzoyl isoquinoline-5,8-hydroquinone formed colorless needles from alcohol, m. p. 162–163°.

Anal. Calcd. for $C_{23}H_{15}O_4N$: C, 74.78; H, 4.10. Found: C, 74.80; H, 4.28.

Diacetyl 5(8)-amino-8(5)-hydroxyisoquinoline.—This derivative was obtained from the dihydrochloride of the aminohydroxy compound with acetic anhydride and sodium acetate either in an aqueous solution (60% yield) or without a solvent (69% yield). It crystallizes from dilute alcohol as long, colorless needles, m. p. 208–209°.

Anal. Calcd. for $C_{13}H_{12}O_3N_2$: C, 63.91; H, 4.96. Found: C, 64.02; H, 5.13.

5-Acetylamino-7-(*p*-sulfobenzeneazo)-8-hydroxyisoquinoline (or 8,6,5).—The above diacetyl compound (2.41 g.) was dissolved in a cold solution of 1 g. of sodium hydroxide in 25 cc. of water (hydrolysis of the O-acetyl group) and the solution was treated at 0° with a suspension of the diazo compound from 2.09 g. of sulfanilic acid. A portion of the deep purple-red solution after being diluted yielded a brown, crystalline precipitate of the azo compound on acidification.

Anal. Calcd. for $C_{17}H_{14}O_5N_4S$: C, 52.82; H, 3.65. Found: C, 52.40; H, 3.99.

5-Acetylamino-7-amino-8-hydroxyisoquinoline Dihydrochloride, VIII (or 8,6,5).—The remainder of the solution of the azo compound was treated with sodium hydrosulfite and warmed gently until the color was discharged. The crystalline, yellow precipitate was dissolved in 20 cc. of water and 4 cc. of concentrated hydrochloric acid, and the clarified solution was saturated with hydrogen chloride at 0°, when fine yellow needles of the dihydrochloride soon separated; yield, 1.3 g. (43%). The salt is only moderately soluble in water but it is slow to crystallize.

Anal. Calcd. for $C_{11}H_{11}O_2N_3 \cdot 2HCl$: C, 45.52; H, 4.52. Found: C, 45.12; H, 4.70.

5-Acetylaminoisoquinoline-7,8-quinone Hydrochloride, IX (or 8,6,5).—A solution of 0.29 g. of VIII in 4 cc. of water and 0.5 cc. of concentrated hydrochloric acid was treated at 10° with 2 cc. of 20% ferric chloride solution added in one portion. The solution became red and fine, yellow needles soon separated. The product was washed free of dark mother liquor with concentrated acid, dissolved in 10 cc. of water, and 1 cc. of concentrated acid was added to the clarified solution. Golden yellow needles soon separated in 51% yield. Without isolating any of the intermediates, the yield from diacetyl aminohydroxyisoquinoline was 38%.

Anal. Calcd. for $C_{11}H_8O_3N_2 \cdot HCl$: Cl, 14.03. Found: 13.93, 13.94.

Summary

Isoquinoline-5,8-hydroquinone has been prepared by three methods, and the oxido-reduction systems from this reductant and from the known quinoline-5,8-hydroquinone have been studied potentiometrically. An analysis is presented of the results obtained in this series of investigations of the degree of aromaticity of various heterocyclic rings.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS

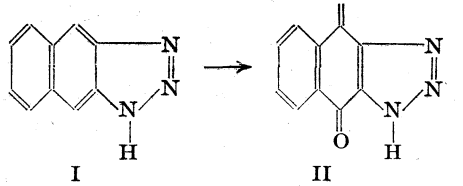
RECEIVED JULY 6, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A Comparison of Heterocyclic Systems with Benzene. VII. Isologs of Anthraquinone Containing One and Two Triazole Rings

BY LOUIS F. FIESER AND ELMORE L. MARTIN

When this work was undertaken no unsubstituted quinones of the type indicated in the title were known, but in a paper published in March of this year Fries, Walter and Schilling[1] described the preparation of *lin*-naphthotriazole-8,9-quinone (II) by the oxidation of *lin*-naphthotriazole (I) with chromic anhydride. We had at the time performed a similar experiment, but the succession of steps leading to II was so generally unsatisfactory that a better method was developed.



I II

Ullmann and Ettisch[2] worked out an excellent method of preparing 2,3-dichloro-1,4-naphthoquinone from α-naphthol and found that one of the two chlorine atoms is easily replaced by reaction with ammonia. The halogen atom of the amino compound (III) is resistant to attack by amines under comparable conditions, but Fries and Ochwat[3] found that the acetyl derivative IV reacts normally with aromatic amines to give arylamino derivatives. On treating the acetyl compound IV with dry ammonia in nitrobenzene solution, we found that the substance is converted

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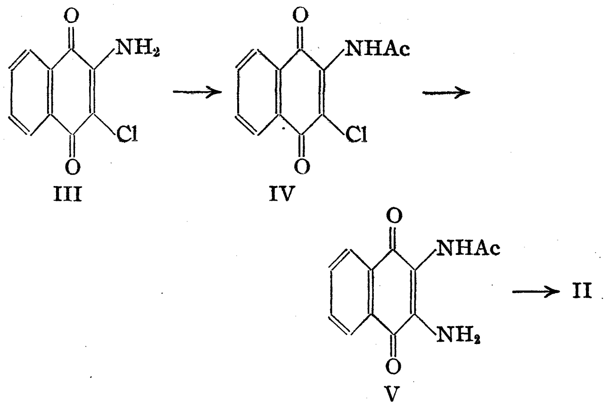
(1) Fries, Walter and Schilling, *Ann.*, **516**, 248 (1935).

(2) Ullmann and Ettisch, *Ber.*, **54**, 270 (1921).

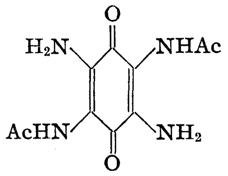
(3) Fries and Ochwat, *ibid.*, **56**, 1295 (1923).



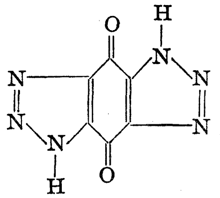
III IV V

smoothly into the amine V. We were at first unable to bring about a reaction of this substance with nitrous acid although the structure assigned was confirmed by the preparation of various derivatives. It was found that the difficulty is connected with the sparing solubility of the amine. When a solution of the colorless hydroquinone of V in dilute acid was treated with excess nitrous acid, a red precipitate of the quinone was produced in fine suspension, and in this condition it slowly reacted with the reagent with the formation of the desired *lin*-naphthotriazole-8,9-quinone, II, the acetyl group being hydrolyzed either during the reaction or in working up the product. On methylating the quinone II by the method described by Fries and co-workers,[1] we obtained a product identical with the 1-methyl-*lin*-naphthotriazole-8,9-quinone synthesized by Hartwell[4] by a method which establishes the structure.

Following the method described above, it was possible to prepare a *lin*-bis-triazoloquinone. Two of the halogen atoms of chloranil are easily replaced by amino groups, and it was found that after acetylation of these groups the remaining halogens can be caused to react with ammonia, giving VI. This substance is very sparingly soluble in most solvents and no reaction with nitrous acid could be brought about in an aqueous medium, even through the expedient found serviceable in the other series. The desired result was achieved by adding sodium nitrite to a suspension of VI in glacial acetic acid at 100°. The red diacetate gradually was transformed to a yellow, crystalline solid which proved to be the monosodium salt of 2,3,5,6-bis-triazolo-1,4-benzoquinone, VII. The quinone, which evidently is a very strongly acidic substance, was obtained by acidifying an aqueous solution of the salt with mineral acid. It decomposes explosively at a high temperature, and gives a characteristic anthraquinone vat test. The pure quinone is completely colorless, a remarkable property for substances of this class.[5]



VI



VII

Attempts to obtain the angular isomer of VII by the oxidation of 1,2,3,4-bis-triazolobenzene met with no success, but some improvements were made in the synthesis of the tricyclic compound and the details are recorded in the experimental part.

Unfortunately the two tricyclic quinones reported above do not dissolve to any appreciable extent in water, and a complete electrochemical characterization could not be made. In the case of *lin*-naphthotriazole-8,9-quinone it was possible to perform titrations of the reductant in alcoholic solutions, the potentials at half-oxidation against a hydrogen electrode in the same buffer at 25° being as follows: 0.4345 v. in 50% alcohol, 0.1 *N* in hydrochloric acid and 0.2 *N* in lithium chloride; 0.3450 v. in 37% alcohol, 0.047 *M* in monopotassium phosphate and 0.047 *M* in disodium phosphate. The difference between these two figures is in the direction which would be expected in a system whose oxidant has a strongly acidic group and whose reductant is basic.

Discussion

Although the results are very meager, an interesting inference can be drawn from a comparison of the potential of *lir*-naphthotriazole-8,9-quinone in alcoholic hydrochloric acid (0.435 v.) with that of other tricyclic quinones in the same solvent. Since *lin*-naphthindazolequinone (E_0 = 0.155 v.) has practically the same potential as its 1-methyl ether VIII,[4] it would be safe to predict that the hydrogen compound corresponding to IX would have a potential close to that of IX. The fact that the value found for *lin*-naphthotriazole-8,9-quinone is so decidedly different, suggests that the structure may be represented more accurately by formula X.[6]

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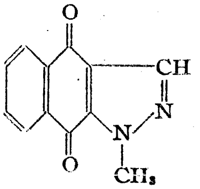
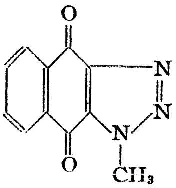
[4] Fieser and Hartwell, THIS JOURNAL, **57**, 1479 (1935).

[5] Compare *lin*-naphthindazolequinone, Fieser and Peters, *ibid.*, **53**, 4080 (1931).

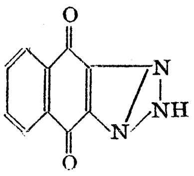
[6] Compare, Fieser and Ames, *ibid.*, **49**, 2604 (1927).



$E_0 = 0.160$ v.
VIII

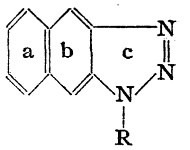


$E_0 = 0.235$ v.
IX

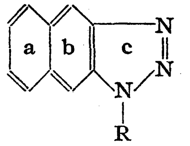


$E_0 = 0.435$ v.
X

As for the fine structure of the isologs of anthrahydroquinone or of anthracene containing a triazole nucleus, the electrochemical results favor the formulation XI, which indicates that Ring c, being less aromatic than Ring a, is the one which assumes the *o*-quinonoid or dihydride structure.

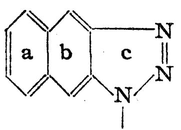


XI



XII

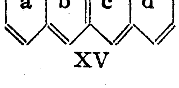
Fries,[1] on the basis of hydrogenation experiments, writes the alternate structure XII, in which Ring a is quinonoid, and the question is still open. We are in complete agreement with this author with regard to the principle involved, and indeed this was discussed previously by one of us with Ames.[6] At that time we failed to recognize a second principle set forth in the important paper by Fries, Walter and Schilling[1] to the effect that every ring of a polynuclear aromatic compound strives to approach as nearly as possible the condition of a true benzoid ring. According to this principle, to which we now subscribe, a structure such as XIII (or a similar structure for anthracene) is highly improbable, for two of the rings (b, c) have the dihydride structure.



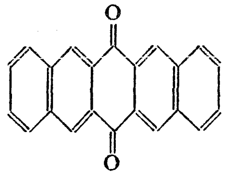
XIII

From a consideration of both of the influences determining the positions of the bonds, the formula for naphthacene XIV previously discussed[7] should be revised as in XV. In each formula two rings are quinonoid, but in XIV they are combined to form a highly unstable 2,3-naphthoquinonoid grouping (Rings a and b), while in XV two isolated and less reactive *o*-benzoquinonoid rings (a and d) are present. The fine structure previously written for naphthacenequinone[7] accords with the principle of greatest stability and it is similar to that assigned by Fries to pentacenequinone, XVI. Fries has expressed the view that, because of the special bond structure of the central nucleus, XVI is no *p*-quinone, and he considers that this explains the failure of the substance to form a vat. We do not share this view, but believe, rather, that the reluctance of XVI to undergo reduction is conditioned by a very low reduction potential. This is determined, not by the special structure of the quinone, but by the reactive quinonoid bond structure of the hydroquinone. This explanation has been advanced to account for a similar property of naphthacenequinone.[7] Clar's "2,3-phthaloylphenanthrene,"[8] which can be assigned the structure XVII, does not contain an ordinary *p*-quinone ring but it nevertheless gives the vat test (because the angular ring stabilizes the anthracene structure of the hydroquinone, giving a higher oxido-reduction potential).[9] Arguments have been advanced[10] for attributing to 1,4-anthraquinone the structure of XVIII, and the substance has all the properties of a true *p*-quinone in spite of the tetraketonic structure of the terminal ring.

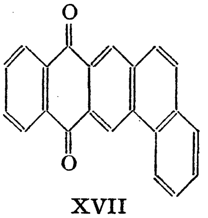
XIV



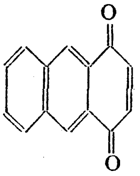
XV



XVI



XVII



XVIII

Experimental Part

1. *lin*-Naphthotriazole-8,9-quinone

2-Acetylamino-3-amino-1,4-naphthoquinone (V).—Dry ammonia was passed into a boiling solution of 2.1 g. of pure 2-acetylamino-3-chloro-1,4-naphthoquinone[3] (m. p. 217–219°) in 15 cc. of nitrobenzene until there was no further color change and no further separation of ammonium chloride. The deep red solution on cooling deposited red crystals of the reaction product. The collected solid was washed with ether–ligroin, dried and washed with water to remove ammonium chloride; yield, 1.6 g. (83%); m. p. 225–230°. Crystallized from alcohol, in which it is only slightly soluble, the substance formed beautiful bright red needles, m. p. 233–234°. It dissolves

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[7] Fieser, This Journal, **53**, 2329 (1931).

[8] Clar, *Ber.*, **62**, 1574 (1929).

[9] Fieser and Dietz, This Journal, **53**, 1128 (1931).

[10] Fieser, *ibid.*, **50**, 465 (1928).

in alcoholic alkali with a deep red-purple coloration and is precipitated unchanged by acids; the solution in concentrated sulfuric acid has a light orange color.

Anal. Calcd. for $C_{12}H_{10}O_3N_2$: C, 62.58; H, 4.38; N, 12.2. Found: C, 62.19; H, 4.38; N, 11.9.

2,3 - Di - (acetylamino) - 1,4 - naphthohydroquinone.—An aqueous suspension of the quinone V was treated with sodium hydrosulfite and stirred until the red crystals disappeared and the colorless hydroquinone separated. This substance was dissolved in dilute hydrochloric acid, and one equivalent of acetic anhydride was added, followed by sodium acetate solution. The diacetyl derivative soon separated and it was recrystallized from dilute alcohol, forming colorless crystals, m. p. 255° dec., which turned yellow on storage.

Anal. Calcd. for $C_{14}H_{14}O_4N_2$: C, 61.29; H, 5.15. Found: C, 60.96; H, 5.19.

***lin*-Naphthotriazole-8,9-quinone (II).**—2-Acetylamino-3-amino-1,4-naphthoquinone (1.5 g.) was reduced as above and the nearly colorless product was collected and dissolved in 25 cc. of water and 3 cc. of concentrated hydrochloric acid. The slightly yellow solution was completely decolorized by filtration through a layer of Norite, and the filtrate, diluted to 50 cc., was treated at 0° with 10 cc. of 10% sodium nitrite solution. A fine, bright red precipitate separated immediately (collected at once, it was found to be the pure starting material), but on standing at 10–20° for two to three hours with the occasional addition of nitrite solution the color faded and finally a nearly colorless product resulted. This was collected, clarified in a dilute solution in alkali, and reprecipitated from the yellow filtrate. A solution of the faintly yellow material in hot acetone was decolorized with Norite, diluted with two volumes of warm water, and allowed to cool, when thin, glistening plates separated; yield 0.6 g. (46%). These crystals have a barely visible yellow tinge and they contain one molecule of water of crystallization which is lost on heating slightly above room temperature. The anhydrous compound decomposes at 240–245°. It does not dissolve in dilute acids. With alkaline hydrosulfite it forms a light red vat with an intensely green intermediate stage (quinhydrone).

Anal. Calcd. for $C_{10}H_5O_2N_3$: C, 60.28; H, 2.53. Found: C, 60.24; H, 2.82.

Fries, Walter and Schilling[1] state that their sample of this quinone was yellow and that the solution in dilute alkali was nearly colorless. Our quinone was nearly colorless and gave a faintly yellow solution in alkali. We obtained the same compound by the oxidation of *lin*-naphthotriazole in glacial acetic acid with chromic anhydride, but the yield was poor and the product was not obtained in a nearly colorless condition.

The N-methyl derivative, prepared by alkylation with dimethyl sulfate and alkali, formed colorless crystals from benzene, m. p. 248–250°. A mixture with Hartwell's sample[4] melted at 250–251°.

2. *lin*-bis-Triazoloquinone

2,5-Diamino-3,6-dichloroquinone.—The method of von Knapp and Schultz[11] was improved considerably by passing dry ammonia into a suspension of 12.3 g. of finely powdered chloranil in 150 cc. of boiling alcohol until the yellow crystals had dissolved. Dark red crystals of the diamine separated along with the ammonium chloride. After cooling, the solid was washed with water, alcohol, and ether, leaving 7.8 g. (75%) of deep red needles. Finding no suitable recrystallizing solvent, the material was purified as follows. A suspension of 1 g. of the quinone in aqueous hydrosulfite solution was warmed slightly to effect reduction. The nearly colorless hydroquinone was dissolved in dilute hydrochloric acid and the solution was decolorized by filtration through a layer of Norite, diluted to 200 cc., and treated at 90° with excess ferric chloride solution. The quinone separated slowly as long fine, deep red needles (0.8 g.).

2,5-Di-(acetylamino)-3,6-dichloroquinone.—A suspension of 8.2 g. of the diaminoquinone in 25 cc. of acetic anhydride was treated with ten drops of concentrated sulfuric acid and stirred at room temperature until conversion to bright yellow crystals of the diacetyl compound was complete. Alcohol was added to the cooled mixture and the product was collected; yield, 8.7 g. (75%); m. p. 240–245°. The substance is moderately soluble in glacial acetic acid and slightly soluble in alcohol. It crystallizes well from either solvent as yellow needles, m. p. 253–254°.

Anal. Calcd. for $C_{10}H_8O_4N_2Cl_2$: C, 41.24; H, 2.77. Found: C, 41.36; H, 2.95.

2,5-Di-(acetylamino)-3,6-diaminoquinone (VI).—The reaction of the diacetylaminodichloroquinone with ammonia did not proceed well in boiling nitrobenzene solution, the material being largely destroyed. A better method consisted in passing dry ammonia into a suspension of 8.2 g. of the finely powdered material in 100 cc. of boiling alcohol and allowing most of the alcohol to evaporate as the reaction progressed. A reddish-brown product separated, and after cooling this was collected and washed with water, alcohol and ether, giving 5.6 g. (79%) of material suitable for the next step. The quinone is sparingly soluble in most solvents and no recrystallizing solvent was found. A purification was accomplished by dissolving the brown-red material (0.25 g.) in a mixture of 25 cc. each of alcohol and water containing 1 cc. of 10% alkali, filtering the purple-red solution, and acidifying. Fine, dark red needles separated slowly. The substance has no characteristic point of decomposition; the solution in concentrated sulfuric acid is deep red and becomes yellow on the addition of a small amount of water. Carbon–hydrogen analyses were unsatisfactory.

2,3,5,6-Bistriazolo-1,4-benzoquinone (VII).—A suspension of 0.5 g. of the crude quinone VI in 20 cc. of glacial acetic acid was warmed on the steam-bath and treated with 20 cc. of 10% sodium nitrite solution, added slowly in portions. The dark starting material slowly dissolved and the color of the solution faded to a light red. Solid sodium nitrite was added until the color changed to a light yellow and yellow crystals of the sodium salt of the reaction product separated. After cooling, the crystals were washed with cold water, alcohol and ether. The substance crystallized from water as stout, bright yellow needles of the monosodium salt dihydrate; yield, 0.2 g.

Anal. Calcd. for $C_6HN_6O_2Na \cdot 2H_2O$: N, 33.9. Found: N, 34.0.

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(11) Von Knapp and Schultz, *Ann.*, **210**, 183 (1881).

The quinone itself separated as completely colorless microcrystals on acidifying a hot, clarified, aqueous solution of the sodium salt; yield, 0.15 g. (40%). The substance is insoluble in the usual solvents and it could not be recrystallized, but the above material appeared to be pure.

Anal. Calcd. for $C_6H_2O_2N_4$: C, 37.89; H, 1.06. Found: C, 38.12; H, 1.20.

The colorless quinone gives a yellow vat with alkaline hydrosulfite solution, and on shaking with air the solution acquires a beautiful blue color, probably as the result of quinhydrone formation. In the presence of excess reducing agent the color fades to yellow on standing, and the test can be repeated until the reagent is exhausted, when the sparingly soluble sodium salt of the quinone separates. The quinone is unaffected at temperatures up to 300°; when heated on a spatula it decomposes with explosive violence.

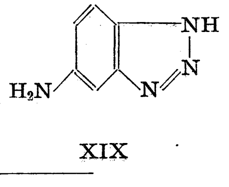
3. Preparation of *lin*-Naphthotriazole (I)

As the procedure of Friedländer and v. Zakrzewski[12] for preparing **potassium 2,3-dihydroxynaphthalene-6-sulfonate** gave very poor results, the following method was developed. Technical 2-naphthol-3,6-disulfonic acid (120 g.) was added rapidly with stirring to a melt at 200° from 460 g. of potassium hydroxide, 20 g. of sodium hydroxide, and 6 cc. of water. In the course of twenty minutes the temperature was raised to 250°, when the yellow melt changed to an even paste. The melt while hot was transferred in portions to 1 kg. of ice and 730 cc. of concentrated hydrochloric acid, and the red-brown solution was treated with active charcoal, filtered and acidified. The slightly colored salt which separated on cooling was dissolved in hot water saturated with sulfur dioxide and after clarifying the solution with active charcoal, the colorless filtrate deposited 50 g. (52%) of glistening, colorless plates. The addition of ferric chloride to the aqueous solution produces a beautiful intense blue-violet coloration.

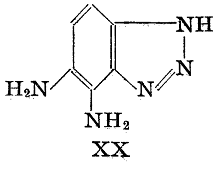
2,3-Dihydroxynaphthalene[12] was obtained by heating 30 g. of the above sulfonate with 240 cc. of water and 45 cc. of concentrated sulfuric acid for twelve hours in an autoclave at 150–160°; yield, 13 g. (65%); m. p. 158–159°. This was converted into 2,3-diaminonaphthalene by the method of Morgan and Godden.[13] The conversion was nearly quantitative in successful experiments, but few tubes withstood the drastic conditions. The method of the above authors was used for closing the triazole ring.

4. Preparation of 1,2,3,4-bis-Triazolobenzene

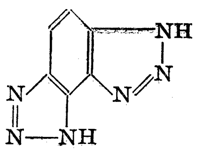
This compound (XXI) has been obtained[14] from 5-aminobenzotriazole (XIX) through the diamino compound XX.



XIX

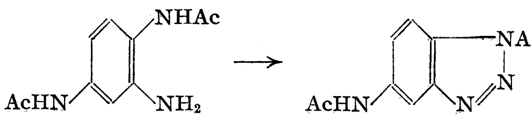


XX



XXI

An improved method of preparing XIX was found in nitrating diacetyl *p*-phenylenediamine, reducing the nitro compound catalytically, converting the amine XXII with nitrous acid into the diacetyl compound XXIII and hydrolyzing the latter compound.



XXII XXIII

2,5-Di-(acetylamino)-aniline (XXII).—2,5-Di-(acetylamino)-nitrobenzene, m. p. 186–188°, was obtained in 83% yield by Ladenburg's method,[15] and 19.7 g. of this material dissolved in 300 cc. of hot alcohol was hydrogenated in the presence of 0.1 g. of Adams catalyst. The amino compound (XXII) was collected and a solution of the material in dilute acid was clarified with Norite. On neutralization the substance separated in a colorless condition; yield, 15 g. (87%); m. p. 235–237° (recrystallized from alcohol, m. p. 236–237°).[16]

5-Aminobenzotriazole Dihydrochloride.—The slow addition of 70 cc. of 10% sodium nitrite solution to a cold solution of 20.7 g. of XXII in 150 cc. of water and 17.7 cc. of concentrated hydrochloric acid gave 20.6 g. (95%) of 5-aminobenzotriazole diacetate, m. p. 182–184° (recrystallized from acetone–water, m. p. 184–185°, literature,[17] 184°). For the hydrolysis, 4.36 g. of the diacetate was boiled with 10 cc. of concentrated hydrochloric acid for one hour, adding a trace of stannous chloride to discharge a faint yellow color. On cooling at 0°, stout colorless needles of the dihydrochloride separated; yield, 4 g. (90%).

4,5-Diaminobenzotriazole (XX) was prepared from XIX through the benzeneazo compound. The latter substance was obtained by coupling in the presence of sodium acetate according to Fries, Güterbock and Kühn,[17] but it was more conveniently collected as the hydrochloride. This was obtained as a mass of fine, bright red needles by adding dilute acid to the orange, gelatinous precipitate of the azo compound, yield 95%. The substance dissolves in dilute alkali and an excess of reagent precipitates the orange sodium salt. For the reduction, 5.49 g. of the hydrochloride was stirred at room temperature with a solution of 9 g. of stannous chloride crystals in 50 cc. of concentrated hydrochloric acid. After gentle warming the resultant yellow mixture was cooled and the precipitated material was recrystallized twice from hydrochloric acid solution; fine yellow needles, 3.2 g. (69%).

1,2,3,4-bis-Triazolobenzene (XXI).—On treating XX with nitrous acid according to Nietzki and Prinz,[14] most of the material was destroyed by oxidation. This was

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[12] Friedländer and v. Zakrzewski, *Ber.*, **27**, 761 (1894).

[13] Morgan and Godden, *J. Chem. Soc.*, **97**, 1718 (1910).

[14] Nietzki and Prinz, *Ber.*, **26**, 2960 (1893).

[15] Ladenburg, *ibid.*, **17**, 148 (1884).

[16] Bülow and Mann, *ibid.*, **30**, 986 (1897), prepared the compound by reduction with iron and acetic acid and reported a melting point of 231–232°.

[17] Fries, Güterbock and Kühn, *Ann.*, **511**, 221 (1934).

prevented to some extent by protecting one of the amino groups by acetylation.

A solution of 1.16 g. of 4,5-diaminobenzotriazole dihydrochloride and 0.6 cc. of acetic anhydride in 100 cc. of water was treated quickly with a solution of 1 g. of fused sodium acetate in water. The light yellow solution was clarified with charcoal, cooled to 0°, and treated slowly with 4 cc. of 10% sodium nitrite solution. The nearly colorless precipitate (acetate) was dissolved in warm 2% sodium hydroxide solution and precipitated with dilute acid, giving 0.2 g. (25%) of the almost colorless bis-triazolobenzene.

Summary

Methods have been developed for the synthesis of isologs of anthraquinone with either one or two of the benzene rings replaced by a triazole ring. Unfortunately these compounds proved to be so sparingly soluble that only a very limited potentiometric characterization was possible, but the results obtained have some bearing on the problem of the fine structure of the triazole nucleus. This paper includes also a comparison with the views of Fries concerning the bond structure of polynuclear hydrocarbons and quinones.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS
RECEIVED JULY 9, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY, TEACHERS COLLEGE, COLUMBIA UNIVERSITY]

Studies of Crystalline Vitamin B_1.[1] X. Sulfite Cleavage. III. Chemistry of the Basic Product

BY EDWIN R. BUCHMAN, ROBERT R. WILLIAMS AND JOHN C. KERESZTESY

By cleavage of vitamin B_1 with sulfite Williams[2] obtained a basic substance C_6H_9NSO (II), easily isolated as the crystalline hydrochloride in yields up to 97%. The free base is a colorless, rather viscous oil with a characteristic faint basic odor, easily soluble in water, alcohol and chloroform and less readily in ether. It is a mono acid base giving well-defined crystalline derivatives with chloroplatinic, picric and picrolonic acids.

The evidence[3] points to the presence of a free hydroxyl group in the vitamin. Since the oxygen in (II) is evidently derived directly from the vitamin, attempts were made to demonstrate an hydroxyl in (II). With concentrated hydrochloric acid at 150° it was found, as expected, that —OH is replaced by non-ionic chlorine

$$C_6H_9NSO\ (II) \xrightarrow{HCl} C_6H_8NSCl\ (V)$$

(V), obtained in good yield in the form of its crystalline hydrochloride, closely resembles the oxy base (II); the ultraviolet absorption spectra are nearly identical.[4]

When treated with excess *p*-nitrobenzoyl chloride in pyridine, (II) gave a crystalline mononitrobenzoate which still exhibited basic properties. Evidently only the —OH group reacts with acyl chlorides and it may be assumed that the nitrogen in (II) is tertiary in character.

The action on (II) of nitrous acid and of methyl iodide was studied to secure further evidence on this point. With nitrous acid a crystalline product was obtained in good yield, but its analysis and properties showed it to be the nitrate of the original base, $C_6H_9NSO \cdot HNO_3$. With methyl iodide a typical quaternary salt was obtained by allowing the two components to combine slowly at room temperature.

$$C_6H_9NSO\ (II) \xrightarrow{CH_3I} C_6H_9NSO \cdot CH_3I\ (VI)$$

Treatment of the salt (VI) with alkali regenerated no ether-soluble base. In striking contrast to (II) which after heating with 20% alkali at 100° can be recovered unchanged, (VI) under the same conditions was completely destroyed with formation of alkali sulfide. The vitamin itself is readily attacked by hot alkali, also splitting out sulfide.[5] This analogy is consistent with the view that the vitamin is a quaternary salt of (II).[6]

While this investigation was in progress there appeared an article[7] by Windaus, Tschesche and Grewe describing the splitting of the vitamin with nitric acid and the isolation of two well-characterized degradation products, one a sulfur-containing acid $C_5H_5NSO_2$. Oxidation of (II) with nitric acid at 40° gave sulfuric acid and 30% of an acid (VII).

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[1] Presented before the Organic Division of the American Chemical Society at the New York Meeting, April, 1935.

[2] R. R. Williams, R. E. Waterman, J. C. Keresztesy and E. R. Buchman, THIS JOURNAL, **57**, 536 (1935).

[3] E. R. Buchman and R. R. Williams, *ibid.*, **57**, 1751 (1935).

[4] A. E. Ruehle, *ibid.*, **57**, 1887 (1935).

[5] A. Windaus, R. Tschesche, H. Ruhkopf, F. Laquer and F. Schultz, *Nachr. Ges. Wiss. Göttingen. Math.-phys. Klasse*, III, 211 (1931).

[6] R. R. Williams, THIS JOURNAL, **57**, 229 (1935).

[7] A. Windaus, R. Tschesche and R. Grewe, *Z. physiol. Chem.*, **228**, 27 (1934).

$$\underset{\text{(II)}}{(C_4H_4NS)\text{—}C_2H_4OH} \xrightarrow{HNO_3} \underset{\text{(VII)}}{(C_4H_4NS)\text{—}COOH}$$

A comparison of the properties of (VII) with those listed[7] by Windaus for his acid showed that the two substances are identical. The similarity in ultraviolet absorption spectra[4,7] of (II) and (VII) strengthens the view that these substances have a common heterocyclic nucleus C_4H_4NS—.[8] The side chain —C_2H_4OH may be written —$CHOHCH_3$ or —CH_2CH_2OH. The optical inactivity of the vitamin argues against the first formulation. When treated with iodine and alkali (II) gave no iodoform,[9] further indicating that the —OH is in the β position.

Experimental

Basic Cleavage Product C_6H_9NSO (II).—The hydrochloride[2] was available for this work in amounts equivalent to approximately 2 g. of vitamin. It is the salt of a weak[10] base crystallizing in thin bars, readily soluble in water and alcohol, practically insoluble in ether, chloroform and acetone and subliming essentially unchanged at 50° *in vacuo*. Due to its extreme hygroscopicity, great care was necessary in the handling of this substance.

The free base was liberated by making alkaline the aqueous solution of the hydrochloride, shaking out with ether or chloroform and evaporating off the solvent. There was obtained a colorless oil miscible with water but almost insoluble in 20% sodium hydroxide.

An aqueous solution of the hydrochloride gave with phosphotungstic acid an immediate white microcrystalline precipitate. The picrolonate was made by treating an aqueous solution of the hydrochloride with picrolonic acid in methanol. After standing for two days, well-formed yellow crystals had deposited, m. p. 184°[11] (dec.). *Anal.* Calcd. for $C_6H_9NSO{\cdot}C_{10}H_8N_4O_5$: S, 7.87. Found: S, 8.09. With chloroplatinic acid in alcoholic solution, there was an immediate orange-yellow crystalline precipitate of m. p. 181° (dec.). Under similar conditions with gold chloride, an oil was obtained. The addition of ethereal picric acid to an ether solution of the free base threw down a picrate, m. p. 162–163°, difficultly soluble in ether and in alcohol but moderately soluble in water.

A few crystals of the hydrochloride were subjected to pyrolysis and a pine splinter moistened with hydrochloric acid introduced into the vapors. There was no color formed; the vitamin under the same conditions also gave a negative test. However, the characteristic color which the vitamin develops with diazotized sulfanilic acid was not given by (II). Also, unlike the vitamin, the basic cleavage product was found to be quite stable to hot alkali. A weighed amount (*circa* 20 mg.) of the crystalline hydrochloride was heated at 100° for three-fourths of an hour with 1 cc. of 20% sodium hydroxide. The reaction mixture gave a definitely negative test with nitroprusside[12] solution. A recovery of 90% of the starting material was effected by extraction of the base with ether and conversion into the hydrochloride.

Action of Concentrated Hydrochloric Acid on (II).—26.0 mg. of the hydrochloride of the basic cleavage product was heated in a sealed tube for three hours at 145° with 0.5 cc. of concentrated hydrochloric acid (d. 1.19). The contents of the tube were evaporated to dryness *in vacuo* and taken up in absolute alcohol, yield 27.4 mg. Recrystallization was effected by adding dry ether to the alcoholic solution. After standing overnight 14.5 mg. of cube-like crystals had formed. *Anal.* Calcd. for $C_6H_8NSCl{\cdot}HCl$: Cl, 35.81; Cl^-, 17.91; N, 7.07; S, 16.19. Found: Cl, 35.47; Cl^-, 18.29; N (Dumas), 7.06; S, 16.36. The substance is much like the hydrochloride of (II) in its solubilities, but it is decidedly less hygroscopic. Also it is noticeably more volatile. *Circa* 10 mg. was dried for analysis at room temperature in a phosphorus pentoxide desiccator connected to a water pump and after twenty-four hours it was found that the entire sample had been volatilized. The free base has a pyridine-like odor. The nitroprusside test was negative.

Action of *p*-Nitrobenzoyl Chloride on (II).—79.4 mg. of the hydrochloride was refluxed for one-half hour in pyridine solution with excess of *p*-nitrobenzoyl chloride. The reaction mixture was diluted with water and sodium carbonate was added. Extraction with ether and subsequent evaporation of solvent yielded 41.5 mg. of crystalline product (low yield indicative of side reaction). The 41.5 mg. was purified by dissolving in alcohol and adding water. Fine nearly white needles melting sharply at 131° were obtained and dried *in vacuo* at 55° for analysis; yield 22.7 mg. *Anal.* Calcd. for $C_{13}H_{12}N_2SO_4$: S, 10.97; N, 9.59. Found: S, 11.06; N (Dumas), 9.44. The *p*-nitrobenzoate is practically insoluble in water but soluble in ether, in alcohol, and readily in dilute hydrochloric acid. A crystalline hydrochloride was obtained by evaporating the hydrochloric acid solution.

Action of Nitrous Acid on (II).—A portion of the hydrochloride was treated in aqueous solution with sodium nitrite and the mixture extracted with ether. On evaporation of the ether an oil was obtained which in a few minutes changed to an ether-insoluble[13] crystalline mass. After crystallization from ethanol–ether the substance was dried at 55° *in vacuo*. *Anal.* Calcd. for $C_6H_9NSO{\cdot}HNO_3$: N, 13.59; S, 15.55. Found: N (Dumas), 13.33; S, 15.75. The above product is hygroscopic, sublimes when heated *in vacuo*, is almost insoluble in ether and chloroform, soluble in acetone and readily soluble in alcohol and water. The aqueous solution was found to have a strong acid reaction and to give a copious precipitate with nitron reagent. The nitrate of (II), prepared from the hydrochloride and the theoretical amount of silver nitrate, behaved in a similar fashion.

Action of Methyl Iodide on (II).—65.3 mg. of the hydrochloride was converted into the free base, which was then allowed to stand for two days at room temperature with excess methyl iodide. After removal of excess methyl

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[8] H. T. Clarke and S. Gurin, THIS JOURNAL, **57**, 1876 (1935).

[9] A. Lieben, *Ann. Suppl.*, **7**, 231 (1870).

[10] R. R. Williams and A. E. Ruehle, THIS JOURNAL, **57**, 1856 (1935).

[11] All melting points in this paper are uncorrected.

[12] All nitroprusside tests in this paper were performed in a like manner except that much less substance was usually used.

[13] A somewhat similar phenomenon is described by Pummerer, *Ber.*, **43**, 1405 (1910).

iodide *in vacuo* the partly crystalline colored residue weighed 94.8 mg. This was purified by taking up in alcohol (acetone may be used) and precipitating with dry ether; 59.6 mg. of not quite colorless leaf-like crystals was obtained and a portion dried for analysis *in vacuo* at room temperature. *Anal.* Calcd. for $C_7H_{12}NSOI$: N, 4.91; S, 11.25. Found: N (Dumas), 4.70; S, 11.25. The methiodide is hygroscopic, quite insoluble in ether and chloroform, soluble in acetone and alcohol and readily soluble in water. It is extremely unstable toward alkali. A portion treated with 20% sodium hydroxide liberated no ether-soluble base but on standing at room temperature a dark tar was formed, insoluble in water and acid. The nitroprusside test was strongly positive. The methiodide as well as the other compounds described here has no vitamin B_1 activity.

Action of Nitric Acid on (II).—The hydrochloride of (II) was first converted into the nitrate or better into the free base and then oxidized with nitric acid (d. 1.42); 101 mg. of the hydrochloride gave with silver nitrate 115.7 mg. of the nitrate which was dissolved in 1 cc. of nitric acid. After short heating at 40° the reaction started, as evidenced by the darkening of the solution and the evolution of nitrogen oxides. The solution was kept at about 40° until no more gas bubbles formed and then most of the nitric acid was removed *in vacuo*. Quantitative removal of sulfate with baryta gave 50.2 mg. of barium sulfate. The remaining solution was evaporated to dryness, the residue suspended in water and extracted repeatedly with ether. Evaporation of the ether gave 42.0 mg. of white crystalline material which crystallized from methanol in cubes; yield 20.7 mg. After drying at 55° *in vacuo* it was analyzed. *Anal.* Calcd. for $C_5H_5NSO_2$: C, 41.93; H, 3.52; N, 9.79; S, 22.40. Found: C, 41.70; H, 3.51; N (Dumas), 9.20; S, 22.99. In later experiments it was found more convenient, instead of extracting the substance from its aqueous suspension with ether, to dissolve it in alkali and reprecipitate it by bringing to neutrality with acid. The properties of the substance are identical with those given by Windaus[7] for an acid of the same constitution obtained from the vitamin. It sublimes *in vacuo* at about 160°; on heating in a capillary tube it becomes colored above 200° and decomposes at about 250° with gas evolution. It is rather difficultly soluble in hot water and ether, soluble in alcohol and readily soluble in acids and in alkali. It gave a weak positive nitroprusside reaction. When heated with concentrated nitric acid no sulfate was formed. With ethereal diazomethane the methyl ester of m. p. 74° described by Windaus was obtained.

Action of Iodine and Alkali on (II).—The reaction was carried out on a 10-mg. portion of the hydrochloride according to the technique described by Mulliken.[14] No iodoform was formed.

We wish to acknowledge our indebtedness to Drs. H. T. Clarke and O. Wintersteiner for securing the microanalyses and to the Carnegie Corporation for a grant of funds through the Carnegie Institution of Washington.

Summary

1. The basic cleavage product (II) gives on oxidation an acid $C_4H_4NS—COOH$ identical with the product obtained by Windaus directly from the vitamin.

2. Evidence is presented for regarding (II) as a tertiary heterocyclic base with a β-hydroxyethyl side chain $C_4H_4NS—CH_2CH_2OH$.

3. Evidence is presented consistent with the view that the vitamin is a quaternary salt of the base (II).

NEW YORK, N. Y. RECEIVED JULY 11, 1935

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[14] "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, Vol. I, p. 166.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Synthesis of Phenanthrene and Hydrophenanthrene Derivatives. I. The Bougault Reaction

BY LOUIS F. FIESER AND EMANUEL B. HERSHBERG

In recent years γ-arylbutyric acids have acquired a position of considerable importance in the synthesis of polynuclear hydrocarbons, and several excellent methods have been developed for the preparation of these acids. Butyric acids of the benzene, naphthalene, phenanthrene, anthracene, and pyrene series are readily available as starting materials, as are many of their derivatives substituted in either the nucleus or the side-chain.[1] It occurred to us to submit some of these acids in the form of the esters to a special cyclization procedure which hitherto has been applied only to the simplest member of the series.

Bougault[2] discovered that the condensation product from β-phenylpropionic ester and oxalic ester is converted by concentrated sulfuric acid into the diester of indene-1,2-dicarboxylic acid,

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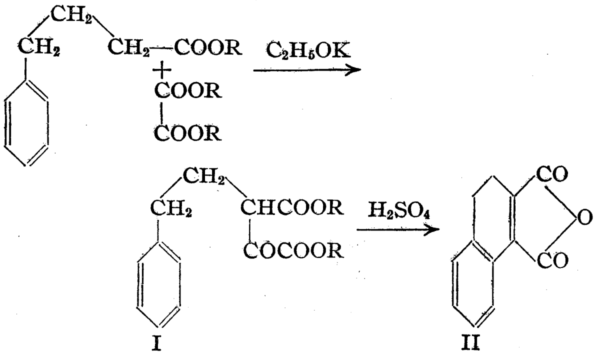
[1] "Organic Syntheses," John Wiley and Sons, Inc., 440 Fourth Ave., New York City, 1935, Vol. XV, p. 64; Haworth and coworkers, *J. Chem. Soc.*, 1125, 1784, 2248, 2717, 2720 (1932); 1012 (1933); 454 (1934); Cook and Hewett, *ibid.*, 398 (1933); Cook and Haslewood, *ibid.*, 767 (1935); Fieser and Peters, THIS JOURNAL, **54**, 4347, 4373 (1932).

[2] Bougault, *Compt. rend.*, **159**, 745 (1915).

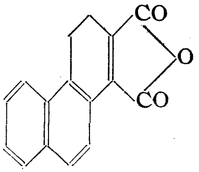
and von Auwers and Möller[3] applied the Bougault cyclization reaction to the next higher homolog. α-Oxalyl-γ-phenylbutyric acid (I) was prepared by these investigators in excellent yield by the condensation of phenylbutyric ester and oxalic ester with potassium ethylate.



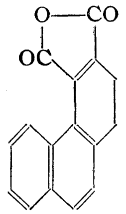
I II

At −15° the ester (I) was converted by sulfuric acid into the diethyl ester of 3,4-dihydronaphthalene-1,2-dicarboxylic acid, while at room temperature the reaction product was obtained in the form of the corresponding anhydride, II, in nearly quantitative yield. In repeating the work of von Auwers and Möller it has been found that the ester condensation can be carried out with equally satisfactory results using sodium ethylate.

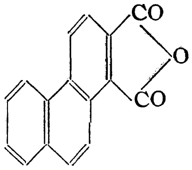
Starting with γ-(1-naphthyl)-butyric ester and γ-(2-naphthyl)-butyric ester we prepared the oxalic ester condensation products and submitted them to the Bougault reaction. With concentrated sulfuric acid there was extensive sulfonation, but the esters were converted smoothly by 80% acid into the cyclic anhydrides III and IV.[3a]



III



IV



V

The structure of III is established by the method of synthesis and the fact that the new ring can be aromatized, 3,4-dihydrophenanthrene-1,2-dicarboxylic acid anhydride (III) being converted in good yield into phenanthrene-1,2-dicarboxylic acid anhydride (V) on treatment with sulfur. This method was applied with equally good results to the dihydronaphthalene derivative, II, whereas von Auwers and Möller found that dehydrogenation with bromine proceeds very poorly. The anhydride of naphthalene-1,2-dicarboxylic acid may now be classed as a readily available compound.

The new phenanthrene and hydrophenanthrene derivatives substituted in the 1,2-positions (III and V) offer many interesting possibilities for further synthesis, and we are investigating particularly the synthesis of substances related to the oestrogenic hormones and their transformation products. Preliminary results indicate that both phenanthrene-1,2-dicarboxylic acid anhydride and the 3,4-dihydro derivative have oestrogenic activity.

We are indebted to Dr. G. Pincus of the Harvard Biological Laboratory for studying the physiological activity of the compounds. He reports that the anhydrides produced prolonged oestrus in mice, the effect lasting over a period of as much as two weeks. Cornification resulted in every case after the administration of as little as 0.05 mg. of either compound. The completely aromatic anhydride V acts slightly more rapidly than the dihydro compound III. Because of the protracted action it is difficult to make a direct comparison with the follicular hormone, but on the basis of the ordinary method of assay the minimum activity of both phenanthrene-1,2-dicarboxylic acid anhydride and the 3,4-dihydro compound is approximately 20,000 mouse units per gram.

The investigation of various substitution products and derivatives of the above compounds and related substances is in progress.

Experimental Part[4]

3,4-Dihydronaphthalene-1,2-dicarboxylic Acid Anhydride.—After several experiments on the ester condensation, the procedure of von Auwers and Möller[3] was modified in certain respects. The proportions of reagents found most satisfactory were as follows: 50 g. of ethyl phenylbutyrate, 57 g. of diethyl oxalate (1.5 equiv.), 10.4 g. of potassium (1.02 equiv.) and 12.6 g. of absolute ethyl alcohol (1.05 equiv.). The amount of alcohol is about one-third that specified,[3] and to promote a rapid reaction it was necessary to use powdered potassium. The metal was cleaned by melting it under toluene and powdered in the same solvent in an all-glass apparatus. After cooling, the metal powder was washed by decantation with ether in an atmosphere of nitrogen. After the completion of the condensation reaction the mixture containing

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(3) Von Auwers and Möller, *J. prakt. Chem.*, **217**, 124 (1925).

(3a) Bardhan, *Nature*, **134**, 217 (1934), has reported the synthesis of a dihydrophenanthrene derivative by a similar cyclization.

(4) All melting points are corrected. Analyses by Mrs. G. M. Wellwood, Dr. R. G. Larsen and Mr. E. L. Martin. For a part of the synthetical work we are indebted to Mary Fieser.

the potassium salt was decomposed with dilute acid and the ethereal solution of the oxalyl ester and excess oxalic ester was washed, dried with sodium sulfate and the solvent was evaporated in vacuum. In our experience the separation of the potassium salt from the mixture is incomplete.

In other experiments an equivalent amount of sodium ethylate, prepared as above, was found equally satisfactory, the only difference being that it was necessary to reflux the mixture for twenty-four hours in order to bring the reaction to completion.

For the cyclization the residual light yellow oil (containing oxalic ester) was dissolved in 500 cc. of concentrated sulfuric acid, keeping the temperature below 25°. After one and one-half hours the deep red solution was poured onto ice and the crude anhydride (m. p. 117–122°) was collected and washed. One distillation in vacuum gave 42–44 g. (81–85%) of light yellow material, m. p. 122–124°, b. p. 227–230° at 23 mm. The distillate exhibits triboluminescence. Once crystallized from benzene–ligroin the product melted at 126–127°.

Naphthalene-1,2-dicarboxylic Acid Anhydride.—A mixture of 17.8 g. of the dihydro compound and 2.85 g. of sulfur was heated with shaking in a nitrate bath at 230° until the sulfur had dissolved, and the bath temperature was then raised to 240–250° until the evolution of hydrogen sulfide was at an end (about thirty minutes). The residue was then distilled (b. p. 211–214° at 11 mm.) and crystallized from benzene–ligroin, giving 13.3 g. (76%) of pale yellow needles, m. p. 164–165°.

Condensation with β-Methoxynaphthalene.—The reaction of naphthalene-1,2-dicarboxylic acid anhydride with this ether was investigated in preliminary work which was later abandoned. The Friedel and Crafts reaction in warm tetrachloroethane solution gave, as in the case of phthalic anhydride,[5] a lactone: pale yellow prisms, m. p. 238–239°.

Anal. Calcd. for $C_{22}H_{12}O_3$: C, 81.49; H, 3.71. Found: C, 81.85; H, 3.98.

Heated in tetrachloroethane solution with aluminum chloride for three hours on the steam-bath, the lactone was isomerized to a naphthaloylnaphthol; thick yellow prisms from toluene, m. p. 264–265°.

Anal. Calcd. for $C_{22}H_{12}O_3$: C, 81.49; H, 3.71. Found: C, 81.91; H, 3.52.

3,4-Dihydrophenanthrene-1,2-dicarboxylic Acid Anhydride.—Ethyl γ-(1-naphthyl)-butyrate was prepared in 91% yield by esterification with alcohol and hydrogen chloride; b. p. 210–211° at 14 mm. The condensation with oxalic ester was carried out by the original procedure of von Auwers and Möller,[3] using excess alcohol and lumps of potassium. The potassium salt of the oxalyl ester in this case separated very completely from the ethereal solution, and it was collected, washed with ether and decomposed with ice-cold, dilute sulfuric acid. The oil which separated was collected and dried in ether, and after distillation of the solvent at diminished pressure, the product was obtained as a viscous yellow oil in 80% yield.

The oxalyl ester was warmed with 7–10 parts by volume of 80% sulfuric acid on the steam-bath with vigorous shaking, when it was soon converted into a bright yellow, granular solid. The product was collected after diluting the mixture with water. This material was practically pure and the yield of the anhydride was quantitative.

The anhydride is sparingly soluble in glacial acetic acid or benzene and moderately soluble in dioxane. The solutions exhibit a brilliant greenish-yellow fluorescence. Crystallized from dioxane or acetic anhydride it formed golden yellow needles, m. p. 263.5–264.5°.

Anal. Calcd. for $C_{16}H_{10}O_3$: C, 76.77; H, 4.04. Found: C, 76.83; H, 4.37.

A solution of the anhydride in acetone, diluted with water, neutralized only one equivalent of methyl alcoholic potassium hydroxide, probably because of the formation of a mono-ester; neutralization equivalent found, 239; molecular weight 250.

Phenanthrene-1,2-dicarboxylic Acid Anhydride.—For the dehydrogenation, 5.7 g. of the above anhydride was heated with 0.73 g. of sulfur at 320–325° for ten minutes, and the residue was distilled at 15 mm. pressure directly from the bath. The yellow solid was crystallized from acetic anhydride, when it formed long yellow needles of m. p. 311–312°; yield, 5.1 g. (91%). The substance is only sparingly soluble in dioxane or acetic anhydride; it gives a phthalein test with resorcinol and sulfuric acid.

Anal. Calcd. for $C_{16}H_8O_3$: mol. wt., 248; C, 77.39; H, 3.25. Found: C, 77.55; H, 3.62; neutralization equivalent, 245.

1,2-Dihydrophenanthrene-3,4-dicarboxylic Acid Anhydride.—Ethyl γ-(2-naphthyl)-butyric ester (b. p. 227–228° at 25 mm.) was condensed with oxalic ester in the presence of potassium ethylate, exactly as described above for ethyl γ-phenylbutyrate. The potassium salt of the product remained dissolved in the ethereal reaction mixture, and the oil obtained on shaking the solution with dilute acid, drying and removing the solvent, contained ethyl oxalate. The crude oil from 19.6 g. of the arylbutyric ester was mechanically stirred with 125 cc. of 80% sulfuric acid at 80–90° for one hour. The oil partially dissolved at the start and after about ten minutes a yellow solid separated from the dark acid liquor. After cooling, the solid was collected on a glass funnel, washed with 80% sulfuric acid and, after thorough draining, with a liberal quantity of alcohol. The product was bright yellow and nearly pure; yield, 16.5 g. (81%). The anhydride is readily soluble in benzene; it dissolves only slowly in boiling alcohol or glacial acetic acid and tends to remain in solution. It crystallizes well from benzene–ligroin as bright greenish-yellow needles, m. p. 151–152°. The solution in concentrated sulfuric acid is bright red.

Anal. Calcd. for $C_{16}H_{10}O_3$: C, 76.77; H, 4.04. Found: C, 76.68, 76.65; H, 4.22, 4.28.

Summary

The anhydrides of dihydrophenanthrene-*o*-dicarboxylic acids can be prepared in good yield by extending an adaptation of the cyclization reaction of Bougault to α-oxalyl-γ-arylbutyric esters of the naphthalene series. These and other similar substances are being investigated both for use in the synthesis described in the

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[5] Fieser, THIS JOURNAL, **53**, 3546 (1931).

second paper of this series, and because the Bougault reaction provides a convenient route to 1,2-substituted phenanthrenes of a type which may prove useful in the synthesis of compounds related to the sex hormones. It has been found that the anhydrides of both 3,4-dihydrophenanthrene-1,2-dicarboxylic acid and phenanthrene-1,2-dicarboxylic acid have oestrogenic properties.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS

RECEIVED AUGUST 19, 1935

[CONTRIBUTION FROM THE UNIVERSITY OF MARYLAND]

Cerin and Friedelin. II. Some Functional Derivatives[1]

BY NATHAN L. DRAKE AND STERL A. SHRADER

Earlier investigation has shown[2] that cerin and friedelin possess the same polycyclic nucleus of thirty carbon atoms. It is the purpose of this paper to describe certain functional derivatives of these substances, thereby confirming the carbonyl nature of friedelin and demonstrating that cerin is an hydroxy ketone.

In keeping with its carbonyl nature friedelin reacts with hydroxylamine, with *p*-nitrophenylhydrazine, and with 2,4-dinitrophenylhydrazine, yielding the corresponding derivatives of the carbonyl group. Friedelin oxime is converted by treatment with phosphorus pentachloride into an isomeric substance which is no longer an oxime. This rearrangement product is not at all altered by any hydrolytic agent which does not decompose it, does not form an acetate with acetic anhydride and cannot be reconverted to friedelin by any method that we have been able to discover. The oxime, on the other hand, can be hydrolyzed readily to friedelin, and gives an acetate with acetic anhydride.

Cerin, like friedelin, can be converted into an oxime and a 2,4-dinitrophenylhydrazone. When treated with Purdie's reagents, cerin yields a monomethyl ether. An oxime or a 2,4-dinitrophenylhydrazone can be prepared from this ether without removal of the methyl group. When reduced in *n*-amyl alcohol by means of sodium, cerin yields a dihydroxy derivative which is characterized by the formation of a diacetate. It is apparent, therefore, that cerin must contain a carbonyl and an hydroxyl group. Whether the hydroxyl or the carbonyl of cerin occupies the same position in the nucleus as the carbonyl group of friedelin we do not know, for all attempts to obtain friedelin from cerin have failed.

Experimental

Friedelin Oxime.—Ten grams of friedelin was dissolved in 200 ml. of benzene containing 50 ml. of alcohol, and 3.5 g. of hydroxylamine hydrochloride, dissolved in 25 ml. of alcohol, was added. Three grams of potassium hydroxide dissolved in 25 ml. of alcohol was added to the reaction mixture through the reflux condenser and the mixture was refluxed for one hour, cooled and poured into 400 ml. of water. The resulting solution was acidified with sulfuric acid, and the product filtered, washed and recrystallized from a 2 to 1 mixture of benzene–ethyl acetate; 7.9 g. of oxime was obtained. The substance melts at 290–294° and crystallizes in thin hexagonal plates.

Anal. Calcd. for $C_{30}H_{51}ON$: C, 81.56; H, 11.65; N, 3.17. Found: C, 81.29, 81.25; H, 11.57, 11.71; N, 3.32, 3.25.[3]

Hydrolysis of Friedelin Oxime.—One-half gram of friedelin oxime was dissolved in 90 ml. of *n*-amyl alcohol and 6 ml. of 50% phosphoric acid was added. The mixture was refluxed for seven hours, and 50 ml. of alcohol was removed by distillation. The crystals which separated overnight were recrystallized from an ethyl acetate–benzene mixture, and melted at 257–262°. No change in the melting range was observed when this material was melted mixed with friedelin.

Anal. Calcd. for $C_{30}H_{50}O$: C, 84.43; H, 11.82. Found: C, 84.26, 84.00; H, 11.88, 11.71.

Friedelin Oxime Acetate.—0.6 g. of friedelin oxime was dissolved in 20 ml. of acetic anhydride and refluxed for one-half hour. The acetate which separated from the cold solution was recrystallized from ethyl acetate from which it separates in the form of hexagonal plates. The product melted at 237–239°.

Anal. Calcd. for $C_{32}H_{53}NO_2$: C, 79.28; H, 11.23. Found: C, 79.52; H, 10.97.

The Beckmann Rearrangement of Friedelin Oxime.—7.5 g. of friedelin oxime was dissolved in 2500 ml. of dry chloroform, the solution was cooled to −5°, and 4.5 g. of phosphorus pentachloride added in small portions during the course of fifteen minutes. The mixture was allowed to stand in an ice- and salt-bath for twelve hours, and then allowed to warm up to room temperature; 80% of the

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[1] From the Ph.D. dissertation of Sterl A. Shrader.

[2] Drake and Jacobsen, THIS JOURNAL, **57**, 1570 (1935).

[3] We are indebted to Dr. T. B. Smith for the nitrogen determinations.

chloroform was distilled off and the remainder poured into ice water. After neutralization of the acid with 10% potassium hydroxide solution, the chloroform was removed by distillation, and the solid filtered and recrystallized from benzene containing one-fourth its volume of alcohol; 6.5 g. of product was obtained. Recrystallization from ethyl acetate–chloroform–ethyl alcohol, and finally from dioxane yielded a product which melted at 316–318°. The substance crystallizes in the form of hexagonal plates.

Anal. Calcd. for $C_{30}H_{51}ON$: C, 81.56; H, 11.65; N, 3.17. Found: C, 81.32, 81.38; H, 11.87, 11.67; N, 3.34, 3.32.[4]

Attempts to Hydrolyze the Rearrangement Product.—Many attempts were made to hydrolyze the product obtained by the action of phosphorus pentachloride on friedelin oxime, but none were successful. Alkali or acid in aqueous *n*-amyl alcohol under reflux or in a sealed tube at 200–250° did not effect a cleavage of the substance. Aqueous ethylene glycol and phosphoric acid at the reflux temperature were without effect. Phenol containing some water and hydriodic acid had no effect under reflux. Likewise, acetic acid and phosphoric acid containing water did not effect hydrolysis. Sulfuric acid and sodium nitrite in *n*-amyl alcohol were similarly without effect. In all but one of these experiments the original substance was recovered; phenol, hydriodic acid and the material heated in a sealed tube produced a tar.

Friedelin-2,4-dinitrophenylhydrazone.—One-half gram of friedelin was dissolved in 60 ml. of hot methyl cellosolve, and 0.3 g. of 2,4-dinitrophenylhydrazine added. The mixture was warmed until homogeneous. Two drops of concentrated hydrochloric acid were added and the mixture boiled for five to ten minutes. On cooling, the solution deposited narrow orange-colored lath-like crystals which were recrystallized from benzene. The product melted with decomposition at 297–299°.

Anal. Calcd. for $C_{36}H_{54}N_4O_4$: C, 71.24; H, 8.98; N, 9.23. Found: C, 71.50, 71.24; H, 9.05, 8.92; N, 9.26, 9.27.

Friedelin *p*-nitrophenylhydrazone was prepared by a method similar to that described above for the 2,4-dinitrophenylhydrazone; the *p*-nitrophenylhydrazone melted with decomposition at 277–279°.

Anal. Calcd. for $C_{36}H_{55}N_3O_2$: C, 76.95; H, 9.85; N, 7.47. Found: C, 77.41, 77.58, 77.42; H, 9.95, 9.78, 9.89; N, 7.58, 7.52.

We are unable to account for the poor carbon determinations. Further crystallization from dioxane, benzene and ethyl acetate–benzene results in a product whose percentage composition is essentially that recorded above. This substance crystallizes in the form of narrow hexagonal laths.

Cerin Methyl Ether.—Ten grams of cerin was dissolved in 500 ml. of dry dioxane, and treated with 50 g. of methyl iodide and 4 g. of silver oxide. The mixture was refluxed for nine hours with the addition of a gram of fresh silver oxide every two hours. The solution was then freed of silver oxide and iodide by filtration, and concentrated to about 50 ml.; 4.5 g. of methylated product separated from the cold solution. This substance melted at 235–245°. An additional gram of product which melted at 204–230° was obtained by concentrating the solution to about 30 ml. The remainder of the material would not crystallize, and was obtained as an amorphous white precipitate by adding water. We were unable to obtain this material in crystalline form by use of any of the usual solvents or solvent combinations. The two crystalline fractions were combined and again treated with methyl iodide and silver oxide using dioxane as a solvent; 3.5 g. of a product melting at 259–262° and 2 g. melting at 200–215° were obtained from this methylation. Recrystallization of the high melting product from benzene–acetone yielded a substance that crystallized in narrow laths and melted at 265–270°. Extensive recrystallizations did not serve to raise the melting point of the low-melting fraction very much and analysis indicated it to be considerably deficient in methoxyl content.

Anal. Calcd. for $C_{31}H_{52}O_2$: C, 81.58; H, 11.48; OCH_3, 6.80. Found: C, 81.55, 81.47; H, 11.44, 11.28; OCH_3, 6.81, 6.84, 6.82, 6.73.

The specific rotation of cerin methyl ether in chloroform solution is $[\alpha]^{26}_{5461}$ $-58.9°$ ($C = 2.76$).

The Oxime of Cerin Methyl Ether.—Cerin methyl ether (0.5 g.), dissolved in a 2 to 1 mixture of benzene and alcohol, was converted by refluxing for an hour with hydroxylamine hydrochloride (0.2 g.) and potassium hydroxide (0.5 g.) into an oxime. The product crystallized in narrow laths and melted at 258–262°.

Anal. Calcd. for $C_{31}H_{54}NO_2$: C, 78.71; H, 11.52; N, 3.06; OCH_3, 6.57. Found: C, 78.72, 78.93; H, 11.29, 11.24; N, 3.37, 3.17; OCH_3, 6.66, 6.83, 6.79.

2,4-Dinitrophenylhydrazone of Cerin Methyl Ether.—The method employed was identical with the one described above for preparing the 2,4-dinitrophenylhydrazone of friedelin. The product crystallizes in narrow laths, almost needle-like, and melts with decomposition at 284–285°.

Anal. Calcd. for $C_{37}H_{56}N_4O_5$: C, 69.82; H, 8.86; N, 8.80. Found: C, 69.81, 69.83; H, 8.78, 8.89; N, 8.87, 8.90.

2,4-Dinitrophenylhydrazone of Cerin.—Prepared as above, this product crystallized from a benzene–alcohol mixture in the form of orange laths with a pronounced tendency to form spherulites and melted with decomposition at 253–255°.

Anal. Calcd. for $C_{36}H_{54}N_4O_5$: C, 69.42; H, 8.74; N, 9.00. Found: C, 69.50, 69.53; H, 8.78, 8.86; N, 9.04, 9.36.

Cerin Oxime.—One and nine-tenths grams of cerin dissolved in a mixture of 150 ml. of benzene and 100 ml. of ethyl alcohol was heated under reflux for three hours with hydroxylamine hydrochloride (0.8 g.) and potassium hydroxide (1 g.). Water was then added and the mixture made acid to Congo red. The benzene was removed by steam distillation and the crude product recrystallized from benzene–ethyl acetate. A final recrystallization from ethyl alcohol yielded a product which crystallized in lath-like plates and melted at 266–272°.

Anal. Calcd. for $C_{30}H_{51}NO_2$: C, 78.71; H, 11.24. Found: C, 78.56, 78.57; H, 11.62, 11.35.

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[4] We wish to thank Dr. J. R. Spies for these analyses.

Dihydrocerin (Cerinol).—One and one-half grams of cerin in 100 ml. of *n*-amyl alcohol was reduced by adding 3 g. of sodium to the hot solution over a period of fifteen minutes. After the sodium had dissolved completely, the alcohol was removed by steam distillation and the product recrystallized from dioxane. The dicarbinol, for which we propose the name *cerinol*, crystallized from dioxane in narrow white laths, which melted at 293–295°; $[\alpha]^{25}_{5461}$ +9.4 (C = 0.48).

Anal. Calcd. for $C_{30}H_{52}O_2$: C, 81.01; H, 11.75. Found: C, 81.05, 80.86; H, 11.63, 11.77.

Cerinol Diacetate.—Cerinol is smoothly converted by acetic anhydride alone into a diacetate. This product crystallizes from ethyl acetate–ethyl alcohol in narrow almost needle-like laths which melt at 267–269°.

Anal. Calcd. for $C_{34}H_{56}O_4$: C, 77.22; H, 10.67. Found: C, 77.04, 77.05; H, 10.35, 10.40.

The Purification of Cerin.—Several recrystallizations of crude material from chloroform are necessary to obtain pure cerin. A properly purified sample should melt at 250–256°; at least six recrystallizations are necessary starting with crude extract. A sample so prepared yielded the following analytical results. Calcd. for $C_{30}H_{50}O_2$: C, 81.38; H, 11.39. Found: C, 81.37; H, 11.35. Less extended recrystallizations result in products with a broader melting range and a considerably lower carbon content. Cerin is not at all affected by refluxing with alcoholic potassium hydroxide, but is very sensitive to mineral acids.

Cerin Acetate.—The treatment of cerin with boiling acetic anhydride alone or with boiling acetic anhydride containing a trace of sulfuric acid results in the formation of a mixture of products from which it is not possible to obtain a pure substance. The reaction products, even after many recrystallizations, possess carbon and hydrogen contents which do not correspond to any of those demanded by cerin monoacetate, cerin diacetate or the acetate of a dehydration product, $C_{30}H_{48}(OCOCH_3)$. Under much milder conditions, however, by the use of pyridine and acetic anhydride at room temperature, it is possible to obtain a monoacetate of cerin; 1 g. of cerin was dissolved in 80 ml. of dry pyridine and 10 ml. of acetic anhydride was added over a period of about five minutes. The mixture was allowed to stand at room temperature overnight (*ca.* 25°). The product was isolated by dilution of the pyridine with water, and recrystallized in succession from benzene–ethyl acetate, ethyl acetate, benzene, ethyl acetate, glacial acetic acid and ethyl acetate. The substance melted at 256–259° with decomposition.

Anal. Calcd. for $C_{30}H_{52}O_3$: C, 79.28; H, 10.82. Found: C, 79.05, 79.19; H, 10.82, 10.88.

This product was further crystallized from glacial acetic acid, and finally from ethyl acetate, from which it separated in narrow almost needle-like laths which melted at 259–261°.

Summary

1. Friedelin oxime, 2,4-dinitrophenylhydrazone and *p*-nitrophenylhydrazone have been prepared.
2. Friedelin oxime undergoes the Beckmann rearrangement and yields a product which so far has defied all attempts to cleave it by hydrolysis.
3. Cerin methyl ether, its oxime and 2,4-dinitrophenylhydrazone have been prepared.
4. Cerin has been reduced to a dihydroxy compound which was characterized by the formation of a diacetate.
5. Cerin has been characterized by the formation of an oxime and a 2,4-dinitrophenylhydrazone.
6. The monoacetate of cerin has been prepared by acetylation in pyridine at room temperature.

College Park, Md. Received July 24, 1935

[Contribution from the Department of Physiological Chemistry, Teachers College, Columbia University]

Studies of Crystalline Vitamin B_1. XI. Presence of Quaternary Nitrogen[1]

By Robert R. Williams and A. E. Ruehle

The necessity for reconciling the chemical characteristics of the basic cleavage product[2] of vitamin B_1 with the undoubted binuclear character of the vitamin led our associate, Dr. E. R. Buchman, to suggest the presence of quaternary nitrogen in the latter. If present, the tetrasubstituted nitrogen should be recognizable by its strong basicity. On titrating the vitamin hydrochloride with sodium hydroxide the presence of a moderately strong basic nitrogen was revealed, too strong for a tertiary base though not strong enough for a true quaternary base. The basic cleavage product behaved as a typical tertiary base but its methiodide[2b] closely resembled the vitamin not only in basic strength but also in exhibiting an unusual pseudo basic behavior. Both the vitamin and the methiodide of its basic cleavage product required an additional molecular equivalent of alkali for com-

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[1] Presented before the Division of Organic Chemistry at the New York Meeting of the American Chemical Society, April 22, 1935.

[2] (a) R. R. Williams, R. E. Waterman, J. C. Keresztesy and E. R. Buchman, This Journal, **57**, 536 (1935); (b) Paper X of this series, E. R. Buchman, R. R. Williams and J. C. Keresztesy, *ibid.*, **57**, 1849 (1935).

plete liberation of the base. This parallelism of behavior constituted strong evidence of a close structural resemblance between these compounds, associated with a quaternary nitrogen in each. In view of Dr. H. T. Clarke's suggestion[3] of the presence of a thiazole nucleus in the vitamin, it was of interest to secure similar data regarding synthetic thiazolium compounds. 4-Methylthiazole ethiodide behaved similarly to the methiodide of the basic cleavage product while 2,4-dimethylthiazole ethiodide exhibited the characteristics of a salt of a true quaternary base. These observations furnish strong confirmation of this feature of the structural formula of the vitamin recently announced by Williams.[3]

Birch and Harris[4] and Moggridge and Ogston[5] have recently described titrations of vitamin B_1 similar to our own. These authors, however, are neither in complete agreement with each other nor with us as to the interpretation to be placed on such curves. For that reason we feel the necessity of discussing our results somewhat in detail.

Experimental

Apparatus

The indicator electrode used was the MacInnes and Dole membrane type of glass elctrode,[6] made from Corning 015 glass and supported by lime glass tubing. The reference electrode was a normal calomel half-cell. The potential measurements were made with a Leeds and Northrup type K potentiometer and 2500-e galvanometer used in conjunction with a vacuum tube electrometer.[7] The titrations were carried out in a small cell through which a slow stream of nitrogen was passed to exclude carbon dioxide and to stir the solution. All measurements were made in an air thermostat kept at 25.0°.

No attempt was made to maintain a constant salt concentration because of the difficulty which would thereby be introduced in recovering the vitamin from the solution for other uses. Neither was any attempt made to evaluate liquid junction potentials except in so far as correcting for the "asymmetry potential" of the glass electrode, using calibrated buffers would eliminate this error. It is also recognized that the change in volume during titration introduces a small error in the values of the dissociation constants obtained.

Materials

NaOH and HCl.—0.1 *N* solutions were used in all titrations.

Vitamin B_1 was obtained by the method of Williams, Waterman and Keresztesy;[8] 50 mg. of the crystalline vitamin dissolved in 10 cc. of water served as the sample for titration.

The basic cleavage product (**hydrochloride**) was prepared by cleaving the vitamin with sodium sulfite.[2a]

Methiodide of Basic Cleavage Product.—Prepared by addition of methyl iodide to the cleavage product.[2b]

4-Methylthiazole Ethiodide.—Prepared as described elsewhere.[9]

2,4-Dimethylthiazole Ethiodide.—Prepared as described elsewhere.[9]

Experimental Results

The results obtained are shown graphically in Figs. 1–4. The pK_B values given in Table I represent the half neutralization points on the curves and are calculated from the relation $p\text{H} + p\text{OH} = 14$ for aqueous solution at 25° and the approximation[10] $p\text{OH} = pK_B$ at half the neutralization point of a weak base.

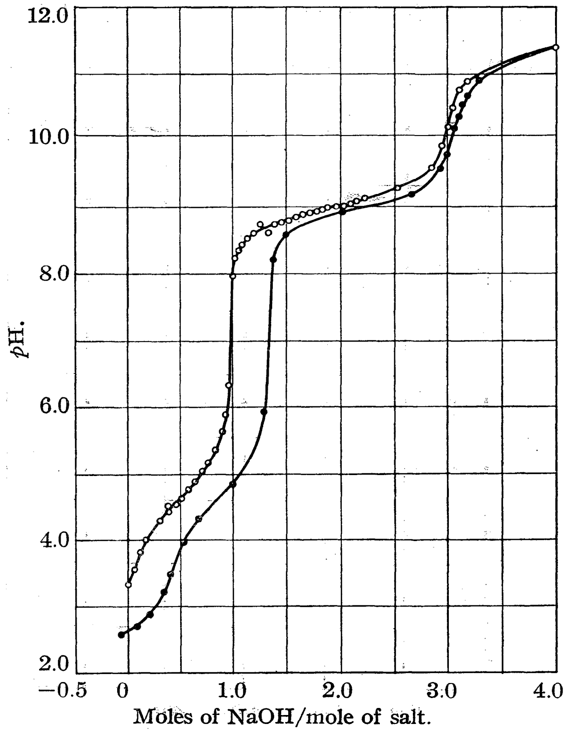

Fig. 1.—Titration of vitamin B_1: ○—○, titration with NaOH, ●—●, back titration with HCl.

The titrations demonstrate seven important points, six of which are illustrated directly by the figures.

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[3] R. R. Williams, THIS JOURNAL, **57**, 229 (1935).

[4] T. W. Birch and L. J. Harris, *Nature*, **135**, 654 (1935).

[5] R. C. G. Moggridge and A. G. Ogston, *Biochem. J.*, **29**, 866 (1935).

[6] D. A. MacInnes and M. Dole, *Ind. Eng. Chem.*, *Anal. Ed.*, **1**, 57 (1929).

[7] K. G. Compton and H. E. Haring, *Trans. Am. Electrochem. Soc.*, **62**, 345 (1932).

[8] R. R. Williams, R. E. Waterman and J. C. Keresztesy, THIS JOURNAL, **56**, 1187 (1934).

[9] Paper XII of this series, H. T. Clarke and S. Gurin, THIS JOURNAL, **57**, 1876 (1935).

[10] This approximation holds strictly only for weak bases. Hence the absolute values given in Table I for stronger bases are somewhat in error.

TABLE I

Base	pK_B
Vitamin B_1 (stronger base)	5.0
Vitamin B_1 (weaker base)	9.5
Basic cleavage product (quaternary)	4.1
Basic cleavage product (tertiary)	10.6
4 Methylthiazole (quaternary)	4.5
4 Methylthiazole (tertiary) (curve not shown)	10.4
2,4-Dimethylthiazole (quaternary)	2.8

1. Two bases are liberated, in titrating the vitamin with sodium hydroxide, one of which is considerably stronger than the other. The stronger base is somewhat weaker than would be expected for a quaternary base, but the strength of the base liberated from the methiodide of the basic cleavage product is of the same order of strength as the stronger base in the vitamin.

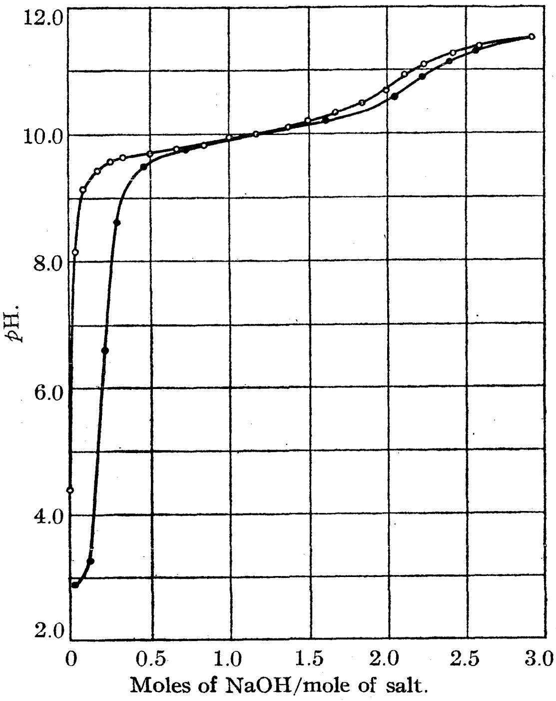

Fig. 2.—Titration of methiodide of basic cleavage product: ○—○, titration with NaOH; ●—●, back titration with HCl.

2. Both the vitamin and the methiodide of its basic cleavage product require an additional equivalent of alkali to liberate completely the strong base present in each.

3. During the portion of the titration referred to in (2) there is a marked slowness in coming to equilibrium. With each addition of reagent a large change in potential occurs, but after ten to fifteen minutes there is only a small net change. The behavior suggests the liberation of a very strong base with a slow rearrangement to a much weaker one. The additional equivalent of alkali required in this portion of the titration suggests that this "weaker base" gives rise to an acid which is neutralized as it is formed.

4. The back titrations of both the stronger base of the vitamin ($pK_B = 5.0$) and the methiodide of the basic cleavage product show a loss of material amounting to 10–20% of the original amount present. The slowness in attainment of equilibrium is equally evident in the back titration. The weaker base in the vitamin ($pK_B = 9.5$) is reneutralized by exactly one equivalent of acid, showing no alteration of the portion of the molecule associated with it.

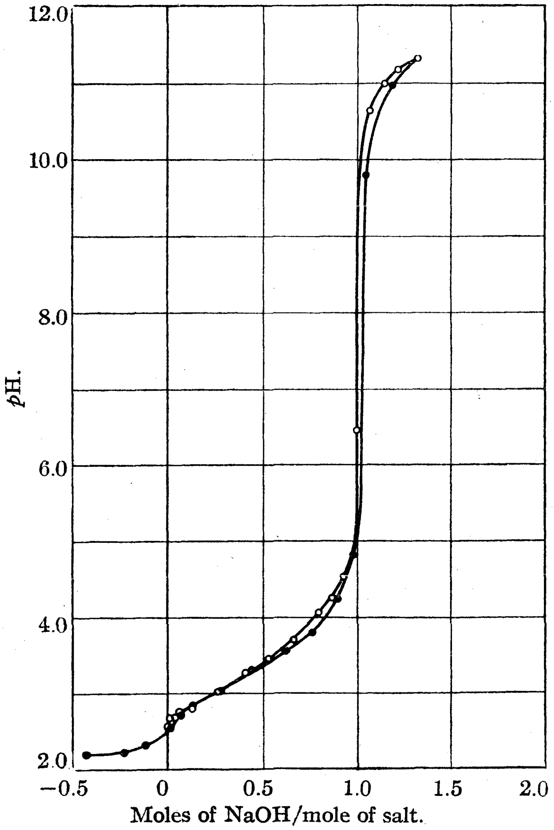

Fig. 3.—Titration of hydrochloride of basic cleavage product: ○—○, titration with NaOH; ●—●, back titration with HCl.

5. The hydrochloride of the basic cleavage product is demonstrated to be the salt of a very weak base which requires only one equivalent of reagent to liberate it. Equilibrium is attained almost instantaneously after each addition of sodium hydroxide. There is no loss of material on back titration.

6. The curve of 4-methylthiazole ethiodide is entirely analogous in form to that of the methiodide of the basic cleavage product. The same phenomenon of slowness in coming to equilibrium is manifest in both the forward and back titrations. Two equivalents of alkali are required to liberate the base and less than two of acid to reneutralize it.

7. The curve of 2,4-dimethylthiazole ethiodide, on the other hand, is the curve of a typical quaternary base, as is evident by comparison with the water curve. Evidently the methyl group in position 2 modifies the behavior of thiazolium salts in a marked way. A mauve color developed in this case on addition of the first drops of alkali (thiazolo-cyanine dye formation).[11] The back titration of this substance showed no significant points of inflection, apparently due to the relative stability of the colored substance, but afforded additional assurance of an entirely different behavior when position 2 is occupied by a methyl group.

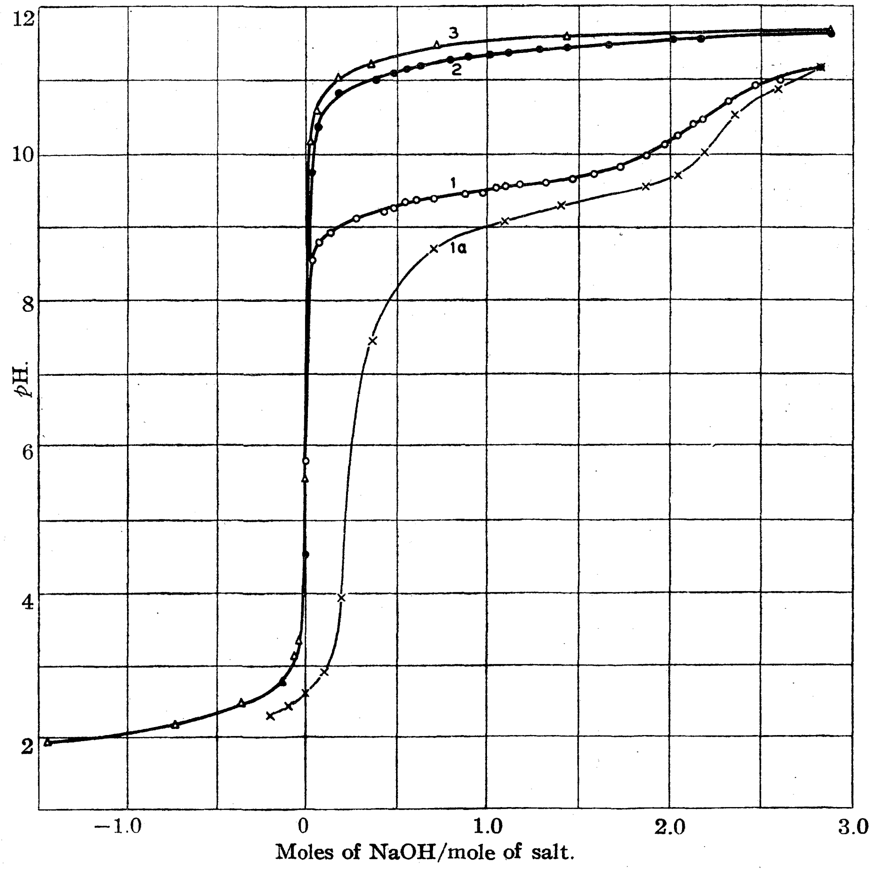

Fig. 4.—(1), Titration of 4-methylthiazole ethiodide with NaOH; (1a), back titration with HCl; (2), titration of 2,4-dimethylthiazole ethiodide with NaOH; (3), water curve.

Discussion of Results

There can be no doubt that the vitamin reacts exactly like the quaternary salt of its basic cleavage product toward sodium hydroxide, whereas its behavior is markedly different from that of the salt of the tertiary base. Furthermore, this behavior is not associated with the amino group contained in the vitamin, contrary to the suggestion of Moggridge and Ogston, since this group is not present in this cleavage product.[2b] Moggridge and Ogston have partially avoided the effect of the slow drift mentioned above by performing a rapid titration, which gives an indication of the actual strength of the stronger base. The curve is similar to that of the salt of a very strong base, although they conclude that there is no quaternary base present. It is unfortunate that their titration curve with equilibrium values is not shown above *p*H 7, as this should also reveal the presence of the quaternary base.

A study of the mechanism associated with the formation and neutralization of the pseudo base is in progress and will appear shortly in a paper by Dr. H. T. Clarke and associates. For the present it is sufficient to point out that the anomalous behavior of the vitamin closely resembles that of the quaternary salt of the basic cleavage product but not that of the salt of the basic cleavage product itself.

We are indebted to Dr. H. T. Clarke for advice and for furnishing us with samples of the synthetic thiazolium salts used in this study. We also wish to acknowledge financial aid by the Carnegie Corporation of New York through the Carnegie Institution of Washington.

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[11] L. G. S. Brooker, F. M. Hamer and C. E. K. Mees, *J. Opt. Soc. Am.*, **23**, 216 (1933).

Summary

1. Vitamin B_1 contains two basic groups, one of which is of the same order of strength as the nitrogen in the quaternary salt of its basic cleavage product and in 4-methylthiazole ethiodide.

2. The vitamin and the methiodide of its basic cleavage product, like 4-methylthiazole ethiodide, form pseudo bases in alkaline solutions, but this phenomenon is not exhibited by a 2-methyl substituted thiazolium base or by simple thiazoles.

NEW YORK CITY RECEIVED JULY 6, 1935

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 130]

The Dehydrogenation of Nicotine in Toluene as a Solvent

BY AVERY A. MORTON AND DAVID HORVITZ[1]

The experiments reported in this paper show that nicotine can be dehydrogenated by sulfur in boiling toluene as a solvent. This temperature is the lowest at which a dehydrogenation by sulfur or selenium has been carried out and is one of the few instances of the application of such a reaction to an alkaloid.[2] The object of this work was to perfect the exceedingly important method of dehydrogenation by lowering the temperature, controlling the concentrations, and changing the solvent so that the correctness of conclusions relative to the carbon framework of organic compounds might be subject to less doubt.[3] It was also desired to extend the application of dehydrogenation to nitrogen-containing compounds. Nicotine was chosen as suitable for study because the product of the proposed reaction is already known, having been prepared from nicotine by oxidation with potassium ferricyanide[4] or silver oxide[5] or by dehydrogenation over platinized asbestos at 320°.[6] Fusion of nicotine with sulfur has also been carried out by Cahours and Étard.[4]

Under the mild conditions attending the use of toluene as a solvent the amount of hydrogen sulfide evolved corresponds to 69% of the theoretical as given in equation 1 for the formation of nicotyrine, $C_{10}H_{10}N_2$. Actually nicotyrine was

$$C_{10}H_{14}N_2 + 2S = C_{10}H_{10}N_2 + 2H_2S \qquad (1)$$

obtained in only about 2.5% yield, the larger amount of material being thiodinicotyrine[7] $C_{20}H_{18}N_4S$ (equation 2), from which nicotyrine can be obtained by distillation over copper.[4] The yield of this substance when purified was about 18%.

$$2C_{10}H_{14}N_2 + 6S = C_{20}H_{18}N_4S + 5H_2S \qquad (2)$$

No appreciable quantities of tar were formed. The remainder of the material appeared to be unchanged nicotine and possibly products not completely dehydrogenated. Cahours and Étard[4] obtained this sulfur compound by the action of sulfur on nicotine in the absence of a solvent but failed to observe any nicotyrine.

Under a wide variety of conditions such as were possible by changing the concentrations and quantities of reagents the amount of hydrogen sulfide liberated could not be increased. Addition of acid at the end of the experiment failed to reveal any combined hydrogen sulfide. Iron, which has been claimed by Cheung[8] to break up sulfur addition compounds at higher temperatures, had no effect on the velocity or extent of hydrogen sulfide evolution. The addition of a small quantity of diphenylguanidine in the hope that it would act catalytically was found to inhibit greatly the rate and the completion of the reaction. Other solvents, boiling within the range of 99–121°, which were tried were epichlorohydrin, tetrachloroethylene, glacial acetic acid, and a gasoline fraction (99–102° b. p.). These solvents were far inferior to toluene both in the quantity of hydrogen sulfide formed and in the freedom from tarry products. Even the addition of acetic acid to toluene retarded greatly the rate of gas evolution although the total amount finally ap-

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(1) From the thesis of David Horvitz submitted in partial fulfilment of the requirements for the degree of Bachelor of Science, 1934.

(2) See Blount [*J. Chem. Soc.*, 124 (1935)] for leading references to the application of dehydrogenation of alkaloids by selenium.

(3) See Vocke, *Ann.*, **497**, 248 (1932); Cook and Hewett, *J. Chem. Soc.*, 1103 (1933); 365 (1934); Clemo and Ormston, *ibid.*, 352 (1933), for criticisms of the present method of fusion.

(4) Cahours and Étard, *Bull. soc. chim.*, **34**, 449 (1880).

(5) Blau, *Ber.*, **27**, 2535 (1894).

(6) Wibaut and Overhoff, *Rec. trav. chim.*, **47**, 935 (1928).

(7) This compound was named thiotetrapyridine by Cahours and Étard on the basis of the erroneous belief that nicotyrine contained two pyridine rings. A more correct name would be thiodinicotyrine.

(8) Cheung, *Bull. inst. pin*, 108 (1929); *C. A.*, **23**, 3467 (1929).

proached the same value obtained for toluene alone.

The success of this study has given encouragement to extend the use of solvents to the cases of cholesterol and abietic acid, which have heretofore given compounds of disputed structure[9] or yielded small amounts[10] of substances. Strychnine is also being investigated by this method. Solvents which boil higher than toluene are preferred in these cases. The results will be published shortly. The work on nicotine is being reported at this time because the recent paper of Blount,[2] in which the dehydrogenation of an alkaloid by selenium is mentioned, indicates a growing interest in this field.

Experiments

Choice of Solvent and Conditions.—Preliminary tests showed that no hydrogen sulfide was evolved when 0.5 g. of sulfur was refluxed for fifteen hours with 15 ml. each of epichlorohydrin, tetrachloroethylene, gasoline (99–102° fraction), glacial acetic acid, and toluene. Under the same conditions isopropyl propionate reacted with sulfur. Of the five suitable solvents toluene proved the best with respect to freedom from tarry products and quantity of hydrogen sulfide evolved when tested by refluxing 20 ml. of each with 0.5 g. (0.016 mole) of sulfur and 0.97 g. (0.006 mole) of nicotine (freshly distilled) for fifty hours. The hydrogen sulfide evolved was absorbed in ammoniacal zinc sulfate and titrated with standard iodine solution. Systematic variation of the quantities of sulfur, nicotine, and solvent showed that the largest quantity of sulfide gas, amounting to 69% calcd. according to equation 1, was obtained with 0.01 mole (1.6 g.) of nicotine, 0.225 mole (0.80 g.) of sulfur, and 20 ml. of toluene. Higher concentrations of nicotine produced some tar. Addition of 1.1 g. of alcoholized iron powder caused a somewhat decreased rate and quantity of gas. Diphenylguanidine, 0.2 g., reduced the total evolution of gas by 30%. Glacial acetic acid, 2.4 g., cut down the velocity to a fifth at the start but affected the amount finally obtained by only 11%. A huge excess of sulfur, amounting to over 100 times the theoretical, had no appreciable influence. No odor of methyl mercaptan was detected in any experiment.

Isolation of Nicotyrine and Thiotetrapyridine.—The quantities given above as being best were increased 25 times. The reaction was carried out by refluxing in a 2-liter flask heated in an oil-bath. At the end of ninety-one hours the evolution of gas had practically ceased. The resulting dark green solution was heated on a steam-bath under the vacuum created by a water pump until the distillation of toluene had ceased. The dark green viscous residue stood for two days without crystallization, a procedure which had been effective in causing solidification in other experiments. After placing the flask over solid carbon dioxide for two hours and then allowing to stand overnight, a large deposit of green crystals resulted. The supernatant liquid was poured off and the crystals washed with ether. They were then recrystallized twice from warm alcohol, yielding 7.6 g. of bright yellow crystals. The melting point after a third recrystallization remained at 151.5–153.5°. Cahours and Étard give 155° for this compound, thiodinicotyrine. Since no previous determination of its molecular weight had been made, the boiling point elevation in benzene was observed with the differential thermometer apparatus of Menzies: found with 0.0939 g. in 35.4 ml. of solvent, 303; with 0.1640 g., 314; calculated for $C_{20}H_{18}N_4S$, 346.

Upon distilling the solution, which had been poured off from the crude product, under 17 mm. vacuum a considerable additional amount of hydrogen sulfide was evolved. The fraction boiling from 143 to 153°, amounting to 1 ml., was collected. When redistilled at atmospheric pressure the main portion boiled at 268–274°. It is not as pure as the nicotyrine prepared by Wibaut and Overhoff[6] who found a boiling point of 280°. It was recognized as consisting chiefly of nicotyrine by its insolubility[11] in water, and by the melting point of its picrate derivative, which after six recrystallizations from alcohol melted at 160–161°. Blau gives 163–164; Wibaut 168–169°.

The above method of separation of the products proved much superior to extraction of the toluene solution with 5% alkali followed by distillation at atmospheric pressure of the toluene solution. Some nicotyrine was obtained together with tar and decomposition products. An attempt to precipitate the thiodinicotyrine by adding alcohol to the toluene concentrate before the crystals had formed was made. In spite of the fact that thiodinicotyrine is insoluble in alcohol, no crystals separated even on seeding and standing for several days at low temperatures.

Conclusions

Toluene has been found to be preferred over several other solvents of similar boiling point as a medium for the dehydrogenation of nicotine by sulfur. The temperature is lower than any hitherto employed for this purpose. The products are thiodinicotyrine and a small quantity of nicotyrine with practically no tarry materials.

CAMBRIDGE, MASS. RECEIVED JULY 12, 1935

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[9] Diels and Rickert, *Ber.*, **68**, 267, 325 (1935).

[10] Vesterberg, *ibid.*, **36**, 4200 (1903); Virtanen, *Ann.*, **424**, 198 (1921); Ruzicka and Meyer, *Helv. Chim. Acta*, **5**, 581 (1922).

[11] For a comparison with other possible dehydrogenation products see Pinner and Wolffenstein, *Ber.*, **25**, 1430 (1892); Pinner, *ibid.*, **28**, 456 (1895); Pictet and Crépieux, *ibid.*, **31**, 2018 (1898); Pictet and Rotschy, *ibid.*, **34**, 696 (1901).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INDUSTRIAL SCIENCE DIVISION, WEST VIRGINIA UNIVERSITY]

Some β-Alkoxyethyl Esters of *p*-Aminobenzoic Acid

BY H. V. ASHBURN, A. R. COLLETT AND C. L. LAZZELL

In view of the fact that an ether linkage usually increases the solubility of organic substances in lipoids, it was thought worth while to prepare and study the physiological properties of a series of compounds of the anesthesine type but containing an ether linkage in the alcohol portion of the molecule.

The starting materials for this work were the mono-ethers of glycol. The methyl, ethyl and butyl ethers were obtained from the Carbide and Carbon Chemicals Corporation. The propyl, isopropyl, isobutyl and secondary butyl ethers were prepared by heating the corresponding alcohols with ethylene oxide in the presence of a small amount of sulfuric acid as a catalyst.[1] The tertiary butyl ether was prepared in the same manner except that acid aluminum fluosilicate was used as the catalyst.[2]

The ethers were purified by fractional distillation, using a distillation column packed with jack chain. Only samples having a boiling range of 0.5° or less were used.

p-Nitrobenzoates

The *p*-nitrobenzoates of these monoglycol ethers were prepared according to the method of Conn, Collett and Lazzell.[3] These esters are viscous, practically odorless liquids having a pale yellow color. They are insoluble in water but soluble in all the common organic solvents.

TABLE I

p-NITROBENZOATES

R in β-R-ethyl	Yield, %	B. p., °C.	$d^{25}_{\text{abs.}}$	n^{25}_{D}	γ^{25}	Formula	Nitrogen analyses, % Calcd.	Found	
Propoxy	84	181.6–182.6	1.1763	1.5165	37.8	$C_{12}H_{15}O_5N$	5.53	5.70	5.67
Isopropoxy	86	172.0–172.8	1.1741	1.5148	36.5	$C_{12}H_{15}O_5N$	5.53	5.50	5.55
Isobutoxy	83	184.8–185.6	1.1532	1.5118	35.4	$C_{13}H_{17}O_5N$	5.24	5.28	5.19
s-Butoxy	80	183.5–184.5	1.1560	1.5124	36.1	$C_{13}H_{17}O_5N$	5.24	5.18	5.31
t-Butoxy	97	174.8–175.8	1.1579	1.5123	35.1	$C_{13}H_{17}O_5N$	5.24	5.29	5.30

Table I lists the analyses, physical constants and yields of all the new *p*-nitrobenzoates prepared. The analyses were made by titration with titanous chloride solution. All boiling points were taken under a pressure of 4.0 mm. with a thermometer completely immersed in the vapor. Refractive indices were determined by means of an Abbé refractometer at 25°. Surface tensions were obtained by means of a Du Noüy tensiometer at 25° and Harkins' correction for the ring method was applied. The yields are based upon the amount of glycol ether used.

p-Aminobenzoates

The *p*-aminobenzoates were obtained from the nitro compounds by reduction with hydrogen using Adams platinum–platinum oxide catalyst.[4]

One-tenth mole of the nitro compound was dissolved in 150 cc. of alcohol, 0.2 g. of Adams platinum–platinum oxide catalyst added and the solution shaken with hydrogen under an initial pressure of 45 lb./sq. in. until the theoretical amount of hydrogen was absorbed. The shaking with hydrogen was allowed to continue for an additional half-hour to ensure complete reduction. The catalyst was then filtered off and the alcohol removed by evaporation on the steam-bath. The red colored viscous oil remaining was dissolved in ether. The solution was then dried over anhydrous sodium sulfate, filtered, and dry hydrogen chloride passed in with cooling until precipitation was complete. The hydrochloride was filtered off, washed with dry ether until perfectly white and finally dried. To obtain the free base, the hydrochloride was dissolved in water, the solution cooled to 0–10° and dilute sodium carbonate solution added until the solution was alkaline. The free base was then filtered off and washed with cold water. The isobutyl, secondary butyl and tertiary butyl compounds were distilled under reduced pressure immediately after removing the alcohol.

Table II lists the analyses, physical constants and yields of these compounds. The analyses for nitrogen were made by the Kjeldahl method.

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(1) German Patent 580,075, July 5, 1933; *C. A.*, **27**, 4814 (1933).

(2) French Patent 39,773, Feb. 17, 1931; *C. A.*, **26**, 4826 (1932).

(3) Conn, Collett and Lazzell, THIS JOURNAL, **54**, 4370 (1932).

(4) Adams, "Organic Syntheses," John Wiley & Sons, Inc., 440 Fourth Ave., New York City, 1928, Vol. VIII, pp. 10–16, 92–99.

TABLE II

p-AMINOBENZOATES

R in β-R-ethyl	Yield, %	M. p., °C. base	M. p., °C. picramide	Formula	Nitrogen analyses, %		
					Calcd.	Found	
Methoxy	94	75.9	132.0	$C_{10}H_{13}O_3N$	7.18	7.15	7.24
Ethoxy	93	79.2	136.7	$C_{11}H_{15}O_3N$	6.69	6.40	6.56
Propoxy	87	44.5	138.4	$C_{12}H_{17}O_3N$	6.27	6.20	6.18
Isopropoxy	86	95.4	156.0	$C_{12}H_{17}O_3N$	6.27	6.23	6.30
Butoxy	79	34.0	123.1	$C_{13}H_{19}O_3N$	5.90	6.07	5.71
Isobutoxy	77	..	150.3	$C_{13}H_{19}O_3N$[a]	5.90	5.88	5.86
s-Butoxy	84	..	132.5	$C_{13}H_{19}O_3N$[b]	5.90	5.87	5.89
t-Butoxy	84	77.4	140.0	$C_{13}H_{19}O_3N$[c]	5.90	5.94	5.88

[a] B. p. 176.5–177.5° at 0.7 mm. [b] B. p. 177.0–178.0° at 0.7 mm. [c] B. p. 173.5–174.5° at 0.3 mm.

The picramides were prepared by the method given by Mulliken.[5]

The melting points of the hydrochlorides are not given since they apparently decompose before melting. The bases were all crystallized from ligroin with the exception of the tertiary butoxy compound which was crystallized from a water–alcohol mixture and the isobutoxy and secondary butoxy compounds which solidified after distillation when placed in a cool place for a few days, but these did not give definite melting points and could not be recrystallized. They apparently melt near room temperature. The yields are based upon the amount of glycol ether used.

Physiological data on these compounds will be reported in a later paper.

Summary

Five new β-alkoxy ethyl *p*-nitrobenzoates and a series of eight *p*-aminobenzoates have been prepared and some of their physical constants determined.

MORGANTOWN, WEST VIRGINIA RECEIVED JUNE 29, 1935

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[5] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., 440 Fourth Ave., New York City (1916), Vol. II, p. 32.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

A Gaseous Discharge Tube Especially Designed as an Intense Source of Continuous Ultraviolet Radiation

BY R. H. MUNCH

In the study of certain gaseous absorption lines, during the course of some research work under the direction of Dr. F. T. Gucker, Jr., the author required an intense source of continuous ultraviolet radiation which was simpler and more efficient than any that could be found described in the literature. This article deals with the development of such a source. Beyond about 3500 Å. there are only three sources of continuous radiation: the so-called Lyman continuum[1] (to 300 Å.), the hydrogen continuum[2] (3657–1216 Å.) and the helium continuum[3] (1125–500 Å.). The hydrogen continuum, which is the most useful, may be excited with considerable intensity if about 1500 v. is applied to an ordinary discharge tube made with a long capillary viewed from the end. Such a tube, dissipating as much as 18 kw., must be made of quartz and water cooled. It is, therefore, expensive and is comparatively inefficient. A more convenient method of exciting the hydrogen continuum without using high voltage and water cooling is by means of thermoelectrons from a hot cathode as in the low voltage arc of Duffendack and Manley.[4] This arc passed between a heated tungsten filament and a disk anode, in a tube containing a palladium tube to admit hydrogen and a quartz window sealed on with wax. We built a tube differing from this only in having an oxide coated

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[1] V. Schumann, "Smithsonian Contributions to Knowledge," **29**, No. 1413, 13 (1903); T. Lyman, *Astrophys. J.*, **60**, 1 (1924); *Nature*, **118**, 156 (1926); G. H. Dieke and J. J. Hopfield, *Z. Physik*, **40**, 299 (1926); *Phys. Rev.*, **30**, 400 (1927); G. Rathenau, *Z. Physik*, **87**, 32 (1933); Collins and Price, *Rev. Sci. Inst.*, **5**, 423 (1934).

[2] V. Schumann, *loc. cit.*, E. Gehrcke and E. Laue, *Ann. Physik*, **76**, 673 (1925); Bay and Steiner, *Z. Physik*, **45**, 337 (1927); Lawrence and Edlefsen, *Rev. Sci. Inst.*, **1**, 45 (1930); Kistiakowsky, *ibid.*, **2**, 549 (1931); Stevens, *ibid.*, **6**, 40 (1935).

[3] J. J. Hopfield, *Astrophys. J.*, **72**, 137 (1930).

[4] Duffendack and Manley, *J. Opt. Soc. Am.*, **24**, 222 (1934); **23**, 101 (1933).

cathode and a thin Pyrex window[5] equivalent to 1 mm. of quartz, but it was too weak a source even with ten times the current Duffendack and Manley used. Starting from this tube we finally evolved a source which combined the intensity of the high voltage tube with the simplicity of the low voltage arc.

Construction and Operation of the Tube.—Figure 1 shows the construction of this tube. The oxide coated cathode, C, is a 0.48 × 15.25 cm. piece of nickel gauze woven of 0.25 mm. wires 19 per inch, bent into a corrugated form having a 0.48 cm. cross section. One end is spot welded to the top of the cathode shield, S, and the other to a 0.10 cm. nickel wire. It is then painted with a water suspension of equal parts of barium and strontium carbonates and dried in an oven. Successive layers are applied until a heavy coating is obtained, since the life of the cathode in a hydrogen tube is proportional to the amount of oxide it has on it.

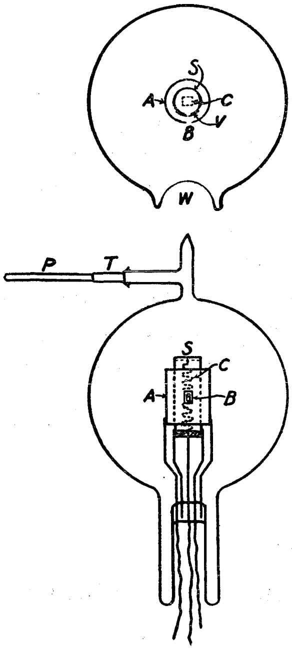

Fig. 1.

The cathode is surrounded by a cylindrical shield, S, of 0.125 mm. nickel, 4.06 cm. long and 1.25 cm. in diameter, which forms one lead to the cathode and is closed at the bottom by means of a porcelain disk (cross hatched) through which the second cathode lead passes. The only opening in the shield is a 0.66 × 3 mm. slit cut in a piece of 0.25 mm. sheet tungsten[6] welded in the side.

The anode, A, is a 2.2 × 2.86 cm. nickel cylinder made from 0.25 mm. sheet with a 0.32 cm. × 0.64 cm. hole, B, to correspond with the slit in the cathode shield. These parts are mounted as shown on a five wire stem which is then sealed into a 10 cm. Pyrex bulb. When the tube is in operation, the whole discharge between the cathode and the anode must pass through the small slit in the shield, and is viewed through the opening in the anode. This arrangement of parts gives a rectangular light source most suitable for a spectrograph or any instrument having a collimating slit. The extremely efficient source of electrons furnished by the oxide coated cathode, together with the short distance between anode and cathode, enable this tube to pass a given current at about 5% of the voltage required for an ordinary capillary tube. It requires no water cooling and could operate continuously at a current of 1.5 amp., or run for a short time at a higher current. Since the slit area was 2 sq. mm., the current density through the slit was 75 amp. per square centimeter for continuous operation and could be increased considerably for short periods. The use of a smaller slit was not practical, since it made the discharge hard to start.

The thin window, W, is made opposite the slits by first blowing a bubble about 3.2 cm. in diameter, then melting it back to about half its height and sucking it in carefully. The palladium tube, P, is now silver soldered to a copper tube, T, the end of which is flared and sealed on the *outside* of a piece of Nonex which is fused to the Pyrex from which the bulb is made. The external copper seal withstands sudden heating without developing cracks. The tube must now be evacuated and freed of all traces of moisture or carbon monoxide which might deactivate the cathode and would certainly produce line or band spectra. It is connected through a liquid air trap and large stopcock to a vacuum pump. The glass and metal parts are outgassed thoroughly by passing a discharge through the tube and sweeping it out with a stream of hydrogen at 2–4 mm. pressure. This is admitted by holding a Bunsen burner flame under the palladium tube, and its removal is regulated by the stopcock. When the spectrum becomes continuous, below 3657 Å., the tube is sealed off.

The electrical connections are similar to those of a "tungar" or a hot cathode mercury arc rectifier. The cathode, which requires 9 amp. at about 3 v., is supplied by a step-down transformer and connected in series with a rheostat and ammeter. The anode circuit, also containing a rheostat and ammeter, may be connected to any 110 volt circuit. The use of a. c. to heat the cathode and d. c. for the anode circuit gives the maximum cathode life. In operation, the fall of potential between anode and cathode is 30–35 v. If the discharge fails to start (before the tube has been outgassed or when the cathode is nearly spent) it may be started by touching the palladium tube with the type of Tesla coil used in testing for leaks in a vacuum system.

Performance of the Tube.—The improved hydrogen arc was found to be about thirty times as intense (for the same current) as the original type of Duffendack and Manley. Since the latter only used 50 m. a. as against 1.5 amp. as a moderate rating for the improved type, the total increase is about nine hundred fold since the intensity is proportional to the current density.[7]

We did not have the equipment necessary to compare the improved lamp with the high voltage arc, but if the intensity here also is proportional to the current, the increased efficiency of the new tube can be judged by the fact that it passes 1.5 amps. for about 75 watts total energy, instead of over 2 kw.

The determination of the absolute intensity of the continuum emitted by the lamp was outside

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(5) Simon Sonkin, *J. Opt. Soc. Am.*, **19**, 65 (1929).

(6) When the slit was made in the nickel, or even in a molybdenum section, its edges melted and lines appeared in the continuum. Tungsten proved completely satisfactory, although harder to work. It must be cut with a thin abrasive wheel, since shears splinter it. The slit was cut by means of carborundum dust on a copper disk run at high speed.

(7) Bay and Steiner, *loc. cit.;* Lawrence and Edlefsen, *loc. cit.*

the scope of our work. However, a comparison was made with the mercury arc lines emitted by a G. E. "Labarc" when both sources were run at 1 amp. The continuum was 25% as intense as the 2483 and 2652 Å. lines, 7% as intense as the 2894 and 3022 Å. lines and 12% as intense as the 3350 Å. line. These figures should give anyone familiar with this field a satisfactory idea of the performance of the lamp.

The Tube as a Line Spectral Source.—This type of lamp operates when filled with helium, argon, or a mixture of argon and mercury; and presumably when filled with the other rare gases. The argon mercury mixture gave a spectrum from which the far ultraviolet lines, particularly the resonance line, were nearly absent due to the quenching effect of argon while the visible and near ultraviolet lines were very strong.

Acknowledgments.—The author wishes to express his appreciation to Dr. F. T. Gucker, Jr., for his encouragement and assistance in the course of this work and for his assistance in the preparation of the manuscript for publication. It is also a pleasure to acknowledge the helpful advice given by Dr. R. A. Fisher and Dr. W. S. Huxford of the Physics Department of Northwestern University.

Summary

A simple, low voltage hydrogen discharge tube especially designed as an intense source of continuous ultraviolet has been developed. It requires no water cooling, since it produces the same light intensity with only about 5% of the electrical power required by a high voltage hydrogen discharge tube. Details of construction and operation are given.

In addition to being useful as a source of continuous radiation it has been used as a source of the line spectra of mercury and the rare gases.

EVANSTON, ILLINOIS RECEIVED JUNE 22, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

Some Thermodynamic Properties of Uni-univalent Halide Mixtures in Aqueous Solution

BY HERBERT S. HARNED

It has been shown experimentally by Güntelberg and by Harned that the logarithm of the activity coefficient of hydrochloric acid in chloride mixtures of constant total ionic strength varies linearly with the molality of the acid. Since these earlier studies, other investigations have confirmed this result.[1]

Recently, from a number of sources, sufficient evidence has been acquired to permit more extended observations of this relation, particularly with respect to concentration and temperature. The results obtained will have a special interest in connection with some recent generalizations made by Åkerlöf[2] regarding the behavior of these mixtures. Of still greater interest will be the limitations which the newer knowledge imposes upon Brönsted's theory of the specific interaction of ions.[3]

For our purposes, the law of the linear variation of the logarithm of the activity coefficient at constant ionic strength may be expressed for the systems of uni-univalent halide acid–halide salt mixtures in the following manner. Thus

$$\begin{aligned}\log \gamma_1 &= \alpha_1 m_1 + \log \gamma_1^0 = \log \gamma_{1(0)} - \alpha_1 m_1 \\ \log \gamma_2 &= \alpha_2 m_2 + \log \gamma_2^0 = \log \gamma_{2(0)} - \alpha_2 m_2\end{aligned} \quad (1)$$

where the ionic strength, $\mu = m_1 + m_2 =$ constant. The first of these equations refers to the acid (subscript 1) in the mixture, and second to the salt (subscript 2) in the same mixture. γ_1^0 and γ_2^0 are the activity coefficients of the acid at zero concentration in the salt solution and that of the salt at zero concentration in the acid solution, respectively. $\gamma_{1(0)}$ and $\gamma_{2(0)}$ are the activity coefficients of the acid and salt in pure aqueous solution of the acid and salt, respectively. Equation (1) is taken to be valid at any total ionic strength, μ.

The present communication contains measurements of the cells

H_2 (1 atm.) | HCl (0.01), NaCl(m) | AgCl | Ag Type I

which will serve to supplement the available accurate data on this subject. Results have been

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(1) Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926); Harned, THIS JOURNAL, **48**, 326 (1926); see also Harned and Mason, *ibid.*, **53**, 3377 (1931); Hawkins, *ibid.*, **54**, 4480 (1932); Mason and Kellam, *J. Phys. Chem.*, **38**, 689 (1934); Bates and Urmston, THIS JOURNAL, **55**, 4068 (1933); Murdoch and Barton, *ibid.*, **55**, 4074 (1933).

(2) Åkerlöf and Thomas, *ibid.*, **56**, 593 (1934); Åkerlöf, *ibid.*, **56**, 1439 (1934).

(3) Brönsted, *ibid.*, **44**, 877 (1922).

obtained from 0 to 60° at 5° intervals and at salt concentrations which vary from 0 to 3 *M*. These in combination with the results of Harned and Ehlers, and Harned and Nims[4] make it possible to compute α_1 and α_2 in these mixtures from 0 to 40° and throughout wide ranges of total concentrations. Further data are now available for computing α_1 and α_2 of a number of uni-univalent halide acid–salt mixtures at 25°. The information derivable from these results, namely, the behaviors of α_1 and α_2 as functions of temperature and concentration, is an important addition to the knowledge of such mixtures.

Experimental Results[5]

The measurements of the cells (Type I) were carried out by a technique similar to that employed by Harned and Hamer,[6] and the results were obtained at round concentrations by the method described by them. Measurements at each concentration were made from 0 to 60° at 5° intervals. These were expressed to within ±0.05 mg. by the quadratic equation

$$E = E_{25} + a(t - 25) + b(t - 25)^2 \qquad (2)$$

The values of E_{25} and the constants *a* and *b* are given in Table I.

TABLE I

CONSTANTS OF EQUATION (2)

$m_1 = 0.01 \quad \mu = m_1 + m_2$

	E_{25}	$a \times 10^6$	$b \times 10^6$
0.01	0.46416	175	−3.0
.02	.44815	124	−3.0
.03	.43891	94	−2.95
.06	.42330	50	−2.9
.11	.40996	12	−2.8
.21	.39550	− 35	−2.8
.51	.37422	− 97	−2.65
1.01	.35502	−149	−2.5
2.01	.32949	−210	−2.0
3.01	.30906	−247	−1.5

Method of Computation of α_1 and α_2.—The values of α_1 may be computed directly at a given concentration if the activity coefficient of the acid in pure water and the activity coefficient of the acid in the salt solution are known. The first of these has been derived from measurements of the cells

$$H_2 \mid HX(m) \mid AgX \mid Ag;\ X = Cl:Br \qquad \text{Type II}$$

and the second from cells of Type I, or

$$H_2 \mid HX(m_1),\ MX(m_2) \mid AgX \mid Ag;\ \begin{cases} X = Cl:Br \\ M = Li, Na, K, Cs \end{cases} \qquad \text{Type I}$$

Thus

$$\alpha_1 = (\log \gamma_{1(0)} - \log \gamma_1)/(m - m_1) \qquad (3)$$

where the subscript 1(0) refers to the acid in pure water at a concentration μ.

The computation of α_2 from the values of α_1 and other known data may be made by the use of the Gibbs–Duhem equation in the form.

$$m_H \, d \ln a_H a_X + m_M \, d \ln a_M a_X = -55.5 \, d \ln a_W \qquad (4)$$

where a_H, a_M, a_X represent the activities of the ionic species denoted by subscripts and a_W is the activity of water. Since the anion is common in all the mixtures under consideration, $m = m_X = m_H + m_M$ = constant, this equation becomes

$$2m_1 \, d \log \gamma_1 + 2m_2 \, d \log \gamma_2 = -55.5 \, d \log a_w \qquad (5)$$

γ_1 and γ_2 equal the activity coefficients $(\gamma_H\gamma_X)^{1/2}$ and $(\gamma_M\gamma_X)^{1/2}$, respectively. According to equation (1), $d \log \gamma_1 = \alpha_1 \, d\, m_1$ and $d \log \gamma_2 = \alpha_2 \, d\, m_2$, whence equation (5) becomes

$$2\alpha_1 m_1 \, d\, m_1 + 2\alpha_2 m_2 d\, m_2 = -55.5 \, d \log a_w \qquad (6)$$

Let $m_1 = mx$; then $m_2 = (1 - x)m$, where x can have any value from 0 to 1. Employing these values in equation (6) and performing the integration, we obtain

$$x^2(\alpha_1 + \alpha_2) - 2\alpha_2 x = -55.5/m^2 \int_0^x d \log a_w \qquad (7)$$

an equation which is fundamental to all subsequent discussion.

Upon integration from x equals 0 to 1 or from the pure salt to pure acid solution, we readily obtain

$$\alpha_2 = \alpha_1 + (55.5/m^2) \log (a_1/a_2) \qquad (8)$$

where a_1 and a_2 are the activities of water of the pure acid and pure salt solutions, respectively. Equation (8) gives us a means of computing α_2 from α_1. Since the thermodynamic data of the halide electrolytes in water have been expressed in terms of activity coefficients, we have evaluated the activity ratio in equation (8) by means of the equation

$$\ln \frac{a_0}{a} = \frac{m}{55.5}\left[\nu + \frac{\nu}{m}\int_1^\gamma d \ln \gamma\right] \qquad (9)^7$$

a_0 is the activity of the pure solvent, and ν for the uni-univalent salts in question equals 2. The logarithm of the ratio of the activities of water of

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(4) Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933); Harned and Nims, *ibid.*, **54**, 423 (1932).

(5) These results formed part of a Thesis presented by George E. Mannweiler to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Master of Science, June, 1934. The principal part of the work in this Thesis will be published in a subsequent article.

(6) Harned and Hamer, THIS JOURNAL, **55**, 2194 (1933); **55**, 4496 (1933).

(7) Harned in Taylor, "Treatise on Physical Chemistry," 2d ed., D. Van Nostrand Co., New York, 1931, Chap. XII, Equation 102, Vol. I, p. 779.

TABLE II

THE VALUES OF (α_1) AND ($-\alpha_2$) FOR UNI-UNIVALENT HALIDE SOLUTION AT 25°

					α_1				
m..........	0.1	0.5	1	1.5	2	3	4	5	6
LiCl[a]	0.007[b]	0.0060	0.0050	0.0054	0.0052	0.0037	−0.0025[c]	....	−0.0086[c]
NaCl[d]	.042[b]	.0035	.0324	....	.0308	.0306	.0296[c]	0.0297[c]	.0287[c]
KCl[e]	.080[b]	.0624	.0563	.0552	.0567	.0625	.0660[c]	.0722[c]	....
CsCl[f]	.140[b]	.1046	.1004	.0992	.0992	.0980	....	....	....
LiBr[g]	....	.0055	.0055	.0054	.0041	....	....	....	....
NaBr[h]	(.050)	.0383	.0375	.0364	.0385	....	....	....	....
KBr[h]	(.098)	.0884	.0800	.0808	.0802	.0860	....	....	....
γ_{HCl}	.796	.757	.809	.896	1.009	1.316	1.762[i]	2.374[i]	3.220[i]
γ_{HBr}	.802	.788	.873	....	1.169	1.671	....	....	....
	[log $\gamma_{0.1}$ + 10]				($-\alpha_2$)				
LiCl	9.8982	0.011	0.012	0.011	0.012	0.013	....	....	....
NaCl	9.8910	.057	.058	....	.058	.058	....	....	....
KCl	9.8842	.074	.072	.069	.064	.054	....	....	....
CaCl	9.8762	.070	.060	.053	.046	.041	....	....	....
LiBr	9.8998	.034	.030	.030	.030	....	....	....	....
NaBr	9.8915	.070	.068	.067	.063	....	....	....	....
KBr	9.8847	.076	.069	.065	.065	....	....	....	....

[a] Harned and Copson, THIS JOURNAL, **55**, 2206 (1933). [b] Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926); Harned, THIS JOURNAL, **48**, 326 (1926). [c] Hawkins, *ibid.*, **54**, 4480 (1932). [d] Present communication, Table I. [e] Harned and Hamer, THIS JOURNAL, **55**, 2194 (1933). [f] Harned and Schupp, *ibid.*, **52**, 3892 (1930). [g] Vance, *ibid.*, **55**, 4518 (1933). [h] Harned and Hamer, *ibid.*, **55**, 4496 (1933). [i] Randall and Young, *ibid.*, **50**, 989 (1928).

solutions of two uni-univalent electrolytes at a given concentration, m, is readily found from two of these equations to be

$$\log \frac{a_1}{a_2} = \frac{2}{55.5}\left[\int_1^{\gamma_{2(0)}} m \, d \log \gamma_2 - \int_1^{\gamma_{1(0)}} m \, d \log \gamma_1\right. \tag{10}$$

whence from equation (8)

$$\alpha_2 = \alpha_1 + \frac{2}{m^2}\left[\int_1^{\gamma_{2(0)}} m \, d \log \gamma_2 - \int_1^{\gamma_{1(0)}} m \, d \log \gamma_1\right] \tag{11}$$

The subscript (0) refers to activity coefficients of pure aqueous solutions of the acid or the salt. When this subscript is omitted, the activity coefficient of the substance in question in the mixture is under consideration. Since α_1 is known by experiment and since the integrals on the right may be computed, α_2 may be calculated. This equation has been derived upon the assumption that equations (1) are valid. From experimental evidence we know that the first of these relations is true for the variation of log γ_1 with m_1 in the cases of hydrochloric and hydrobromic acids in their corresponding alkali salt solutions. Indeed judging from electromotive force and solubility measurements the law is valid within narrow limits in dilute solutions and also in solutions of potassium chloride or sodium chloride at 5 M and 6 M, respectively. No direct experimental data confirm the linear law for the logarithm of the activity coefficient of the salt in the acid solution, that is to say, the constancy of α_2. Since so much evidence confirms the validity of the first of the relations given by equation (1), we shall proceed by assuming the second of these relations to be valid.

The Halide Acid–Alkali Salt Mixtures at 25°. —The values of α_1 for hydrochloric acid in lithium, sodium, potassium and cesium chloride solutions and for hydrobromic acid in lithium, sodium, and potassium bromide solutions computed by equation (3) are compiled in Table II. The activity coefficient of hydrochloric acid in pure aqueous solution was obtained from the data of Harned and Ehlers and Randall and Young[8] and is given in the eighth row of the table. The ninth row of the table contains the activity coefficient of hydrobromic acid taken from the data compiled by Harned.[9] The preceding rows contain α_1 of the acids in the halide solutions designated. The sources of the data are given in the references below the table. The accuracy of this determination is difficult to estimate since it depends on the concentration. If we assume errors of ±0.05, ±0.1, ±0.2, and ±0.2 mv., at 0.1, 0.5, 1, and 3 M, respectively, then the maximum error in α_1 is ±0.004, ±0.0034, ±0.0034, and ±0.0011 at these concentrations. At 0.1 M Güntelberg's results are consistent to within

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[8] Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933); Randall and Young, *ibid.*, **50**, 989 (1928).

[9] Ref. 7, Chap. XII, p. 772.

±0.02 mv. and are in agreement with Harned's values. The consistency of the present results as judged from graphs is of the order of ±0.001 at 0.1 *M*, ±0.0006 at 0.5 *M* and 1 *M*, and ±0.0004 at the higher concentrations.

The values of $(-\alpha_2)$ given in the second part of the table were obtained from α_1 and the activity coefficient data by means of equation (11). The values of $\log \gamma$ employed in the graphical integration for the sodium and potassium chloride and bromide solutions were taken from the data of Harned and Robinson and Sinclair, and for the case of cesium chloride from the combined data of Robinson and Sinclair and Schupp.[10] The values of $\log \gamma$ for the lithium chloride solutions were those of Robinson and Sinclair. In some cases, the earlier results were changed slightly to conform with the values of $\log \gamma_{0.1}$ given in Table II. Since we have employed data from so many sources, it is difficult to estimate the accuracy of the computation of $(-\alpha_2)$. From 0.5 to 3 *M* the consistency of the data as judged from graphs is of the order of ±0.002 and it appears that on the whole the results may be relied on to this extent.

Hydrochloric Acid–Sodium Chloride Mixtures from 0 to 40°.—For mixtures of hydrochloric acid and sodium chloride, accurate data are available which make possible the computation of α_1 and α_2 from 0 to 40° and from 0.3 to 3 *M*. The integral on the right of equation (11) was computed from activity coefficients of Harned and Ehlers (hydrochloric acid) and Harned and Nims (sodium chloride).[11] The values of α_1 were obtained from the electromotive forces given in Table I of the present communication and the electromotive force data of Harned and Ehlers.[12] The values at 0.1 *M* were obtained from the very careful measurements of Güntelberg (20°) and also those of Harned (25°). From 0.5 *M* to 3 *M*, the results are consistent to within the limit of ±0.0006 in the case of α_1 and ±0.001 in the case of α_2. Table III contains the values of these quantities at 25° and at 10° intervals from 0 to 40°.

TABLE III

THE VALUES OF α_1 AND $(-\alpha_2)$ FOR HYDROCHLORIC ACID–SODIUM CHLORIDE MIXTURES FROM 0 TO 40°

tm	0.1	0.3	0.5	1	2	3
			(α_1)			
0	(0.052)	0.048	0.0444	0.0421	0.0410	0.0406
10	..	.044	.0402	.0381	.0370	.0366
20	.044[a]	.040	.0361	.0341	.0330	.0326
25[c]	.042[b]	.0375	.0341	.0322	.0311	.0306
30	..	.035	.0320	.0302	.0290	.0286
40	(.035)	.030	.0280	.0263	.0251	.0246
			($-\alpha_2$)			
0		0.081	0.0816	0.0785	0.0724	0.0702
10		.068	.0702	.0685	.0658	.0644
20		.060	.0625	.0619	.0600	.0594
25		.057	.0587	.0577	.0578	.0574
30		.054	.0550	.0549	.0552	...
40		.047	.0474	.0482	.0493	...

[a] Güntelberg, *loc. cit.* [b] Harned, *loc. cit.* [c] The results at 25° differ slightly from those in Table II. This is due to the fact that the values in this table were smoothed against *T*.

Limitations of Empirical Rules of Åkerlöf and Thomas.—We shall first consider two empirical relations which Åkerlöf and Thomas have employed[2] for computing solubility data in concentrated solutions.

The first of these rules is expressed by

$$\log (\gamma_{1(0)}/\gamma_{2(0)}) = Bm \qquad (12)$$

where B is a constant. If this relation be employed in conjunction with equation (11), it is found that at constant temperature

$$(\alpha_1 - \alpha_2) = B \neq f(m) \qquad (13)$$

Further, if both this and equations (1) are valid, in other words if all these relations are linear, then

$$\left.\begin{aligned} (\alpha_1 - \alpha_2)\, m &= \log (\gamma_{1(0)}/\gamma_{2(0)}) \\ \log \gamma_1^0 &= \log \gamma_2^0 \end{aligned}\right\} \qquad (14)$$

and according to equation (11)

$$\log \frac{\gamma_{1(0)}}{\gamma_{2(0)}} = -\frac{2}{m}\left[\int_1^{\gamma_{2(0)}} m \,\mathrm{d} \log \gamma_2 - \int_1^{\gamma_{1(0)}} m \,\mathrm{d} \log \gamma_1\right] \qquad (15)$$

We may readily test these relations by means of the above data. From the activity coefficients of the acids and the pure salts at various concentrations, the left side of equation (12) was computed, and the value of B at each concentration was determined. For example in the case of the chlorides $\gamma_{1(0)}$ is the activity coefficient of hydrochloric acid and $\gamma_{2(0)}$ that of the designated chloride at a concentration, m. The results are given in Table IV.

It is to be noticed that when B is small, the variation of B with concentration is small, but that in general B decreases with increasing concentration. Where B is larger, the actual and

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(10) Harned, THIS JOURNAL, **51**, 416 (1929); Harned and Schupp, *ibid.*, **52**, 3886 (1930); Robinson and Sinclair, *ibid.*, **56**, 1830 (1934).

(11) The activity coefficients of Harned and Nims were recomputed from the electromotive forces. The values of $(-\log \gamma)$ at 0.1 *M* were found to be 0.1070, 0.1070, 0.1080, 0.1090, 0.1100 and 0.1109 at 0, 10, 20, 25, 30 and 40°, respectively. All other values of γ were adjusted to these values.

(12) Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933); Harned and Nims, *ibid.*, **54**, 423 (1932).

TABLE IV

VALUES OF B AT DIFFERENT CONCENTRATIONS

m	0.5	1	2	3
LiCl	0.020	0.017	0.018	0.018
NaCl	.096	.091	.089	.084
KCl	.140	.132	.124	.121
CsCl	.200	.175	.156	.150
LiBr	.036	.035	.034	
NaBr	.112	.104	.102	
KBr	.168	.155	.149	

percentage deviation of B with concentration is greater. In Fig. 1, B is plotted against m and the variation of B with m is represented by the crosses and dashed lines. The solid lines in the figure represent the values of $(\alpha_1 - \alpha_2)$ obtained from Table II. In the cases of the lithium chloride–hydrochloric acid and lithium bromide–hydrobromic acid mixtures B does not vary appreciably with m and therefore $(\alpha_1 - \alpha_2) = B$ according to equation (13). This equality may not be exact but it is within the experimental error. In the case of the sodium salt mixtures B is slightly different from $(\alpha_1 - \alpha_2)$ and a similar but greater difference occurs with the potassium salt mixtures and finally a still greater difference with the cesium salt mixture. This is in accord with the character of equation (11) and the nature of the variation of B with m as well as the linear variations represented by equations (1).

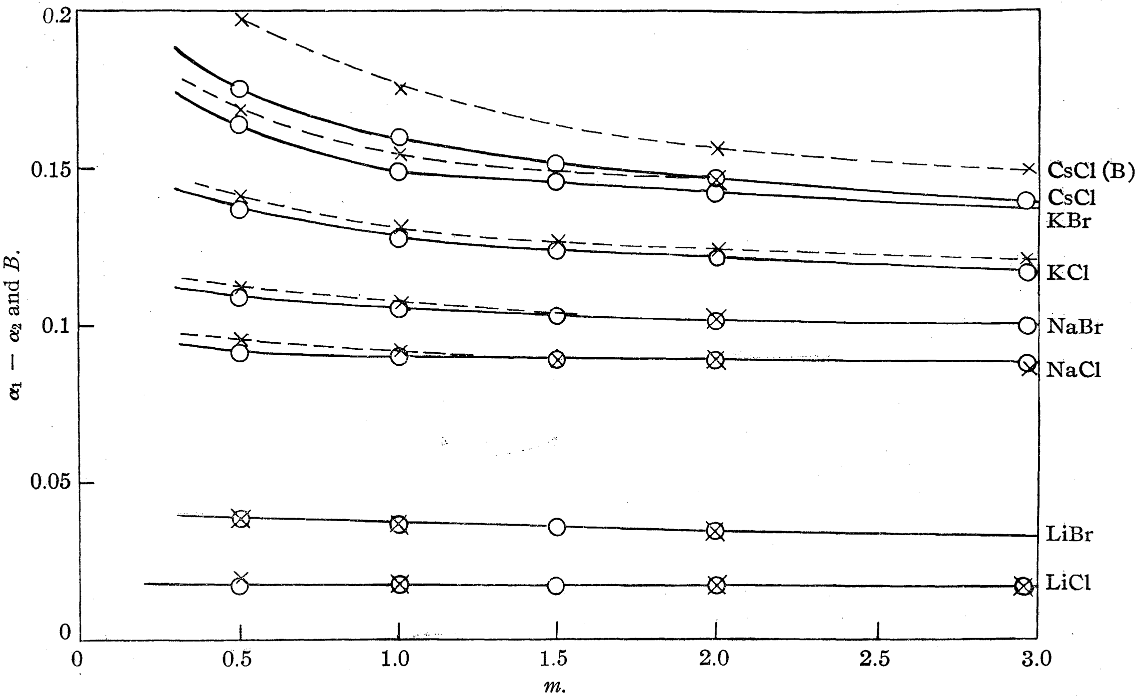

Fig. 1.—Plots of B and $\alpha_1 - \alpha_2$ vs. m for uni-univalent halide solutions: ×, B; ○, $\alpha_1 - \alpha_2$.

The variation of B with m conforms with the contentions of Robinson, and Scatchard and Prentiss,[13] who concluded from heat of dilution data and freezing point data, respectively, that B is not constant and is $f(m)$ in dilute solutions. Even in concentrated solutions care must be employed in the use of these relations while in dilute solutions it is obvious that it is not valid.

The second rule postulated by Åkerlöf and Thomas states that α_1 and α_2 are constants which do not vary with m. In dilute solutions, reference to Tables II and III and Figs. 2 and 3 shows that this is not the case. Since their observations refer particularly to concentrated solutions, we note that there is a general tendency for α_1 and α_2 to vary less as the concentration increases. But even in very concentrated solutions, these quantities still appear to be a function of m. For example, in the case of sodium chloride–hydrochloric acid mixtures α_1 tends to decrease somewhat up to 6 M while for the potassium chloride mixtures it passes through a minimum at about 1.5 M and then increases. We must conclude therefore that at constant temperature α_1 and α_2 are not characteristic constants of a given pair of electrolytes.

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[13] Robinson, THIS JOURNAL, **56**, 2312 (1934); Scatchard and Prentiss, *ibid.*, **56**, 2320 (1934).

Further Discussion of the Derived Parameters, α_1 and α_2.—The curves in Fig. 2 which represent the values of α_1 and $-\alpha_2$ for hydrochloric acid–chloride mixtures are typical of all the results in Table II. In fact, the bromide mixtures exhibit behaviors which parallel those of the chloride mixtures. At higher concentrations, α_1 does not equal $(-\alpha_2)$. As the concentration decreases, there seems to be a tendency in some cases (*e. g.*, CsCl, NaCl, NaBr) for the values to approach each other somewhat. Potassium chloride and bromide mixtures exhibit a more complex behavior since the curves representing the variation of these constants with concentration cross. In some cases, $(-\alpha_2) > \alpha_1$ (*e. g.*, NaCl, LiCl) while in others (*e. g.*, CsCl) $\alpha_1 > (-\alpha_2)$.

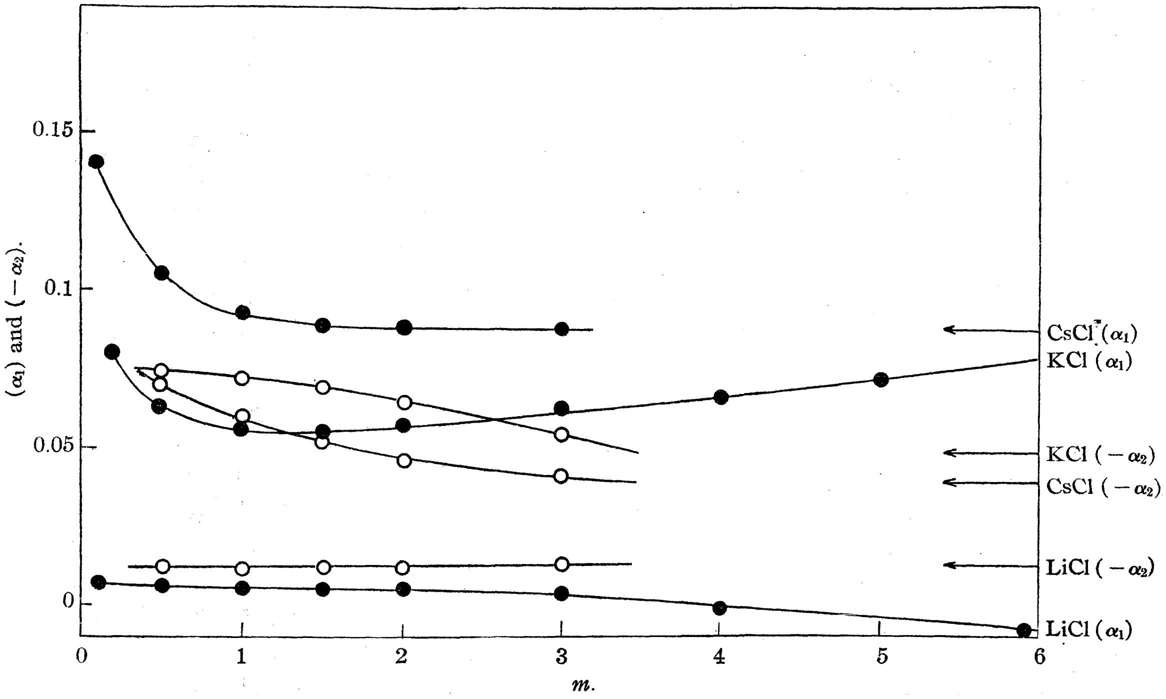

Fig. 2.—Plots of α_1 and $-\alpha_2$ *vs.* m for uni-univalent chloride–hydrochloric acid mixtures.

The best illustration of these behaviors is given by the sodium chloride mixtures and is shown by Fig. 3 in which the parameters, α_1 and $(-\alpha_2)$ are plotted against m at 0, 25 and 40°. As the concentration decreases, there is a tendency for the corresponding curves of α_1 and $-\alpha_2$ to approach each other somewhat but the evidence indicates that they do not meet even in the dilute solutions.

It is important to note that the values reported for α_1 and $-\alpha_2$ have been derived from electromotive force measurements which have been checked by measurements from various sources. The mixture data have been tested in a number of ways. For example, from mixture data by purely formal methods,[14] Harned was able to compute the activity coefficients of some single electrolytes. Another test of these data consists in computing dissociation constants and total heats of ionization of water in the salt solutions. Agreement was obtained with the best calorimetric data by Harned and Hamer for potassium chloride solutions. The values of α_1 for the chloride solutions at 0.1 *M* were obtained from the closely agreeing values of Güntelberg and Harned.[14] All the data of the activity coefficients of single electrolytes have been checked in a number of ways. The activity coefficients of hydrochloric acid agree with colorimetric data as shown by Harned and Ehlers. Those of the salt solutions at 25° have been found to be in agreement with the vapor pressure data of Robinson and Sinclair and Robinson.[15] At 0.5 *M* sodium chloride $(-\alpha_2)$ was found to be 0.0820 from the electromotive force data of Harned and Nims and 0.0814 from the freezing point data of Scatchard and Prentiss.[16] Further the reference value of γ in 0.1 *M* sodium chloride employed, namely, 0.778, agrees very

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[14] Harned, This Journal, **48**, 326 (1926); Harned and Hamer, *ibid.*, **55**, 4496 (1933); Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

[15] Robinson, This Journal, **57**, 1161 (1935).

[16] Scatchard and Prentiss, *ibid.*, **55**, 4355 (1933).

closely with 0.7784 recently obtained by Brown and MacInnes.[17] In view of these facts, we believe the results are within the limits of accuracy previously discussed.

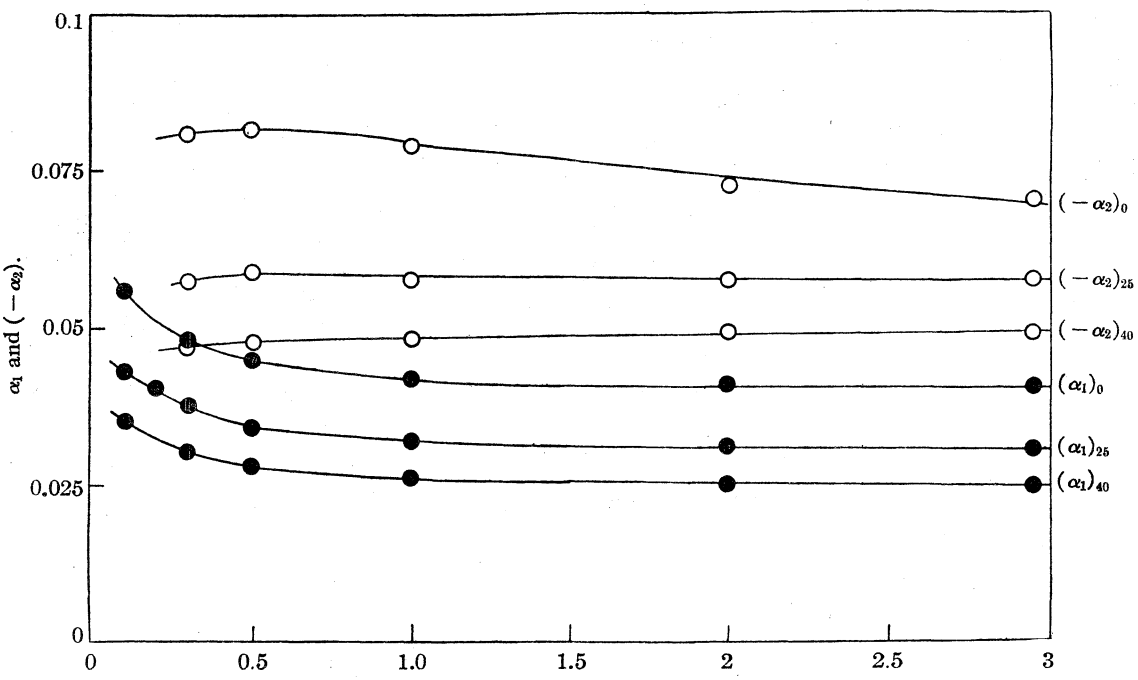

Fig. 3.—Plots of α_1 and $-\alpha_2$ *vs. m* for sodium chloride–hydrochloric acid mixtures at 0, 25 and 40°.

Theory of Specific Ionic Interaction

Since these results are of interest in relation to Brönsted's theory of specific ionic interaction, we shall introduce a few of the consequences of this theory.[18] The osmotic coefficient, ϕ, may be introduced into equation (7) by means of the relation

$$-\partial \log a_v = (\nu m/55.5 \times 2.303)\, \partial\phi \qquad (16)$$

and the equation for the variation of the osmotic coefficient in mixtures at constant total molality, *m*, may be obtained. Thus

$$x^2(\alpha_1 + \alpha_2) - 2\alpha_2 x = \frac{1}{m^2}\int_0^x \frac{\nu m}{2.303}\, \partial\phi \qquad (17)$$

As pointed by Güntelberg, the left side of this equation is quadratic. Brönsted's theory of specific ionic interaction applied to these mixtures leads to the conclusion that both the osmotic coefficient and the logarithm of the activity coefficient vary linearly with the composition. Thus

$$2.303B'm\partial x = \partial\phi \qquad (18)$$

where B' is a constant. Combining this equation with equation (17) and integrating, we find that

$$x(\alpha_1 + \alpha_2) - 2\alpha_2 = \nu B' \qquad (19)$$

for all values of *x* between 0 and 1. Consequently

$$\begin{aligned} \alpha_1 &= -\alpha_2 \\ \alpha_2 &= -(\nu/2)B' = -B' \text{ (1-1 Electrolytes)} \end{aligned} \qquad (20)$$

The theory of specific ionic interaction as originally formulated requires: (1) the linear variation of log γ at constant total molality (Eq. 1); (2) the linear variation of ϕ (Eq. 18); (3) that $\alpha_1 = -\alpha_2$. These results follow from the assumption that ions of like sign uniformly influence each other in a dilute salt solution. According to this formulation of the theory the factor $(\alpha_1 + \alpha_2)$ is a measure of the deviation from the theory, caused by specific interaction between ions of like sign. Upon the basis of the validity of (1) (Eq. 1), we have computed the factor $(\alpha_1 + \alpha_2)$ and found that at high concentrations it is finite. In this connection, we note that the thermodynamic result given by equation (17) does not require the equality, $\alpha_1 = -\alpha_2$, at any concentration including $m = 0$. Since this depends on the hypothesis of ionic interaction, we have not extended the curves in the figures to lower concentrations where the uncertainty becomes large. This consideration raises the interesting question as to whether $(\alpha_1 + \alpha_2)$ vanishes at any concentration. In Fig. 4, we have plotted the values of this factor against *m*. The dots and

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(17) Brown and MacInnes, THIS JOURNAL, **57**, 1356 (1935).

(18) Brönsted, *ibid.*, **44**, 877 (1922); **45**, 2898 (1923).

the solid lines represent the results of this investigation. It is apparent that at higher concentrations, 0.3 *M* and above, $(\alpha_1 + \alpha_2)$ is finite and there is no definite indication that this quantity approaches zero as the concentration decreases. Since Brönsted's theory was never intended to apply to concentrations greater than 0.1 *M*, these results do not seriously contradict the theory although they definitely show that it is not valid at the higher concentrations.

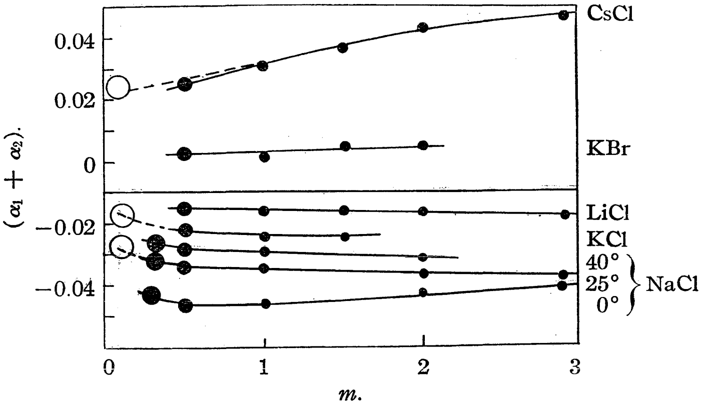

Fig. 4.—Plots of $(\alpha_1 + \alpha_2)$ *vs.* *m*.

It is apparent (Fig. 4) that the values of $(\alpha_1 + \alpha_2)$ of cesium chloride and sodium chloride mixtures differ considerably. The most recent results for activity coefficients at 0.1 *M* determined since these calculations were made conform to this distribution. According to our earlier discussion $\log \gamma_{1(0)} - \log \gamma_{2(0)} = \alpha_1 - \alpha_2$ if we neglect the small difference between $(\alpha_1 - \alpha_2)$ and *B*. Harned and Ehlers obtained −0.0989, and Randall and Young[19] obtained −0.0993 for $\log \gamma_{0.1}$ for hydrochloric acid at 25°. If we employ the mean of these results, and Brown and MacInnes' value of −0.1088 for $\log \gamma_{0.1}$ of sodium chloride, then $(\alpha_1 - \alpha_2) = 0.0097$. From Güntelberg's value of α_1 at 20°, we obtain 0.040 at 25°. Hence, $-\alpha_2 = 0.057$ and $(\alpha_1 + \alpha_2) = -0.017$. For cesium chloride, we use Robinson and Sinclair's value of 0.1238 for $-\log \gamma_{0.1}$. Güntelberg obtained 0.146 for α_1 at 20°. From the temperature coefficient of this quantity, we find that $\alpha_1 = 0.143$ at 25°. Therefore $-\alpha_2 = 0.1040$, and $(\alpha_1 + \alpha_2) = 0.0039$. If we introduce a correction due to the fact that $B > (\alpha_1 - \alpha_2)$, then the value of $(\alpha_1 + \alpha_2)$ is even higher. In the same manner by employing the values of $\log \gamma$ and α_1 given in Table II, we obtain 0.013 and −0.007 for $(\alpha_1 + \alpha_2)$ of the lithium and potassium chloride mixtures, respectively, which appear to lie between the values obtained for the other two salts. The circles in Fig. 4 represent these values with the exception of that of the lithium chloride mixtures, and the dashed lines a prolongation of the plots obtained from our data. Since a computation at this concentration is very sensitive, care must be exercised in drawing conclusions from the results. However, we believe that the spread and distribution of the results are significant. In the case of sodium chloride $(\alpha_1 + \alpha_2)$ seems to tend toward zero but it is too early to draw any conclusion regarding this matter.

These observations lead to some interesting alternative propositions. (1) If $\log \gamma$ varies exactly linearly with *m* at constant total molality (Eq. 1), then ϕ does not and specific effects between ions of like sign may occur. If this is the case, $(\alpha_1 + \alpha_2)$ may be finite when $m = 0$. (2) If $\log \gamma$ does not vary linearly with *m* at constant total molality, then the present results require that ϕ does not. Since $\log \gamma_1$ has been shown to obey the linear relationship within very narrow limits, we conclude that in the case of these mixtures any departure from a linear variation is greater for ϕ than for $\log \gamma$.

All our results depend upon the assumption that α_2 is constant, or that the second of the relations in equation (1) is valid. If this is not true, then the above indications of specific effects between ions of like sign may be subject to another interpretation. For instance, Scatchard and Prentiss have extended the theory of specific ionic interaction to terms including higher powers of the concentration. Without abandoning the fundamental postulate of the theory, they arrive at the conclusion that "neither $\log \gamma$ or ϕ need vary linearly except in very dilute solutions, and that α_1 need equal $-\alpha_2$ only at zero concentration."[20,21] It is possible that such an extended theory will account for the deviation from the original theory and exclude specific interaction between ions of like sign.

Summary

1. Measurements of the cells $H_2 \mid HCl(0.01), NaCl(m) \mid AgCl \mid Ag$ from 0 to 60° have been reported.

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(19) Randall and Young, THIS JOURNAL, **50**, 989 (1928).

(20) Quoted from a private communication from Prof. George Scatchard.

(21) Scatchard and Prentiss, THIS JOURNAL, **56**, 2320 (1934).

2. From these and other suitable data, the values of α_1 and α_2 defined by equation (1) have been computed for a number of halide acid-halide mixtures.

3. It has been shown that the empirical rules of Åkerlöf and Thomas that (1) B is a constant and does not vary with the concentration, (2) α_1 and α_2 are not functions of m, are not valid. Neither B, α_1 or α_2 can be regarded as constants characteristic of a given pair of electrolytes.

4. The results have been discussed in relation to the original and extended theory of specific ionic interaction.

NEW HAVEN, CONN. RECEIVED JUNE 18, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Thermodynamics of Ionized Water in Sodium Chloride Solutions

BY HERBERT S. HARNED AND GEORGE E. MANNWEILER[1]

From measurements of the cells

$$H_2 \mid MOH(m_0), MX(m) \mid AgX \mid Ag, \text{ and} \qquad (A)$$

$$H_2 \mid HX(m_0), MX(m) \mid AgX \mid Ag \qquad (B)$$

$$M = Li, Na, K\ X = Cl^-, Br^-$$

the thermodynamic properties of the ions of water in potassium and lithium chloride solutions, and potassium and sodium bromide solutions, have been studied over wide temperature and concentration ranges.[2] The only determination of the activity coefficient and dissociation of water in sodium chloride solutions is contained in the contribution by Harned where the method of determining these quantities from cells without liquid junction was first developed.[3] Since these results were obtained from scattered data at 25° only, they have been redetermined from measurements of the above cells by employing a consistent and more accurate technique. Further, the results have been extended to cover a temperature range from 0 to 60°. From these results we have computed: (1) the ionization constant of water; (2) the ionic activity coefficient product of water in sodium chloride solutions; (3) the ionization of water in sodium chloride solutions; and (4) the heat of ionization of water and the partial molal heat of ionization of water in sodium chloride solutions.

Experimental Results

The electromotive forces of cells of types (A) and (B) may be expressed as functions of the temperature by means of the quadratic equations

$$E_A = E_{A(25)} + c\,(t - 25) + d\,(t - 25)^2 \qquad (1)$$

$$E_B = E_{B(25)} + a\,(t - 25) + b\,(t - 25)^2 \qquad (2)$$

The values of $E_{B(25)}$, a, and b are given in Table I of an earlier investigation[4] and the values of $E_{A(25)}$, c, and d are contained in Table I of this communication. Measurements were made by a technique similar to that employed by Harned and Hamer[2] and Harned and Copson.[2] The experimental results were the mean of three cells which were measured at the concentrations specified from 0 to 60° at 5° intervals. The deviations from the mean were ±0.04 mv. and the experimental results smoothed to round concentrations agree with those computed by equation (2) to within approximately this limit.

TABLE I

$E_{A(25)}$ AND CONSTANTS OF EQUATION (1), $m_0 = 0.01$

μ	$E_{A(25)}$	$c \times 10^6$	$d \times 10^6$
0.02	1.05027	167.4	0.28
.03	1.03244	109.25	.25
.05	1.00887	34.65	.13
.11	0.99098	− 27.40	.12
.21	.97303	− 87.45	.11
.51	.94905	−162.00	.0
1.01	.93055	−225.35	− .07
2.01	.91132	−279.5	− .35
3.01	.89950	−309.1	− .62

The Ionization Constant of Water, the Ionic Activity Coefficient and Dissociation of Water in Sodium Chloride Solutions.—The ionization constant of water was determined from these results by the two methods developed by Harned and Hamer. The equation for the cells of type A may be written in the form

$$E_A - E_0 + \frac{RT}{NF}\ln\frac{m}{m_0} = \frac{RT}{NF}\ln\frac{\gamma_H\gamma_{OH}}{a_{H_2O}} - \frac{RT}{NF}\ln\gamma_H\gamma_{Cl} - \frac{RT}{NF}\ln K \qquad (3)$$

which corresponds to equation (4) of Harned and Hamer. By employing the values of molal po-

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[1] The present communication contains material from a thesis presented by George E. Mannweiler to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Master of Science, June, 1934.

[2] Harned and Hamer, THIS JOURNAL, **55**, 2194 (1933); (b) **55**, 4496 (1933); Harned and Copson, *ibid.*, **55**, 2206 (1933).

[3] Harned, *ibid.*, **47**, 930 (1925).

[4] Harned, *ibid.*, **57**, 1865 (1935).

tential of the silver chloride electrode, E_0, determined by Harned and Ehlers,[5] the left side of this equation was evaluated. This quantity was plotted against μ and extrapolated to zero μ, at which point it is equal to $(-RT/NF \ln K)$. From these values K was computed at 5° temperature intervals from 0 to 60°. This extrapolation is unusually favorable for the evaluation of K since the plots are straight lines with small slopes.

As a check of this determination, we have also evaluated K from our measurements of both cells of types A and B. This procedure does not require the values of E_0 determined by others and consequently serves as a good test of the general accuracy of the data. From the equations of the cells and the limiting equation of the theory of Debye and Hückel to which a term linear with μ is added, the equation

$$E_A - E_B - \frac{RT}{NF}\ln\frac{m_0^2\,(m + m_0)}{m} + \frac{RT}{NF}\,\frac{5.908 \times 10^6}{D^{3/2}\,T^{3/2}}\sqrt{2\mu} = \beta\mu - \frac{RT}{NF}\ln K \qquad (4)$$

may be derived. This equation corresponds to equation (16) given by Harned and Hamer. The left-hand member of this equation was evaluated, plotted against μ, and from its value at $\mu = 0$, K was computed. This method is not as favorable for the determination of K as the one previously described since the plots possess a greater slope. However, a good extrapolation was possible and the results checked those obtained by the first method within the experimental error. The values of the ionization constant thus obtained are in close agreement with the results of Harned and Hamer with the exception of the value at 0° where the difference was 1%. At the temperatures of 20 to 50° inclusive, the agreement is 0.1% or better, at 5, 10, 15, 55 and 60°, the agreement is 0.3 to 0.4%. The results at the designated temperatures are given in Table II.

TABLE II

THE IONIC ACTIVITY COEFFICIENT PRODUCT OF WATER IN SODIUM CHLORIDE SOLUTIONS, $\gamma_H\gamma_{OH}/a_{H_2O}$

μ	0	10	20	25	30	40	50	60
0.02	0.761	0.763	0.760	0.759	0.759	0.752	0.751	0.751
.03	.723	.732	.726	.725	.725	.717	.715	710
.06	.680	.666	.664	.664	.663	.653	.649	.643
.11	.610	.613	.608	.607	.605	.595	.589	.583
.21	.560	.559	.557	.556	.553	.544	.538	.532
.51	.517	.520	.516	.514	.513	.502	.497	.488
1.01	.540	.542	.537	.535	.531	.517	.507	.495
2.01	.691	.699	.691	686	.681	.654	.629	.600
3.01	.971	.985	.972	.962	.948	.898	.855	.791
$K \times 10^{14}$	.1134	.2919	.681	1.007	1.470	2.914	5.482	9.651

By substitution of these values of K and the values of $\gamma_H\gamma_{Cl}$ in sodium chloride solutions computed from the electromotive forces of cells of type B in equation (3), the ionic activity coefficient product of water, $\gamma_H\gamma_{OH}/a_{H_2O}$, may be computed since the left side of this equation is known. The values of this quantity are given at convenient temperatures in Table II. Values at intermediate temperatures may be interpolated.

Because of the importance of this quantity for the study of ionic equilibria in aqueous solutions, we have given at convenient salt concentrations in Table III the values recently determined at 25° for cases of a number of uni-univalent salt solutions. Although on the whole the agreement with the results of Harned, Harned and Swindells, and Harned and James[6] is good when allowance is made for the differences in reference values, the recent results are the more accurate since a simpler method is used which permits better extrapolations.

TABLE III

THE VALUES OF [LOG $(\gamma_H\gamma_{OH}/a_{H_2O}) + 1$] OF UNI-UNIVALENT HALIDE SOLUTIONS AT 25°

$\mu^{1/2}$	CsCl[a]	KCl[b]	NaCl	LiCl[c]	KBr[d]	NaBr[d]	LiBr[e]
0.04	0.962	0.962	0.962	0.962	0.962	0.962	0.962
.07	.935	.935	.935	.935	.935	.935	.935
.1	.912	.912	.912	.912	.912	.912	.912
.2	.848	.847	.845	.839	.847	.845	.839
.3	.810	.802	.797	.777	.804	.797	.777
.4	.783	.771	.760	.728	.773	.761	.728
.5	.761	.747	.735	.690	.749	.738	.690
.6	.746	.732	.719	.662	.733	.723	.662
.7	.741	.727	.711	.640	.726	.716	.641
.8	.748	.735	.710	.624	.732	.715	.626
.9	.763	.750	.716	.611	.747	.721	.614
1.0	.785	.769	.728	.602	.766	.734	.606
1.2	..	.819	.772	.598	.811	.779	.610
1.4	..	.891	.838	.612	.874	.842	..
1.7	..	1.010	.966	.664	.980	.953	..
2.0	..	..	..	.746	..	..	..

[a] Harned and Schupp, Jr., THIS JOURNAL, **52**, 3892 (1930). [b] Harned and Hamer, *ibid.*, **55**, 2194 (1933). [c] Harned and Copson, *ibid.*, **55**, 2206 (1933). [d] Harned and Hamer, *ibid.*, **55**, 4496 (1933). [e] Vance, *ibid.*, **55**, 4518 (1933).

There is one result characteristic of this quantity which is of interest. In Fig. 1, we have plotted [log $(\gamma_H\gamma_{OH}/a_{H_2O}) + 1$] against the quantity $\Sigma(1/a)$, or $(1/a_+ + 1/a_-)$ at concentrations of $\mu^{1/2}$ equal to 0.5 and 1. The ionic radii employed were taken from the values derived by Pauling[7] from crystallographic data for all ions except hydrogen ion. In the latter case, Bragg's[8]

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(5) Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933).

(6) Harned, *ibid.*, **47**, 930 (1925); Harned and Swindells, *ibid.*, **48**, 126 (1926); Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926).

(7) Pauling, THIS JOURNAL, **49**, 765 (1927).

(8) Bragg, *Phil. Mag.*, [6] **40**, 169 (1920).

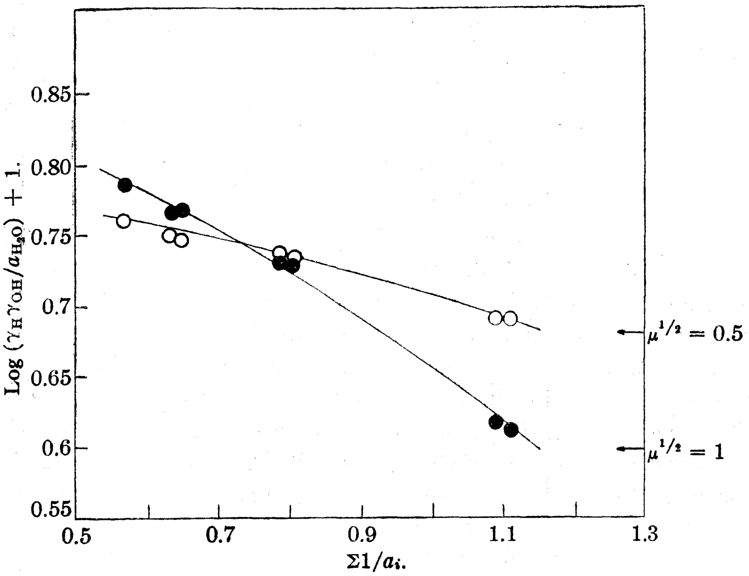


Fig. 1.—Plots of [log $(\gamma_H\gamma_{OH}/a_{H_2O}) + 1$] against $\Sigma 1/a_i$ at constant molality.

value was employed. $\Sigma 1/a$ was found to be 1.09, 1.11, 0.78, 0.80, 0.63, 0.65 and 0.57 for lithium bromide and chloride, sodium bromide and chloride, potassium bromide and chloride, and cesium chloride, respectively. The values are in the order $\Sigma 1/a$. Since the curves drawn through the points show only a slight curvature and since this result must be regarded as a rough approximation, we may represent it by a linear equation. Thus

$$\log \frac{\gamma_H\gamma_{OH}}{a_{H_2O}} = \log \frac{K}{m_H m_{OH}} = A - B\Sigma \frac{1}{a}; \quad [\mu = \text{constant}] \quad (5)$$

where K is the thermodynamic ionization constant, m_H and m_{OH} the molalities of the ions, and A and B are positive constants. Consequently

$$\log m_H m_{OH} = C + B\Sigma 1/a \quad (6)$$

where C is a constant. Thus, the smaller the value of $\Sigma 1/a$ for the ions of the salt, the greater the ionization of the solvent. This result is in the expected direction. The value of $B/\mu^{1/2}$ is a function of μ.

The Total Heat of Ionization of Water in Sodium Chloride Solutions

As shown by Harned and Hamer,[2b] the total heat of ionization of water may be computed from these results by the equation

$$\Delta H = -F(E_B - E_A)_{25} + FT(A) + F[(A) - 2T(B)]\ (t - 25) + F(B)\ (t - 25)^2 \quad (7)$$

where $(E_B - E_A)_{25}$ are the differences in electromotive forces of the cells at 25° and at a given concentration, t is °C., (A) equals $(c-a)$, and (B) equals $(d-b)$. a, b, c, and d are the constants of equations (1) and (2). The results may be expressed within the experimental error, estimated to be of the order of ±50 cal. or ±0.4%, by the equation

$$\Delta H = \Delta H_i + \omega\mu^{1/2} \quad (8)$$

The values of ΔH_i obtained by extrapolation agreed with those of Harned and Hamer to within this limit from 25 to 60°. At the lower temperatures the values obtained were about 80 cal. greater than those given by Harned and Hamer. The average value of ΔH_i is well represented by the equation

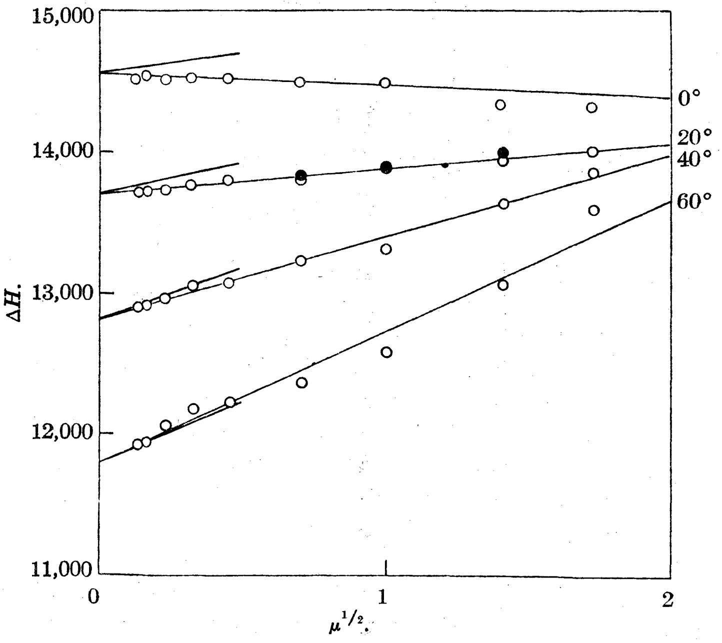


Fig. 2.—Plots of the total heat of ionization of water in sodium chloride solutions against $\mu^{1/2}$.

$$\Delta H_i = 20{,}182 + 0.026117T - 0.078067T^2 + 0.0000079127T^3 \quad (9)$$

In Table IV, the values of ω obtained from plots of ΔH *versus* $\mu^{1/2}$ are given at the temperatures designated.

Table IV

Values of the Constant of Equation (8)

t	ω	t	ω	t	ω
0	−40	25	290	50	700
5	0	30	370	55	780
10	50	35	460	60	860
15	130	40	550		
20	210	45	640		

In Fig. 2, we have plotted ΔH against $\mu^{1/2}$ at 0, 20, 40 and 60°. We have also indicated the limiting slope of the Debye and Hückel theory for the relative partial molal heat content of the ions of water. Our results should approach these slopes in very dilute solution ($m = 0.001$ or less). Since they cannot be extended to low dilutions with a high accuracy, no attempt has been made to employ the limiting laws for the purpose of extrapolation. As a confirmation of the correct character of the results at higher concentrations, we may compare our data with values of the same quantity determined from calorimetric measurements of the heat of neutralization of hydrochloric acid and sodium hydroxide by Richards and Rowe[9] at 20°. Their results are represented by the dots in Fig. 2. The agreement is within the limit of 40 cal.

Summary

1. Measurements of the cells

H_2 | NaOH (0.01), NaCl (m) | AgCl | Ag

H_2 | HCl (0.01), NaCl (m) | AgCl | Ag

in aqueous solution from 0 to 60° have been made.

2. From these the value of the ionic activity coefficient product of water in sodium chloride solutions has been computed.

3. It is shown that the logarithm of the ionization in alkaline halide solutious, $\log m_{\mathrm{H}}m_{\mathrm{OH}}$, at a given concentration varies nearly linearly with the sum of the reciprocal of the ionic radii. This is only a rough approximation but serves to show that ions of smaller radii cause the greater dissociation of the solvent.

4. The total heat content of the ionization of water and the relative partial molal heat content of the hydrogen and hydroxyl ions in sodium chloride solutions has been determined from 0 to 60°. Good agreement with the calorimetric heat of neutralization is found at 20°.

New Haven, Connecticut Received June 18, 1935

[9] Richards and Rowe, This Journal, **44**, 684 (1922).

[Contribution from the Department of Biological Chemistry, Columbia University]

Studies of Crystalline Vitamin B_1. XII. The Sulfur-Containing Moiety

By H. T. Clarke and S. Gurin

The chemical investigation of vitamin B_1 was undertaken in this Laboratory on the invitation of Mr. R. R. Williams, who acquainted us with the sulfite cleavage reaction[1] and kindly furnished a supply of the crystalline vitamin and its basic cleavage product. Early in the course of our work we were able to suggest the presence of a thiazole nucleus in vitamin B_1, and this suggestion was incorporated by Williams in his tentative formula.[2]

In view of the presence of sulfur in the vitamin molecule,[3] our attention was primarily directed toward elucidation of the manner in which this element is combined, by the use of methods recently developed[4] for the study of sulfur in proteins. In the preliminary stages of this investigation, the recognition of the vitamin and its basic cleavage product as derivatives of thiazole was greatly aided by a study of their behavior toward alkaline plumbite and toward bromine water. Striking contrasts were observed between the two compounds with both reagents. When heated with the lead reagent, the vitamin yields lead sulfide relatively rapidly, while the thiazole base gives a visible precipitate only after several hours. Conversely, on treatment with bromine the base is largely oxidized to sulfuric acid under conditions in which the vitamin remains almost entirely unchanged and suffers little or no loss of physiological activity. On the basis of considerations discussed elsewhere,[4] the conclusion was almost inescapable that the sulfur atom in the base is linked to two carbon atoms in a structure of which the carbon groupings are more susceptible to oxidative attack than is the sulfur.

While this study was in progress, it was re-

[1] Williams, Waterman, Keresztesy and Buchman, This Journal, **57**, 536 (1935).

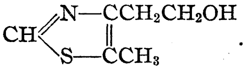
[2] Williams, *ibid.*, **57**, 229 (1935).

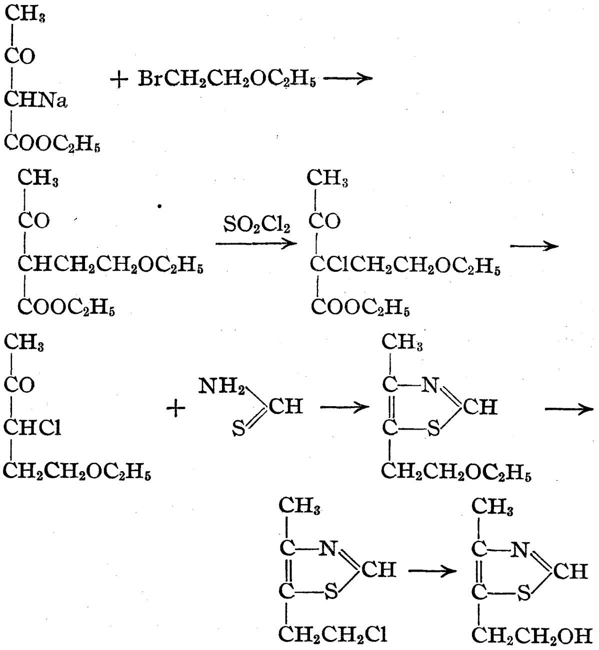
[3] Windaus, Tschesche, Ruhkopf, Laquer and Schultz, *Z. physiol. Chem.*, **204**, 123 (1932).

[4] Blumenthal and Clarke, *J. Biol. Chem.*, **110**, 343 (1935).

ported by Windaus, Tschesche and Grewe[5] that the vitamin could be split by the action of nitric acid into two fragments of which one contained the atom of sulfur originally present in the vitamin. Buchman, Williams and Keresztesy[6] then established the close relationship of the basic cleavage product to the acid $C_5H_5O_2NS$ of Windaus by demonstrating the formation of the acid from the base by oxidation with nitric acid.

A striking feature of this acid is its property of yielding lead sulfide on treatment with alkaline plumbite,[5] a clear indication of the bivalent condition of the sulfur. This resistance of sulfur to oxidation by nitric acid is characteristic of the thiazole nucleus; Roubleff[7] found dimethylthiazole-carboxylic acid to be stable toward boiling nitric acid, though other oxidizing agents broke down the ring with formation of sulfuric acid. Among the descriptions of the known methylthiazole-carboxylic acids, that of the 4,5 isomer[8] seemed to agree most closely with the observed properties of the acid prepared from the vitamin. Synthesis of this compound by an application of the simplified procedure of Willstätter and Wirth,[9] followed by a comparison of the methyl esters, established the identity of the two. The absorption spectra of the acids, determined in this Laboratory by Mr. A. E. Ruehle, showed almost exact coincidence.[10]

On oxidation with nitric acid, the basic cleavage product of the vitamin loses one carbon atom,[6] the resulting carboxyl group being derived from a hydroxyethyl group. The base may therefore be assigned the constitution  $\mathrm{CH}\left\langle\begin{matrix}\mathrm{N{-}CCH_2CH_2OH}\\ \| \\ \mathrm{S{-}CCH_3}\end{matrix}\right.$. The position of the hydroxyl group was inferred by Buchman, Williams and Keresztesy[6] from the optical inactivity and failure of the iodoform test; it can be rigorously established only by synthesis.[11] This has been accomplished by the accompanying scheme.



The last two products were found to be identical with the corresponding compounds derived from vitamin B. Attempts to employ ethylene chlorohydrin or β-chloroethyl acetate in the first step were unsuccessful. In the second step, reliance was placed on the specific action of sulfuryl chloride, which causes the introduction of chlorine exclusively at the α position in acetoacetic esters.

Reference has been made above to the contrasting behavior of the vitamin and the thiazole cleavage product toward plumbite and bromine. Precisely similar differences obtain with synthetic thiazoles and their quaternary salts; the former yield lead sulfide with difficulty and sulfate readily, the latter yield lead sulfide relatively rapidly[12] and sulfate slowly or not at all. This parallelism supports the idea[1] that in vitamin B_1 the thiazole moiety exists in the form of a quaternary salt.

This view is strengthened by the results obtained by Birch and Harris,[13] Moggridge and Ogston[14] and Williams and Ruehle[15] in electrometric titrations of the vitamin hydrochloride. These indicate reversible reaction with three instead of the anticipated two equivalents of alkali, the extra equivalent reacting at around *p*H 9, as if a pseudo acid were formed. 4-Methyl-

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(5) Windaus, Tschesche and Grewe, *Z. physiol. Chem.*, **228**, 27 (1934).

(6) Buchman, Williams and Keresztesy, THIS JOURNAL, **57**, 1849 (1935).

(7) Roubleff, *Ann.*, **259**, 253 (1890).

(8) Wohmann, *ibid.*, **259**, 299 (1890).

(9) Willstätter and Wirth, *Ber.*, **42**, 1908 (1909).

(10) Ruehle, THIS JOURNAL **57**, 1887 (1935).

(11) At the New York Meeting of the Society (April, 1935) Dr. E. R. Buchman announced the synthesis of the base by condensation of brominated acetopropyl alcohol with thioformamide.

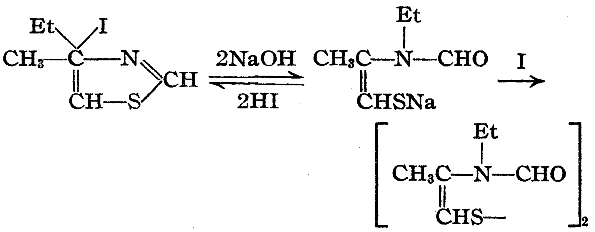
(12) The methylthiazole-carboxylic acid forms an exception to this generalization, in that its response to plumbite is nearly as rapid as that of the quaternary thiazolium salts. This effect is undoubtedly a reflection of the influence of the carboxylic group, which largely determines the instability to alkali in the case of cysteine and its derivatives.

(13) Birch and Harris, *Nature*, **135**, 654 (1935).

(14) Moggridge and Ogston, *Biochem. J.*, **29**, 866 (1935).

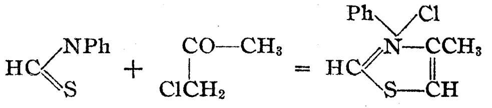
(15) Williams and Ruehle, THIS JOURNAL, **57**, 1856 (1935).

thiazole ethiodide behaves in a strictly analogous fashion.[15] We find that when this substance is treated with two equivalents of alkali in dilute solution, it acquires the ability to reduce one equivalent of iodine. The resulting product, which contains no iodine and is devoid of basic properties, is also formed by the action of air upon an alkaline solution of 4-methylthiazole ethiodide. Mills, Clark and Aeschlimann[16] have shown that alkali reversibly opens the thiazole ring in benzothiazole methiodide, with the formation of a sulfhydryl compound. It seems possible that a similar reaction occurs with the simple quaternary thiazolium base



Alkaline solutions of the vitamin also reduce iodine, but (possibly owing to side reactions attributable to the pyrimidine moiety) in considerably larger proportions. These questions are under investigation.

The reaction between vitamin B_1 and sulfite appears to be a function of the pyrimidine portion of the molecule, for attempts to regenerate thiazole bases from their ethiodides by the action of sulfite were uniformly unsuccessful; nor was cleavage under the same conditions observed with N-phenylthiazolium salts. The readiness with which this type of salt is synthesized



by the action of chloroacetone upon thioacylanilides is worthy of attention. These compounds, like vitamin B_1 and the thiazole ethiodides, respond readily to the alkaline plumbite test but not to that with bromine.

It seems probable that the opening of the ring by the action of alkali upon thiazolium salts is responsible for the readiness with which vitamin B_1 and other quaternary thiazole derivatives yield lead sulfide upon treatment with plumbite. The free thiazole bases presumably exist in the ammonium form to only a minute extent in the presence of alkali, and it is therefore not surprising that they break down extremely slowly under the experimental conditions.

Experimental

Action of Bromine on Vitamin B_1.—The extent to which sulfate is formed from the vitamin hydrochloride by bromine depends largely upon the concentration, as well as upon the temperature.

No sulfate is formed from relatively concentrated solutions. To a solution of 5.685 mg. of vitamin hydrochloride in 0.2 cc. of water bromine vapor was added by aspiration. A yellow, oily precipitate formed; the mixture was heated in boiling water, when the oil dissolved and the bromine escaped. This process was repeated twice. The resulting solution gave no precipitate with barium chloride. On heating with alkaline plumbite a black precipitate formed.

A solution of 3.07 mg. of vitamin hydrochloride in 1 cc. of water containing a visible excess of bromine was allowed to stand at room temperature for two hours, then warmed on the water-bath. On addition of barium chloride, 0.29 mg. of barium sulfate precipitated. This corresponds to 13.4% of the sulfur. In a similar experiment in which the warming was omitted, only 4.9% of the sulfur was converted into sulfate. When, on the other hand, a solution of 6.66 mg. of vitamin hydrochloride in 2.5 cc. of water was heated with excess of bromine for six hours at about 95°, the yield of sulfate was 71%.

Action of Iodine upon Vitamin B_1.—Addition of iodine in potassium iodide to solutions of the vitamin hydrochloride caused, even in very high dilutions, the precipitation of a resinous addition product which is almost insoluble in water or dilute mineral acid, readily soluble in alcohol, but not in chloroform. It dissociates on shaking with water and ether, the iodine passing into the ether; the vitamin was found, with unimpaired physiological activity, in the aqueous phase. No sulfate was produced.

Action of Alkaline Plumbite upon Vitamin B_1.—To 5.62 mg. of the vitamin hydrochloride were added 0.1 cc. of 10% lead acetate solution and 1 cc. of 10% sodium hydroxide. The clear, yellow solution was heated in a sealed tube under nitrogen at 90–95°. Precipitation of lead sulfide became apparent almost immediately, and appeared complete at the end of forty hours. After seventy-two hours the precipitate was collected and oxidized; it yielded 3.28 mg. of barium sulfate (80% of the theoretical amount). In a similar experiment, a 61% yield of sulfate was obtained after three hours' heating.

Action of Bromine upon $C_6H_9ONS \cdot HCl$.—A solution of 5.87 mg. of the hydrochloride of the basic cleavage product of the vitamin in 1 cc. of water was treated with bromine vapor as above. After being allowed to stand for twenty hours at room temperature, barium chloride was added: the resulting barium sulfate weighed 5.60 mg., corresponding to 73.3% of the sulfur. The supernatant solution was again treated with bromine; after twenty-four hours a further 0.23 mg. of barium sulfate had formed, bringing the total yield of sulfate to 76.4% of the theoretical amount. More sulfate was readily obtained from the supernatant by warming with bromine after neutralization with barium hydroxide.

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(16) Mills, Clark and Aeschlimann, *J. Chem. Soc.*, **123**, 2353 (1923).

Action of Alkaline Plumbite on C_6H_9ONS.—To 6.00 mg. of the hydrochloride was added 1 cc. of a solution prepared by adding to 10% lead acetate solution twice the volume of 2 *N* sodium hydroxide necessary to form a clear solution. The mixture was heated in a sealed tube at 95°. After sixteen hours a small amount of lead sulfide had precipitated. After one hundred and twelve hours, the contents were acidified with hydrochloric acid and the liberated hydrogen sulfide distilled into a solution of bromine in dilute alkali. The resulting sulfate yielded 2.01 mg. of barium sulfate, corresponding to 25.7% of the sulfur. The volatile base in the residual solution required 1.15 cc. of 0.01 *N* acid, corresponding to 34.5% of the nitrogen; on treatment with mercuric oxide according to the process of Weber and Wilson,[17] the base removed corresponded to 0.65 cc. of 0.01 *N* acid, whence the yield of ammonia was 19.5% of the theoretical. This figure is undoubtedly too low owing to incomplete reaction with the mercuric oxide.

In the ensuing account, the temperatures indicated are uncorrected.

4-Methylthiazole.—This substance, previously prepared by reduction of 4-methyl-2-oxythiazole[18] and by diazotization of 4-methyl-2-aminothiazole,[19] was more conveniently obtained by an adaptation of the method of Willstätter and Wirth.[9] A solution of 5 g. of crude thioformamide[20] in 20 cc. of absolute alcohol was boiled with 8 g. of chloroacetone for one hour under reflux. Some ammonium chloride was filtered off; the filtrate was made distinctly acid with hydrochloric acid and evaporated to dryness. The residue was made alkaline and distilled; the distillate was freed from moisture and ammonia by warming with solid potassium hydroxide. The product, amounting to 3–4 g., distilled at 130°.

On treatment with bromine, a dilute solution of the hydrochloride yielded a yellow oily precipitate, soluble in acetic acid or alcohol; sulfate is rapidly formed in the cold. When heated with alkaline plumbite in a sealed tube at 95°, lead sulfide is formed, but so slowly as to be perceptible only after about four hours.

The ethiodide, prepared by heating the base with twice its volume of ethyl iodide in a sealed tube for forty hours at 95°, crystallizes from absolute alcohol in colorless bars, m. p. 144.5°.

Anal. Calcd. for $C_6H_{10}NSI$: I, 49.77. Found: I, 49.94.

On treatment in aqueous solution with bromine it yields an oily precipitate, but no sulfate is formed in the cold. With plumbite at 95°, lead sulfide forms rapidly, and precipitation appears to be complete after three hours.

On adding platinic chloride to a solution of the base in 0.2 *N* hydrochloric acid, a precipitate separated slowly. This was recrystallized from 0.1 *N* hydrochloric acid in 50% alcohol. The composition of the product, which melted without decomposition at 198°, indicated that the platinichloride had lost the elements of hydrochloric acid.[21]

Anal. Calcd. for $C_8H_{12}N_2S_2Cl_4Pt$: Pt, 36.35; S, 11.95. Found: Pt, 35.90; S, 11.41; after a second recrystallization, Pt, 37.08; S, 12.16.

2,4-Dimethylthiazole.—The base, b. p. 140°, was prepared from thioacetamide and chloroacetone in the same manner as the 4-methylthiazole; the yield was twice as large. The ethiodide[22] melted with decomposition at 212°.

Anal. Calcd. for $C_7H_{12}NSI$: I, 47.18. Found: I, 47.76.

4-Methylthiazole-5-carboxylic Acid.—To a solution of 5 g. of thioformamide in 100 cc. of ether was added 14 g. of ethyl α-chloroacetoacetate.[23] The mixture was allowed to stand for ninety-six hours at 0–5°, during which time 8.5 g. of thiazole carboxylic ester hydrochloride separated in colorless needles. After washing with ether, this was dissolved in water; the solution was made alkaline to thymolphthalein and shaken with five 20-cc. portions of ether. The ethereal solution was dried with sodium sulfate and evaporated. The residue, which crystallized on chilling, was distilled under reduced pressure; b. p. 140° (12 mm.); yield, 5.0 g. of ethyl 4-methylthiazole-5-carboxylate,[24] m. p. 28°.

The ethyl ester was hydrolyzed by boiling a solution of 1.2 g. of it in 25 cc. of alcohol containing 1.4 g. of sodium hydroxide for fifteen minutes under reflux. The alcohol was evaporated under reduced pressure, and the residue, dissolved in 10 cc. of water, was acidified to *p*H 3–4 with concentrated hydrochloric acid. The resulting precipitate was twice recrystallized from 150-cc. portions of boiling water; yield, 0.8 g. of colorless bars which sublimed at 255°.

Anal. Calcd. for $C_5H_5O_2NS$: C, 41.93; H, 3.52; N, 9.78; S, 22.4. Found: C, 42.03; H, 3.59; N, 9.51; S, 22.55.

The methyl ester, prepared by adding ethereal diazomethane to a suspension of the acid in dry ether, and evaporating to dryness, formed needles which melted sharply at 75° without recrystallization.

Anal. Calcd. for $C_6H_7O_2NS$: C, 45.82; H, 4.49; N, 8.92; S, 20.4. Found: C, 45.90; H, 4.52; N, 8.61; S, 20.34.

The melting point was unchanged by admixture of the methyl ester of the acid[6] prepared from vitamin B_1.

As observed by Windaus, Tschesche and Grewe,[5] the acid readily yields lead sulfide and ammonia on heating with alkaline plumbite. At 95°, the precipitation of sulfide was noticeable after less than an hour; after forty-four hours the yield of ammonia was 95% of the theoretical amount. On treating a solution in 0.05 *N* hydrochloric acid with bromine, sulfate is formed very slowly in the cold but rapidly on warming.

Ethyl α-2-Ethoxyethylacetoacetate.—To a solution of 11.5 g. of sodium in 350 cc. of absolute alcohol 65 g. of ethyl acetoacetate was added; to the gently boiling solution there was added 84 g. of ethyl β-bromoethyl ether during one and one-half hours. Heating was continued for ten hours under reflux with stirring. A small amount

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(17) Weber and Wilson, *J. Biol. Chem.*, **35**, 385 (1918).

(18) Arapides, *Ann.*, **249**, 23 (1888).

(19) Popp, *ibid.*, **250**, 277 (1888).

(20) Gabriel, *Ber.*, **49**, 1115 (1916).

(21) An analogous change was observed in the case of thiazole by Willstätter and Wirth.[4]

(22) Fisher and Hamer, *J. Chem. Soc.*, 2509 (1930).

(23) Allihn, *Ber.*, **11**, 567 (1878).

(24) Wohmann, *Ann.*, **259**, 298 (1890).

of unreacted alkali was neutralized with alcoholic hydrogen chloride, the salts were precipitated with ether, and the filtrate evaporated under reduced pressure at room temperature. The residue, weighing 80 g., was fractionally distilled and the principal fraction collected at 85–90° (10 mm.). The yield was 56 g. (55% of the theoretical amount) of a colorless liquid.

Anal. Calcd. for $C_{10}H_{18}O_4$: C, 59.40; H, 8.91. Found: C, 59.20; H, 8.82.

Ethyl α-Chloro-α-2-ethoxyethylacetoacetate.—To 20.2 g. of ethyl α-2-ethoxyethylacetoacetate 15.2 g. of sulfuryl chloride was added, with stirring and ice-cooling, during thirty to forty minutes. Stirring was continued for an hour, while the temperature rose to 20–25°; 50 cc. of the ether was then added, and the mixture gently boiled for an hour to complete the evolution of sulfur dioxide and hydrogen chloride. The ether was distilled off and the residue fractionally distilled *in vacuo*. The first fraction (85–90° (12 mm.)), amounting to 6.7 g., consisted mainly of unchanged starting material; the principal fraction (115–118° (12 mm.)), weighing 15 g., was found by analysis to be not quite pure, but was not improved on further fractionation. It formed a colorless liquid with a pungent odor.

Anal. Calcd. for $C_{10}H_{17}O_4Cl$: Cl, 15.0. Found: Cl, 16.8.

Methyl α-Chloro-γ-ethoxypropyl Ketone.—A solution of 10 g. of the above chlorinated ester in a mixture of 20 cc. of acetic acid and 20 cc. of 15% aqueous sulfuric acid was boiled for four hours under reflux. Ethyl acetate and alcohol were then distilled off under slightly reduced pressure at 30–40°. A mixture of 20 cc. each of acetic acid and 15% sulfuric acid was added, and the whole again boiled for four hours. It was then diluted with an equal volume of water and shaken repeatedly with ether. After removal of moisture with sodium sulfate and evaporation of ether, the residue from the ethereal solution was distilled under reduced pressure; yield, 3.5 g. (50% of the theoretical amount), b. p. 72–73° (12 mm.).

Anal. Calcd. for $C_7H_{13}O_2Cl$: Cl, 21.6. Found: Cl, 22.7.

4-Methyl-5-β-ethoxyethylthiazole.—A mixture of 3.0 g. of the above chloroketone and 2.0 g. of thioformamide was allowed to stand for two days at 0–5° and was then warmed at 100° for one hour; 1.0 g. more of thioformamide was added and the mixture again heated for one hour. It was then dissolved in 10 cc. of water, acidified to Congo Red with concentrated hydrochloric acid, shaken repeatedly with ether, boiled to expel hydrogen sulfide, and made alkaline to thymolphthalein. After expelling the bulk of the ammonia by boiling under reflux, the volatile organic base was distilled out with steam. There was thus obtained 1.5 g. of a pale yellow oil, slightly soluble in water, miscible with alcohol and ether; b. p. 235° (with decomp.) by the capillary tube method of Emich.

No attempt was made to purify the base. It formed with platinic chloride a crystalline, sparingly soluble precipitate, consisting of orange needles, melting with decomposition at 154–155°.

Anal. Calcd. for $C_{16}H_{28}O_2N_2S_2Cl_6Pt$: S, 8.51; Pt, 25.95. Found: S, 8.69; Pt, 25.98.

On recrystallization from hot 50% acetone this changed, by loss of the elements of hydrogen chloride, into a nearly colorless, crystalline substance which melted without decomposition at 144–145°.

Anal. Calcd. for $C_{16}H_{26}O_2N_2S_2Cl_4Pt$: S, 9.42; Pt, 28.74. Found: S, 9.22; Pt, 27.8.

The base, on treatment with ethereal picric acid, yielded a sparingly soluble picrate, which after recrystallization from alcohol melted at 112°.

Anal. Calcd. for $C_{14}H_{16}O_8N_4S$: S, 8.00. Found: S, 8.02.

4-Methyl-5-β-chloroethylthiazole.—A solution of 0.627 g. of the ethoxy base in 5 cc. of concentrated hydrochloric acid was heated in a sealed tube for three hours at 150°. Ethyl chloride and excess hydrochloric acid were evaporated, and the residue was twice recrystallized from a mixture of absolute alcohol and ether; yield, 0.206 g.

Anal. Calcd. for $C_6H_8NSCl{\cdot}HCl$: N, 7.07; S, 16.16; Cl, 35.85; Cl^-, 17.93. Found: N, 7.32; S, 16.13; Cl, 35.55; Cl^-, 18.07.

The melting point, 127–128°, was unchanged on admixture of a sample (m. p. 130°) of the product originating[6] from vitamin B_1.

On treatment with picric acid in 50% alcohol, the hydrochloride yielded a sparingly soluble picrate, crystallizing in needles from absolute alcohol.

Anal. Calcd. for $C_{12}H_{11}O_7N_4SCl$: S, 8.19; Cl, 9.09. Found: S, 8.33; Cl, 9.04.

Its melting point, 138°, was unchanged on addition of the picrate (m. p. 139°) of the compound secured from the vitamin.

4-Methyl-5-β-hydroxyethylthiazole.—The mother liquor from the above hydrochloride was evaporated to dryness, dissolved in 5 cc. of water, heated in a sealed tube for four hours at 150°, and again evaporated to dryness. The hygroscopic, crystalline residue was recrystallized from a mixture of absolute alcohol with ether or dioxane; yield, 0.223 g.

Anal. Calcd. for $C_6H_9ONS{\cdot}HCl$: N, 7.80; S, 17.85; Cl, 19.74. Found: N, 7.89; S, 17.70; Cl, 19.90.

In crystalline form it was indistinguishable from the hydrochloride of the basic product from the vitamin.

A picrate separated on the addition of ethereal picric acid to the hydrochloride in alcohol. On recrystallization from absolute alcohol it melted at 162°.

Anal. Calcd. for $C_{12}H_{12}O_8N_4S$: N, 15.00; S, 8.60. Found: N, 15.05; S, 8.74.

The corresponding picrate originating from the vitamin melted at 162–163°; mixed m. p. 162–163°.

Action of Alkali and Iodine upon 4-Methylthiazole Ethiodide.—To a solution of 0.1244 g. of 4-methylthiazole ethiodide (4.88 millimole) in 10 cc. of water was added 13.1 cc. of 0.076 *N* sodium hydroxide. The colorless solution was titrated with 0.10 *N* iodine. On the addition of each drop, a red-brown precipitate formed which rapidly dissolved; 5.00 cc. was required (102% of the theoretical amount).

The solution, on being allowed to stand, deposited needles which after washing with water and recrystallizing from aqueous alcohol melted at 101–102°. Further crops were obtained by concentrating the mother liquors and recrystallizing; yield, 0.0578 g. The product is sparingly soluble in cold water and dilute hydrochloric acid, readily soluble in alcohol and in ether.

Anal. Calcd. for $C_{12}H_{20}O_2N_2S_2$: N, 9.72; S, 22.22. Found: N, 9.53; S, 22.36.

The same product was obtained by aeration: to a solution of 0.2 g. of the ethiodide in 10 cc. of water, 2 *N* sodium hydroxide was added until the *p*H was 10. A trace of ferrous sulfate was added and air was bubbled through the solution for forty hours. A yield of 0.072 g. of colorless needles, m. p. 101–102°, separated during the aeration; further quantities were obtained by extraction with ether.

2,4-Dimethyl-3-phenylthiazolium Salts.—A mixture of 7.0 g. of thioacetanilide, 5.7 g. of chloroacetone, and 5 cc. of absolute alcohol was boiled gently under reflux for one and one-half hours and then evaporated at 100°. The sirupy residue was repeatedly stirred with ether; the insoluble portion was dissolved in water and decolorized with charcoal. The chloride could not be crystallized; addition of picric acid caused the precipitation of an oil. Platinic chloride yielded a crystalline platinichloride, insoluble in water and in alcohol, which melted with decomposition at 245° after darkening at 240°.

Anal. Calcd. for $C_{22}H_{24}N_2S_2Cl_6Pt$: C, 33.49; H, 3.05; S, 8.13; Pt, 24.77. Found: C, 33.50; H, 2.80; S, 8.35; Pt, 24.86.

On adding potassium iodide in excess to an aqueous solution of the chloride, the iodide crystallized in the form of colorless needles, soluble in water, ethyl alcohol, chloroform, and ethylene chloride, sparingly soluble in butyl alcohol, insoluble in acetone, m. p. 210°.

Anal. Calcd. for $C_{11}H_{12}NSI$: C, 41.77; H, 3.79; N, 4.42; S, 10.09; I, 40.1. Found: C, 41.73; H, 3.49; N, 4.47; S, 10.19; I, 39.76.

No sulfate is formed by the action of bromine upon this substance, either in the cold or on warming for a short time. With alkaline plumbite, lead sulfide is rapidly produced at 95°.

4-Methyl-3-phenylthiazolium Iodide.—A mixture of 2.0 g. of thioformanilide and 5 cc. of chloroacetone was warmed to 50° for a few minutes; the resulting solution was allowed to cool to room temperature during two hours. On addition of ether, the product precipitated as a liquid. This was dissolved in 50 cc. of water, decolorized with charcoal, and treated with 3 g. of potassium iodide. The crystals which formed were recrystallized from water: colorless, rectangular plates, m. p. 241°.

Anal. Calcd. for $C_{10}H_{10}NSI$: S, 10.56; I, 41.9. Found: S, 10.67; I, 41.9.

The properties of this iodide closely resemble those of the 2,4-dimethyl compound.

Summary

1. The acid $C_5H_5O_2NS$ obtained by Windaus and collaborators by the action of nitric acid upon vitamin B_1 is shown to be 4-methylthiazole-5-carboxylic acid.

2. The basic product, obtained by Williams and his colleagues by treating vitamin B_1 with sulfite, is shown to be 4-methyl-5-β-hydroxyethylthiazole. This substance has been synthesized.

3. Experimental evidence is given in support of the view that the thiazole exists in the vitamin in the form of a quaternary salt.

NEW YORK, N. Y. RECEIVED JUNE 20, 1935

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

The Action of Hydrogen Bromide on the Nitrogen Afterglow

BY W. H. RODEBUSH AND M. L. SPEALMAN

Rodebush and Ewart[1] reported that the addition of hydrogen bromide to the nitrogen afterglow, produced in moist nitrogen by means of the electrodeless discharge, caused quenching of the nitrogen afterglow with the simultaneous production of a brilliant orange glow at the point where the gases mixed. When this orange light was viewed with a small spectroscope, it appeared to consist of the prominent red and yellow first positive bands of nitrogen, and an orange band which they also attributed to nitrogen. With hydrogen iodide they observed that the nitrogen afterglow was quenched, and that a blue afterglow was produced which extended from the point where the gases mixed to the liquid–air cooled trap of the mercury vapor diffusion pump. This blue afterglow was attributed to iodine. With both hydrogen bromide and hydrogen iodide, considerable quantities of the corresponding ammonium halide were produced in the reaction tube.

It has been suggested, however, that the orange bands might be bromine bands. If this were true, the reactions of hydrogen bromide and hydrogen iodide with active nitrogen would be entirely similar since there was no doubt that the spectrum obtained when hydrogen iodide is added to active nitrogen is due to the iodine molecule. The behavior in the two cases, however, is so different as to cast doubt upon this point of view. The

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[1] Ewart and Rodebush, THIS JOURNAL, **56**, 97 (1934).

luminescence of the hydrogen bromide is emitted in the immediate vicinity of the point of mixing, no matter how rapid the flow of gases. The primary reaction is presumably

$$N + HBr = NH + Br$$

Bromine molecules would therefore have to be formed by a following reaction which must be slow, and the concentration of bromine molecules must therefore be very low at the point of admission of the hydrogen bromide. It is possible for a bromine molecule to be formed by direct combination of an excited and unexcited bromine atom, but the probability of this process is extremely small.[2] A spectrographic investigation was the obvious solution to this question. The only difficulty is that, on account of the low intensities, it is not possible to use a very high dispersion.

Experimental

The electrical apparatus used with the electrodeless discharge was identical with that used in the work mentioned previously. A flowing system was used in which nitrogen was pumped through a Pyrex glass tube having a length of a meter or more, and an internal diameter of about 2.5 cm. The exciting coil was wrapped around this tube at the inlet end. The light from the discharge was prevented from reaching the slit of the spectrograph by surrounding the discharge region with a box, and by means of two right angle bends in the glass tube. The photographs were taken end-on of a 25-cm. section of the tube through either quartz or Pyrex glass windows. The connection to the vacuum pumps was about 3 cm. from the window. At the other end of this 25-cm. section of the tube the gas to be added to the nitrogen afterglow was introduced. A right angle bend in the reaction tube at this point served to prevent quite completely the superposition of the nitrogen afterglow spectrum on the photographic plate when something else was being photographed.

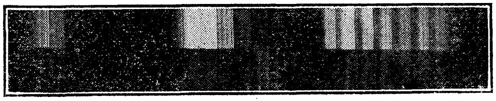

Fig. 1.

The upper photograph in Fig. 1 is a four-hour exposure of the nitrogen afterglow; the lower photograph is a two-hour exposure of the light produced on adding hydrogen bromide to the nitrogen afterglow. These pictures were taken consecutively on the same plate by using adjacent openings in the slide covering the slit of the spectrograph. Great care was taken not to jar the spectrograph or move the plate-holder during these exposures. A Hilger E-1 spectrograph having a glass optical system was used for these photographs. The slit width was about 0.05 mm.; the plate was a Type I-F Eastman spectroscopic plate.

Since the two exposures are of unequal length, no comparison of intensities may be made between them. The important point is that no bands appear in one exposure which are not present in the other. Under a low dispersion the first positive (afterglow) bands of nitrogen appear to have four or five heads. The effect of the presence of the hydrogen bromide is greatly to intensify two of these heads in certain bands while certain other bands as a whole are greatly weakened. The following tabulation of results may be made.

TABLE I

Transition (V′ − V″)	Effect	Transition (V′ − V″)	Effect
11–6	Greatly diminished intensity	13–9	Marked increase in intensity of two heads
10–5		9–5	
9–4		8–4	
12–8		7–3	
11–7		6–2	
10–6		12–9	
		11–8	
		10–7	
		9–6	

In connection with this action of hydrogen bromide it is of interest that bromine produced the same effects as hydrogen bromide on the distribution of intensities, so far as one could tell from spectrograms taken with a Bausch and Lomb quartz spectrograph. The Bausch and Lomb instrument, however, has a much lower dispersion than the Hilger spectrograph used. However, the similarity was so marked as to leave little doubt, and it therefore seems that it is the bromine atom rather than the hydrogen bromide molecule which is responsible for the effects observed.[3]

The blue afterglow produced by adding hydrogen iodide to the nitrogen afterglow was photographed with a Bausch and Lomb quartz spectrograph, and was found to consist of a continuum extending from 4800 to 2200 Å. interspersed with a great many broad, diffuse bands. Presumably this is a fluorescence spectrum of iodine.

Summary

The relative intensity of certain transitions in the nitrogen afterglow is greatly altered by the presence of hydrogen bromide or bromine, but the band spectrum of bromine was not observed.

URBANA, ILLINOIS RECEIVED JULY 2, 1935

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(2) Urey and Bates, *Phys. Rev.*, **34**, 1541 (1929).

(3) On adding Br_2 there was considerable attack of the glass with the production of pale yellow transparent flakes. The product was not identified, but was found to be insoluble in hot and cold dilute acid and alkali.

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, COLLEGE OF ENGINEERING, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Critical Increment of Ionic Reactions. Influence of Dielectric Constant and Ionic Strength

BY W. J. SVIRBELY AND J. C. WARNER

Due to the pronounced influence of the properties of the medium upon the rate of reactions involving ions[1] and the fact that in all solvents these properties are usually functions of the temperature, it seems certain that these factors should be considered in discussions of the critical increment or energy of activation[2] of reactions in solution.

Influence of Dielectric Constant.—Salt effects may be eliminated by considering the velocity constant at zero ionic strength (k^0). In ionic reactions, the factor having the most pronounced influence upon k^0 at constant temperature is very likely the dielectric constant of the solvent. With this assumption, we may write

$$\log k^0 = f\,(D,T)$$

and

$$\frac{\mathrm{d}\log k^0}{\mathrm{d}T} = \left(\frac{\partial \log k^0}{\partial T}\right)_D + \left(\frac{\partial \log k^0}{\partial D}\right)_T \frac{\mathrm{d}D}{\mathrm{d}T} \qquad (1)$$

Multiplying Eq. (1) by $2.3RT^2$, one obtains a relation between the critical increment in a solvent of fixed composition and a medium of constant dielectric constant.

$$(E^0)_{\text{fixed comp.}} = (E^{0*})_D + 2.3RT^2\left(\frac{\partial \log k^0}{\partial D}\right)_T \frac{\mathrm{d}D}{\mathrm{d}T} \qquad (2)$$

For all common solvents and solvent mixtures, the dielectric constant decreases with increasing temperature and Eq. (2) predicts that if an increase in D causes a decrease in k^0, E^0 will be greater than E^{0*}. In attempting to decide which value should be considered the true energy of activation, one encounters the fundamental difficulty of splitting the rate equation into the customary kinetic and energy of activation terms. The success of the Brönsted–Christiansen–Scatchard theory would lead one to believe that changes in k^0 due to change of D with T should be included in the kinetic term. One should, therefore, consider E^* the true energy of activation since it arises from $(\partial \log k^0/\partial T)_D$. To the best of our knowledge, all investigators in the field of solution kinetics have called E, which is obtained from $\mathrm{d}\log k^0/\mathrm{d}T$ or $\mathrm{d}\log k/\mathrm{d}T$, the energy of activation. However, Eq. (2) is independent of any theory and gives the relation between the two critical increments when rate constants depend only on D and T.

The dielectric constants of most solvents and solvent mixtures may be expressed[3] in the form

$$D = ae^{-bT} \qquad (3)$$

where a and b are empirical constants. Hence, at any given temperature

$$\mathrm{d}D/\mathrm{d}T = -bD \qquad (4)$$

From experiments to determine the variation of k^0 with D at constant temperature, one may evaluate $(\partial \log k^0/\partial D)_T$ and then calculate E^* from E using Eqs. (2) and (4). For reactions between two ions, the Scatchard theory[1a] yields the relations

$$\log k^0 = -\frac{\epsilon^2 Z_A Z_B}{2.3rkDT} + C \qquad (5)$$

and

$$\left(\frac{\partial \log k^0}{\partial D}\right)_T = \frac{\epsilon^2 Z_A Z_B}{2.3rkD^2T} \qquad (6)$$

This predicts for reactions between ions of unlike sign $E > E^*$ and for reactions between ions of like sign $E < E^*$.

The whole treatment may be made more general, but more difficult to apply, by obtaining E^* from $(\partial \log k^0/\partial T)_{x_1, x_2 \ldots x_n}$ where $x_1, x_2 \ldots x_n$ represent all properties of the solvent which influence the rate and vary with the temperature.

Influence of Ionic Strength.—Knowing the velocity constants, at fixed temperature and dielectric constant as a function of the ionic strength (μ), one may find a relation between the critical increments at zero ionic strength (E^0) and at some fixed ionic strength by methods similar to those used in the previous section. For reactions between ions and uncharged molecules, the primary salt effect is generally small, and E should not change much with ionic strength. For reactions between ions, the usually valid Brönsted–Christiansen relation may be used.

$$\log k = \log k^0 + \log \frac{f_A f_B}{f_X} \qquad (7)$$

Assuming that the ion activity coefficients may

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[1] (a) Scatchard, *Chem. Rev.*, **10**, 229 (1932); (b) Harned and Samaras, THIS JOURNAL, **54**, 1, 9 (1932); (c) Warner and Warrick, *ibid.*, **57**, 1491 (1935).

[2] (a) Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford University Press, 1933; (b) La Mer, *J. Chem. Phys.*, **1**, 289 (1933).

[3] Åkerlöf, THIS JOURNAL, **54**, 4125 (1932).

TABLE I

LIMITING VELOCITY CONSTANTS IN WATER AND IN MEDIA OF FIXED DIELECTRIC CONSTANT

	H_2O Variable D			CH_3OH-H_2O $D = 63.5$			CH_3OH-H_2O $D = 55.0$	
Temp., °C.	k^0_s	k^0_G	Wt. % CH_3OH	k^0_s	k^0_G	Wt. % CH_3OH	k^0_s	k_G
30	0.00625	0.00647	28.3	0.0159	0.0166	46.6	0.0304	0.0330
40	.0217	.0227	21.4	.0413	.0432	39.6	.0785	.0833
50	.0680	.0710	14.8	.106	.110	33.4	.192	.207
60	.205	.212	8.1	.263	.270	27.5	.468	.502
70	.584	.609	0.0	.584	.609	..	....	....

TABLE II

VELOCITY CONSTANTS AT $\sqrt{\mu} = 0.194$ IN WATER AND IN MEDIA OF FIXED DIELECTRIC CONSTANT

	H_2O Variable D			CH_3OH-H_2O $D = 63.5$			CH_3OH-H_2O $D = 55.0$	
Temp., °C.	k_1	k_2	k_3	k_1	k_2	k_3	k_1	k_2	k_3
30	0.00429	0.00432	0.00435	0.00990	0.00989	0.00963	0.0173	0.0175	0.0166
40	.0148	.0150	.0149	.0262	.0261	.0265	.0457	.0446	.0445
50	.0460	.0465	.0469	.0683	.....	.....	.114	.114	.113
60	.137	.137	.137	.172	.171	.170	.283	.283	.284
70	.388	.....	.385	.388	.....	.385	....	....	....

be expressed by the Debye theory, taking into account ion diameters, Eq. (7) becomes[1a,c]

$$\log k = \log k^0 + \frac{\epsilon^2 Z_A Z_B \kappa}{DkT(1 + \kappa b)} \qquad (8)$$

By differentiating Eq. (8) and multiplying by RT^2, one obtains a relation between E^0 and E at a fixed ionic strength. This treatment permits the interesting observation that for reactions between ions of unlike sign in solvents such as water, alcohols and water–alcohol mixtures, an increase in ionic strength should increase the critical increment in media of fixed dielectric constant but decrease it in solvents of fixed composition.

In the following sections these predictions concerning the influence of dielectric constant and ionic strength upon the critical increment will be compared with observed effects in the conversion of ammonium cyanate into urea.

Experimental

In this part, experiments are reported on the rate of reaction between ammonium ion and cyanate ion over the temperature range 30 to 70° in water (dielectric constant varying with temperature) and in mixtures of water with methyl alcohol at constant dielectric constants for the mixtures of 63.5 and 55.0. All materials were prepared or purified as described in previous papers,[4,1c] which also describe the procedure used in this investigation. All temperatures were checked against a thermometer recently calibrated by the Bureau of Standards. Thermostat temperatures were maintained constant within ±0.03°. Dielectric constants for water and for water–methyl alcohol mixtures were taken from the work of Åkerlöf.[3]

The limiting velocity constants (k^0) were calculated by Scatchard's[5] method which yields the integrated velocity equation[1c]

$$k^0 t = \left\{\frac{1 + 4A\sqrt{C}}{C}\right\} - \left\{\frac{1 + 4A\sqrt{C^0}}{C^0}\right\} \qquad (9)$$

A is the Debye–Hückel constant in $\ln f_i = -AZ_i^2 \sqrt{\mu}$. Average values of the limiting velocity constant (k^0_s) obtained by this method are listed in Table I. Deviations (δ) of the experimental value of $C/(1+4A\sqrt{C})$ from the value calculated from the average k^0_s are plotted against the experimental value of this function in Fig. 1.[1c] The filled circles represent values of $C^0/(1+4A\sqrt{C^0})$. Limiting velocity constants were also calculated from bimolecular constants determined by the method of slopes[1c,4] by Eq. (8) which applied to our reaction becomes

$$\log k^0 = \log k + \frac{3.63 \times 10^6 \sqrt{\mu}}{(TD)^{3/2} + 100.6\, DT \sqrt{\mu}} \qquad (10)$$

Average values of these limiting rate constants (k^0_G) are also given in Table I. In Table II, we give velocity constants at $\sqrt{\mu} = 0.194$ obtained by three methods: k_1 is obtained from k^0_s by the relation[1c]

$$k_1 = k^0_s/(1 + 2A\sqrt{\mu}) \qquad (11)$$

k_2 from k^0_G by Eq. (10), and k_3 is obtained directly from the slope[1c] of t (minutes) against $1/C$ at $\sqrt{\mu} = 0.194$. All data at 50° are taken from the work of Warner and Warrick[1c] and velocity constants at 70° were recalculated from the data of Warner and Stitt.[4] In Fig. 2, log k^0_s and log k_1

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(4) Warner and Stitt, THIS JOURNAL, **55**, 4807 (1933).

(5) Scatchard, *ibid.*, **52**, 52 (1930).

are plotted against $1/T$ for water and the methyl alcohol–water mixtures of $D = 63.5$ and 55.0. (Lines obtained by plotting $\log k_G^0$ against $1/T$ are parallel to those obtained using $\log k_s^0$.) In each case, the deviations of experimental points from the best straight line are almost within the possible experimental error. There is, however, some indication of a trend toward decreased slopes in the lower temperature range. The linear relations shown in Fig. 2 may be expressed by the equations

H_2O, variable D

$$\log k_s^0 = 14.77 - 23{,}580/4.58T$$
$$\log k_1 = 14.36 - 23{,}240/4.58T \qquad (12)$$

CH_3OH–H_2O, $D = 63.5$

$$\log k_s^0 = 11.79 - 18{,}840/4.58T$$
$$\log k_1 = 11.92 - 19{,}380/4.58T \qquad (13)$$

CH_3OH–H_2O, $D = 55.0$

$$\log k_s^0 = 11.79 - 18{,}500/4.58T$$
$$\log k_1 = 11.80 - 18{,}850/4.58T \qquad (14)$$

The difference between the zero ionic strength critical increments at the fixed dielectric constants of (Table III) 63.5 and 55.0 is within the possible experimental error of ±150 cal. Due to salting out there is some uncertainty as to the actual dielectric constants of these mixed solvents which may contribute to the difference in critical increments. However, these experiments do lend some support to the hypothesis that the critical increment of reactions between ions should be fairly independent of the dielectric constant when the dielectric constant does not change with temperature. There is a large and significant difference between the critical increment in water and in the media of fixed dielectric constant. These differences are compared with the difference calculated by Eq. (2) in Table III. Eq. (2) applied to the conversion of ammonium cyanate into urea becomes

$$(E^0)_{H_2O} - E^{0*} = \frac{1050\,T}{D} \qquad (15)$$

In obtaining Eq. (15), $(\partial \log k_s^0/\partial D)_T$ is the experimental limiting slope of $\log k_s^0$ against D in CH_3OH–H_2O mixtures. dD/dT for water is taken from the work of Åkerlöf.[3] Since D decreases with increase in T, Eqs. (2) and (15) imply that if E^{0*} is constant $(E^0)_{H_2O}$ will increase with T. Unfortunately our experiments are not sufficiently precise to test this implication. Eq. (2) also predicts that E^0 will change from one solvent of fixed composition to another through changes in $(\partial \log k^0/\partial D)_T$ and dD/dT. By interpolation of our

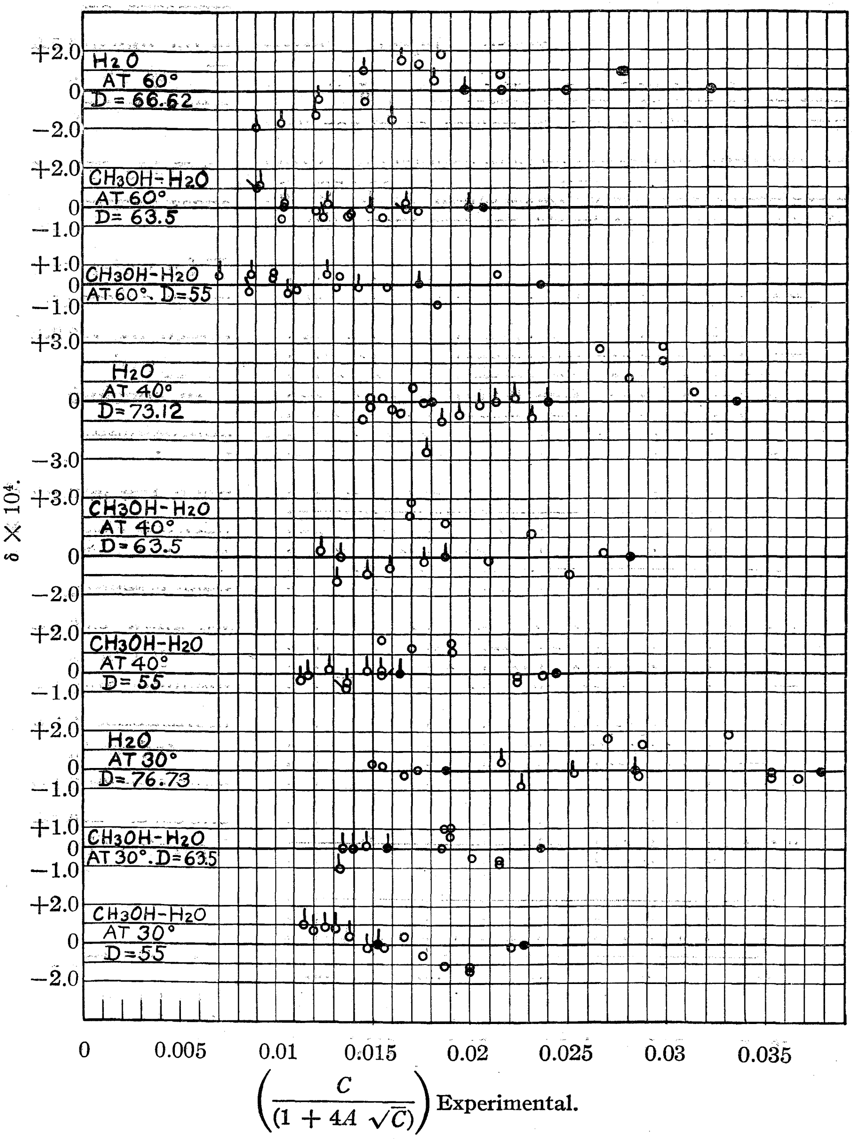

Fig. 1.

TABLE III

SUMMARY OF CRITICAL INCREMENT DATA

	H_2O	CH_3OH-H_2O $D = 63.5$	$D = 55.0$
E^0 (Exptl. at $\sqrt{\mu} = 0$)	23,580	18,840	18,500
$(E^0)_{H_2O} - E^{0*}$(Exptl.)		4,740	5,080
$(E^0)_{H_2O} -$ E^{0*}(Calcd. by Eq. 2 at 50°)		4,860	4,860
E(Exptl. at $\sqrt{\mu} = 0.194$)	23,240	19,380	18,850
E(Calcd. from E^0's Eq. 17 at 50°)	23,360	19,280	18,950
E(Calcd. from E^0's using Eq. (11) at 50°)	23,380	19,270	19,000

data at 40 and 50° and a slight extrapolation at 60° we are able to obtain values of k_s^0 for 28.3 wt. per cent. of methyl alcohol as solvent. From these data we obtain $(E^0)_{28.3\%\ CH_3OH} = 23{,}050$ cal., which is approximately 500 cal. less than $(E^0)_{H_2O}$.

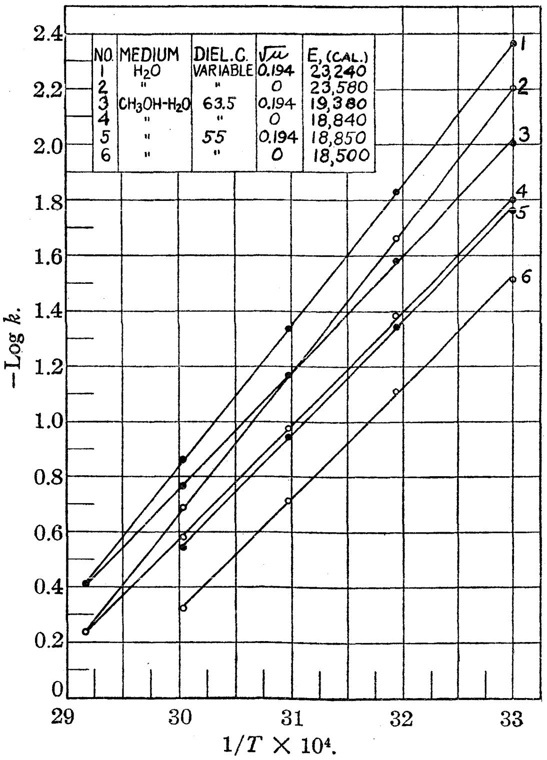

Fig. 2.—Influence of temperature on the rate of conversion of ammonium cyanate to urea in different media.

If $(\partial \log k_s^0/\partial D)_T$ is obtained from the experimental slope of log k_s^0 against D at 28.3% of methyl alcohol and dD/dT is obtained by interpolation of Åkerlöf's[3] data, Eq. (2) becomes

$$(E^0)_{28.3\%\ CH_3OH} - E^{0*} = 735\ T/D \qquad (16)$$

Assuming $E^{0*} = (E^0)_{D = 63.5}$, one calculates by Eq. (16), $(E^0)_{28.3\%\ CH_3OH} = 22{,}970$ cal.

By differentiating Eq. (10) and multiplying by RT^2, one obtains the following relation between the critical increments at $\sqrt{\mu} = 0$ (E^0) and at some fixed ionic strength

$$E = E^0 + 8.35 \times 10^6\ RT^2 \sqrt{\mu} \left\{ \frac{{}^3/{}_2T^{1/2}D^{3/2} + 100.6\ D \sqrt{\mu}}{(T^{3/2}D^{3/2} + 100.6\ DT \sqrt{\mu})^2} \right\} \left\{ 1 + \frac{\mathrm{d} \ln D}{\mathrm{d} \ln T} \right\} \qquad (17)$$

Using Eq. (17), we have calculated $(E)_{\sqrt{\mu} = 0.194}$ from E^0 for water and the two media of fixed dielectric constant. These calculated critical increments are compared to experimental values in the fourth and fifth rows of Table III. E and E^0 may also be related by taking logarithms and differentiating Eq. (11). Values of E calculated from E^0 by this method are given in the last row of Table III. There are no significant differences between these values and those calculated by Eq. (17). If E at $\mu = 0.1$ is calculated from E^0 for water, one obtains $(E)_{\mu = 0.1} = 23{,}280$ cal., which differs by about 0.5% from the values obtained by Walker and Hambly[6] and by Doyle[2a] at approximately the above ionic strength.

In conclusion, we must call attention to the approximate character of the relationships which have been derived and used. They are based upon the assumption that the rate of reactions between ions depends only upon the temperature, the dielectric constant of the medium and the ionic strength. From previous investigations,[1c,4] we know that this assumption is only approximately true for the rate of reaction between ammonium and cyanate ions. Considering these limitations, we believe we have satisfactorily accounted for the influence of dielectric constant and ionic strength upon the critical increments in this one case. The ideas presented in this paper are being tested with data on the rates of other ionic reactions which can be followed with greater precision.

Summary

1. On the assumption that the rates of ionic reactions are functions only of the temperature, dielectric constant and ionic strength, equations are derived which predict the influence of dielectric constant and ionic strength upon critical increments.

2. These predictions are in satisfactory agreement with observed effects in the reaction between ammonium and cyanate ions which was studied over the temperature range 30 to 70° in water, dielectric constant varying with temperature, and in mixtures of water with methyl alcohol at fixed dielectric constants for the mixtures of 63.5 and 55.0.

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[6] Walker and Hambly, *J. Chem. Soc.*, **67**, 746 (1895).

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, COLLEGE OF PHYSICIANS AND SURGEONS, COLUMBIA UNIVERSITY]

Studies of Crystalline Vitamin B_1. XIII. Ultraviolet Absorption of Some Derivatives of the Basic Cleavage Product and their Synthetic Analogs[1]

BY A. E. RUEHLE

Similarity in absorption of an unknown and a known compound is often insufficient to establish an identification. When, however, such a similarity is found to extend to a series of derivatives of each, a high degree of certainty of identification may be achieved. These principles are well illustrated by the case of the basic cleavage product[2] of vitamin B_1 and certain of its derivatives. Smakula[3] pointed out a similarity which now appears fortuitous between the absorption spectrum of a cleavage product of the vitamin and the spectra of certain pyrrole derivatives. In the present study a similarity in absorption is shown between the basic cleavage product and its derivatives and a corresponding series of synthetic thiazole derivatives amounting to virtual identification of the nucleus present. This result is in accord with the structural formula for vitamin B_1 recently announced by Williams[4] and the further chemical evidence adduced by Clarke and Gurin.[5]

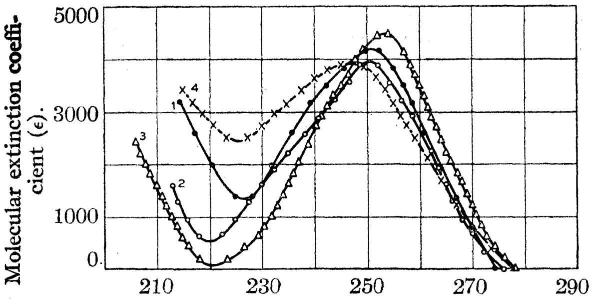

Fig. 1.—1, ●——● Basic cleavage product hydrochloride; 2, ○——○ 4-methylthiazole hydrochloride; 3, △——△ 2,4-dimethylthiazole hydrochloride; 4, ×——× 2-oxy-4-methylthiazole hydrochloride.

Experimental

The method of determining extinction coefficients was that used in obtaining the absorption curve of the vitamin,[6] namely, the use of the Hilger rotating sector photometer and E316 quartz spectrograph. The only innovation was the use of a hydrogen discharge tube as the source in rechecking most of the curves. Eastman I-O ultraviolet sensitized plates were used in exploratory work due to their greater range and latitude, while a more contrasting plate (Eastman DC Ortho) was used for final determination of the absorption spectrum.

I am indebted to my colleagues for samples of the basic cleavage product and its derivatives as well as for samples of synthetic thiazoles.[2,5,7] All samples were dissolved in distilled water and made slightly acid with sufficient hydrochloric acid to ensure the absence of excess free base.

Results and Discussion

The absorption curve of the basic cleavage product is seen in Fig. 1 to be similar to the curves of 4-methylthiazole 2,4-dimethylthiazole, and 2-oxy-4-methylthiazole. In Fig. 2 are shown the curves of the methiodide of the basic cleavage product and of 4-methylthiazole ethiodide. Again there is close correspondence, although the maximum appears at a shorter wave length when the nitrogen is quaternary. The oxidation product of the basic cleavage substance (identical with Windaus' oxidation product from the vitamin) is shown in Fig. 3. This curve agrees moderately well with that shown by Smakula.[3] In the same figure is shown the curve of synthetic 4-methylthiazole-5-carboxylic acid. The correspondence in absorption amounts to identity and the two

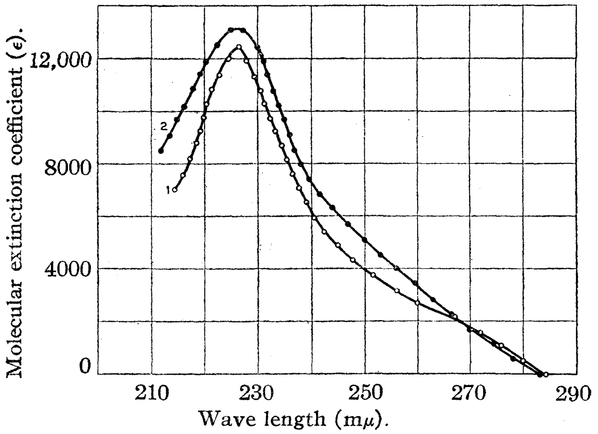

Fig. 2.—1, ○——○ Basic cleavage product methiodide; 2, ●——● 4-methylthiazole ethiodide.

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(1) Presented before the Organic Division of the American Chemical Society at the San Francisco Meeting, August 19, 1935.

(2) R. R. Williams, R. E. Waterman, J. C. Keresztesy and E. R. Buchman, THIS JOURNAL, **57**, 536 (1935).

(3) A. Smakula, *Z. physiol. Chem.*, **230**, 231 (1934).

(4) R. R. Williams, THIS JOURNAL, **57**, 229 (1935).

(5) H. T. Clarke and S. Gurin, *ibid.*, **57**, 1876 (1935).

(6) O. Wintersteiner, R. R. Williams and A. E. Ruehle, *ibid.*, **57**, 517 (1935). Nomenclature of V. Henri, "International Critical Tables," 1929, Vol. V, p. 359.

(7) E. R. Buchman, R. R. Williams and J. C. Keresztesy, THIS JOURNAL, **57**, 1849 (1935).

compounds have in fact been shown by chemical methods to be identical.[5] Absorption curves obtained subsequently on synthetic 4-methyl-5-β-hydroxyethylthiazole and its methiodide show equally close correspondence to the curves of the basic cleavage product and its methiodide, respectively, but are omitted from Figs. 1 and 2 for purposes of clarity. A case in which substitution produced little change in absorption is shown in Fig. 4, where the curves of the basic cleavage product and its chloro derivative (V)[7] are compared. The replacement of the β-hydroxyl group by chlorine apparently does not involve the portion of the molecule associated with the observed absorption.

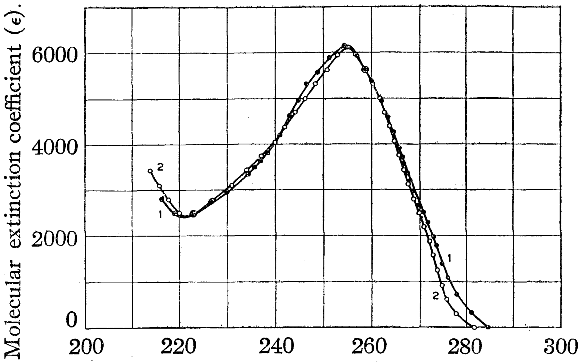

Fig. 3.—1, ●——● Oxidation product of basic cleavage product; 2, ○——○ 4-methylthiazole, 5-carboxylic acid.

I wish to thank Dr. R. R. Williams for suggesting this problem to me and for helpful criticism and advice. I am indebted to Drs. H. T. Clarke, E. R. Buchman and S. Gurin for generously supplying me with the samples used, and especially to Dr. Clarke for the use of the spectrographic facilities in his laboratory. I am further indebted to the Carnegie Corporation of New York through the Carnegie Institution of Washington for financial support in the purchase of materials necessary in the work.

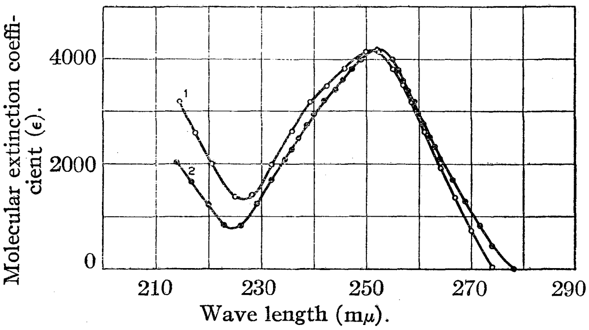

Fig. 4.—1, ○——○ Basic cleavage product hydrochloride; 2, ●——● chloro derivative of basic cleavage product hydrochloride.

Summary

The ultraviolet absorption of the basic cleavage product of vitamin B_1 is not only similar to that of the thiazoles but its derivatives exhibit absorption similar to that of corresponding thiazole derivatives.

NEW YORK, N. Y. RECEIVED JULY 11, 1935

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Nitroso Compounds. IV. Reaction of Ethyl Nitrite with Certain Isopropyl and Cyclohexyl Ketones

BY JOHN G. ASTON AND M. GLENN MAYBERRY

In the present paper further[1] experiments with a variety of ketones and catalysts are described. It was found that when ethyl nitrite reacts with certain isopropyl or cyclohexyl ketones in the presence of concentrated aqueous hydrogen chloride as catalyst, substitution usually occurs both on the branched alpha carbon atom to yield the true nitroso compound and on the primary alkyl group to yield the α isonitroso compound.

$$2(CH_3)_2CHCOCH_2R + 2HNO_2 \longrightarrow 2H_2O + (CH_3)_2C(NO)COCH_2R$$

$$(CH_3)_2CHCOCH_2R + HNO_2 \longrightarrow H_2O + (CH_3)_2CHCOC(NOH)R$$

However, better yields of both products are obtained if acetyl chloride or dry hydrogen chloride is used as catalyst.[2]

The numerical results appear in Tables I, II and III.

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[1] See Aston, Menard and Mayberry, THIS JOURNAL, **54**, 1530 (1932).

[2] In nitrosating menthone to the bisnitroso compound acetyl chloride gave better yields than aqueous hydrochloric acid. (a) Baeyer and Manasse, *Ber.*, **27**, 1912 (1894); (b) Baeyer, *ibid.*, **28**, 1586 (1895).

TABLE I

KETONES WITH ETHYL NITRITE IN THE PRESENCE OF AQ. HCl

Ketone	% EtONO absorbed	% NO	M. p., °C.	% NOH	M. p., °C.	M. p. of dioxime, °C.	% Ketone recovered
i-Pr *i*-bu	..	4.3	85.9–86.7	7.3	liquid	162–163	10
Me cyclohexyl	..	12.9	114.5–115	0.0	.....	......	39.6
Et cyclohexyl	83.3	3.8	119.5–120	14.7	78–78.2	......	49.4

TABLE II

KETONES WITH ETHYL NITRITE IN THE PRESENCE OF ACETYL CHLORIDE

Ketone	% EtONO absorbed	% NO	M. p., °C.	% NOH	M. p., °C.	M. p. of dioxime, °C.	% Ketone recovered
Me *i*-Pr	70	43.2	99–99.5	0.0	.....	....	35.7
Et *i*-Pr	53.3	49	122–123	34.2	92–93	....	27.1
Pr *i*-Pr	77.5	0.0	....	35.4	liquid	148.5–149	69
n-Bu *i*-Pr	43.7	.0	....	45.8	liquid	140–140.3	50
i-Bu *i*-Pr	71.4	50.1	89.2–90	8.4	liquid	162–163	40.8
Me cyclohexyl	48.0	17.0	114.5–115	0.0	.....	....	50
Et cyclohexyl	39.0	3.0	119.5–120	25.6	78–78.2	....	52.2

TABLE III

KETONES WITH ETHYL NITRITE IN THE PRESENCE OF HYDROGEN CHLORIDE GAS

Ketone	% EtONO absorbed	% NO	M. p., °C.	% NOH	M. p., °C.	M. p. of dioxime, °C.	% Ketone recovered
Me *i*-Pr	61.8	38.8	99–99.5	0.0	.....	....	29.7
Et *i*-Pr	62.4	30.3	122–123	53.2	92–93	....	23.3
Pr *i*-Pr	69.7	0.0	....	46.5	liquid	148–149	60.3
n-Bu *i*-Pr	73.7	.0	....	28.7	liquid	140–140.3	36
i-Bu *i*-Pr	51.3	51.7	89.2–90	19.0	liquid	162–163	45.1
Me cyclohexyl	60.9	43.5	114.5–115	0.0	.....	....	56.2
Et cyclohexyl	63.6	3.7	119.5–120	38.5	78–78.2	....	31

The results using dry hydrogen chloride and acetyl chloride should be considered together as in the absence of any information concerning the mechanism[3] there is, *a priori*, nothing to distinguish between them. The somewhat surprising fact already discussed[1] is that with ethyl isopropyl ketone substitution occurs to an approximately equal extent on either alkyl group.

Another significant fact is that in the case of propyl isopropyl and *n*-butyl isopropyl ketones, no substitution occurred on the isopropyl group. However, only about 40% of the ketone yielded the isonitroso compound with the fate of the rest still in doubt. As it does not seem likely that there would be any difficulty in isolating the true nitroso compound, if formed, either due to increased solubility or rapid decomposition, we are tempted to believe that in these cases substitution only involved the primary alkyl group. The fact that the isonitroso compound was liquid necessitated conversion into its oxime with consequent loss, so that our inability to account for the rest of the ketone may be due to this cause.

With isobutyl isopropyl ketone the results are practically the same as with ethyl isopropyl ketone if one considers that the lower yield of isonitroso ketone is due to the fact that the isonitroso compound was isolated by converting it into its oxime. It is difficult to reconcile this fact with the immediately previous one. Speculating one might attribute the non-activity of the alpha hydrogen on the isopropyl group of *n*-propyl and *n*-butyl isopropyl ketones to (a) steric hindrance by the far end of the other alkyl group through incipient ring formation, or (b) to a higher relative activity (rate) of the alpha carbon on the *n*-propyl and *n*-butyl groups, inasmuch as Ponzio found that branching reduced the tendency for (rate of) substitution on the alpha carbon atom of a ketone by nitrous acid.[4]

Experimental

The Results with Aqueous Hydrogen Chloride.—These have been given in Table I. The procedure followed was in general the same as already given[1] with the following exceptions. The isopropyl α-isonitrosoisobutyl ketone is a liquid[5] and was isolated as the dioxime. The unreacted ketone and low boiling material was distilled off under reduced pressure, and the remaining liquid converted into diisopropyl glyoxime as described later. The isonitrosoethyl cyclohexyl ketone, which did not crystallize by simple evaporation of the reaction mixture, was isolated by

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[3] Rate studies are precluded because of practical restrictions obvious from the experimental details of this paper.

[4] Ponzio, *J. prakt. Chem.*, [2] **58**, 394 (1898).

[5] Locquin, *Bull. soc. chim.*, [3] **31**, 1166 (1904).

the method described below for isolating isonitrosoethyl isopropyl ketone from the reaction using acetyl chloride as catalyst.

The Results Using Acetyl Chloride.—The procedure followed is given below for ethyl isopropyl ketone. The yields, given in Table II, are based on the amount of ethyl nitrite absorbed except in cases where the amount of ketone reacted (unrecovered) was less than the amount of ethyl nitrite absorbed. Then the yield is based on the unrecovered ketone. The isonitroso compounds of propyl isopropyl and butyl isopropyl ketones, being liquids, were converted into the corresponding dioximes which were then isolated and identified as described under "Diisopropyl Glyoxime."

Products from Ethyl Isopropyl Ketone Using Acetyl Chloride as Catalyst.—To 45 g. (0.45 mole) of ethyl isopropyl ketone was added 5 g. of acetyl chloride. The theoretical amount of dry gaseous ethyl nitrite was passed in over a period of two and one-half hours, keeping the temperature between 45–55°. During the process, the reaction mixture turned green; 18 g. (0.24 mole) of ethyl nitrite was absorbed during the reaction. The reaction mixture deposited 15.2 g. (0.117 mole) of almost pure bimolecular ethyl α-nitrosoisopropyl ketone on standing overnight in the icebox.

The α-isonitrosoethyl isopropyl ketone was isolated from the mother liquor; 31.7 g. of the liquid was cooled in ice, shaken with 40 cc. of 10% solution of sodium hydroxide and 9 g. of a non-aqueous upper layer removed. The aqueous layer, after extraction with ether, was cooled in ice and acidified with dilute sulfuric acid. Precipitation of the isonitroso ketone was complete when the solution was neutral; 5.7 g. (0.0044 mole) was thus obtained nearly pure after washing with water.

The ether extract of the basic solution was then evaporated. The liquid remaining was combined with the liquid insoluble in sodium hydroxide solution and distilled; 7.3 g. (0.073 mole) of ketone, identified by refractive index and by isolation of its semicarbazone, was recovered.

The Results, Using Dry Hydrogen Chloride.—The yields in Table III were calculated on the same basis as in Table II. The isonitroso compounds were isolated as described above.

Products from Isopropyl Isobutyl Ketone Using Dry Hydrogen Chloride as Catalyst.—The theoretical quantity of dry gaseous ethyl nitrite was passed through a solution of 0.6 g. of dry hydrogen chloride in 32.5 g. of ketone over a period of one hour, starting at a temperature of 18°. After about ten minutes the liquid which had turned blue was heated to 45° and thus maintained for the remainder of the reaction; 9.6 g. (0.128 mole) of ethyl nitrite was absorbed. The reaction mixture after standing for two days in the icebox deposited 8.7 g. (0.055 mole) of white crystals of bimolecular α-nitrosoisopropyl isobutyl ketone which was almost pure after washing with ether.

Diisopropyl Glyoxime.—After filtering off the above solid, 15.7 g. of mother liquor was cooled in ice and shaken with 40 cc. of a 10% aqueous solution of sodium hydroxide; 9.5 g. of liquid did not dissolve. The aqueous layer, after separation and extraction with ether, was cooled in ice and made slightly acid with dilute sulfuric acid. The acid solution was extracted with ether, and the ether solution evaporated; 3.5 g. of liquid remained.

This liquid, containing the isonitrosoisobutyl isopropyl ketone was cooled in ice and shaken with a solution containing 4.7 g. of sodium hydroxide in 27.8 cc. of water. To this solution, with continued cooling, was added 2.7 g. of hydroxylamine hydrochloride dissolved in 11.7 cc. of water. The solution was then warmed to 40–50° for ten minutes and kept at room temperature for two days. After cooling in ice 1.8 g. (0.01 mole) of dioxime was precipitated by acidification with sulfuric acid. After recrystallization from chloroform it melted at 162–163°.[6]

The ether extract of the basic solution was evaporated and the remaining liquid combined with the material insoluble in the sodium hydroxide solution. When this was distilled, 6.7 g. of ketone identified by refractive index and by isolation of its semicarbazone was obtained.

Analyses and Molecular Weights.—The results of the necessary analyses on new compounds are given in Table IV and those of the molecular weight determinations in Table V.

TABLE IV

ANALYSES

Compound	Source	Calcd.		Found	
		C, %	H, %	C, %	H, %
Methyl nitrosocyclohexyl ketone	A	61.89	8.44	61.67	8.43
Ethyl nitrosocyclohexyl ketone	A	63.9	8.87	63.75	8.9
α-Isonitrosoethyl cyclohexyl ketone	A	63.9	8.87	63.75	8.88
α - Nitrosoisopropyl isobutyl ketone	A	61.1	9.62	61.22	9.72
Ethyl isopropyl glyoxime	B	53.12	8.92	53.41	9.11
Propyl isopropyl glyoxime	C	55.77	9.37	55.76	9.37

TABLE V

MOLECULAR WEIGHT DETERMINATIONS

Compound	Source	Calcd.	Found
(a) Cryoscopic in Benzene			
Bimolecular methyl nitrosocyclohexyl ketone	A	310	291
Bimolecular α-nitrosoisopropyl isobutyl ketone	B	314	316
(b) Rast Camphor Method			
Isonitrosoethyl cyclohexyl ketone	B	169.1	167.2
Ethyl isopropyl glyoxime	B	158.1	159.2
Propyl isopropyl glyoxime	C	172.1	175.7

In Tables IV and V the materials marked "A" were obtained by the action of ethyl nitrite on the ketones in the presence of aqueous hydrogen chloride, "B," of acetyl chloride and "C," of dry hydrogen chloride.

Known compounds were identified by melting point and with the exception of diisopropyl glyoxime by mixed melting point.

Structure of Nitroso Derivatives.—That a compound was a true nitroso derivative was shown by a double molecular weight and that the colorless crystals yielded a

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[6] (a) Bouveault and Locquin, *Bull. soc. chim.*, [3] **35**, 653 (1906); (b) Ponzio, *J. prakt. Chem.*, [2] **63**, 368 (1901)

blue liquid on melting or when dissolved in solvents. The identity of an isonitroso compound was shown beyond reasonable doubt by a "normal" molecular weight together with lack of color and by solubility in alkali.

Summary

1. The action of ethyl nitrite on certain ketones using aqueous hydrogen chloride, acetyl chloride and dry hydrogen chloride as catalysts has been studied. The results are expressed in tabular form.

2. Certain new compounds prepared are listed in Table IV.

STATE COLLEGE, PENNSYLVANIA

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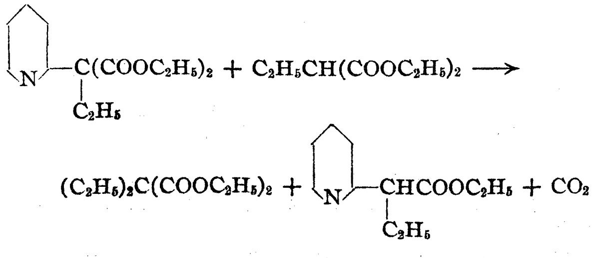
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Ethyl-2-pyridylmalonic Ester

BY L. A. WALTER AND S. M. MCELVAIN

The observation that the presence of a pyridine nucleus in certain types of therapeutic agents definitely lowers the intravenous toxicities of these substances[1] suggested the preparation and pharmacological evaluation of some pyridyl substituted barbituric acids. The first work along this line was directed toward the preparation of 5-ethyl-5-(2-pyridyl)-barbituric acid. Although it has not been possible to obtain this barbituric acid by the condensation of urea with the corresponding malonic ester, the preparation and properties of the ethyl-2-pyridylmalonic ester seem to be of sufficient interest to report.

This ester was prepared by the reaction of 2-bromopyridine with sodio-ethylmalonic ester in the absence of alcohol. When the reaction was carried out in alcoholic solution practically all of the bromopyridine which reacted was converted into 2-ethoxypyridine. Even in the absence of alcohol the yield of the pyridyl substituted malonic ester was not high (19%). Considerable amounts of ethyl α-(2-pyridyl)-butyrate and diethylmalonic ester were obtained as by-products of the reaction. These products apparently were the result of the alkylation of ethylmalonic ester by the ethyl-2-pyridylmalonic ester, thus



All attempts to condense ethyl-2-pyridylmalonic ester with urea either by means of dry or alcoholic sodium ethoxide were unsuccessful. The reaction product was in each case α-(2-pyridyl)-butyramide. Thus the behavior of this pyridyl substituted malonic ester parallels that which has been observed[2] for diphenylmalonic ester. It appears, therefore, that the 2-pyridyl group when substituted in a malonic ester approaches the effectiveness of two phenyl groups in promoting the cleavage of the ester. When compared to a single phenyl group the 2-pyridyl group is certainly very much more effective in increasing the sensitivity of the malonic ester to cleavage. For example, it was found that after refluxing for one hour with alcoholic sodium ethoxide, ethyl phenylmalonic ester suffered alcoholysis to ethyl carbonate and the corresponding acetic ester to the extent of 31% while under the same conditions ethyl-2-pyridylmalonic ester underwent alcoholysis to the extent of 93%.

The unusual labilizing effect of the 2-pyridyl group on the carbethoxy group of this pyridylmalonic ester is probably associated with the 2-linkage. It is well known that certain pyridine substituents, such as methyl, halogen, etc., are most reactive when they are in the 2-position. In the 4-position they are somewhat less reactive, while in the 3-position they are least reactive and resemble more closely the corresponding benzene derivatives in their behavior. It would be reasonable to expect, therefore, that a 3-pyridylmalonic ester, when it is made, will be found to have a resistance to alcoholysis comparable to that of a monophenyl substituted malonic ester and consequently be the most promising intermediate for the preparation of a 5-pyridylbarbituric acid.

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[1] Strong and McElvain, THIS JOURNAL, **55**, 816 (1933); Snell and McElvain, *ibid.*, **56**, 1612 (1934).

[2] Dox and Thomas, *ibid.*, **45**, 1811 (1923); Cope and McElvain, *ibid.*, **54**, 4319 (1932).

Experimental

Ethyl-2-pyridylmalonic Ester.—To a suspension of 13.6 g. (1 mol) of sodium ethoxide in 100 cc. of absolute ether was added 38 g. (1 mol) of diethyl ethylmalonate. The mixture was warmed until the solid material had dissolved and then the ether and alcohol were removed under diminished pressure. To the remaining sodio-ethylmalonic ester 50 g. of 2-bromopyridine[3] was added and the mixture heated, with stirring, in an oil-bath at 140–150° for thirty hours. The reaction mixture then was treated with 150 cc. of ether and the ethereal solution washed with water and dried. Distillation of this solution gave the following products: 2 g. of 2-ethoxypyridine, b. p. 66° (25 mm.); 30 g. of 2-bromopyridine, b. p. 92–93° (25 mm.); 15 g. of a mixture of ethyl and diethyl malonic esters, b. p. 108–114° (25 mm.); 9 g. of ethyl α-(2-pyridyl)-butyrate, b. p. 97–98° (2 mm.), d_4^{25} 1.0330, n_D^{25} 1.4873; 9 g. of ethyl-2-pyridylmalonic ester, b. p. 136–137° (2 mm.), d_4^{25} 1.0950, n_D^{25} 1.4849.

Anal. Ethyl α-(2-pyridyl)-butyrate. Calcd. for $C_{11}H_{15}O_2N$: C, 68.35; H, 7.83. Found: C, 68.20; H, 7.94. Diethyl ethyl-2-pyridylmalonate. Calcd. for $C_{14}H_{19}O_4N$: C, 63.35; H, 7.37. Found: C, 63.10; H, 7.39.

An attempt was made to prepare ethyl-2-pyridylmalonic ester by reaction of 2-bromopyridine with an alcoholic solution of sodio-ethylmalonic ester. From a run using 53 g. of 2-bromopyridine the only reaction product isolated was 20 g. (49%) of 2-ethoxypyridine. This compound was found to boil at 66° (25 mm.) and 160–161° (740 mm.); mercuric chloride derivative,[4] m. p. 152–153; hydrochloride, m. p. 90–91°.

Anal. Hydrochloride. Calcd. for $C_7H_{10}ONCl$: Cl, 22.21. Found: Cl, 22.17.

Reaction of Ethyl-2-pyridylmalonic Ester with Urea and Sodium Ethoxide.—To a solution of 7.9 g. of sodium ethoxide in 50 cc. of absolute alcohol was added 3.3 g. of urea and 7.5 g. of ethyl-2-pyridylmalonic ester. This solution was heated in a sealed tube at 100° for seven hours. After this time the alcoholic solution was diluted with 50 cc. of water and treated with the exact quantity of acetic acid necessary to react with the sodium ethoxide used. The alcohol then was removed under diminished pressure and the remaining aqueous solution extracted with ether. This ether extract was evaporated and the residue washed with petroleum ether to remove any unreacted ester. The tar-like material remaining was recrystallized from 25 cc. of water and gave 0.1 g. of crystals which after several recrystallizations from hexone melted at 188°. This material was shown not to be a barbituric acid by its elementary analysis.

The aqueous mother liquor from this crystallization together with the original aqueous solution was concentrated and from them was obtained 3.8 g. (80%) of α-(2-pyridyl)-butyramide, m. p. 125–126°. This same amide resulted from the ammonolysis of ethyl α-(2-pyridyl)-butyrate.

Anal. Calcd. for $C_9H_{12}ON_2$: C, 65.81; H, 5.85. Found: C, 65.79; H, 5.73.

When the ethyl-2-pyridylmalonic ester was heated with urea and dry sodium ethoxide the principal product of reaction was likewise the α-(2-pyridyl)-butyramide.

Alcoholysis of Ethyl-2-pyridylmalonic Ester and of Ethylphenylmalonic Ester.—A 3.0736-g. sample of each of these substituted malonic esters was refluxed for one hour with 50 cc. of absolute alcohol containing 1.2 g. of sodium ethoxide. The alcohol and any diethyl carbonate then was distilled off under diminished pressure and condensed by passing through a spiral surrounded by an ice-salt mixture. The residue remaining in the reaction flask was washed with ether to remove any unreacted malonic ester. The alcohol and ethyl carbonate, which previously had been distilled off, together with a small amount of water, were added to the residue and the resulting alkaline solution refluxed for thirty minutes. The solution was then acidified with sulfuric acid and the carbon dioxide evolved absorbed in ascarite and weighed. The carbon dioxide obtained from ethyl 2-pyridylmalonic ester weighed 0.4730 g. (92.7%) while that obtained from ethyl phenylmalonic ester amounted to 0.1548 g. (30.8%).

Summary

The preparation and properties of ethyl-2-pyridylmalonic ester are described.

Madison, Wisconsin

Received July 19, 1935

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[3] Craig, This Journal, **56**, 231 (1934).

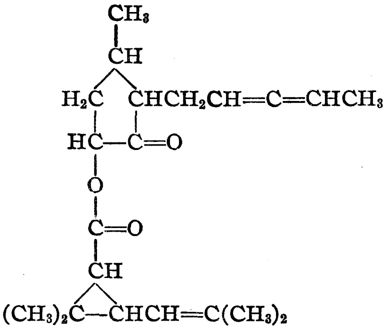
[4] Von Pechmann and Baltzer [*Ber.*, **24**, 3148 (1891)] report the b. p. of this compound as 156° and the m. p. of its mercuric chloride derivative as 141°.

[CONTRIBUTION FROM DIVISION OF INSECTICIDE INVESTIGATIONS, BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, UNITED STATES DEPARTMENT OF AGRICULTURE]

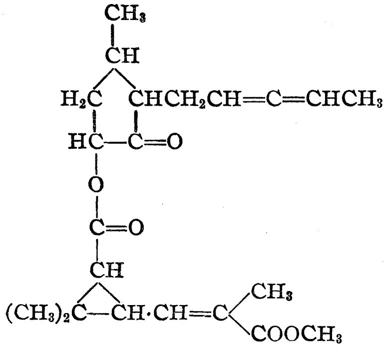
Constituents of Pyrethrum Flowers.[1] II. Isolation of Pyrethrin II

BY F. B. LAFORGE AND H. L. HALLER

The researches of Staudinger and Ruzicka[2] on the insecticidal principles of pyrethrum flowers are too well known to require detailed comment. In brief, the two active constituents, pyrethrin I and pyrethrin II, were shown to be esters of the cyclic ketonic alcohol pyrethrolone with chrysanthemum monocarboxylic acid and chrysanthemum dicarboxylic acid methyl ester, respectively, as represented by the formulas



Pyrethrin I



Pyrethrin II

Pyrethrin I was isolated from a partly purified extract of the flowers as the crystalline semicarbazone, which was hydrolyzed to the free ester, a liquid that could be distilled in a high vacuum. It was also prepared by esterification of pyrethrolone with chrysanthemum monocarboxylic acid.

The semicarbazone of pyrethrum II was not obtained pure, and the free ester was prepared only by esterification of pyrethrolone with chrysanthemum dicarboxylic acid methyl ester. The alcoholic and acidic components used in these partial syntheses of the two pyrethrins were obtained from mixtures of the semicarbazones of both.

Although the formulas of the pyrethrins proposed by Staudinger and Ruzicka have remained unquestioned, the authors themselves refer to the unsatisfactory properties of the semicarbazones, especially of the resynthesized pyrethrins, and point to the possibility of a change in the arrangement of the double bonds in the side chain of the alcoholic component and to possible steric changes during the reaction processes.[3]

To reduce the risk of changes that may occur in connection with the employment of semicarbazones, the pyrethrins should be prepared directly and under as mild conditions as possible.

Pyrethrum flowers are now purchased on the basis of their total pyrethrin content which is usually up to 1% or slightly more. Various analytical methods have been developed for their evaluation, some of which indicate only the total pyrethrin content, others the separate amounts of the two pyrethrins.

Because a wide difference of opinion exists as to the insecticidal value of each of the two compounds, it is of practical as well as of scientific importance to establish their relative toxicities. This can be best accomplished by isolating both pyrethrin I and pyrethrin II in pure condition and testing each one separately on insects.[4]

Extracts of the flowers made with organic solvents contain, in addition to the pyrethrins, comparatively large quantities of fats, waxes, fatty acids and other known and unknown substances which are regarded as inert from an insecticidal standpoint. The separation of the pyrethrins from these substances, which must constitute the first step in their isolation, has offered such unusual difficulties as to discourage attempts for its accomplishment.

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(1) The first paper in this series by Haller and Acree, "Determination of Pyrethrin II," appeared in *Ind. Eng. Chem., Anal. Ed.*, **7**, 343 (1935).

(2) H. Staudinger and L. Ruzicka, *Helv. Chim. Acta*, **7**, 177 (1924).

(3) Staudinger and Ruzicka, *ibid.*, **7**, 448 (1924).

(4) With this object in view Gnadinger and Corl, THIS JOURNAL, **51**, 3054 (1929), have repeated the isolation of the mixed semicarbazones by the method of Staudinger and Ruzicka, and have separated that of pyrethrin II to the extent of obtaining a product melting at 56–59°. The analytical figures given by them for the free ester obtained from their semicarbazone indicate, however, that it was still a mixture of about 70% pyrethrin II and 30% pyrethrin I.

Staudinger and Ruzicka and all subsequent investigators have employed petroleum ether extractives as starting material. Dissolving this material in methyl alcohol containing a little water and refrigerating, effects a partial separation of fats and waxes. The material remaining in solution is transferred to petroleum ether, and the fatty acids are removed by extraction with aqueous alkali carbonate, an operation that is exceedingly unsatisfactory owing to the formation of emulsions. By this method preparations of 50 to 60% total pyrethrin content are obtained. These are employed for the isolation of the pyrethrins as semicarbazones.

The initial difficulties in the isolation of the pyrethrins, involving the removal of the fats, waxes and acids from the original extractive, are eliminated in the following process, which is described in detail in the experimental part of this article.

The petroleum ether extractive used contained about 30% of total pyrethrins, pyrethrin I and pyrethrin II being present in about equal amounts. Addition of a small quantity of water to an acetic acid solution of this material precipitated the fats and waxes in a semi-solid form, which, after hardening by cooling, were readily removed by filtration.

By addition of water to the filtrate and extraction with petroleum ether, a product was obtained with a total pyrethrin content of 60 to 65% but still containing fatty acids and other impurities.

For the extraction of the acids, the only suitable solvent that did not involve the formation of emulsions was aniline. By agitation of the pyrethrin concentrate in this solvent with aqueous potassium carbonate the fatty acids were removed. The product separated from the aniline by acid was a concentrate containing 65 to 70% of total pyrethrins.

When this mixture was dissolved in a mixture of acetic acid and petroleum ether and sufficient water was added to cause separation of the two liquids, the pyrethrin II tended to concentrate in the acid layer, and the pyrethrin I, together with most of the impurities, concentrated in the petroleum ether layer. By isolation of the material in the acid layer and several repetitions of the process, a concentrate was obtained containing 80 to 83% pyrethrin II and 3 to 8% of pyrethrin I.

For the final purification the concentrates were fractionated in a molecular still at a comparatively low temperature, yielding pyrethrin II of practically 100% purity.

Although it is possible to obtain fairly large quantities of the concentrate containing about 80% pyrethrin II, the losses in distillation are considerable. Pyrethrin II so obtained is a colorless, very viscous liquid. Instead of being dextrorotatory, as recorded by Staudinger and Ruzicka for the synthetic compound, it showed a slight levo rotation.

It is to be regarded as probable that the pyrethrin II which is isolated by the process described in this article is different from the pyrethrin II obtained by partial synthesis. It is also quite possible that one or more other compounds having the same empirical formula and general nature as pyrethrin II are present in pyrethrum extracts.

Work is now in progress on this phase of the problem and on the direct isolation of pyrethrin I.

Experimental

Preliminary Purification of Oleoresin.—The starting material, a commercial concentrated petroleum ether extract, consisted of a thick brown liquid with a total pyrethrin content of about 30%, in which the pyrethrins were present in about equal amounts. After removal of the remaining solvent by warming under reduced pressure (an essential step), 450 g. of the material was divided into nine 50-g. portions.

To each portion 75 cc. of glacial acetic acid was added, and the mixture was stirred until practically all had dissolved. The same quantity of acetic acid to which 15 cc. of water had been added was mixed with the solution, causing the separation of a semi-solid mass of material. The containers were then cooled in an ice-bath for about half an hour, after which the contents were filtered separately on cold Büchner funnels. The solid material consisted of fats and waxes with comparatively little occluded pyrethrins. The green filtrates were combined and after addition of decolorizing carbon were again filtered. The acetic acid solution was then divided into two or three portions and strongly diluted with water, and the separated oil was extracted with petroleum ether. A small quantity of insoluble dark sirup was discarded. The petroleum ether solution was washed with water, a little sodium chloride being added to break slight emulsions. After the solution had been dried with sodium sulfate, most of the solvent was recovered by distillation on the steam-bath; the remainder was removed under reduced pressure. The same method was used in isolating all pyrethrum concentrates referred to below from their acetic acid solutions.

The quantity of concentrate obtained from 450 g. of the original material was 140 g. It contained, besides other impurities, fatty acids, which were removed by dissolving the material in 400 cc. of freshly distilled aniline and agitating the solution for about ten hours at −10° with a solution of 140 g. of potassium carbonate in 600 cc. of water. The aniline solution readily separated from the slimy soap solution, which was drawn off and on acidification yielded the extracted fatty acids. The aniline solution was washed three times with saturated bicarbonate solution and then, with constant stirring, was slowly run into 400 cc. of concentrated hydrochloric acid and 400 g. of cracked ice. These procedures were usually carried out in two operations with half the quantities stated. The separated oil was taken up in a suitable quantity of petroleum ether. A small quantity of insoluble material was discarded. The residue obtained from the washed and dried petroleum ether solution consisted of 90 g. of yellow oil containing 38.9% of pyrethrin II and 29.2% of pyrethrin I. Only slight variations from these values were observed in similar runs.

The analytical results for pyrethrin II were obtained by the methoxyl method of Haller and Acree,[5] those for pyrethrin I by the method of Seil.[6] In some instances pyrethrin II was also determined by the method of Seil as a check on the methoxyl method. It was observed that concentrates with a content of pyrethrin II of the order of 80% as determined by the methoxyl method showed a value about 5 or 6% higher by the Seil method. Practically 100% pyrethrin II usually showed an apparent pyrethrin I content of 2 to 3% by the Seil method. This is not surprising, because abnormally large samples had to be employed to obtain a significant volume in the titration, and the values observed evidently were very close to the limits of error of the method.

Separation of Pyrethrin II from Pyrethrin I by Differential Solubility.—The 90 g. of partly purified material obtained by the process just described was dissolved in 200 cc. of glacial acetic acid and 400 cc. of petroleum ether in a separatory funnel, and 20 cc. of water was added in small portions with vigorous shaking.

The addition of water caused the solution to separate into two layers, a petroleum ether fraction (P) and an acetic acid fraction (A). The latter was washed with six 40-cc. portions of petroleum ether, yielding an acid fraction (A-1).

The combined petroleum ether washings were added to the petroleum ether fraction (P), and the resulting solution was washed with six 40-cc. portions of acetic acid containing 10 to 12% of water. These acid washings were combined (A-2).

The acid-washed petroleum ether solution (P-1) yielded about 35 g. of a product containing 43% pyrethrin I and 14.4% pyrethrin II. This was set aside for the isolation of pyrethrin I.

The acid solution A-2 was extracted once with 240 cc. of petroleum ether and then with two 60-cc. portions of the same solvent. The combined petroleum ether washings were designated P-2, and the washed acid solution was designated A-3.

The two acetic acid solutions A-1 and A-3 were combined, and the dissolved material was isolated by the addition of water and extraction with petroleum ether. The quantity of concentrate so obtained was 30 g. It contained 72.2% of pyrethrin II and 14.2% of pyrethrin I. The material will be referred to as of stage I.

This product was dissolved in 100 cc. of acetic acid and 200 cc. of petroleum ether, and 14 cc. of water was added in small portions, with vigorous shaking after each addition. The separated acid solution was washed with four 20-cc. portions of petroleum ether. The washings and the separated petroleum ether layer were added to solution P-2.

The dissolved material in the acid solution (A-4) was isolated by dilution with water and extraction with petroleum ether and 20 g. of material containing 76.5% of pyrethrin II and 7.4% of pyrethrin I was obtained (stage II).

At stage III, which is reached by repeating the solution in acetic acid–petroleum ether, addition of water and subsequent washing of the acid layer with petroleum ether, using corresponding quantities of solvents, the yield was about 14 g. of material containing 82.7% of pyrethrin II and 6% of pyrethrin I. It is necessary to repeat the process whenever at stage III the pyrethrin II content falls below 80%, but it is not possible by further repetition to raise it much above 83% when the proportions originally present were of the order given.

All petroleum ether extracts except P-1 were combined with P-2. The quantity of material obtained from these combined extracts was 25 g. When treated in a second series of operations according to the procedure described, it yielded 8 g. of concentrate containing at stage III about the same percentages of the two pyrethrins as the corresponding final product from the first series.

As the separation and concentration of pyrethrin II proceeds, the concentrates become progressively more viscous and lighter in color and more difficultly soluble in petroleum ether. A concentrate of more than 70% of pyrethrin II separates in part even from a moderately dilute petroleum ether solution on cooling, but this is of no advantage in purification, as the separated product carries the impurities with it.

The process described could probably be replaced by a continuous one involving the same principle, if the object were to prepare large quantities of concentrates of high pyrethrin II content.

Preparation of Pure Pyrethrin II from the Concentrate by Distillation in a Molecular Still.—From 8 to 10 g. of solvent-free concentrate containing about 80% of pyrethrin II and 3 to 8% of pyrethrin I was distilled in a Hickman-type molecular still of suitable size.[7] The still was heated in a small oil-bath kept at the constant temperature of boiling chlorobenzene (131°), the pressure as recorded by the mercury gage being about 10^{-6} mm. The distillation usually required eight to ten hours.

In the earlier trial runs a number of fractions were collected and analyzed to determine at which points the distillation should be interrupted. In later distillations three fractions were usually collected. The first fractions contained most of the pyrethrin I and the more volatile impurities. The second fractions generally consisted of 80 to 90% of pyrethrin II and were combined for redistillation. The third fractions were practically 100%

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(5) H. L. Haller and Fred Acree, Jr., *Ind. Eng. Chem., Anal. Ed.*, **7**, 343 (1935).

(6) H. A. Seil, *Soap*, [5] **10**, 89 (1934).

(7) K. Hickman, *J. Franklin Inst.*, **213**, 119 (1932).

pyrethrin II. There was always more than 50% loss due to polymerization in the still, and the still residue consisted of a glassy mass almost insoluble in all solvents. The yield of pure pyrethrin II was in no case more than 20% of the quantity of material distilled, but an additional quantity was obtained on redistillation of the second fractions.

The analytical results and physical constants for several samples are given below.

Preparation A.—*Anal.* Calcd. for $C_{22}H_{30}O_5$: C, 70.54; H, 8.08; $1CH_3O$, 8.28. Found: C, 70.63, 70.84; H, 7.69, 7.69; CH_3O, 8.10. Calcd. to pyrethrin II (mol. wt. 374), 97.72; n^{30}_{D} 1.5247; n^{20}_{D} 1.5285. *Rotation:* 0.135 g. in 2.28 cc. ether at 20° rotated $-0.34°$; $l = 0.96$ dm.; $[\alpha]^{20}_{\mathrm{D}}$ -6.0. 0.235 g. in 2.28 cc. benzene at 20° rotated $-0.42°$; $l = 0.96$ dm.; $[\alpha]^{20}_{\mathrm{D}}$ -4.2.

Preparation B.—*Anal.* Found: CH_3O, 8.24, 8.33. calcd. to pyrethrin II (mol. wt. 374), 99.66, 100.38; n^{29}_{D} 1.5258.

Preparation C.—*Anal.* Found: CH_3O, 8.07, 8.04; n^{20}_{D} 1.5259.

Preparation D.—*Anal.* Found: CH_3O, 8.00; n^{20}_{D} 1.5247.

It will be noted that none of the samples shows a pyrethrin II content of appreciably more than 100% as determined by the methoxyl method, indicating that none of them contained methyl pyrethrolone, alkyl esters of the chrysanthemum acids or other methoxyl containing impurities. These may have been present in the concentrates before distillation, but, being of much lower molecular weight, they would be removed in the more volatile fractions.

Summary

A procedure for the preparation of pyrethrin II is described.

Petroleum ether extractives of pyrethrum flowers are separated from fats and waxes by the employment of acetic acid.

The acids are removed from the concentrate by extraction in aniline solution with potassium carbonate.

Partial separation of pyrethrin II from pyrethrin I is accomplished by taking advantage of their different solubilities in a system consisting of diluted acetic acid and petroleum ether. Pyrethrin II tends to concentrate in the acid solution, pyrethrin I in the petroleum ether.

Concentrates so obtained containing about 80% of pyrethrin II and about 6% of pyrethrin I are distilled in a molecular still and yield pure pyrethrin II.

WASHINGTON, D. C.

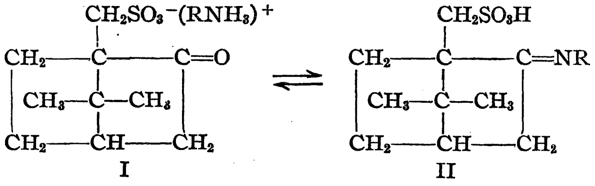
RECEIVED JULY 26, 1935

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

Anomalous Mutarotation of Salts of Reychler's Acid. III. Reduction of Ketimines of *d*-Camphor-10-sulfonic Acid. Formation of Sultams

BY R. S. SCHREIBER AND R. L. SHRINER

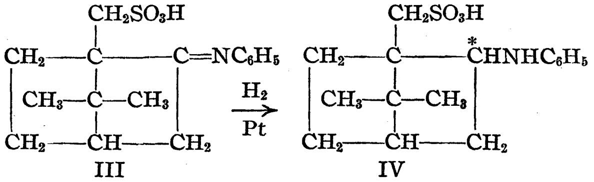
The mutarotation of salts of primary amines and Reychler's acid was ascribed[1] to the establishment of an equilibrium between the *d*-salt (I) and the *l*-ketimine (II).



I II

In order to establish the ketimine structure beyond question, the product of this reaction was subjected to catalytic reduction, since it is known that ketimines may be hydrogenated to secondary amines.[2]

The ketimine (III) obtained by the dehydration of the aniline salt of Reychler's acid readily absorbed one mole of hydrogen in the presence of platinum black and the hydrogenated product, 2-(N-phenylamino)-10-camphane-sulfonic acid (IV) was found to consist of the two diastereoisomers which would be expected because of the creation of a new asymmetric carbon atom at position 2. These isomers were separated by fractional crystallization. The α-form melted at 300–302° and had a specific rotation[3] of $-88.5°$ whereas the β-form melted at 350–351° and was dextrorotatory, $+8.5°$.



III IV

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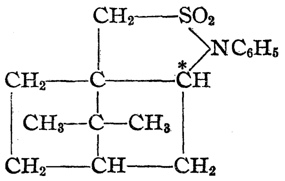
(1) Schreiber and Shriner, THIS JOURNAL, **57**, 1306, 1445 (1935).

(2) Mignonac, *Compt. rend.*, **171**, 114 (1920); Rupe and Vogler, *Helv. Chim. Acta*, **8**, 832 (1925); Rupe and Metzger, *ibid.*, **8**, 838 (1925); **13**, 457 (1930).

(3) All specific rotations reported in this paper were determined at 25° with sodium D light.

Further evidence supporting the above structures was obtained by causing each of the isomers of IV to undergo ring closure leading to the formation of two isomeric sultams of the structure shown in V.

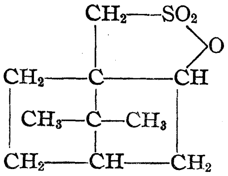


V

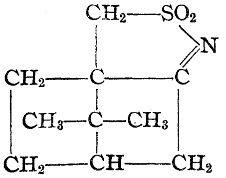
Treatment of the α-form of IV with either benzene-sulfonyl chloride or acetic anhydride produced the α-sultam (V) which melted at 172–173° and had a specific rotation of $-110°$ in chloroform. The β-form of IV could be converted to the β-sultam (V) by slightly more drastic conditions. The β-sultam melted at 137–138° and had a rotation of $+140.5°$ in chloroform.

These sultams were neutral compounds and their structure was proved not only by their analyses but by the fact that each isomer could be hydrolyzed by means of concentrated hydrochloric acid to the original α- and β-forms of 2-(N-phenylamino)-camphane-10-sulfonic acids (IV) in exactly the same fashion as other substituted sulfonanilides.[4]

The cyclization of the two forms of IV into the sultams shows that no rearrangements, which often occur in the camphor series, took place during the dehydration of the aniline salt. Examination of the literature revealed two similar cases of ring formation in the camphane series. Lipp and Holl[5] prepared a sultone VI by dehydrating 2-hydroxycamphane-10-sulfonic acid and Reychler prepared *d*-camphor-10-sulfonanhydramide[6] (VII).



VI



VII

Other sultams recorded are 1,8-naphthsultam prepared by Dannerth[7] and the sultam of 8-(2-aminophenyl)-naphthalene-1-sulfonic acid.[8]

Construction of the molecular models of the two isomeric forms of IV showed that in one model the sulfonic acid group and the amino group may approach closer to each other than in the isomeric model. Also, one model of the two isomeric sultams (V) possessed much more strain than the other. This difference is reflected in the properties of the two sultams. The β-sultam was formed with greater difficulty and hydrolyzed more easily than the α-sultam.

Experimental

Reduction of the Anil of *d*-Camphor-10-sulfonic Acid.—Thirteen grams of the anil, prepared by dehydration[1] of the aniline salt of Reychler's acid, was dissolved in 50 cc. of methyl alcohol and hydrogenated catalytically with 0.1 g. of platinum oxide-platinum black.[9] One mole of hydrogen was absorbed in four hours after which time the absorption of hydrogen stopped. The mixture was heated and the catalyst removed by filtration. When cool, the filtrate deposited 4.6 g. of crystals which melted at 288–295° (Maquenne block) and had a specific rotation[2] of $-78.0°$ in a mixture of equal volumes of chloroform and methyl alcohol. Several recrystallizations from methyl alcohol of this first crop gave 1.1 g. of the α-form in a pure state, with a constant melting point of 300–302° (Maquenne block) and a constant specific rotation of $-88.5°$. The mother liquor was evaporated to dryness, and then dissolved in 35 cc. of concentrated hydrochloric acid, which was heated to boiling and diluted with 150 cc. of water. This solution was allowed to stand overnight, during which time 4.6 g. of crystals separated. Recrystallization from dilute hydrochloric acid yielded 1.3 g. of the pure β-form. This form had a melting point of 350–351°, and a constant specific rotation of $+8.5°$ in a mixture of chloroform and methyl alcohol.

α-Form of 2-(N-Phenylamino)-camphane-10-sulfonic Acid (IV).—*Anal.* Calcd. for $C_{16}H_{23}O_3NS$: N, 4.53; S, 10.35; neut. eq. by titration, 309. Found: N, 4.49; S, 10.30; neut. eq., 308.3.

β-Form of 2-(N-Phenylamino)-camphane-10-sulfonic Acid (IV).—*Anal.* Calcd. for $C_{16}H_{23}O_3NS$: N, 4.53; S, 10.35; neut. eq. by titration, 309. Found: N, 4.34; S, 10.21; neut. eq., 309.2.

Sultam of α-Form of 2-(N-Phenylamino)-camphane-10-sulfonic Acid (V).—Five grams of the α-form of IV was heated with 15 g. of benzenesulfonyl chloride on a steam-bath until solution was complete (one to two hours). The mixture was then poured into excess of 5% sodium hydroxide to destroy the unreacted sulfonyl chloride, and the solution then acidified with hydrochloric acid. The insoluble product was recrystallized from methyl alcohol. The yield was 3.1 g. or 65% of the theoretical, m. p. 172–173°.

Anal. Calcd. for $C_{16}H_{21}O_2NS$: N, 4.71; S, 10.99. Found: N, 4.81; S, 10.92.

This compound was neutral, and did not give a neutral equivalent. The same compound was prepared by heating the α-form of IV with acetic anhydride for an hour on a

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[4] Schreiber and Shriner, THIS JOURNAL, **56**, 1618 (1934).

[5] Lipp and Holl, *Ber.*, **62**, 499 (1929).

[6] Reychler, *Bull. soc. chim.*, **19**, 127 (1898).

[7] Dannerth, THIS JOURNAL, **29**, 1319 (1907).

[8] Steiger, *Bull. soc. chim.*, **53**, 1254 (1933).

[9] Adams and Shriner, THIS JOURNAL, **45**, 2171 (1923).

steam-bath. On dilution with water the sultam was precipitated. Recrystallized from methyl alcohol, it gave a melting point of 172–173°. No depression in melting point occurred when mixed with the product obtained above. Its specific rotation[2] in chloroform was −110°; in acetone −117.5°.

Sultam of β-Form of 2-(N-Phenylamino)-camphane-10-sulfonic Acid (V).—The β-form of IV could not be converted into a sultam by either of the two procedures used for the preparation of the α-form. In each case the original acid was recovered unchanged. It was prepared, however, by a slightly modified procedure. Two grams of the above β-form of IV was dissolved in 3 g. of pyridine to which was added 1.2 g. of benzenesulfonyl chloride. The mixture was warmed on a steam-bath for two hours, diluted with 10–15 cc. of water and filtered and recrystallized from ethyl alcohol. The yield was 1.2 g. or 64%. It melted at 137–138° and had a specific rotation in chloroform of +140.5°.

Anal. Calcd. for $C_{16}H_{21}O_2NS$: N, 4.81; S, 10.99. Found: N, 4.73; S, 10.99.

Hydrolysis of the α-Sultam of 2-(N-Phenylamino)-camphane-10-sulfonic Acid.—One gram of the sultam was refluxed with 35 cc. of concentrated hydrochloric acid for thirty-six hours, at the end of which time the insoluble material had disappeared. The solution was then evaporated to about 10 cc. and cooled. Filtration yielded 0.6 g. of crystals. The product melted at 300–302° and had the same specific rotation as the α-form of 2-(N-phenylamino)-camphane-10-sulfonic acid.

Hydrolysis of the β-Sultam of 2-(N-Phenylamino)-camphane-10-sulfonic Acid.—Four-tenths of a gram of the β-sultam was refluxed for eight hours with 20 cc. of concentrated hydrochloric acid. The solution was diluted with 25 cc. of water and evaporated nearly to dryness. On cooling, the β-form of 2-(N-phenylamino)-camphane-10-sulfonic acid crystallized. The yield was 0.25 g. or 60%. The melting point was 350–351° on the Maquenne block and the specific rotation checked that of the original β-isomer of IV.

Summary

The catalytic hydrogenation of the anil of *d*-camphor-10-sulfonic acid yielded two diastereoisomeric forms of 2-(N-phenylamino)-camphane-10-sulfonic acid. Loss of water converted each of these isomers into its corresponding sultam, and each of the latter could be hydrolyzed to their respective original isomers. These reactions constitute further evidence that the *levo*-rotatory products obtained by the dehydration of primary amine salts of Reychler's acid are ketimines.

URBANA, ILLINOIS RECEIVED AUGUST 3, 1935

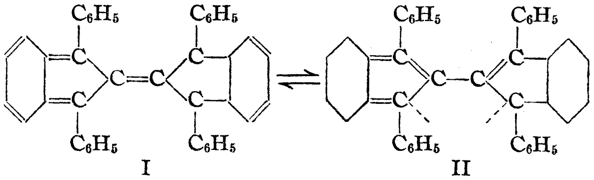
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Synthesis of Bis-2,2'-(1,3-diphenylindenol-3). A Contribution to the Rubrene Problem

BY J. C. ECK AND C. S. MARVEL

The question of the structure of rubrene has become of considerable interest to us because of its relationship to the problems involved in the rearrangement of certain types of polyynes. Recently Dufraisse and Willemart[1] have reported that Moureu's hydrocarbon $C_{42}H_{30}$, which is formed by the spontaneous rearrangement of tetraphenyldiphenylethynylethane,[2] can be oxidized with lead dioxide to give a 34% yield of rubrene. This observation is somewhat surprising since previous work has shown that chromic acid converts rubrene to *o*-dibenzoylbenzene,[3] whereas the same reagent oxidizes Moureu's hydrocarbon to *o*-benzoylbenzoic acid.[4]

The discoverers of rubrene[5] have considered it to be a difulvene of structure I which may be in equilibrium with a diindenyl form containing two trivalent carbon atoms, II. This diradical structure has also been advocated by Schönberg.[6]



I II

The structural formulas which have been assigned to rubrene and its many known derivatives are based on the reactions of the compounds and no confirmatory synthesis has been given for any compound in the series. The present work was undertaken with the hope of accomplishing the synthesis of rubrene or its closely related derivative, dihydroxydihydrorubrene, which has been assigned structure III.

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(1) Dufraisse and Willemart, *Bull. soc. chim.*, [5] **1**, 576 (1934).

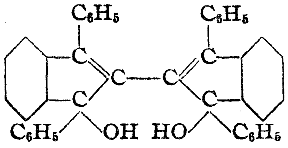
(2) Munro and Marvel, THIS JOURNAL, **54**, 4445 (1932).

(3) Moureu, Dufraisse and Enderlin, *Compt. rend.*, **187**, 406 (1928); Dufraisse and Enderlin, *Bull. soc. chim.*, [4] **51**, 132 (1932).

(4) Halley and Marvel, THIS JOURNAL, **54**, 4450 (1932).

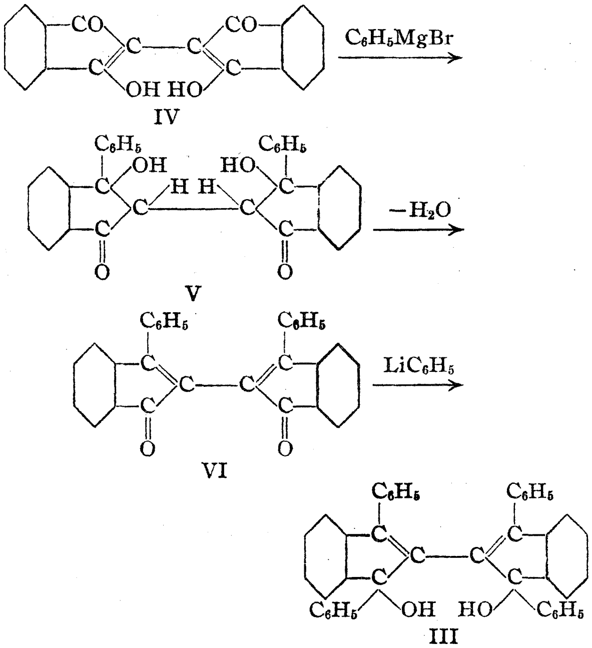
(5) The literature on rubrene has been summarized by Dufraisse, *Bull. soc. chim.*, [4] **53**, 789 (1933).

(6) Schönberg, *Ber.*, **67**, 633 (1934).



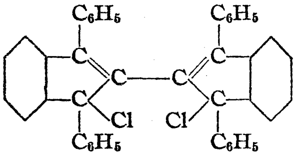
III

The starting point in our synthesis was bis-2,2′-(1,3-indandione) (IV) which was prepared by the method of Gabriel and Leupold.[7] This was converted to bis-2,2′-(1-phenylindanone-3-ol-1) (V) by the action of excess phenylmagnesium bromide. Since only two phenyl groups can be introduced into the molecule by this treatment, the bis-indandione (IV) must exist largely in the di-enolic form. Dehydration of compound V gave a good yield of bis-2,2′-(1-phenylindenone-3) (VI) which, with lithium phenyl, gave bis-2,2′-(1,3-diphenylindenol-3) (III). Lithium phenyl was used in this step to lessen the chance of 1,4 addition to the conjugated systems involved.[8] That the final product of these reactions had the formula (III) expected from the synthesis was established by its oxidation to *o*-dibenzoylbenzene in yields of 88% of the theoretical amount, and by the fact that the two hydroxyl groups could be replaced by chlorine atoms.



According to Dufraisse and Badoche[9] dihydroxydihydrorubrene, to which they assign structure III, melts at 307–308°; moderate heat converts it to rubrene monoxide by loss of water; dehydrating agents convert it to a white compound whose solutions have an intense violet fluorescence; and reduction converts it to rubrene. Our synthetic bis-2,2′-(1,3-diphenylindenol-3) (III) melts at 293°; sublimes unchanged at 280° at 3 mm. pressure; heating it with potassium acid sulfate at 250° or with phosphorus pentoxide at 100° affects it only very slightly, giving a trace of a substance which, in solution, shows a greenish fluorescence; reduction with iron in hydrochloric or acetic acid does not affect it.

The chloride VII which was prepared from the dihydro compound was treated with silver in the hope that the diradical II could be prepared. This reaction has not been studied extensively but sufficient work has been done to show that rubrene is not produced.



VII

Inspection of the formula of bis-2,2′-(1,3-diphenylindenol-3) (III) shows that it may exist in meso and racemic forms. It is possible that we have obtained one of these forms by our synthesis, whereas the other results from the oxidation of rubrene. However, the difference in chemical properties between our synthetic product and that obtained from rubrene seems to us to be too marked for these products to be meso and racemic forms.[10]

Experimental

Bis-2,2′-(1-phenylindanone-3-ol-1).—To a solution of phenylmagnesium bromide prepared from 15.7 g. of bromobenzene and 2.4 g. of magnesium in 200 cc. of anhydrous ether was added 10 g. of bis-2,2′-(1,3-indandione) suspended in 200 cc. of dry benzene. The reaction mixture was stirred for about twelve hours, and then the solvent was decanted from the black unreacted material into an aqueous solution of ammonium chloride. The reaction product precipitated in the ether–benzene mixture as soon as hydrolysis of the magnesium complex occurred. The straw-colored precipitate was collected on a filter, washed with water and dried in the air. The yield was 10 g. (65%).

This product was recrystallized by suspending it in about 300 cc. of dioxane, heating the solvent to boiling

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[7] Gabriel and Leupold, *Ber.*, **31**, 1159 (1898).

[8] Lüttringhaus, *ibid.*, **67**, 1602 (1934).

[9] Dufraisse and Badoche, *Compt. rend.*, **193**, 63 (1931).

[10] Koelsch and Richter have synthesized bis-2,2′-(1,3-diphenylindenol-3) and the corresponding dichloride by another series of reactions. Their products are identical in physical properties with the compounds which we have obtained. See Koelsch and Richter, THIS JOURNAL, **57**, 2010 (1935).

and filtering hot. On cooling the first extract, a yellow crystalline compound, melting at 345° (bloc Maquenne), was obtained.

Anal. Calcd. for $C_{30}H_{22}O_4$: C, 80.71; H, 4.93. Found: C, 80.78; H, 4.92.

The filtrate from this first fraction was used to re-extract the material which did not dissolve in the first treatment with hot dioxane. On cooling the second extract, a mixed product was obtained. However, when the filtrate from this portion was again used to extract the undissolved portion of the original material, a second isomer of the hydroxy ketone, melting at 358° (bloc Maquenne), was obtained.

Anal. Calcd. for $C_{30}H_{22}O_4$: C, 80.71; H, 4.93. Found: C, 80.91; H, 5.00.

Either of these products or the mixture of the two gave satisfactory results in the following experiment.

Bis-2,2′-(1-phenylindenone-3).—An intimate mixture of 10 g. of bis-2,2′-(1-phenylindanone-3-ol-1) and 10 g. of powdered, freshly-fused, potassium acid sulfate was placed in a large Pyrex test-tube and slowly immersed in a Wood's metal bath previously heated to 250°. This temperature was then maintained for twenty-five minutes. The reaction mass was occasionally stirred with a glass rod. The reaction mixture was cooled and extracted with water. The water-insoluble material was dissolved in 200 cc. of benzene and boiled with 2 g. of decolorizing carbon for about a half hour. This solution was filtered and concentrated to 25 cc. Slow addition of an excess of low-boiling petroleum ether precipitated the product as beautiful, red crystals. The yield was 7.8 g. (80%) of a product melting at 213–214°.

Anal. Calcd. for $C_{30}H_{18}O_2$: C, 87.8; H, 4.39. Found: C, 87.52; H, 4.44.

Bis-2,2′-(1,3-diphenylindenol-3).—A solution of lithium phenyl was prepared from 0.5 g. of lithium and 5.7 g. of bromobenzene in 150 cc. of anhydrous ether.[11] Unreacted lithium was removed and then 5 g. of bis-2,2′-(1-phenylindenone-3) dissolved in 200 cc. of dry benzene was added dropwise. The reaction mixture was stirred during this addition, and for about an hour afterward. This solution was hydrolyzed with aqueous ammonium chloride solution, the ether–benzene solution was washed thoroughly with water and dried over anhydrous sodium sulfate. The solution was then concentrated and, on cooling, the product separated. The yield was 4.9 g. (70%) of a product which melted at 293° (bloc Maquenne).

Anal. Calcd. for $C_{42}H_{30}O_2$: C, 89.04; H, 5.30. Found: C, 88.76; H, 5.28.

This reaction product was separated into two isomers by careful recrystallization from benzene. The less soluble form was yellow, and melted at 273° (bloc Maquenne). The more soluble form melted at 293° (bloc Maquenne). Heating the lower-melting product or allowing it to stand converted it to the higher-melting product.

Anal. Calcd. for $C_{42}H_{30}O_2$: C, 89.04; H, 5.30. Found: (low-melting isomer) C, 89.28; H, 5.57; (high-melting isomer) C, 89.20; H, 5.48.

Oxidation of Bis-2,2′-(1,3-diphenylindenol-3).—A mixture of 0.5 g. of the dihydroxy compound and 2.5 g. of potassium dichromate in 50 cc. of glacial acetic acid was heated under a reflux condenser for ten hours. The reaction mixture was poured into water and filtered. The precipitate was taken up in ether and the ether solution was extracted with aqueous sodium carbonate. The ether was removed in a current of air, and the residue taken up in alcohol, decolorized by boiling with norite, filtered and concentrated to a small volume. On cooling, 0.44 g. (88%) of *o*-dibenzoylbenzene, m. p. 145–146°, separated. The product showed no depression in melting point when mixed with a known specimen of *o*-dibenzoylbenzene.

Bis-2,2′-(1,3-diphenyl-3-chloroindenyl).—A solution of 0.1 g. of bis-2,2′-(1,3-diphenylindenol-3) in 25 cc. of anhydrous ether was saturated with hydrogen chloride and allowed to stand overnight. The solvent was evaporated and the residue recrystallized three times from acetone. The yield was 0.07 g. of a light yellow product which melted at 245–247° (bloc Maquenne).

Anal. Calcd. for $C_{42}H_{28}Cl_2$: Cl, 11.77. Found: Cl, 11.86.

A solution of this chloride in benzene was shaken with molecular silver for several days. The solution became greenish-yellow, and there was no indication of the red color of rubrene in solution.

Attempted Dehydration of Bis-2,2′-(1,3-diphenylindenol-3).—A small sample of the dihydroxy compound was heated for ten minutes at 250° with potassium acid sulfate. When the dehydrating reagent was removed, the organic material was dissolved in benzene. This solution showed a slight green fluorescence which was not shown by the original dihydroxy compound in benzene solution. However, no product except the starting material could be isolated from the reaction mixture. Treatment of the dihydroxy compound with phosphorus pentoxide at 100° for ten minutes gave the same results. The dihydroxy compound itself was heated to 280° at 3 mm. Under these conditions it sublimed undecomposed.

Attempted Reduction of Bis-2,2′-(1,3-diphenylindenol-3).—A suspension of the dihydroxy compound in hydrochloric acid was treated with iron filings but, after the iron had dissolved, the unchanged starting material was recovered. Likewise, treating the dihydroxy compound with iron and glacial acetic acid did not affect it.

Summary

Bis-2,2′-(1,3-diphenylindenol-3) has been synthesized and shown not to be identical with the product known as dihydroxydihydrorubrene.

Urbana, Illinois Received August 2, 1935

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[11] Gilman, Zoellner and Selby, This Journal, **55**, 1252 (1933).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

The Reactions between Mercury Diaryls and Diarylselenium Dihalides

BY HENRY M. LEICESTER

In previous work on the synthesis of aromatic selenonium salts[1] it was shown that triarylselenonium chlorides could be prepared by fusing together diarylselenium dichlorides and mercury diaryls. Since at that time the chief interest lay in the study of the selenonium salts, the mechanism of their synthesis was not worked out. The course of this reaction has now been studied.

Since mercury diaryls were found to react with diarylselenium dihalides in solution, the mechanism of this reaction was first investigated. Both diarylselenium dibromides and dichlorides were used, and the procedure was the same in all cases. The equimolecular amounts of the reagents shown in Table I were mixed in the dry state and treated with about 25 cc. of carbon disulfide. The mixture was shaken for five minutes at room temperature. The mercury diaryls dissolved at once; the dihalides somewhat more slowly. When the dibromides were used, a white precipitate began to appear almost immediately, and the red color of the dibromide faded. After shaking, the mixture was allowed to stand for five to ten minutes. Precipitation was then complete. In the case of the dichlorides, the precipitation required from one to three days before it was complete. The precipitate was filtered off and crystallized from benzene if necessary, though usually it was very pure. The carbon disulfide was distilled from the filtrate and the residue dissolved in ether. A little aryl mercuric halide which remained undissolved was added to the main precipitate. The ether was then distilled off and the residue fractionated.

TABLE I

	Starting Compounds				Reaction Products								
No.	R_2Hg R =	Amt., g.	R_2SeX_2 R =	Amt., g.	R_2Se R =	Amt., g.	Yld., %	RX R =	Amt., g.	Yld., %	RHgX R =	Amt., g.	Yld., %
1	Tol.[a]	1.8	Tol.[b]	2.1	Tol.	1.2[c]	97	Tol.[b]	0.5[c]	62	Tol.[b]	1.5	85
2	Tol.	0.76	Ph.[b]	0.79	..	..	..	Tol.[b]	.15	44	Tol.[b]	0.66	89
3	Ph.	.70	Tol.[b]	.84	Tol.	0.37	71	Ph.[b]	.27	87	Ph.[b]	.71	100
4	Ph.	.70	Ph.[b]	.78	Ph.	.37	80	Ph.[b]	.07	23	Ph.[b]	.67	94
5	Tol.	.90	Tol.[d]	.80	Tol.	.50	82	..	..	..	Tol.[d]	.60	78

[a] Tol. = *p*-tolyl; Ph. = phenyl. [b] X = Br. [c] The amounts of selenide and bromotoluene were determined in separate experiments. [d] X = Cl.

The reactions which were studied quantitatively are summarized in Table I. The three reactions which correspond for the dichlorides to reactions 2 to 4 for the dibromides were studied only qualitatively, but the analogous reaction products were identified in each case.

Di-*p*-tolyl selenide, phenyl and *p*-tolyl mercuric bromides and chlorides were identified by mixed melting points with the known compounds; diphenyl selenide was converted to the dibromide for identification; *p*-bromotoluene was oxidized to *p*-bromobenzoic acid which was proved by mixed melting point; and bromobenzene was identified by conversion to *p*-nitrobromobenzene, and by mixed melting point of the latter with an authentic specimen.

It is therefore evident that the course of the reaction can be represented by the following general equation

$$R_2Hg + R_2SeX_2 = RHgX + RX + R'_2Se$$

where X is a halogen. The ease with which the selenium dihalides, especially the dibromides, halogenate the mercury compounds is noteworthy.

The reaction was next tried in acetone. When diaryl selenium dibromides were dissolved alone in this solvent, the powerful effect of bromoacetone on the eyes soon became apparent, and the red color faded from the solution. Evaporation of the solvent left diaryl selenides, which were identified as described above. The reaction occurred more rapidly in the case of di-*p*-tolylselenium dibromide than when diphenylselenium dibromide was used. This bromination of the solvent rendered study of the reaction with mercury diaryls unsatisfactory.

However, no corresponding chlorination occurred with diarylselenium dichlorides. In the cold, these reacted with mercury diaryls just as they did in carbon disulfide solution. When,

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[1] Leicester and Bergstrom, THIS JOURNAL, **53**, 4428 (1931).

however, the reaction mixture was refluxed, a second reaction was observed. Thus, when diphenylselenium dichloride and mercury diphenyl were heated in acetone, a compound precipitated which was insoluble in boiling benzene, and could thus be separated from the phenyl mercuric chloride which was also formed. The amount of this new compound produced increased as the time of refluxing was lengthened. The substance was not very soluble in alcohol, but could be crystallized from this solvent in short needles, m. p. 259–260° (uncorrected). When it was treated with sodium hydroxide solution, mercuric oxide was precipitated. Triphenylselenonium chloride was isolated from the filtrate by the method previously described.[1] The compound was thus the double salt, triphenylselenonium chloride–mercuric chloride, a fact which was proved by comparing it with a sample of the double salt prepared directly from mercuric chloride and triphenylselenonium chloride. The behavior of the two substances was identical.

The reactions described above, with the exception of the second step in hot acetone, obviously differ from that which was previously observed in the fusion of the mercury and selenium compounds, since no selenonium salt was formed. Therefore, a more detailed study of the fusion of di-*p*-tolylselenium dichloride and mercury di-*p*-tolyl was made. This reaction has been earlier described[1] (p. 4434) but the proportions of the reagents there used were determined empirically. When an equimolecular mixture of the two compounds was heated to 140–150°, it fused to a brown liquid which cooled to a thick tar. When this was treated with ether, it was converted to a yellow powder. A hot benzene extract of the latter gave crystals of *p*-tolyl mercuric chloride when it cooled. The material which did not dissolve in benzene crystallized from alcohol in granular crystals, m. p. 216–217°. These gave mercuric oxide and tri-*p*-tolylselenonium chloride when they were treated with sodium hydroxide.

When a mixture of 0.76 g. of mercury di-*p*-tolyl and 1.30 g. of di-*p*-tolylselenium dichloride, a ratio of 1:2, was fused and treated as above, no *p*-tolymercuric chloride was isolated. However, from the ether extract was obtained di-*p*-tolyl selenide, and the odor of *p*-chlorotoluene was noticed. A yield of 1.29 g. or 98% of the mercuric chloride double salt, m. p. 216–217°, was obtained. When this was worked up in the usual way, it gave 86% of the tri-*p*-tolylselenonium salt which was identified by conversion to the iodide.

These facts show that the reaction which took place in carbon disulfide and cold acetone also occurred in the fusion, but that a further reaction then occurred between the aryl mercuric chloride, which now was not removed from the sphere of the reaction, and a second molecule of diarylselenium dichloride. The two steps in the reaction are

$$(CH_3C_6H_4)_2SeCl_2 + (CH_3C_6H_4)_2Hg = (CH_3C_6H_4)_2Se + CH_3C_6H_4Cl + CH_3C_6H_4HgCl$$

$$CH_3C_6H_4HgCl + (CH_3C_6H_4)_2SeCl_2 = (CH_3C_6H_4)_3SeCl{\cdot}HgCl_2$$

The occurrence of the second step in hot acetone is no doubt due to the solubility of the aryl mercuric chlorides in this solvent.

For further proof of the occurrence of the second reaction, equimolecular mixtures of di-*p*-tolylselenium dichloride and *p*-tolyl mercuric chloride were fused at 150–160° for one minute. The liquid bubbled at first, and became dark red-brown. It cooled to a hard solid. This was converted to an orange powder by stirring under ether. The ether extract contained a very small amount of an oily product which was not identified. A yield of 73% of tri-*p*-tolylselenonium chloride–mercuric chloride, m. p. 215–216°, was obtained.

Entirely analogous results were obtained by fusing together equimolecular amounts of diphenylselenium dichloride with *p*-tolyl mercuric chloride, and of di-*p*-tolylselenium dichloride with phenyl mercuric chloride. In the latter case, the selenonium iodide and picrate prepared from the reaction product had low melting points, as had been found for the corresponding products from the fusion of di-*p*-tolylselenium dichloride with mercury diphenyl.

Summary

1. In carbon disulfide solution, mercury diaryls react with diarylselenium dihalides to form aryl mercuric halides, aryl halides and diaryl selenides.

2. In the fusion of mercury diaryls and diarylselenium dichlorides, aryl mercuric chlorides are produced, and these react with more diarylselenium dichloride to form the mercuric chloride double salt of a triarylselenonium chloride.

3. In acetone solutions, diarylselenium dibromides brominate the solvent, and diarylselenium dichlorides in the cold react as in carbon disulfide and when heated, as in the fusion reactions.

STANFORD UNIVERSITY, CALIF. RECEIVED JULY 8, 1935

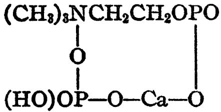
[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

The Mono and Tricholine Esters of Orthophosphoric Acid[1,2]

BY ERNEST L. JACKSON

Of the three possible simple choline esters of orthophosphoric acid, the triester hitherto has not been reported and only the diester seems to have been obtained pure. Abderhalden, Paffrath and Sickel[3] described crystalline, apparently pure di-(choline bromide) phosphate which they prepared by the reaction of ethyl metaphosphate with choline bromide. The mixed ester, dimethyl mono-(choline chloride) phosphate, was prepared crystalline by Renshaw and Hopkins[4] while Langheld[5] reported the amorphous, impure chloroplatinate of ethyl mono-(choline chloride) phosphate and Abderhalden, Paffrath and Sickel[3] the sirupy, likewise impure ethyl mono-(choline bromide) phosphate. The present paper pertains to the mono and tricholine esters, particularly the preparation of the esters or a suitable derivative in high purity.

By heating choline chloride with a mixture of orthophosphoric acid and phosphorus pentoxide Schmidt[6] obtained a sirup which, by analogy with the reaction of choline chloride with sulfuric acid, he inferred to contain a phosphoric acid ester of choline. The further investigation of this reaction has now led to the preparation of the amorphous calcium salt of the monocholine ester (1)

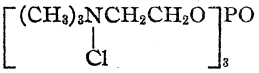


$$\begin{array}{l}(CH_3)_3NCH_2CH_2OPO(OH)\\ \qquad\quad | \qquad\qquad\qquad\quad |\\ \qquad\quad O \qquad\qquad\qquad\quad |\\ \qquad\quad | \qquad\qquad\qquad\quad |\\ (HO)OP{-}O{-}Ca{-}O\end{array}$$

I

, which, though free from choline, was contaminated with 3–4% of dicholine phosphate as shown by the isolation of its crystalline chloroaurate. Monocholine phosphate chloroaurate prepared from the calcium salt was crystalline, but contained a little impurity which could not be eliminated. The chloroplatinate, however, could be prepared pure and crystalline from the chloroaurate by removing the gold with finely divided silver[7] and forming the chloroplatinate from the resulting monoester. The pure chloroplatinate is suitable as a source of the monoester for pharmacological study as the platinum is eliminated readily by metallic silver and the monoester is stable in aqueous solution.

Trimethylamine condenses slowly with tri-β-chloroethyl phosphate either in toluene solution or without a solvent, but the products are sirups, probably mixtures consisting mostly of insoluble intermediate condensation products. Pure, crystalline tri(choline chloride) phosphate (II)



$$\left[\begin{array}{l}(CH_3)_3NCH_2CH_2O\\ \qquad\ \ |\\ \qquad\ Cl\end{array}\right]_3 PO$$

was prepared, however, by carrying out the reaction in anhydrous ethanol solution under selected conditions of temperature and concentration. When heated at 90° for two hours the pure triester, though showing no change in appearance and elementary analysis, acquires a considerably increased physiological activity,[2] evidently due to a partial conversion to a more active compound, perhaps through an intramolecular reaction with neurine chloride as a possible product. The triester yields readily a crystalline chloroaurate.

Experimental

Calcium Phosphato-ethyltrimethylammonium Phosphate (I).—A mixture of 12 g. of pure dry choline chloride, 8.4 g. of 100% orthophosphoric acid and 12 g. of phosphorus pentoxide was heated at 100° under reduced pressure for thirty minutes, the sirup stirred, the stirrer left in the mixture and the heating continued for thirteen hours. The glassy mass was dissolved in 150 cc. of cold water, the solution shaken with excess of calcium carbonate, some activated carbon added, and the solids filtered off and washed with water. The filtrate was neutralized to phenol red with calcium hydroxide solution, the calcium phosphate filtered off after adding some carbon, and the filtrate concentrated immediately under reduced pressure (bath, 60°) to about 100 cc., again neutralized to phenol red with calcium hydroxide solution, some carbon added and filtered off. The concentration was continued to a thin, colorless sirup which was poured slowly into 350 cc. of absolute ethanol, and the precipitated sirup stirred until completely solid and powdered. It was filtered off and washed with absolute ethanol; yield, 16–19 g. The amorphous, hygroscopic calcium salt was precipitated

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

[2] The preparation of the esters was undertaken at the suggestion of Dr. Maurice I. Smith in connection with his studies on the pharmacology of the phosphoric acid esters. The physiological action of the compounds, including triethyl and tri-β-chloroethyl phosphates, will be published by him in *Bull. Nat. Inst. of Health*, No. 165 (1935). The investigation was greatly facilitated by the analytical coöperation of Dr. E. Elvove and Mr. C. G. Remsburg of this Institute, to whom we express our thanks.

[3] Abderhalden, Paffrath and Sickel, *Arch. ges. Physiol.* (*Pflugers*), **207**, 249 (1925).

[4] Renshaw and Hopkins, THIS JOURNAL, **51**, 953 (1929).

[5] Langheld, *Ber.*, **44**, 2084 (1911).

[6] Schmidt, *Ann.*, **337**, 55 (1904); *cf.* Grün and Limpächer, *Ber.*, **59**, 1350 (1926); **60**, 147 (1927).

[7] *Cf.* Dudley, *Biochem. J.*, **23**, 1071 (1929).

thrice from its solution in 20 cc. of water by ethanol. It was then free from choline,[2] but contained less than 5% of dicholine phosphate. The substance showed no hydrolysis[2] by *N* hydrochloric acid at 100° during fifty minutes.

Anal. Calcd. for $C_5H_{15}O_8NP_2Ca$: C, 18.79; H, 4.74; N, 4.39; P (ionizable), 9.72; P (total), 19.43; Ca, 12.55. Found (dried at 75° *in vacuo*): C, 18.85; H, 4.59; N, 4.17; P (ionizable), 11.65; P (total), 20.40; Ca, 12.73; Cl, 0.00.

Monocholine Phosphate Chloroaurate.—To 10.5 g. of thrice precipitated calcium salt dissolved in 50 cc. of cold 2 *N* hydrochloric acid was added an equimolecular amount of auric chloride in 50 cc. of the same solvent. The precipitate (0.9 g.) was filtered off, washed with cold 2 *N* hydrochloric acid and recrystallized twice from about forty parts of hot *N* hydrochloric acid (clusters of light yellow, short prismatic needles difficultly soluble in water); m. p. 271.5–272° (corr., decomp.). Its composition agreed with that of dicholine phosphate chloroaurate.

Anal. Calcd. for $C_{10}H_{27}O_4N_2PAu_2Cl_8$: C, 12.65; H, 2.87; N, 2.95; P, 3.27; Au, 41.59. Found (dried at 25° *in vacuo* over phosphorus pentoxide): C, 12.78; H, 2.80; N, 3.03; P, 3.27; Au, 41.40.

The principal product was the chloroaurate of monocholine phosphate which was obtained in fractions as homogeneous, long, yellow needles by repeated concentration of the filtrate under reduced pressure (bath, 50°); yield, 14.3 g. or 83%. The crude substance was recrystallized five times from 2 *N* hydrochloric acid, washed with cold water and dried at 80° *in vacuo;* m. p. 174–176° (corr.). The compound, though showing substantially the same analysis after another recrystallization, was somewhat impure. It is hygroscopic and easily soluble in water.

Anal. Calcd. for $C_5H_{15}O_4NPAuCl_4$: C, 11.47; H, 2.89; N, 2.68; P, 5.93; Au, 37.69; Cl, 27.11. Found: C, 12.56; H, 3.10; N, 2.91; P, 6.32; Au, 36.18; Cl, 26.03; Ca, 0.14.

Chloroplatinate.—An aqueous solution (30 cc.) of 2.5 g. of thrice recrystallized monocholine phosphate chloroaurate was shaken for a few minutes with 5 g. of finely divided silver,[7] the solids filtered off and the colorless filtrate concentrated under reduced pressure to a sirup, which was dissolved in 5 cc. of *N* hydrochloric acid and mixed with 33% excess of the theoretical chloroplatinic acid in 5 cc. of water. After adding ethanol to turbidity it was kept at 5° for several hours, the crystals filtered off, washed first with ice-cold 50% ethanol and then with absolute ethanol. A second crop was obtained by concentrating the filtrate under reduced pressure (bath, 50°) to about 5 cc. and adding ethanol to turbidity; yield, 1.7 g. or 92%. One recrystallization by dissolving it in 5 cc. of 0.5 *N* hydrochloric acid at 35–40° and adding 4 cc. of ethanol gave the pure chloroplatinate (1.3 g.) as clusters of orange-colored prismatic needles. For analysis the hygroscopic crystals were dried to constant weight at 25° *in vacuo* over phosphorus pentoxide; m. p. 207–208° (corr., decomp.).

Anal. Calcd. for $C_{10}H_{30}O_8N_2P_2PtCl_6 + 2H_2O$: H_2O, 4.44. Found:[8] H_2O, 4.28. Calcd. for $C_{10}H_{30}O_8N_2P_2PtCl_6$: C, 15.46; H, 3.90; N, 3.61; P, 7.99; Pt, 25.15; Cl, 27.41. Found:[9] C, 15.55, 15.59; H, 4.06, 4.07; N, 3.57, 3.65; P, 8.02, 8.13; Pt, 25.41, 25.67; Cl, 28.03.

Tri-β-chloroethyl Phosphate.—Sixty-four grams of phosphoryl chloride was added during twenty minutes to a mechanically stirred mixture of 106 g. of pure ethylene chlorohydrin and 125 cc. of dry carbon tetrachloride[4] at room temperature. After stirring for thirty minutes it was refluxed gently for sixteen hours, kept at 25° for two days, the carbon tetrachloride and a little ethylene chlorohydrin distilled off through a seven-bulb column (15 mm. at end) and the residue fractionated at 2–3 mm.; yield, 75 g. (60% on the chlorohydrin); b. p. 180–182° (2–3 mm.); $d^{20}{}_{20}$ 1.428. About 20 g. of product boiling above 215° (2–3 mm.) showed considerable decomposition on attempted distillation. Plimmer and Burch[10] reported about 12% yield, b. p. 140° (40 mm.) and *d* 1.39. The cause of the disagreement in boiling points is not apparent.

Anal. Calcd. for $C_6H_{12}O_4Cl_3P$: C, 25.22; H, 4.24; Cl, 37.26; P, 10.87. Found: C, 25.26; H, 4.39; Cl, 37.27; P, 10.69.

Tri-(choline chloride) Phosphate (Phosphato-tri-(ethyltrimethylammonium chloride)) (II).—A solution of 6.5 g. (0.11 mole) of trimethylamine and 10 g. (0.035 mole) of pure tri-β-chloroethyl phosphate in 12 cc. of anhydrous ethanol[11] was sealed at 0° and then kept at 30–33° for seven days, well-built prisms starting to separate after two to three days. After cooling to 0° the crystals were filtered off, washed with 8 cc. of cold isopropanol and dried at 25° *in vacuo* over calcium chloride; yield, 7.7 g. (48%). The filtrate, diluted with 25 cc. of isopropanol, gave on long standing at 5° about 0.3 g. of crystals. When dissolved in about six parts of absolute ethanol at 60° and decolorized with activated carbon, the triester crystallizes as colorless prismatic needles or elongated prisms in 80–85% yield with little, if any, alcoholysis. It is somewhat hygroscopic, is practically insoluble in benzene, chloroform and ether, difficultly soluble in warm isopropanol, soluble in warm ethanol and readily soluble in cold water to yield a neutral solution from which the chlorine is removed quantitatively by silver nitrate. Its decomposition point (incomplete) of about 245° (uncorr.) is not a suitable criterion of purity. Analyses of thrice recrystallized samples were essentially the same when dried to constant weight at 25° *in vacuo* over phosphorus pentoxide or at 90° *in vacuo*, but the physiological activity[2] was considerably increased by the two hours of heating at 90°.

Anal. Calcd. for $C_{15}H_{39}O_4N_3Cl_3P$: C, 38.90; H, 8.50; N, 9.08; Cl, 22.99; P, 6.70. Found: (dried at 25°) C, 38.68; H, 8.84; N, 8.97; Cl, 22.90; P, 6.85; (dried at 90°) C, 38.85; H, 8.68; N, 8.97; Cl, 22.76; P, 6.71.

Toluene was found unsuitable as a solvent in the prepa-

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(8) Sample previously dried overnight at 25° *in vacuo* over calcium chloride.

(9) Prior to the determination of nitrogen (Kjeldahl) and phosphorus, the sample was digested for two hours with hot concentrated sulfuric acid and the platinum filtered off.

(10) Plimmer and Burch, *J. Chem. Soc.*, 284 (1929).

(11) It is important to use the specified proportions of tri-β-chloroethyl phosphate and ethanol. When 8 cc. of ethanol was used, the separation of a sirup with the crystals of the triester necessitated the interruption of the reaction after three days, removal of the crystals and dilution with ethanol. With 18 cc. the reaction time was considerably greater (twelve days) and the yield of triester was smaller (30%).

ration of the triester. Trimethylamine (6.5 g.) and tri-β-chloroethyl phosphate (10 g.) in 100 cc. of dry toluene, kept sealed at 25–30° for several days or at 78–80° for two days, gave a sirup. A solution of the sirup, prepared at 78–80°, in a mixture of isopropanol and ether yielded at 5° crystals (0.6 g.) which could be recrystallized from isopropanol (needles), but was not investigated further.

Chloroaurate.—The compound was precipitated by adding an aqueous solution (7 cc.) of 1 g. of pure triester to 10% excess of the calculated auric chloride in 10 cc. of water; yield, 2.7 g. It crystallizes from water (difficultly soluble) as clusters of short, yellow prismatic needles melting incompletely at 216° (uncorr.) and to a clear red liquid at 230°.

Anal. Calcd. for $C_{15}H_{39}O_4N_3PAu_3Cl_{12}$: C, 13.11; H, 2.86; N, 3.06; P, 2.26; Au, 43.07. Found (dried at 25° *in vacuo* over phosphorus pentoxide): C, 13.17; H, 2.88; N, 3.07; P, 2.28; Au, 43.20.

Summary

From the products of the phosphorylation of choline chloride with orthophosphoric acid and phosphorus pentoxide the amorphous calcium salt of the monocholine ester of phosphoric acid has been prepared free from choline but containing 3–4% of dicholine phosphate, a new chloroaurate of which is described. Monocholine phosphate chloroaurate prepared from the calcium salt was somewhat impure, but from it could be obtained the pure, crystalline chloroplatinate.

Trimethylamine condenses with tri-β-chloroethyl phosphate under appropriate conditions to give crystalline tri-(choline chloride) phosphate which yields a crystalline chloroaurate. An effect of heat on the pure triester is pointed out.

Improvements have been made in Plimmer and Burch's procedure for the preparation of tri-β-chloroethyl phosphate.

WASHINGTON, D. C. RECEIVED JULY 8, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

The Predominant Role of Association in the Dissociation of Simple Straight-Chain Sulfonic Acids in Water. I. Conductivity[1]

BY J. W. MCBAIN AND MARGARET D. BETZ

Among the simplest uni-univalent organic electrolytes are the straight-chain saturated alkyl sulfonic acids, RSO_3H, the higher members of which have been made for the first time and generously placed at our disposal by Prof. C. R. Noller and J. J. Gordon.[2] In a series of communications it will be shown that their behavior at great dilution is that of simple partially dissociated acids, but that in more concentrated solutions, such as from $N/20$ upward, a radical change takes place in their physical chemical properties, such as conductivity, freezing point and electromotive force.

This change is the opposite of that which the interionic attraction theory was set up to explain. It would appear to be due to association in the sense in which this term has so long been used in chemical science, as for example in describing the occurrence of double molecules in the vapor of acetic acid or in solutions of acetic and other acids in benzene. This association is not caused by Coulomb attraction of opposite charges, but it is due to van der Waals cohesive forces. It occurs even in spite of electrostatic repulsion, for it is very marked in the association of ions of like charge.

Since in all the more concentrated solutions the effect of association is so dominant as to submerge the ordinary behavior of interionic attraction, it must surely be a force of universal occurrence and a factor which is seldom negligible. This association must affect not merely ions but also the molecules from which they are derived. Since one of the authors introduced the conceptions of colloidal electrolytes and of neutral and ionic micelles more than twenty years ago,[3] it has been known that the group of colloidal electrolytes embraces more substances than the acids and bases put together.[4] However, it is not sufficiently recognized that colloidal electrolytes appear to be the rule rather than the exception in non-aqueous solutions and that even fairly simple substances in aqueous solution, such as

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(1) Experiments by Miss Betz.

(2) C. R. Noller and J. J. Gordon, THIS JOURNAL, **55**, 1090 (1933); for cetyl sulfonic acid see J. W. McBain and R. C. Williams, *ibid.*, **55**, 2250 (1933); B. Flaschenträger and G. Wannschaff, *Ber.*, **67**, 1121 (1934); R. C. Murray, *J. Chem. Soc.*, 739 (1933).

(3) J. W. McBain and C. S. Salmon, THIS JOURNAL, **42**, 426 (1920); *Proc. Roy. Soc.* (London), **A97**, 44 (1920); J. W. McBain and H. E. Martin, *J. Chem. Soc.*, **105**, 957 (1914); J. W. McBain, *Trans. Faraday Soc.*, **9**, 99 (1913); *Kolloid-Z.*, **12**, 256 (1913); J. W. McBain, M. E. Laing and A. F. Titley, *J. Chem. Soc.*, **115**, 1279 (1919).

(4) Compare the extensive international symposium on colloidal electrolytes of September, 1934, *Trans. Faraday Soc.*, **31**, 1 (1935).

butyric acid[5] or potassium iodate,[6] partake of this behavior in measurable degree.

These sulfonic acids offer exceptionally favorable material for study on account of their ready solubility and complete freedom from hydrolysis. These hydrogen soaps are more colloidal than the ordinary alkali soaps of similar length of carbon chain.

Experimental

Macroscopic Observations on the Hydrogen Soaps.—The hydrogen soaps undecyl (C_{11}), lauryl (C_{12}) and myristyl (C_{14}), sulfonic acids, were in the form of very hygroscopic powders containing one molecule of water of crystallization. When added to water, the soaps form concentrated liquid crystal solutions which, when preparing the higher concentrations of isotropic solution, require several hours of heating at temperatures above 25° to redissolve completely in additional water. The highest concentrations of the sulfonic acids prepared in this manner were 1.13 N_w undecyl, 0.85 N_w lauryl, and 0.53 N_w myristyl. The more concentrated solutions of the undecyl and lauryl sulfonic acids were still stable at 0°. Myristyl sulfonic acid is less soluble and therefore above the freezing point of water has separated as an opaque white gel. As the temperature is raised, the myristyl sulfonic acid progressively dissolves, the curd becoming clearer and "melting" to a transparent solution at 15–16°. The sodium and potassium salts are so much less soluble that they require heating to 25 or 30°. All of the isotropic soap solutions froth freely, and undecyl and lauryl sulfonic acids yield a generous lather even at 0°.

Purest available potassium chloride and water (0.5×10^{-6} mhos) were used. Solutions were made up by weight and concentrations were determined by titration after being checked by refractive index with the Zeiss dipping refractometer with prism No. 1 and auxiliary prism. The readings in scale divisions were as follows.

Sulfonic acid		
Undecyl	$C_{11}H_{23}SO_3H$	$15 + 80\,m$ at 19.0°
Lauryl	$C_{12}H_{25}SO_3H$	$15 + 80\,m$ at 19.4°
Myristyl	$C_{14}H_{29}SO_3H$	$15 + 99\,m$ at 19.0°

As is well known, association does not much affect the value of molar refraction in solution.

The solubilities in grams per 100 g. of water of the calcium sulfonates were very approximately determined as follows.[7]

	Undecyl	Lauryl	Myristyl
Calcium	0.2	0.02	0.02

The densities at 25.00/4° were measured by Dr. M. E. L. McBain as follows, where molality, $m = N_w$ or weight normality.

Undecyl		Lauryl		Myristyl	
Concn., N_w	Density	Concn., N_w	Density	Concn., N_w	Density
0.3688	1.00171	0.375	0.99933	0.098738	0.99749
.4641	1.00301	.635	1.00063	.2369	.99829
.7823	1.00686	.820	1.00123	.4504	.99964

Conductivity measurements were made with the Grinnell Jones–Dykes type of bridge, supplied by Leeds and Northrup, with an oil thermostat at 25 ± 0.01° and the H-shaped cell of McBain and Titley with cell constant 13.239. The conductivity of lauryl sulfonic acid solutions at 25° was unaltered by lapse of time or by previous heating and quick cooling.

The conductivity data are recorded in Tables I, II and III. In column 4 is given the Arrhenius ratio μ_v/μ_∞ where however μ_∞ is taken as 378 for the most dilute solutions below and including

Table I

Conductivity of Undecyl Sulfonic Acid at 25°

N_w	K	μ_v	$100\ \mu_v/\mu_\infty$	$100\ \mu_v/\mu_\epsilon$
0.000950	0.000349	368.5	97.51	98.5
.00950	.00308	325.8	86.21	89.3
.04330	.008903	208.20	49.12	58.72
.06134	.010693	177.23	41.81	50.30
.0800	.013846	176.69	41.69	50.69
.1049	.017452	170.70	40.28	49.53
.3688	.062810	184.64	43.56	(59.0)
.4641	.08050	191.87	45.30	
.7761	.13196	199.81	47.14	
1.1375	.18337	202.25	47.72	

Table II

Conductivity of Lauryl Sulfonic Acid at 25°

N_w	K	μ_v	$100\ \mu_v/\mu_\infty$	$100\ \mu_v/\mu_\epsilon$
0.001	0.000347	348.1	92.11	93.04
.0061	.001987	327.2	86.58	89.08
.010	.003212	322.9	85.44	88.64
.0525	.00783	151.5	35.72	42.50
.075	.00954	129.9	30.63	36.71
.1025	.01479	148.3	34.97	(42.69)
.2550	.03860	161.3	38.03	
.35	.05238	162.9	38.41	
.511	.0796	175.7	41.43	
.75	.1112	175.9	41.48	
.814	.1196	176.6	41.64	

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(5) C. R. Bury and D. G. Davies, *J. Chem. Soc.*, 2413 (1932); Jones and Bury, *Phil. Mag.*, **4**, 841 (1927); Bury, *ibid.*, p. 980; Grindley and Bury, *J. Chem. Soc.*, 679 (1929); 1665 (1930); E. A. Goode, N. S. Bayliss and A. C. D. Rivett, *ibid.*, 1950 (1928).

(6) J. W. McBain, S. S. Kistler and W. McClatchie, *J. Phys. Chem.*, **35**, 130 (1931).

(7) Compare the values found for the corresponding sulfates by S. Lenher [*Am. Dye Reporter*, 6/11/33, 663–667].

TABLE III

CONDUCTIVITY OF MYRISTYL SULFONIC ACID AT 25°

N_w	K	μ_v	$100\ \mu_v/\mu_\infty$	$100\ \mu_v/\mu_\epsilon$
0.00122	0.000422	347.0	91.82	93.0
.010	.001696	170.6	40.23	46.35
.015	.001874	125.8	29.66	33.73
.031	.003536	115.4	27.21	31.73
.0514	.0605	119.7	28.23	33.62
.09873	.0114	118.9	28.04	(33.90)
.2369	.0281	126.7	29.88	
.4504	.06694	167.3	39.45	
.543	.0762	161.5	38.08	
.543	.07551	160.0	37.76	

0.01 N_w. For all the more concentrated solutions, as will be explained later, μ_∞ was taken as 426; probably (see later) this should have been increased to 546 in the most concentrated solutions, which would have decreased the final values of the ratio by about one-fourth.

During the past few years, it has become customary to calculate the degree of dissociation of uni-univalent electrolytes, $\alpha = \mu_v/\mu_\epsilon$, following the method of Sherrill and Noyes and MacInnes as developed by Shedlovsky, Davies, and others, upon the basis of the Debye–Hückel–Onsager and other equations. Incidentally, several authors have thus found that certain electrolytes, such as potassium nitrate or the potassium iodate already referred to, are not as fully dissociated as potassium chloride.

From the meager data available for large organic ions, we have taken the value for μ_∞ as $350 + 28 = 378$, where hydrogen ion accounts for 96.2% of the total. The initial Onsager slope for complete dissociation is therefore $\mu_\epsilon = 378 - 145.7\sqrt{N_v}$.

These conductivity data are plotted in Fig. 1. The curves are of the same form as those which have become familiar for ordinary soaps such as potassium laurate. The initial parts of the curves show that dissociation is definitely not complete and that the observed values for $\alpha = \mu_v/\mu_\epsilon$ correspond to approximate dissociation constants of the order of K = 0.01, 0.05 and 0.07. This compares with the value 0.3 for potassium laurate at 18°, that of hydrochloric acid and potassium chloride being taken as infinity. The values are only approximate on account of the associative factors which are beginning to assert themselves with increase in concentration. Figure 1 also includes for comparison the conductivity curves which are exhibited by fully dissociated uni-univalent and uni-decivalent electrolytes for 100% dissociation. In the latter case, according to Mukherjee,[8] the numerical factor in the final term of the Onsager equation is increased to 2925 (instead of our 145.7), and for a uni-centivalent electrolyte to 40,572. (That is, there would be no observable μ_v in all solutions accessible to measurement.) It is quite obvious that although the actual data lie below the limit for uni-univalent electrolytes, they all very greatly exceed the values possible for an ionic micelle regarded as a polyvalent ion in the ordinary sense. They show that the treatment of the ionic micelle as an ordinary polyvalent ion is wholly insufficient.[9]

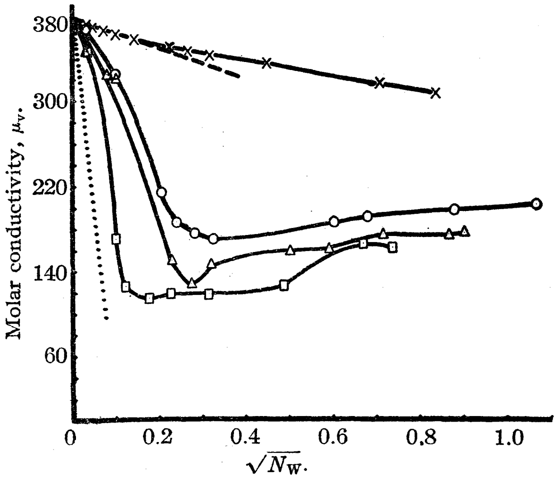

Fig. 1.—Molar conductivity: ×, hydrochloric acid "International Critical Tables"; ○, undecyl sulfonic acid; △, lauryl sulfonic acid; □, myristyl sulfonic acid. Dashed line indicates the slope for 100% for a uni-univalent electrolyte; dotted line indicates the slope for a uni-decivalent electrolyte.

The Behavior of these Acids at Ordinary Concentrations.—The most striking and remarkable feature exhibited by the conductivity of our sulfonic acids is the minimum at 0.1, 0.075, and 0.031 N_w solutions of undecyl lauryl, and myristyl, respectively. After passing through a minimum in these moderately dilute solutions, the conductivity rises markedly with increase of concentration. Such behavior in aqueous solution is unparalleled except by the higher sodium

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(8) I. Mukherjee, *Kolloid-Z.*, **62**, 264 (1933); **65**, 72 (1933).

(9) Thus, this suggestion thrown out by Van Rysselberghe and others is inappropriate since it is not in accordance with experiment [P. J. Van Rysselberghe, *J. Phys. Chem.*, **38**, 645 (1934)]. Similarly, the discussion of J. L. Moilliet, B. Collie, C. Robinson and G. S. Hartley [*Trans. Faraday Soc.*, **31**, 120 (1935)] is crippled by the same invalid assumption and also by the failure to recognize the existence of undissociated molecules and of their association products, the neutral micelles. Again, the conductivity, freezing point and electromotive force curves for soaps and for these sulfonic acids are not in accord with the simple mass action equation [compare R. C. Murray and G. S. Hartley, *ibid.*, p. 186].

and potassium soaps studied by McBain and collaborators[10] and the alkyl sulfates (salts and free acid) recently studied by Lottermoser and Püschel which closely parallel our findings.[11]

Figure 1 emphasizes by comparison with the initial Onsager slope the increasingly excellent conductivity of these acids in concentrated solution. It is enormously greater than that consonant with the behavior of a weak electrolyte as exhibited in the very dilute solutions, and still more so with the increasing weakness indicated in the slightly less dilute solutions before the minimum in conductivity is attained.

The conductivity rises above the minimum by 18, 36, and for myristyl no less than 45%. The old hypothesis of McBain and Salmon, which appears still valid, is that simple anions of low mobility associate to form ionic micelles of high mobility in accordance with Stokes' law, since they have retained their electrical charges. However, it is here necessary to assume an extraordinarily high mobility for the ionic micelle, rising to that of the hydroxyl ion for each charge on the ionic micelle. If the equivalent conductivity of the charges of the ionic micelle had been raised only to that of the chlorine ion, the maximum increase of conductivity would be the inadequate value 424/378 = 1.125 fold. That found by McBain and Williams[2] for acetyl sulfonic acid at 90° was likewise larger, namely, 1.25 fold. The existence of this remarkable enhancement of conductivity is therefore beyond dispute.

The alternative hypothesis adopted by Franklin and Kraus for solutions in liquid ammonia, to the effect that a large portion of the current may be borne by free electrons and be semi-metallic in nature, seems unnecessarily bold for these aqueous solutions. Also, the recent hypothesis of Fuoss and Kraus[12] applies only to minima in solvents of low dielectric constant and of very low dissociating power.

The Debye–Hückel theory was set up to explain why ions show less conductivity than that which corresponds to their intrinsic mobility. We have here the opposite phenomenon, a great and increasing conductivity in spite of inter-ionic attraction.

The intrinsic mobilities of ions in strong aqueous solutions are, however, really high. For example, in the diffusion of potassium chloride where the effects of interionic attraction almost completely eliminate themselves, the potassium and chloride ions actually move much faster than at infinite dilution.[13] The differential or "instantaneous" diffusion coefficients are far larger in concentrated solutions of potassium chloride than they are in pure water.

Equally relevant is the demonstration by McBain and Van Rysselberghe[14] by means of migration data that in all concentrated solutions containing even one ion that is more than univalent, complex anions are formed in large amount. Similarly, by means of ultra-filtration, McBain, Kistler and McClatchie[6] have shown that moderate concentrations of such salts as cadmium iodide or potassium or sodium iodates contain appreciable proportions of constituents so large that they are held back by an ultrafilter that is permeable to all simple ions and molecules.

A high conductivity per electrical charge must always occur where the linear velocity in cm./sec./volt/cm. is exceptionally high, as is the case with air bubbles and suspended hydrocarbons.[15] When further, the number of charges is equal to the number of chemical equivalents in the particle, we observe a very high total conductivity as in the present case.

Freezing point experiments to be described do not allow of any alternative hypothesis of increased relative concentration of hydrogen ion in stronger solutions, nor do they admit of measurable amounts of simple free molecules; nor is it apparent how a Grotthuss mechanism can be invoked in explanation of our data.

The enhanced mobility of the ionic micelle is not due merely to close packing as compared with the original ions, it is also due to the stripping off of the water of hydration from those ions in order that they may come into contact and be close packed and anhydrous in the interior of the particle.

Finally, the association here irresistibly dem-

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[10] However, in 0.0025 *N* potassium, sodium, lithium and calcium (but not strontium nor strychnine) salts of gum arabic, D. R. Briggs observed a minimum [*J. Phys. Chem.*, **38**, 872 (1934)].

[11] A. Lottermoser and F. Püschel, *Kolloid-Z.*, **63**, 175 (1933). See also the maximum obtained in moderately dilute solutions of methylene blue by C. Robinson and H. E. Garrett, *Trans. Faraday Soc.*, **31**, 253 (1935).

[12] R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 2387 (1933).

[13] B. W. Clack, *Proc. Phys. Soc.* (London), **27**, 116 (1925); **36**, 313 (1924); *Phil. Mag.*, **15**, 1061 (1933); J. W. McBain and C. R. Dawson, *Proc. Roy. Soc.* (London), **A148**, 32 (1935); see also M. E. L. McBain, This Journal, **55**, 545 (1933), and private communication regarding Sky Blue F.F. by Dr. L. M. Neale, Manchester, England.

[14] J. W. McBain and P. J. Van Rysselberghe, This Journal, **52**, 2336 (1930).

[15] See for example R. DuBois and A. H. Roberts, *J. Phys. Chem.*, **35**, 3070 (1931).

onstrated is real association, not the electrostatic clustering of ions in Bjerrum's well-known modification of the interionic theory that currently passes under the name. It is association of like parts of the uncharged portions of the molecules and ions under the influence of van der Waals forces.

Since neutral molecules are admittedly present in large proportion in dilute solutions, it would be very strange if these too did not associate with each other to form neutral micelles. Indeed, if it occurs with the ions in spite of electrostatic repulsion, it must be far more complete with the similar neutral molecules. For ordinary soaps, McBain and collaborators have deduced the presence of practically uncharged neutral micelles, using several distinct lines of evidence, none of which can otherwise be even semiquantitatively explained—ultrafiltration, ultracentrifuge and electrolytic migration.

Surely, if association can play so predominant a role in these simple cases, it must be of practically universal occurrence and only seldom completely negligible.

Summary

In dilute solutions, the straight chain sulfonic acids are simple partially dissociated electrolytes.

A remarkable transformation sets in at about $N/20$ where the conductivity is at a minimum, increasing with concentration by 18, 36 and 45% for the three sulfonic acids here studied.

The only explanation so far found is association of *like* ions to form ionic micelle, whose *equivalent* conductivity in concentrated solutions attains to that of the hydroxyl ion.

Association is so dominant that it completely submerges the ordinary features of interionic attraction.

STANFORD UNIVERSITY, CALIFORNIA

RECEIVED JUNE 18, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Association in the Dissociation of Simple Straight-Chain Sulfonic Acids in Water. II. Freezing Point[1]

BY J. W. MCBAIN AND MARGARET D. BETZ

Conductivity has shown that in dilute solution the sulfonic acids are simple and moderately weak, but that with increasing concentration a transformation takes place, due to formation of ionic micelles whose equivalent conductivity rivals that of the hydroxyl ion itself. Here we present freezing point data which likewise show this great influence of association. The molal freezing point lowerings fall rapidly in very dilute solution, pass through a minimum, and steadily increase with rising concentration—again the opposite effect from such factors as usually determine dissociation constant and interionic attraction. Association of like ions, overcoming Coulomb repulsion, produces ionic micelles. Neutral molecules associate even more readily to form neutral micelles.

Freezing point measurements of free sulfonic acids are untroubled by the hydrolysis whose effects are often disturbing with ordinary soaps.[2] Myristyl sulfonic acid, like most of the soaps, is too insoluble for study at 0°. The lowering observed with sulfonic acids, like that with octoates, decoate, laurate and oleates, is readily measurable, but except in concentrated solution, much less than that for an acetate or hydrochloric acid.

Experimental Data

More concentrated solutions were investigated by the Beckmann method, which of necessity gives too low a freezing point, since a solution cannot continue to freeze except below its freezing point; however, undercooling was confined to 0.10°. More dilute solutions were measured by the Richards method, in some cases using a 0° room and a Beckmann thermometer, in others using a platinum resistance thermometer with a Leeds and Northrup Mueller bridge and high sensitivity type H galvanometer of 17 ohms resistance, reading more closely than 1/10,000

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(1) Experiments by Miss Betz, except where indicated.

(2) J. W. McBain, M. E. Laing and A. F. Titley, *J. Chem. Soc.*, (London,) **115**, 1289 (1919). Errata: On page 1289, twenty-third line, after "solutions" insert "due to separation of acid potassium laurate." Page 1289, Table VI, last column, the next to the last number should read 1.355* instead of 0.355; the next to the last number in each column should be marked with an asterisk. Page 1290, second line, delete "soap" and insert "acid potassium laurate"; Table VII, first number of fifth column should be 0.206 instead of 1.196; in the last column the first seven numbers should be marked with an asterisk.

ohm. Temperature readings were standardized against a Bureau of Standards calibrated mercury thermometer and analyses were made by means of a Zeiss dipping refractometer. The sulfonic acids froth freely at 0°. Fifty-four solutions were measured; all results are given in the graphs, but only those for rounded concentrations are given in Tables I and II. The values for the activity coefficient γ were obtained following the procedure of Randall,[3] neglecting heat of dilution.

Table I

Molal Lowering of Freezing Point (Θ/m) and Activity Coefficients (γ) of Undecyl Sulfonic Acid in Aqueous Solution; $g = i/2 = \Theta/2\lambda m = 1 - j$

m	Θ/m	g	γ
0.01	3.452	0.929	0.838
.02	2.775	.747	.575
.04	1.850	.498	.358
.05	1.590	.428	.298
.09	1.005	.270	.175
.16	0.689	.186	.102
.25	.537	.145	.0680
.36	.539	.145	.0493
.49	.576	.155	.0383
.64	.608	.164	.0308
.81	.641	.173	.0252

Table II

Molal Lowering of Freezing Point (Θ/m) and Activity Coefficients (γ) of Lauryl Sulfonic Acid in Aqueous Solution; $g = i/2 = \Theta/2\lambda m = 1 - j$[a]

m	Θ/m	g	γ
0.001	3.6	0.99	0.957
.002	3.6	.99	.933
.005	3.46	.959	.874
.01	3.34	.897	.789
.02	2.65	.712	.604
.05	1.524	.410	.290
.09	0.669	.180	.151
.10	.604	.163	.136
.16	.576	.155	.091
.20	.554	.149	.074
.25	.550	.148	.062
.36	.539	.145	.045
.50	.544	.146	.034
.64	.576	.155	.028
.81	.591	.159	.023

[a] Experiments by M. E. L. McBain.

The Osmotic Coefficient, g.—Activity coefficients have been so commonly employed, especially in this country, that there appears to be a tendency to forget that the osmotic coefficient of Bjerrum, g, and the i value of van't Hoff have exactly equal thermodynamic validity and significance. Bjerrum's g is identical with van't Hoff's i/v where v is the total number of ions producible at infinite dilution from one formula weight. g is $\Theta/v\lambda m$ and is also equal to the $1-j$ of Lewis and Randall. Following Guggenheim's notation[4]

$$\ln 1/N_0 f_0 \equiv g \ln 1/N_0 = L_F^\circ \Theta/RT^{\circ 2} = gm$$

and for freezing points of aqueous solutions within the experimental error even of the best determinations, $g = \Theta/\lambda m$. $N_0 \text{ d} \log f_0 = -N_S \text{ d} \log F_S$.

For ideal solutions, g, like the activity coefficient of the solvent, f_0, and that of the solute, f_S, becomes unity. However, as we have just seen, g varies directly with the actual lowering of freezing point just as directly as m, while the change in the activity coefficients is far more indirect.

The relation between osmotic coefficient g and activity coefficient f is very similar to that between concentration of the hydrogen ion and pH in that the first varies directly when the second is changing as the inverse logarithm.

So intent have workers in this field been during the last dozen years upon discussing the interionic attraction explanation of the deviation of electrolytes from the behavior of ideal solutions, that it seems to have been commonly forgotten that the actual freezing point lowering of hydrochloric acid never deviates from that of a truly ideal solution by more than 6% over the whole range of concentration from infinite dilution to 1 molar. Indeed, according to the "International Critical Tables," the greatest deficit is that for 0.1 *N* solution, amounting to only 5.2%. Thereafter, it approaches more closely to the lowering of an ideal solution, equaling it below 0.6 *M* and surpassing it by 6% in 1 *M* solution. Similarly, in 1 *M* solution, the lowering for sucrose is 10.9% above that of an ideal solution and that of potassium chloride only 12.5% below the ideal value.

Nevertheless, the numerical scale in which activity coefficients are expressed exaggerates these deviations, making the activity coefficients for these three solutes in 1 *M* solution 0.8404,[5] 1.221 and 0.601,[6] respectively. It is interesting that the activity coefficient of hydrochloric acid should be so much less than unity when its actual freezing point lowering exceeds that of an ideal solution. Activity is a partial quantity and possesses no more *direct* significance than does any other partial quantity such as partial specific

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[3] M. Randall, This Journal, **48**, 2512 (1926).

[4] E. A. Guggenheim, "Modern Thermodynamics by the Methods of Willard Gibbs," Methuen and Company, Ltd., London, 1933.

[5] M. Randall and L. E. Young, This Journal, **50**, 995 (1928).

[6] M. Randall and A. M. White, *ibid.*, **48**, 2514 (1926).

volume. For example, as shown by Lewis and Randall, the partial specific volume of magnesium sulfate is negative, which has very indirect connection with its real positive volume.

The Graphs of $j/\sqrt{m}$ Against $\sqrt{m}$.—The $j/\sqrt{m}$ graphs of Lewis and Randall here assume a characteristic form, decidedly different from that either of weak or of strong electrolytes (see Fig. 1). All crystalloidal electrolytes, from the strongest, like potassium chloride, through progressively weaker ones, like acetic acid, to the weakest, such as sucrose, must lie between the graph marked KCl and $K = 0$, as Randall and Allen[7] also have shown. For $K = 1$, the graph is a straight line. For weaker electrolytes, the height of the "hump" is a measure of the weakness and it rises to a value of 46 for acetic acid at $m = 10^{-5}$, all curves approaching the same limit as KCl for infinite dilution.

In very dilute solutions, the sulfonic acids exhibit this normal behavior of weak electrolytes and they are drawn with the slopes corresponding with the conductivity results. However, the heights of the maxima, 2.6 and 2.8 for the sulfonic acids, are those of a still weaker electrolyte for which $K = 0.005$; but this maximum does not lie at the position for such a weak electrolyte, namely, $m = 0.01$, but in the much stronger solution $m = 0.05$. Most striking and significant however is the disregard shown for the theoretical limiting curve $K = 0$. The graphs before reaching their maximum cut sharply across this boundary into the region forbidden for crystalloids whether electrolytes or not. Hence colloid is present in large quantity.

It is not enough to assume that the undissociated acid associates to form a colloid because of the very high conductivity which forces us to recognize the anions also as colloid. On the other hand, as will be shown in the next paper of this series dealing with electromotive force, it is not enough to assume that only the anions are colloid. Both molecules and anions must be colloidal for the total freezing point lowering is far less than that corresponding to the hydrogen ion indicated by the usual method of calculating e. m. f.

Cetyl sulfonic acid exhibits at 90° a similar high value of $j/\sqrt{m}$, apparently rising to a maximum of 2.5 at $m = 0.01$,[8] although this is in a dilution where the vapor pressure method becomes inaccurate. On the other hand, not even the highest soaps of sodium or potassium yield at 90° a value exceeding 1.2. For the laurates, it is only 0.64 and 0.67 at 90°, but at 0° the curve rises to a maximum of 1.65 for potassium laurate at $m = 0.1$ with the sudden nearly vertical dip in more dilute solutions which we have here found for the sulfonic acids.

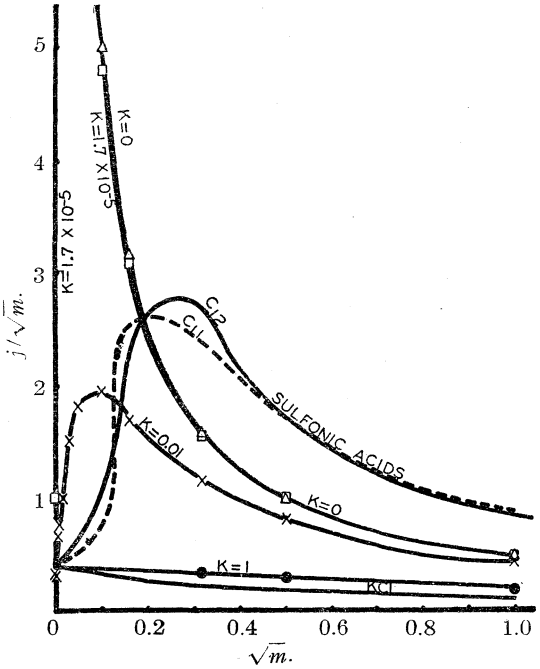

Fig. 1.—$j/\sqrt{m}$ graphs for sulfonic acids, showing their very different dehavior from that characteristic of either strong or weak electrolytes except in very dilute solution.

Discussion

Figure 2 exhibits the value of g of the sulfonic acids in comparison with hydrochloric acid. It will be noted that they too pass through a minimum and rise again with increase of concentration to the extent of 25 and 26%, respectively.

Figure 3 compares the activity coefficients[9] of lauryl, which is very similar to that of undecyl, with those of hydrochloric acid and of potassium laurate. The latter would appear to refute the suggestion of Linderstrøm-Lang[10] that soaps might be regarded as simple electrolytes 100% dissociated provided that the cations become lost as far as osmotic effects are concerned, upon

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[7] M. Randall and C. Allen, This Journal, **52**, 1818 (1930). Dissociation constants deduced by their rule from freezing point data would not be legitimate or free from ambiguity for these substances.

[8] J. W. McBain and R. C. Williams, *ibid.*, **55**, 2254 (1933).

[9] Compare the discussion of J. W. McBain and M. M. Barker, *Trans. Faraday Soc.*, **31**, 149 (1935).

[10] K. Linderstrøm-Lang, *Compt. rend. trav. lab. Carlsberg*, **16**, No. 6, 1-47 (1926); for other incompatible evidence see J. W. McBain, This Journal, **50**, 1636 (1928).

finding themselves among the comparatively long anions (at most only 17 Å. long, but probably far less[11] or even spherical). It would further be necessary to assume that the anions are lost among each other and that ordinary ions added are not lost since, as is well known, they exert in soap solutions the full osmotic effects that they do in water. Since this is true for added potassium, sodium or hydrogen ions, it must be equally true of the same ions already present in the soap itself. In Fig. 3 for $m = 0.048$, $m = 0.22$, the activity coefficient of potassium laurate is almost that of the highly dissociated hydrochloric acid, whereas that of lauryl sulfonic acid with identical length of hydrocarbon chain is much less than half as great. According to his suggestion, the results should have been identical if only simple ions are present in both cases instead of differing by 2.5-fold.

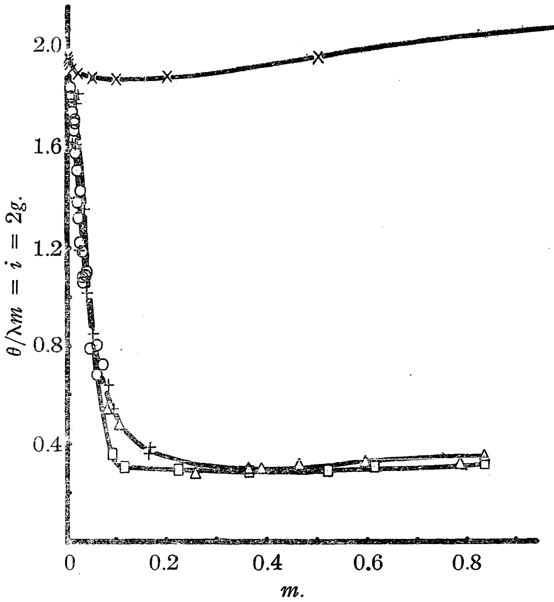

Fig. 2.—Osmotic coefficients of hydrochloric acid (×) and of undecyl (△) and lauryl (□) sulfonic acids.

It is obvious from the figures that the ionic micelle does not behave like a polyvalent ion whose charges are coincident. McBain,[12] in accordance with the suggestion of Bjerrum in 1923 and later corroborated by Scatchard and Kirkwood, explained this as being due to the distance apart of like charges on a single ionic micellar particle being greater than the average distance between ordinary ions in ordinary solutions such as potassium chloride. Simms,[13] whose work has not been accorded the attention it deserves for its fundamental importance in colloid phenomena and in the application of interionic attraction theory as the basis of electro-kinetics, has discussed the theory of widely spaced charges. He, in agreement with *ad hoc* calculations of Debye, formulated the influence of ionic strength for the two extreme cases; first where polyvalent charges coincide as in the Debye–Hückel theory of ordinary ions, and second where molecules or particles are polyvalent but with widely separated charges of like sign and behave effectively as univalent ions.

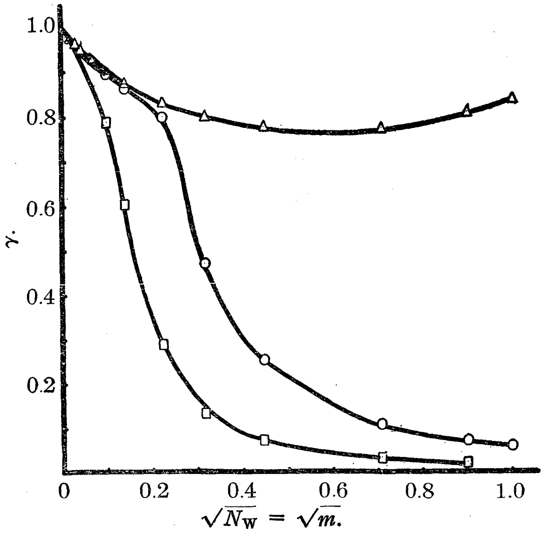

Fig. 3.—Activity coefficients of lauryl sulfonic acid (□), potassium laurate (○) and hydrochloric acid (△).

Summary

The osmotic coefficients of undecyl and lauryl sulfonic acids pass through a minimum in dilute solution, rising again with concentration by about 25%.

The graphs of $j/\sqrt{m}$ against $\sqrt{m}$ exhibit a highly characteristic form which departs strikingly from that of strong electrolytes or that for any simple weak electrolyte or non-electrolyte.

The only consistent interpretation of all the data is that whereas in dilute solutions they are simple moderately weak electrolytes, with increased concentration molecules and ions associate into neutral and ionic micelle, respectively, but that ionic micelles, owing to the wide spacing of their charges, have the ionic strength similar to uni-univalent electrolytes.

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[11] I. Langmuir, Chap. 29, Vol. I of Jerome Alexander's "Colloid Chemistry," 1926, p. 838.

[12] J. W. McBain, This Journal, **50**, 1636 (1928); G. Scatchard and J. G. Kirkwood, *Physik. Z.*, **33**, 297 (1932).

[13] H. S. Simms, This Journal, **48**, 1239, 1251 (1926); *J. Phys. Chem.*, **32**, 1121 (1928); and *J. Gen. Physiol.*, **11**, 613 (1928).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Straight-Chain Sulfonic Acids in Water. III. Electromotive Force[1]

BY J. W. MCBAIN AND MARGARET D. BETZ

Before attempting to determine concentration of hydrogen ion using a hydrogen electrode separated from a 0.1 N calomel electrode by a 3.5 N potassium chloride bridge, it is advisable to refer to the standard data on hydrochloric acid[2] and to compare them with the predicted values from $E = E_0 + E_D + 0.05915 \log 1/N_w f_H$ at 25°.

E_0 has been shown by Guggenheim and Schindler[3] to be equal to 0.3337 volt. E_D is calculable from the two extreme formulas, that of Henderson for a diffuse boundary

$$E_D = \frac{-RT}{F} \frac{C_1(U_1 - V_1) - C_2(U_2 - V_2)}{C_1(U_1 + V_1) - C_2(U_2 + V_2)} \log \frac{C_1(U_1 + V_1)}{C_2(U_2 + V_2)}$$

where $-RT/F = -0.05915$; $C_1 = C_{KCl} = 3.5$; $U_1 = 73.50$; $V_1 = 76.32 = V_2$; $C_2 = C_{HCl}$; $U_2 = 349.72$; and the transcendental equation of Planck for a sharp boundary $E_D = 0.05915 \log \xi$ where ξ is defined by the equation

$$\frac{\xi C_1 V_1 - C_2 V_2}{C_1 V_1 - \xi C_2 V_2} = \frac{\log (C_1/C_2) - \log \xi}{\log (C_1/C_2) + \log \xi} \times \frac{\xi C_1 - C_2}{C_1 - \xi C_2}$$

which may be solved by a short series of approximations. Both formulas neglect the actual laws of diffusion as revealed experimentally and in particular the acceleration, retardation and collision[4] effects exerted by different diffusion columns upon each other, which may even reverse the direction of diffusion.

It is interesting to note the large values of computed diffusion potentials and the minima and changes of sign in Table I. The familiar Bjerrum correction, subtracting values for saturated and half saturated salt bridges from each other, is not well supported by the data of the table, for the two formulas differ from each other and the last two columns of the table likewise differ. For dilute solutions, the Henderson formula agrees with the Bjerrum value within one millivolt if the Scatchard value for KCl/KCl be adopted, but then the Planck equation deviates from Bjerrum by +1 to −1.5 millivolts. The deviation for normal acid is very large in all cases.

TABLE I

COMPUTED VALUES FOR DIFFUSION POTENTIALS OF THE LIQUID JUNCTIONS HCl/KCl AND HCl/KCl/0.1 KCl

	HCl/KCl			HCl/KCl/0.1 KCl		
N_v HCl	1.75 KCl, m. v.	3.5 KCl, m. v.	Difference	1.75 KCl, m. v.	3.5 KCl, m. v.	Difference
By Henderson's Formula						
0.991	21.1	15.2	−5.9	19.7	13.5	−6.2
.09812	6.8	4.9	−1.9	5.4	3.2	−2.2
.009715	3.2	3.0	−0.2	1.8	1.3	−0.5
.001	4.0	3.5	− .5	2.6	1.8	− .8
.0001	4.2	4.6	+ .4	2.8	2.9	+ .1
By Planck's Equation						
1.0	21.9	16.0	−5.9	20.5	14.3	−6.2
0.1	8.0	5.7	−2.3	6.6	4.0	−2.6
.01	3.9	2.7	−1.2	2.5	1.0	−1.5
.001	3.9	3.9	−0.0	2.5	2.2	−0.3
.0001	5.0	4.6	− .4	3.6	2.9	− .7
.0000001		7.4			5.7	

In the opposite direction come the diffusion potentials of 3.5 KCl/0.1 KCl, 1.72 millivolts from the Henderson formula, 2.7 from the Cummings modification; 2.4 to 2.7 Scatchard,[3] 1.85 Guggenheim and Schindler,[3] and for 1.75 KCl/0.1 KCl, 1.38 by the Henderson formula. $n_{KCl} = 0.510$ from $m = 0$ to 0.5.

Our e. m. f. values for hydrochloric acid as compared with the best data for the nearest round concentrations are 0.991 N_v 0.3400 (0.3427, 0.3423); 0.0981 N_v 0.4010 (0.4020, 0.4012, 0.4010, 0.4004, 0.4000, 0.3998, 0.3995); 0.00972 N_v 0.4584 (0.4582, 0.4579); 0.000962 N_v 0.5165; 0.0000952 N_v 0.5739 volt.

f_{HCl} is taken from the calculations of Randall and Young.[5] If the assumption is made that $f_{H^+} = f_{HCl} = f_{Cl^-}$, we are able to compare the computed values with the best observed values for e. m. f. of hydrochloric acid in Table II, which shows a discrepancy of no less than 10 millivolts for N hydrochloric acid. Either the activity of the hydrogen ion in hydrochloric acid solution has been very greatly overestimated or the diffus-

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[1] Experiments by Miss Betz.

[2] All the best data are collected in "Abhandlungen der Deutsche Bunsen-Gesellschaft"; *Messungen Elektromotorischer Kräfte galvanischer Kelten*, No. **5**, 116 (1911); *Erster Ergänzungsheft*, 22 (1915); *Zweiter Ergänzungsheft*, 71, 72, 73 and **74** (1929).

[3] E. A. Guggenheim and T. D. Schindler, *J. Phys. Chem.*, **38**, 533 (1934). If Scatchard's maximum difference between flowing junctions and diffused junctions, 3.5 millivolts, be subtracted from his chosen value, −0.3373 volt, for E_0 with flowing junction, the result for a diffused boundary is 0.3338 volt, in excellent agreement with Guggenheim [G. Scatchard, THIS JOURNAL, **47**, 707 (1925)]. We used a calomel electrode of Guggenheim's pattern and hydrogen electrodes used in 1914 by McBain and Martin. All results were corrected to 760 mm. pressure of hydrogen.

[4] For references see J. W. McBain and C. R. Dawson, THIS JOURNAL, **56**, 52 (1934).

[5] M. Randall and L. E. Young, *ibid.*, **50**, 989 (1928).

Table II

Computed Values for E. m. f. of HCl Solutions at 25°

$E = E_0 + E_D + 0.05915 \log 1/N_w f_H$ for the cell

$$\begin{array}{l|l|l|l|l} (\mathrm{Pt})_2\mathrm{H}_2 & \mathrm{HCl} & \mathrm{KCl} & \mathrm{KCl, HgCl} & \mathrm{Hg, where}\ E_0 = 0.3337 \\ & N_w & 3.5 & 0.1 & \end{array}$$

N_v	N_w	f_H = activity	0.05915 × $1/N_w f_H$	E_D H^a	P^b	Total H^a	P^b	Observed
1.0	1.019	0.843	0.0044	0.0135	0.0143	0.3516	0.3524	0.3417
0.1	0.1004	.802	.0648	.0032	.0040	.4017	.4025	.4006
.01	.01	.906	.1208	.0013	.0010	.4558	.4555	.4582
.001	.001	.966	.1783	.0018	.0022	.5138	.5142	.5163
.0001	.0001	.99	.2369	.0029	.0029	.5735	.5735	.5739

[a] Henderson formula. [b] Planck equation.

sion potential is very different from that calculated from either the Planck or Henderson formula. The e. m. f. data for more dilute solutions agree with the computed values only within 2 millivolts.

E. m. f. Data for Sulfonic Acids and their Mixtures with Hydrochloric Acid.—Before presenting the e. m. f. data for the sulfonic acids themselves, we give Table III to show that as a first approximation the addition of hydrochloric acid to water and to a solution of sulfonic acid produces the same effect upon e. m. f. In other words, the activity of hydrochloric acid is not profoundly affected by the presence of the ionic micelle of the sulfonic acid. This is a result of general significance confirming similar previous findings with soaps and cetyl sulfonic acid, for it would indicate that in all mixtures containing polyvalent organic compounds or any other ions or particles where the charges are not concentrated in a point the effect of multivalence almost wholly disappears. Ordinarily the Debye–Hückel theory would postulate an ionic strength sufficient almost completely to obliterate the lowering of freezing point or the production of e. m. f. by any univalent ions present. Hence the principle of ionic strength as regards valency definitely does not apply; even the data for *p*H for the sulfonic acid solutions alone would serve to substantiate this important truth.

Since it is difficult exactly to predict what the hydrogen-ion concentration of a mixture of colloidal electrolytes with hydrochloric acid should be, we have inserted as a guide the last two columns as a comparison with the observations. One gives the mean of the two concentrations before mixing and the other assumes that the weight normality of the hydrogen ion referred to the solvent water in each of the separate solutions is maintained constant apart from the actual increase in the amount of water present; that is, that the degree of dissociation of neither sulfonic acid nor hydrochloric acid nor their activities is affected by mixing. Upon referring to the table, it will be seen that the concentration of hydrogen ion observed, with two exceptions, actually ex-

Table III

Hydrogen-Ion Concentration of Mixtures of Equal Volumes of Sulfonic Acid Solutions with Hydrochloric Acid Solutions at 25°

HCl N_w	Sulfonic acid alone N_w	E. m. f.	N_w of H	Mixture E. m. f.	N_w of H	Mean of Columns 1 and 4	Mean N_w
			Undecyl				
0.00972	0.0324	0.4303	0.0290	0.4382	0.0214	0.0194	0.0193
.00972	.112	.4100	.0661	.4273	.0327	.0379	.0376
.0981	.112	.4097	.0668	.4023	.0902	.0825	.0826
.0981	.238	.3939	.126	.3947	.1216	.1120	.1117
			Lauryl				
0.01	0.01	0.4615	0.00845	0.4580	0.00966	0.00923	0.00923
.1	.1	.4152	.0537	.4109	.0634	.0769	.0771
1.0	.810	.3655	.389	.3463	.838	.695	.719
			Myristyl				
0.01	0.029	0.4498	0.0135	0.4513	0.0127	0.0117	0.0117
.1	.1066	.4197	.0447	.4081	.0713	.0723	.0727
.1	.313	.3962	.115	.3975	.108	.107	.107

ceeds both of these values. The acidity of the mixture and the activity of the hydrogen ion is greater than that predicted, even though we have completely ignored in the computation any driving back of the dissociation of the incompletely dissociated colloidal electrolyte and also any effect of valency. Apparently, both of these items are insignificant in comparison even with the relatively minor effect of hydration.

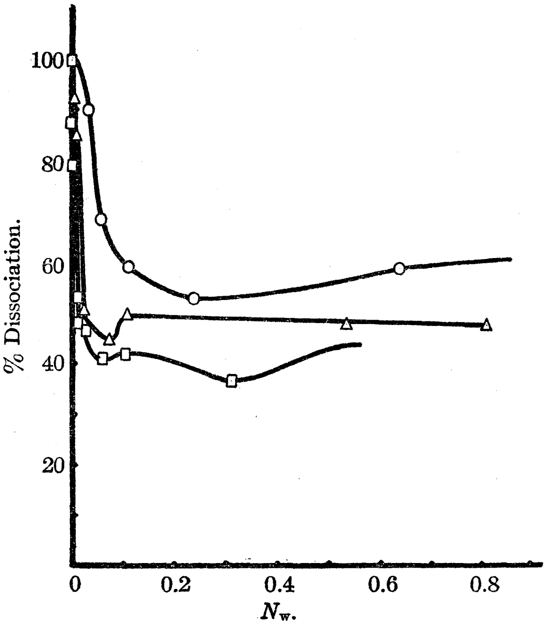

Fig. 1.—Degree of dissociation of undecyl (○), lauryl (△), and myristyl (□), sulfonic acids at 25°.

The method of calculation of hydrogen-ion concentration used in Table II is justified by its results, especially in view of the foregoing discussion of diffusion potentials. What we have done is to assume that the activity of the hydrogen ion is the same in solutions of hydrochloric acid as in solutions of sulfonic acids or their mixtures with hydrochloric acid that give the same e. m. f. This assumes equality of diffusion potential in both cases and also 100% dissociation of hydrochloric acid. We therefore plotted the best values for e. m. f. of hydrochloric acid against the logarithm of the concentration N_w and read off the concentration of hydrochloric acid and therefore of hydrogen ion responsible for each value of e. m. f. observed in all further experiments. The data are given in Table IV and the degrees of dissociation shown in Fig. 1. Less accurate data for 0° are given in Fig. 2, where if anything the hydrogen-ion concentrations appear greater.

TABLE IV

HYDROGEN-ION CONCENTRATION OF SULFONIC ACID SOLUTIONS FROM E. M. F. MEASUREMENTS AT 25°, WITH 0.1 *N* CALOMEL ELECTRODE

N_w	E. m. f.	N_w of H^+	% Dissociation
	Undecyl		
0.0324	0.4303	0.0292	90.0
.0595	.4220	.0407	68.5
.112	.4097	.0668	60.0
.112	.4100	.0661	59.0
.238	.3939	.126	52.9
.637	.3666	.374	58.7
1.138	.3515	.684	60.1
	Lauryl		
0.0061	0.4716	0.00562	92.2
.01	.4615	.00849	84.9
.025	.4515	.0126	50.4
.075	.4266	.0335	44.7
.1085	.4152	.0537	49.5
.535	.3762	.256	47.8
.814	.3655	.389	47.8
	Myristyl		
0.00032	0.5466	0.000279	87.3
.00122	.5104	.00120	98.5
.00259	.4970	.00205	79.2
.0126	.4673	.00668	53.0
.01317	.4689	.00631	47.9
.029	.4498	.0135	46.5
.0625	.4336	.0257	41.1
.1066	.4197	.0447	41.9
.313	.3962	.115	36.7
.543	.3672	.366	67.3

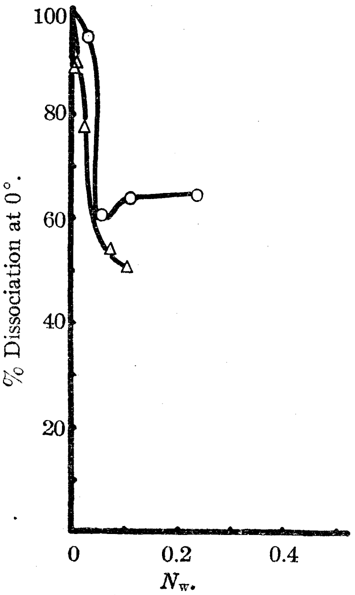

Fig. 2.—Degree of dissociation of undecyl (○), and lauryl (△), sulfonic acids at 0°.

Summary

Existing e. m. f. data for hydrochloric acid with a 3.5 N potassium chloride bridge have been compared with values computed from diffusion potentials and the activity coefficients of hydrochloric acid on the assumption that $f_H = f_{Cl} = f_{HCl}$. Discrepancies are noted which become very large, rising to 10 millivolts for 1 N hydrochloric acid.

Hydrochloric acid added to these colloidal electrolyte solutions of sulfonic acids produces slightly more effect upon e. m. f. even than it does in water, showing that the ionic micelles cannot be regarded as equivalent to polyvalent ions in which the charges are concentrated in one point.

In very dilute solution, the sulfonic acids behave like weak electrolytes and the degree of dissociation rapidly falls, but in more concentrated solution remains almost constant or tends to rise again.[6]

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(6) Still larger readings in the most concentrated solutions are robbed of significance because precipitate forms between the sulfonic acid and the salt bridge and they change rapidly with time.

STANFORD UNIVERSITY, CALIFORNIA
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Straight-Chain Sulfonic Acids in Water. IV. Comparison of Results, and So-called "Hammarsten Effects"

BY JAMES W. MCBAIN

Colloidal electrolytes were discovered through comparison of conductivity with osmotic coefficient. Preceding parts of this series have shown that undecyl, lauryl and myristyl sulfonic acids, although conforming in dilute solution to the behavior of a simple half weak electrolyte, form the ionic micelle and neutral micelle characteristic of colloidal electrolytes in all stronger solutions. Further significant results follow from the comparison of these three kinds of data for the solutions between 0.1 and 1.0 N where the graphs tend to rise with concentration. The data are collected in Figs. 1, 2 and 3.

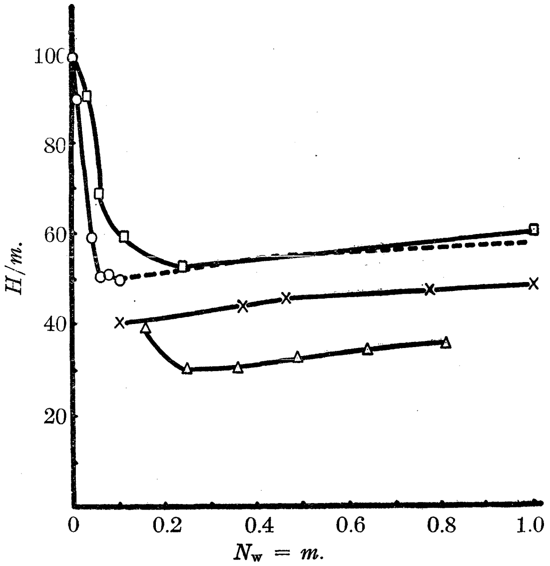

Fig. 1.—Hydrogen-ion concentration of undecyl sulfonic acid: □ is e. m. f.; ○ is conductivity, $100\mu\nu/\mu_\epsilon$; × is Arrhenius ratio, $100\mu/\mu_\infty$; △ is freezing point.

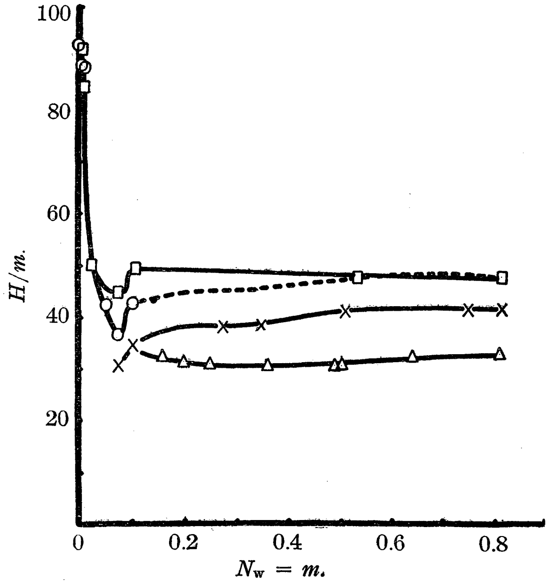

Fig. 2.—Hydrogen-ion concentration of lauryl sulfonic acid: □ is e. m. f.; ⊙ is conductivity, $100\mu\nu/\mu_\epsilon$; × is Arrhenius ratio, $100\mu_T/\mu_\infty$; △ is freezing point.

Before comparing the graphs on each figure, it is necessary to recall how they arise. Those for e. m. f. call for no comment, except that we have omitted the most concentrated solution for myristyl sulfonic acid on account of precipitation at the salt bridge. Those for undecyl sulfonic acid, judging from the dilute solutions, appear somewhat too high.

The first part of the conductivity curve, with points marked by circles, is the degree of dissociation according to the modern ionic attraction theory; but it passes through a minimum and leaves thereafter no basis for the calculation, since the results are already affected by the transition from simple electrolyte to colloidal electrolyte. Below and parallel to the last two circles lie the crosses representing Arrhenius conductivity ratios, $\mu v/\mu_\infty$ (where $\mu_\infty = \mu_{\mathrm{Cl}}$) showing how much is the dual effect of interionic attraction and of the assumption that hydrochloric acid is fully dissociated. The graph of circles is continued by us as a dashed line parallel to the crosses. This gives us an approximate value for the hydrogen-ion concentration, on the assumption that the steadily increasing correction upward for interionic attraction is balanced by the steadily increasing correction downward due to the steady increase in mobility of the ionic micelle from that of chloride ion to that of hydroxyl ion.

It is to be noted that these two curves for concentration of hydrogen ion or degree of dissociation practically coincide. Within the experimental error, conductivity and electromotive force have given the same result. The concentration of hydrogen ion increases faster than the total concentration. The degree of dissociation —doubtless into a changing product—increases with concentration, contrary in appearance to Le Chatelier's principle.

As regards freezing point lowering, there are only two curves because of the insolubility of myristyl sulfonic acid below 15°. In dilute solution they have no direct significance on this diagram because freezing point counts all molecules and ions, not merely hydrogen ion. Only after the transition to colloidal electrolyte is complete does freezing point measure hydrogen ion alone, because no simple molecules and no simple ions other than hydrogen ion are present.

We may therefore for these more concentrated solutions calculate the degree of dissociation of the total sulfonic acid into hydrogen ion and corresponding equivalents of ionic micelle by making use of exactly the same assumptions that we have employed in calculating e. m. f. If we assume that $f_{\mathrm{H}^+} = f_{\mathrm{Cl}^-} = f_\pm$ for hydrochloric acid, and if we assume that the activity coefficient of the hydrogen ion from the sulfonic acid is identical with that of hydrogen ion in hydrochloric acid solution containing exactly the same concentration of hydrogen ion, we need only compare the actual lowering of freezing point, Θ, of the sulfonic acid with one-half the lowering observed for solutions of hydrochloric acid itself, as recorded in "I. C. T.," in order to identify the concentration of hydrogen ion causing the whole of the freezing point lowering of the sulfonic acid and causing exactly one-half the lowering in the hydrochloric acid solution. In other words, we have assumed that the effect of interionic attraction upon hydrogen ion in the sulfonic acid solution is exactly the same as in hydrochloric acid solution of the same actual concentration of the hydrogen ion. We find per cent. dissociation at once by dividing this concentration so obtained by the molality of the sulfonic acid solution. In dilute solutions, where the colloidal electrolyte is breaking down into a simple electrolyte, this relation can no longer hold and the results are not included in the figures.

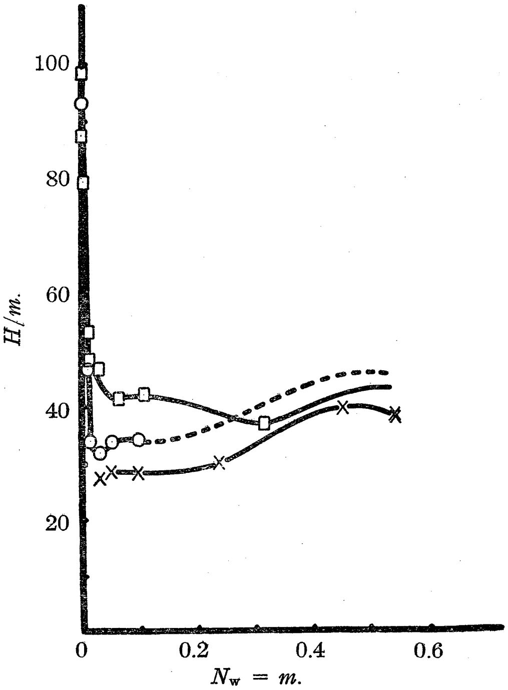

Fig. 3.—Hydrogen-ion concentration of myristyl sulfonic acid: □ is e. m. f.; ○ is conductivity, $100\mu v/\mu_\epsilon$; × is Arrhenius ratio, $100\ \mu v/\mu_\infty$.

It will be noted in the foregoing that precisely the same basis of assumption is made in calculating e. m. f. and freezing points. Incidentally, we take advantage of the direct proportionality between Θ and g, derived as follows, using the nomenclature of Guggenheim $g \ln 1/N_0 = L^0_F\Theta/RT^{\circ 2}$ with good approximation for aqueous solutions.

$$g \ln \frac{1}{N_0} \equiv \ln \frac{1}{N_0 f_0} \equiv g\left(N_S + \frac{N_S^2}{2} + \frac{N_S^2}{3} + \text{etc.}\right) = g\,N_S = gm$$

since $N_0 = 1 - N_S$. Whence $g = \Theta/\lambda m$.

The freezing point lowering is only about three-fifths that required for the concentration of hydrogen ion shown to be present by conductivity and electromotive force. This contradiction has to be accepted as a fact because it is far beyond any possible error of experiment, and we see no way of explaining it away as unreal without introducing some fantastic and unjustified assumption, such as that the actual conductivity observed is partly metallic or that some new class of impurity is present which does not lower freezing point but yet has a high conductivity. It cannot be due to any non-electrolyte or electrolyte present as impurity because the effect would be in the opposite direction of that here observed. It must be recalled that all three measurements were made on identical solutions.

Similarly, with 0.5 *N* cetyl sulfonic acid[1] at 90° the hydrogen-ion concentration, according to e. m. f., appeared nearly double that deduced from vapor pressure lowering. The only other authenticated instance is that of thymonucleic acid as studied by the Hammarstens, to which we shall return.

No such discrepancy has ever been observed between the many methods used to measure ordinary soaps.

So-Called "Hammarsten Effects."—Confusion has arisen through calling different things, some of them long since known,[2] "Hammarsten effect." Unquestionably, it is wholly legitimate to follow the usage of Linderstrøm-Lang[3] in defining as genuine "Hammarsten effect" the fact that the osmotic coefficient of thymonucleates depends upon the size of the cation. Thus the Bjerrum osmotic coefficient, g, $= i/v = \Theta/v\lambda m$, which is approximately equal to the osmotic pressure observed divided by the osmotic pressure of an ideal non-electrolyte of the same concentration, was observed by E. and H. Hammarsten[4] to be as follows

Cation	H^+	Na^+	NH_4^+	$(CH_3)_3NH^+$	$(CH_3)_4N^+$	$(C_2H_3)N^+$	$(C_3H_7)_3NH^+$
	0.70	0.80	1.20	1.35	1.45	1.50	1.74

Linderstrøm-Lang, however, did not agree with Hammarsten's explanation which assumed that "the small ions, I_1, are able to penetrate into the I_n ions and thus become osmotically inactive, whereas large ions I_2, are not capable of this." He concluded "that there must be far different and more profound causes and that Hammarsten's explanation, though perhaps necessary, is not sufficient." Jorpes and Hillgrew[5] also observed this kind of Hammarsten effect with various salts of Congo red.

For this genuine Hammarsten effect we may advance here a new explanation. The formation of neutral micelles is a process of association of molecules through orderly array of like parts. It is the organic radical which possesses this property. This close packing of parallel molecules can only occur if the cationic radicals, such as hydrogen, are so small as not to interfere. When these "heads" of the molecules, as they are commonly referred to in the literature on insoluble monomolecular films, become too large, their bulk interferes with the association of molecules to form neutral micelle. Meanwhile, the formation of ionic micelle, stripped of these cations, proceeds as usual. Thus the effect of large heads is to leave in the solution more ions and more simple molecules even if formation of ionic micelle is somewhat favored. Hence the lowering of freezing point or any other expression of g is measurably increased, the original genuine Hammarsten effect. This would explain the series of thymonucleates and the series of Congo reds.

The same principle or genuine Hammarsten effect also serves for the first time to explain many phenomena known to soap boilers who blend their raw materials to yield soaps of definite physical properties.[6] It also explains why hydrogen soaps

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(1) J. W. McBain and R. C. Williams, THIS JOURNAL, **55**, 2256 (1933).

(2) Van Rysselberghe's use of the term which he defines as observing a value of van't Hoff's *i* of the order of 1 or less, was in fact the basis of the older work on dyes and soaps and the reason for recognizing the existence of colloidal electrolytes and their most characteristic feature, the ionic micelle. His suggestion [*J. Phys. Chem.*, **38**, 645 (1934)] that the ionic micelle may be treated as an ordinary polyvalent ion was based upon lack of data for other measurements and appears to be invalidated by the data referred to in the previous parts of this series. Similarly, F. G. Donnan's new definition "that the value of *g* may be affected by the action of the Coulomb field of the G^+ ions on the Cl^- ions, or by a variety of actions (Hammarsten effect)" likewise appears to be invalidated by its postulation of significant interionic attraction at great distances apart of ions.

(3) K. Linderstrøm-Lang, *Compt. rend. trav. lab. Carlsberg*, **16**, 1 (1926).

(4) E. and H. Hammarsten, *Arch. Kemi. Geol. og. Mineralogi. Medd. Kngl. Vetensk. Akad.*, **8**, No. 27 (1913); E. Hammarsten, *Biochem. Z.*, **144**, 383 (1924); H. Hammarsten, *ibid.*, **147**, 481 (1924).

(5) E. Jorpes and G. Hillgrew, *Biochem. Z.*, **145**, 57 (1925).

(6) Compare J. L. Bowen and R. Thomas, *Trans. Faraday Soc.*, **31**, 172 (1935).

are more colloidal than those of sodium and potassium.

Following Pauli and his collaborators,[7] McBain and Williams,[1] and Adair and Adair[8] conferred the name "Hammarsten effect" upon the divergence observed where the total freezing point lowering or osmotic coefficient g, is far less than that necessary to account for the hydrogen ion alone as measured by e. m. f. The only example was that of thymonucleic acid itself, not its salts, studied by E. Hammarsten in 1924.[4] Now, with four sulfonic acids, we have five examples altogether.[9] Linderstrøm-Lang's explanation[3] has been shown to be untenable. We shall now suggest a general explanation.

The Activity Coefficients of Individual Ions.—Guggenheim convincingly emphasized that activity coefficients of single ions had no meaning, since in measurements of activity hitherto the results had been a function of both ions, not separated from each other. However, this is not to say that the ions do not exist and do not each contribute a partial molal free energy, but merely that the individual activity coefficients had not been experimentally isolated.

Guggenheim himself, however, has defined an activity coefficient of hydrogen ion f_{H^+} which is arbitrarily set equal to $f_{\pm}$ or f_{HCl} the mean activity coefficient of the salt, and in which the definition is used only for dilute solutions. This is a different convention from that of MacInnes and Scatchard, who set f_{K^+} equal to f_{Cl^-} and equal to $f_{\pm}$ or f_{KCl}.

We will now show that if the experimental data here presented are valid they lead to a more definite evaluation of f_{H^+} which is not a mere arbitrary convention but which is fixed by the data themselves.

This is a direct result and explanation of McBain and Pauli's "Hammarsten effect," which otherwise has recently been referred to as "an affront to the second law of thermodynamics." This so-called Hammarsten effect is that hydrogen-ion concentration measured by e. m. f. with a liquid junction salt bridge appears far greater than as measured by freezing point or osmotic pressure.

The reason is, as was shown in deriving Figs. 1 and 2, that the conventional assumption was made that f_{H^+} equals f_{HCl} in these more concentrated solutions. Since added hydrochloric acid affects e. m. f. and freezing point of these solutions by approximately the same amount as it does in water, it was, and is, approximately correct to identify the concentration of hydrogen ion of a sulfonic acid solution with that of a solution of hydrochloric acid giving the same e. m. f. However, as regards freezing point lowering, although f_{H^+} may be taken as approximately the same for both cases, the freezing point lowering was quite arbitrarily ascribed equally to hydrogen and chlorine ions. That is, it was assumed that f_{H^+} equals f_{Cl^-} and this resulted in finding that the concentration of hydrogen ion so arrived at was only 60% of that corresponding to the e. m. f. data.

To reconcile freezing point with e. m. f. and explain away such "Hammarsten effect," it is only necessary to assume that f_{H^+} is only about one-half f_{Cl^-} and that the freezing point lowering of these more concentrated solutions is therefore more largely due to the chlorine ion than to the hydrogen ion. This brings up the values for hydrogen-ion concentration derived from freezing point to approximate equality to those from e. m. f. for the latter remain unchanged.

It is evident that this new approach toward measuring the activity coefficient of a single ion lends itself to further experimental test, since all data with single electrodes must conform if they are real. It is also evident that no information is obtainable from cells without liquid junctions because they measure, like freezing point in ordinary solutions, the geometric mean of both ions or the stoichiometric activity coefficient of the salt itself.

It is not without interest that in the preceding section devoted to e. m. f. it was shown that the existing data for e. m. f. of 1 N hydrochloric acid differ by no less than 10 millivolts from the value predicted on the assumption that $f_{H^+} = f_{HCl}$. This would corroborate the conclusion thus reached that $f_{H^+} < f_{HCl} < f_{Cl^-}$.

Constitution Diagram.—The constitution diagrams of these solutions resemble those of the soaps such as published by Miss Norris[10] for cetyl sulfonic acid, or more closely that of potas-

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[7] W. Pauli and E. Valkó, "Elektrochemie der Kolloide," Julius Springer, Vienna, 1929, p. 258; *Kolloid-Z.*, **48**, 1 (1929); **57**, 312 (1931); **62**, 162 (1933); **66**, 312 (1934).

[8] G. S. Adair and M. E. Adair, *Trans. Faraday Soc.*, **31**, 131 (1935).

[9] Possibly also gum arabic should be added to the list (D. R. Buggs, "Symposium on Quantitative Biology," Cold Springs Harbor, **1**, 152 (1933); *J. Phys. Chem.*, **38**, 873 (1934); Thomas and Murray, *ibid.*, **32**, 676 (1928); H. B. Oakley, *Trans. Faraday Soc.*, **31**, 146 (1935).

[10] M. H. Norris, *J. Chem. Soc.*, **121**, 2161 (1922).

sium oleate at 18,[11] except that in previous diagrams boundaries should be raised by a few per cent. to allow for interionic attraction and 100% dissociation of hydrochloric acid. The middle line of the diagram is given from e. m. f. and conductivity data of Figs. 1, 2 and 3. Most of the transition between simple crystalloidal and colloidal electrolytes takes place between 0.05 and 0.15 *N* for undecyl and lauryl sulfonic acids and in still more dilute solution in myristyl sulfonic acid. Above 0.1 or 0.2 *N* there can be but little else than colloid and hydrogen ions. The concentration of ionic micelles will be equal to that of the hydrogen ion, the remaining sulfonic acid forming neutral micelles.

Summary

Hydrogen-ion concentration deduced from conductivity, freezing point lowering, and electromotive force for solutions of simple sulfonic acids above 0.1 *N* are compared.

Conductivity and e. m. f. (single electrode) agree in showing that the dissociation of the colloidal electrolyte is about 50%.

If the data for thymonucleic acid and for undecyl, lauryl, myristyl, and cetyl sulfonic acids are valid, it is shown that the activity coefficients of single ions may be measured. For example, in more concentrated solutions of hydrochloric acid, the activity coefficient of the hydrogen ion appears to be about half that of the chlorine ion and $f_{H^+} < f_{HCl} < f_{Cl^-}$ where $f_{H^+} f_{Cl^-} = f_{HCl}$.

A new explanation of the genuine Hammarsten effect is given, based upon steric hindrance to close packing.

STANFORD UNIVERSITY, CALIFORNIA

RECEIVED JUNE 18, 1935

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[11] J. W. McBain and R. C. Bowden, *J. Chem. Soc.*, **123**, 2427 (1923).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Nitroso Compounds. III. Reactions of Organo-metallic Compounds with Alpha Halo Nitroso Compounds[1]

BY JOHN G. ASTON AND DAVID F. MENARD

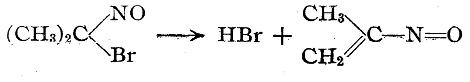
Introduction

This investigation originated in an attempt to obtain true nitroso hydrocarbons by the action of zinc alkyl on compounds of the type CR_1R_2-$Br(NO)$ in a way similar to that by which Bewad had obtained nitro compounds from their alpha bromo derivatives.[2]

Although this attempt failed, certain reactions involving the nitroso group were observed which were interesting from the standpoint of possible analogies between true nitroso compounds and aldehydes or ketones.

Splitting Out of the Hydrogen Halide

When 2,2-bromonitrosopropane was treated with anhydrous ammonia, only ammonium bromide resulted along with acetoxime. To explain this splitting out of hydrobromic acid the first step in the reaction may be tentatively written

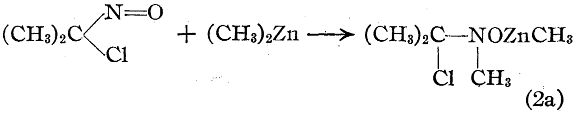


$$(CH_3)_2C\begin{matrix}NO\\Br\end{matrix} \longrightarrow HBr + \begin{matrix}CH_3\\CH_2\end{matrix}{>}C{-}N{=}O \qquad (1)$$

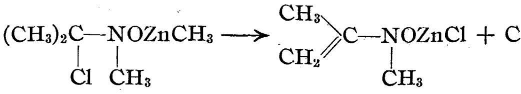
inasmuch as the unsaturated nitroso compound might well react to give acetoxime. It is not surprising therefore that the alpha halo nitroso compounds with dimethylzinc yield methane almost quantitatively by inducing the splitting out of hydrogen bromide and then reacting with it.

Reaction with Zinc Alkyls

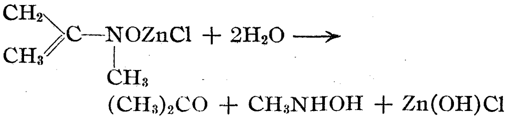
In the reaction of one mole of dimethylzinc and one mole of 2-chloro-2-nitrosopropane, one mole of methane is evolved per mole of chloronitroso compound. In the products of hydrolysis of the solid addition product methylhydroxylamine, acetone and acetoxime were observed. The first two arise from addition. The net reaction may be written



$$(CH_3)_2C\begin{matrix}N{=}O\\Cl\end{matrix} + (CH_3)_2Zn \longrightarrow (CH_3)_2\underset{Cl}{C}{-}\underset{CH_3}{N}OZnCH_3 \qquad (2a)$$



$$(CH_3)_2\underset{Cl}{C}{-}\underset{CH_3}{N}OZnCH_3 \longrightarrow \begin{matrix}CH_3\\CH_2\end{matrix}{>}C{-}\underset{CH_3}{N}OZnCl + CH_4 \qquad (2b)$$



$$\begin{matrix}CH_2\\CH_3\end{matrix}{>}C{-}\underset{CH_3}{N}OZnCl + 2H_2O \longrightarrow (CH_3)_2CO + CH_3NHOH + Zn(OH)Cl \qquad (2c)$$

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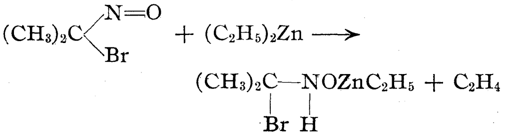
[1] From a thesis presented by David F. Menard in partial fulfilment of the requirements for the Ph.D. degree, June, 1934.

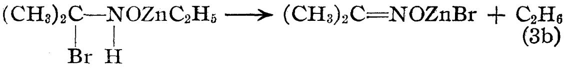
[2] Bewad, *J. prakt. Chem.*, [2] **48**, 368 (1893).

In this reaction and following ones, HX is represented as splitting out after addition and then reacting with the remaining zinc methyl linkage in the addition product. The reaction might as well have been represented as occurring by first splitting out HX and then adding of zinc methyl to the unsaturated nitroso compound. Indeed the presence of acetoxime indicates that some splitting out of HX from the chloronitroso compound does occur directly, followed by decomposition of the unsaturated nitroso compound. The yields of the various products show that no other reaction of importance occurs.

Diethyl zinc reacted with 2-bromo-2-nitrosopropane in the same way that dimethylzinc reacted on the chloro compound, yielding ethane with acetone and ethylhydroxylamine as the hydrolysis products. However, only about 70% reacted in this way while the remaining 30% was reduced as shown by the presence of ethylene in the gaseous mixture. It was assumed that one mole of ethane was formed for each mole of ethylene and the secondary reaction written



$$(CH_3)_2C\begin{matrix}\diagup N{=}O\\ \diagdown Br\end{matrix} + (C_2H_5)_2Zn \longrightarrow \underset{\substack{|\\Br}}{(CH_3)_2C}{-}\underset{\substack{|\\H}}{N}OZnC_2H_5 + C_2H_4 \quad (3a)$$



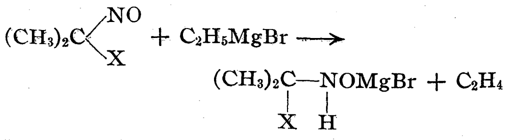
$$\underset{\substack{|\\Br}}{(CH_3)_2C}{-}\underset{\substack{|\\H}}{N}OZnC_2H_5 \longrightarrow (CH_3)_2C{=}NOZnBr + C_2H_6 \quad (3b)$$

$$(CH_3)_2CNOZnBr + H_2O \longrightarrow (CH_3)_2C{=}NOH + Zn(OH)Br \quad (3c)$$

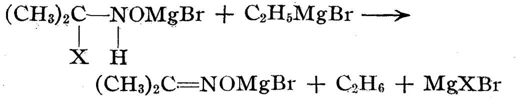
In keeping with this, acetoxime was also found in the products of hydrolysis of the mixed insoluble addition product.

Reaction with Grignard Reagents

When 2-chloro or 2-bromo-2-nitrosopropane was treated with ethylmagnesium bromide (2 moles of Grignard per mole of compound), no addition was observed; the principal reaction was a reduction similar to the secondary reaction observed with diethylzinc



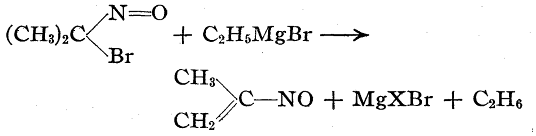
$$(CH_3)_2C\begin{matrix}\diagup NO\\ \diagdown X\end{matrix} + C_2H_5MgBr \longrightarrow \underset{\substack{|\\X}}{(CH_3)_2C}{-}\underset{\substack{|\\H}}{N}OMgBr + C_2H_4 \quad (4a)$$



$$\underset{\substack{|\\X}}{(CH_3)_2C}{-}\underset{\substack{|\\H}}{N}OMgBr + C_2H_5MgBr \longrightarrow (CH_3)_2C{=}NOMgBr + C_2H_6 + MgXBr \quad (4b)$$

$$(CH_3)_2C{=}NOMgBr + H_2O \longrightarrow (CH_3)_2C{=}NOH + Mg(OH)Br \quad (4c)$$

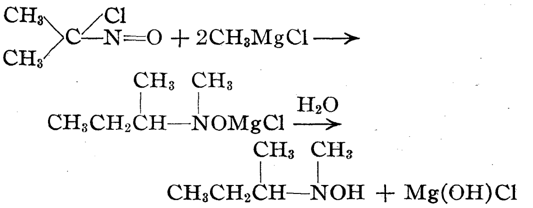
The products were ethane and ethylene and after hydrolysis of the insoluble addition compound, acetoxime and its hydrolysis products (acetone and hydroxylamine). Whereas reactions (4a and 4b) require equal molal quantities of ethane and ethylene, the ethane produced in both cases considerably exceeded the ethylene. This indicated a reaction



$$(CH_3)_2C\begin{matrix}\diagup N{=}O\\ \diagdown Br\end{matrix} + C_2H_5MgBr \longrightarrow \begin{matrix}CH_3\diagdown\\ CH_2\diagup\!\!\diagup\end{matrix}C{-}NO + MgXBr + C_2H_6 \quad (5)$$

involving the splitting out of hydrogen bromide, which reacted with the Grignard to yield ethane while the hypothetical unsaturated nitroso compound after hydrolysis yielded hydroxylamine as in the reaction with ammonia (1).

The reaction of one mole of methylmagnesium chloride on one mole of 2-chloro-2-nitrosopropane resulted in addition to the N=O group as the main reaction. Hydrolysis yielded methylhydroxylamine. The reaction of two moles of methylmagnesium chloride resulted in addition to the N=O group and simultaneous replacement of the halogen by the methyl group with rearrangement, yielding 68% of β-s-butyl-β-methylhydroxylamine



$$\begin{matrix}CH_3\diagdown\\ CH_3\diagup\end{matrix}C\overset{\diagup Cl}{-}N{=}O + 2CH_3MgCl \longrightarrow CH_3CH_2\overset{\substack{CH_3\\|}}{C}H{-}\overset{\substack{CH_3\\|}}{N}OMgCl \xrightarrow{H_2O} CH_3CH_2\overset{\substack{CH_3\\|}}{C}H{-}\overset{\substack{CH_3\\|}}{N}OH + Mg(OH)Cl \quad (6)$$

Methylmagnesium chloride acted similarly with 2-bromo-2-nitrosopropane. In this case a small amount of β-methyl-β-*t*-butylhydroxylamine was identified as well.

With phenylmagnesium bromide there was no addition or replacement of bromine by the phenyl radical. However, a 20% yield of benzene indicated splitting out of hydrogen bromide by a reaction similar to (5).

Kohler and Tishler[3] have discussed the analogous α-halo-ketone problem and have shown that Grignard reagents often react with ketones of the type $R_2C(X)COR$ to replace halogen by magnesium with the simultaneous production of the alkyl halide

$$R_2C(X)COR + R^1MgX^1 \longrightarrow R^1X + R_2C(MgX^1)COR \quad (7)$$

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[3] Kohler and Tishler, THIS JOURNAL, **54**, 1595 (1932); **57**, 217 (1935).

In none of our experiments was there ever a detectable amount of alkyl halide which might have been produced by an analogous reaction.

Experimental

Preparation of 2-Bromo-2-nitrosopropane.[4]—Four hundred and twenty-seven grams (3.15 moles) of $NaAc\cdot 3H_2O$ dissolved in 500 cc. of water was added to a solution of 110 g. (1.5 moles) of acetoxime dissolved in 200 cc. of water. Five hundred grams of ice was added. With constant stirring and cooling, 239 g. (1.5 moles) of bromine was dropped in at such a rate that the solution was kept below 0°.

The dark blue oil was separated after standing for twenty minutes, washed with ice water and dried over 10 g. of anhydrous sodium sulfate in the cold. The last traces of water were removed by cooling in ether–carbon dioxide snow and filtering off the ice; yield, 46–54 g. (20–30%). The product was over 90% pure (bromine analysis).

Preparation of 2-Chloro-2-nitrosopropane.[5]—The procedure was as described for the bromo compound, the chlorine being introduced as a rapid stream; yield, 62%.

Reaction of 2-Bromo-2-nitrosopropane with Ammonia.—Dry ammonia was bubbled through a solution of 32 g. of 2-bromo-2-nitrosopropane in 50 cc. of anhydrous ether at 20–25° for four hours, when no further precipitation of ammonium bromide took place. The 2-bromo-2-nitrosopropane, carried over into a condenser cooled in ice–salt, was returned to the reaction flask from time to time. Fourteen grams of solid ammonium bromide (identified by analysis) was filtered off. The ether solution was fractionated, yielding 4.2 g. of bromo acetone, 2.8 g. of acetoxime and 2.4 g. of tar.

Reaction of Dimethylzinc with 2-Chloro-2-nitrosopropane.—The apparatus and procedure already described[6] were used. To a solution of 21.8 g. (0.204 mole) 2-chloro-2-nitrosopropane in 150 cc. of anhydrous ether at 0° was added 19.4 g. (0.204 mole) of dimethylzinc. The resulting mixture stood at room temperature for twenty-five hours. Analyses of the gas showed that 2.64 g. (0.165 mole) of methane was formed, or 81% based on reaction (2b).

No products were found in the ether solution. An insoluble solid addition product was hydrolyzed with dilute sulfuric acid. Analysis of the gas corresponded to a yield of 0.67 g. (0.042 mole) of methane, or 10.3% based on the zinc methyl used.

Continuous ether extraction of the aqueous solution yielded 5.67 g. (0.079 mole) of acetoxime and 0.60 g. of tar. In the aqueous portion 0.204 mole of zinc and 0.204 mole of chloride were identified. This was distilled and 5.58 g. (0.96 mole) of acetone was identified in the distillate. The residue, which reduced ammoniacal silver nitrate and iodine solutions, was reduced with 20 g. of zinc dust and 50 cc. of 6 *N* hydrochloric acid. It was then made alkaline and distilled into standard hydrochloric acid (free methylhydroxylamine is decomposed in hot aqueous alkali),[7] yielding 0.109 mole of methylamine hydrochloride, identified by analysis and by conversion to N-methyl-*p*-toluene-sulfonamide, m. p. 78–78.5°,[8] (confirmed by mixed melting point).

Reaction of Diethylzinc with 2-Bromo-2-nitrosopropane.—Thirty-five grams (0.289 mole) of diethylzinc was added to a solution of 44 g. (0.289 mole) of 2-bromo-2-nitrosopropane in 125 cc. of anhydrous ether as above; 2.09 g. (0.075 mole) of ethylene and 6.28 g. (0.209 mole) of ethane were found in the gases.

In the ether solution, 2.0 g. of bromoacetone and 1.7 g. of tar were identified.

On hydrolysis of the addition product 0.17 g. (0.006 mole) of ethylene, 2.61 g. (0.087 mole) of ethane, 9.4 g. (0.127 mole) of acetoxime, 2.89 mole of zinc, 0.265 mole of bromide, 8.0 g. (0.138 mole) of acetone and 0.118 mole of ethylhydroxylamine were found. The ethylhydroxylamine was reduced and converted to N-ethyl-*p*-toluenesulfonamide, m. p. 63°,[8] and identified by a mixed melting point.

Reaction of Two Moles of Ethylmagnesium Bromide with 2-Chloro-2-nitrosopropane.—An ether solution containing 0.748 mole of ethylmagnesium bromide was added to a solution of 40 g. (0.374 mole) of 2-chloro-2-nitrosopropane in 150 cc. of anhydrous ether as above except that nitrogen replaced the carbon dioxide; 4.15 g. (0.148 mole) of ethylene and 6.05 g. (0.201 mole) of ethane were found in the gas.

From the ether 3.9 g. of unreacted 2-chloro-2-nitrosopropane was obtained. No gas was evolved on hydrolysis of the insoluble addition product. From the ether extract 6.8 g. of liquid (b. p. 60–120°), 6.6 g. (0.90 mole) of acetoxime and 4.1 g. of tar were obtained. In the aqueous portion, 1.03 moles of halide, 11.0 g. (0.189 mole) of acetone and 0.123 mole of hydroxylamine[9] were identified. No other products were found.

Reaction of Two Moles of Ethylmagnesium Bromide with 2-Bromo-2-nitrosopropane.—An ether solution containing 0.0528 mole of ethylmagnesium bromide was added to a solution of 40 g. (0.264 mole) of 2-bromo-2-nitrosopropane in 170 cc. of anhydrous ether; 2.60 g. (0.294 mole) of ethane was found in the gas.

No products were found in the ether and no gas was evolved on hydrolysis of the insoluble addition product. From the ether extract 5.6 g. of unidentified liquids (b. p. 60–120°), 3.2 g. (0.044 mole) of acetoxime and 4.2 g. of tar were obtained. In the aqueous portion, 0.796 mole of bromide, 0.68 g. (0.012 mole) of acetone and 0.042 mole of hydroxylamine were identified.

Reaction of Two Moles of Methylmagnesium Chloride with 2-Chloro-2-nitrosopropane.—An ether solution containing 0.546 mole of methylmagnesium chloride was added to a solution of 29 g. (0.268 mole) of 2-chloro-2-nitrosopropane in 50 cc. of anhydrous ether. No gas was evolved.

The entire reaction mixture was hydrolyzed and continuously extracted with ether as previously. In the ether portion, after hydrolysis and continuous extraction of the entire reaction mixture, only 0.4 g. of chloroacetone

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(4) Following the method of Piloty [*Ber.*, **31**, 454 (1898)], the yields were erratic and the material very impure.

(5) This method is superior to that of Ponzio, *Chem. Zentr.*, **77**, I, 1692 (1906).

(6) Menard and Aston, THIS JOURNAL, **56**, 1601 (1934).

(7) Kjellin, *Ber.*, **26**, 2382 (1893).

(8) Remsen and Palmer, *Am. Chem. J.*, **8**, 241 (1886).

(9) Acree and Johnson, *ibid.*, **38**, 316 (1907).

and 4.0 g. of tarry residue were identified. In the aqueous portion, 0.751 mole of chloride and 3.0 g. of acetone (0.054 mole) were identified.

The free base was steam distilled from the aqueous portion into hydrochloric acid solution after making alkaline without reduction. Evaporation of the distillate yielded a very hygroscopic hydrochloride which was entirely soluble in absolute alcohol. It reduced ammoniacal silver nitrate. Nineteen grams (0.14 mole) of this hydrochloride was reduced with 40.0 g. of stannous chloride (0.21 mole) and 40 cc. of concd. hydrochloric acid in the cold. After making alkaline, distilling the base into hydrochloric acid and evaporating to dryness, a solid hydrochloride was obtained; recrystallized twice from absolute alcohol, m. p. 242–244° in a sealed tube. *Anal.* Calcd. for $C_5H_{14}NCl$: Cl, 28.63. Found: (Volhard) Cl, 28.68.

The hydrochloride was converted into the oxalate (twice recryst. from absolute alcohol) m. p. 109–110°. *Anal.* Calcd. for $C_7H_{15}O_4N$: C, 46.90; H, 8.57. Found: C, 46.84, 46.75; H, 8.76, 8.60.

This was identified as N-methyl-*s*-butylamine oxalate by a mixed melting point with a known sample of oxalate. The known sample was prepared by the methylation of *s*-butylamine obtained by the reduction of methyl ethyl ketoxime.[10] The base[11] thus obtained was purified through the *p*-toluenesulfonamide, and converted into the oxalate, m. p. 110–111° (from absolute alcohol). (The oxalate of N-methyl-*t*-butylamine melts with decomposition at 166°.[12])

β-*s*-Butyl-β-methylhydroxylamine.—The reaction of methylmagnesium chloride with 2-chloro-2-nitrosopropane was repeated and the free β-*s*-butyl-β-methylhydroxylamine was extracted with ether after making alkaline, without previous reduction or distillation. A solid product, m. p. 59–60°, b. p. 86° at 101 mm., was obtained, but was difficult to keep pure. *Equivalent weight.* Calcd. for $C_5H_{12}ON$: 103.1. Found: 102.5–103.0.

In handling, this compound apparently absorbed water of recrystallization. *Anal.* Calcd. for $C_5H_{12}ON{\cdot}H_2O$: C, 49.54; H, 12.48. Found: C, 48.80, 48.81; H, 12.29, 12.49.

Reaction of Two Moles of Methylmagnesium Chloride with 2-Bromo-2-nitrosopropane.—An ether solution containing 0.474 mole of methylmagnesium chloride was added to 36 g. (0.237 mole) of 2-bromo-2-nitrosopropane dissolved in 100 cc. of dry ether.

After hydrolysis and extraction, in the ether layer were identified 0.3 g. of bromoacetone, 1.8 g. of acetoxime and 4.3 g. of tar. In the aqueous portion, 0.413 mole of halide and 1.3 g. of acetone were identified, and 4 g. of impure β-*s*-butyl-β-methylhydroxylamine, b. p. 85–93° at 115 mm. (a yield of 17%), and 3.4 g. of tar were extracted from it after making alkaline.

The entire portion (b. p. 85–93°) was reduced as in the previous experiment. The hydrochloride of the resulting amine, melting at 190–200°, was converted into the oxalate. Fractional recrystallization of the product from alcohol (2.0 g.) yielded (in order of increasing solubility) 0.1 g. of oxalic acid, m. p. 187°, 0.1 g. of oxalate, decomp. 166–167° (probably N-methyl-*t*-butylamine oxalate) and 1.4 g. of N-methyl-*s*-butylamine oxalate, m. p. 110–111°.

Reaction of One Mole of Methylmagnesium Chloride with One Mole of 2-Chloro-2-nitrosopropane.—An ether solution containing 0.400 mole of methylmagnesium chloride was added to a solution of 43 g. (0.400 mole) of the chloronitrosopropane. After standing overnight the blue ether solution was decanted from the solid addition product. Fractional distillation yielded only 4.0 g. of chloronitrosopropane. The solid addition product was hydrolyzed in the cold with dilute sulfuric acid. By continuous extraction with ether 0.78 g. of acetone, 3.40 g. of unreacted chloronitrosopropane, 0.07 g. of acetoxime (m. p. 60°), 3.0 g. of tar were obtained and separated by distillation. The aqueous portion after extraction was distilled to half its volume to remove 0.041 mole of acetone as ascertained by analysis of the distillate. The residue was reduced with zinc dust and hydrochloric acid, made alkaline, and the volatile bases (0.115 mole) distilled into standard hydrochloric acid. Evaporation of the distillate yielded a hygroscopic reducing salt. This was further reduced with stannous chloride and concentrated hydrochloric acid. The hydrochloride obtained after the usual procedure was crystallized from absolute alcohol (m. p. 137–159°). *Anal.* Calcd. for CH_6NCl: Cl, 52.50. Found: Cl, 47.1. This salt was undoubtedly methylamine hydrochloride while the impurity was probably N-methyl-*s*-butylamine.

Reaction of Phenylmagnesium Bromide with 2-Bromo-2-nitrosopropane.—This reaction was carried out in the same manner as the methyl Grignard experiments. To a solution of 54 g. (0.363 mole) of 2-bromo-2-nitrosopropane was added an ether solution containing 0.495 mole of phenylmagnesium bromide. The resulting mixture contained no excess phenylmagnesium bromide. It was worked up as before. Upon distillation the following products were identified in the ether layer, 13.1 g. of bromoacetone, a little diphenyl (corresponding only to that found originally present in the phenylmagnesium bromide solution) and 5.0 g. of tar.

The addition product was hydrolyzed and continuously extracted for sixty-eight hours to dissolve all tar and colored material. The following products were identified from the ether extract of the aqueous portion: 5.6 g. (0.096 mole) of acetone, 0.096 mole of hydroxylamine, 4.16 g. (0.057 mole) of acetoxime, 5.8 g. (0.074 mole) of benzene and 14.1 g. of tar.

Summary

1. The reactions of dimethyl- and diethylzinc on 2-bromo and 2-chloro-2-nitrosopropane have been studied and found to involve the nitroso group.

2. The reactions of methyl and ethyl Grignard reagents have also been studied with these same compounds and found to involve the nitroso group.

3. The β-*s*-butyl-β-methylhydroxylamine obtained by the reaction of two moles of methyl

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[10] "Organic Syntheses," Vol. XI, p. 58.

[11] See also Löffler, *Ber.*, **43**, 2041 (1910), for another method of preparation.

[12] Sabatier and Mailhe, *Ann. chim. phys.*, [3] **16**, 87 (1909).

Grignard reagent and both nitroso compounds is a rearrangement product. It is the only case where the bromine is replaced by the action of the organometallic compound.

4. All the organometallic compounds except the methyl Grignard reagent, tended to some extent to split out HX.

STATE COLLEGE, PA. RECEIVED JULY 22, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Conductance of Non-aqueous Solutions. I. Sodium Triphenylboron and Disodium Tri-α-naphthylboron in Diethyl Ether

BY HENRY E. BENT AND MAURICE DORFMAN

Considerable work has been published recently from this Laboratory dealing with the alkali metal derivatives of various organic compounds. These compounds are salt-like in their character and conduct an electric current in non-aqueous solutions. The dissociation constants of these salts are not known but the assumption has been made that they are all of the same order of magnitude.[1,2] The data of this paper will be used later to test this assumption and are of immediate interest in establishing the structure of disodium tri-α-naphthylboron. A preliminary report of the experimental method[3] is given.

Sodium triphenylboron is a peculiar compound.[4] Triphenylboron is saturated as far as primary valence forces are concerned. It is true that it may readily add other molecules such as ammonia by means of a coördinate covalence but this can hardly be the case for sodium. The sodium addition compound conducts an electric current in diethyl ether solution and therefore presumably the sodium ion is held to the triphenylboron ion by electrostatic force.[5] The stability of sodium triphenylboron is therefore apparently due to a large electron affinity of triphenylboron. This in turn is probably due to the fact that the negative ion may be represented by a large number of structures, which result in a stabilization as a result of the phenomenon of resonance.[6]

The compound disodium tri-α-naphthylboron is still more curious. The second sodium is held rather loosely.[7] It was not possible, however, to measure ΔF for the addition of the second sodium due to the fact that an amalgam which might be in equilibrium with the compound would be solid at ordinary temperatures.

It seemed quite possible that a study of the conductance of solutions of these compounds, especially when compared with sodium triphenylmethyl, might shed some light on their structure and properties.

The method used experimentally was the ordinary a. c. procedure for resistances up to about 10^6 ohms. For higher resistance a d. c. method was adopted. The two methods were found to check in the region in which they overlapped.

Experimental Part

The cell "A," buret "B," and the tube in which the sodium addition compound was prepared are shown in Fig. 1. Two sheets of platinum, 1 cm. wide by 2 cm. long, were held rigidly about 1 mm. apart as indicated at the right in Fig. 1. Six holes were drilled in the sheets and soft glass rods pulled down to the size of the holes. A small bead was placed at the middle of each rod, the platinum sheets slipped over the ends and then by means of a small flame the end heated until sufficiently soft to allow it to be mashed down with a graphite rod. Heavy platinum wires were welded to the sheets of bright platinum and these in turn welded to No. 40 platinum ribbon, the latter being sealed into Pyrex as described by Bent and Gilfillan.[8] The cell constant was 0.00898.

The sodium addition compound was prepared in "C" by shaking a known weight of the boron compound with 40% sodium amalgam. The product was poured into the buret quantitatively by distilling ether back into "C"

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[1] Bent, *et al.*, THIS JOURNAL, **52**, 1498 (1930); **53**, 1786 (1931); **54**, 1393, 3250 (1932); **57**, 1217, 1242, 1259 (1935).

[2] Conant and Wheland, *ibid.*, **54**, 1212 (1932); McEwen, work soon to be published.

[3] This work was in progress before the first paper of Fuoss and Kraus [*ibid.*, **55**, 476 (1933)] appeared. In order to minimize the importance of polarization potentials they found it convenient to work with potentials as high as 150 v. In order to avoid the same difficulty we used potentials as small as possible, in most cases not more than 20 mv. A high sensitivity galvanometer made possible the use of these small potentials. Under these conditions polarization potentials gave no trouble.

[4] The stability of this compound has been reported in an earlier communication, Bent and Dorfman, *ibid.*, **57**, 1259 (1935).

[5] Krause and Polack [*Ber.*, **59**, 777 (1926)] state that sodium triphenylboron has a small conductivity in ether solution but give no quantitative data.

[6] Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

[7] Bent and Dorfman, *loc. cit.*

[8] Bent and Gilfillan, THIS JOURNAL, **55**, 3989 (1933).

thereby washing the amalgam. Tube "C" was sealed off at the constriction. Solution was then poured into "A." Dilutions were accomplished by pouring a given quantity into "B" and distilling ether back into the cell. This procedure made it possible to work with extremely dilute solutions without introducing uncertainty due to water given off by the glass. The small amount of water liberated during the early part of a run would not affect appreciably the concentration of the original concentrated solution. Experiments on the most dilute solutions were then made in glass which had been in contact with the solution so long as to introduce no further appreciable error from this source.[9] The procedure of pouring all of the material into the cell and repeating the run with the same sample of material served as a check on the unimportance of decomposition due to water given off by the glass.

In making d. c. measurements a Wolf potentiometer, direct reading to 0.01 mv., was used to apply a variable potential to the cell. In series with the cell was a Leeds and Northrup type HS galvanometer, mounted on a Julius suspension. This instrument has a sensitivity of 1 mm. for 10^{-11} amp. The procedure consisted in determining the potential necessary to produce 10 cm. deflection of the galvanometer when applied through a standard resistance. The cell was then added to the circuit and the potential determined which would give the same deflection of the galvanometer. The accuracy of the measurement, therefore, is essentially that of the Wolf potentiometer. With the technique described above it was quite easy to obtain an accuracy of from 1–5% in the measurement of the resistance of the cells over the range from 2×10^4 to 5×10^8 ohms. When the specific conductance became as small as 5×10^{-10} further dilution had no effect. This was probably due to adsorbed material as the specific conductance of ether is less than 4×10^{-18}. This final value of 5×10^{-10} was taken as the specific conductance of the solvent and subtracted from the observed reading for the most dilute solutions where it would begin to be important.

TABLE I

CONDUCTANCE OF DISODIUM TRI-α-NAPHTHYLBORON IN DIETHYL ETHER SOLUTION AT 0°

Equiv. per liter $\times 10^7$	Λ	Equiv. per liter $\times 10^7$	Λ
792,000	0.00674	792,000	0.00672
162,000	.00539	368,000	.00544
34,900	.00742	66,300	.00636
6,560	.0143	8,500	.0126
1,204	.040	272	.0116
144.4	.187	29.6	.0510
2.92	3.1	1.27	.036

TABLE II

CONDUCTANCE OF SODIUM TRIPHENYLBORON IN DIETHYL ETHER SOLUTION AT 0°

Equiv. per liter $\times 10^7$	Λ	Equiv. per liter $\times 10^7$	Λ
26,860	0.0284	26,860	0.0284
14,000	.0357	5,290	.0517
3,210	.0588	332	.117
695	.0921	34.4	.286
106	.146	2.50	1.07
9.8	.476	0.257	3.07

TABLE III

CONDUCTANCE OF DISODIUM TRI-α-NAPHTHYLBORON IN DIETHYL ETHER SOLUTION AT 25°

Equiv. per liter $\times 10^7$	Λ
758,000	0.00598
154,400	.00455
32,840	.00598
7,260	.00955
1,150	.0318
136	.170

TABLE IV

CONDUCTANCE OF SODIUM TRIPHENYLBORON IN DIETHYL ETHER SOLUTION AT 25°

Equiv. per liter $\times 10^7$	Λ
25,990	0.0243
13,500	.0296
3,100	.0491
665	.0778

The experimental results are given in Tables I, II, III and IV and in Fig. 2.

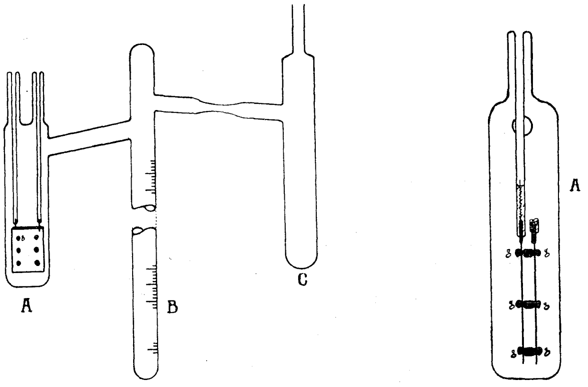
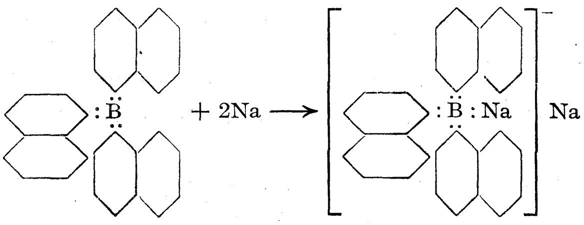


Fig. 1.

Discussion of Results

The fact that tri-α-naphthylboron can add two electrons suggested that the reaction with two atoms of sodium might be represented by the structural formulas



The two electrons from the sodium atoms are here assumed to complete a group of eight about a boron atom. One of the sodium ions is drawn to the boron atom by the strong electrostatic

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(9) Bent and Lesnick, THIS JOURNAL, **57**, **1246** (1935).

force but the other is unable to approach so closely on account of the three phenyl groups attached to the boron. If this picture is correct, one would expect one of the sodium ions to dissociate very readily, giving rise to a relatively strong electrolyte.

A second possibility is that a quinonoid structure results in the localization of the negative charge at the para position of one of the benzene rings. If such a structure represents the molecule the absence of steric hindrance would permit both sodium ions to come close to the carbon atom, one on either side of the ring. A further argument in favor of the quinonoid structure is to be found in the fact that triphenylboron is not able to add a second atom of sodium. The oxidation potential of 1,4-naphthoquinone is 0.495 and of 1,4-benzoquinone is 0.711 v.[10] The larger oxidation potential is exhibited by that compound for which the quinonoid structure is relatively less stable. If this second hypothesis is correct then we would expect triphenylboron to add a second atom of sodium less readily than tri-α-naphthylboron. We attempted to prepare trianthracylboron (9, 10-anthraquinone has a potential of 0.157 v.) in order to test the influence of the oxidation–reduction potential. However, the methods used in preparing triphenylboron and tri-α-naphthylboron were not successful.

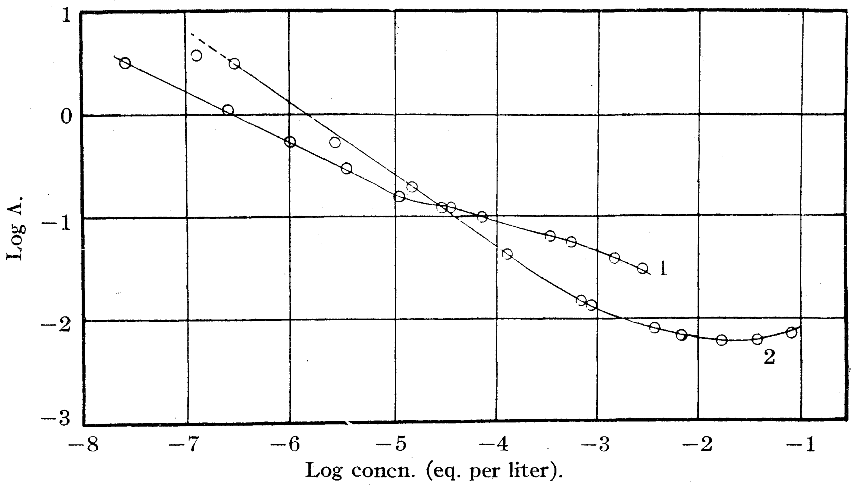

Fig. 2.—Curve 1, sodium triphenylboron; curve 2, disodium tri-α-naphthylboron.

It was in order to test these hypotheses with regard to the nature of the union of the two sodium atoms that the conductance experiments were initiated. To our great surprise we obtained the curves reported in Fig. 2. The curve for sodium triphenylboron (curve No. 1) which was run for comparison seems quite normal. There is a little kink in the curve at a rather smaller concentration than one might expect. The slope of the curve is −0.5, as one would expect for a uni-univalent electrolyte.[11]

It follows from Oswald's dilution law that if we are working at concentrations such that only a small fraction of the material is ionized we may write

$$K = \frac{(\mathrm{Na}^+)(\mathrm{R}^-)}{(\mathrm{NaR})} = \frac{\alpha^2 C}{(1-\alpha)} = \alpha^2 C = \frac{\Lambda^2}{\Lambda^2_\infty}\,C$$

$$\text{or } \log \Lambda = \log \Lambda_\infty K^{1/2} - {}^1/_2 \log C$$

Plotting log Λ against log C the slope should be −0.5. As is evident from the figure, however, disodium tri-α-naphthylboron is neither a much stronger electrolyte than sodium triphenylboron nor is the slope of the curve −0.5. On the contrary, the slope of the curve plotting log Λ against log C is −0.69 ± 0.02. This slope of approximately $^2/_3$ can be accounted for in the following way. If we assume that both sodium atoms ionize simultaneously, then we obtain the following equations.

$$K = \frac{(\mathrm{Na}^+)^2(\mathrm{R}^=)}{\mathrm{Na_2R}} = \frac{(\alpha C)^2(\alpha C)}{(1-\alpha)C} = \alpha^3 C^2 = \frac{\Lambda^3}{\Lambda^3_\infty}\,C^2$$

$$\text{or } \log \Lambda = \log \Lambda_\infty K^{1/3} - {}^2/_3 \log C$$

This gives an explanation for the slope of the conductance curve of $-{}^2/_3$ but leads to the very surprising conclusion that here we are dealing with a weak electrolyte presumably capable of ionizing in steps and yet both sodium atoms come off simultaneously. This cannot be accounted for by assuming simply that the two atoms are distantly located in the molecule, for, as has been shown by Adams,[12] such an assumption leads to the conclusion that the statistical factor would only double the apparent ionization constant. Evidently there must be possible some rearrangement of the molecule which can take place only when both sodium ions have been removed, or which, taking place when one ion is gone, suffi-

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[10] "I. C. T.," Vol. 6, p. 334. These values are for 0.5 N HCl, 95% ethyl alcohol.

[11] Kraus and Fuoss, THIS JOURNAL, **55**, 21 (1933).

[12] Adams, *ibid.*, **38**, 1503 (1916).

ciently weakens the force of attraction for the second ion that it ionizes readily. The energy change for this rearrangement must be sufficiently large to more than offset the coulomb energy which would normally make the second sodium ion ionize with much less ease.

On the basis of these facts the following hypothesis is suggested. The two electrons furnished by the two sodium atoms are localized in the ion, on a carbon atom in a quinonoid ring. The two sodium ions are held closely to the negative charge, one on either side of the atom on which the electrons are localized. When one of the sodium ions leaves, the coulomb force of the single sodium ion then becomes too small to cause this localization of the electrons to continue. The pair of electrons then resonates among all of the various quinonoid structures which can be written for the molecule with the result that the effective size of the ion is greatly increased, the coulomb force weakened and the second sodium ionizes as though the salt were a strong electrolyte.

Referring now to the equilibrium data[13] we find what at first glance would appear to be a contradiction. One of the sodium atoms can be removed easily by shaking disodium tri-α-naphthylboron with an amalgam while the other sodium atom is removed only by shaking with a more dilute amalgam. This turns out not to be a contradiction, however, but is quite capable of being explained without modifying the above theory. If we are right in assuming that both electrons are located on the same atom and that they resonate together, then we would expect a large coulomb repulsion term on account of the proximity of the two negative charges. This would account for the difficulty of adding a second sodium atom to monosodium tri-α-naphthylboron. When we consider the process of ionization, however, we are not removing electrons and hence this coulomb term does not enter into the dissociation constants of the ions.

The theory which has just been outlined is in harmony with all of the observations which we have made on these compounds. It is of course desirable to have more data in order to test further the theory.

In a later communication the significance of the temperature coefficient of conductance will be considered. It is not unusual for weak electrolytes in non-aqueous solution to exhibit a negative coefficient.[14]

Summary

A simple method is described for measuring the specific resistance of non-aqueous solutions. This method has been used for specific resistances up to 5×10^{10} ohms.

The equivalent conductance for sodium triphenylboron and disodium tri-α-naphthylboron in ether solution has been determined at 0 and 25° and from 10^{-1} to 10^{-7} mole per liter.

The bearing of these results on the structure of disodium tri-α-naphthylboron is discussed.

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[13] Bent and Dorfman, *loc. cit.*

[14] Kraus, "The Properties of Electrically Conducting Systems," Chemical Catalog Co., New York City, 1922, p. 144.

CAMBRIDGE, MASS. RECEIVED JUNE 4, 1935

[CONTRIBUTION OF THE CHEMICAL LABORATORIES OF THE RICE INSTITUTE]

Synthesis of Certain Pyridine Derivatives of Barbituric Acid

BY CARL SELLNER KUHN AND G. HOLMES RICHTER

The discovery of the substituted barbituric acids as hypnotics was followed by their administration in conjunction with various other drugs which enhanced their effectiveness. The analgesics and antipyretics are the most commonly used for this purpose. Since many of these drugs are basic, such as the alkaloids and other heterocyclic nitrogen compounds, they will form very definite "molecular compounds" with the acidic barbituric acid derivatives.

The effectiveness of drugs of this type suggests that the heterocyclic substituted barbituric acids would be interesting compounds. In contrast to the easy preparation of the molecular compounds or salts mentioned above, the introduction of a heterocyclic residue in the 5-position of barbituric acids presents a much more difficult problem, since the active halides and the aldehydes of this class of compounds are limited in number or are difficult to synthesize. A review of the literature on barbituric acids of this type shows that pyrazole,[1,2,3] imidazole,[4] piperidine,[5] indole,[6] thiazole,[7] furan[8] and tetrahydrofuran[9] rings have been introduced into the molecule.

Our laboratory has succeeded in preparing four new barbituric acids all containing the pyridine nucleus. Pure β-picoline was brominated to give β-picolyl bromide; this was then condensed with a substituted malonic ester to give an alkyl-β-picolylmalonic ester. The malonic ester was then condensed with urea in the usual fashion to give the 5,5-disubstituted barbituric acids.

Several attempts were made to join the pyridine ring directly to malonic ester and barbituric acid. Notwithstanding reported easy reactions of α-bromopyridine with many reagents, we were unable to condense α-bromopyridine with malonic ester. An effort was made to obtain the pyridine malonic ester through a Ladenburg rearrangement by treating pyridine with brominated malonic esters in the presence of catalysts but the easy decomposition of the malonic esters prevented the success of the experiment.

Experimental Part

(1) **β-Picoline.**—The β-picoline required for the preparation of the β-picolyl bromide was made by the method of P. Schwarz,[10] and gives a product free from the α and γ isomers.

Melting Points and Analyses of the Products

Name	M. p., °C.	Formula	% C Calcd.	% H Calcd.	% C Found	% H Found
5-(β-Picolyl)-5-ethylbarbituric acid	213–214	$C_{12}H_{13}O_3N_3$	58.28	5.30	58.80	5.71
5-(β-Picolyl)-5-*n*-propyl barbituric acid	250 dec.	$C_{13}H_{15}O_3N_3$	59.74	5.79	59.61	5.77
5-(β-Picolyl)-5-*n*-butyl barbituric acid	218–219	$C_{14}H_{17}O_3N_3$	61.06	6.23	61.73	6.81
5-(β-Picolyl)-5-*i*-amyl barbituric acid	229–230	$C_{15}H_{19}O_3N_3$	62.25	6.62	62.70	6.62

(2) **β-Picolyl Bromide.**—The preparation of this product by dissolving β-picoline in concentrated hydrochloric acid and brominating with two molecules of bromine at 150° is described by Dehnel.[11] The isolation of the bromide by treating the solution with sulfur dioxide, neutralizing with sodium carbonate, and extracting with ether must be carried out as rapidly as possible since the bromide may react with itself to give high molecular weight tars. β-Picolyl bromide is a lachrymator and a marked irritant for the skin, hence care must be taken in opening the sealed tubes and in handling the product.

(3) **Ethyl β-Picolylalkylmalonates.**—β-Picolyl bromide was condensed with ethyl ethylmalonate, ethyl *n*-propylmalonate, ethyl *n*-butylmalonate and ethyl *n*-amylmalonate. Since the method of condensation and purification was the same in all cases it will be described only for ethyl ethylmalonate.

One and six-tenths grams of sodium was dissolved in 22 cc. of absolute alcohol placed in a two-necked 200-cc. flask fitted with a condenser and stirrer. The resulting solution of sodium ethylate was cooled to 50° and 13.2 g. of ethyl ethylmalonate added. The β-picolyl bromide, which must be prepared shortly before each reaction due to its unstable nature, was thoroughly dried over anhydrous magnesium sulfate in ether solution. The ether solution of the bromide was added as rapidly as possible, the ether being distilled off during the addition by heating on the steam-bath. The mixture was heated for an hour on the steam-bath to complete the reaction. At the end of the reaction the remainder of the ether and the alcohol were distilled off.

The oily liquid and sodium bromide were washed with water to remove the salt and the oily layer removed with ether and extracted with 15% hydrochloric acid to remove the picolylmalonic ester. This acid solution was subsequently made alkaline and extracted with ether. The ether solution was dried over anhydrous magnesium sulfate and distilled, about 2 g. of a viscous red oil remained which apparently started to boil when the temperature of the bath reached 145–150° but due to the small amount of material and the obvious decomposition, no further attempts were made to distil the product.

(4) **5-(β-Picolyl)-5-ethyl Barbituric Acid.**—One and one-half grams of ethyl β-picolylethylmalonate, 0.62 g. of sodium, and 0.775 g. of urea were dissolved in 15 cc. of absolute alcohol in a Pyrex tube. The tube was sealed and heated with steam for twelve hours. At the end of this time the tube was opened and the contents washed in an evaporating dish, and the alcohol was removed on the hot-plate. The aqueous solution was carefully treated, dropwise addition, with 5% hydrochloric acid. At the turning point of congo red no precipitation took place, but when the solution was made slightly more acid an amorphous solid separated out of solution. This was recrystallized from 95% alcohol several times, yield 0.65 g.

The compound is soluble in dilute alkali and concentrated hydrochloric acid and warm alcohol; it is slightly soluble in hot water.

(5) **5-(β-Picolyl)-5-*n*-propylbarbituric Acid.**—The synthesis of this material was carried out in the same manner as described for the picolylethylbarbituric acid. Four grams of the β-picolyl-*n*-propyl ethylmalonate gave 0.52 g. of the barbituric acid. It was recrystallized four times from 95% alcohol.

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(1) A. Meyer, *Compt. rend.*, **152**, 1677 (1911).

(2) A. Sonn and Litten, *Ber.*, **66B**, 1512 (1933).

(3) Räth and Gebauer, German Patent 589,146.

(4) Taggart and Richter, This Journal, **55**, 1110 (1933).

(5) French Patent 776,449.

(6) Akabari, *J. Chem. Soc. Japan*, **52**, 601 (1931).

(7) Hooper and Johnston, This Journal, **56**, 484 (1934).

(8) Kirner and Richter, *ibid.*, **51**, 3131 (1929).

(9) Dox and Jones, *ibid.*, **50**, 2033 (1928).

(10) Schwarz, *Ber.*, **24**, 1676 (1891).

(11) Dehnel, *ibid.*, **33**, 3496 (1900).

(6) **5-(β-Picolyl)-5-*n*-butylbarbituric Acid.**—The synthesis was essentially the same as for the lower homologs. Two and one-half grams of the substituted malonic ester gave 0.71 g. of the product when recrystallized three times from 95% alcohol.

(7) **5-(β-Picolyl)-5-isoamylbarbituric Acid.**—The method of preparation was the same as above. Four grams of the substituted malonic ester gave 1.4 g. of the product when recrystallized three times from alcohol.

Summary

1. The synthesis of four new heterocyclic derivatives of barbituric acid which contain the β-picolyl group in the 5-position is described.

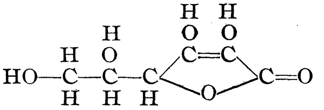
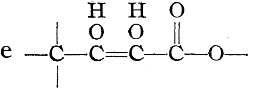
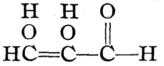
HOUSTON, TEXAS RECEIVED JUNE 22, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA AND THE COLLEGE OF PHARMACY OF THE UNIVERSITY OF CALIFORNIA]

Titration Curves and Dissociation Constants of *l*-Ascorbic Acid (Vitamin C) and Diethyl Dihydroxymaleate

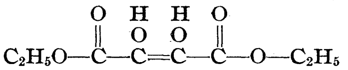
BY W. D. KUMLER AND T. C. DANIELS

Birch and Harris[1] using a micro method found the pK_a values of *l*-ascorbic acid at 16–18° to be $pK_{a_1} = 4.17$ and $pK_{a_2} = 11.57$. We have redetermined these constants at 22–23° using a macrohydrogen electrode and find values in agreement with theirs, namely, $pK_{a_1} = 4.12$ and $pK_{a_2} = 11.51$.

Although *l*-ascorbic acid is about four times as strong as acetic acid the generally accepted formula[2]  contains no carboxyl group, the acidity being attributed to the  $-\overset{|}{\underset{|}{C}}-\overset{\overset{H}{O}}{C}=\overset{\overset{H}{O}}{C}-\overset{\overset{O}{\|}}{C}-O-$ grouping.[2] As evidence that a structure of this type may give rise to relatively strong acid properties the case of reductone (glucose-reductone, gluco-reductone)  $H\overset{\overset{H}{O}}{C}=\overset{\overset{H}{O}}{C}-\overset{\overset{O}{\|}}{C}-H$ has been cited[2] which has a $pK_a = 5.0$.[3]

Reductone is the enol form of a 1,3-dialdehyde and these compounds like the enol forms of 1,3-diketones are undoubtedly much stronger acids than the enol form of the β-ketonic esters to which type of compound the structure assigned to *l*-ascorbic acid belongs. The enol form of acetylacetone has a $K_{a_{enol.}} = 1.3 \times 10^{-5}$ and the enol form of ethyl acetoacetate has a $K_{a_{enol.}} = 5 \times 10^{-9}$.[4] Thus for comparing acid strength reductone is not a correct analog of *l*-ascorbic acid.

We have measured the pK_a values of a β ketonic ester, diethyldihydroxymaleate



$$C_2H_5O-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{O}}{C}=\overset{\overset{H}{O}}{C}-\overset{\overset{O}{\|}}{C}-O-C_2H_5$$

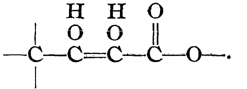
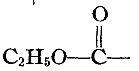
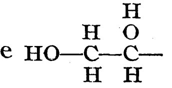
which contains the grouping to which the acidity of *l*-ascorbic acid has been attributed[2]  $-\overset{|}{\underset{|}{C}}-\overset{\overset{H}{O}}{C}=\overset{\overset{H}{O}}{C}-\overset{\overset{O}{\|}}{C}-O-$. Since the negativity of the  $C_2H_5O-\overset{\overset{O}{\|}}{C}-$ group is considerably greater than that of the  $HO-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{O}{C}}-$ group and the ester has two equivalent hydrogens it should actually be a stronger acid than *l*-ascorbic. However, from the pK_a values in Table I it is seen that *l*-ascorbic is much the stronger acid, its first dissociation constant being 1000 times as great as that of the other compound.

TABLE I

ALCOHOL–WATER SOLUTION

	pK_{a_1}	pK_{a_2}
l-Ascorbic acid	4.85	12.0
Diethyl dihydroxymaleate	7.88	12.3
Dimethyl dihydroxymaleate	7.85	12.3
WATER		
l-Ascorbic acid	4.12	11.51

The second dissociation constants have very nearly the same value, and in both cases are un-

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[1] Birch and Harris, *Biochem. J.*, **27**, 595 (1933).

[2] Herbert, Hirst, Percival, Reynolds, Smith, *J. Chem. Soc.*, 1270 (1933).

[3] Von Euler and Martins, *Ann.*, **505**, 73 (1933).

[4] Acetylacetone $K_a = 1.5 \times 10^{-6}$, ethyl acetoacetate $K_a = 2 \times 10^{-11}$ (Landolt–Börnstein), acetylacetone $K_{enolization} = 0.132$, ethylacetoacetate $K_{enolization} = 0.004$ (Rice, "Mechanism of Homogeneous Organic Reactions," Chemical Catalog Co., p. 92). The $K_{a_{enol.}}$ constants were calculated from the above K_a's by use of the equation

$$K_{a_{enol.}} = K_a \frac{(K_{enolization} + 1)}{K_{enolization}}$$

doubtedly due to an enolic type of structure. The first constant of *l*-ascorbic acid is too strong to be attributed to an enolized α-hydroxy-β-ketonic ester but might be due to some other grouping such as the enol form of a hydroxy, 1,3-diketone, a free carboxyl group, or the opening of the lactone ring. We are aware of the various arguments which have been advanced against these types of structures[2] but in view of inability of the enolized α-hydroxy-β-ketonic ester structure to account for the first dissociation constant these arguments should be checked.

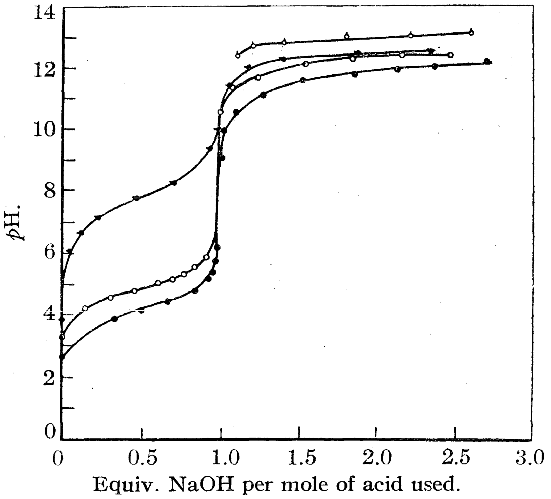

Fig. 1.—*l*-Ascorbic acid, ○: 0.0574 g. of acid, 4 ml. of alcohol, 4 ml. of water at beginning. Diethyldihydroxymaleate, -●: 0.0436 g. of compound, 4 ml. of alcohol, 4 ml. of water at beginning. No evidence of hydrolysis after thirty minutes at end of titration. Blank salt solution, ȯ: 0.109 g. of $NaC_2H_3O_2 \cdot 3H_2O$, 4 ml. of alcohol, 4 ml. of water. *l*-Ascorbic acid, ●: 0.0647 g. of acid, 5 ml. of water at beginning.

Experimental

A Hildebrand type hydrogen electrode and saturated calomel cell were used. These were checked against a standard phosphate buffer. A potentiometer–galvanometer circuit was used in obtaining the electromotive forces.

Due to the insolubility of the diethyl dihydroxymaleate in water the titrations were made in ethyl alcohol–water solutions which were 50% by volume at the start of the titration. Although the pK_a values are higher[5] in the alcohol solutions than in pure water they are strictly comparable with each other. The pK_{a_1} of *l*-ascorbic acid is 0.73 higher in the alcohol solution than in pure water.

As a check on the pK_a values of diethyl dihydroxymaleate the dimethyl ester was measured. Theoretically one would expect very little difference in the acidity of these two compounds and very little was observed as is shown by the pK_a values in Table I. However, since in the case of the dimethyl compound it was necessary to start with a 60% alcohol solution the values are not strictly comparable with the other two compounds but the errors thus introduced are less than 0.06 of a pK_a unit.

To demonstrate that the second pK_a is real and not an apparent effect due to the dilution of the 0.1 N sodium hydroxide, the curve for a sodium acetate blank is shown which falls definitely above the other curves.

Materials

Synthetic *l*-ascorbic acid was obtained from Hoffmann–LaRoche, Inc., and was used without further purification, m. p. 190°; literature m. p. 189, 190, 192°; molecular weight by titration 175.7, theoretical 176.1.

Dimethyl dihydroxymaleate was prepared by dissolving anhydrous dihydroxymaleic acid in the least quantity of anhydrous methyl alcohol and passing dry hydrogen chloride into the solution;[6] m. p. 150–151°, literature m. p. 151°.

Diethyl dihydroxymaleate was prepared by dissolving anhydrous dihydroxymaleic acid in anhydrous ethyl alcohol and passing dry hydrogen chloride into the solution;[7] m. p. 71–73°, literature 72–73°.

Dihydroxymaleic acid was prepared by oxidizing tartaric acid with hydrogen peroxide in the presence of ferrous iron[6] (p. 899).

Summary

The titration curves of *l*-ascorbic acid in water and of *l*-ascorbic acid and diethyl dihydroxymaleate in alcohol–water solution have been determined. The pK_a values of these compounds and of dimethyl dihydroxymaleate were measured. *l*-Ascorbic acid is 1000 times as strong as diethyl dihydroxymaleate. The apparent inability of the enolized α-hydroxy-β-ketonic ester type of compound to account for the acid properties of *l*-ascorbic acid suggests that some other grouping is responsible for its large first dissociation constant.

BERKELEY, CALIF.
SAN FRANCISCO, CALIF.

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(5) Branch, Yabroff and Bettman, THIS JOURNAL, **56**, 937 (1934).

(6) Fenton, *J. Chem. Soc.*, **65**, 905 (1894).

(7) Fenton, *ibid.*, **69**, 555 (1896).

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

The Use of the Ortho–Para Hydrogen Conversion in the Detection of Free Radicals Produced in Photo-dissociation[1]

BY W. WEST

In considering the properties to be anticipated of the lighter free radicals which might be utilized to demonstrate their presence or absence in photochemical experiments, the paramagnetic properties which they should exhibit as the result of their possession of an odd electrom seem worthy of investigation. As, however, the low concentration of radicals to be expected in these experiments would make a direct determination of any change of susceptibility extremely difficult by ordinary magnetic methods, it was proposed to investigate the possibility of using the discovery of Farkas and Sachsse[2] that paramagnetic substances are capable of catalyzing the interconversion of ortho and para hydrogen for their detection. The method has already been used by Farkas and Sachsse in an investigation of the magnetic properties of B_2H_6,[3] and the possibility of its application to the problem considered here has also been stated by A. Farkas in his monograph.[4] If, for instance, methyl iodide vapor is dissociated by light to methyl radicals and iodine atoms in the presence of a mixture of ortho and para hydrogen which is not in equilibrium at the temperature of the experiment, the paramagnetic radicals should, during their period of free existence, be capable of changing the ortho–para ratio toward the equilibrium value, and the experimental finding of such a change could be taken as evidence of the production of paramagnetic substances, which, in this case, could scarcely be other than the methyl group or iodine atom. The result of absorption of radiation might also be the production of a molecule, without dissociation, in a paramagnetic excited state, which on collision with a hydrogen molecule might bring about conversion; but unless the excited state were metastable, its short life would cause such conversion to be negligibly rare in comparison with those brought about by the comparatively long lived free radicals.

Since the thermal conductivity method of Bonhoeffer and Harteck[5] will give false results for the ortho-para composition of a hydrogen mixture, if more than traces of gas other than hydrogen are admitted to the conductivity gage, it was necessary in these experiments, in which only liquid air was available as a refrigerant, to choose reactions in which the products contain little or no methane; carbon monoxide also is not removed by liquid air, but these experiments show that it can be fairly adequately removed by the usual cuprous-ammonium reagent. The production of molecular hydrogen is of course to be avoided, and also, as the conversion efficiency of hydrogen atoms is of the order of 10^6 times as great as that of substances effective in virtue of paramagnetic properties, the conversion in a reaction in which these are produced will mask that produced by other radicals. Methyl iodide, acetone, propionyl aldehyde and benzene were the substances examined.

Procedure

The platinum wire of the conductivity cell, spot welded to platinum leads, was 15 cm. long, 10 μ thick, with a resistance of some 50 Ω when carrying a heating current of 50 m. a. in hydrogen at 58 mm., the cell being immersed in liquid air maintained at constant level. In series with the wire was an accurate resistance of 50 Ω. From a measurement of the potential fall across this resistance by means of a Leeds and Northrup Student Type Potentiometer the current passing through the gage wire was calculated, and a measurement of the potential drop across the gage enabled its resistance to be determined. The heating current through the gage wire was made accurately the same for the different hydrogen samples required in a determination of the amount of conversion by adjusting a rheostat until a given potential difference existed across the standard 50 Ω resistance. Reproducibility of the gage resistance was usually within 0.01 Ω.

Dry hydrogen, freed from oxygen, from a 2-liter reservoir could be passed either directly to the gage ("ordinary" hydrogen, $o/p = 3/1$) or to the "converter" containing charcoal at liquid air temperature, where it was changed to approximately a 1:1 mixture ("converted" hydrogen). The converted hydrogen could be passed directly to the gage or bubbled through methyl iodide, etc., into the reaction vessel, a quartz tube 30 cm. long and 2.6 cm. in diameter, cemented to glass by silver chloride cement, and into a similar "blank" vessel (of glass, but with a silver chloride joint exactly like that in the reaction vessel) in

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[1] The results given here were reported at the meeting of the American Chemical Society held in New York, April 22–26, 1935.

[2] L. Farkas and H. Sachsse, *Z. physik. Chem.*, **B23**, 1 (1933).

[3] L. Farkas and H. Sachsse, *Trans. Faraday Soc.*, **30**, 331 (1934).

[4] A. Farkas, "Ortho-Hydrogen, Para-Hydrogen, Heavy Hydrogen," Cambridge University Press, 1935, p. 102.

[5] K. F. Bonhoeffer and P. Harteck, *Z. physik. Chem.*, **B4**, 113 (1929).

parallel with the reaction vessel. These vessels were filled to a total pressure of 1 atmosphere, the organic compounds being at a partial pressure equal to their vapor pressure at 20°. From these the contents could be passed through any necessary chemical absorbent and through a liquid air trap to the gage, which was filled by means of a capillary control to 58 mm. of mercury. The conversion was measured from gage resistance measurements in the presence of "ordinary," "converted," "illuminated" and "blank" hydrogen made immediately after one another. High vacuum technique was used throughout. Illumination was effected by two "cold" quartz mercury arcs 38 cm. long, placed as close as possible to the reaction tube, one consuming 300 watts at 3000 v., the other 500 watts at 5000 v. A large proportion of their luminous energy is at wave length 2537 Å. A fan directed on the arcs and reaction vessel kept the temperature practically that of the room. Radiation of wave length 1849 Å. was excluded by wrapping the reaction vessel in two layers of cellophane, 0.025 mm. thick.

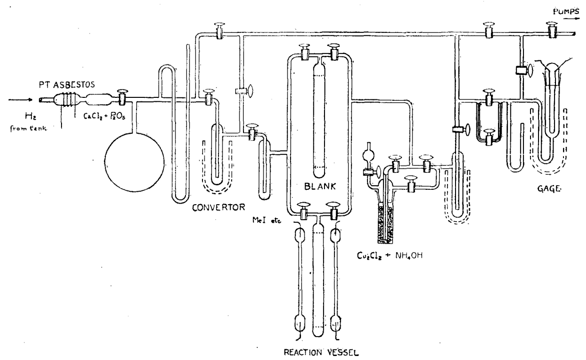

Fig. 1.—Reaction vessel.

Results

Preliminary experiments showed (a) a difference of about 1.8 Ω in the resistance of the gage wire in the presence of "ordinary" and completely "converted" hydrogen (b) a linear para-hydrogen concentration—resistance curve, (c) no change in the *o-p* ratio when a sample of converted hydrogen was left in the reaction vessel, without illumination, or in the blank overnight, whether in the presence or absence of methyl iodide vapor. Table I gives some representative results.

ΔR_1 is the difference in the gage resistance immersed in "illuminated" and "blank" hydrogen, respectively, and ΔR_0 the corresponding difference for "ordinary" and "converted."[6]

Table I

Substance	Exposure, min.	ΔR_1 ohms	ΔR_0	Corrected ΔR	% Conversion
Methyl	90	0.17	1.42	0.14	10
iodide	80	.21	1.79	.18	10[a]
	225	.68	1.79	.60	34[a]
	180	−.01	1.78		0[b]
Acetone	210	.60	.71	.31	44
	453	.90	1.03	.34	33
Propyl	187	.11	1.82	Probably	0
aldehyde	143	.12	1.15	0	0
Benzene	110	.20	1.21		?
	128	.12	1.80		?

[a] The bracketed data refer to the same run. [b] Illumination through glass.

Corrections.—Since the presence of only a few per cent. of methane or carbon monoxide in the gas which reaches the gage will give completely fallacious results, special experiments were carried out on methyl iodide and acetone to find how much carbonaceous material escaped the traps. Methyl iodide was chosen in the first place because, although it has a strong continuous absorption at 2537 Å., the actual decomposition effected by illumination is very small. The iodine recovered after two hours of exposure of methyl iodide and hydrogen under the same conditions as in the conversion experiments required only 2.49 cc. of 5×10^{-3} *N* thiosulfate for its titration, equivalent, if one atom of iodine is produced for every molecule of iodide decomposed, to the decomposition of rather less than 0.5% of the iodide initially present. To determine directly the amount of methane produced under the conditions of these experiments, the gas resulting from two hours' exposure of methyl iodide and hydrogen under the conditions of the conversion experiments was passed by means of a Töpler pump through a liquid air trap into a gas buret. This was analyzed by slow combustion in excess oxygen over a heated platinum spiral by Dennis' method, and the products passed into an absorption pipet containing an accurately known volume (some 5 cc.) of 0.02 *N* baryta. A turbidity was produced, showing the presence of carbon dioxide; the excess baryta was titrated by 0.01 *N* hydrochloric acid (microburet) and an apparent methane percentage of 0.46 was found in the hydrogen. Mercury was used throughout the gas analysis, as confining liquid. A blank experiment on the hydrogen, unmixed with methyl iodide, but otherwise treated in the same way as in the former experiment, also gave a turbidity with baryta, apparently arising from carbon compounds in the short pieces of connecting rubber tubing and stopcock grease in the gas analysis apparatus, equivalent to 0.34% methane, so that a methane con-

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[6] Values of ΔR_0 less than 1.8 Ω are due to a loss of efficiency of the charcoal in bringing about conversion to the low temperature equilibrium. After the introduction of air to the converter thorough baking out was found to be necessary to obtain a subsequent complete conversion to the 1:1 mixture.

tent of 0.12% is indicated in the hydrogen after two hours of illumination with methyl iodide.

The effect of this on the resistance of the gage wire can be estimated approximately in this way. From the calculated values of the rotational specific heats of ortho and para hydrogen at 93°K.,[7] one can calculate from the equation $\kappa = k\eta C_v$ the ratio of the thermal conductivities of 1/1 and 3/1 mixtures on the assumption that the viscosities are the same and that k is given by the somewhat uncertain equation[8]

$$k = {}^1/_4\,(9C_p/C_v - 5)$$

This ratio thus calculated is 0.963 for $\kappa(3/1):\kappa(1/1)$.

The thermal conductivity of hydrogen at 81°K. is given as 13.24×10^{-5},[9] and assuming this was for normal (3/1) hydrogen, the thermal conductivity for the 1/1 mixture is 13.77×10^{-5} and $\Delta\kappa = 0.53 \times 10^{-5}$. This corresponds to a difference in resistance in the gage wire of 1.79 Ω. In the experiment on methyl iodide in which an apparent change in resistance of 0.68 Ω was produced as the result of 225 minutes of illumination, 0.23% of methane might have been present in the hydrogen measured in the gage. The thermal conductivity of methane at 91.4°K. is given as 2.248×10^{-5},[10] and the conductivity of a mixture of 99.77% hydrogen (1/1) and 0.23% of methane would be 13.745×10^{-5}. The change in resistance in the gage wire produced by the presence of this amount of methane in the 1/1 mixture would be 0.085 Ω, compared with an observed change of 0.68 Ω, many times larger than could be accounted for by the production of methane. The change in gage resistance brought about in these experiments as the result of illumination seems attributable only to an actual change in the ortho–para ratio.

The acetone experiments were carried out with pure dry material in order to avoid the condensation reactions which take place in the presence of moisture.[11] The quantum yield in the photodecomposition of the vapor at wave length 26504 Å. is 0.33; half of the gaseous products consists of carbon monoxide and most of the rest of ethane; Damon and Daniels[11] report 10% of hydrogen in the product from the vapor, while Berthelot and Gaudechon[12] apparently from the photodecomposition of liquid acetone at the boiling point, find no hydrogen, but 5% methane in the products.

Removal of carbon monoxide by the cuprous ammonium complex ordinarily used for that purpose seemed the only method which would not disturb the ortho–para ratio, and the gas from the reaction vessel was slowly bubbled through a sludge of concentrated cuprous ammonium reagent and broken glass filling a trap between the reaction vessel and the liquid air trap. Special experiments showed that no conversion was brought about in this process. A direct determination of carbonaceous matter which escaped the traps, by the method previously described, showed the presence of 1.35% of such material estimated as methane or carbon monoxide as the result of three hours of exposure. The corrections have been made as before on the assumption that the interfering gas is methane; they would not be essentially changed if carbon monoxide were the disturbing substance. Although the corrections are considerable, there still remains a large resistance change in the gage as the result of illumination which cannot be accounted for by any methane or carbon monoxide possibly present.

Special significance is to be attached to the difference in the resistance changes produced by illuminating acetone and propionyl aldehyde, respectively. The quantum yield for the aldehyde decomposition of wave length 2537 Å. is about 1;[13] the principal products of decomposition are carbon monoxide and ethane, and an amount of hydrogen equal to 4% that of the carbon monoxide is reported. The products are of the same nature as and more in quantity than those from acetone; nevertheless, the observed change in resistance after illumination is only about one-sixth that produced by acetone. If the resistance change in the acetone experiments had been spurious, there would have been as large a change in the aldehyde experiments. The change of resistance observed in the aldehyde experiments is smaller than the corrections for the acetone experiments estimated as described above, and it seems very probable that it is entirely the effect of interfering material escaping the traps and that no appreciable ortho–para conversion is brought about by illuminated propionyl aldehyde. The

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(7) *E. g.*, K. F. Bonhoeffer and P. Harteck, *Z. physik. Chem.*, **B4**, 117 (1929).

(8) J. Jeans, "Dynamical Theory of Gases," Cambridge University Press, 1925, 4th ed., p. 302.

(9) Landolt–Börnstein, "Tabellen," 5th ed., Vol. II, p. 1305.

(10) Landolt–Börnstein, "Tabellen," 5th ed., Vol. II, p. 1306.

(11) G. H. Damon and F. Daniels, THIS JOURNAL, **55**, 2368 (1933).

(12) Berthelot and Gaudechon, *Compt. rend.*, **151**, 480 (1910).

(13) P. A. Leighton and F. E. Blacet, THIS JOURNAL, **54**, 3165 (1932).

magnitude of the correction to be subtracted from the observed change of resistance in the acetone experiments seems therefore overestimated rather than underestimated.

There is a small decomposition of benzene vapor on illumination by the mercury arc,[14] and if the products are the same as in the mercury-sensitized photo-decomposition, hydrogen and methane will be present. In any case, the observed change of resistance was relatively small, and probably is almost entirely to be attributed to uncondensable products.[15]

Discussion

The net result of these experiments is that the illumination of 1/1 ortho-para hydrogen mixture in the presence of methyl iodide and of acetone vapor at room temperature by light of wave lengths in the continuous absorption region of the organic compounds leads to a greater change in the thermal conductivity of the hydrogen than can be accounted for by the spurious presence of uncondensable gas; and the only reasonable interpretation is that appreciable conversion of the hydrogen mixture toward the room temperature equilibrium has been brought about. As, apart from solid catalysts and atomic hydrogen, the only substances known to bring about this conversion at an appreciable rate at room temperature are paramagnetic substances, the only conclusion to be drawn is that the organic substances under the action of the light gave paramagnetic entities capable of bringing about the conversion. That these were free radicals, or possibly, also, from methyl iodide, iodine atoms, allows of no reasonable doubt. The primary dissociation of methyl iodide in the region of continuous absorption into methyl radicals and iodine atoms can therefore be taken as certain.

The difference in the behavior of acetone and of propionyl aldehyde with respect to ortho–para conversion is completely in accord with the conclusions of Norrish[16] that photodecomposition of the aliphatic ketones occurs with the production of free radicals and of the aldehydes with a primary separation of carbon monoxide and formation of a saturated hydrocarbon. It seems certain from the experiments reported here that any free radical production on illumination of propionyl aldehyde is either much smaller or involves a much shorter life than in acetone under the same conditions. Although the experiments of Leermakers[17] point conclusively to the existence of a chain reaction in the photo-decomposition of acetaldehyde at high temperature and hence presumably to the presence of radicals, the "chain yield" at 25° is only 0.03 and, to quote this author, "It is possible that there are two modes of decompositions of aldehydes, one resulting in radicals, the other in carbon monoxide and hydrocarbon directly." Also, the experiments on the ortho–para conversion are in satisfactory agreement with those of Pearson,[18] who, employing the mirror methods of Paneth for the detection of free radicals, showed that mirrors could be removed by the products of illuminated acetone, and to a much less degree by those of propionyl aldehyde, and concluded that acetone exposed to light produces radicals and propionyl aldehyde does not.

Summary

An attempt has been made to detect the presence of free radicals in photo-dissociations by making use of the effect discovered by Farkas and Sachsse of the paramagnetic interconversion of ortho and para hydrogen.

Conversion in excess of any possible spurious effect was found to be produced by methyl iodide and acetone vapors illuminated to radiation of frequency in their continuous absorption regions, and not by propionyl aldehyde nor benzene.

The results are interpreted as indicating the production of paramagnetic free radicals on illumination of methyl iodide and acetone. The occurrence of conversion from acetone and not from propionyl iodide is strong evidence in support of Norrish's hypothesis of a difference in mechanism in the photo dissociation of aliphatic aldehydes and ketones.

New York, N. Y. Received July 18, 1935

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(14) J. R. Bates and H. S. Taylor, This Journal, **49**, 2450 (1927).

(15) The effect of benzene and of other hydrogen containing compounds reported by Farkas and Sachsse (*loc. cit.*) in bringing about ortho–para conversion is much too small to be detected in these experiments; that, for instance, methyl iodide itself does not bring about a conversion comparable to those noted here is shown conclusively by the blank experiments on methyl iodide, without illumination, and by the experiment on illumination through glass.

(16) R. G. W. Norrish, *Trans. Faraday Soc.*, **30**, 107 (1934).

(17) J. A. Leermakers, This Journal, **56**, 1537 (1934).

(18) T. G. Pearson, *J. Chem. Soc.*, 1718 (1934).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Photolysis of Azomethane

BY GEORGE S. FORBES, LAWRENCE J. HEIDT AND DARRELL V. SICKMAN

Measurements of quantum yields provide a valuable check upon hypotheses regarding energy chains in the corresponding thermal reactions. Carried out in monochromatic light, and at temperatures where a wholly negligible fraction of molecules present can be activated in unit time by collisions, the energy available after reaction can be calculated, and then apportioned among various combinations of molecules presumably involved in subsequent collisions. The temperature coefficients, also, of such photolyses have an obvious bearing upon the interpretation of the data for the thermal reactions.

Ramsperger[1] reported a quantum yield somewhat over two for the photolysis of azomethane, using the treacherous method of light-filters. Under his experimental conditions the nonactinic light was from one-third to five times the light absorbed, and he apparently overestimated the necessary corrections. The initial reaction he wrote $CH_3—N{=}N—CH_3 + h\nu \longrightarrow C_2H_6 + N_2$. The energy of the photon at 366 mμ, 83,000 cal./mole and the heat of reaction, 20,000 cal./mole add up to 103,000 cal./mole of which the ethane would be expected to retain the greater part. Ramsperger has argued that each newly formed ethane molecule might provide energy of activation (51,000 cal./mole) for one new azomethane molecule, and thus bring the total decomposition up to the value observed.

We found it hard to understand why the quantum yield, if two, should be independent of both temperature and pressure as stated by Ramsperger. We were convinced that measurements at additional wave lengths (Ramsperger made use of λ 366 mμ only) would afford additional information.

We carried out four series of measurements, at initial pressures of 664, 377, 184 and 181 mm., respectively. Six wave lengths of monochromatic light were employed. We found that the quantum yield, ϕ, approaches unity as its upper limit for initial decomposition at low pressures. The photochemical temperature coefficient if $t \ngtr 226°$ was found to be zero, in agreement with Ramsperger, as became reasonable in the light of the revised quantum yield. But at 260° this coefficient was no longer negligible.

Experimental

The monochromator, spark source, uranyl oxalate actinometer and trapezoidal gas reaction cell, as well as details of operation and the necessary corrections, were essentially the same as in recent work on ozone in this Laboratory.[2,3] At λλ 366 and 313 mμ a constricted mercury arc[4] replaced the spark; its oscillations were controlled by thin annular films of mercury within ground joints.[5] The monochromatic intensities back of the exit slit ranged from 3.8×10^{16} to 7.4×10^{17} quanta per minute.

The actinometer cell used at λλ 366 and 335 mμ was trapezoidal in form, 3 cm. deep, and held 11 cc. of a solution containing 0.003 mole of washed uranyl oxalate and 0.003 mole of oxalic acid per liter. At λ 313 mμ the same solution was used in a rectangular cell 5 mm. thick, and holding 5 cc. The quantum yields have been shown by Forbes and Heidt[6] to be identical with those previously established by W. G. Leighton and Forbes.[7] At λλ 254 and 208 mμ the rectangular cell was used with a solution 0.001 *M* in uranyl sulfate and 0.005 molal in oxalic acid, standardized in this wave length range by Brackett and Forbes.[8] Since the gas cell and the actinometer cell were exposed alternately as described below, the fluctuations in intensity of the light source were not followed radiometrically.

The reaction cell was fused into the wall of a quartz beaker which served as a thermostat. A ring of felt surrounding the space between the front window and the exit slit tended to hold the temperature of the former at the temperature inside the cell. Two immersion heaters regulated automatically, or by hand, held temperatures constant within 0.05°. A layer of thermostating liquid over the meniscus of the mercury in the regulator in each case was found to increase greatly the sensitivity of the make-and-break to temperature changes. Water was used in the thermostat from 0 to 70°, diethylene glycol 70 to 125°, *n*-butyl phthalate 125 to 200° and castor oil 200 to 300°. Temperatures were recorded with a set of Anschütz thermometers. The monochromator was pivoted under the light source[9] so that its exit slit could swing into line with reaction cell or actinometer cell as desired.

Previous experience with the photolysis of ozone[2,3] had convinced us of the fundamental importance of rigorous purification of reactants and the elimination of stopcocks. The purifying train as well as the reaction cell was thoroughly flamed, and degassed by means of a diffu-

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(1) Ramsperger, THIS JOURNAL, **50**, 123 (1928).

(2) Forbes and Heidt, *ibid.*, **56**, 1671 (1934).

(3) Heidt and Forbes, *ibid.*, **56**, 2365 (1934).

(4) Forbes and Harrison, *J. Opt. Soc. Am.*, **11**, 99 (1925).

(5) Forbes and Heidt, THIS JOURNAL, **53**, 4349 (1931).

(6) Forbes and Heidt, *ibid.*, **56**, 2363 (1934).

(7) W. G. Leighton and Forbes, *ibid.*, **52**, 3139 (1930).

(8) Brackett and Forbes, *ibid.*, **55**, 4459 (1933).

(9) Forbes, Kistiakowsky and Heidt, *ibid.*, **54**, 3246 (1932).

TABLE I

Serial number	λ in mμ	$\bar{P}$	$\bar{p}$	t	Q	A	B	Time	ΔP	ϕ	k
1–1 a	208–4 Zn	181.8	(181)	20.5	7.5	100	7.5	25.0	1.18	0.96	
b		183.0	(180)	20.2	6.8	100	6.8	44.5	1.76	.90	
1–2 a	335–1 Zn	184.4	(179)	22.4	9.9	45	4.4	46.0	1.15	.87	4.5
b		185.5	(178)	22.2	9.1	45	4.1	50.0	1.20	.89	
c		186.8	(176)	22.4	8.8	45	4.0	53.5	1.32	.94	
1–3 a	208–4 Zn	188.4	(175)	22.7	10.0	100	10.0	53.0	2.34	.68	
b		190.6	(172)	23.0	6.8	100	6.8	48.5	1.55	.72	
c		192.1	(171)	23.2	6.7	100	6.6	51.5	1.35	.61	
d		193.2	(170)	22.2	9.2	100	9.2	51.0	1.53	.50	
e		194.9	(168)	22.5	8.2	100	8.2	59.0	1.51	.48	
f		196.1	(167)	21.5	8.1	100	8.1	50.0	1.29	.49	
g		197.2	(166)	22.1	6.5	100	6.5	51.0	0.98	.46	
1–4	335–1 Zn	198.1	(165)	21.2	12.2	44	5.4	57.0	1.54	.77	4.5
1–5		199.4	(164)	21.2	11.5	43	5.1	50.0	1.22	.73	
1–6	208–4 Zn	200.9	(162)	22.6	13.1	100	13.0	55.0	1.56	.33	
1–7 a		201.8	(161)	21.9	11.8	100	12.0	55.0	2.16	.50	
b		203.3	(160)	22.1	6.8	100	6.8	54.0	0.83	.35	
c		203.9	(159)	21.5	5.5	100	5.5	56.5	.65	.32	
1–8	335–1 Zn	204.6	(158)	22.3	10.3	42	4.3	52.0	.86	.59	4.5
1–9		205.4	(157)	21.3	10.3	41	4.2	54.5	.85	.57	

TABLE II

Serial number	λ in mμ	$\bar{P}$	$\bar{p}$	t	Q	A	B	Time	ΔP	ϕ	k
2–1 a	208–4 Zn	377.8	(376)	23.9	6.2	100	6.2	52.0	1.62	0.77	
b		378.9	(375)	23.1	7.0	100	7.0	58.5	1.43	(.54)	
2 a	254–2 Zn	379.8	(374)	23.6	5.1	20	1.0	58.5	0.1	.26	0.8
b		379.9	(374)	23.8	6.8	20	1.4	65.5	.15	.25	
3	208–4 Zn	380.0	(374)	22.1	5.7	100	5.7	58.5	0.93	.43	complete
4 a	335–1 Zn	381.3	(373)	22.7	8.3	70	5.8	54.5	1.80	.87	4.5
b		382.7	(371)	21.6	11.3	70	7.9	52.0	2.25	.84	
5 a	366 Hg	384.9	(369)	21.2	6.2	56	3.5	207.0	1.42	.30	3.0
b		386.0	(368)	21.5	3.3	56	1.9	225.0	0.89	.32	
6 a	313 Hg	386.9	(367)	21.8	9.1	48	4.4	307.0	.3	.041	3.0
b		387.2	(366)	22.0	4.0	47	1.9	271.0	.2	.06	

TABLE III

Serial number	λ in mμ	$\bar{P}$	$\bar{p}$	t	Q	A	B	Time	ΔP	ϕ	k
3–1 a	208–4 Zn	666	(664)	25.0	16.7	100	16.7	26.0	2.2	0.77	
b		668	(662)	25.0	14.5	100	14.5	28.5	2.1	.77	
c		670	(660)	25.0	16.0	100	16.0	21.5	1.5	.67	
2 a	335–1 Zn	672	(658)	25.0	18.5	88	16.3	26.5	1.95	.69	4.5
b		674	(656)	25.0	16.2	88	14.2	24.5	1.5	.66	
c		675	(655)	25.0	15.5	88	13.6	22.5	1.15	.58	
3 a	366 Hg	678	(652)	24.9	74.0	75	56.0	52.0	3.60	.19	3.0
b		680	(650)	25.2	58.0	75	44.0	38.0	2.25	.21	
c		688	(647)	25.3	56.0	75	42.0	46.3	2.40	.19	
d		691	(644)	26.1	56.0	74	41.0	54.0	2.45	.17	
4 a		693	(642)	99.8	67.0	75	50.0	42.5	1.85	.13	
b		696	(639)	100.0	67.0	74	50.0	32.5	1.3	.12	
c		697	(638)	100.0	67.0	74	50.0	43.0	1.80	.13	
5		725	(610)	226.0	55.5	74	41.0	120.0	3.1	.097	
6		727	(608)	25.0	34.4	73	25.0	57.5	0.50	.077	

sion pump backed by an oil pump. The supply of azomethane (two samples separately prepared) was fractionated before each filling of the cell with rectification in a tower packed with glass beads and held at −80°. The distillate, entirely free from color in the liquid state, was outgassed at −80° until about a third of it had evaporated,

TABLE IV

TEMPERATURE COEFFICIENT OF ϕ FOR AZOMETHANE

$\lambda = 366$ mμ, $k = 3.0$

$\overline{P}$	$\overline{p}$	t	Q	A	B	Time	ΔP	ϕ
184.2	184.2					0		
185	(183)	26.6	23	0.33	7.6	34.5	1.90	1.1
187	(181)	26.3	26	.33	8.6	52.0	2.75	0.94
190	(178)	26.3	31	.32	10.0	37.5	1.95	.79
209	(159)	260.0	32	.30	9.5	38.0	(4.4–1.3)	1.3
213	(151)	260.0	29	.29	8.5	20.0	(2.05–0.75)	1.2
219	(149)	260.0	29	.29	8.5	33.5	(3.15–1.2)	1.1
227	(141)	28.2	27	.27	7.2	60.5	2.1	0.73
230	(138)	28.2	27	.26	7.0	95.5	3.0	0.69

and then stored in a liter bulb. In view of these precautions it appeared proper to assume that initial pressures in the reaction cell represented azomethane exclusively. After introduction of gas, this cell, together with the spiral quartz manometer, was sealed off from the rest of the apparatus. The mercury manometer to which the zero readings of the quartz manometer were referred reproduced pressure changes within 0.05 mm.

Tables I to IV include all our photolytic measurements where Q and B are respectively quanta incident upon, and absorbed by, the gas per minute, with omission of the factor 10^{16}. A is the percentage of incident light absorbed by the gas. The average total pressure during a photolysis is $\overline{P}$ and the average partial pressure of azomethane calculated from Ramsperger's mechanism is $\overline{p}$. The temperature of the cell, t, follows. Time of a given photolysis is in minutes. The manometer and barometer readings in millimeters of mercury have been corrected to 0°, and the gas pressures reduced to 0° by means of the simple gas law. Following Ramsperger, our quantum yields, ϕ, represent the increase in the number of molecules, in the reacting system, per quantum absorbed, and were calculated by use of Ramsperger's absorption coefficients, k, except at 208 mμ, beyond the spectral range covered by him, where the absorption, in our cell, was evidently complete. As he obtained these data by using a spectrograph and calibrated screens, after the method of Ramsperger and Porter,[10] the uncertainties inherent in the filter method could not have vitiated the results. We were, however, obliged to make the undesirable assumption that the variation of extinction coefficients with temperature is unimportant over a range of 240°. Except at 260°, the highest temperature employed by us, the velocity of decomposition in the absence of light was negligible.

Discussion of Results

In order to make the corrections for transmitted light as small as possible the wave lengths 208 and 335 mμ (the latter corresponding to an absorption maximum of azomethane) were first employed. The *initial* value of ϕ is seen to be close to unity at 181 mm., a pressure intermediate between Ramsperger's greatest pressure and his next smaller one. But at 377 and 665 mm. $\phi = 0.77$, indicating clearly the increase in deactivation with pressure. The decrease in ϕ at all pressures, as decomposition increased at room temperature, is very striking. Ramsperger gives four averaged quantum yields only, one for each of four initial pressures, but we calculated relative values of ϕ for each of his twenty separate experiments, and found that his values also decreased with increasing decomposition at room temperature. The decrease of ϕ with increase of initial pressure was less noticeable in Ramsperger's results, because three out of four of his pressures were much smaller than any of ours. He observed that "a very slight deposit was formed on the front window of the reaction chamber" upon raising temperature from 20 to 100°. Such a deposit was evident to us almost immediately after beginning of illumination by λ 208 mμ in the pressure range in which we operated. No deposit was formed at λ 366 mμ. The photolysis of even one millimeter of gas was attended by a decrease in ϕ far greater than experimental error whenever a deposit was formed. As our material was insufficient in amount to permit of refilling the cell after each twenty-minute run, we had to resort to graphical treatment of results to eliminate this complication. In Fig. 1, plots of ϕ against pressure change yield a straight line within the limits of experimental error, which might be expected if the falling off in the light entering the cell, for *small* changes in extinction by the deposit on the window, were roughly proportional to the thickness of this de-

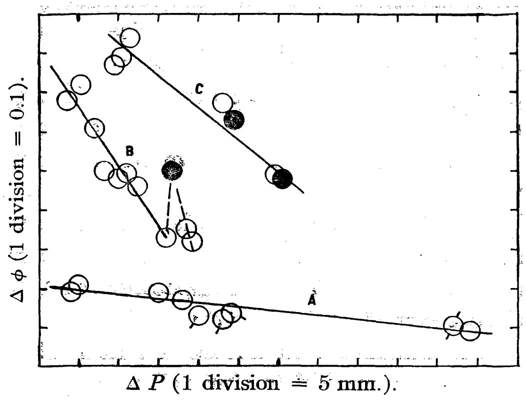

Fig. 1.—Δ ϕ/Δ P shown as independent of t (if $t \ngtr 226°$), and dependent on wave length only. Curve A at λ 366 mμ; circles at 25°, single-flag circles at 100°, double-flag circles at 226°. Curve B at λ 208 mμ; all experiments at 21°. The solid circle resulted just after heating the front window to 100° for twelve hours. Curve C at λ 335 mμ; all experiments at 21°. No break resulted (solid circles) upon heating the front window to 100° for twelve hours.

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[10] Ramsperger and Porter, THIS JOURNAL, **48**, 1267 (1926).

posit. The opacity of the deposit is greatest at λ 208 mμ due in part to increased scattering. Interference rings were plainly seen after the deposit had become well developed, an observation in harmony with the fact that the light intensity was greatest at the center of the window, and fell off toward the edges. The deposit could be partially dispelled by gentle heating of the front windows over twelve hours, as is evident from Fig. 1 upon comparing experiment 1–6 with 1–7a at 208 mμ. On the other hand, no increase in transmission at λ 335 mμ was observable—compare 1–4 with 1–5, also 1–8 with 1–9. The falling off in ϕ with increase in decomposition was likewise much less rapid at λ 335 mμ than at λ 208 mμ—compare series 1–2, 1–4, 1–5, 1–8, 1–9 all at 335 mμ with 1–1, 1–3, 1–6 and 1–7 all at 208 mμ.

Unfortunately we had material insufficient to trace the relation between ϕ and λ over the entire wave length range. Still, series 2a where $\phi = 0.25$ at λ 254 mμ may properly be compared with the average of series 2–1 and experiment 2–3 at λ 208 mμ, $\phi = 0.54$. This increase in ϕ with size of the quantum indicates that the probability of dissociation before deactivation increases in the same sense. At λ 254 mμ the light energy, 110,000 cal./mole, is more than twice the activation energy, 51,000 cal./mole while at 208 mμ the ratio is nearly three. But even with this great excess of energy there is no evidence that a second azomethane molecule is activated and subsequently decomposed.

In view of the fact that ϕ is halved in going from λ 208 mμ back to λ 254 mμ, the approximate equality in ϕ for initial decomposition at λλ 366, 335 and 208 mμ is at first sight unexpected. However, the maximum in absorption at λ 335 mμ appears to correspond to absorption in the N=N bond, for the N–C bond does not absorb in this region as is evident upon examining for instance the absorption curve of acetamide.[11] Owing to the stability of the N=N bond and the fact that the two N–C linkages are *both* adjacent to it, a smaller quantum might well produce dissociation than in the case where a larger quantum is absorbed beyond the first absorption maximum, presumably by a single N–C bond.

The temperatures represented by the various points in Fig. 1, plot a, are distributed in random fashion along the (approximately) straight line, the slope of which, as pointed out above, is to be referred to the increase in the deposit upon the front window. It therefore seems permissible to draw the conclusion that the effect upon ϕ of an increase in temperature of 206° is incapable of detection. If the photolysis were a chain reaction at 226° the large percentage of molecules in high vibrational states at this temperature might contribute noticeably to the quantum yields.[12,13] At 260°, however, the dark reaction has become equal to one-third of the photochemical reaction, and the contribution of such molecules to the photochemical reaction rate is no longer negligible.

We are indebted to Dr. O. K. Rice for the opportunity to discuss with him various aspects of this research.

A subsequent paper will deal with approximate physical analyses of the reaction products both thermal and photochemical. In the light of these data it would appear that the reaction mechanism is closely similar in both cases.

Summary

Quantum yields, ϕ, for photolysis of azomethane at 181, 184, 377 and 665 mm. were measured by reference to a uranyl oxalate actinometer. Purification and photolysis alike were carried out in a train without stopcocks, following the technique and precautions developed in previous researches. Six monochromatic radiations were employed. By graphical methods allowance was made for deposition of difficultly volatile decomposition products upon the front window.

The quantum yield ϕ approaches unity as its upper limit for initial decomposition at low pressures.

A temperature increase, 20 to 226°, had no effect on ϕ. Evidently reaction chains are absent in this temperature interval. But in the vicinity of 260° the photochemical temperature coefficient became measurable.

With increasing pressure ϕ falls off rapidly, apparently because of collisional deactivation.

In the region 366 to 335 mμ approximately, ϕ passes through a maximum apparently corresponding to a maximum of absorption by the N=N bond. With increasing quanta ϕ next decreases to a minimum, then increases again when the N–C bond begins to absorb.

CAMBRIDGE, MASSACHUSETTS RECEIVED JUNE 20, 1935

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[11] "International Critical Tables," Vol. V, p. 364.

[12] Sickman and Allen, THIS JOURNAL, **56**, 1251 (1934).

[13] Leermakers, *ibid.*, **56**, 1537, 1899 (1934).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 352]

The Chemiluminescence of 3-Aminophthalhydrazide

BY LOUIS HARRIS AND ALMON S. PARKER

The oxidation of 3-aminophthalhydrazide in alkaline solution is accompanied by considerable light emission.[1] A knowledge of the quantum efficiency under various conditions may assist in interpreting the mechanism of this light emission. Measurements of the quantum efficiency have been reported for certain chemiluminescent reactions,[2,3] and while conclusions have been drawn from measurements with dilute flames, data for condensed phases are meager. In this investigation, measurements were made to determine the maximum quantum efficiency of the chemiluminescence of 3-aminophthalhydrazide and the effect of various factors on this efficiency.

A thermopile offers a more direct measure of the chemiluminescent energy than photometric measurements, but is usually too insensitive. However, if the light reaction zone is made to approach a point source, a larger fraction of the emitted light energy may be focused on the thermopile surface. A number of preliminary measurements indicated that if a solution of sodium luminol[4] containing hydrogen peroxide was thoroughly mixed with a large excess of strong oxidizing agent (alkaline hypochlorite), the light reaction could be confined to a small volume. Accordingly, a suitable reaction chamber was designed and the energy measurements effected with a thermopile.

Materials.—**1. Sodium luminol** was prepared according to directions.[5]

2. Hydrogen peroxide (3% U. S. P.) was analyzed before its addition to the sodium luminol solutions.

3. Sodium hypochlorite was prepared by bubbling commercial (tank) chlorine slowly through a solution *N* in sodium hydroxide and 2 *N* in sodium carbonate, with continuous stirring until the solution contained about 5% (by weight) available chlorine (as Cl_2). This solution was diluted to a chlorine content of 0.5 or 1.0%, and sodium carbonate added to bring the alkali concentration to 0.350 *N* (carbonate).

Any other chemicals used were of C. P. quality and distilled water was employed throughout.

Apparatus.—A number of reaction chambers were tested; that illustrated in Fig. 1 proved the most satisfactory. This chamber could be so operated that a brilliant spherical spot of light (2 mm. in diameter; slightly larger for the concentrated solutions) appeared at the point where the reactants met, with no residual light in the effluent. The chamber was constructed of standard size glass tubing with quartz tubing around the reaction zone. The sodium luminol plus hydrogen peroxide feed nozzle was 0.483 mm. in diameter. Stopcocks in the connecting lines from two 18-liter aspirator bottles, containing the reactants, regulated the gravity flow. The spot of light was focused by a quartz lens, 3.8 cm. in diameter and 19.1 cm. away, on the sensitive surface of a Kipp (micro) thermopile. (The image of this spot, formed by the lens, was slightly smaller than the active surface of the pile which was 28.26 sq. mm.) The thermopile was connected to a Leeds and Northrup H. S. type galvanometer. The thermopile–galvanometer system was calibrated with two standard lamps (Bureau of Standards).

Experimental Procedure

It was necessary to determine what part of the galvanometer deflection was due to heat of mixing or to any other extraneous effects. Proper shielding of the system prevented stray light from entering the thermopile. Preliminary measurements showed that it was advisable to store the bottles containing the reactants for twenty-four hours, before making measurements, in a thermally insulated room (24 to 25°) with the thermopile–galvanometer system. When sodium luminol solution (in the absence of hydrogen peroxide) was mixed in the chamber with the hypochlorite, the galvanometer deflection obtained was less than 1% of the maximum deflection when hydrogen peroxide was present. Likewise, when hydrogen peroxide solution alone was mixed with the hypochlorite, the deflection obtained was a negligible fraction of that obtained under normal conditions of operation.

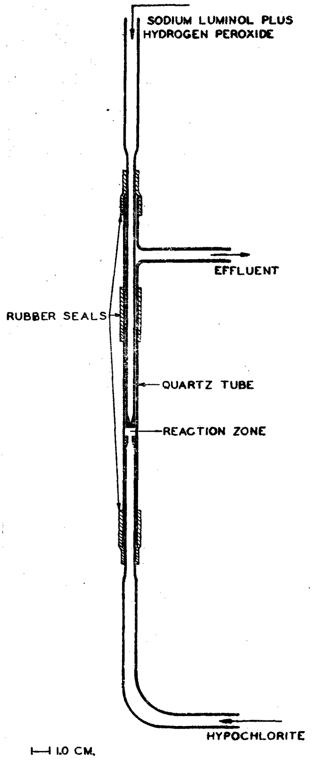

Fig. 1.—Reaction chamber.

The maximum flow of sodium luminol plus hydrogen peroxide was limited by the liquid head (about 1.5 m.) and the capillary feed nozzle (Fig. 1). After the rate of sodium luminol plus peroxide had been fixed, the flow of

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[1] Albrecht, *Z. physik. Chem.*, **136**, 321 (1928).

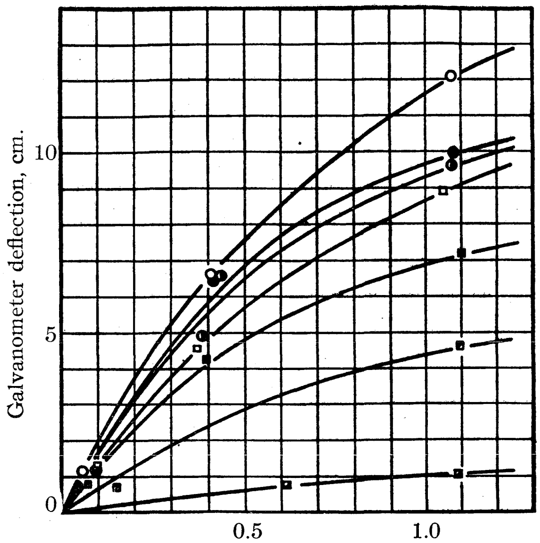
[2] Polanyi and co-workers, *ibid.*, **B1**, 3–73 (1928).

[3] Thomas and Dufford, *J. Opt. Soc. Am.*, **23**, 251 (1933).

[4] The sodium salt of 3-aminophthalhydrazide will be designated as sodium luminol.

[5] Huntress, Stanley and Parker, THIS JOURNAL, **56**, 241 (1934).

hypochlorite was adjusted to give a small spot of light on the lens-side of the reaction zone. Under these conditions, moderate variations (as high as 15%) in the rate of flow of hypochlorite had no influence on the galvanometer deflection. When potassium ferricyanide plus sodium hydroxide was tried as the oxidizing agent, in place of hypochlorite, the light was no longer confined to a spot but filled the reaction zone and appeared dimmer than before.



Rate of flow of sodium luminol plus hydrogen peroxide, ml./sec.

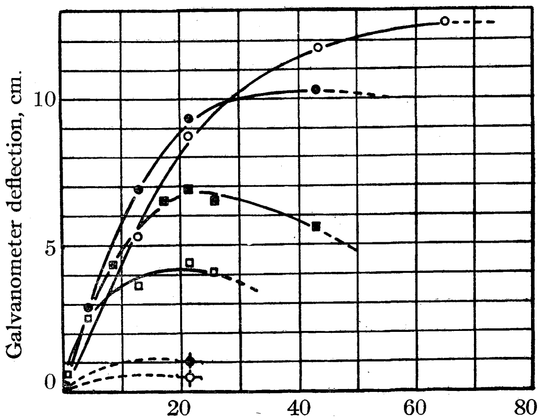
Fig. 2.—Variation of galvanometer deflection with rate of flow of sodium luminol plus hydrogen peroxide.

Curve	Conc. sodium luminol, g. mole/liter	Conc. hydrogen peroxide, g.mole/liter	Conc. hypochlorite, % Cl_2	Conc. alkali, *N*
○	0.0251	0.0434	1.0	0.350
●	.0251	.0215	0.5	.350
◑	.0126	.0215	1.0	.350
□	.0251	.0215	1.0	.350
■	.0050	.0215	1.0	.350
◩	.0025	.0215	1.0	.350
◪	.00050	.0215	1.0	.350

Data.—The data are presented in Figs. 2 and 3. Each of the galvanometer deflections plotted is the average of ten observations. The average deviation was 3%. Different batches of the reactant solutions gave the same deflections within 5%. The change in galvanometer deflection with varying rate of flow of sodium luminol plus hydrogen peroxide is shown in Fig. 2. By interpolation of these data, it was found possible to express all data for other rates of flow. The data, interpolated in this way, are presented in Fig. 3, which also shows how variations in the hydrogen peroxide concentration affect the galvanometer deflections.

Quantum Efficiency

It was assumed that the chemiluminescent intensity was equal in all directions and that the source might be considered as a point. The latter assumption was validated by measurements with a larger lens. Therefore, the galvanometer deflections were an easily calculated fraction of the total energy emitted.



Concentration of hydrogen peroxide, g. mole × 10^3/liter.

Fig. 3.—Variation of galvanometer deflection with hydrogen peroxide concentration; hypochlorite, 1% Cl_2; alkali, 0.350 *N;* rate of flow of sodium luminol plus hydrogen peroxide, 1 ml./sec.; rate of flow of hypochlorite, 3 ml./sec. (approx).

Curve	Conc. sodium luminol, g. mole/liter	Curve	Conc. sodium luminol, g. mole/liter
○	0.0251	□	0.0025
●	.0126	-●-	.00050
■	.0050	-○-	.00025

A spectroscope showed that the chemiluminescence extended from the violet, deep into the red. A quartz cell filled with distilled water, placed between the reaction zone and the thermopile, reduced the galvanometer deflections by about 10%. Jena filter OG2b, which transmits nearly 100% from 5780 to 20,000 Å., reduced the galvanometer deflection by about 98%, showing that only 2% of the chemiluminescent energy was of wave lengths longer than 5780 Å.

Photographs of the chemiluminescence and of the emission from a standardized lamp, taken with a Hilger E315 spectrograph and III-L Eastman Kodak plates, assisted in evaluating the energy distribution of the chemiluminescence. Most of the chemiluminescent radiation was in the wave length region 3800 to 5000 Å. with a flat maximum from 4100 to 4400 Å.

Inasmuch as the sodium luminol, hypochlorite and the product of the chemiluminescence each absorbs light of wave lengths shorter than 3700 Å., the energy observed may be only a fraction of the total produced.

The following constants and variables were used in the calculation of the quantum efficiency (Eff).

Eff = quanta emitted per molecule of sodium luminol introduced.
d = galvanometer deflection (cm.).
v = rate of flow of sodium luminol plus hydrogen peroxide (ml. per sec.).
a = concentration of sodium luminol (g. mole per ml.).
f = galvanometer calibration factor (8.556 ergs per sec. per cm. deflection).
λ = wave length of the maximum chemiluminescent intensity (4250×10^{-8} cm.).
l = fraction of the total emitted light focused on the thermopile (0.00246) (calculated from the geometry of the system).
t = fraction of light transmitted by lens and chamber wall (0.9).
h = Planck's constant (6.554×10^{-27} erg. sec. per quantum).
c = velocity of light (3.00×10^{10} cm. per sec.).
N = Avogadro's number (6.063×10^{23}).

$$\text{Eff} = \frac{d}{v \times a} \times \frac{f \times \lambda}{l \times t \times c \times h \times N}$$

Figure 4 shows how the quantum efficiency varies with the concentration of sodium luminol and with the rate of flow of sodium luminol plus hydrogen peroxide. The numerical value for the quantum efficiency, from the maximum of the lowest curve of Fig. 4, was calculated to be 2.8×10^{-3} quanta per molecule of sodium luminol introduced. At lower rates of flow of sodium luminol plus hydrogen peroxide the efficiency increased but never more than doubled.

Fluorescence Experiments

Even though the chemiluminescence extended over a rather broad band in the spectrum, it seemed of interest to study the emission of light from aqueous solutions of sodium luminol when they were illuminated by an external source. Most of the experiments were performed under daylight illumination with window glass interposed between the light and the solutions ($\lambda >$ 3400 Å.). The fluorescence was found to be much stronger when hydrogen peroxide was added to the sodium luminol. The fluorescence intensity was a maximum for concentrations of sodium luminol between 0.00025 and 0.00005 molal. Although the maximum quantum efficiency is also in this concentration range, no correlation between the two is implied. It is more likely that the dependence of the fluorescence on concentration is determined by the molal absorption coefficient (ϵ = 8000 approx. for wave lengths shorter than 3700 Å.).

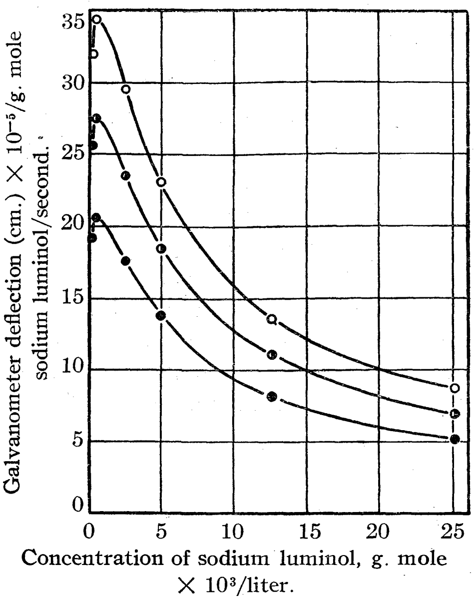


Fig. 4.—Variation of energy emitted per mole of sodium luminol, with its concentration. Concentration of hydrogen peroxide: maxima of Fig. 3. Concentration of hypochlorite, 1% Cl_2: concentration of alkali, 0.350 N.

Curve	Rate of flow of sodium luminol plus hydrogen peroxide
○	0.1 ml./sec.
◑	0.5 ml./sec.
●	1.0 ml./sec.

Absorption Spectra Measurements

Quantitative measurements of the absorption spectra were made, in order to obtain further information concerning the reactants and products. The absorption of aqueous solutions of sodium luminol, and of mixtures of sodium luminol with hydrogen peroxide, extended from 3970 to 2400 Å. Each solution showed absorption maxima at 3500 and 2900 Å., and evidence of another maximum at shorter wave lengths than 2500 Å. Below 3600 Å. the absorption by sodium luminol is slightly but definitely different from that of solutions containing hydrogen peroxide, the necessary corrections having been made for absorption by hydrogen peroxide alone. Absorption by aqueous solutions of the product from the chemiluminescence extends from 5000 to below 2300 Å. The amount and character of the absorption depended upon the manner in which the reactants were brought together. The results indicate that the internal absorption, by the final products, and possibly by the intermediate products, reduces the light emission, especially for concentrated solutions. In evaluating the quantum efficiencies, however, the internal absorption has been neglected.

Discussion of Results

The change in energy emission with changing hydrogen peroxide concentration (Fig. 3) indicates that hydrogen peroxide plays a major role in the chemiluminescence. The fluorescence and the absorption spectra point to the same conclusion. Figure 3 indicates that each molecule of sodium luminol is associated with about four molecules of hydrogen peroxide. This, in conjunction with the other results, suggests a compound between sodium luminol and hydrogen peroxide. The binding between the two types of molecule is probably a loose one and the molecular ratio in the compound itself is not necessarily four to one.

The quantum efficiency, though low, is about 10,000 times higher than any thus far reported for condensed systems.[3] The comparatively high efficiency is, no doubt, assisted by the successful mixing. The prolonged chemiluminescence customarily observed seems to indicate that in those instances, the rate of reaction is limited by the rate of diffusion. The fact that the rate observed with potassium ferricyanide is less than with hypochlorite, indicates that a smaller concentration of the active oxidizing agent is produced in the former case. Recently,[6] there was reported an intense chemiluminescence in the oxidation of alkaline solutions of dimethyldiacridylium nitrate by hydrogen peroxide. The luminescent interval was shortened from hours to seconds and the light intensity increased considerably by the addition of a catalyst, osmium tetroxide, which decomposed the hydrogen peroxide. A similar result is obtained in the oxidation of sodium luminol by physical rather than chemical means.

Mechanism of Chemiluminescence

It seems fairly definitely established that sodium luminol plus hydrogen peroxide is the light-emitting molecule or its parent substance. The light-emitting molecule is brought to its energized state by reactions of the parent with some oxidizing substance. The relatively low quantum efficiency would then be explained by one or more of the following non-light producing processes: (a) simultaneous reactions of the reactants to form other substances; (b) reactions of the excited molecule with the oxidizing substance; (c) collisions "of the second kind" involving the excited molecules or the oxidizing substance. In addition, if transitions corresponding to the ultraviolet occur, the quantum efficiency is reduced, due to internal absorption.

Since the light-emitting process may consist of several steps, where the excited molecules do not fall directly to the ground level, it is difficult to draw conclusions concerning the energetics of the over-all reaction.

Summary

The oxidation of the sodium salt of 3-aminophthalhydrazide has been carried out under conditions to give a maximum light intensity. The quantum efficiency was found to be about 0.3%. Evidence for compound formation between hydrogen peroxide and the sodium salt has been presented. The mechanism of the chemiluminescence has been discussed.

CAMBRIDGE, MASS. RECEIVED JUNE 26, 1935

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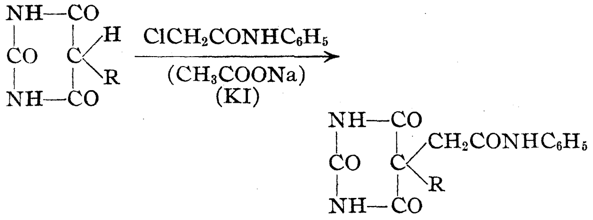
[6] Gleu and Petsch, *Z. angew. Chem.*, **48**, 57 (1935).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Alkyl-acetanilido-barbituric Acids

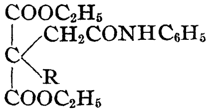
BY JOHN A. TIMM

Of the many derivatives of barbituric acid, which have been prepared and tested for their value as sedatives and hypnotics, the molecules of none, as far as the author is aware, contain the acetanilido group attached to the 5 carbon atom. The well-known use of acetanilide as an antipyretic suggested its use as a substituent in the barbituric acid ring. Accordingly various 5-alkylbarbituric acids have been condensed with chloroacetanilide using a modification of the method of Dox and Houston[1] who used sodium acetate to condense chloroacetone and barbituric acid in alcohol–water solution. In our experiments it was found that sodium acetate alone would not effect condensation but that if potassium iodide were added also condensation proceeded with satisfactory yields as follows.



The following barbituric acids were prepared by this method: 5-ethyl-5-acetanilido-; 5-*n*-butyl-5-acetanilido-; 5-isobutyl-5-acetanilido-; 5-isoamyl-5-acetanilido-; and 5-allyl-5-acetanilido-. Their possible pharmacological activity will be tested and published elsewhere.

Attempts were made to condense chloroacetanilide with the sodium salts of various ethyl monoalkylmalonates in absolute alcohol solution to obtain malonic esters of the type



which might then have been condensed with urea to form the desired barbituric acids. These attempts failed as did the similar ones of Dox and Houston[1] in which they attempted to condense chloroacetone with alkylmalonic esters.

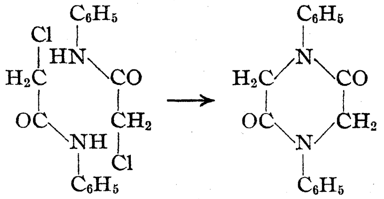
Experimental Part

Barbituric Acids Containing the Acetanilido Group.—One molecular proportion of the appropriate alkyl-barbituric acid was dissolved in 35% alcohol by gentle heating on a water-bath in a flask provided with a stirrer and a reflux condenser. An equimolecular proportion of chloroacetanilide,[2] a one and one-half molecular proportion of sodium acetate, and a quarter molecular proportion of potassium iodide were dissolved in warm 80% alcohol. The second solution was added slowly to the first and the mixture refluxed with stirring for seven hours. The desired product crystallized partially during the process of the reaction. The mixture was cooled in an ice-bath and the product filtered off. Partial evaporation of the filtrate yielded a second crop of crystals. The product in each case was recrystallized from 80% alcohol. All are colorless, crystalline solids which melt with decomposition. Physical and analytical data of these new compounds are summarized in Table I.

TABLE I

	Barbituric acid, 5-acetanilido-	Melting range, °C., with dec.	Yield, %	N Analyses, % Calcd.	Found	
1	5-Ethyl-	243–247	52	14.53	14.40	14.39
2	5-*n*-Butyl-	250–256	47	13.25	13.32	13.24
3	5-Isobutyl-	250–255	57	13.25	13.29	13.34
4	5-Isoamyl-	245–250	65	12.69	12.64	12.73
5	5-Allyl-	237–242	58	13.95	13.98	13.92

Attempt to Prepare Ethyl Acetanilidoethylmalonate.—When an equimolecular proportion of chloroacetanilide was warmed on a water-bath with the sodium salt of ethyl ethylmalonate until the absolute alcohol solution became neutral, condensation did not take place in the desired manner to form ethyl acetanilidoethylmalonate. A white solid separated which proved to be diphenyl-diketo-piperazine (m. p. 263°)[3] formed from the condensation of two molecules of chloroacetanilide:



The oily layer was extracted with ether; dried over sodium sulfate; the ether removed and the remaining oil distilled *in vacuo*. A colorless oil was obtained, b. p. 164° (9 mm.), which contained 7.24% of nitrogen. This could not have been ethyl acetanilidoethylmalonate whose nitrogen content is 4.36%. It might have been ethoxyacetanilide (N, 7.8%).

The author wishes to express his appreciation to Dr. Arthur J. Hill for his helpful suggestions during the progress of this work and to Mr. John B. Howard for his help in the analysis of these new compounds.

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[1] Dox and Houston, THIS JOURNAL, **46**, 252 (1924).

[2] Prepared by the method of Jacobs and Heidelberger, *J. Biol. Chem.*, **21**, 104 (1915).

[3] Abenius, *Ber.*, **21**, 1665 (1888).

Summary

The following 5,5-barbituric acid derivatives have been prepared: ethyl-acetanilido-, *n*-butyl-acetanilido-, isobutyl-acetanilido-, isoamyl-acetanilido- and allyl-acetanilido-.

NEW HAVEN, CONN. RECEIVED JULY 13, 1935

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Studies in the Ketone Sugar Series. V. The Validity of Hudson's Rules of Isorotation in the Ketose Group. Preparation of the True α-Pentaacetylfructose<2,6>

BY EUGENE PACSU AND FRANCIS B. CRAMER

Twenty years ago Hudson and Brauns[1] prepared a positively rotating pentaacetylfructose by acetylation of β-tetraacetylfructose<2,6> in the presence of zinc chloride. Since this pentaacetate was different from the β-pentaacetylfructose<2,6> obtained[2] from the same tetraacetate by using sulfuric acid with acetic anhydride for the acetylation, it was allocated to the α-series. Five years later Brauns[3] prepared from β-tetraacetylfructose<2,6> two chloroacetylfructoses, designating the one having specific rotation[4] -161 in chloroform as the α-, and the one having 45.3 in chloroform as the β-form. Subsequently, Brauns' allocations were reversed at the suggestion of Hudson,[5] the dextrorotatory compound becoming the α-, and the levorotatory the β-chloroacetylfructose. On the assumption that these two isomers constituted an α,β-pair with the same ring which is present in the parent β-tetraacetylfructose, Hudson[5] calculated the rotation of carbon 2 to be $a_{\text{Cl}} = 37{,}800$, and that of the acetylated basal chain common to them, comprising asymmetric carbon atoms 3,4 and 5, to be $b_{\text{fruct. ac.}} = -21{,}200$. The fact that the constant a_{Cl} was found to be the same both in sign and magnitude as $A_{\text{Cl}} = 37{,}900$[6] for the aldoses was regarded as evidence that the substitution of —CH_2OAc for —H does not change the rotation of carbon atom 2. This conclusion seemed to be confirmed by the additional fact that the values of a_{F} and a_{Br} in the ketose group also have been found to be practically equal to the corresponding values of A_{F} and A_{Br} for the aldose group. It appeared therefore, safe to assume that $a_{\text{Ac}} = A_{\text{Ac}} = 19{,}100$, which is the average value for the aldoses. However, combining $a_{\text{Ac}} = 19{,}100$ with the constant $b_{\text{fruct. ac.}} = -21{,}200$, the specific rotations for α-, and β-pentaacetylfructoses become -5 and $-103°$, respectively, in chloroform, whereas the two known pentaacetates of fructose show 34.7 and $-121.0°$, respectively. In view of this disagreement, Hudson concluded that "it seems very unlikely that the dextrorotatory pentaacetate can be the expected α-form." As to the other known pentaacetate, of specific rotation $-121.0°$, Hudson stated that "it may be the expected β-form, though the difference of 18° in specific rotation makes such a conclusion uncertain." However, it was recently proved[7] that neither "α-chloroacetylfructose" nor "α-pentaacetylfructose" possesses a ring structure in its molecule, but both of these "α"-isomers are derivatives of the open-chain fructose, the former being 1,3,4,5-tetraacetyl 6-chloro*keto*fructose, and the latter 1,3,4,5,6-pentaacetyl*keto*fructose. Consequently, all calculations and conclusions based on the assumption that either the two chloro acetates or the two pentaacetates of fructose constitute α,β-stereoisomeric pairs, are invalid. This discovery *ipso facto* invalidated the above inference that the values of the different A_{x} constants for the aldoses are equal to those of the corresponding a_{x} constants in the ketose group. It also reopened the problem of the validity of the principle of optical superposition in the ketose series for further investigation. In order to test this principle it is necessary to know the optical rotations of a true α,β-stereoisomeric pair of any ketose or ketose derivative. It is remarkable that in the ketose series, contrasting with the aldose, no such true, α,β-pair has hitherto been known with cer-

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(1) Hudson and Brauns, THIS JOURNAL, **37**, 2736 (1915).

(2) Hudson and Brauns, *ibid.*, **37**, 1283 (1915).

(3) Brauns, *ibid.*, **42**, 1846 (1920).

(4) Unless otherwise stated the rotations given are all for sodium light and 20°.

(5) Hudson, THIS JOURNAL, **46**, 477 (1924).

(6) The revised mean value of this constant is $A_{\text{Cl}} = 39{,}450$. It is obtained by using $A_{\text{Cl}} = 38{,}100$ found by Hudson and Kunz [THIS JOURNAL, **47**, 2052 (1925)] for chloroacetyllactose instead of the old value of $A_{\text{Cl}} = 30{,}300$ [Hudson, *ibid.*, **46**, 462 (1924)].

(7) Pacsu and Rich, *ibid.*, **54**, 1697 (1932); **55**, 3018 (1933).

tainty. To be sure, Schlubach and Schröter[8] prepared a crystalline methylfructoside tetraacetate, which they regarded as representing the α-isomeride of the known β-methylfructoside tetraacetate<2,6>. However, the allocation of their substance to the α-series was made on a premise that was shown in Part IV[9] of this series to be incorrect. It seemed, therefore, advisable to search for another α-derivative of fructose that might be used as a key substance to test the validity of the principle of optical superposition in the ketose group. Such a substance has now been provided by the discovery of the true α-pentaacetylfructose<2,6>. On replacement of the chlorine atom in β-acetochlorofructose<2,6> by an acetoxyl radical, no Walden inversion occurs on carbon atom 2, if the reaction be carried out in acetic anhydride solution with silver acetate.[10] The reaction product represents the pure β-pentaacetylfructose<2,6>. However, a partial Walden inversion does take place on carbon atom 2, if the same exchange reaction be carried out in boiling acetic anhydride solution with anhydrous sodium acetate. The mixture so obtained was found to consist of about 71% of the β-pentaacetate and 29% of the α-isomeride. After separation from the β-compound, the α-pentaacetylfructose<2,6> was isolated in pure, crystalline form; m. p. 122–123°; specific rotation 47.4° in chloroform. Using the molecular rotation of the β-pentaacetate ([M] −47,200) and the new acetate ([M] 18,500), the constants $a_{\text{Ac}} = 32{,}850$ and $b_{\text{fruct. ac.}} = -14{,}350$ were obtained from the two equations: $-47{,}200 = -a_{\text{Ac}} + b_{\text{fruct. ac.}}$ and $18{,}500 = +a_{\text{Ac}} + b_{\text{fruct. ac.}}$. It is seen that $a_{\text{Ac}} = 32{,}850$ for the ketoses is very much larger than $A_{\text{Ac}} = 19{,}100$ for the aldoses. Knowing the value of $b_{\text{fruct. ac.}}$, it is now possible to calculate the different a_{x} values for the ketoses, and the specific rotations of the α-isomerides from the corresponding β-derivatives. For instance, the value of a_{OMe} is calculated from the molecular rotation of the known β-methylfructoside tetraacetate<2,6> ([M] −45,200) to be $a_{\text{OMe}} = 45{,}200\text{–}14{,}350 = 30{,}850$. Hence, the specific rotation of α-methylfructoside tetraacetate<2,6> will be $(30{,}850 - 14{,}350)/362 = 45.5°$. Schlubach's crystalline tetraacetylmethylfructoside is recorded as having specific rotation 45.0° in chloroform. The excellent agreement between these two values indicates that Schlubach's compound is really the α-isomeride of the tetraacetyl-β-methylfructoside<2,6>. Fifteen years ago Brauns[11] prepared a crystalline β-ethylfructoside tetraacetate<2,6> from tetraacetyl-β-fructose-<2,6> by ethylation and reported for the pure substance m. p. 83° and specific rotation −127.6° in chloroform. From the molecular rotation ([M] −48,000) of this compound, and using the above constant of $b_{\text{fruct. ac.}} = -14{,}350$, the value of $a_{\text{OEt}} = 48{,}000 - 14{,}350 = 33{,}650$ is obtained. Hence, the specific rotation of the α-isomeride is calculated to be $(33{,}650 - 14{,}350)/376.2 = 51.3°$ in chloroform. In Part IV[9] of this series, there has been described a new crystalline ethylfructoside tetraacetate with m. p. 103–104°, and specific rotation 51.6° in chloroform. Here again, the agreement between the calculated and the observed value is excellent, and it supports the conclusion that the new fructoside represents the α-form of Brauns' β-ethylfructoside tetraacetate <2,6>.

In Table I there are shown the values of the different a_{x} constants for the ketoses calculated from the known β-derivatives of fructose, and the corresponding A_{x} values for the aldoses. It is seen that these constants, with the exception of a_{OH}, are throughout larger in the ketose than in the aldose series. Table I also shows the calculated specific rotations of the α-isomerides. The very satisfactory agreement between calculated and observed rotations in the case of methyl- and ethylfructoside tetraacetate leads to the conclusion that Hudson's rules of isorotation hold closely in the ketose series. It will be attempted to prepare some of the unknown α-derivatives from the new fructose pentaacetate.

Experimental Part

Preparation of α-Pentaacetylfructose <2,6>.—To a gently boiling mixture of 7 g. of anhydrous sodium acetate and 70 g. of freshly distilled acetic anhydride there was added 13.7 g. of β-acetochlorofructose<2,6> in one portion. A rapid reaction took place and sodium chloride precipitated. After thirty minutes of boiling, the solution was filtered from the sodium salts and the filtrate was concentrated *in vacuo* to a sirup which was mixed with 300 cc. of ice-cold water. The oily precipitate obtained soon turned into a crystalline solid (10.8 g.) which showed specific rotation −71.6° in chloroform solution. The filtrate was neutralized with solid sodium bicarbonate, extracted with chloroform, the chloroform layer dried with calcium chloride and evaporated *in vacuo* to a thick sirup. The ether solution of the latter soon deposited crystals at 0°;

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[8] Schlubach and Schröter, *Ber.*, **61**, 1216 (1928).

[9] Pacsu, THIS JOURNAL, **57**, 745 (1935).

[10] Pacsu and Rich, *ibid.*, **55**, 3023 (1933).

[11] Brauns, *ibid.*, **42**, 1846 (1920).

TABLE I

Comparison of the calculated a_x values for the ketoses with the corresponding A_x values for the aldoses; calculated and observed rotations of the α-isomerides of some β-fructose derivatives.

Substance	Mol. wt.	M. p., °C.	$[\alpha]_D$ in $CHCl_3$	Mol. rot. in $CHCl_3$	a_x for ketoses	A_x for aldoses	$[\alpha]_D$ of the α-isomers in $CHCl_3$ Calcd.	Obsd.
β-Tetraacetylmethylfructoside<2,6>	362	76	−125.0°	−45,200	a_{OMe} = 30,850	A_{OMe} = 26,900	+ 45.5°	+45.0°
β-Tetraacetylethylfructoside<2,6>	376.2	83	−127.6°	−48,000	a_{OEt} = 33,650	A_{OEt} = 29,100[a]	+ 51.3°	+51.6°
β-Acetofluorofructose<2,6>	350	112	− 90.0°	−31,500	a_F = 17,150	A_F = 9,800	+ 8.0°	Unknown
β-Acetochlorofructose<2,6>	367	83	−161.0°	−59,100	a_{Cl} = 44,750	A_{Cl} = 39,450[b]	+ 82.0°	Unknown
β-Acetobromofructose<2,6>	411	65	−189.0°	−77,700	a_{Br} = 63,350	A_{Br} = 60,000[c]	+119.2°	Unknown
β-Tetraacetylfructose<2,6>	348	132	− 91.6°	−31,900	a_{OH} = 17,750	A_{OH} = 20,700	+ 9.2°	Unknown
β-Pentaacetylfructose<2,6>	390	109	−121.0°	−47,200	a_{OAc} = 32,850	A_{OAc} = 19,100	......	+47.4°

[a] From α- and β-ethylglucoside tetraacetate [J. H. Ferguson, THIS JOURNAL, **54**, 4086 (1932)]. [b] See Footnote 6. [c] This revised mean value is obtained by using A_{Br} = 59,300 [Hudson and Kunz, *ibid.*, **47**, 2052 (1925)] for bromoacetyllactose instead of A_{Br} = 56,500 [Hudson, *ibid.*, **46**, 462 (1924) .

yield, 1.1 g.; specific rotation −110.0° in chloroform. Since pure β-pentaacetylfructose<2,6> has the value of −120.9° in chloroform, and the pure α-pentaacetate has later been found to show specific rotation 47.4° in chloroform, the first crop (10.8 g.) of the reaction product obtained consisted of about 28.8% (3.1 g.) of the α- and 71.2% (7.7 g.) of the β-pentaacetate. The isolation of the isomerides was accomplished by a rough mechanical separation followed by one recrystallization from alcohol. The mixture (10.8 g.) was dissolved at room temperature in 250 cc. of absolute ether, and the solution was kept undisturbed in the icebox for several days. During this time 4 g. of crystalline material separated consisting of large crystals of the β-pentaacetate and small crystals of different appearance of the α-isomeride. The large crystals were sorted out (2.6 g.) and showed specific rotation −111.3° in chloroform; the small prismatic crystals of the α-isomeride (1.4 g.) showed the value of 26.5° in the same solvent. After one recrystallization from 10 cc. of absolute alcohol, the latter substance had m. p. 122–123°, $[\alpha]^{20}{}_D$ 47.4°; $[\alpha]^{20}_{6563}$ 38.0°; $[\alpha]^{20}_{5463}$ 56.0°; $[\alpha]^{20}_{4861}$ 73.0° and $[\alpha]^{20}_{4358}$ 94.3° in chloroform (0.2774 g. of substance, 10 cc. of solution; 2-dm. semi-micro tube; rotations, 2.63, 2.11, 3.11, 4.05 and 5.23° to the right, respectively); yield, 1.1 g. Another recrystallization from alcohol and a final one from chloroform by addition of ether at 0° did not change the rotation or melting point. The new acetate is soluble in most organic solvents except petroleum ether and cold alcohol. It is fairly soluble in hot water. In an acetyl estimation 0.2228 g. of the substance required 28.5 cc. of 0.1 *N* sodium hydroxide solution. The value calculated for the hydrolysis of five acetyl groups is 28.5 cc. The titrated solution (56.5 cc.) which contained 0.1028 g. of *d*-fructose, rotated sodium light 0.67° to the left in a 4-dm. tube at 20°, corresponding to specific rotation −92.0°, which is the constant rotation of *d*-fructose in water solution.

Summary

1. The true α-pentaacetylfructose<2,6> with m. p. 122–123° and specific rotation 47.4° in chloroform has been prepared. By the aid of this key substance it has been possible to calculate the correct a_x values for the ketone sugar derivatives.

2. The different a_x values for the ketoses are, with the exception of a_{OH}, throughout larger than the corresponding A_x values for the aldoses.

3. From the a_x values, the specific rotations of several α-fructose derivatives have been calculated. The excellent agreement between calculated and observed values of the methylfructoside tetraacetate of Schlubach as well as the ethylfructoside tetraacetate of Pacsu leads to the conclusion that (a) both compounds belong to the α-series (b) Hudson's rules of isorotation hold closely in the ketose group.

PRINCETON, NEW JERSEY

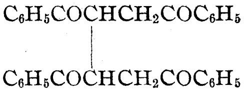
RECEIVED AUGUST 5, 1935

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

The Structures of the Dimolecular Reduction Products of Dibenzoylethylene

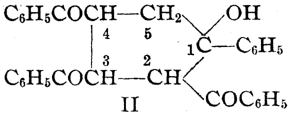
BY ROBERT E. LUTZ AND FRED S. PALMER

A dimolecular product has been obtained from the reduction of dibenzoylethylene (III) with the heterogeneous combination zinc and glacial acetic acid,[1] and further studies described in this and the two following papers have led to the isolation from the various reductions of a total of five isomers which are closely related structurally as is evident from the intertransformations described under Diagram 1. The results of our studies show that these five compounds are of two types. Two of them are *dl* and *meso* isomers of I and are designated for convenience as bis-dibenzoylethanes-A and -B. The other three appear to be cyclic internal ketols of these (II) and are named *cyclo*-bis-dibenzoylethanes-A, -B and -C.



$$\begin{array}{c} C_6H_5COCHCH_2COC_6H_5 \\ | \\ C_6H_5COCHCH_2COC_6H_5 \end{array}$$

I



II

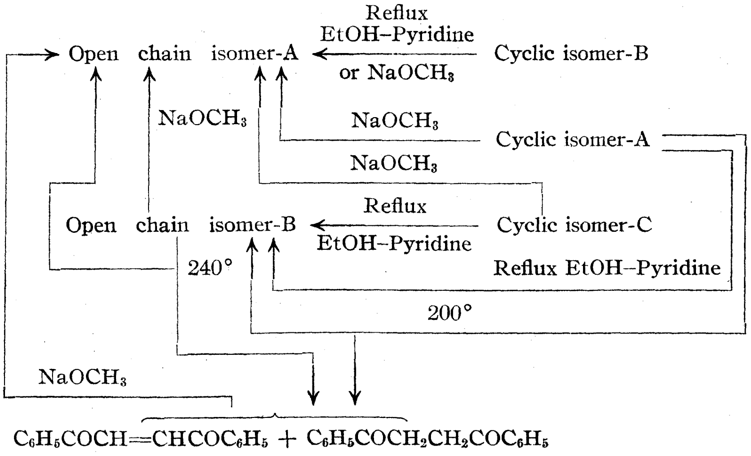


DIAGRAM 1.

All of these isomers are rearranged by sodium methylate into the open chain bis-dibenzoylethane-A which presumably separates from an equilibrium mixture through its exceeding insolubility in alcohol. In three of these transformations ring fission has taken place, presumably through reversal of an internal ketol condensation, and in at least two instances the configurations with respect to carbons 3 and 4 (formula II) have been reversed. The rearrangement of the cyclic isomers-A and -C into the open chain isomer-B may be accomplished also by refluxing in 85% ethanol containing pyridine; and the cyclic isomer-B under these conditions goes to the open chain isomer-A. The ring fissions in the latter cases, in contrast with those brought about with sodium alcoholate, take place without change in configuration, as is evident from the fact that both open chain stereoisomers are obtainable and are stable in boiling alcoholic pyridine. The open chain isomer-B is partly rearranged into the open chain isomer-A at 240° with some decomposition into dibenzoylethylene, dibenzoylethane and resinous materials; the open chain isomer-A slowly distils unchanged in the vacuum oven at this temperature. The cyclic isomers are unstable at temperatures above 200°; *cyclo*-bis-dibenzoylethane-A under these conditions is rearranged in excellent yield into the open chain isomer-B, accompanied by some decomposition giving small amounts of dibenzoylethylene and dibenzoylethane, III and IV.

It is very evident that the open chain isomers are the stable types and are formed easily by fission of the ring. The closure of the ring, however, has not been effected in any instance except during the actual formation of the dimolecular compounds in the reduction of dibenzoylethylene.

From the above facts it is clear that the configurations of the cyclic isomers-A and -C with respect to carbons 3 and 4 correspond to that of the open chain isomer-B, and the configuration of *cyclo*-B to that of the open chain isomer-A. The fact that, of the open chain isomers, A is the stable one (at 250°) and is the higher melting and the less soluble, suggests that possibly this is the *meso* form and that the isomer-B is *dl*,[2] and consequently that the cyclic isomer-B has the *cis* arrangement of

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[1] Lutz, THIS JOURNAL, **51**, 3008 (1929).

[2] *Cf.* the *dl*- and *meso*-dibenzoyldihalogenoethanes [Lutz, *ibid.*, **48**, 2905, 2916 (1926); **49**, 1106 (1927)] and the dihalogenosuccinic acids.

benzoyl groups on carbons 3 and 4, and -A and -C the *trans*.

All of the reactions and relationships described in Diagram 1 are consistent with the formulation of the dimolecular compounds either as open chain polyketones (I) or as cyclic internal ketols of these (II).

Dehydration either with acetic anhydride and sulfuric acid or with acetyl chloride was found to confirm the structures assigned above to the two types of dimolecular products. The open chain compounds, as diastereoisomeric bis-saturated 1,4-diketones, lose two molecules of water under these conditions and give one and the same bisfuran V whereas the cyclic isomers behave like β-hydroxy ketones and lose only one molecule of water, as would be expected from the formula II, to give the cyclic α,β-unsaturated ketone IX.

The dehydration of the open chain bis-dibenzoylethanes-A and -B is illustrated in Diagram 2. The structure of the product, bis-2,5-diphenylfuran V, is clear from the fact that upon oxidation with the nitric and glacial acetic acid reagent, a yellow compound is obtained which corresponds in analysis and properties with bis-dibenzoylethylene VI, and which is easily reduced by means of sodium hydrosulfite to bis-dibenzoylethane-A. The reactions involved are characteristic,[3] and constitute adequate evidence for the open chain formulation of the dimolecular compounds in question, particularly in view of the fact that the cyclic isomers behave consistently in a different sense.

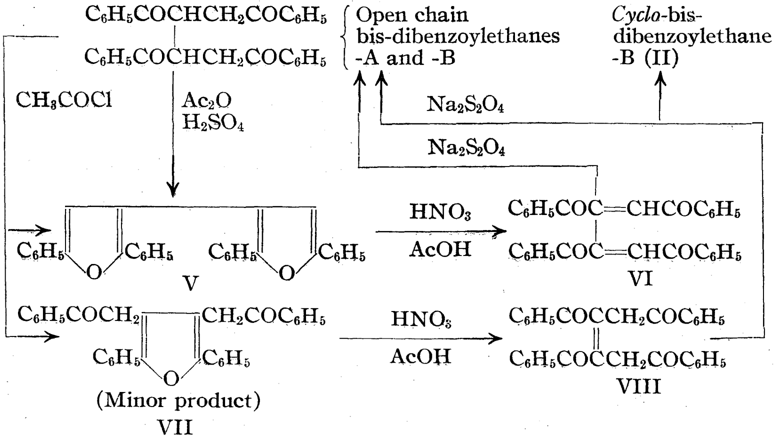

DIAGRAM 2.

A mono-dehydro compound, diphenacyldiphenylfuran (VII) theoretically could be formed also upon dehydration, since the open chain dimolecular compounds should be able to act also in the sense of the diphenacyl saturated 1,4-diketone. A search based on this consideration revealed such a product which was present in small amounts in the crude residues from the purification of the products of the dehydrations using acetyl chloride. This compound is oxidized by the nitric–glacial acetic acid reagent to a diphenacyldibenzoylethylene VIII (presumably the *cis* form), which in turn is reduced to a mixture of the dimolecular products by means of sodium hydrosulfite. These results are in complete accord with the various structures assigned in Diagram 2.

Bis-dibenzoylethane-A was synthesized by the direct condensation of dibenzoylethylene and dibenzoylethane by means of sodium methylate. This reaction (illustrated in Diagram 1) is analogous to the Michael condensation with α,β-unsaturated ketones and may be regarded as confirming the nature of the carbon chain in the dimolecular products. However, since all of the dimolecular compounds including the cyclic isomers are rearranged by means of sodium methylate into this same bis-dibenzoylethane-A, the reaction does not add further information concerning the isomerism. In connection with this reaction it is noteworthy that, whereas the condensation product is very stable and distils in high vacuum at 250°, the stereoisomeric bis-dibenzoylethane-B breaks down at this temperature, giving partly the more stable isomer-A (I) and also approximately equivalent amounts of dibenzoylethylene and dibenzoylethane, the products of a reversal of the Michael condensation.

The cyclic bis-dibenzoylethanes-A, -B and -C, in contrast with the open chain isomers, give on dehydration with acetic anhydride and sulfuric acid or with acetyl chloride only one product which is formed through the loss of one molecule of water and which is different from the diphenacylfuran obtained as described above. This characteristic reaction supports our formulation of the cyclic dimolecular compounds as substituted β-hydroxy ketones, and the dehydro compound as the cyclic

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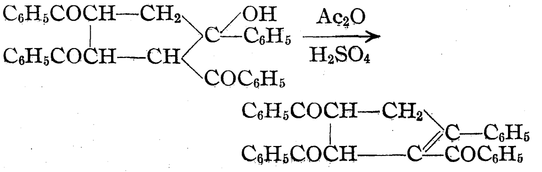
(3) *Cf.* Lutz and Wilder, THIS JOURNAL, **56**, 978 (1934).

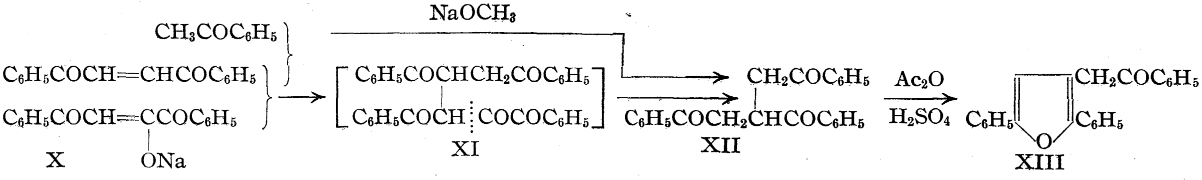
α,β-unsaturated ketone, 1-phenyl-2,3,4-tribenzoylcyclopentene, IX.[4] This hypothesis appears to be the only reasonable one available and is in complete accord with all of the facts.[5]



IX

Theoretically this dehydration product IX should exist in two diastereoisomeric forms, but only one has been obtained. Obviously in at least one instance reversal of configuration with respect to the groups about carbons 3 and 4 has occurred. The dehydro compound, unlike the true furans derived from I, does not react readily with the nitric–glacial acetic acid reagent under the usual conditions.

We had hoped through ozonization of this dehydro compound IX to accomplish fission of the ring and to obtain the pentaketone XI. We attempted to synthesize this pentaketone by the condensation of the sodium derivative of dibenzoylethenol and dibenzoylethylene. The reaction gave, however, tribenzoylpropane XII, a product clearly formed by hydrolytic cleavage of the desired and probably intermediate pentaketone. This hydrolytic product XII was synthesized also by the condensation of acetophenone and dibenzoylethylene, and its structure was confirmed by dehydration with acetic anhydride and sulfuric acid to the known phenacyldiphenylfuran XIII.[6]



X XI XII XIII

The ozonization of the cyclopentene IX did not proceed as expected, but nevertheless gave an ultimate result which was understandable and consistent with our formulation of the various compounds and reactions involved. The colorless compound obtained on hydrolysis of the noncrystalline product of ozonization proved to be a peroxide (XIV) from which the cyclopentene IX could be regenerated by gentle heating or by the action of potassium iodide, oxygen and iodine, respectively, being liberated. These reactions, particularly the latter, are typical of the peroxides of this type which are known.[7] Under the influence of sodium methylate the peroxide XIV is converted directly into tribenzoylpropane in small but significant yield; the reaction probably either involves rearrangement to the hypothetical pentaketone XI followed by hydrolytic fission, or proceeds through XV. The peroxide XIV when refluxed with 70% ethanol for twelve hours gave a new substance which according to analysis and molecular weight could be formed only through the loss of an atom of oxygen; this product must be the oxido compound of formula XV. The rearrangement with loss of oxygen of an α,β-peroxide to a β-diketone has been reported[8] but in the case in hand, since such a rearrangement is impossible without fission of the ring, it is not unreasonable to suppose that an oxide is formed. This compound under the influence of sodium methylate gives tribenzoylpropane XII in good yield. The reaction is accounted for in a reasonable way through a series of steps such as is illustrated in Diagram 3, namely, hydrolysis of the oxide system, ring fission involving a typical reversal of a ketol condensation (as in the change II $\xrightarrow{NaOCH_3}$ I), and hydrolytic splitting of the resulting product into tribenzoylpropane and phenylglyoxal (the latter would hardly be expected to be stable under the circumstances, and was not isolated).

While some of the steps in this degradation of the *cyclic* bis-dibenzoylethanes to tribenzoylpropane are not established with certainty, we believe nevertheless that the results constitute confirmatory evidence in support of the various structures assigned.

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(4) *Cf.* the internal condensation of the dimolecular reduction products of α,β-unsaturated ketones such as mesityl oxide, phorone, benzalacetone, and benzalacetophenone [Harries and Hübner, *Ann.*, **296**, 295 (1897); Harries and Eschenbach, *Ber.*, **29**, 2121 (1896); Conant and Cutter, THIS JOURNAL, **48**, 1016 (1926)].

(5) A hydroxydihydro-1,4-pyran formula for the cyclic dimolecular compounds is a possible but very improbable alternative to the cyclic ketol formulation because, while it might account for the stereoisomerism and some of the reactions, it involves a cyclic hemiacetal linkage between an enol hydroxyl and a carbonyl group, for which there is no analogy.

(6) Paal and Schulze, *Ber.*, **36**, 2435 (1903).

(7) *Cf.* Houben, "Die Methoden der organischen Chemie," Vol. III, 1923, p. 254; Reiche, "Alkylperoxide und Ozonide," 1931, p. 71.

(8) *Cf.* Ref. 6, p. 257.

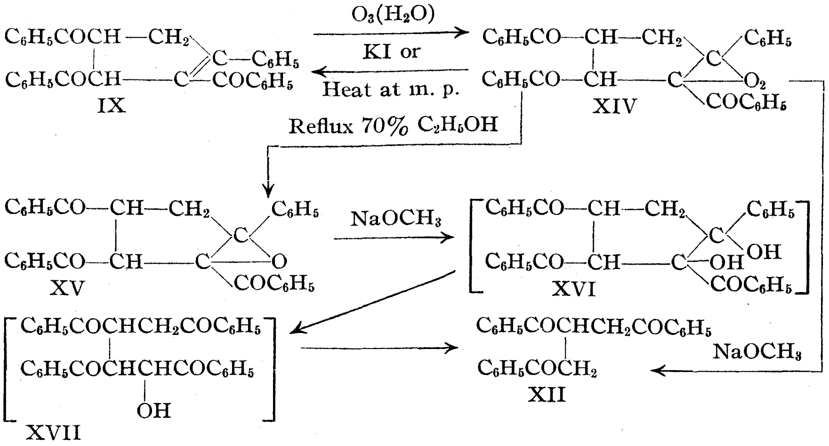

DIAGRAM 3.

Experimental Part

Bis-dibenzoylethane-A (1,6-diphenyl-3,4-dibenzoylhexanedione-1,6), I, is best prepared by the condensation of dibenzoylethane and dibenzoylethylene. A suspension of 2 g. of dibenzoylethane in 125 cc. of absolute ethanol was treated with a solution of 0.25 g. of sodium in 30 cc. of absolute ethanol, and the resulting mixture added with stirring over a period of three hours to a suspension of 2 g. of dibenzoylethylene in 100 cc. of absolute ethanol. The solids dissolved and a fine crystalline precipitate appeared. On standing for two hours, 2.5 g. of nearly pure product was obtained (yield 62%). It crystallized as short prisms from chloroform (adding a little petroleum ether) and from chlorobenzene; m. p. 202° (corr.). The method works equally well on a larger scale, and with methanol as the solvent. The compound is very difficultly soluble in hot ethanol (about 0.15 g. per 100 cc. at the boiling point), and acetone.

Anal. Calcd. for $C_{32}H_{26}O_4$: C, 81.01; H, 5.48. Found: C, 80.79; 80.66; H, 5.47; 5.69.

This isomer may also be prepared as follows: (a) 1 g. of *cyclo*-bis-dibenzoylethane-A was shaken with 100 cc. of absolute ethanol containing 0.4 g. of dissolved sodium. On standing for fifteen hours the crystalline precipitate was filtered from the red solution (0.2 g.), was recrystallized from chlorobenzene, and identified as bis-dibenzoylethane-A by mixed m. p. (b) A mixture of *cyclo*-bis-dibenzoylethane-B (0.01 g.) in 2 cc. of ethanol with 1 drop of pyridine was refluxed for twenty-four hours and deposited a cake of the characteristic granular crystals of the open chain bis-dibenzoylethane-A (identified by mixed m. p.).

This isomer is unaffected by fusion at 240–250° in the vacuum oven and distils slowly onto the cold finger condenser with a slight amount of decomposition. It is unaffected by prolonged refluxing in chlorobenzene or ethanol.

Bis-dibenzoylethane-B (1,6-diphenyl-3,4-dibenzoylbutanedione-1,6), I, is formed in small amounts in some of the reductions described in the following two papers, but it is difficult to isolate since it is the most soluble of the five dimolecular compounds. It is best prepared by rearrangement of *cyclo*-bis-dibenzoylethane-A in either of the following two ways: (a) a mixture of 5 g. of *cyclo*-bis-dibenzoylethane-A, 280 cc. of 85% ethanol, and 3.4 g. of pyridine was refluxed for twenty-four hours. On cooling and filtering 2.4 g. of nearly pure open chain isomer-B was obtained. A second crop was obtained from the filtrate (total yield 65–75%). (b) *Cyclo*-bis-dibenzoylethane-A was fused at 200° in the vacuum oven for one hour, giving a small amount of distillate which collected on the cold finger condenser (this was shown to be a mixture of approximately equal amounts of dibenzoylethane and dibenzoylethylene which were isolated and identified by mixed melting points). The fused mass, on crystallization from alcohol, proved to be nearly pure bis-dibenzoylethane-B. This isomer was obtained also as follows: 0.05 g. of *cyclo*-bis-dibenzoylethane-C was refluxed in 5 cc. of 95% ethanol with 4 drops of pyridine for twenty-one hours. On dilution with water 0.04 g. of nearly pure bis-dibenzoylethane-B was obtained and identified.

The compound crystallizes as characteristic thin square plates from ethanol; m. p. 168° (corr.).

Anal. Calcd. for $C_{32}H_{26}O_4$: C, 81.01; H, 5.48. Found: C, 80.84, 80.75; H, 5.49, 5.47.

The compound is not affected by long refluxing in ethanol.

Pyrolysis and distillation of 1 g. in the vacuum oven at 230–240° gave a distillate containing some bis-dibenzoylethane-A and considerable amounts of dibenzoylethane and dibenzoylethylene (identified by mixed melting points).

Rearrangement.—A solution of 0.07 g. in 5 cc. of methanol containing 0.05 g. of dissolved sodium, on standing for twenty-four hours, gave a crystalline deposit of the open chain isomer-A (0.05 g., identified by mixed m. p.).

3,3′-Bis-2,5-diphenylfuran, V.—Ten grams of bis-dibenzoylethane-A (or -B) was suspended in 50 cc. of acetic anhydride and 10–15 drops of concd. sulfuric acid. The resulting solution on standing for fifteen minutes was decomposed in ice water, giving 7.1 g. of nearly pure product which was crystallized from acetone; m. p. 195–196° (corr.).

Anal. Calcd. for $C_{32}H_{22}O_2$: C, 87.67; H, 5.02. Found: C, 87.57, 87.67; H, 5.08, 5.08.

One-gram samples of both isomers, I-A and I-B, on standing for eighteen hours in 50 cc. of acetyl chloride, with subsequent hydrolysis, gave mixtures consisting largely of the bis-diphenylfuran. The crude product was washed with hot alcohol, leaving the bis-furan as the residue; the washings contained the diphenacylfuran which is described below.

Bis-1,2-dibenzoylethylene (1,6-Diphenyl-3,4-dibenzoyl-2,4-hexadiene-1,6-dione), VI.—Ten grams of V was suspended in 75 cc. of glacial acetic acid and a solution of 5 cc. of concd. nitric acid in 25 cc. of glacial acetic acid was added slowly, the temperature maintained at 30–35°. The crystals went into solution and a yellow solid then separated. After ten minutes this was filtered; yield 6.3 g. of m. p. 205–210°. It was recrystallized from chloroform–acetone mixtures and from butanone; m. p. 214–218° (corr.).

Anal. Calcd. for $C_{32}H_{22}O_4$: C, 81.67; H, 4.72. Found: C, 81.61; H, 4.79.

Reduction of 0.5 g. with 3 g. of sodium hydrosulfite in 100 cc. of 70% ethanol (refluxing two hours) gave 0.24 g. of bis-dibenzoylethane-A (identified by mixed melting point). Catalytic reduction (platinum) in ethyl acetate was stopped when the reaction rate slowed down with the absorption of approximately one molecule of hydrogen, but gave largely non-crystalline products and a small yield of bis-dibenzoylethane-A. Zinc and glacial acetic acid reduction appeared to give two new products (*cf.* m. p. 160–165° and 199–200°) which have not yet been investigated.

2,5-Diphenyl-3,4-diphenacylfuran, VII.—The residue from evaporation of the alcohol washings from the main fractions in the above-described dehydration of the open chain bis-dibenzoylethanes with acetyl chloride, was fractionally crystallized from ethanol and gave a very small amount of the second product which melted at 164–165° (corr.).

Anal. Calcd. for $C_{32}H_{24}O_3$: C, 84.17; H, 5.31. Found: C, 84.10; H, 5.51.

(*Cis*)-1,2-diphenacyl-1,2-dibenzoylethylene (1,6-Diphenyl-3,4-dibenzoyl-3-hexene-1,6-dione) VIII.—A suspension of 0.1 g. of VII in 0.7 cc. of glacial acetic acid was treated with 0.05 cc. of concd. nitric acid in 0.25 cc. of glacial acetic acid. Immediate reaction at room temperature took place, a new crystalline product appearing. After standing ten minutes, cooling, and filtering, 0.085 g. of nearly pure product was obtained which, after several crystallizations from ethanol, melted at 183–184° (corr.).

Anal. Calcd. for $C_{32}H_{24}O_4$: C, 81.31; H, 5.12. Found: C, 81.19; H, 5.17.

Reduction of 0.016 g. with 2 g. of sodium hydrosulfite in 2 cc. of 70% ethanol (refluxing fifteen minutes) gave 0.015 g. of a mixture of bis-dibenzoylethanes melting at 182–183° which showed a mixed melting point depression with *cyclo*-bis-dibenzoylethane-C, but none with the cyclic isomer-B and the open chain isomer-A. The microscopic examination of the crystals indicated that the product is really the mixture of the latter two isomers as shown by the mixed melting points.

1-Phenyl-2,3,4-tribenzoylcyclopentene-1, IX.—Ten grams of *cyclo*-bis-dibenzoylethane-A was dissolved in 75 cc. of acetic anhydride at 90° and 8 drops of concd. sulfuric acid added, the mixture then being heated for twenty minutes at 90° and decomposed in ice water. On completion of hydrolysis the solid was precipitated nearly pure and was filtered and washed with water; yield 8.1 g. It crystallized from ethanol as large thin rhombic needles; m. p. 182° (corr.).

Anal. Calcd. for $C_{32}H_{24}O_3$: C, 84.17; H, 5.31. Found: C, 84.10, 84.09; H, 5.34, 5.31.

The 1-Phenyl-2,3,4-tribenzoylcyclopentene-1 Peroxide, XIV.—Ozonized oxygen was passed for four hours through a solution of 5 g. of IX in 30 cc. of dry chloroform. The solvent was then evaporated in a current of moist air and the residue allowed to stand in contact with water. The product was extracted with ether, and on concentrating a total of 3.5 g. of crystals was isolated; m. p. 115–118° (with effervescence). Recrystallization from chloroform–ether or ethyl acetate–ligroin mixtures gave the m. p. 132–133° (corr.) (with effervescence). Alcohol was not used for recrystallization since decomposition occurs in this solvent. Attempts to induce the oily ozonide to crystallize were unsuccessful, and digestion with water appeared necessary to obtain a crystalline product. Ozonization carried out in 80% glacial acetic acid gave directly the peroxide.

Anal. Calcd. for $C_{32}H_{24}O_5$: C, 78.66; H, 4.95. Found: C, 78.38; H, 4.88.

Pyrolysis of the peroxide by heating slowly to 140° gave a fused mass from which on crystallization from ethanol only IX was obtained (identified by mixed melting point). When pyrolysis was effected by sudden heating of the sample in an oil-bath at 140–150°, violent evolution of gas occurred with deposition of benzoic acid on the walls of the vessel. Crystallization of the residue from acetone gave a new substance of m. p. 217–219° (corr.) which gave the analysis, C, 82.52; H, 5.28; and molecular weight (Rast) 308, 291.

The action of potassium iodide in ethanol on the peroxide liberated free iodine and regenerated IX which was identified by mixed melting point.

Hydrolysis of 0.5 g. with 10 cc. of methanol containing 0.05 g. of dissolved sodium (standing twenty-four hours) gave a red solution from which 0.1 g. of tribenzoylpropane crystallized and was identified by mixed melting point.

1-Phenyl-2,3,4-tribenzoyl-1,2-epoxycyclopentane, XV.—Two grams of the peroxide XIV, on refluxing in 75 cc. of 70% ethanol for twelve hours, gave 1.35 g. of a new product which on repeated crystallization from butanone and from methanol (containing a little acetone) was obtained as thin rectangular scales of m. p. 117–119° (corr.) (a mixed melting point with the peroxide gave a sharp depression).

Anal. Calcd. for $C_{32}H_{24}O_4$: C, 81.31; H, 5.12; mol. wt. 472. Found: C, 81.48, 81.50; H, 5.35, 5.35; mol. wt. (freezing point in benzene), 450.

Hydrolysis of 0.5 g. in 10 cc. of methanol containing 0.05 g. of dissolved sodium (standing one week) gave a red solution from which 0.24 g. of solid crystallized. The product was washed with ethanol and identified by melting point (120–121°) and mixed melting point as tribenzoylpropane. From the filtrates 0.03 g. of benzoic acid was isolated.

Acetic anhydride containing concd. sulfuric acid reacts with the oxide to give a deep indigo-blue solution from which, even after refluxing, the oxide is recovered on hydrolysis.

Tribenzoylpropane (1,4-Diphenyl-2-phenacyl-1,4-butanedione), XII.—The structure of the true tribenzoylpropane is evident from the mode of formation and dehydration to the furan as described in the foregoing discussion.

The product obtained by the Friedel and Crafts reaction on tricarballylic acid chloride[9] (XVIII) and supposed without evidence to be tribenzoylpropane, is different from our compound the structure of which is certain

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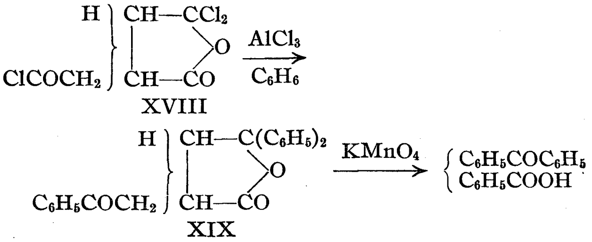
[9] Emery, *Ber.*, **24**, 601 (1891).

from the above data. Since it is an isomer, this product must be either α- or β-phenacyl-γ,γ-diphenylbutyro-γ-lactone (XIX), a structure which finds strong support from the following facts; with phenylhydrazine only a monophenylhydrazone is formed[6] and on oxidation with alkaline permanganate approximately equivalent amounts of benzophenone and benzoic acid are produced.



Tribenzoylpropane (1,4-Diphenyl-2-phenacyl-1,4-butanedione) XII.—Three grams each of dibenzoylethanol and dibenzoylethylene were added to a solution of 0.3 g. of sodium in 30 cc. of methanol. On standing for twenty-four hours the substances dissolved and new crystals deposited. On cooling 1.3 g. of product was obtained which after repeated crystallization from ethanol melted at 122° (corr.). When the equivalent amount of the sodium salt of dibenzoylethanol was substituted in the reaction for the free enol and sodium methylate, the yield was raised to 50–60%. A third procedure is as follows: 2 g. of dibenzoylethylene in 25 cc. of methanol and 1.8 g. of acetophenone was treated with 0.2 g. of sodium dissolved in methanol. After several hours 0.5 g. of tribenzoylpropane crystallized.

Anal. Calcd. for $C_{24}H_{20}O_3$: C, 80.86; H, 5.66. Found: C, 80.51, 80.84; H, 5.61, 5.66.

Conversion into the known 2,5-diphenyl-3-phenacylfuran XIII was accomplished as follows: 0.2 g. of XII was dissolved in hot acetic anhydride containing one drop of concd. sulfuric acid. On decomposition with water 0.15 g. of diphenylphenacylfuran crystallized (m. p. 115–116° after repeated crystallization from ethanol [Paal and Schulze[6] reported 113°]). This product when treated with 40% hydrazine hydrate gave the characteristic ketazine melting at 214–215° (*cf.* Ref. 5).

α- or β-Phenacyl-γ,γ-diphenylbutyro-γ-lactone, XIX, (the so-called tribenzoylpropane of Emery[9]) was prepared from tricarballylic acid chloride exactly as described by Emery[9] in a yield of 48% (the rest of the material was an intractable resin). It gave a sharp mixed melting point depression with the true tribenzoylpropane XII described above. Tricarballylic acid chloride is hydrolyzed by water on standing for several hours, the acid being regenerated. A sample of the lactone XIX was suspended in alkaline permanganate (excess) and the mixture distilled. Pure benzophenone was obtained in the steam distillate in a yield of 50%. A similar yield of benzoic acid was recovered from the residual mixture.

Summary

The intertransformations and relationships of the five isomeric dimolecular reduction products of dibenzoylethylene are described. Two are open chain compounds and three are cyclic internal ketols.

Evidence for the open chain structures involves dehydration to mono- and bis-furans, oxidation to the unsaturated 1,4-diketone types, and reduction again to the original compounds. One of the open chain isomers was synthesized by condensation of dibenzoylethylene and dibenzoylethane.

The dehydration of the cyclic isomers gives a cyclic α,β-unsaturated ketone which is degraded by ozonization, through a peroxide and an oxide to tribenzoylpropane which was synthesized by condensation of acetophenone and dibenzoylethylene. The interpretation of these reactions and the bearing on the problem of structure is considered.

The product of the Friedel–Crafts reaction on tricarballylic acid chloride is shown to be a phenacyl-γ,γ-diphenylbutyro-γ-lactone.

UNIVERSITY, VIRGINIA
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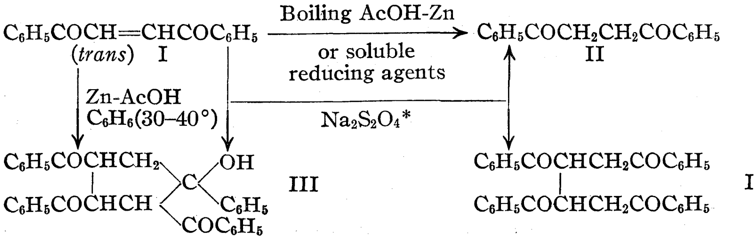
[Contribution from the Cobb Chemical Laboratory, University of Virginia]

The Reductions of Unsaturated 1,4-Diketones with Zinc Combinations. The Formation of the Cyclic Dimolecular Products

By Robert E. Lutz, Lowry Love, Jr., and Fred S. Palmer

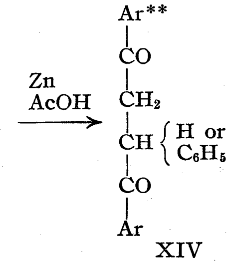
The reduction of unsaturated 1,4-diketones in homogeneous solution with soluble reducing agents leads exclusively to monomolecular products, the saturated 1,4-diketones or the corresponding furans. The mechanism undoubtedly involves initially the 1,6-addition of hydrogens or their equivalent at the oxygen atoms at the ends of the conjugated system, with oxidation–reduction potential a measure of the driving force in the reaction. The reduction with metal combinations, however, presents a more complex picture. *Trans*-dibenzoylethylene, which is reduced chiefly to dibenzoylethane (II) by zinc dust in hot glacial acetic acid, gives on slower reduction in the cold smaller amounts of II and very considerable yields of the dimolecular product, *cyclo*-bis-dibenzoylethane-A (III), the structure of which has been elucidated in the preceding paper. With zinc and benzene–glacial acetic acid mixtures at 30–35° (conditions most favorable to dimolecular reduction), there is produced largely the dimolecular product III and very little dibenzoylethane. In this type of reduction, therefore, dibenzoylethylene behaves to some extent like a simple α,β-unsaturated ketone.



* Special conditions (see experimental part).

Of the various unsaturated 1,4-diketones, *trans*-dibenzoylethylene is the one most prone to give dimolecular reduction products. Using zinc and glacial acetic acid at room temperature (typical conditions under which *trans*-dibenzoylethylene gives largely the dimolecular product) only monomolecular products are obtained from the following

V *Cis*-$C_6H_5COCH=CHCOC_6H_5$
VI *Cis*- and *trans*-$ClC_6H_4COCH=CHCOC_6H_4Cl$
VII *Trans*-$CH_3C_6H_4COCH=CHCOC_6H_4CH_3$
VIII *Trans*-$(CH_3)_3C_6H_2COCH=CHCOC_6H_2(CH_3)_3$
IX *Cis*-$C_6H_5COCBr=CBrCOC_6H_5$
X *Cis*-$C_6H_5COCH=C(C_6H_5)COC_6H_5$***
XI *Cis*-$C_6H_5COCBr=C(C_6H_5)COC_6H_5$
XII $C_6H_5COCH_2CHX$*COC_6H_5
XIII *dl*- or *meso*-C_6H_5COCHX*$CHXCOC_6H_5$



$$\mathrm{Ar^{**}\!-\!CO\!-\!CH_2\!-\!CH\{H\ or\ C_6H_5\}\!-\!CO\!-\!Ar}$$

XIV

*X = Cl or Br. **Ar = Corresponding aromatic group. *** Gave mainly the corresponding furan.

Other examples have been described in earlier papers.[1]

It is a striking fact that in reductions with zinc and glacial acetic acid at room temperature *trans*-dibenzoylethylene gives largely *cyclo*-bis-dibenzoylethane-A (III) whereas the *cis* isomer gives a nearly quantitative yield of the monomolecular product II (although other conditions were found under which the *cis* isomer also gave III in considerable amounts).

The Mechanism of Dimolecular Reduction.—The fact that *cyclo*-bis-dibenzoylethane-A is obtained under reducing conditions under which the open chain isomers are stable, definitely excludes the possibility that the ethylene linkage alone is involved, and indicates that a conjugate reaction occurs with cyclization taking place through the intermediate enolic groups. The results therefore furnish positive evidence for the generally accepted hypothesis that the reduction of α,β-unsaturated ketones by metal combinations involves a conjugate mechanism with the reaction beginning on oxygen.

The usual 1,4-dimolecular reduction mechanism might seem to find support from the fact that under comparable conditions the *trans* isomer in

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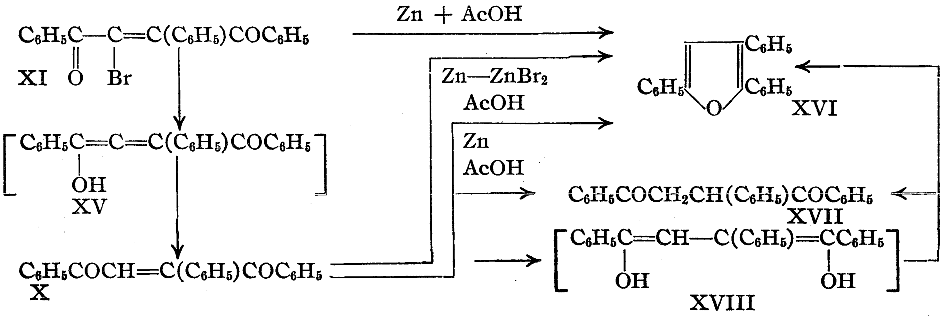
[1] (a) Lutz, This Journal, **51**, 3008 (1929); (b) Lutz and Taylor, *ibid.*, **55**, 1593 (1933); (c) Lutz and Wilder, *ibid.*, **56**, 2065 (1934).

contrast with the *cis* gives chiefly the dimolecular product, although both stereoisomers are reduced with comparable ease.[2] The stereochemical factor, however, may be without significance in view of the fact that *trans*-dibenzoylethylene with respect to tendency to undergo dimolecular reduction is unique among the unsaturated 1,4-diketones including *cis*-dibenzoylethylene. In consideration of this fact and in view of the known reactivity of enolic intermediates, an alternative and equally plausible mechanism is 1,6-reduction followed by condensation between the resulting enol or enolate and the reactive conjugated system of another molecule of unreacted dibenzoylethylene.

The zinc–glacial acetic acid reduction of dibenzoylphenylbromoethylene XI is of interest in connection with the catalytic effect of zinc bromide which is generated during the reduction.[3] The furan XVI is the chief product of this reaction. It is produced in much smaller yield in the reduction of dibenzoylphenylethylene X, but becomes the major product when zinc bromide is added to the reagents. The fact that dibenzoylphenylethane XVII and triphenylbromofuran are stable under the reaction conditions shows that the loss of bromine and the dehydrations to the furan XVI occur at some intermediate stage, and indicates that in both reductions there is formed in the final step the same intermediate dienol or dienolate (XVIII). The elimination of bromine from XI undoubtedly takes place through 1,4-reduction of the α-bromo ketone to the allenic enol or enolate XV.[4]



The zinc–acetone reductions of *dl*- and *meso*-dibenzoyldibromoethanes XIX are of interest because, in contrast with the dibenzoyldichloro- and monohalogeno-ethanes (XIII and XII), considerable yields of *cyclo*-bis-dibenzoylethane-A are obtained. *Trans*-dibenzoylethylene does not react under these conditions but does so when zinc bromide is added to the reagent, the products being the same as those obtained in the reduction of the dibromides where the zinc bromide is generated during the reaction.[5] Dibenzoylbromoethylene is not reducible by the Zn–ZnBr$_2$–acetone reagent. These facts suggest that the reduction of the dibromides under these conditions proceeds partly at least through elimination of bromine with the intermediate formation of dibenzoylethylene, followed by competing mono- and dimolecular reduction.

$$\underset{\text{XIX}\quad dl \text{ or } meso}{C_6H_5COCHBrCHBrCOC_6H_5} \longrightarrow \left[\underset{trans}{C_6H_5COCH{=}CHCOC_6H_5}\right] \longrightarrow \text{I} + \text{II}$$

This mechanism is consistent with the following facts: (a) the yield of *cyclo*-bis-dibenzoylethane-A is much higher in the reduction of dibenzoylethylene than in the case of the dibromides, as would be expected in view of the necessarily higher concentration of dibenzoylethylene during the reaction; (b) the monomolecular product predominates when *trans*-dibenzoylethylene is added slowly to the Zn–ZnBr$_2$–acetone mixture over a period of several hours so that the concentration during reaction is very low, thus simulating conditions involved in the reduction of the dibromides; and (c) dibenzoylbromoethane (XII) which could not

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(2) Conant and Lutz, THIS JOURNAL, **45**, 1047 (1923). In homogeneous solution where the configuration is without appreciable effect, both carbonyl groups of either *cis* or *trans* isomers are surrounded by reductant ions and may be supposed to react practically simultaneously. In the reduction of the *cis* compound by metal combinations, the spatially proximate carbonyl groups also should be able to react in quick succession or simultaneously at the metal surface, whereas the reaction with the *trans* compound, initiated at one carbonyl oxygen with the other spatially removed from the immediate source of hydrogen, could hardly be completed as easily and would afford the maximum opportunity for the dimolecular coupling to become a competing or even the dominant reaction.

(3) Lutz, Tyson, Sanders and Fink, THIS JOURNAL, **56**, 2679 (1934).

(4) Such a hypothesis has been suggested in an earlier paper (Refs. 1c, 3). *Cf.* the formation of the allenic halogenomagnesium enolate by the action of the Grignard reagent on α-bromo-β-phenylbenzalacetophenone [Kohler and Tishler, THIS JOURNAL, **57**, 217 (1935)], and also the reactions between the Grignard reagent or magnesium [Fisher, *ibid.*, **57**, 381 (1935)] and α-halogeno ketones.

(5) Probably the effective reducing agent is a Zn–ZnBr$_2$ combination analogous to the Mg–MgI$_2$ reagent of Gomberg and Bachmann [THIS JOURNAL, **49**, 237 (1927)].

form dibenzoylethylene or its equivalent in an intermediate step, does not undergo dimolecular reduction.

Cis-dibenzoylethylene in contrast with the *trans* isomer is reduced by the Zn–$ZnBr_2$–acetone reagent to a mixture in which the monomolecular product predominates. From this fact, if the mechanism of reduction of the *dl* and *meso* dibromides suggested above is correct, it would follow that the *trans* isomer and not the *cis* is involved as intermediate, and that the elimination of halogen from the *dl* and *meso* dibromides does not take place in a consistent stereochemical sense.[6]

Experimental Part

Separation of the mixtures obtained in reductions where the dimolecular products are formed is exceedingly difficult and involves laborious fractional crystallizations. Mixtures of dibenzoylethane and *cyclo*-bis-dibenzoylethane-A were usually partly separated by taking advantage of the higher solubility and higher rate of solution, and also the more rapid rate of crystallization (despite its greater solubility) of the monomolecular product. Such mixtures were usually digested for a very short time with boiling ethanol and filtered quickly; the residue consisted chiefly of the dimolecular compound, and the first fraction crystallizing quickly from solution was largely dibenzoylethane. The last fractions of crystals thrown out from the alcohol solution by dilution with water, on similar digestion with hot alcohol, at times yielded the cyclic dimolecular isomers -B and -C when these were present in small amounts. The following method was used in the separation of some of the mixtures resulting from the sodium hydrosulfite reductions. The crude product was precipitated by diluting the reaction mixture with water, the aqueous solution containing the bisulfite addition compound XIX being worked up as described separately below. This crude residue was digested for a short time with boiling ethanol. The insoluble residue was filtered off quickly, and digested with hot benzene, again leaving an insoluble residue consisting largely of *cyclo*-bis-dibenzoylethane-C (which was purified by recrystallization from chlorobenzene). The benzene filtrate gave a crystalline product which on fractionally crystallizing from benzene or chloroform gave a pure sample of *cyclo*-bis-dibenzoylethane-B. From the alcohol filtrate from the first digestion, a small crop of *cyclo*-bis-dibenzoylethanes-B and -C was obtained, and then a mixture of *cyclo*-bis-dibenzoylethane-A and dibenzoylethane. The latter mixture was separated by fractional crystallization from ethanol; or when small samples were involved, by the following procedure: the mixture was dissolved in boiling ethanol and allowed to crystallize quietly, long needles of dibenzoylethane forming first; when these appeared to be fully developed, the mixture was filtered suddenly, and immediately a granular crystalline precipitate formed in the filtrate (with a little luck and care, this separation may be semi-quantitative, and was so used in several instances).

Cyclo - bis - dibenzoylethane-A (1 - phenyl - 2,3,4 - tribenzoylcyclopentanol-1) III, is best obtained by the action of zinc dust on *trans*-dibenzoylethylene in 6–1 benzene–glacial acetic acid solution at 30–40°. It is best purified by repeated recrystallization from benzene, and is obtained as short prisms of m. p. 161° (corr.).

Anal. Calcd. for $C_{32}H_{26}O_4$: C, 80.95; H, 5.53; mol. wt., 474. Found: C, 80.60, 81.08, 80.95, 80.92; H, 5.76, 5.77, 5.59, 5.53; mol. wt., 483, 499, 460.

Both dibenzoylethane and the above dimolecular product III have been found to be stable under the various reducing conditions. The very considerable amounts of resinous by-products found in various of the reductions are therefore not due to secondary reactions.

Cyclo-bis-dibenzoylethane-B (1-phenyl-2,3,4-tribenzoylcyclopentanol-1) III, was obtained from the sodium hydrosulfite reductions described above. It crystallized as tufts of needles from benzene, chlorobenzene, or ethanol; m. p. 202–203° (corr.).

Anal. Calcd. for $C_{32}H_{26}O_4$: C, 81.01; H, 5.48. Found: (dried *in vacuo* at 120°) C, 80.36, 80.44; H, 5.51, 5.76.

A solution of 0.05 g. in 2.5 cc. of methanol containing 0.03 g. of dissolved sodium was allowed to stand for three hours and deposited 0.05 g. of bis-dibenzoylethane-A which was identified by mixed melting point.

A solution of 1 g. in 30 cc. of warm acetic anhydride containing one drop of concd. sulfuric acid was decomposed in water and gave considerable brown resin from which 0.4 g. of the dehydro compound (1-phenyl-2,3,4-tribenzoylcyclopentene-1) was isolated and identified by mixed melting point.

Cyclo - bis - dibenzoylethane-C (1 - phenyl - 2,3,4 - tribenzoylcyclopentanol-1) III, was obtained in only small amounts from the fractional crystallization of the products of reduction of dibenzoylethylene with sodium hydrosulfite or with the Zn–$ZnBr_2$–acetone combination. It crystallized from benzene, chlorobenzene, or large volumes of ethanol as square plates; m. p. 204–205° (corr.).

Anal. Calcd. for $C_{32}H_{26}O_4$: C, 81.01; H, 5.48. Found: C, 80.68; H, 5.64.

A solution of 0.1 g. in 5 cc. of ethanol containing 0.06 g. of dissolved sodium was allowed to stand for three hours and 0.06 g. of nearly pure bis-dibenzoylethane-A crystallized and was identified by mixed melting point.

Dehydration of 1 g. with 30 cc. of acetic anhydride and one drop of concd. sulfuric acid (warmed to solution) gave 0.92 g. of nearly pure dehydro compound of m. p. 179° (identified by mixed m. p.).

Sodium hydrosulfite reduction of dibenzoylethylene, carried out in 60–65% ethanol, produces almost exclusively monomolecular reduction. However, it was found that certain sam-

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[6] The elimination of bromine might perhaps be pictured as taking place stepwise, involving 1,4-reaction of the effective reducing agent with the α-bromo ketone system (*cf.* Ref. 4) rather than with the system Br–C–C–Br, since this would account for the failure of configuration to influence the reduction. The actual dimolecular coupling may take place according to the mechanisms described above or possibly through condensation of the intermediate dibenzoylethylene with unchanged dibromide or an enolate such as $C_6H_5COCHBrCH{=}C(OZnBr)C_6H_5$ (a 1,4-Reformatsky reaction).

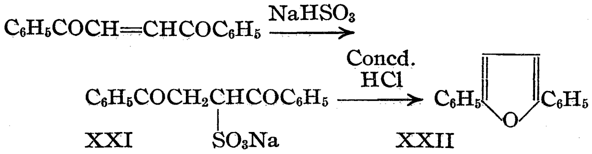
SOME TYPICAL REDUCTIONS OF UNSATURATED 1,4-DIKETONES

Subst., g.	Red. agent, g.	Conditions of the experiment	Yield of products, %		
			Mono-mol.[a]	*Cyclo*-[b] dimol.-A	Other[c] products
		Trans-Dibenzoylethylene—Reductions with Sodium Hydrosulfite			
1	1	60 cc. 90% EtOH, refluxed 1 hr.	N. q.[d]	. . .	. . . . . .
. .	. .[e]	90% EtOH$_3$ (several runs)	L[f]	S	S (II-B, II-C) 30–60% (XXI)
10	8	200 cc. 73% EtOH; 2 hrs. shaking at 25–30°	S	L	L (II-B, II-C); 45% (XXI)
1	1	60 cc. 90% EtOH; 4 hrs. shaking at 25–30°	L	. . .	S (II-B, II-C)
10	4	70 cc. 90% EtOH; $Na_2S_2O_4$ added slowly; 25–30°	vs.	vl	vs (II-B, II-C); S (XXI)
75	140[g]	300 cc. H_2O soln. of $Na_2S_2O_4$ added to boiling soln. of I in 800 cc. 95% EtOH	S[h]	. . .	L (XXI); 40% (IV-B)
		Trans-Dibenzoylethylene—Reductions with Zinc Dust			
10	40	200 cc. acetone; 4 g. $ZnBr_2$; 2 g. ZnO; reflux 8 hrs.	10–20	55–60[i]	
10	40	Subst. in acetone added over 2.5 hrs. to boiling acetone–Zn dust mixture +4 g. $ZnBr_2$ + 2 g. ZnO	L	. . .[j]	
2	10–20	Add Zn to boiling 25 cc. AcOH (duplicated)	N. q.	. . .	
5	10	Add Zn to boiling 100 cc. AcOH	68	26	
2	4	50 cc. AcOH; 2.5 hrs.; 25–30°	15	45	
2	4	10 cc. AcOH; 2.5 hrs.; 25–30°	30	50	
10	20	150 cc. C_6H_6, 25 cc. AcOH; 5–15°; Zn added slowly	. .	41[k]	
20	20	150 cc. C_6H_5; 5–15°; 50 cc. AcOH added slowly	. .	50[k]	
20	20	150 cc. C_6H_6 + 25 cc. AcOH; 5–30° (4 runs)	S	50–55[k]	
20	20	150 cc. C_6H_6 + 25 cc. AcOH; 30–40°	. .	70–88[k]	
20	20	150 cc. C_6H_6 + 25 cc. AcOH; 44–47°	S	60	
1	4	Add Zn slowly to boiling 12 cc. AcOH + 3 cc. Ac_2O	85	7	
		Cis-Dibenzoylethylene (V)			
2	4	10 cc. AcOH; 3 hrs. at 25–30°	95	tr	
2	2	10 cc. AcOH + 2 cc. C_6H_6; 10 hrs. at 25–30°	100	. .	
2	2	5 cc. AcOH + 15 cc. C_6H_6; 24 hrs. at 25–30°	18	80	
25	100	400 cc. acetone + 8 g. $ZnBr_2$ + 4 g. ZnO; reflux 7 hrs.	36	20	
		dl- and *meso*-dibenzoyldibromoethanes (XIX)			
. .	. .	AcOH (ordinary conditions)	N. q.	. .	
15	40	Acetone; refluxing 8 hrs. (both give identical yields)	45	50[l]	
. .	. .	Acetone cont. 10% EtOH; refluxing 8 hrs.	vl	. .	
		Dibenzoylchloroethane (XII)			
3	4	Acetone + 6 g. KI; reflux 1.5 hrs.	97		

[a] The corresponding saturated 1,4-diketone. [b] *Cyclo*-bis-dibenzoylethane-A. [c] The various products are indicated by symbol. The open chain bis-dibenzoylethanes = IV-A and -B and the cyclic isomers III-A, -B and -C; dibenzoylethane sulfonate = XXI. [d] N. q. = nearly quantitative. This was the case, however, only when good sodium hydrosulfite was used. [e] Using samples of sodium hydrosulfite which had been standing in the laboratory for several years and which had very evidently deteriorated and contained considerable amounts of $NaHSO_3$. [f] Due to the difficulty of separating the mixtures many of the yields were determined only roughly, and indicated by the symbols: L = large amounts, vl = very large, S and vs = small and very small, tr = trace. [g] Technical $Na_2S_2O_4$ used. [h] A considerable amount of unchanged material was recovered. [i] There was isolated also a 5% yield of II-C. [j] A considerable yield of a new compound of m. p. 248.5° (long thin rectangular scales from butanone) was isolated but has not yet been identified. It is probably not a simple dimolecular isomer since it is unaffected by boiling Ac_2O and H_2SO_4. [k] The product was nearly pure and the rest of the material resinous. [l] Traces of by-products were isolated from larger scale runs but not enough material was obtained for study.

ples of the reagent which had deteriorated gave considerable quantities of dimolecular products and of sodium bisulfite addition compound XXI. These results could be partially duplicated with the best grades of sodium hydrosulfite only under special conditions, namely, adding the solid reagent slowly to a 90% ethanol solution of dibenzoylethylene. Under these conditions there were produced large amounts of *cyclo*-bis-dibenzoylethane-A and smaller amounts of the cyclic isomers-B and -C, dibenzoylethane, and the sodium bisulfite addition compound. In one experiment when a concentrated aqueous solution of technical sodium hydrosulfite was added to a hot alcohol solution of dibenzoylethylene, the *open chain* bis-dibenzoylethane-B (IV) was obtained as the chief product; this is the only case aside from catalytic reduction where an open chain dimolecular product was formed in considerable amounts and isolated.

The sodium bisulfite addition compound XIX is a typical product of a 1,4-addition, and is formed nearly quantitatively when dibenzoylethylene is treated in 90% ethanol with sodium bisulfite. It is not easily hydrolyzed and is converted into diphenylfuran XXII by the action of boiling concd. hydrochloric acid.



The sulfonate was best prepared by allowing a mixture of 5 g. of *trans*-dibenzoylethylene, 4 g. of sodium bisulfite, and 110 cc. of 85% ethanol to stand for two hours. The solution was evaporated and the residue crystallized from ethanol: yield 84%; m. p. 255–262° (corr.). The analyses for S, C and H were unsatisfactory but approximated the values calculated for the formula XXI.

When refluxed for one hour with concd. hydrochloric acid, the sulfonate was converted into 2,5-diphenylfuran which was identified by mixed melting point with an authentic sample prepared by the action of acetic anhydride and a trace of concd. sulfuric acid on dibenzoylethane.[7]

Summary

The reduction of *trans*-dibenzoylethylene with zinc and acetic acid under varying conditions leads to the formation of dibenzoylethane and the cyclic dimolecular reduction product, *cyclo*-bis-dibenzoylethane-A, but *cis*-dibenzoylethylene gives largely, and other unsaturated 1,4-diketones exclusively, monomolecular products.

The formation of the cyclic dimolecular product is regarded as evidence for the conjugate mechanism.

The catalytic effect of zinc bromide in the reductions of dibenzoylphenylethylene and dibenzoylphenylbromoethylene is discussed, together with the probable mechanism.

The zinc–acetone reductions of the halogeno derivatives of dibenzoylethane are considered and a mechanism for the dimolecular reduction of the dibenzoyldibromoethanes is proposed.

Circumstances are described under which sodium hydrosulfite reduction of dibenzoylethylene gives large amounts of dimolecular products and sodium bisulfite addition compound.

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[7] *Cf.* Kapf and Paal, *Ber.*, **21**, 3057 (1888).

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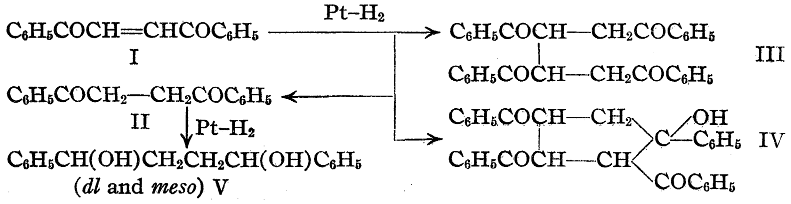
[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

The Catalytic Hydrogenation of Unsaturated 1,4-Diketones

BY ROBERT E. LUTZ AND FRED S. PALMER

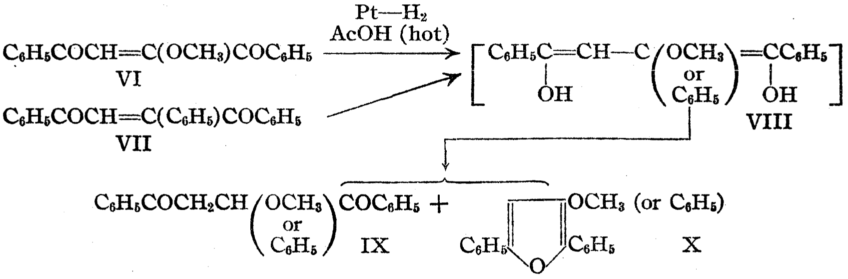
These studies were made in order to compare the catalytic hydrogenation of the unsaturated 1,4-diketones with reductions utilizing ordinary homogeneous and heterogeneous combinations. In the case of *trans*-dibenzoylethylene (Table I) chiefly the platinum catalyst was used with the following as solvents: methanol, 95% ethanol, dilute ethanol, acidified ethanol, glacial acetic acid, dioxane, ethyl acetate and decalin. With few exceptions there resulted mixtures of dibenzoylethane II and open chain and cyclic bis-dibenzoylethanes-A, III and IV, the relative yields varying considerably. Small yields of bis-dibenzoylethane-B also were obtained in many cases, but neither *cyclo*-bis-dibenzoylethane-B nor -C was isolated.



The yields of the difficultly soluble bis-dibenzoylethane-A, which crystallizes out during reaction, are probably fairly accurate as listed in the tables. However, the yields of the other products could be determined only approximately in many cases because of the difficulty of separating the mixtures and because there was undoubtedly some loss through further reduction. The primary stage of the reaction goes very rapidly, but the products are all reducible further slowly, as was shown in separate experiments, with the absorption of sufficient hydrogen to account for reduction of all of the carbonyl groups. The reductions listed in Table I were all stopped after the first and rapid phase of the reactions appeared to be complete, and involved usually the absorption of approximately 0.7–0.8 molecule of hydrogen. The dimolecular products upon further hydrogenation gave only non-crystalline products, but dibenzoylethane gave the two known stereoisomeric diphenylbutane-1,4-glycols V which were isolated in one experiment and identified. The material not accounted for in the tables was non-crystalline and was not identified.

When the rate of reduction is diminished through the use of smaller amounts of catalyst or lowered temperature, the *cyclic* dimolecular isomer-A (IV) predominates and very little of the open chain isomer III is formed. On the other hand, when the reaction proceeds very rapidly through the use of an excess of catalyst, the open chain isomer-A predominates and the yields of the monomolecular product and of the *cyclo*-bis-dibenzoylethane-A drop to a minimum. The total yield of dimolecular products, however, remains approximately constant.

In view of the effectiveness of small amounts of acid in promoting normal saturation of the alicyclic double bond in pseudocodeine,[1] two runs were made on dibenzoylethylene in alcohol with added hydrochloric or sulfuric acid. A striking increase in the yield of dibenzoylethane was observed (from 5–20 to 40%) and the yields of dimolecular products dropped almost to zero. Unfortunately the larger part of the product was non-crystalline and not identified, but the marked effect of the added acid on the course of the reduction was nevertheless unmistakable.



In glacial acetic acid the yield of the dimolecular product, *cyclo*-bis-dibenzoylethane-A, is consistently high (40–60%) regardless of the addition of ammonium chloride (to simulate conditions in the reduction of pseudocodeine hydrochloride) or of sodium acetate or hydrochloric acid. Only traces of the open chain bis-dibenzoylethane-A were found, together with bis-dibenzoylethane-B in yields varying from 5–20%. Considering all of the catalytic reductions undertaken, the yield of the normal reduction product, dibenzoylethane, reaches a minimum of 0–5% when glacial acetic acid–0.5% hydrochloric acid is the solvent. In all of the reductions in glacial acetic acid the main product is the same cyclic dimolecular isomer-A which is obtained in the zinc dust reductions under approximately similar solvent conditions.

It is noteworthy that reduction with platinum catalyst in dioxane as the solvent gives largely, and in ethyl acetate almost exclusively, monomolecular reduction. The use of Raney nickel catalyst in ethanol and in decalin also decidedly favors monomolecular reduction. In the inert solvents, then, the normal saturation of the ethylene double bond reaches a maximum.

It is a striking fact that *cis*-dibenzoylethylene, upon reduction under conditions wherein the *trans* isomer is converted chiefly into dimolecular products, gives largely the monomolecular product, dibenzoylethane, in 45–50% yields, together with about a 20% yield of a mixture of dimolecular products. This result finds a close parallel in the zinc–glacial acetic acid reduction where the *cis* isomer also shows a far greater reluctance to undergo dimolecular reduction than does the *trans* isomer.

In Table II is listed a series of experiments on various other unsaturated 1,4-diketones and related compounds. In every case the only crystalline products isolated were monomolecular, and no crystalline dimolecular products were found. Some dimolecular reduction may have occurred since in many cases considerable amounts of non-crystalline and unidentified by-products were formed. In any case the yields of monomolecular product were usually much greater than in the case of reduction of *trans*-dibenzoylethylene under comparable conditions. These results show dibenzoylethylene to be unique and the only compound of the series to undergo di-

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[1] Lutz and Small, THIS JOURNAL, **54**, 4715 (1932).

molecular reduction easily, a phenomenon already noted in the zinc–glacial acetic acid reductions.

The reduction of dibenzoylmethoxyethylene VI and of dibenzoylphenylethylene VII is of particular interest because furans are formed to a considerable extent, the conditions chosen being similar to those which lead to furan formation in zinc dust reductions.[2]

The mono and dibromo derivatives of both dibenzoylethylene and dibenzoylethane are reduced catalytically (using platinum) to dibenzoylethane without the formation in any case of appreciable amounts of the dimolecular products.

$$\left.\begin{array}{ll} \mathrm{C_6H_5COCH{=}CBrCOC_6H_5} & \mathrm{XI} \\ \mathrm{C_6H_5COCBr{=}CBrCOC_6H_5} & \mathrm{XII} \\ \mathrm{C_6H_5COCH_2CHBrCOC_6H_5} & \mathrm{XIII} \\ \mathrm{C_6H_5COCHBrCHBrCOC_6H_5} & \mathrm{XIV} \end{array}\right\} \xrightarrow[\mathrm{EtOH}]{\substack{\mathrm{Pt} \\ \mathrm{H_2}}} \begin{array}{l} \mathrm{COC_6H_5} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{COC_6H_5} \end{array}$$

Discussion of Results.—The formation of dimolecular products in catalytic hydrogenation was unexpected because, despite the many compounds that have been studied, this phenomenon has been observed in very few cases, namely, citral, dibenzalacetone, and certain α,β-unsaturated nitro compounds.[3]

A striking and significant parallelism exists between catalytic and zinc–acetic acid reductions of the unsaturated 1,4-diketones. The following facts are established in both types of reduction: (a) dimolecular reduction occurs to a very considerable extent with *trans*-dibenzoylethylene, (b) the same *cyclo*-bis-dibenzoylethane-A is obtained as the chief dimolecular product when glacial acetic acid is the solvent, (c) *cis*-dibenzoylethylene shows a far greater tendency to undergo normal saturation of the ethylene linkage than the *trans* isomer, (d) *trans*-dibenzoylethylene is the only unsaturated 1,4-diketone to give large yields of the dimolecular products under ordinary conditions, and (e) roughly the same degree of furan formation occurs during the reductions of VI and VII. It is quite likely therefore that the mechanism of the main course of catalytic and metal combination reductions of *these unsaturated 1,4-diketones* under conditions involved in the experiments covered by the above five points is similar.

The formation of the stable cyclic dimolecular compounds and furans during catalytic reduction in alcohol or in glacial acetic acid may be regarded as proof that in respect to the main course of these reactions a direct addition of hydrogen to the ethylene linkage does not occur but rather conjugate reactions involving one or both carbonyl groups, in the case of dibenzoylethylene giving enolic intermediates such as $\mathrm{C_6H_5}\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{C}}{=}\mathrm{CHCH}{=}\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{C}}\mathrm{C_6H_5}$ and $\mathrm{C_6H_5COCHCH{=}C(OH)C_6H_5}$, and in the cases of

$$\begin{array}{l} \mathrm{C_6H_5CO\underset{|}{C}HCH{=}C(OH)C_6H_5} \\ \mathrm{C_6H_5COCHCH{=}C(OH)C_6H_5} \end{array}$$

VI and VII leading to the results summarized in the diagram (*cf.* discussion of mechanism in the preceding paper). The conjugate mechanism for catalytic hydrogenations of α,β-unsaturated ketones, which has been assumed without proof,[4] is open to some question.[5] Our results constitute positive evidence for the existence of such a mechanism in some cases, but it is obviously far from certain that the phenomenon is general.

In this connection it is noteworthy that sorbic and muconic acids[6] to some extent undergo conjugate hydrogenation but it is uncertain as to whether or not the carbonyl oxygens are involved.

Pertinent to this discussion is the work of Conant and co-workers[7] on irreversible reductions. Soluble reducing reagents are regarded as acting through electron transfer, and catalytic hydrogen by addition of a hydrogen molecule, the latter occurring in cases where the hydrogen electrode potential is considerably above the "apparent reduction potential" (*i. e.*, the highest potential of reducing agents which will cause appreciable reduction in a reasonable time).[8] Catalytic reduction of dibenzoylethylene which has an "apparent reduction potential" above that of the hydrogen electrode, involves, as might have been predicted, a mechanism in which hydrogen or more likely electrons add to oxygen; however, dibenzoylphenylethylene, which on catalytic hydrogenation also undergoes conjugate addition involving the oxygens, has an "apparent reduction potential" which is very considerably below that of the hydrogen electrode.[8]

Catalytic hydrogen, while it may add at the ends of conjugated systems which include ter-

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(2) (a) Lutz, THIS JOURNAL, **51,** 3008 (1929); (b) Lutz and Taylor, *ibid.*, **55,** 1593 (1933).

(3) Skita, *Ber.*, **42,** 1634 (1909); Vavon, *Ann. chim.*, [9] **1,** 144 (1914); Borsche, *Ber.*, **45,** 46 (1912); A. M. Kinney, Dissertation, Harvard University, 1921; Sonn and Schellenberg, *Ber.*, **50,** 1513 (1917); Kohler and Drake, THIS JOURNAL, **45,** 1281 (1923).

(4) Straus and Grindel, *Ann.*, **439,** 276 (1924).

(5) *Cf.* Kern, Shriner and Adams, THIS JOURNAL, **47,** 1147 (1925).

(6) Farmer and Galley, *J. Chem. Soc.*, 430 (1932); Farmer and Hughes, *ibid.*, 304 (1934).

(7) *Cf.* Conant and Cutter, *J. Phys. Chem.*, **28,** 1096 (1924).

(8) *Cf.* Conant and Lutz, THIS JOURNAL, **45,** 1047 (1923).

minal oxygen atoms and does so to a considerable extent in the case of *trans*-dibenzoylethylene, probably does not involve the conjugate mechanism exclusively. Under some conditions, notably in the solvents ethyl acetate, dioxan, decalin or acidified ethanol, *trans*-dibenzoylethylene gives largely dibenzoylethane. Possibly the ethylene linkage in these cases reacts to a large degree directly with hydrogen. Pertinent to this point is the problem of the stereochemistry of addition which can be followed when completely substituted ethylenes are used as in the case of salts of dimethylmaleic and fumaric acids and the dimethylstilbenes.[9] Addition of hydrogen to the oxygens in the case of unsaturated 1,4-dicarbonyl compounds would undoubtedly destroy the stereoisomerism and no oriented addition would be possible; this appears to be the case for example in the zinc–acetic acid reduction of *cis* and *trans* di-(2,4,6-trimethylbenzoyl)-dimethylethylenes where identical products are obtained regardless of the configuration of the starting material.[2b] When consistent *cis* addition does occur it seems reasonable to suppose that only the ethylene linkage is involved, as is undoubtedly the case in the catalytic hydrogenation of the dimethylstilbenes.[3] In the reduction of the salts of dimethyl maleic and fumaric acids both 1,6 and 1,2 reductions are possible; slow catalytic hydrogenation favors stereochemical orientation, and probably therefore involves exclusively 1,2 addition to the ethylene linkage; but in the case of metal combinations leading to unoriented addition, the conjugate type of reduction undoubtedly predominates.[10] We had hoped to obtain evidence along this line by catalytic hydrogenation of the diaroyldimethylethylenes, $\mathrm{ArCOC(CH_3){=}C(CH_3)COAr}$; while zinc and acetic acid reductions have been successful,[2b] catalytic hydrogenations proceed very slowly and fail to give the expected and known crystalline primary reduction products.

Experimental Part

The various hydrogenations described in Tables I and II were carried out in the usual way. In the case of dibenzoylethylene in alcohol as solvent the material was partly in suspension at the beginning. Reduction with platinum catalyst proceeds very rapidly with absorption of from 10–50 cc. per minute in small runs of from 2–10 g. When the dibenzoylethylene is used up (evident from disappearance of the yellow color), the rate of absorption drops to 0.5–1.0 cc. per minute, at which point the absorption usually reached from 0.7–0.8 mole. The reaction ordinarily was stopped at this point to minimize the secondary stages of the reduction. Probably the oils and resins which comprise the residue of material not accounted for in the yields listed in the tables are partly the result of the secondary reductions involving one or more of the carbonyl groups of the various primary reduction products. In separate experiments it was shown that each of the dimolecular products slowly absorbs approximately 3–4 molecules of hydrogen under the usual conditions (platinum in alcohol), accounting for reduction of all of the carbonyl groups.

TABLE I

SOME TYPICAL CATALYTIC REDUCTIONS OF *TRANS*-DIBENZOYLETHYLENE AT 25–27° AND ATMOSPHERE PRESSURE

The material not accounted for was non-crystalline.

Pt oxide catalyst per g. subs., g.	Solvent per g. subs., g.	Solvent	Dibenzoylethane %	% Dimolecular Cyclo A	% Dimolecular Open chain A	% Dimolecular Open chain B
0.002–0.004	..	95% ethanol	15–25	35–45	5–15	5–15
.01	..	95% ethanol	15–20	15–20	30–40	trace
.02	..	95% ethanol	5–10	5–10	25–30	trace
.1	..	95% ethanol	...	...	30	...
.1	70	70% ethanol	5–15	25–30	25–30	5–15
.1	60	95% EtOH-3% H_2SO_4	40	...	...	...
.1	60	95% EtOH-1% HCl	40	...	...	...
.01	40	Glacial AcOH	15	40–45	trace	10–15
.01	35	AcOH-5% NH_4Cl	5–10	50–60	0–5	5–10
.01	35	AcOH-0.5% HCl	0–5	55–60	trace	10–15
.01	30	AcOH-2.7% NaOAc	15–20	40–45	trace	5–10
.08	75	Dioxane	55–60	...	...	trace
.05	30	Ethylacetate	90–95[a]	...	...	5–10
Ni[c]	25	95% ethanol	60–65	S[b]	S	S
Ni[c]	30	Decalin	75[a]	...	...	...

A few qualitative experiments which were not worked up adequately deserve mention. With platinum catalyst (1–100 g. of substance) in 95% ethanol at 0°, results were obtained similar to those found with smaller amounts of catalyst at ordinary temperature, largely *cyclo*-bis-dibenzoylethane-A being obtained with smaller amounts of the open chain isomer-A. When ethanolic sodium acetate was used as solvent at room temperature chiefly the open chain bis-dibenzoylethane-A was obtained and little else but resinous material. Substitution of the palladium on barium sulfate catalyst in a few instances was without significant effect on the course of reduction.

[a] In some runs considerable amounts of the dimolecular product was formed and correspondingly less of dibenzoylethane. [b] S = small amounts, possibly as high as 10–15%. [c] Raney catalyst.

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(9) Ott, *Ber.*, **61**, 2124 (1928).

(10) The unoriented addition of hydrogen in the metal combination reduction of the dimethylstilbenes may possibly involve one or both of the phenyl groups through conjugate addition with consequent destruction of stereoisomerism in the intermediate step.

Hydrogenation of dibenzoylethane using platinum catalyst in ethanol proceeded with absorption of 2 moles of hydrogen, giving an oil which on fractional crystallization was separated into the *dl*- and *meso*-diphenylbutane-1,4-glycols which were identified by mixed melting points with authentic samples prepared by the catalytic reduction of the acetylenic glycols.[11]

TABLE II

CATALYTIC REDUCTION OF SOME TYPICAL UNSATURATED 1,4-DIKETONES AND RELATED COMPOUNDS

Except as otherwise indicated these reductions were carried out at 25–27° and atmospheric pressure, using the platinum oxide catalyst (0.01–0.02 g. per g. of substance) in 95% ethanol as solvent (35–70 cc. per gram of substance).

Compound	Yield of monomolecular product, %
Cis-dibenzoylethylene	45–50[a]
Trans-dibenzoylmethylethylene	75
Cis-dibenzoylphenylethylene	62 (25[b])
Trans-di(2,4,6-trimethylbenzoyl)ethylene	86
Trans-di(4-chlorobenzoyl)ethylene	44
Trans-di(4-methylbenzoyl)ethylene	19
Dibenzoylmethoxyethylene	[c]
Cis-dibenzoylbromoethylene[d]	40
Cis-dibenzoyldibromoethylene[d]	84
Dibenzoylbromoethane[d]	68
dl-Dibenzoyldibromoethane[d]	44

[a] The rest of the material was accounted for as oils and small amounts of dimolecular products totaling 10–20% in yield. [b] This yield was obtained from an experiment carried out in glacial acetic acid at 100°, and triphenylfuran was obtained also in yields of 45–50%. Dibenzoylphenylethane is unaffected by these conditions and catalyst, and was recovered nearly quantitatively unchanged in a typical experiment. [c] This experiment, carried out in glacial acetic acid at 75–80°, gave largely the oily dibenzoylmethoxyethane (not identified) and a yield of 35–40% of diphenylmethoxyfuran (identified by mixed melting point with an authentic sample). [d] Palladium on barium sulfate as catalyst (0.1–0.15 g. per g. of substance).

Summary

The catalytic hydrogenation of *trans*-dibenzoylethylene under different conditions results in both mono- and dimolecular products, while other unsaturated 1,4-diketones, including *cis*-dibenzoylethylene and the halogen derivatives, undergo largely monomolecular reduction.

The striking parallelism between catalytic and zinc combination reductions is shown and is regarded as indicative of a common reaction mechanism.

The formation of furans and of cyclic dimolecular products is adduced as evidence that in these cases catalytic hydrogenation involves conjugate addition.

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[11] *Cf.* Zalkind and Isakowitch, *J. Russ. Phys.-Chem. Soc.*, **45**, 1902 (1913).

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[CONTRIBUTION FROM THE ABBOTT LABORATORIES, NORTH CHICAGO, ILLINOIS]

Sulfur-Containing Barbiturate Hypnotics

BY D. L. TABERN AND E. H. VOLWILER

Early in the history of barbituric acid synthesis, two or three simple 5,5-disubstituted 2-thio derivatives were made, with the aim of preparing from them by removal of the sulfur atom, the therapeutically promising oxygen analogs. Einhorn[1] and others studied the sulfur elimination through reduction, then oxidation and by the action of strong acids under pressure. They noted the comparative instability of the thiobarbiturate ring, reduction of the diethyl derivative by sodium amalgam, for instance, yielding chiefly the malonic diamide.

No serious attempt at pharmacologic evaluation seems to have been reported, and no study of higher homologs has been made as in the case of the simple barbituric analogs. Fischer and Mering[2] gave a 7-kilogram dog orally a dose of one gram of diethylthiobarbituric acid with the result that "one hour later he slept, did not react to any stimulation, and died after eight hours."

Dox and Hjort[3] have included mention of the same compound in a series of simple and N-alkyl barbiturates. They state that fine and coarse tremors mask the anesthesia which is characterized by preanesthetic excitement and cyanosis.

In spite of these unfavorable pharmacologic indications, the desire to secure hypnotics more readily broken down in the body for the production of short hypnosis and even surgical anesthesia, led to the decision several years ago to make a

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[1] Einhorn, *Ann.*, **359**, 145 (1908); see also German Patents 165,649, 166,266, 172,404, 182,764.

[2] Fischer and Mering, *Therapie der Gegenwart*, **44**, 100 (1903); Fränkel, "Arzneimittel Synthese," 6th ed., p. 510.

[3] Dox and Hjort, *J. Pharmacol.*, **31**, 455 (1927).

critical and systematic study of the higher alkyl substituted thiobarbiturates. The recent appearance of a note by Miller, Munch and Crossley[4] prompts the present publication of our earlier studies which have subsequently progressed to the stage of extensive clinical application.

Preliminary experiments demonstrated that not only could the desired compounds be synthesized by conventional methods in satisfactory yields, but that from the pharmacological and clinical side, certain members of the group were indeed powerful hypnotics of very brief action. In proper dosage, the results were frequently striking; following intravenous administration, sleep followed at once; surgical anesthesia ensued within five minutes; and not more than twenty minutes later the animal was again on its feet almost normal.

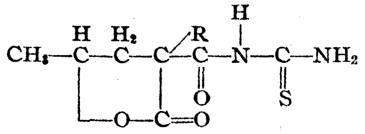
In general, the thio analogs of those disubstituted barbituric acids previously found most valuable as hypnotics, ranked highest in efficiency. Furthermore, certain thiobarbiturates were definitely more active as hypnotics than the oxygen analogs. Toxicities were not in general correspondingly higher, and it is possible to select several members of the series possessing very favorable ratios of effective to toxic doses.

The sulfur atom seemed to exert an additional influence in shortening the period of destruction within the body, and hence the duration of the hypnotic action.

Experimental

While the thiobarbituric acid derivatives may be prepared by several methods, we have found it convenient for experimental purposes to use the requisite malonic esters with somewhat more than the calculated amount of dry powdered thiourea in alcoholic sodium ethylate or its equivalent at 100–120°. Purification is best effected by dissolving in sodium hydroxide and reprecipitating by carbon dioxide followed by recrystallization from alcohol (75–90%). The pure acids are all somewhat yellowish solids that crystallize more readily than the oxygen analogs.

Johnson and Hill[5] have reported that under essentially these conditions, diallyl and benzyl allyl malonic esters yield open-chain compounds of the formula



We have repeated these experiments with much larger quantities of materials; our compounds melt somewhat higher, and both analyses and pharmacologic evaluations show that they *must be* only the normally expected thiobarbiturates.

The following example illustrates the method of preparation.

The Ethyl (1-Methylbutyl) Thiobarbituric Acid.—One hundred and thirty grams of ethyl (1-methylbutyl)-malonic ester is added to a concentrated solution of sodium ethylate prepared from 34 g. of sodium in absolute alcohol; with stirring, 60 g. of finely divided thiourea is added, and the mixture refluxed for ten hours. Most or all of the solvent is evaporated and the residual mass dissolved in cold water. The barbituric acid derivative so formed is precipitated by the addition of dilute hydrochloric acid. It may be purified by solution in dilute sodium hydroxide solution and precipitation by carbon dioxide.

Final purification is best carried out by solution in cold alcohol, heating to 50° and dilution with water to a 50% alcohol content. The ethyl (1-methylbutyl)-thiobarbituric acid so obtained is a white crystalline solid melting at 158–159° and readily forming salts with alkalies.

While the thiobarbiturates readily form stable salts, these are sometimes not easily obtained in the crystalline state. For instance, when ethyl isoamyl thiobarbituric acid in alcoholic solution is treated with one mole of alkali, the solution may be evaporated to dryness, leaving a glass which is rendered friable only by drying completely in a good vacuum.

In other instances, crystals were ultimately secured which permitted seeding of the concentrated alcoholic solutions and the separation of crystalline salts.

Such salts are hygroscopic and dissolve readily in water and alcohol to give strongly alkaline solutions. For instance, sodium ethyl (1-methylbutyl)-thiobarbiturate, in 2.5% solution, has a *p*H of approximately 10.4 to 10.6 (as determined by the glass electrode).

Another characteristic of the sodium salts is the avidity with which they hold solvents of crystallization (alcohols, chloroform, benzene, etc.) even on drying *in vacuo* at 80–100°.

Solutions of the sodium salts are rather unstable, being decomposed quite completely at the end of thirty-six hours at 60°. In the case of the ethyl *s*-butyl thiobarbituric acid, an alkali-insoluble compound, melting point about 100°, being probably the amide, was first secured; on the addition of acid, much carbon dioxide, but no hydrogen sulfide, was evolved and a compound, probably the acetyl urea, melting at 155–156°, was precipitated.

The calcium salts are best prepared by adding strong calcium chloride solution to a solution of the sodium salt in water. Mono and dialkylamine salts may be prepared

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(4) Miller, Munch and Crossley, *Science*, **81**, 615 (1935).

(5) Johnson and Hill, *Am. Chem. J.*, **46**, 356 (1911).

by dissolving the thiobarbituric acid in an excess of amine and removing the excess *in vacuo*. These salts are likewise readily soluble in water, but easily hydrolyzed.

The salts give intense green or brown solutions or precipitates with compounds of copper, iron, nickel, cobalt, etc. These appear to be analogous to the colored cobalt salts which Koppanyi[6] and others have employed for the colorimetric estimation of simple barbiturates. Here, however, the greater residual valence of the sulfur permits the use of aqueous rather than anhydrous media.

On attempting to prepare the N-(or S)-allyl derivatives by the method normally used for the synthesis of N-alkyl barbiturates, that is the reaction of allyl bromide with the sodium salts in aqueous or alcoholic solutions, unstable semi-solids gradually evolving allyl mercaptan were secured. Synthesis through the use of the N-alkyl thioureas is being studied.

The action of potassium permanganate on ethyl-(1-methylbutyl)-thiobarbituric acid in alkaline solution, yielded the oxygen analog (Nembutal); when an unsaturated group was present, however, extensive change of a still undetermined nature took place. Hydrogen peroxide in alkaline solution either left the acid unchanged or, if used in sufficient excess, led to poorly defined products. Freshly precipitated silver oxide formed a complex addition product soluble in sodium hydroxide, but insoluble in ammonium hydroxide, water, alcohol, and acids.

TABLE I

THIOBARBITURATES

	M. p., °C.	Nitrogen Calcd.	Found
Ethyl allyl	172–173	13.2	13.1
Ethyl isopropyl	192	13.1	12.76
Ethyl *n*-butyl	144–145	12.3	12.07
Ethyl *s*-butyl	163–165	12.3	12.4
Ethyl (2-methylallyl)	160–161	12.3	12.4
Ethyl isoamyl	167–169	11.6	11.52
Ethyl (1-methylbutyl)	158–159	11.6	11.7
Ethyl *n*-hexyl	136–137	10.9	11.1
Ethyl 2-ethylbutyl	137–138	10.9	10.8
Ethyl cyclohexyl	205–207	11.03	11.1
Ethyl phenyl	215–217	11.3	11.2
Methyl (2-methylallyl)	128–130	13.2	13.45
Diallyl	134	12.5	12.5
Allyl 2-methyl allyl	180–182	11.7	11.67
Allyl *s*-butyl	142–143	11.7	11.83
Allyl (1-methylbutyl)	127–129	11.0	11.04
Allyl benzyl	140–150	10.2	10.38
Ethyl (3-chloro-2-butenyl)	128–130	10.7	10.85

Pharmacologic

We are indebted to Mr. H. C. Spruth of the Pharmacologic Department, Abbott Laboratories, for the pharmacologic investigation of the thiobarbiturates, which will be reported in detail elsewhere. It is of interest, however, to record here preliminary data regarding certain of the most promising compounds. Intravenous injection into rabbits has been found to be the method of choice because it is thus possible to evaluate not only the effective and toxic doses, but also gain some information regarding relative depths of depression and sleeping times. The latter point is important since for compounds designed for the production of brief surgical anesthesia the sleeping time must be as brief as is consistent with proper depth of hypnosis and recovery must be rapid.

TABLE II

THIOBARBITURATES

	Minimum effective dose mg./kg.	Minimum lethal dose, mg./kg.	Sleeping time min. mg./kg.
Diethyl	75	>200	64 at 100
Ethyl isopropyl	30	80–100	97 at 40
Ethyl *n*-butyl	20	90–100	22 at 40
Ethyl *s*-butyl	15	>50	15 at 25
Ethyl (2-methylallyl)	30		
Ethyl isoamyl	30	55–60	78 at 40
Ethyl (1-methylbutyl)	10	35–40	14 at 20
Ethyl (2-ethylbutyl)	10	40	
Diallyl	30	>125	
Allyl (2-methylallyl)	20		
Allyl *s*-butyl	10	50	13 at 20
Ethyl (3-chloro-2-butenyl)	Convulsions 20 mg./kg.		

It will be seen that several of the compounds indicated fulfil to a considerable degree the properties desired. In clinical experience they have also proved of practical value.

Summary

A series of disubstituted thiobarbituric acids has been synthesized and characterized. Several of these compounds are powerful hypnotics. When injected intravenously into animals, they produce very prompt sleep, from which the animals recover rapidly. The sulfur in these compounds appears to accelerate their destruction in the body.

NORTH CHICAGO, ILLINOIS

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(6) Koppanyi, *J. Am. Pharm. Assoc.*, **23**, 1074 (1934).

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

Studies in the Physical Chemistry of Betaines and Related Substances. I. Studies of Dielectric Constants and Apparent Molal Volume[1]

BY JOHN T. EDSALL AND JEFFRIES WYMAN, JR.

Introduction

The betaines and the amino acids occupy a distinctive place among organic substances. Both these classes of compounds are distinguished by their unusually high melting points, by their high solubility in water and insolubility in truly nonpolar solvents, and by the fact that in all cases their solutions have a dielectric constant greater than that of the solvent. All these properties find a natural explanation in terms of their structure as zwitterions.

In additon to these general resemblances, however, there are certain notable differences between the two classes of compounds. Instead of the $—^+NH_3$ group found in the amino acids, the betaines contain the group $—^+NR_1R_2R_3$, where the R's may be almost any organic radicals, but are generally methyl groups. This structure greatly increases both the volume and the basic strength of the nitrogenous radical, and results in important modifications in the properties of the molecules. Moreover, the betaines, unlike the amino acids, are soluble not only in water but in alcohol and in mixtures of alcohol with ether or benzene. Furthermore, their dissociation constants and other properties indicate that they remain as zwitterions, and do not pass over to the uncharged form, in all of these solvents. This has made possible the present study of their dielectric behavior in solvents both of very high and very low dielectric constant, which reveals certain new relationships between the dielectric effect of zwitterions and the properties of the solvent. One highly polar molecule closely related to the betaines, N-dimethylanthranilic acid, is very soluble in pure benzene, and its dipole moment in this solvent has been directly determined, as well as its dielectric increment in other solvents, and its dissociation constants.

Moreover, in the case of the betaines, in distinction from the amino acids, it is possible to obtain in pure form the uncharged molecule corresponding to a given zwitterion. Thus, to a betaine of the type $(CH_3)_3{}^+NRCOO^-$, there corresponds the uncharged ester $(CH_3)_2NRCOOCH_3$. We have made an experimental study of one such pair, namely, ortho benz betaine and its isomer, dimethylanthranilic acid methyl ester. The striking contrasts found between them throw considerable light on the relation of the electric charges to the properties of the molecule.

In one important class of these substances, namely, the benz betaines, the electric charges on the zwitterion are closely attached to the benzene ring. Owing to the rigid nature of this structure the moments of these compounds can then be calculated with greater reliability than has hitherto been possible in other cases, and considered in relation to their dielectric effects in polar solvents.

Zwitterions, like ions, produce electrostriction of the solvent, an effect which in theory should decrease as the radius of the charged group or ion increases. The increase in bulk of the charged nitrogenous group in the betaines as compared with amino acids should therefore lead to a decrease of electrostriction, and our density measurements confirm this conclusion. The electrostriction due to the betaines becomes much greater in media of low dielectric constant than in water. A fairly extensive study of this phenomenon has been carried out, and the results obtained are in general accord with theoretical expectations.

Preparation of Materials

Betaine [N-Trimethylglycine, $(CH_3)_3N^+CH_2COO^-$] was obtained from a pure sample of betaine hydrochloride (Eastman Kodak Co.) by the action of silver oxide, recrystallized four times from absolute alcohol by gradual addition of anhydrous ether, and dried forty-eight hours in a vacuum desiccator over phosphorus pentoxide; m. p. 293°.[2]

Other betaines described below were liberated from their halogen salts and purified by the same method.

Pyridine Betaine [$C_5H_5N^+CH_2COO^-$].—The hydrochloride was prepared by heating pyridine with chloroacetic acid.[3] Heating for five hours at about 60° gave a purer product than a shorter heating at a higher tempera-

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[1] A preliminary account of part of this work was published in *J. Biol. Chem.*, **105**, Proc. XXIV (1934).

[2] Willstätter, *Ber.*, **35**, 584 (1902).

[3] E. von Gerichten, *ibid.*, **15**, 1251 (1882).

ture. The hydrochloride was dissolved in alcohol and crystallized by addition of ether. The free betaine was liberated and purified as described above. Its behavior on heating was exactly as described by von Gerichten.

Dimethylphenyl Betaine [$C_6H_5(CH_3)_2N^+CH_2COO^-$].—The hydrochloride was prepared by heating dimethylaniline with chloroacetic acid.[4] The reaction proceeded much more slowly than for pyridine betaine: twelve to eighteen hours heating on the water-bath was required, and the yield even then was less good than for pyridine betaine. A considerable amount of an impurity with a deep blue color was present, which went into solution with the free betaine when the latter was liberated from the hydrochloride. The impurity, like the betaine, was soluble in water and alcohol and insoluble in ether; but it proved to be soluble in acetone, or in a mixture of 90% acetone and 10% alcohol, in which the betaine is insoluble, and the two substances were separated by this means. The purified betaine melted at 124–126° (in agreement with Willstätter and Kahn).

Dimethylanthranilic Acid Methyl Ester [ortho $(CH_3)_2N$-$C_6H_4COOCH_3$].—To a solution of 340 g. of anthranilic acid (2.5 moles) in 500 cc. of water containing just enough potassium hydroxide to allow a faintly alkaline solution, 1600 g. (12.7 moles) of dimethyl sulfate is added, with stirring, during two and a half hours; 40% potassium hydroxide is added simultaneously at such a rate as to maintain a faintly alkaline reaction. The temperature is held at about 10° during the addition of the first half; it is then gradually raised to 65°. The resulting oily ester is taken up in ether, dried over calcium chloride, and distilled under reduced pressure. The yield was 150 g. (33% of the theoretical amount); b. p. 139° at 16 mm.

Dr. W. D. Peterson, who developed this method in Professor E. P. Kohler's laboratory, obtained in one preparation a yield as high as 75%, using smaller quantities of material than those above given.

Dimethylanthranilic acid [ortho$(CH_3)_2NC_6H_4COOH$] was obtained almost quantitatively by heating its methyl ester with excess of water for eight hours in a reflux condenser.[5] It was purified by recrystallization from ether and melted at 68°.

Ortho Benz Betaine [$(CH_3)_3N^+C_6H_4COO^-$].—Methyl iodide was added to dimethylanthranilic acid methyl ester (1.5 moles of iodide per mole of ester) and the solution left to stand. The iodide of the methyl ester of ortho benz betaine slowly crystallized out. The yield after one week in the cold was 15–20%, in agreement with Willstätter and Kahn. A large additional yield was obtained when the reacting mixture was allowed to stand for several weeks longer.

The iodide of the betaine ester, after crystallization from alcohol, was treated with silver oxide, whereby the free betaine is liberated. Subsequent purification as described above; m. p. 223–224°.

Meta Benz Betaine.—The iodide was prepared from meta aminobenzoic acid and three moles of methyl iodide, following the method of Griess[6] as modified by Cumming,[7] and the free betaine liberated and purified as described above (m. p. 236–238°).

The betaine was also prepared by the action of dimethyl sulfate (4 moles) on *m*-aminobenzoic acid. When the reaction was complete, most of the salt in the system was precipitated by addition of alcohol; the filtrate was concentrated *in vacuo* until nearly all alcohol was removed; the betaine was then precipitated as the triiodide by addition of iodine dissolved in hydriodic acid. The triiodide was converted to the iodide, as described by Willstätter and Kahn for the triiodide of *p*-benz betaine.

Para Benz Betaine.[4,8]—The iodide was prepared from para aminobenzoic acid and methyl iodide, by essentially the same procedure as the meta compound. The melting point of the free betaine was 252–255°.

Methods and Experimental Results

Dielectric Constant.—The dielectric constant of solutions of the betaines and related compounds in various solvents was determined by a resonance method previously developed.[9] Measurements were made at 25°, at a variety of wave lengths between 3 and 26 meters. In no case was there any indication of variation of dielectric constant with frequency in this range. The settings were least sharp, indicating relatively greatest absorption, for solutions in alcohol and solvents containing a large proportion of alcohol. In all cases, excepting a few involving solvents of relatively low dielectric constant, the dielectric constant was found to be strictly linear in the concentration of solute in moles per liter, and the experimental results can be expressed in terms of a first degree equation involving the dielectric constant of the solvent ϵ_0 and the slope of the dielectric constant concentration curve δ. In the small number of cases where this was not so the deviation from linearity was generally slight and the limiting value of δ for infinite dilution could be estimated from a graph with considerable accuracy. In Table I the data in regard to dielectric constant are given on this basis in terms of ϵ_0 and δ. Cases in which the curves were not linear are marked with an asterisk and the limiting value of δ is followed by the value, enclosed in brackets, reckoned from the difference between the dielectric constant of the most concentrated solution and that of the solvent. In the right-hand column of Table I is given in each case the range of concentration studied. The contents of this table are shown graphically in Fig. 1.

Several of these substances have also been studied by Devoto, although only in aqueous

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[4] Reitzenstein, *Ann.*, **326**, 326 (1903); Willstätter and Kahn, *Ber.*, **37**, 401 (1904).

[5] Willstätter and Kahn, *ibid.*, **37**, 401 (1904).

[6] Griess, *ibid.*, **6**, 585 (1873).

[7] Cumming, *Proc. Roy. Soc.* (London), **78A**, 138 (1906–1907).

[8] Michael and Wing, *Am. Chem. J.*, **7**, 195 (1885).

[9] Wyman, *Phys. Rev.*, **35**, 623 (1930).

TABLE I

Substance	Solvent	ϵ_0	δ	Range of concentration
N-Dimethylanthranilic acid methyl ester	Benzene	2.275	+ 0.570 ± 0.002	0.18–0.39
	53.1% Benzene–ethanol	11.49	− 1.2 ± 0.1	.14–0.29
	Ethanol	24.50	− 4.21 ± 0.04	.15–0.25
	49.17% Ethanol–water	49.37	− 9.4 ± 0.1	.21–0.33
N-Dimethylanthranilic acid	*Benzene	2.273	+ 5.1 ± 0.1(5.55 ± 0.05)	.00038–0.43
	71.1% Benzene–ethanol	6.868	+10.7 ± 0.1	.12–0.17
	51.0% Benzene–ethanol	12.05	+12.1 ± 0.5	.049–0.12
	28.66% Benzene–ethanol	17.91	+11.2 ± 0.3	.026–0.16
	Ethanol	24.36	+10.3 ± 0.2	.041–0.23
	83.25% Ethanol–water	31.41	+14.9 ± 0.3	.080–0.12
	73.0% Ethanol–water	35.96	+16.2 ± 0.2	.14
	65.37% Ethanol–water	40.09	+16.5 ± 0.6	.055–0.13
	49.08% Ethanol–water	49.37	+16.2 ± 0.2	.082–0.16
	29.94% Ethanol–water	66.05	+13.6 ± 0.8	.048–0.12
	Water	78.54	+12.0 ± 0.3	.045–0.15
Betaine	89.95% Benzene–ethanol	3.205	+ 7.0 ± 0.7	.00089–0.0042
	*79.90% Benzene–ethanol	4.913	+12.5 ± 1.0 (8.9 ± 0.2)	.0016–0.017
	*68.9% Benzene–ethanol	7.427	+22 ± 2 (10.9 ± 0.1)	.0034–0.065
	*50.9% Benzene–ethanol	12.19	+19 ± 2 (13.5 ± 0.2)	.012–0.11
	*27.6% Benzene–ethanol	18.15	+17.3 ± 0.5 (16.0 ± 0.2)	.074–0.17
	*Ethanol	24.42	+19.3 ± 0.3 (17.1 ± 0.3)	.042–0.18
	44.3% Ethanol–water	52.29	+19.5 ± 0.2	.20–0.29
	Water	78.54	+18.2 ± 0.3	.034–0.16
Pyridine betaine	Water	78.54	+18.5 ± 0.2	.11–0.33
Ortho benz betaine	81.48% Benzene–ethanol	4.579	+10.7 ± 0.2	.020–0.046
	72.74% Benzene–ethanol	6.501	+13.1 ± 0.2	.039–0.077
	59.27% Benzene–ethanol	9.90	+17.0 ± 0.2	.054–0.11
	34.86% Benzene–ethanol	16.33	+20.3 ± 0.4	.054–0.12
	Ethanol	24.26	+22.4 ± 0.2	.17–0.40
	73.71% Ethanol–water	35.70	+23.6 ± 0.2	.12–0.24
	52.34% Ethanol–water	47.37	+23.2 ± 0.4	.10–0.22
	31.70% Ethanol–water	60.43	+21.3 ± 0.2	.082–0.20
	Water	78.54	+18.7 ± 0.2	.055–0.56
Meta benz betaine	90.11% Benzene–ethanol	3.191	+10.1 ± 0.5	.0015–0.0037
	83.2% Benzene–ethanol	4.234	+12.3 ± 1.0	.0065–0.017
	75.70% Benzene–ethanol	5.825	+24.2 ± 0.8	.012–0.048
	61.78% Benzene–ethanol	9.27	+40.5 ± 0.4	.042–0.073
	48.59% Benzene–ethanol	12.74	+47.9 ± 0.4	.048–0.089
	25.45% Benzene–ethanol	18.63	+54.0 ± 0.5	.057–0.30
	Ethanol	24.42	+52.3 ± 0.5	.062–0.094
	42.78% Ethanol–water	53.50	+57.2 ± 0.5	.062–0.089
	Water	78.54	+48.4 ± 0.4	.032–0.084
Para benz betaine	19.90% Benzene–ethanol	19.97	+83.4 ± 4.0	.00078–0.0031
	*Ethanol	24.41	+77.4 ± 2.5 (70.0 ± 0.7)	.0043–0.019
	67.80% Ethanol–water	38.71	+76.5 ± 0.7	.0054–0.023
	43.37% Ethanol–water	53.21	+76.1 ± 0.7	.021–0.039
	Water	78.54	+72.4 ± 0.7	.011–0.043

solution, and his δ values, which differ somewhat from ours, may be given for comparison: betaine, +25[10]; N-dimethylanthranilic acid, +16.7[11]; *o*-benz betaine, +20;[11] *m*-benz betaine, +58;[11] *p*-benz betaine, +68.[11]

Optical Polarizations

In the case of N-dimethylanthranilic acid and its methyl ester, values of the optical polarization were determined from measurements of the refractive index for sodium light made with a Pulfrich Zeiss refractometer. The index of refraction of the pure ester at 25° was found to be 1.55743 and the density was 1.0950. This gives a polarization of 52.69 cc. The polarization of the ester was also calculated from the index of refraction at 25° of a 0.3867 molar solution in

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[10] Devoto, *Gazz. chim. ital.*, **64**, 76 (1934).

[11] Devoto and Ardissone, *ibid.*, **64**, 371 (1934).

benzene and the value obtained was 52.3 cc.

The index of refraction of the pure acid, which melts at 68°, could not well be measured; the optical polarization was therefore calculated from measurements of the refractive index at 25° of aqueous solutions at three concentrations with the following results: 0.1631 molar, 45.9 cc.; 0.1295 molar, 46.4 cc.; 0.0925 molar, 45.6 cc. We may accept 45.9 cc. as a value correct to at least 1%.

Total Polarizations and Electric Moments

In the case of N-dimethylanthranilic acid and its ester it is possible on the basis of the foregoing data and that on the densities given in the following section to calculate the polarizations and electric moments in benzene. The results, extrapolated to infinite dilution, are as follows: for the acid, 879 cc. for the polarization and 6.31×10^{-18} e. s. u. for the moment; for the ester, 140 cc. for the polarization and 2.05×10^{-18} e. s. u. for the moment.

Densities and Apparent Molal Volumes

The density of N-dimethylanthranilic acid methyl ester, measured with a pycnometer at 25°, was found to be 1.0950. The densities of the solid *o*-, *m*-, and *p*-benz betaines were determined to an accuracy of about 0.2% by flotation in benzene–chloroform mixtures, in which they are insoluble, with the following results: *o*-benz betaine, 1.290; *m*-benz betaine, 1.299; *p*-benz betaine, 1.261.

The apparent molal volumes of the various substances studied were calculated in the usual way from the density of the solutions, together with the density of the solvents, measured with a pycnometer. Each substance was measured at two or three concentrations in each solvent studied (concentration of solute 1 to 4% by weight, generally from 2 to 3% by weight) and the apparent molal volumes listed in Table II are the averages of these individual determinations. There was no evidence of any significant change with concentration. The apparent molal volumes in water are probably reliable to within 1 cc. and the others to within 2 cc., except in the very volatile alcohol ether mixtures, where the error may be 4 or 5 cc.

Dissociation Constants of N-Dimethylanthranilic Acid and its Methyl Ester.—The dissociation constants were determined at 25° with the hydrogen electrode, using a bubbling electrode of the Simms type.[12] Before titration dimethylanthranilic acid methyl ester was converted into its hydrochloride (m. p. 145–146°, after recrystallization) which is readily soluble in water, and the hydrochloride was titrated with sodium hydroxide. The following values of the logarithmic dissociation constants (pK') were obtained (pK'_1 and pK'_2 refer to dimethylanthranilic acid, pK'_E to its methyl ester; concentration of substances titrated was 0.04 molar).

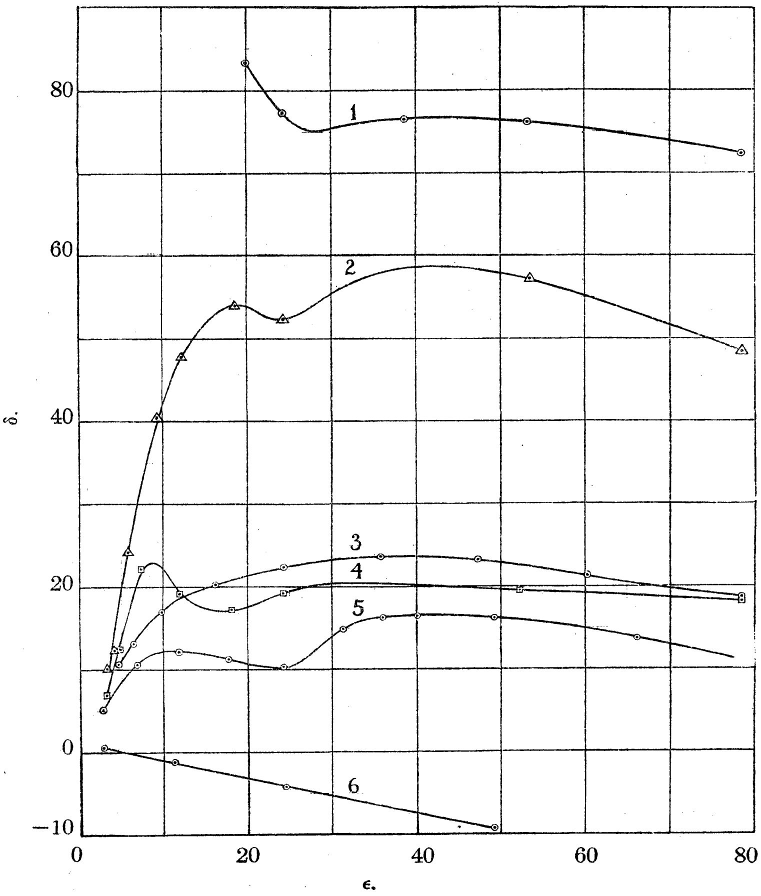

Fig. 1.—Dielectric increments in relation to dielectric constant of solvent: 1, *p*-benz betaine; 2, *m*-benz betaine; 3, *o*-benz betaine; 4, glycine betaine; 5, N-dimethylanthranilic acid; 6, N-dimethylanthranilic acid methyl ester.

The acidity of the solution in 90% ethanol was

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[12] For details of method and calculation of pK' see Edsall and Blanchard, THIS JOURNAL, **55**, 2337 (1933).

TABLE II

APPARENT MOLAL VOLUMES (CC.) IN VARIOUS SOLVENTS AT 25°

Solvent	Dielectric constant	Apparent molal volume: Betaine	Dimethyl phenyl betaine	Ortho benz betaine	Meta benz betaine	Para benz betaine	Dimethyl-anthranilic acid
Water	78.54	97.7	146.8	146.5	145	141.3	134.6
70% Water–30% alcohol	60					135	
50% Water–50% alcohol	47					133	134
25% Water–75% alcohol	34				133	130	
Absolute ethyl alcohol	24.3	91.9	133	133	124	119	132
70% Alcohol–30% ether	17.2	93.0	122	124			
55% Alcohol–45% ether	13.7			121			
50% Alcohol–50% benzene	12.5	89.0	137	134			
30% Alcohol–70% benzene	7.0		131	132			
Benzene	2.275						137.2

Dimethylanthranilic acid methyl ester: apparent molal volume in alcohol 159.0 cc.; in benzene 159.6 cc.

TABLE III

Solvent	pK_1'	pK_2'	pK_E'
Water	1.4	8.42	5.55
90% Ethanol		8.15	2.4

so great that pK_1' could not be exactly determined. It probably lies between 1 and 2. From the earlier measurements of Cumming[13] (in aqueous solution at 25°) we calculate pK_1' as 1.36, pK_2' as 8.64, and pK_E' as 3.70. This last value diverges greatly from our own. We believe our value to be the more reliable of the two, as it is based on seven different sets of e. m. f. measurements, in which the ratio of ester to ester hydrochloride was varied from 7:1 to 1:7. The values of pK' calculated from these measurements all lay within 0.06 of the value given in Table III. On the other hand Cumming (who employed a catalytic method) obtained shifting values which he himself regarded as not altogether reliable.

Discussion

Dielectric Constant.—In the case of polar solutions the interpretation of the dielectric constant offers a very difficult problem, at the present time lacking a theoretical solution from general principles. Certainly the Clausius–Mosotti relation is inapplicable and indeed yields results probably many times too small for the polarizations. On the other hand consideration of a variety of experimental results in the light of our knowledge of molecular structure suggests that the dielectric constant itself is in a general way proportional to the volume polarization. An attempted rationalization of the situation has been given by one of us[14] which leads to the result that in the case of polar liquids the Clausius–Mosotti relation for the volume polarization p in terms of the dielectric constant ϵ is to be replaced by the expression

$$p = (\epsilon - 1)/3 \qquad (1)$$

This expression would afford a ready explanation of the additive character of the dielectric constant so apparent in the case of polar solutions and of the close correlation between δ, the dielectric increment per mole of solute, and the polarization of the solute in substances for which there is a basis for estimating the polarization, notably the aliphatic amino acids which exist as zwitterions. Hitherto, however, there has always been a considerable degree of uncertainty in such estimates of the polarizations arising principally from the possibility of free rotation of the carbon atoms in the aliphatic chains, involving a change in the distance between the oppositely charged groups of the zwitterionic molecule.

In the benz betaines the groups bearing the positive and negative charges are attached to the relatively rigid benzene ring, and the separation of the charges, and consequently the moments and polarizations, can be reckoned with considerably less uncertainty. We may in fact calculate the separation of the charged groups in *o*-, *m*- and *p*-benz betaine, assuming the molecules to be undistorted, quite simply from models based on data from recent x-ray and electron diffraction studies.[15] In each the positive charge of the zwitterion is assumed to be located at the center of the nitrogen atom, and the negative charge midway between the two oxygens of the carboxyl group, owing to the resonance involving these. The locus of the carboxyl carbon atom is taken to

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[13] Cumming, *Proc. Roy. Soc.* (London), **78A**, 138 (1906–1907).

[14] Wyman, THIS JOURNAL, **56**, 536 (1934). See also Greenstein, Wyman and Cohn, *ibid.*, **57**, 637 (1935).

[15] Pauling and Brockway, *Proc. Nat. Acad. Sci.*, **20**, 336 (1934), and *J. Chem. Physics*, **2**, 867 (1934); Hengstenberg and Lenel, *Z. Krist.*, **77**, 424 (1931); Pauling and Sherman, *Proc. Nat. Acad. Sci.*, **20**, 340 (1934).

be on the straight line passing through the corresponding carbon of the benzene ring and the center of the hexagon, the ring itself being regarded as plane; the same is assumed also for the nitrogen atom. The various interatomic distances (in Ångströms) are taken as follows: carbon to carbon in the ring, 1.39; carboxyl carbon to adjoining carbon in the ring, 1.54; nitrogen to adjoining carbon in the ring, 1.4; oxygen to carboxyl carbon, 1.29. The angle subtended by the two oxygens at the carboxyl carbon atom is taken as 125°. This gives 1.29 cos (125°/2) = 0.6 Å. for the distance from this carbon atom to the locus of the negative charge, and this distance, owing to symmetry, is in a direction radial to the ring. The dipole distances (*i. e.*, distances between the positive and negative charges of the zwitterions) calculated from these models are 3.23, 5.49, and 6.36 Å. for *o*-, *m*- and *p*-benz betaine, respectively.

In the case of *o*-benz betaine the distance calculated in this way would seem to be too small in view of the size of the carboxyl group and of the methyl groups attached to the nitrogen atom. If we take the carbon to hydrogen distance as 1.07, the radius of the hydrogen atom as half the hydrogen to hydrogen distance or 0.75/2, the distance from the nitrogen to the carbons of the methyl groups as 1.4,[16] and assume the tetrahedral arrangement for the four valences of the nitrogen atom, we may estimate the minimum dipole distance as in the neighborhood of 3.9 Å. This estimate[17] is based on the assumption that there is free rotation of both the carboxyl carbon and nitrogen atoms about the valences joining them with corresponding carbon atoms of the ring. It would seem, therefore, that the ortho compound must be somewhat deformed and exist in a state of strain involving a certain amount of potential energy.[18] This would be expected to give rise to an effect of "steric hindrance" to the introduction of the methyl groups into this molecule, and corresponds to the fact that it is indeed much more difficult to effect the complete methylation of the amino group in anthranilic acid than in *m*- and *p*-aminobenzoic acids.[19]

If we adopt for the dipole distances of the *o*-, *m*- and *p*-benz betaines the values 3.9, 5.49, and 6.36, respectively, the corresponding moments are 18.6, 26.2 and 30.4 $\times 10^{-18}$ e. s. u. The same moments calculated from the data on the dielectric constant in water by means of Eq. (1), taking the optical polarization in each case as 52.7 (*i. e.*, the value experimentally determined for the uncharged isomer N-dimethylanthranilic acid methyl ester) are 21.9, 31.0 and 36.4. The values are 18, 18, and 20% too high, respectively. It would seem therefore that the moments, or polarizations, calculated from Eq. 1, though probably somewhat too high, are closely proportional to the true values as far as we can estimate them.

The behavior of the benz betaines as we pass to solvents of lower dielectric constant consisting of alcohol–water mixtures, alcohol, and alcohol–benzene mixtures is apparent from Fig. 1. Unfortunately it is impossible to dissolve these substances in pure benzene itself. If we make use of Eq. (1) to calculate the polarizations from these data, we obtain the results shown graphically in Fig. 2. The polarizations of course follow the δ values quite closely and are fairly constant down to a dielectric constant of about 20. It is impossible to extend the measurements on the para compound below this point owing to its insolubility, but the polarizations of the ortho and meta compounds fall rapidly from here on with diminishing dielectric constant of the solvent. Indeed it is extraordinary that the δ values for both these compounds (and of glycine betaine) seem to be converging toward the value 5.1 actually observed in the case of dimethylanthranilic acid in benzene.

The results obtained for ortho and meta benz betaine in the solvents of lowest dielectric constant actually studied, are given in Table IV. Here we have tabulated, in addition to the dielectric constant of the solvent and the δ value, the molal polarizations (P) and the corresponding moments (μ), calculated first from the Clausius–Mosotti equation at infinite dilution and then from Equation 1. In these calculations the apparent molal volumes are taken to be the same as in alcohol, namely, 133 cc. and 124 cc. for the ortho and meta compounds, respectively (they contribute at most less than 10% to the calculated polarizations), and the optical polarizations are again taken as 52.7 cc. For comparison, the results of similar calculations for betaine are included, in which the volume is taken as 91.9 cc. and the optical polarization as 35 cc.

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[16] Mark, *Z. Elektrochem.*, **40**, 413 (1934).

[17] This would involve a 17° displacement of the valence bonds joining the carboxyl carbon and nitrogen atoms to the ring.

[18] See Weissberger, Sängewald and Hampson, *Trans. Faraday Soc.*, 887 (1934), and discussion by de Laszlo, p. 892, who states: "In the case of 1-8-diiodonaphthalene the I atoms are spread out at 18° from the vertical and in ortho diiodobenzene 4° from the direction joining the C atom to the center of the hexagon."

[19] Willstätter and Kahn, *Ber.*, **37**, 412 (1904).

TABLE IV

Compound	ϵ (Solvent)	δ	P, cc., Clausius–Mosotti	P, cc., Eq. 1	$\mu \times 10^{18}$ Clausius–Mosotti	$\mu \times 10^{1}$ Eq. 1
Ortho B B	4.579	10.7	813	3725	6.05	13.2
Meta B B	3.191	10.1	1177	3457	7.36	12.8
Betaine	3.205	7.0	814	2401	6.11	10.7

It should be noted that in this range the values calculated on any basis are changing rapidly with the dielectric constant of the solvent. Nevertheless, however, we interpret the dielectric constant in this doubtful region, it appears clear that the moments of the betaines in these solvents of very low dielectric constant are decidedly lower than in water. It might be supposed that this effect is due to association of dipoles. Hooper and Kraus[20] have recently shown for certain highly polar molecules dissolved in benzene that the δ value and molal polarization decrease rapidly with increasing concentration at concentrations in the neighborhood of 0.001 molar. Hence the apparent moments deduced from studies at concentrations greater than this are much lower than the true moments determined at very great dilutions. Kraus interprets these phenomena as being due to association of dipoles, with decrease in apparent moment, at the higher concentrations. It seems improbable that our data on the betaines can be explained on this basis. In N-dimethylanthranilic acid in benzene there is actually a slight increase of δ from the value 5.1 observed at the lowest concentration 38×10^{-5} to the value 5.5 obtained at a concentration of 0.43; in the case of *p*-benz betaine in 19.9% benzene–ethanol δ is constant in the range 78×10^{-5} to 31×10^{-4} molar. Only in the case of betaine (N-trimethylglycine) in certain solvents is there anything resembling the effect described by Hooper and Kraus, and for this compound we have based our calculations on the limiting value of δ for the lowest concentrations.

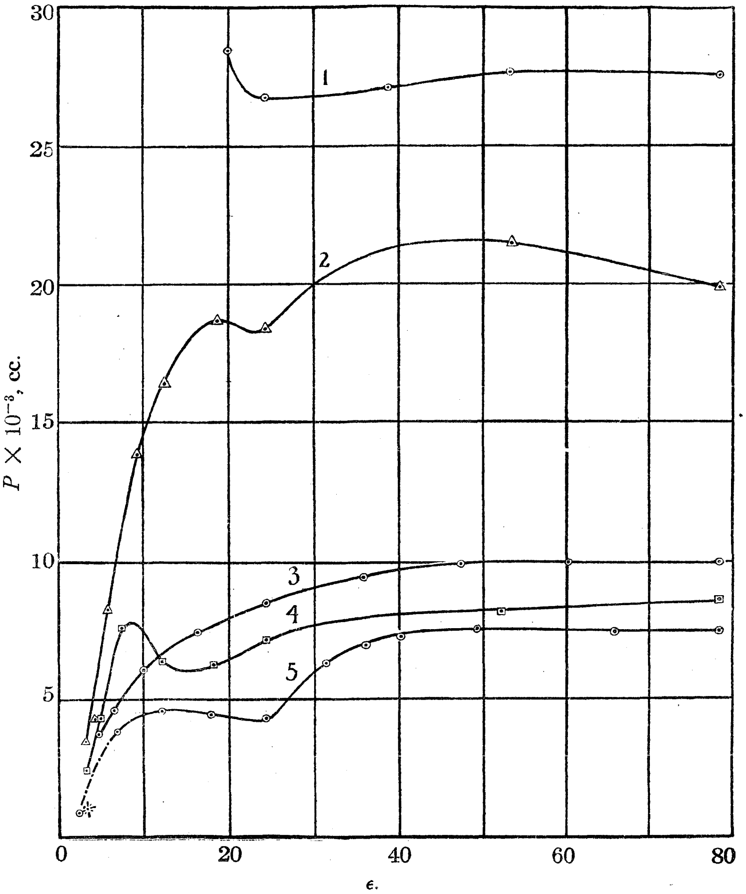

Fig. 2.—Polarizations calculated from Eq. 1, in relation to dielectric constant of solvent. The point marked by an asterisk, corresponding to pure benzene, is calculated by the Clausius–Mosotti relation: 1, *p*-benz betaine; 2, *m*-benz betaine; 3, *o*-benz betaine; 4, glycine betaine; 5, N-dimethylanthranilic acid.

If we accept the reality of the great reduction in moment indicated by the results in solvents of low dielectric constant and reject an explanation based on association, it remains to account for this in terms of a change in the individual molecules. The most natural explanation is probably in terms of a distortion of the valence bonds uniting the carboxyl carbon and the nitrogen atoms to the corresponding carbons of the ring. Such a distortion, involving a decrease in the dipole distance easily reckoned on the basis of simple geometrical considerations, would lead to a decrease of electrostatic energy inversely proportional to the dielectric constant of the solvent. If we regard this energy as that arising from two opposite elementary charges ($\pm e$) uniformly distributed over two equal spheres of radius b whose centers are separated by a distance R, we may apply the formula given by Scatchard[21] for the electrostatic energy E per mole.

$$E = \frac{Ne^2}{\epsilon}\left(\frac{1}{b} - \frac{1}{R}\right)$$

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[20] Hooper and Kraus, THIS JOURNAL, **56**, 2265 (1934).

[21] See Cohn, McMeekin, Edsall and Weare, *ibid.*, **56**, 2270 (1934).

In this expression ϵ denotes the dielectric constant of the medium and N is Avogadro's number. On the basis of this formula and the geometry of the molecule we can calculate the energy change $E_0 - E$ associated with a given angular distortion ω of both the valences uniting the nitrogen and carboxyl carbon atoms to the ring. In the ortho and meta compounds the distortion is assumed to take place in the plane of the ring, which makes it most effective; in the case of the para compound it makes no difference in what plane the bending occurs. The results of the calculation, expressed in calories per mole, for a medium of dielectric constant unity, are given in Fig. 3. This figure shows how much greater must be the tendency for a distortion of the valence bonds in the ortho compound than in the two others and how relatively small is the tendency in para benz betaine. The question then arises how such a decrease of electrostatic energy compares with the corresponding energy increase due to valence distortion itself. Stuart[22] has estimated that the distortion of a valence bond by 10° involves an increase of potential energy of the order of 1000 to 2000 calories per mole. Although we do not know how this varies with the angle, nevertheless it is clear that in solvents of low dielectric constant there will probably be a considerable distortion and corresponding reduction of moment of the ortho and meta molecules. In water, calculation shows that such an effect would be relatively insignificant. It may well be that the greater dipole moment and the smaller tendency for this to reduce itself in less polar solvents accounts for the very much smaller solubility of p-benz betaine in solvents of low dielectric constant. It would appear, however, at least in the case of the ortho compound, that this deformation would demand an approach of the charged groups to a distance actually less than that consistent with the bulk of these groups, discussed above. In regard to this, it is conceivable that when the forces become very great the interfering methyl groups are actually forced aside or that the carboxyl carbon atom is prevented from rotating, or both, with the result that the locus of the negative charge is brought into close proximity to the positively charged nitrogen atom; to this effect might be added the result of an actual polarization of the molecule under the influence of the strong field arising from the zwitterionic charges of the molecule itself in a medium of low dielectric constant.

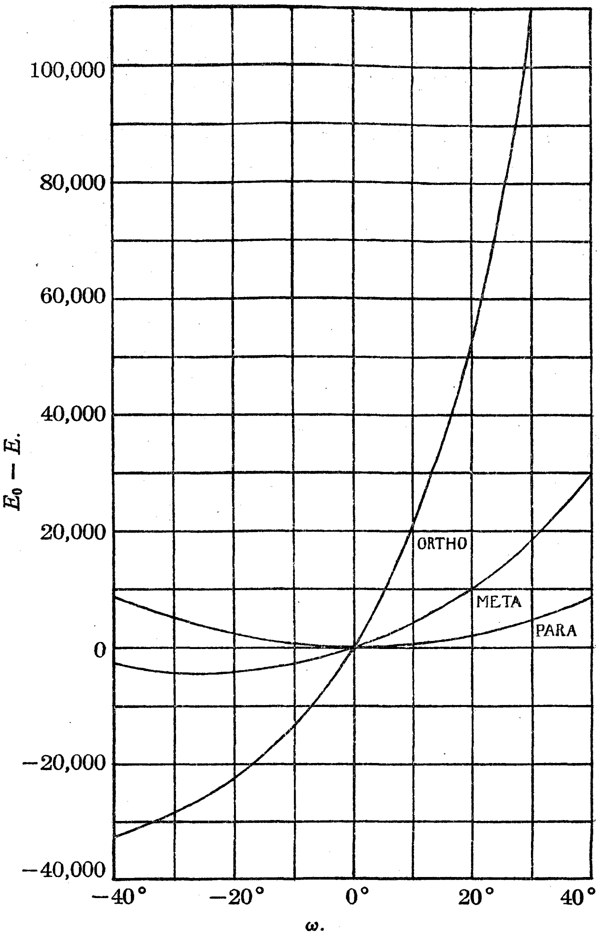

Fig. 3.—Energy change in relation to angular distortion, ω, of valence bonds for the benz betaines. Negative values of ω correspond to an increase of distance between the charges.

Of course the possibility remains of an intramolecular rearrangement of the betaines into their uncharged isomers, with a great resultant decrease in moment. At very high temperatures such a transformation does occur, as Willstätter[23] has shown. Under the conditions of our experiments, however, there has never been any sign of this. The uncharged isomers (*i. e.*, the methyl esters of the dimethylated aminobenzoic acids) are low melting substances, readily soluble in ether and benzene. When the betaines, dissolved in the solvents of lowest dielectric constant studied, were treated with ether, they were quantitatively precipitated, and no trace of ether-soluble material could be found. Furthermore,

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[22] Stuart, *Phys. Rev.*, **38**, 1372 (1931).

[23] Willstätter, *Ber.*, **35**, 584 (1902); Willstätter and Kahn, *ibid.*, **37**, 404 (1904).

the betaine so isolated showed no change of melting point from that of the substance as originally prepared.

For comparison with the betaines, we have studied the properties of one of these uncharged substances, namely, dimethylanthranilic acid methyl ester. This substance, dissolved in benzene, gives a δ value of $+0.570$ and has a moment of 2.05×10^{-18} e. s. u. In solvents of higher dielectric constant the δ value becomes negative. The results are included in Fig. 1 and show the striking contrast in behavior between this moderately polar molecule and the zwitterionic betaines.

The behavior of the ester is in marked contrast with that of N-dimethylanthranilic acid itself. This substance shows throughout a high δ value characteristic of zwitterionic structure, although in details it differs decidedly from glycine betaine, pyridine betaine, and ortho benz betaine in regard to δ. In pure benzene its moment is 6.31×10^{-18} e. s. u. or more than three times that of the ester. The detailed character of the variation both of δ and of the polarization (calculated from Eq. 1) with the dielectric constant of the solvent may be seen from Figs. 1 and 2. It would appear therefore that N-dimethylanthranilic acid remains largely in the zwitterion form even in pure benzene.

The study of its dissociation constants and that of its ester (Table III) further supports the view that this substance is a zwitterion, at least in water and in alcohol–water mixtures. According to the relations developed by Ebert[24] the ratio K_z of zwitterions to uncharged molecules in a solution of a simple ampholyte is given by the equation

$$K_z = (K_1/K_E) - 1$$

where K_1 is the first dissociation constant of the acid and K_E that of its ester, both being expressed as acid dissociation constants. On the basis of the data given in Table III this yields a value of approximately 12,000 for K_z in water and about 10 in 90% alcohol. There seems no doubt whatever therefore that in these solvents dimethylanthranilic acid exists predominantly in the zwitterion form. That a large proportion of zwitterions should remain in pure benzene is certainly surprising on the basis of our general knowledge of dissociation constants as a function of the dielectric constant of the solvent.[2]

It may be noted that N-dimethylanthranilic acid shows very unusual properties in other respects also.[26] Unlike most zwitterions it is very soluble not only in water but also in alcohol, acetone and benzene, and quite soluble even in ether and carbon tetrachloride. It melts at 70° to a clear liquid which solidifies on cooling and the solid so obtained shows all the properties of the original substance. In contrast with this, most zwitterionic acids melt between 200 and 300°, and decompose on melting. Likewise this compound shows markedly different properties from the other ortho, meta and para aminobenzoic acids, whether the nitrogen is unmethylated, monomethylated or dimethylated. These melt at temperatures from 140 to 180°; they are sparingly soluble in water, appreciably more soluble in alcohol or benzene; and their dissociation constants and those of their esters indicate values of K_z in water which are not far from unity.[27] Devoto[28] has indeed reported a δ value of about 40 for meta aminobenzoic acid in water, while that for dimethylanthranilic acid is only 12,[29] but there are no essential inconsistencies here since the charged zwitterions in the meta compound possess higher dipole moments than those in an ortho compound and hence even though they do not predominate so completely over the uncharged molecules they still have a much higher effect on the dielectric constant of the solvent.

It should be noted that the δ value and the polarization of dimethylanthranilic acid calculated from Eq. 1 are lower in all solvents studied than for ortho benz betaine (see Figs. 1 and 2). It seems not improbable that this is because of the substitution of a hydrogen atom for one of the methyl groups, which permits the positive and negative radicals to pack together more closely and results in a decrease of dipole moment. Indeed the moment in water calculated from Eq. 1 is 18.9×10^{-18} e. s. u., or about 14% less than that of ortho benz betaine. 3.23 Å., the dipole dis-

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[24] Ebert, *Z. physik. Chem.*, **121**, 385 (1926). See also Edsall and Blanchard, THIS JOURNAL, **55**, 2337 (1933).

(25) Professor Linus Pauling has suggested to us that the hydrogen atom of the carboxyl group in dimethylanthranilic acid may form a hydrogen bond with the nitrogen of the methylated amino group. Such a structure might account for the high moment and other peculiar properties of this substance.

(26) For previous discussions of this substance, see Cumming, *Proc. Roy. Soc.* (London), **78A**, 138 (1906–1907), and Devoto, *Gazz. chim. ital.*, **64**, 371 (1934).

(27) Ebert, *Z. physik. Chem.*, **121**, 385 (1926).

(28) Devoto, *Gazz. chim. ital.*, **63**, 247 (1933).

(29) Devoto and Ardissone [*Gazz. chim. ital.*, **64**, 371 (1934)] give the higher value, 16.7.

tance calculated from the model of the molecule in the undistorted condition is 17% less than 3.9, the dipole distance of the more bulky benz betaine. In any case the very remarkable properties of dimethylanthranilic acid clearly demand further study for they are unparalleled among all the ampholytes known to us.

Apparent Molal Volumes and Electrostriction of the Solvent

Betaines, possessing charged groups, produce electrostriction of the solvent, similar to that which has been shown to occur in solutions of amino acids.[30] The magnitude of the effect may be estimated by a comparison with similar uncharged substances, and with the aid of Traube's atomic volumes. In Table V are listed the apparent molal volumes in water calculated from Traube's theory for the substances studied, the observed volumes, and the estimated electrostriction, which is given by the difference between the observed and calculated volumes. Certain typical amino acids are also listed for comparison. In the last column is tabulated the value ΔE, which represents the difference in electrostriction between a given betaine and a corresponding amino acid (ortho, meta and para benz betaines are considered to correspond approximately to α, β and γ amino acids, respectively).

TABLE V

BETAINES IN WATER

Substance	Apparent molal vol., cc. Calcd.	Obs.	Electrostriction, cc./mole	ΔE
Betaine	105.9	97.7	8.2	5.1
Dimethyl phenyl betaine	151.4	146.8	4.6	8.7
Ortho benz betaine	151.4	146.5	4.9	8.4
Meta benz betaine	151.4	145.0	6.4	8.0
Para benz betaine	151.4	141.3	10.1	5.8
Pyridine betaine	108.8	99.6	9.2	4.1
Dimethylanthranilic acid	135.2	134.6	0.6	12.7
Glycine	57.0	43.5	13.5	..
α-Aminovaleric acid	105.9	92.7	13.2	..
β-Alanine	73.3	58.9	14.4	..
γ-Aminovaleric acid	105.9	90.0	15.9	..

It is apparent that when hydrogen atoms, surrounding a charged nitrogen, are replaced by the more bulky methyl or phenyl groups, the electrostriction diminishes. In betaine, with three methyl groups, the decrease is 5.1 cc. out of 13.3, an average value for an α-amino acid. Substitution of a phenyl for a methyl group, as in dimethylphenyl glycine, produces a further diminution of 3.6 cc. These results experimentally observed accord closely with what would be expected from the theory of electrostriction produced by ions in solution.[31] The smaller a given ion the more intense will be the electric field in its immediate neighborhood and the greater the orientation and compression effects producing electrostriction of the solvent.

These data suggest an approach to the solution of another problem. It has hitherto been impossible to decide whether most of the electrostriction produced by amino acids is due to the carboxyl or to the amino group since only the effect of the two groups in combination can be observed. In dimethyl phenyl betaine, however, the electrostriction produced is 8.7 cc. less than that characteristic of α amino acids. Almost all this diminution must be due to an effect on the charged nitrogen atom although the electrostriction produced by the carboxylic group may also be slightly diminished by the introduction of the large groups adjacent to it. It seems fair to assume, however, that at least 8.7 cc. of the total electrostriction (13.3 cc.) characteristic of α amino acids is due to the amino group and, therefore, not more than 4.6 cc. to the carboxyl group. Adopting tentatively the same ratio for the two groups when the charges are far apart and the total electrostriction is some 20 cc. per mole, we should assign approximately 13 cc. to the amino and 7 cc. to the carboxyl group. Utilizing the calculations of Vosburgh, Connell and Butler[32] for the relation between electrostriction and ionic radius, we may deduce an apparent radius of 2.25 Å. for the amino and 2.9 Å. for the carboxyl group.

In solvents of lower dielectric constant, the apparent molal volumes of the betaines are invariably smaller than in water. The same is true for salts, as was shown long ago by Carrara and Levi[33] and more recently by the careful and exact measurements of Vosburgh, Connell and Butler.[34] In the betaines the decrease in apparent molal volume is greater the greater the separation of the charged groups. Thus the value for

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(30) Cohn, McMeekin, Edsall and Blanchard, *J. Biol. Chem.*, **100**, Proc. XXVII (1933); THIS JOURNAL, **56**, 784 (1934). Reference may be made to these papers for the details of the calculation of electrostriction values.

(31) See Webb, *ibid.*, **48**, 2589 (1926).

(32) Vosburgh, Connell and Butler, *J. Chem. Soc.*, 933 (1933).

(33) Carrara and Levi, *Gazz. chim. ital.*, [II], **30**, 197 (1900).

(34) Vosburgh, Connell and Butler, *J. Chem. Soc.*, 933 (1933).

ortho benz betaine is 13 cc. per mole lower in absolute alcohol than in water; for para benz betaine, it is 22 cc. lower.

In solvents other than water, the electrostriction of the betaines cannot be calculated directly from Traube's atomic volumes, since the "Covolume" of Traube varies with the solvent employed in a manner depending largely on the particular substance studied.

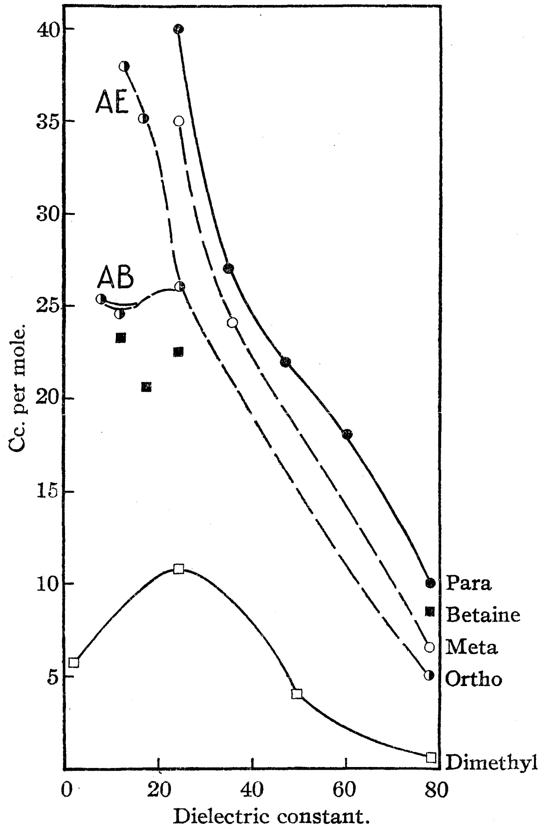

Fig. 4.—Electrostriction of betaines and dimethylanthranilic acid in various solvents: abscissa, dielectric constant of solvent; ordinate, electrostriction in cc. per mole; ◑, *o*-benz betaine; ○, *m*-benz betaine; ●, *p*-benz betaine; ■, betaine; □, dimethylanthranilic acid. The values for dimethylphenyl-betaine (not shown) are almost identical with these for *o*-benz betaine. The branch of the *o*-benz betaine curve marked AE refers to alcohol–ether mixtures; that marked AB, to alcohol–benzene mixtures.

We can, however, estimate the electrostriction directly by comparing a betaine in any given solvent with the isomeric uncharged ester *in the same solvent.* The difference between the two apparent molal volumes gives the contraction of the system due to the reaction $(CH_3)_2NRCOOCH_3 \longrightarrow (CH_3)_3N^+RCOO^-$; *i. e.*, by definition, the electrostriction.

We have taken dimethylanthranilic acid methyl ester as the uncharged isomer for comparison with all the benz betaines and with dimethylphenylglycine.[35] Its apparent molal volume in alcohol and in benzene is shown in Table II. It will be seen that the two volumes are almost identical, and that both are about 8 cc. higher than the value (151.4 cc.) calculated from Traube's theory for water.[36] (The ester is insoluble in water, so that this determination cannot be made directly.) For purposes of interpolation we have assumed the apparent molal volume of the ester in alcohol–water mixtures to vary linearly with the weight fraction of alcohol in the solvent, from 151.4 to 159.0 cc. In other organic solvents the value 159 cc. (identical with that in alcohol and benzene) has been taken.

In the case of betaine (trimethylglycine) we have no data on the uncharged isomer, dimethylglycine methyl ester. We have therefore calculated its volume in water from Traube's theory (see Table V) and have assumed the value in alcohol and other organic solvents to be 8 cc. greater than in water by analogy.

Dimethylanthranilic acid differs from its ester by one CH_2 group, whose contribution to the volume of the molecule is known to be nearly constant and equal to 16.3 cc. per mole in all solvents. To estimate the apparent molal volume of the acid in the uncharged form, therefore, we have subtracted 16.3 cc. from the volume of the ester in the same solvent. The difference between this value and the observed apparent molal volume of the acid yields the electrostriction. The electrostriction of the substances studied is plotted against the dielectric constant of the solvent in Fig. 4.

It may be seen from the figure that the electrostriction produced by the benz betaines is four or five times as great in ethyl alcohol (ϵ = 24.3) as in water (ϵ = 78.5) while that of trimethylglycine is nearly three times as great.

We may compare these experimental results with the effects to be expected theoretically from the calculations of Vosburgh, Connell and Butler for ions. Para benz betaine may be selected for comparison, since in this substance the charged groups are widely separated, and their mutual influence is small. The electrostriction in water is

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[35] Traube [*Sammlung Chem. Vorträge*, **4**, 255 (1899) and references there given] has shown that the apparent molal volumes of uncharged ortho, meta and para isomers are identical within 1 or 2 cc.

[36] This is in harmony with the finding of Traube that apparent molal volumes of uncharged compounds are generally 8 to 13 cc. greater in organic solvents than in water.

10 cc. per mole, of which we may tentatively assign 6 cc. to the carboxyl and 4 cc. to the methylated amino group.[37] Groups producing this amount of electrostriction in water should from the tables of the above-named authors in ethanol produce 23 and 18 cc. of electrostriction respectively, or a total of 41 cc. The observed value in ethanol (Fig. 4) is 40 cc. The agreement is far better than we should have any right to expect, considering the approximations involved in the theory itself and in its application to such substances as the betaines.

The results in mixed solvents are more difficult to interpret. It should be noted, however, that the electrostriction produced by ortho benz betaine is markedly greater in alcohol–ether mixtures than in alcohol–benzene mixtures of the same dielectric constant. It seems probable that this difference is correlated with the fact that ether is much more compressible than benzene.

It will be noted from Fig. 4 that the electrostriction of dimethylanthranilic acid is almost zero in water, and in all solvents is much lower than that of any of the betaines. Qualitatively these low values appear to parallel the relatively low δ values of this substance, and suggest that its electrical constitution must differ in some significant respect from that of the betaines.

Summary

1. Dielectric constant increments and apparent molal volumes have been determined for various betaines, and for N-dimethylanthranilic acid and its methyl ester in a variety of solvents ranging from water to benzene.

2. For the relatively rigid benz betaines, approximate dipole moments have been calculated on the basis of known interatomic distances. These have been compared with the values calculated from the observed dielectric increments with the aid of theoretical considerations.

3. In solvents of low dielectric constant, the dielectric increments (and probably the moments) of all the betaines studied fall far below their values in water. This effect appears to be due to actual deformation of the molecules rather than to association.

4. N-Dimethylanthranilic acid appears to exist largely as a zwitterion, not only in water and alcohol, but also in pure benzene, in which its dipole moment is more than three times as great as that of its methyl ester.

5. The electrostriction of the solvent produced by betaines in water is less than that produced by similar amino acids, presumably due to the greater bulk of the positively charged group in the betaines.

6. The electrostriction due to the betaines is much greater in solvents of low dielectric constant than in water, and the magnitude of the effects observed is in good accord with theoretical predictions.

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[37] The results of the ensuing calculation would not be significantly altered if we assigned 5 cc. to each group, or 7 cc. to one group and 3 to the other.

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

The "Salting-in" of Hydrogen Peroxide by Electrolytes

BY M. H. GORIN

Non-electrolytes are in general salted out of solution by the addition of electrolytes. The magnitude of this effect varies widely with the nature of the electrolyte and non-electrolyte, and in a few cases even changes in sign. However a search of the literature revealed that sodium chloride and sodium sulfate give relatively large salting-out effects with all non-electrolytes so far investigated, excepting hydrogen peroxide; Livingston[1] found the activity coefficient, $\gamma_{H_2O_2}$, of hydrogen peroxide to be less than unity in aqueous solutions of these salts. This is a "salting-in" effect of sodium chloride and sodium sulfate on hydrogen peroxide. On account of the exceptional nature of this result it was considered worth while to check Livingston's work with sodium chloride, and to study the behavior of hydrogen peroxide with several other electrolytes. The data are presented in Table I and plotted together with Livingston's in Fig. 1.

The experimental method used was the same as Livingston's; the distribution ratio of hydrogen peroxide between the salt solutions and iso-

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[1] Livingston, THIS JOURNAL, 50, 3207 (1928).

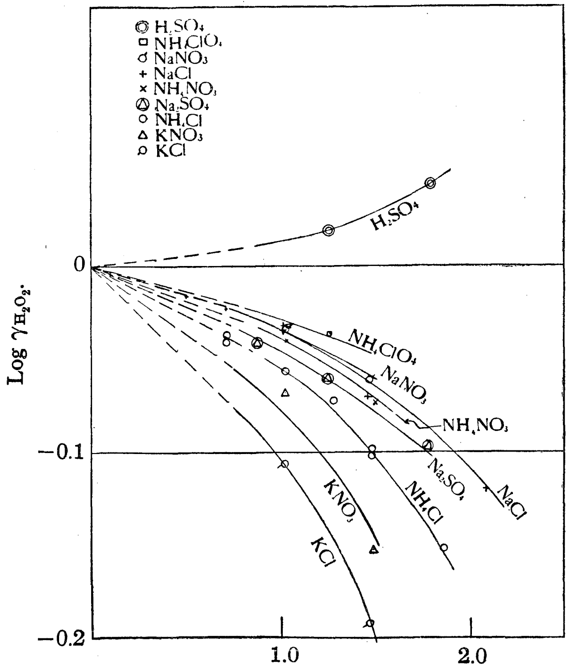
TABLE I

EXPERIMENTAL RESULTS AT 25°

Salt	Ionic strength[c] μ	R	$\gamma_{H_2O_2} = R_0/R$	Log $\gamma_{H_2O_2}$	Log $\gamma_{H_2O_2}/\mu$
$NaCl$[a]	1.02	7.62	0.929	−0.032	−0.032
NH_4Cl[a]	0.51	7.79	.910	− .041	− .080
NH_4Cl[a]	1.04	8.07	.878	− .057	− .055
NH_4Cl[a]	1.60	8.35	.848	− .072	− .045
NH_4Cl[a]	2.17	8.89	.797	− .098	− .045
NH_4Cl[a]	3.41	10.02	.707	− .152	− .045
NH_4Cl[b]	0.51	20.02	.918	− .037	− .073
NH_4Cl[b]	1.60	21.70	.847	− .072	− .045
NH_4Cl[b]	2.17	23.22	.791	− .102	− .047
KCl[a]	1.03	9.04	.784	− .106	− .103
KCl[a]	2.13	11.00	.644	− .192	− .090
$NaNO_3$[a]	1.03	7.66	.925	− .034	− .033
$NaNO_3$[a]	2.13	8.15	.869	− .061	− .029
NH_4NO_3[a]	1.05	7.77	.912	− .040	− .038
NH_4NO_3[a]	2.22	8.39	.845	− .073	− .033
KNO_3[a]	1.04	8.30	.853	− .069	− .066
KNO_3[a]	2.18	10.06	.705	− .152	− .070
NH_4ClO_4[a]	1.07	7.63	.929	− .032	− .030
NH_4ClO_4[a]	1.55	7.70	.922	− .035	− .021
H_2SO_4[a]	1.54	6.79	1.043	+ .018	+ .012
H_2SO_4[a]	3.14	6.39	1.108	+ .044	+ .014

[a] Solvent is isoamyl alcohol. [b] Solvent is 3 parts acetophenone + 1 part carbon tetrachloride. [c] μ is given in moles per 1000 g. of water.

amyl alcohol was determined; $\gamma_{H_2O_2}$ is given by the expression $\gamma_{H_2O_2} = R_0/R$ where R_0 is the distribution ratio of hydrogen peroxide between pure water (*i. e.*, hydrogen peroxide in water/hydrogen peroxide in isoamyl alcohol), and isoamyl alcohol, and R the distribution ratio of hydrogen peroxide between the salt solutions and isoamyl alcohol. The value, 7.08 ± 0.01, was found for R_0, while Livingston[1] used 6.95, an average between his value, 6.87, and that of Calvert,[2] 7.03 ± 0.05. In the case of ammonium chloride a solvent made up by adding one part of carbon tetrachloride to three parts of acetophenone was also used for the partition experiments, in order to confirm the results. R_0 was found to be 18.37 ± 0.07 for this mixture. The partition coefficient for pure acetophenone was found to be 11.55 ± 0.08. This value is far greater than the one previously given in the literature,[3] and is probably very much more nearly correct since the permanganate method used by these investigators[3] was found to give high results in the presence of acetophenone.



Square root of ionic strength.

Fig. 1.

It is seen from Table I and Fig. 1 that $\gamma_{H_2O_2}$ is not only less than unity in sodium chloride and sodium sulfate solutions but also in solutions of all the salts studied; and that only in the case of sulfuric acid is $\gamma_{H_2O_2}$ greater than unity. Furthermore, the order of the "salting-in" of hydrogen peroxide by the ions under consideration as determined from Fig. 1, is as follows: $K^+ > NH_4^+ > Na^+ > H^+$ and for the negative ions, $SO_4^= > Cl^- > NO_3^- > ClO_4^-$. Randall and Failey[4] in an extensive survey of the subject, tentatively arranged these ions along with some others in the following order of decreasing "salting-out" power on non-electrolytes in general: $Na^+ > K^+ > NH_4^+ > H^+$ and $SO_4^= > Cl^- > NO_3^- > ClO_4^-$. A comparison of this classification with that found for hydrogen peroxide reveals that the order for the "salting-in" of hydrogen peroxide by negative ions is exactly the same as the order for the "salting-out" of non-electrolytes in general. The same could be said about the positive ions if sodium ion were excluded.

It should be noted that log $\gamma_{H_2O_2}$ has been plotted against $\mu^{1/2}$ instead of against μ, as would be required by the Debye–McAuley relation, log $\gamma = K\mu$. This was done because when plots of log $\gamma_{H_2O_2}$ against μ were tried, s-shaped curves resulted in the case of ammonium chloride; for this salt the measurements cover a wide range of ionic strength and the individual points were most closely determined. The other curves in Fig. 1

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[2] H. T. Calvert, *Z. physik. Chem.*, **38**, 513 (1901).

[3] See Walton and Lewis, THIS JOURNAL, **38**, 634 (1916).

[4] Randall and Failey, *Chem. Rev.*, **4**, 290 (1927).

were drawn using the one for ammonium chloride as a model. It appears, therefore, that the Debye–McAuley law is not suitable for the case of hydrogen peroxide.

The evidence here presented proves that the behavior of hydrogen peroxide in solutions of electrolytes is different from that of other non-electrolytes; and requires that the hydrogen peroxide molecules tend to displace the water molecules surrounding all ions. However, in the case of the very small hydrogen ion there is a small "salting-out" effect instead of the relatively large "salting-in" effects shown by other ions. This is probably due to the preferential formation of hydronium ion, since it is reasonable to assume that the equilibrium

$$H_3O_2^+ + H_2O = H_3O^+ + H_2O_2$$

lies far to the right; and to the fact that hydronium ion carries relatively little hydrogen peroxide or water.

The displacement of water by hydrogen peroxide can be explained by the higher dipole moment of the peroxide molecule than that of the water molecule in the neighborhood of an ion. The following structure for hydrogen peroxide would yield a dipole moment of 3.01×10^{-18} as compared with 1.84×10^{-18} for water.

This structure differs from the one assigned to hydrogen peroxide in the gas phase by Penney and Sutherland[5] and can only exist in the strong potential fields surrounding an ion.

The dipole moment of gaseous hydrogen peroxide[6] is practically the same as that of water. Penney and Sutherland[5] have found that the most plausible structure of hydrogen peroxide is a highly skewed one, with an oxygen–oxygen single bond and a hydrogen atom on each oxygen, without free rotation around the O—O bond, the most stable configuration being the one in which the O—H bonds make an angle of 90° with each other. The $\mathrm{O{-}O}{\diagup}^{\mathrm{H}}$ bond angle is the same as in water, 110°, and the dipole moment for this model agrees very well with the observed one.[6] But the difference in potential between the model given in Fig. 2 and the stable configuration of the gaseous state was found by Penney and Sutherland[5] to be only of the order of magnitude of 25,000 calories. Therefore, it is probable that the hydrogen peroxide molecule assumes the structure shown in Fig. 2 as it approaches an ion, since the potential at the surface of even a large ion tending to rotate the O—H dipole is far greater in magnitude than 25,000 calories.

The order of the "salting-in" of hydrogen peroxide by the various positive and negative ions remains to be explained. The structure given in Fig. 2 for the hydrogen peroxide molecule is very similar to that of the water molecule as it orients itself around a negative ion; that is, the H—H distances are nearly the same in the two molecules and therefore it would be expected that hydrogen peroxide would tend to displace water around all negative ions since it has a higher dipole moment. Therefore, the order for the "salting-in" of hydrogen peroxide would be identical with the order for the "salting-out" of other non-electrolytes by negative ions, because the ions which hold the most water would be expected to hold the most hydrogen peroxide. This expectation agrees very well with the experimental findings for the four negative ions investigated. When oriented toward a positive ion, however, the water molecules can pack more closely around it than the peroxide molecules, since in this case the oxygen atoms rather than the hydrogen atoms are pointing toward the ion. Therefore, even though hydrogen peroxide has a higher dipole moment than water, it might be expected that in the case of the very smallest positive ions the equilibrium would favor water practically completely and as the ions increased in size hydrogen peroxide would begin to displace water. Only in the case of the larger positive ions, should hydrogen peroxide be "salted-in" in the same order as other non-electrolytes are "salted-out." The above discussion

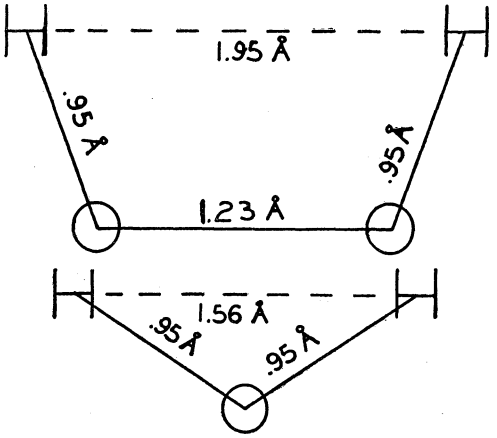

Fig. 2.

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[5] W. G. Penney and G. B. B. M. Sutherland, *J. Chem. Phys.*, **2**, 492 (1934).

[6] See Linton and Maass, *Canadian J. Research*, **7**, 81 (1932).

explains the experimental result that hydrogen peroxide is "salted-in" more by potassium ion than by sodium ion, while other non-electrolytes are "salted-out" more by sodium ion than by potassium ion.

In conclusion I wish to express my gratitude to Professor W. C. Bray for suggesting the problem, and for his very helpful suggestions and criticism during the progress of the work.

BERKELEY, CALIFORNIA RECEIVED JULY 29, 1935

[CONTRIBUTION NO. 159 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

Acetylene Polymers and their Derivatives. XXII. α-Dialkylaminomethyl-β-vinylacetylenes

BY DONALD D. COFFMAN

The reaction of primary acetylenic compounds with formaldehyde and secondary aliphatic amines in dioxane has recently been shown to give good yields of aminomethyl derivatives having the formula $RC{\equiv}CCH_2NR_2$.[1] This reaction has been applied to vinylacetylene, and it proceeds smoothly with low molecular weight secondary aliphatic amines according to the equation

$$CH_2{=}CHC{\equiv}CH + CH_2O + HNR_2 \longrightarrow$$
$$\text{(I)}\ CH_2{=}CHC{\equiv}CCH_2NR_2 + H_2O$$

Members of this new class of amines (I) have been prepared by allowing a dioxane solution of vinylacetylene and paraformaldehyde to react with dimethylamine, diethylamine, piperidine and dicyclohexylamine in an autoclave at 100°. The reaction furnishes the lower members of the series in good yields. The properties of the amines obtained in this way are indicated in Table I. The compounds are stable, colorless liquids with characteristic odors.

TABLE I

PHYSICAL PROPERTIES OF α-DIALKYLAMINOMETHYL-β-VINYLACETYLENES

Nature of amine		B. p., °C.	d^{20}_{4}	n^{20}_{D}	MR Calcd.	MR Found	Exaltation
(II)	$(CH_3)_2N$-	133–135 at 752 mm.	0.8208	1.4700	35.99	37.05	1.06
(III)	$(C_2H_5)_2N$-	166–167 at 766 mm.	.8272	1.4710	45.23	46.34	1.11
(IV)	$(CH_2)_5N$-	207–209 at 766 mm.	.9069	1.5064	47.65	48.89	1.24
(V)	$(C_6H_{11})_2N$-	138–140 at 0.5 mm.	.9492	1.5191	77.78	78.35	0.57

TABLE II

PROPERTIES OF α-DIALKYLAMINOMETHYL CHLOROPRENES

Nature of amine		B. p., °C.	d^{20}_{4}	n^{20}_{D}	MR Calcd.	MR Found	Exaltation
(VI)	$(CH_3)_2N$-	56–58 at 11 mm.	0.9615	1.4895	42.40	43.73	1.33
(VII)	$(C_2H_5)_2N$-	71–73 at 5 mm.	.9500	1.4895	51.63	52.78	1.15
(VIII)	$(CH_2)_5N$-	90–92 at 3.5 mm.	1.0137	1.5193	54.05	55.59	1.54

The reactions of several typical members of this new class of amines have been studied. Compounds (III) and (IV) are readily hydrogenated to the corresponding saturated tertiary amines whose properties and derivatives agree with those already recorded in the literature.

Compounds (II), (III) and (IV) add hydrogen chloride in the presence of cuprous chloride, but they react more slowly with aqueous hydrochloric acid than does the parent hydrocarbon[2] so that elevated temperatures are required. The products (VI), (VII) and (VIII) of the reaction correspond in composition to structure (IX). By analogy with the formation of chloroprene from vinylacetylene, structure (IX) seems most likely.

(IX) $CH_2{=}CHCCl{=}CHCH_2N(R)_2$

(X) $p\text{-}CH_3C_6H_4SCH_2CH_2C{\equiv}CCH_2N(CH_3)_2$

The physical properties of these substituted chloroprenes are indicated in Table II. They are colorless liquids which darken on standing. Like chloroprene, they react with α-naphthoquinone and with maleic anhydride but the products are black tars. Unlike chloroprene, they polymerize very slowly even at 100° or when exposed to light, and no rubber-like polymer has yet been obtained from them. It has already been shown that α-substitution in 1,3-dienes decreases con-

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[1] Mannick and Chang, *Ber.*, **66**, 418 (1933).

[2] Carothers, Williams, Collins and Kirby, THIS JOURNAL, **53**, 4203 (1931).

siderably the rate of polymerization.[3,4] Furthermore, these compounds have polymerization inhibiting groups cast directly in the molecule.

Thio-*p*-cresol readily adds to (II) in the presence of ultraviolet light. The product is a yellow oil corresponding in composition to formula (X). Since the mode of addition of thiophenols has been established thoroughly and since in the case of divinylacetylene only the ethylenic bonds are involved in the addition, the assigned structure seems likely.[5,6] Other addition reactions also take place. One molecule of methanol adds to (II) in the presence of sodium methoxide. The oily product is completely destroyed by permanganate. The theoretical amounts of bromine and iodine are absorbed by (II), but the products were black undistillable sirups. Exhaustive methylation of (II) with methyl iodide and silver oxide gives for the most part a tar, but an unsaturated hydrocarbon C_5H_4 is obtained in poor yield. The compound absorbs oxygen rapidly and when heated gelled and finally exploded violently.

Experimental Part

Preparation of α-Dialkylaminomethyl-β-vinylacetylenes.—The general method of preparation consisted in heating in an autoclave at 100–105° for fourteen to seventeen hours a dioxane solution of secondary aliphatic amine, vinylacetylene and paraformaldehyde. The only especial precaution observed in the preparation consisted in thoroughly cooling in an ice-bath the solution obtained by mixing the amine and paraformaldehyde. After the reaction had ceased for the most part, the vinylacetylene was added. During the heating period, care was taken that the thermal decomposition temperature of vinylacetylene (*ca.* 110°) was not reached. The products of the reaction were isolated in one of two ways. The reaction mixture from small runs was poured into dilute acid, and the aqueous solution was thoroughly ether extracted. The free amine was liberated from its salt by the addition of alkali, and after extraction was dried over potassium hydroxide and distilled under diminished pressure. In the case of large runs, the reaction mixture was separated into its components by fractional distillation under diminished pressure. Table III indicates the condition used and the yields of products obtained. Table IV contains the analytical data for the products.

TABLE III

Product	Amine	Moles of Vinylacetylene	$(CH_2O)_x$	Dioxane solvent, cc.	Time and temp., °C.	Yield of product, %
$(CH_3)_2N$-	14.6	15	4.85	1825	16 hrs. at 50; 12 hrs. at 100	74
	9	9	3	1200	17 hrs. at 45; 7 hrs. at 100	58
	0.5	0.5	0.17	50[a]	12 hrs. at 100	55
$(C_2H_5)_2N$-	.44	.44	.16	60	15 hrs. at 100	91
$(C_2H_5)_2N$-	2.6	2.46	.96	36	8 hrs. at 60; 7 hrs. at 80	72
$(CH_2)_5N$-	0.44	0.44	.16	60	15 hrs. at 100	68
$(C_6H_{11})_2N$-	1.6	1.6	.52	120	14 hrs. at 100	9.6

[a] Dimethylcellosolve was employed as solvent rather than dioxane.

TABLE IV

ANALYSES OF α-DIALKYLAMINOMETHYL-β-VINYLACETYLENES

Nature of amine		Calcd., % N	Found, % N
(II)	$(CH_3)_2N$-	12.84	12.39
(III)	$(C_2H_5)_2N$-	10.22	10.38
(IV)	$(CH_2)_5N$-	9.39	9.26
(V)	$(C_6H_{11})_2N$-	5.71	5.75

Hydrogenation of (III) and (IV) to Corresponding Saturated Tertiary Amines.—α-Diethylaminomethyl-β-vinylacetylene (0.25 mole) and 0.2 g. of platinum catalyst in 100 cc. of absolute ethanol absorbed 0.757 mole of hydrogen (107% of the amount required by theory) during thirty minutes. The catalyst was filtered from the solution and the filtrate was fractionally distilled through a good column. There was received 24 g. (yield 67% of the theoretical amount) of colorless oil identified as *n*-amyldiethylamine. Its constants are: b. p. 155–157° at 760 mm.; d^{20}_4 0.7663; n^{20}_D 1.4250; MR (calcd.), 47.70; MR (obsd.), 47.77.

Anal. Calcd. for $C_9H_{21}N$: N, 9.80. Found: N, 9.96.

The amine readily formed a picrate which melted at 52–53° after recrystallization from ethanol. The constants of the amine and the melting of its picrate are in good agreement with those recorded in the literature.[7] The amine is recorded as boiling at 155–158° at 735 mm. and the picrate as melting at 55°.

α-Pentamethyleneaminomethyl-β-vinylacetylene (0.2 mole) and 0.2 g. of platinum catalyst in 50 cc. absolute ethanol absorbed 0.51 mole of hydrogen (85% of the amount required by theory) during forty minutes. The catalyst was filtered from the ethanol solution and the filtrate was fractionally distilled. There was received 25 g. (yield 80% of the theoretical amount) of N-*n*-amylpiperidine. Its constants are: b. p. 192–195° at 760 mm.; d^{20}_4 0.8412; n^{20}_D 1.4602; MR (calcd.), 50.12; MR (obsd.), 50.55.

Anal. Calcd. for $C_{10}H_{21}N$: N, 9.03. Found: N, 9.15.

The amine readily formed a picrate which melted at 100–101° after recrystallization from ethanol. N-*n*-Amylpiperidine boils at 196° at 769 mm. and its picrate melts at 107°.[8]

Conversion of α-Dialkylaminomethyl-β-vinylacetylenes to α-Substituted Chloroprenes

Addition of Hydrogen Chloride to (II).—The amine (55 g.) was dissolved with cooling in 200 g. of 38% hydrochloric acid containing cuprous chloride (5 g.). The solution was heated at 60° during sixteen hours. It was then added dropwise with cooling to a solution of potas-

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[3] Carothers and Coffman, THIS JOURNAL, **54**, 4071 (1932).

[4] Jacobson and Carothers, *ibid.*, **55**, 1624 (1933).

[5] Ashworth and Burkhardt, *J. Chem. Soc.*, 1791 (1928).

[6] Carothers, THIS JOURNAL, **55**, 2008 (1933).

[7] Meisenheimer and Link, *Ann.*, **479**, 267 (1930).

[8] Robinson and Robinson, *J. Chem. Soc.*, **123**, 541 (1923).

sium hydroxide (112 g.) in 200 cc. of water. The insoluble amine was separated, dried and distilled. There was received 42 g. of colorless product (VI). The yield was 58% of the theoretical amount. After standing a short time, the amine was badly discolored. The substituted chloroprene (VI) reacted very rapidly with maleic anhydride and with naphthoquinone, but the products were black tars. Unlike chloroprene, it polymerized very slowly when exposed to light. After two and one-half months under a 100-watt lamp, a sample contained 10% of insoluble gelatinous polymer.

In the absence of cuprous chloride (II) adds hydrogen chloride very slowly; the product of the reaction is chiefly a tar but a 10% yield of (VI) was received.

Anal. Calcd. for $C_7H_{12}NCl$: Cl, 24.40. Found: Cl, 24.24.

Addition of Hydrogen Chloride to (III).—The amine (68 g.) was dissolved with cooling in 200 g. of 38% hydrochloric acid containing cuprous chloride (5 g). After the solution had been heated sixteen hours at 60°, the amine was freed by the addition of excess alkali, separated, dried and distilled. There was received 40 g. of the monohydrochloride (VII) or 46% of the theoretical amount. The product gave tars when allowed to react with maleic anhydride or naphthoquinone, and it polymerized very slowly. Only a trace of polymer was formed by heating the monomer during forty-three hours at 100°. When exposed to the light of a 100-watt lamp during three months, the monomer formed a semi-granular polymer (less than 10%).

Anal. Calcd. for $C_9H_{16}NCl$: Cl, 20.46. Found: Cl, 20.84.

Addition of Hydrogen Chloride to (IV).—The amine (75 g.) was dissolved with cooling in 200 g. of 38% hydrogen chloride containing cuprous chloride (5 g.). The solution was allowed to stand for sixty-six hours at 35° and was finally heated at 60° for five hours. The product was isolated in the usual manner and there was received a 56% yield of (VIII). This substituted chloroprene contained only a trace of polymer after exposure to the light of a 100-watt lamp during three months.

Anal. Calcd. for $C_{10}H_{16}NCl$: Cl, 19.13. Found: Cl, 18.85.

The Addition of Thio-*p*-cresol to (II).—Thio-*p*-cresol (62 g.) was dissolved in 55 g. of amine (II), and the solution was exposed to the light of a Cooper–Hewitt lamp for twenty-four hours. The pale yellow liquid was washed with dilute alkali and water, and was then dried and distilled in vacuum. There was received 43 g. of dimethylamino-1-pentin-2-yl-5-*p*-thiocresyl ether (X). The yield was 30% of the theoretical amount. Its physical constants are: b. p. 156–158° at 0.5 mm.; d^{20}_4 1.0151; n^{20}_D 1.5620; MR (calcd.), 73.09; MR (obsd.), 74.44.

Anal. Calcd. for $C_{14}H_{19}NS$: N, 6.01. Found: N, 6.18.

The Addition of Methanol to (II).—The amine (2.25 moles) and absolute methanol (2.47 moles) in which sodium (0.22 mole) was dissolved were heated in an autoclave at 100° for twelve hours. The reaction product was poured into a large volume of water, and the water-insoluble material was separated, dried and vacuum distilled. There was received 125 g. of product corresponding in composition to the addition of one molecule of methanol to (II). The product (yield 40%) had a powerful fish-like odor. Its constants are: b. p. 69–71° at 1 mm.; d^{20}_4 0.8987; n^{20}_D 1.5400; MR (obsd.), 48.82.

Anal. Calcd. for $C_8H_{15}NO$: N, 9.93. Found: N, 10.52.

Attempts to establish the structure of this compound by permanganate oxidation were unsuccessful; the amine was completely destroyed. Attempts to add two molecules of methanol to (II) were unsuccessful; the products obtained were tar-like and were for the most part undistillable *in vacuo.*

Exhaustive Methylation of (II).—Exhaustive methylation of (II) with methyl iodide and potassium hydroxide or silver oxide gave for the most part a tar, but a hydrocarbon—presumably pentatetraene ($CH_2{=}C{=}C{=}C{=}CH_2$)—was obtained in poor yields. It absorbed oxygen rapidly and when heated it gelled and finally exploded violently.

The most convenient method for carrying out the methylation consists in treating the methyl iodide quaternary salt of (II) (m. p. 182–184°) with an excess of freshly precipitated silver oxide in aqueous suspension. The quaternary salt (97 g.) in 300 cc. of water was agitated with silver oxide (100 g.) at 45°. When the test for the presence of ionic iodide in the aqueous solution was negative, the silver iodide was filtered off and the filtrate was vacuum distilled. From the condensate there was received 4 g. of hydrocarbon. The residue consisted entirely of tar. The product appeared to boil from 80–90° when distilled immediately; n^{20}_D 1.4778.

Anal. Calcd. for C_5H_4: C, 93.75; H, 6.25. Found: C, 91.97; H, 6.74.

Summary

The reaction between vinylacetylene, paraformaldehyde and secondary aliphatic amines yields α-dialkylaminomethyl-β-vinylacetylenes. Several transformation products of typical members of this new class of amines are described.

WILMINGTON, DELAWARE RECEIVED JULY 17, 1935

[CONTRIBUTION NO. 160 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

Acetylene Polymers and their Derivatives. XXIII. Cyano-4-butadiene-1,3

BY DONALD D. COFFMAN

Compounds of the formula $CH_2{=}C{=}CHCH_2X$ in which X is Cl, Br, I, OH or OAc survive a series of metathetical reactions without undergoing rearrangement.[1] Of these compounds, the chloride and bromide are readily and irreversibly rearranged to $CH{=}CXCH{=}CH_2$, and the iodide rearranges spontaneously.

Because of the ease with which the chloride, bromide and iodide are rearranged, it appeared likely that the action of sodium cyanide on chloro-4-butadiene-1,2 (I) might yield cyanoprene (II), a compound which should be of especial interest as a precursor of synthetic rubber. As a matter of fact cyano-4-butadiene-1,3 (III), isomeric with (II), is obtained in poor yields when an alcoholic solution of sodium cyanide is allowed to react with (I). The reaction evidently proceeds in a normal metathetical manner and is followed by rearrangement of one of the double bonds. Certain by-products formed during the reaction are indicated in subsequent paragraphs.

(I)	$CH_2{=}C{=}CHCH_2Cl$
(II)	$CH_2{=}C(CN)CH{=}CH_2$
(III)	$CH_2{=}CHCH{=}CHCN$
(IV)	$ClCH_2CH{=}CHCH_2CO_2C_2H_5$
(V)	$CH_3OCH_2CH{=}CHCH_2CN$

The structure of cyano-4-butadiene-1,3 (III) is established by its analytical composition and by the following reactions.

It is converted to β-vinylacrylic acid by cold acid hydrolysis and it is readily hydrogenated to *n*-amylamine. Alkaline permanganate oxidizes it to oxalic acid. In ethanol solution, the nitrile adds hydrogen chloride. The reaction consists of 1,4-addition and esterification giving rise to ethyl chloro-5-pentenoate-Δ^3 (IV). The ester (IV) is readily oxidized by alkaline permanganate to chloroacetic acid. When cyano-4-butadiene-1,3 is heated with naphthoquinone or maleic anhydride the only evidence of reaction is the formation of a polymeric mass. However, as has already been pointed out,[2] negative results in the Diels–Alder reaction are of no value in the demonstration of structure, since many 1,3-dienes fail to react.

Results already presented[3] show that to obtain a high rate of polymerization, the terminal carbon atoms in a 1,3-diene must be free of any substituents, but the new nitrile nevertheless polymerizes about twenty times as fast as isoprene and gives a rubber-like product. It polymerizes spontaneously on standing, and the polymerization is greatly accelerated at 100°. After three weeks at ordinary temperature, a 5% yield of α-polymer was obtained. On the other hand, after thirteen hours at 100°, the α-polymer was obtained in 14% yield along with a 42% yield of dimer. Antioxidants act as powerful inhibitors for this transformation. The plastic polymer obtained under the influence of heat may be compounded and cured, and, although the plastic properties of the product were never entirely suppressed, the rubber-like material possessed considerable elasticity. Under the influence of light cyano-4-butadiene-1,3 polymerizes to a granular product identical in appearance with ω-polychloroprene.

Under the conditions of preparation cyano-4-butadiene-1,3 is very reactive. It readily adds methanol to form two chemical individuals obtained as by-products.

The first of these is an unsaturated oil corresponding in composition to the addition of one molecule of methanol to the 1,3-diene (III). Oxidation of the oil with permanganate yields methoxyacetic acid. These facts indicate that it has the structure methoxy-1-cyano-4-butene-2 (V). It evidently is formed by the 1,4-addition of methanol.

The second of these is an oil corresponding in composition to the addition of two molecules of methanol to (III) and apparently it is formed by the addition of one molecule of methanol to (V). It is obtained not only as a by-product in the preparation of (III) but also by allowing (III) to react in a methanol solution of sodium methoxide. When hydrolyzed it yields a dimethoxyvaleric acid. Hydrolysis, demethylation by hydrobromic acid, and elimination of two molecules of water produce an unsaturated lactone which on hydrogenation yields δ-valerolactone.

These facts furnish a basis for a discussion of

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[1] Carothers and Berchet, THIS JOURNAL, **55**, 2807 (1933).

[2] Coffman and Carothers, *ibid.* **55**, 2040 (1933).

[3] Carothers, *Ind. Eng. Chem.*, **26**, 30 (1934).

its structure. Formulas (VI) and (VII) represent the only possibilities consistent with the facts for the structure of a compound formed by the addition of one molecule of methanol to (V).

(VI) $CH_3OCH_2CH_2CH(OCH_3)CH_2CN$
(VII) $CH_3OCH_2CH(OCH_3)CH_2CH_2CN$

No direct experimental method is available for a decision between these two structures since the hydroxy acids derived from each present the possibility of six-membered ring formation required to obtain δ-valerolactone.

Experimental Part

I. Preparation of Cyano-4-butadiene-1,3.—Sodium cyanide (250 g.) was dissolved in a solution of 250 cc. of water and 700 cc. of methanol in a 3-liter flask equipped with stirrer and reflux condenser. Chloro-4-butadiene-1,2 (354 g.) was introduced, and the mixture was heated gently with agitation until the reaction became exothermic. After the reaction had proceeded for an hour, the mixture was cooled and the sodium chloride was removed by filtration. The filtrate was poured into 1.5 liters of water, the water-insoluble layer was separated, and the aqueous solution was twice extracted with ether. The water insoluble layer and the ether extracts were combined and dried over calcium chloride. The ether was evaporated and by distillation of the residue 90 g. of crude product boiling from 36° (50 mm.) to 55° (3 mm.) was received. This material was washed once with cold dilute hydrochloric acid and was dried over magnesium sulfate. Distillation of the dried material gave 64 g. of cyano-4-butadiene-1,3 which boiled at 49–53° (30 mm.).

The physical properties of cyano-4-butadiene-1,3 are: b. p. 135–138° (760 mm.) with polymerization; 65–68° (58 mm.), 48–50° (28 mm.); d^{20}_4 0.8644; $n^{20}D$ 1.4880; *MR* (obsd.), 24.57; *MR* (calcd.), 24.10.

Anal. Calcd. for C_5H_5N: N, 17.72; mol. wt., 79. Found: N, 17.48; mol. wt., 80.

During the preparation of the nitrile considerable amounts of by-products were formed by the addition of methanol to the 1,3-diene. These products obtained along with some polymeric material account, in part, for the utilization of chloro-4-butadiene-1,2.

II. Proof of Structure of Cyano-4-butadiene-1,3

Hydrolysis to β-Vinylacrylic Acid.—Cyano-4-butadiene-1,3 (10 g.) was introduced into a solution of 60 cc. of concd. hydrochloric acid in 100 cc. of ether. After standing for six days at ordinary temperature the solution was diluted with water to 500 cc. total volume, and the solution was continuously ether extracted for twenty-one hours. Distillation of the dried ethereal extract gave a small amount of β-vinylacrylic acid[4] which melted at 71° after recrystallization from petroleum ether. The distillation residue was a polymeric mass.

Anal. Calcd. for $C_5H_6O_2$: C, 61.22; H, 6.12; neut. eq., 98. Found: C, 61.00; H, 6.16; neut. eq., 100.2.

Conversion to Ethyl β-Vinylacrylate.—To well-cooled ethanol (100 g., 95%) in a liter flask was added 100 g. of concd. sulfuric acid. Cyano-4-butadiene-1,3 (40 g.) was then introduced, and the solution was refluxed for seven hours. After three hours the solution was very viscous. The cooled reaction mixture was poured into ice water, and there separated a large amount of soft, plastic and rubber-like polymer. Ether extraction of the solution and distillation of the dried ethereal extract gave a small amount of ethyl β-vinylacrylate which boiled at 65–67° (30 mm.); d^{20}_4 0.9336; $n^{20}D$ 1.4723; *MR* (obsd.) 37.81; *MR* (calcd.), 35.13. The literature[5] records the physical constants of ethyl β-vinylacrylate as b. p. 70–71° (31 mm.); d^{20}_4 0.938.

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.67; H, 7.94. Found: C, 66.69; H, 7.71.

Ethyl β-vinylacrylate failed to form an addition compound when heated with naphthoquinone, and polymerized to a rubber-like mass after ten hours at 100°.

Reduction to *n*-Amylamine.—With a platinum catalyst, cyano-4-butadiene-1,3 (10 g. or 0.126 mole) in 25 g. of acetic anhydride absorbed 94% (0.477 mole) of the theoretical amount of hydrogen during eight hours. The reaction mixture was filtered from the catalyst and distilled, the portion boiling from 200–250° being collected. Redistillation gave 10 g. of colorless liquid which boiled at 112–116° (4 mm.); d^{20}_4 0.9146; $n^{20}D$ 1.4472; *MR* (obsd.), 37.75; *MR* (calcd.), 37.96.

Anal. Calcd. for C_7H_5ON: N, 10.85. Found: N, 10.92.

Hydrolysis of N-*n*-amylacetamide gave *n*-amylamine which boiled at 102–106°; d^{20}_4 0.7584; $n^{20}D$ 1.4093. The literature records the constants for *n*-amylamine as b. p. 104°, d^{19} 0.766. The amine was positively identified by conversion to *p*-bromobenzenesulfon-*n*-amylamide which, after recrystallization from petroleum ether, melted sharply on the block at 54°. The literature[6] records the melting point of *p*-bromobenzene-sulfon-*n*-amylamide as 55°.

Permanganate Oxidation of Cyano-4-butadiene-1,3.—An analytically pure sample of cyano-4-butadiene-1,3 (40 g.) was introduced into an aqueous solution (300 cc.) containing 28 g. of potassium hydroxide. Potassium permanganate (330 g.) was added in small amounts during four hours with vigorous agitation at 30°. The mixture was decolorized with sulfur dioxide, and the manganese dioxide was filtered off and washed with water. The combined filtrates were cooled, strongly acidified and continuously ether extracted. Evaporation of the dried ethereal extract gave a crystalline residue which, after washing with ethyl acetate–petroleum ether mixture, was dissolved in a small amount of water, boiled with Norite, filtered and cooled. The white crystals which separated melted sharply on the block at 101–102° with resolidification either alone or when mixed with an authentic sample of oxalic acid dihydrate.

Neutral equivalent. Calcd. for $H_2C_2O_4 \cdot 2H_2O$: neut. eq., 63.0. Found: neut. eq., 64.0.

Addition of Hydrogen Chloride to Cyano-4-butadiene-1,3.—Cyano-4-butadiene-1,3 (41 g.) was dissolved in 50

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[4] Muskat, THIS JOURNAL, **52**, 326 (1930).

[5] K. v. Auwers, *J. prakt. Chem.*, **105**, 361 (1923).

[6] Demény, *Rec. trav. chim.*, **50**, 51 (1931).

g. of 95% ethanol containing 44 g. of dry hydrogen chloride. After the mixture had stood for sixteen hours at ordinary temperature, it was heated for two hours at 80°. The cooled mixture was poured into ice water, and the water-insoluble layer was separated, washed with water and dried over calcium chloride. Distillation of the crude product (55 g.) in an efficient still gave 21 g. of pure chloro ester and a high boiling residue which could not be distilled without decomposition. The yield of ethyl chloro-5-pentenoate-Δ^3 was 25% of the theoretical amount. It boiled at 67–69° (0.5 mm.), 72–74° (1 mm.), d^{20}_{4} 1.0862; n^{20}_{D} 1.4612, *MR* (obsd.), 41.08; *MR* (calcd.), 40.58.

Anal. Calcd. for $C_7H_{11}O_2Cl$: Cl, 21.85; mol. wt., 162.5. Found: Cl, 22.02; mol. wt., 159.

Ethyl chloro-5-pentenoate-Δ^3 was oxidized to chloroacetic acid by potassium permanganate. The chloro ester (32 g.) was introduced into water (250 cc.) and potassium permanganate (85 g.) was added in small amounts during three hours with vigorous agitation. The mixture was decolorized with sulfur dioxide, and the manganese dioxide was filtered off and thoroughly washed with water. The combined aqueous filtrates were strongly acidified, and the aqueous solution was continuously ether extracted. The dried ethereal solution on evaporation and distillation of the residue gave 8 g. of crude chloroacetic acid which, after recrystallization from petroleum ether and chloroform, melted sharply on the block at 60–61°. The literature records its melting point as 61–63°.

Neutral equivalent. Calcd. for $C_2H_3O_2Cl$: neut. eq., 94.6. Found: neut. eq., 93.4.

Chloroacetanilide was prepared as a solid derivative. It melted sharply on the block at 134–135°. The literature records the melting point as 134–135°.[7]

Polymerization of Cyano-4-butadiene-1,3

Light Polymerization.—A sample of cyano-4-butadiene-1,3 in glass exposed to a 200-watt Mazda lamp for 112 hours at 40–50° was completely converted into a colorless granular mass of rubber-like globules. This granular product is identical in appearance with ω-polychloroprene. In a parallel sample isolated from the light, the only change was a slight increase in viscosity and the appearance of a tarry speck of granular polymer.

Heat Polymerization.—(1) Cyano-4-butadiene-1,3 also polymerized spontaneously on standing; after three weeks a sample of the nitrile gave a 5% yield of alcohol insoluble polymer. This soft, plastic, rather rubber-like mass was compounded with 1% of phenyl-β-naphthylamine and 5% of zinc oxide and was heated at 125° for thirty minutes. Vulcanization was apparently far from complete but the product had good elasticity and fair strength. A sample stretched 1400% without breaking; on release it instantly returned to 250% of its initial length and after ten minutes to 200%.

(2) A sample of the 1,3-diene heated in a glass tube at 100° for thirteen hours was converted to a colorless, viscous sirup which contained 14% of alcohol-insoluble polymer, 42% of high-boiling oil, and 21% of unchanged monomer. The high-boiling material had a molecular weight corresponding to a dimer, but its analytical composition indicated that considerable oxygen had been absorbed. The physical properties of the high-boiling oil are: b. p. 150–165° (3 mm.); d^{20}_{4} 1.0358; n^{20}_{D} 1.5118.

Anal. Calcd. for $C_{10}H_{10}N_2$: N, 17.72; mol. wt., 158. Found: N, 14.68; mol. wt., 160.

The alcohol-insoluble material was a soft, plastic, rubber-like mass. It was compounded with 0.5% of tetramethylthiuram disulfide, 1% benzidine, 3% sulfur, 5% zinc oxide and 1% phenyl-β-naphthylamine and heated at 125° for one hour. The plastic properties were partly suppressed, but the vulcanization was very incomplete. The product could be stretched without breaking to 1800% of its initial length; on release it instantly returned to 400%, and after ten minutes to 200%, its initial length.

(3) Cyano-4-butadiene-1,3 (10 g.) was added to a sodium hydroxide solution (120 g., 17% NaOH), and the mixture was heated to refluxing. During fifteen minutes ammonia was evolved and a polymeric mass commenced to separate from the mixture. After sixteen hours of refluxing all of the nitrile had been converted to a brown, hard, brittle solid (8 g.). The solid was finely ground in a mortar and was repeatedly washed in boiling water. The product after being washed with alcohol and ether was thoroughly dried at 110°. The material was quite hard and very insoluble in common organic solvents.

Anal. Calcd. for $(C_5H_5N)_x$: N, 17.72; C, 75.95; H, 6.33. Found: N, 15.30; C, 76.34; H, 7.38.

IV. By-Products in the Preparation of Cyano-4-butadiene-1,3

In the preparation of cyano-4-butadiene-1,3 large amounts of by-products are formed. The aqueous alcoholic solutions from six preparations of the nitrile (as already described) were continuously ether extracted for twenty-four hours. Fractionation by careful distillation of the dried ethereal extract showed it to consist essentially of three constant-boiling fractions having the compositions of (V) C_6H_9ON, (VI) $C_7H_{13}O_2N$, and (VIII) $C_7H_{10}O_2N$. Considerable amounts of material were discarded as foreshots obtained during the distillation.

(1) Proof of Structure of Methoxy-1-cyano-4-butene-2. Oxidation to Methoxyacetic Acid.—The first fraction (C_6H_9ON) consisted of 63 g. of colorless oil which boiled at 65–67° (7 mm.); d^{20}_{4} 0.9318; n^{20}_{D} 1.4397; MR (obsd.), 31.40; MR (calcd.), 30.90.

Anal. Calcd. for C_6H_9ON: C, 64.86; H, 8.11; N, 12.61; mol. wt., 111. Found: C, 65.40; H, 8.01; N, 12.58; mol. wt., 112.

Methoxy-1-cyano-4-butene-2 (44 g.) was introduced into 200 cc. of water and potassium permanganate (127 g.) was added in small portions during four hours with vigorous agitation. The mixture was decolorized by sulfur dioxide, and the manganese dioxide was filtered off and macerated in a mortar with water. The combined aqueous filtrates, strongly acidified with sulfuric acid, were subjected to continuous ether extraction. The dried ethereal extract was evaporated, and by distillation of the residue there was received 5 g. of organic acid which boiled at 115–117° (29 mm.). The acid was positively identified as methoxyacetic acid by conversion to methoxyacetamide. The amide, after recrystallization from absolute ethanol,

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[7] Meyer, *Ber.*, **8**, 1153 (1875).

melted sharply on the block at 95–96° either alone or when mixed with an authentic specimen of methoxyacetamide. Methoxyacetamide is reported in the literature[8] as melting at 96.5°.

(2) **Conversion of Dimethoxyvaleronitrile to Dimethoxyvaleric Acid and to δ-Valerolactone.**—The second fraction ($C_7H_{13}O_2N$) consisted of 288 g. of colorless oil which boiled at 70–73° (1 mm.); d^{20}_4 0.9788; n^{20}_{D} 1.4288; MR (obsd.) 37.68; MR (calcd.), 37.63.

Anal. Calcd. for $C_7H_{13}O_2N$: C, 58.74; H, 9.09; N, 9.79; mol. wt., 143. Found: C, 58.82; H, 8.81; N, 10.13; mol. wt., 143.

This same nitrile was obtained by the addition of methanol to cyano-4-butadiene-1,3 with sodium methoxide as catalyst. Cyano-4-butadiene-1,3 (79 g.), stabilized by hydroquinone, was added dropwise during half an hour to a vigorously agitated solution of 2 g. of sodium in 64 g. of anhydrous methanol at 60°. After an hour the reaction mixture was cooled, diluted with water and ether extracted. The ethereal solution was washed with dilute acid and dried. From the dried ethereal solution there was received by distillation in an efficient column 32 g. of dimethoxyvaleronitrile which boiled at 72–74° (1 mm.); d^{20}_4 0.9777; n^{20}_{D} 1.4289. The yield was 23% of the theoretical amount. In the absence of alkaline catalysts, the addition of methanol to cyano-4-butadiene-1,3 does not take place. The nitrile (40 g.) and absolute methanol (40 g.) were heated for four hours at 90° in a sealed tube. By distillation there was recovered 32 g. of methanol and 22 g. of nitrile. The residue was polymeric material.

Hydrolysis to Dimethoxyvaleric Acid.—Into a solution of 67 g. of concd. sulfuric acid in 100 cc. of water was introduced 53 g. of dimethoxyvaleronitrile. The solution was refluxed vigorously for four hours and was then repeatedly ether extracted. Evaporation of the dried ethereal solution and distillation of the residue through an efficient column gave 23 g. of recovered nitrile and 15 g. of dimethoxyvaleric acid which boiled at 119–122° (1 mm.); d^{20}_4 1.0800; n^{20}_{D} 1.4428; MR (obsd.), 39.75; MR (calcd.), 39.35.

Anal. Calcd. for $C_7H_{14}O_4$: C, 51.85; H, 8.64; neut. eq., 162. Found: C, 52.40; H, 8.79; neut. eq., 162.

Conversion to δ-Valerolactone.—Dimethoxyvaleronitrile (71 g. or 0.5 mole) was refluxed for eighteen hours with 300 g. of 48% hydrobromic acid. The mixture was diluted to 500 cc. and was continuously ether extracted for seventy hours. The dried ethereal solution was evaporated, and the residue (42 g.) on distillation gave 20 g. of lactone which boiled at 83–85° (3 mm.). The remainder of the material was high boiling, acid to litmus, and contained halogen. The properties of the lactone are: b. p. 226–228° (760 mm.), 83–85° (3 mm.); d^{20}_4 1.1439; n^{20}_{D} 1.4869; MR (obsd.), 24.64; MR (calcd.), 22.43.

Anal. Calcd. for $C_5H_6O_2$: C, 61.22; H, 6.12; mol. wt., 98. Found: C, 60.86; H, 6.33; mol. wt., 100.

The lactone was faintly acid to litmus, but could not be titrated directly with alkali. It absorbed bromine readily, forming a liquid bromide which was not characterized. No solid polymer separated from a sample of lactone heated at 140–150° during eight hours.

The unsaturated lactone (0.234 mole) and a platinum catalyst in 25 cc. of absolute ethanol absorbed 79% (0.184 mole) of the theoretical amount of hydrogen during twenty minutes. The reaction mixture was filtered from the catalyst and distilled. There was received 16 g. of colorless pleasant smelling liquid which had the properties of δ-valerolactone. It boiled at 86–89° (5 mm.), 219–222° (760 mm.); d^{20}_4 1.0794; n^{20}_{D} 1.4503. The lactone formed a solid polymer when heated during eight hours at 150°.

Anal. Calcd. for $C_5H_8O_2$: C, 60.00; H, 8.00. Found: C, 59.76; H, 8.19.

The physical constants for δ-valerolactone as recorded in the literature[9] are b. p. 215–220° (760 mm.), d^{20}_{20} 1.1130; n^{20}_{D} 1.4600. Those recorded for γ-valerolactone[10] are b. p. 207–208 (760 mm.), d^{25} 1.0465; n^{20}_{D} 1.4303. The lactone (1 cc.) when heated with 3 cc. of hydrazine hydrate at 120° for two hours gave a crystalline product. After recrystallization from ethanol–ethyl acetate mixture the product melted sharply on the block at 105° and it had a composition corresponding to the hydrazide of δ-hydroxyvaleric acid.

Anal. Calcd. for $C_5H_{12}O_2N$: N, 21.21. Found: N, 20.97.

(3) The third fraction ($C_5H_{12}ON_2$) was not identified. It consisted of 123 g. of oil which boiled at 131–134° (0.5 mm.); d^{20}_4 1.0293; n^{20}_{D} 1.4480.

Anal. Calcd. for $C_7H_{10}ON_2$: C, 60.89; H, 7.25; N, 20.29; mol. wt., 138. Found: C, 61.76; H, 7.42; N, 19.38; mol. wt., 147.

Summary

The action of alcoholic sodium cyanide on chloro-4-butadiene-1,2 yields cyano-4-butadiene-1,3. The compound polymerizes much faster than isoprene and yields a rubber-like product. It readily undergoes 1,4-addition with hydrogen chloride and with methanol. The transformation products are ethyl chloro-5-pentenoate-Δ^3 and methoxy-1-cyano-4-butene-2.

WILMINGTON, DELAWARE RECEIVED JULY 17, 1935

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[8] Sulo Kilpi, *Z. physik. Chem.*, **80**, 182 (1912).

[9] Marvel and Birkhimer, THIS JOURNAL, **51**, 260 (1929).

[10] Schuette and Thomas, *ibid.*, **52**, 3010 (1930).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

The Crystal Structures of Rubidium and Ammonium Fluoborates

BY J. L. HOARD AND VIRGINIA BLAIR

Introduction

Potassium and rubidium fluoborates have been reported[1] to be isomorphous with the corresponding perchlorates, which are known[2] to possess the barite structure. No crystallographic data have been reported for ammonium fluoborate, a compound of most interesting chemical properties.[3] Although an ammonium salt is expected usually to be isomorphous with the analogous potassium or rubidium salt, the formation in a number of fluorides of hydrogen bonds between nitrogen and fluorine has been observed[4] to result in fundamental changes in structural type. Inasmuch as no fluoborate had been previously studied by x-ray methods, and since, moreover, we considered it quite possible that hydrogen bonds might exist in the ammonium salt and cause it to assume a different structural type, we have carried through structure determinations for rubidium fluoborate and ammonium fluoborate. We have found that both compounds belong to the barium sulfate structural type; the structure of the ammonium salt seems, however, to be somewhat modified as a result of hydrogen bond formation.

Ammonium fluoborate was prepared by adding ammonia to a solution of boric acid in 45% hydrofluoric acid, and evaporating to dryness. The ammonium fluoborate was purified by sublimation and recrystallized from aqueous solution.

Rubidium fluoborate was crystallized from a solution prepared by dissolving equivalent quantities of rubidium chloride and boric acid in 45% hydrofluoric acid. Even after recrystallization under conditions of constant temperature at 0°, no specimen was obtained measuring as much as 1 mm. in its longest dimension.

Data for the x-ray study were obtained from Laue and oscillation photographs.

Determination of the Structure

Using the notation of Wyckoff,[2] which is also the assignment of axes customarily used by crystallographers for crystals with the barite structure, the smallest unit of structure of ammonium fluoborate is an orthorhombic one with $a_0 = 9.06$ Å., $b_0 = 5.64$ Å., $c_0 = 7.23$ Å., containing $4NH_4BF_4$. The similar unit of rubidium fluoborate has $a_0 = 9.07$ Å., $b_0 = 5.60$ Å., $c_0 = 7.23$ Å., also containing four molecules. Although lattice constants are known only to within about half a per cent., it seems sure that b_0 is definitely smaller in the rubidium salt. The units in both cases are confirmed by extensive Laue and oscillation data.

All lattices except the simple orthorhombic are eliminated by the appearance of "forbidden" reflections. The regular vanishings[5] are those required by the space groups C_{2v}^9 and V_h^{16}. The morphology of the crystals is apparently holohedral, and we are able to base a satisfactory structure on V_h^{16}-*Pnma.*

Upon investigation we find it possible to assign both ammonium and rubidium fluoborates to the barite structural type. The positions of the various kinds of atoms together with the parameter values which lead to reasonably good agreement between calculated and observed intensities are given below (the notation is that of Wyckoff, Reference 2, page 283). The positions used are

4(*c*): $u\frac{1}{4}v$; $u + \frac{1}{2}, \frac{1}{4}, \frac{1}{2} - v$, $\bar{u}\frac{3}{4}\bar{v}$; $\frac{1}{2} - u, \frac{3}{4}, v + \frac{1}{2}$, and 8(*d*): xyz; $x, \frac{1}{2} - y, z$; $x + \frac{1}{2}, y, \frac{1}{2} - z$; $x + \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z$; $\bar{x}\bar{y}\bar{z}$; $\bar{x}, y + \frac{1}{2}, \bar{z}$; $\frac{1}{2} - x, y, z + \frac{1}{2}$; $\frac{1}{2} - x, y + \frac{1}{2}, z + \frac{1}{2}$.

We find

$RbBF_4$

4 Rb in 4(*c*) with $u = 0.315$, $v = 0.335$; 4 B in 4(*c*) with $s = 0.932$, $t = 0.696$; 4 F_I in 4(*c*) with $o = 0.069$, $p = 0.597$; 4 F_{II} in 4(*c*) with $m = 0.813$, $n = 0.567$; 4F_{III} in 8(*d*) with $x = 0.923$, $y = 0.043$, $z = 0.810$.

NH_4BF_4

4 NH_4 in 4(*c*) with $u = 0.308$, $v = 0.328$; 4 B in 4(*c*) with $s = 0.947$, $t = 0.697$; 4 F_I in 4(*c*) with $o = 0.086$, $p = 0.603$; 4 F_{II} in 4(*c*) with $m = 0.830$, $n = 0.563$; 4 F_{III} in 8(*d*) with $x = 0.936$, $y = 0.043$, $z = 0.811$.

We next outline the procedure followed in determining the listed parameter values.

The relatively large atomic number of rubidium

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(1) F. Zambonini, *Z. Krist.*, **41**, 57 (1905); T. V. Barker, *J. Chem. Soc.*, **101**, 2484 (1912).

(2) R. W. G. Wyckoff, "The Structure of Crystals," Chemical Catalog Co., New York City, 2d ed., p. 289.

(3) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longman, Green and Co., New York City, 1924, Vol. V, p. 127.

(4) Linus Pauling, *Z. Krist.*, **85**, 380 (1933).

(5) Astbury and Yardley, "Tabulated Data for the Examination of the 230 Space Groups by Homogeneous X-Rays," *Phil. Trans.*, **224**, 221 (1924).

causes it to assume a dominating role in the x-ray scattering by rubidium fluoborate. As a first approximation we neglect the scattering of the lighter atoms, and use the intensity data to fix rough values of the rubidium parameters; because of the near identity in size of NH_4^+ and Rb^+ we may assume that we also obtain by this process approximate values of the ammonium parameters. We then introduce other atoms in the general regions to be anticipated, and calculate intensities for various combinations of the parameter values until we obtain a fairly detailed agreement with the observed intensities. This procedure is greatly simplified by the reasonable assumption of a regular BF_4^- tetrahedron. The size of the tetrahedron thus assumed can be determined, although only roughly, from a consideration of the (0*k*0) reflections, which involve but one degree of freedom. Thermal vibrations of the atoms within the lattice are responsible for a large and unknown decrease in atomic scattering powers. We can say only that observed intensity data fix the parameter of fluorine along *b* so as to limit the B–F separation (assuming a regular tetrahedron) to the range between about 1.40 and 1.47 Å. A value[6] of 1.43 Å. for this interatomic distance, obtained from the theoretical work of Pauling on ionic and covalent radii, is employed in the parameter determinations reported in this paper.

In Table I we give comparisons between calculated and observed intensities of x-ray reflections for a variety of planes. The *f*-values of Pauling and Sherman[7] are employed throughout this paper. No temperature factor is included, so that with increasing sin Θ continually mounting discrepancies between calculated and observed intensities are to be anticipated. By comparison with a scale prepared for the purpose, we have visually estimated the listed intensities; large differences in intensities, irregular crystal shapes, and the collection of data from various photographs combine to make these estimates rather uncertain. We have, nevertheless, attached numerical values to them, for we regard this scheme as more illuminating and somewhat more precise than the appellations "strong," "weak," etc. To compare relative intensities of corresponding reflections between the two salts, the values given for rubidium fluoborate must be multiplied by five.

Table I

Comparison of Calculated with Observed Intensities of x-Ray Reflections

	$RbBF_4$			NH_4BF_4	
	Intensities			Intensities	
(*hkl*)	Calcd.	Obsd.	(*hkl*)	Calcd.	Obsd.
200	14	16	200	42	36
400	4.5	3	400	14	9
600	1.4	1	600	9.6	2
800	33	8	800	28	4
020	86	96	020	54	48
040	65	32	040	62	12
060	16	3	060	11	1.5
080	4.0	0	080	1.4	0
002	43	36	002	53	48
004	14	9	004	8.6	3
006	13	6	006	1.2	<1
008	7.0	2	008	8.4	1.5
011	18	12	011	22.5	32
022	0.3	0	022	49.0	32
031	26	16	031	3.6	2
042	6.0	0	042	0.2	0.5
051	1.6	0	051	10.9	3
101	0.6	0	101	8.9	12
201	3.5	3	201	26.0	32
301	5.1	3	301	15.0	4
401	53	24	401	53.0	32
501	13	2	501	0.3	0
102	34	24	102	1.9	2
103	17	8	103	23.0	12
104	4.5	2	104	2.2	2
105	4.5	1	105	19.0	6
210	79	96	210	43	32
220	41	36	220	52	16
230	7.0	3	230	1.7	1
240	5.1	2	240	2.9	0
410	68	48	410	38	16

In consideration of the many parameters which are involved and the uncertainties already mentioned the intensity data of Table I seem quite consistent. The true parameter values may well differ appreciably from those given; we believe, however, that the structures of these two compounds are actually somewhat different. This point is made clear in the next section.

Discussion of the Structure

A diagram of the structure of ammonium fluoborate is shown in Fig. 1. A list of the interatomic separations which have a direct bearing upon the question of the stability of these structures is given in Table II.

The coördination of fluoride about rubidium ions is such as to place 12 F^- about each Rb^+ at distances ranging from 2.90 to 3.46 Å., with an average value of 3.05 Å. Each NH_4^+ is surrounded by 12 F^- at distances ranging from 2.83 to 3.39 Å., also with an average value of 3.05 Å.

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(6) Private communication from Professor Pauling.

(7) Pauling and Sherman, *Z. Krist.*, **81**, 1 (1932).

TABLE II

INTERATOMIC DISTANCES IN RUBIDIUM AND AMMONIUM FLUOBORATES

$RbBF_4$			NH_4BF_4		
Atom	Neighbor	Separations, Å.	Atom	Neighbor	Separations, Å.
B	F_I, F_{II}, $2F_{III}$	1.43	B	F_I, F_{II}, $2F_{III}$	1.43
Rb	F_I	2.91	N	F_I	2.83
Rb	F_{II}	2.92	N	F_{II}	2.83
Rb	$2F_{III}$	2.89	N	$2F_{III}$	2.86
Rb	$2F_{III}$	2.91	N	$2F_{III}$	2.94
Rb	$2F_{III}$	2.97	N	$2F_{III}$	3.08
Rb	$2F_I$	3.11	N	$2F_I$	3.18
Rb	$2F_{II}$	3.44	N	$2F_{II}$	3.39
F_{II}	$2F_{III}$	3.17	F_{III}	$2F_{III}$	3.01
F_{III}	$2F_{III}$	3.18	F_I	$2F_{II}$	3.16
F_I	$2F_I$	3.28	F_I	F_{II}	3.27

In $(NH_4)_2SiF_6$ each NH_4^+ is equidistant from 12 F^- with NH_4-F = 2.99 Å.

Leaving out of consideration the (seemingly unavoidably) large values of 3.13 and 3.46 Å., we see that the eight smaller Rb-F separations vary within the narrow range from 2.89 to 2.97 Å., with an average of 2.93 Å. This feature of the structure is certainly to be anticipated when dealing with the rubidium ion, which, when isolated, is spherically symmetrical. We find that a similar assignment of parameter values to the ammonium salt leads to intensity predictions which are in some cases rather definitely unsatisfactory; to be entirely rid of these discrepancies, it seems necessary to introduce the type of distortion next to be described.

Examination of an ammonium fluoborate structure with the parameters of the rubidium salt shows that there is just one reasonably satisfactory way in which each ammonium ion might form its maximum number of four hydrogen bonds with fluoride ions. Our assignment of parameter values in ammonium fluoborate surrounds each nitrogen by four fluoride ions at tetrahedron corners, F_I and F_{II} at a distance of 2.83 Å., and 2 F_{III} at 2.86 Å. We find two tetrahedral (bond) angles of 119.5°, a third of 134°, and the fourth of only 84.5°. The interatomic separations indicate that the hydrogen bonds are rather weak, since in NH_4HF_2 the average N-F separation is 2.76 ± 0.06 Å. We believe that the N-F separations in ammonium fluoborate may well be somewhat smaller than those given, for we have introduced what we regard as the minimum amount of distortion from the $RbBF_4$ parameters necessary to account for the intensity data. It seems possible, moreover, that the two hydrogen bonds involving F_I and F_{II} may be somewhat stronger than those involving F_{III}, since the unavoidably large M-F separations of Table II involve F_I and F_{II}. Such an assignment of parameter values, which leads to entirely satisfactory predictions, and to N-F_I = 2.80 Å., N-F_{II} = 2.80 Å., N-F_{III} = 2.87 Å., is as follows: u = 0.308, v = 0.332; s = 0.947, t = 0.693; m = 0.833, n = 0.555; o = 0.089, p = 0.605; x = 0.933, y = 0.043, z = 0.807. We regard it as quite possible that still smaller N-F separations exist within the structure, but we see no possibility of ascertaining the precise state of affairs.

In NH_4F and NH_4HF_2 the formation of hydrogen bonds between nitrogen and fluorine causes these compounds to assume structures belonging to crystal classes entirely different from the corresponding potassium or rubidium salts. That hydrogen bonds in ammonium fluoborate seems quite probable, but their presence results in but slight changes either in parameter values or in lattice constants.

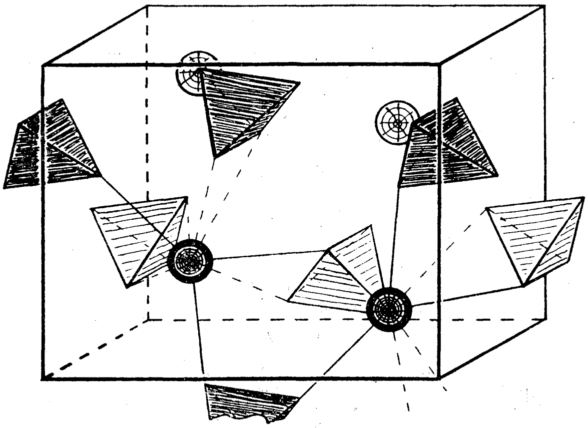


Fig. 1.—The structure of ammonium fluoborate. The positions of nitrogen atoms and of fluoborate ions are indicated respectively by the circles and the regular tetrahedra. Figures heavily shaded are centered in the plane $y = 1/4$, those lightly shaded in $y = 3/4$. The coördination of fluoride about ammonium ions is shown by the lines connecting vertices of the tetrahedra with the circles; the solid lines indicate hydrogen bonds.

Summary

x-Ray data show rubidium fluoborate and ammonium fluoborate to possess similar orthorhombic units of structure with a_0 = 9.07 Å., b_0 = 5.60 Å., c_0 = 7.23 Å. and a_0 = 9.06 Å., b_0 = 5.64 Å., c_0 = 7.23 Å., respectively. Both compounds crystallize with the barium sulfate type of structure, space group V_h^{16}-*Pnma*, being aggregates of

BF_4^- tetrahedra and Rb^+ or NH_4^+ ions. A regular BF_4^- tetrahedron with B-F = 1.43 Å., is assumed in order to determine the eleven parameters of the structure. The rubidium ions are first placed approximately by neglecting the scattering of the other much lighter atoms; these are then assigned parameter values which lead to a generally acceptable agreement between calculated and observed intensities of x-ray reflections. An identical assignment of parameter values in ammonium fluoborate leads to only fair agreement between calculated and observed intensities; these are much improved by the introduction of small distortions which may be interpreted as a tendency toward the formation of hydrogen bonds between nitrogen and fluorine.

STANFORD UNIVERSITY, CALIF.

RECEIVED AUGUST 5, 1935

[CONTRIBUTION FROM THE ORGANIC CHEMICAL LABORATORY OF THE UNIVERSITY OF FLORIDA]

Derivatives of Piperazine. VII. Procaine Analogs, Part I

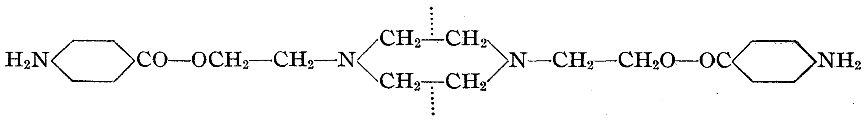
BY DAVID E. ADELSON, L. G. MACDOWELL AND C. B. POLLARD

Considerable work has been done in the field of alkyl *p*-aminobenzoates to ascertain the relationship between chemical constitution and physiological action. Such investigations have included the preparation of procaine analogs containing dissimilar alkylamino groups,[1] aliphatic and aryl aliphatic acids in the place of *p*-aminobenzoic acid[2] and unsaturated groups in the side chain of the acids.[2] Other studies have shown the effect of increase in the length of the carbon chain of the alkyl group and the effect of branched-chain alkyl derivatives in the procaine series.[3] Soderman and Johnson[4] and Roberts and Johnson[5] have studied procaine analogs containing different aromatic acids. Numerous other investigations, far too extensive to list here, have been carried out to determine the effect of increasing molecular weight on the anesthetic properties of compounds of the procaine type.

The purposes of the present investigation were (1) to study the effect of cyclic diamines, such as piperazine, and various types of aliphatic secondary amines on the therapeutic properties of the procaine molecule, (2) to determine the effects thus produced by the increased nitrogen content of the molecule and (3) to devise a simple method for obtaining piperazino-1,4-bis-(β-ethanol) in good yield.

Pyman[6] has prepared the latter compound in 41% yield from piperazine and 2-chloroethanol. The present workers have prepared piperazino-1,4-bis(β-ethanol) in quantitative yield by a method analogous to that used by Horne and Shriner[7] in the preparation of β-diethylaminoethanol.

It is apparent that the di-*p*-aminobenzoate of piperazino-1,4-bis-(β-ethanol) is in reality a "double" procaine molecule. If the molecule is split into symmetrical halves as indicated by the dotted lines, it is logical to consider the molecule as being composed of two similar parts, each of which has a smaller molecular weight than procaine. The percentage of nitrogen in procaine is 11.86, whereas the di-*p*-aminobenzoate of piperazino-1,4-bis-(β-ethanol) contains 13.59% N. Hence the new molecule contains more nitrogen per unit molecular weight than procaine and in addition possesses a cyclic diamino linkage. It will be interesting to learn the modifications which these two effects will produce in the therapeutic properties of procaine.



Experimental

Piperazino-1,4-bis-(β-ethanol).—Twenty-one grams of anhydrous piperazine[8] was dissolved in an equal weight of boiling methanol contained in a flask fitted with a condenser. A stream of ethylene oxide was passed into the solution until the theoretical quantity had been absorbed.

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[1] Brill, THIS JOURNAL, **54**, 2484 (1932).

[2] Brill and Bulow, *ibid.*, **55**, 2059 (1933); Brill and Cook, *ibid.*, **55**, 2062 (1933).

[3] Adams, Rideal, Burnett, Jenkins and Dreger, *ibid.*, **48**, 1758 (1926).

[4] Soderman and Johnson, *ibid.*, **47**, 1390 (1925).

[5] Roberts and Johnson, *ibid.*, **47**, 1396 (1925).

[6] Pyman, *J. Chem. Soc.*, **93**, 1793 (1908).

[7] Horne and Shriner, THIS JOURNAL, **54**, 2925 (1932).

[8] Pollard, Bain and Adelson, *ibid.*, **57**, 199 (1935).

The heat of reaction was sufficient to keep the solution at reflux temperature. Upon cooling the addition compound crystallized out, yield 42 g. (98%). Piperazine-1,4-bis-(β-ethanol) crystallizes from amyl acetate in large prisms which melt at 135–135.5°.

Anal. Calcd. for $C_8H_{18}N_2O_2$: N, 16.09. Found: N, 16.07.

Di-*p*-nitrobenzoate of Piperazino-1,4-bis-(β-ethanol).—This compound is prepared in 50% yield from the above by treatment with *p*-nitrobenzoyl chloride in cold alkaline solution. Recrystallization from xylene gives small yellow granules which melt at 158–158.5°.

Anal. Calcd. for $C_{22}H_{24}N_4O_8$: N, 11.86. Found: N, 11.74.

Di-*p*-aminobenzoate of Piperazino-1,4-bis-(β-ethanol).—Reduction of the di-*p*-nitrobenzoate with a large excess of powdered iron[3] followed by extraction with hot xylene yields this compound. It is purified by solution in dilute hydrochloric acid followed by reprecipitation with dilute alkali and recrystallization from xylene as silky needles, m. p. 203–204°.

Anal. Calcd. for $C_{22}H_{28}N_4O_4$: N, 13.59. Found: N, 13.55.

The tetrahydrochloride of the di-*p*-aminobenzoate of piperazino-1,4-bis-(β-ethanol) is prepared by dissolving the free base in dilute acid and evaporating the solution *in vacuo* at room temperature. The crystals thus formed are very hygroscopic and must be oven-dried prior to analysis. The compound is stable in boiling water.

Anal. Calcd. for $C_{22}H_{32}N_4O_4Cl_4$: N, 10.04. Found: N, 9.83.

Summary

1. Piperazino-1,4-bis-(β-ethanol) has been prepared in good yield. From it have been synthesized the di-*p*-nitrobenzoate, the di-*p*-aminobenzoate and the tetrahydrochloride of the latter.

2. The therapeutic properties of the tetrahydrochloride of the di-*p*-aminobenzoate of piperazino-1,4-bis-(β-ethanol) will be investigated.

GAINESVILLE, FLORIDA RECEIVED AUGUST 17, 1935

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, VIRGINIA MILITARY INSTITUTE]

Normal Fatty Acid Amides of Ethylenediamine

BY N. BEVERLEY TUCKER[1]

The purpose of the work herein reported was to record the physical properties, chiefly the melting points, of the normal fatty acid diamides of ethylenediamine. The amides were all prepared alike, *i. e.*, the diamine was boiled for forty-eight hours with the calculated double molar quantity of the ethyl ester of the desired acid. The resulting solid product was recrystallized to constant melting point, the lower members to the butyric from a mixture of ethyl acetate and alcohol, others from absolute alcohol. The first six members of the series were examined under the polarizing microscope, and their solubilities in three solvents were measured. Results are summarized in the tables.

The diacetyl,[2] dipropionyl and dibutyryl[3] derivatives, as well as several related compounds, have been reported.[3,4]

TABLE I

MELTING POINTS AND SOLUBILITIES

(Melting points were measured with complete stem immersion to eliminate stem correction)

		Solubility at 25°C. in g./100 cc.			N, %	
Derivative	M. p.	Water	Abs. EtOH	Et. acetate	Calcd.	Found
C_2	173–173.5	68.3	13.1	0.25	19.4	...
C_3	189.0	40.8	13.8	.26	16.27	16.22
C_4	191–191.3	4.78	13.7	.28	14.00	13.69
C_5	183.0	0.35		.48	12.28	...
C_6	177–177.3	.02	6.48		10.94	11.18
C_7	171.5	Too small	2.49	.11	9.80	9.82

Melting points of higher members of the series: C_8, 169–169.5; C_{10}, 164.0; C_{11}, 160.5; C_{12}, 159.0; C_{13}, 156–156.4; C_{14}, 154.5; C_{15}, 153.0; C_{16}, 148.5; C_{17}, 149.5–150.

Results of Experiments

In the tables, derivatives of ethylenediamine of the general formula $C_2H_4(NHCOR)_2$, where R is straight chain, are designated as the C_n derivative, where n = the total number of carbon atoms in the acid.

Grateful acknowledgment is made of the assistance of Professor E. Emmet Reid. The writer also wishes to thank Professor Edward Steidtmann for assistance in measuring crystal properties.

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[1] Present address: Chemical Division, Proctor and Gamble Co., Ivorydale, Ohio.

[2] Hofmann, *Ber.*, **21**, 2332 (1888).

[3] Klingenstein, *ibid.*, **28**, 1173 (1895); Chattaway, *J. Chem. Soc.*, **87**, 381 (1905).

[4] Windaus, Dörries and Jensen, *Ber.*, **54**, 2745 (1921); Rosenmund, U. S. Patents 1,926,014 and 1,926,015.

TABLE II

APPEARANCE UNDER THE POLARIZING MICROSCOPE

Derivs.	Crystal system	Habit and extinction	Optical character, biaxial	Elongation	Observed ns[a] Low	Observed ns[a] High
C_2	Triclinic or monoclinic	Flat needles, 40–41°	Negative	Positive	1.53[b]	1.595[c]
C_3	Triclinic	Fibrous, 2–13°	Negative(?)	Positive	1.441–1.442	1.545–1.546
C_4	Triclinic	Flat, elongated, 3–6°	Positive	Positive	1.40–1.45	1.52–1.525
C_5	Triclinic	Flat, some rectangular	....	Positive in needles	1.46	1.52
C_6	Triclinic	Flat, elongated, 5–6°	Positive	Positive	1.46–1.475	1.515–1.520
C_7	Triclinic	Flat, elongated. Rectangular, 0–2°	Positive	Positive	1.48–1.485	1.52–1.530

[a] The ns given above represent those which are observed on the crystals as they lie on the slide in immersion liquids. Since the principal optical directions lie oblique to this surface, the actual minimum index alpha and maximum index gamma cannot be directly measured. [b] Beta. [c] Gamma.

Summary

1. The melting points of the normal fatty acid diamides of ethylenediamine are given, from acetyl to heptadecoyl, less C_9.

2. The solubilities and some crystallographic properties of the first six members of the series are recorded.

LEXINGTON, VIRGINIA RECEIVED JUNE 24, 1935

[CONTRIBUTION FROM SEVERANCE CHEMICAL LABORATORY, OBERLIN COLLEGE]

Preparation of a Potent Vitamin A Concentrate[1]

BY HARRY N. HOLMES, HAROLD CASSIDY, RICHARD S. MANLY AND EVA R. HARTZLER

Since Vitamin A has not yet been isolated, it is highly desirable that improved methods for the preparation of potent concentrates be developed.

Other workers in this field have obtained Vitamin A concentrates of very high values. Karrer, Morf and Schöpp[2] in 1931 succeeded in preparing a pale yellow oil of approximately 105,000 "blue value." (Values based upon the Carr–Price[3] color test and upon Karrer's own calculation that his standard cod-liver oil had a Vitamin A potency of 10 blue value). Heilbron, Heslop, Morton, Webster, Rea and Drummond[4] have published data on a concentrate of 65,000 blue value, while Carr and Jewell[5] have more recently obtained a concentrate of 78,000 blue value. The English workers, like Karrer, based their valuation upon the Carr–Price color test. Their concentrates were prepared by vacuum distillation.

The "blue value" signifies the number of blue units read with a Lovibond tintometer for 0.04 g. of solid dissolved in anhydrous chloroform immediately after reaction with the antimony trichloride reagent. It is obvious that "blue units per gram" could also be calculated by multiplying "blue value" by 25.

Concentration by Freezing.—The liver oil of halibut (Hippoglossus) was saponified in the Parke–Davis laboratories, the non-saponifiable portion removed by a solvent and most of the cholesterol frozen out. In our laboratory the first step was to transfer the concentrate from methyl alcohol to pentane by washing out the alcohol with water.

The pentane solution was next subjected to drastic freezing for a week or ten days in a bath of ethyl alcohol and carbon dioxide snow. To filter out the noticeable precipitate we employed in our earlier work an ultra-filter bomb of heavy metal which could be entirely surrounded by a bath of ethyl alcohol and carbon dioxide snow. Through this strong filter (Fig. 1) the filtrate could be forced by a pressure of 50–100 pounds of nitrogen. This method was very satisfactory when working with small quantities as it prevented any warming up of the mixture with annoying dissolving of the precipitate during filtration and also permitted the exclusion of air. With larger quantities, however, the filtration of such

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(1) This research was made possible through the cordial coöperation of Parke, Davis & Company, of Detroit, and the Abbott Laboratories, of North Chicago. Paper read at the New York Meeting of the A. C. S., Division of Biochemistry, April 22, 1935.

(2) Karrer, Morf and Schöpp, *Helv. Chim. Acta*, **14**, 1036 (1931).

(3) Carr and Price, *Biochem. J.*, **20**, 497 (1926).

(4) Heilbron, Heslop, Morton, Webster, Rea and Drummond, *ibid.*, **26**, 1178 (1932).

(5) Carr and Jewell, *Nature*, **131**, 92 (1933).

gummy material was found to be too slow. In our more recent work we have adopted a suggestion by Dr. Karl Link, using suction filtration through a layer of carbon dioxide snow packed in a coarsely sintered glass filter. Such filtration is rapid, requiring only a few minutes for completion. Moreover, the carbon dioxide snow prevents warming up of the solution and provides an inert atmosphere for protection of the vitamin. The filtrate was then allowed to warm up to room temperature and some of the solvent was removed under suction to remove the dissolved carbon dioxide.

The solution (under nitrogen) was stored in carbon dioxide snow until ready for use. By this process the concentrate usually was improved from the 30,000–40,000 blue value as received in our laboratory to a value of 45,000–50,000. In one instance a blue value of 60,000 was obtained.

Concentration by Tswett Columns.—The column method of filtration through adsorbent powders as originated by the botanist, Tswett,[6] for the separation of plant pigments is peculiarly suited to the concentration of such a heat-sensitive substance as Vitamin A. The more highly adsorbed materials appear in bands near the top of the column, while the less strongly adsorbed materials appear farther down the column.

Karrer and Morf[7] used this method quite extensively in research with vitamin A and with the carotenoid pigments. They used calcium oxide or hydroxide, while Karrer, Morf and Schöpp[2] used alumina, and Karrer and Schöpp employed calcium carbonate.[8]

Although Karrer and his associates cut the adsorbent column into three sections and extracted from the rich middle section, we have found it to be advantageous to obtain fractions of different degrees of potency by washing the entire column with a suitable solvent. The less strongly adsorbed and more soluble materials are washed through first with the more strongly adsorbed and less soluble material following at a slower rate. Frequent changes of the receiver (maintaining an atmosphere of nitrogen) then enable us to obtain filtrate fractions of varying composition.

Although such a well-known adsorbent as carbon must have been tried, its use has not been reported, probably because of serious loss of the vitamin due to oxidation. We have used Norit carbon very extensively with excellent results, but only after taking great precautions in its activation to remove air and replace it with nitrogen.

Since carbon is a non-polar adsorbent while magnesia is somewhat polar it would be expected that the two should show somewhat different preferential adsorption from a complex mixture such as the crude vitamin A concentrate. With this idea in mind we have adopted the procedure of running the solution of concentrate first through carbon and then through a magnesia prepared from the precipitated hydroxide with the idea that the carbon would remove certain impurities and the magnesia others with a resulting product of greater purity than that obtained from either adsorbent alone.

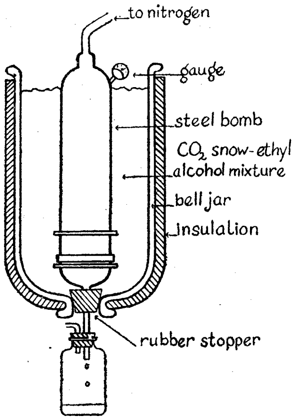

Fig. 1.—Low temperature filtration.

Results.—A large number of filtrate fractions have been obtained in this Laboratory with blue values of 100,000 or higher.

Using carbon alone we have obtained 41 fractions from several different oils with blue values of from 90,000 to 130,000.

TABLE I

No. of fractions	Blue value
23	90,000–100,000
12	100,000–110,000
5	110,000–120,000
2	120,000–130,000
1	130,000

Using magnesia alone two fractions were obtained with blue values between 90,000 and 100,000.

Using carbon followed by magnesia we have obtained 14 fractions with blue values between 90,000 and 140,000. They are distributed as shown in Table II.

Our first attempt using this procedure gave us the best results so far obtained. Circumstances, however, did not permit us to obtain a biological assay although we had about half a gram of the

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(6) Tswett, *Ber. Botan. Ges.*, **24**, 384 (1906).

(7) Karrer and Morf, *Helv. Chim. Acta*, **16**, 625 (1933).

(8) Karrer and Schöpp, *ibid.*, **16**, 745 (1933).

TABLE II

No. of fractions	Blue value
7	90,000–100,000
2	100,000–110,000
1	110,000–120,000
1	120,000–130,000
2	130,000–140,000
1	140,000

richest material. We had removed the solvent from the oily residue under reduced pressure and had stored it under nitrogen in carbon dioxide snow for two days. At the end of that period the oily material had become crystalline, and its blue value had fallen to 1050. We learned too late that our valuable half gram should have been stored at once in cold methyl alcohol for protection.

It may be of interest to note that Karrer considered a standard cod liver as having a "blue value" of 10. Upon this basis our best concentrate was at least 14,000 times as potent in vitamin A as such standard cod-liver oil while Karrer's best concentrate was 10,500 times his standard.

Description of Color Test.—The values given in this paper were all measured by the Carr–Price reaction[3] using antimony trichloride in anhydrous chloroform according to the directions of the "Cod-liver Oil Colour Test Sub-Committee of the British Pharmacopoeia Commission" and reading blue values with a Lovibond tintometer.

Drummond and Morton[9] examined six oils biologically, colorimetrically and spectroscopically and found very good agreement between the three methods. More recently Lathbury[10] has stated that cod-liver oils and vitamin A concentrates show a constant ratio between the results of the biological, chemical and physical methods of measurement.

We read rather consistently, with our particular tintometer, several per cent. higher than Parke, Davis & Company, so all values in this paper have been corrected accordingly. Recently, we found our colorimetric assays of a group of four liver oils in close agreement with those by Parke, Davis & Company in Detroit, and in their English laboratory at Hounslow. Two of these oils had been cross checked with the spectro-absorption instrument in Morton's laboratory (England) and Brode's laboratory (Ohio State University) as well as in Detroit.

Bio-assay of a Potent Concentrate.—Parke, Davis & Company made a bio-assay on one of our earlier potent concentrates which was obtained by use of a carbon column and which gave for us a color assay of 94,000 blue value. The material was dissolved in a commercial cottonseed oil to which had been added 1% of soy bean lecithin as antioxidant. The bio-assay value obtained corresponded to 91,200 blue value, the feeding level required being 0.24 gamma per day, a feeding level remarkably low in comparison with the others recorded in the literature.

The same sample was also analyzed in the Parke–Davis laboratory for vitamin D and found to contain 18,620 Steenbock D units per gram.

Effect of Moist Air on Color Test.—We have recently demonstrated in this Laboratory that an increase in humidity has an inhibiting effect on the formation of the blue color with the antimony trichloride reagent. By enclosing our tintometer, and all apparatus, in a glass case in which we were able to control the humidity to some extent we obtained readings showing an average of over 10% decrease in the blue values with a rise in relative humidity from 35 to about 60%. The best vitamin A values we have so far obtained were read in July, 1934, under humid conditions in our basement, which averaged about 20°F. (11°C.) cooler than the official outdoor temperature. It seems probable, therefore, that our reported values of that month really deserved a higher rating.

Materials

Pentane.—The pentane used was a low boiling petroleum fraction (b. p. 30–45°) obtained from the Viking Distributing Co., Charleston, W. Va.

Chloroform.—U. S. P. grade from the Dow Chemical Co., Midland, Michigan.

Antimony Trichloride.—Baker C. P. anhydrous antimony trichloride. The reagent was made up with especially purified dry chloroform to a concentration of 21–23% of antimony trichloride in chloroform.

Carbon.—Grade "A," pharmaceutical Norit, obtained from L. A. Salamon Co., 216 Pearl St., New York City.

Magnesium Oxide.—In the earlier work we prepared our own magnesium oxide from Parke–Davis milk of magnesia by filtering and drying. This process was quite tedious, however, and we have recently been using a similar magnesia, "Micron Brand," 2641, obtained from the California Chemical Corp., Newark, California. This was used by Strain[11] in the purification of carotenes.

Alumina.—The alumina used was purchased from the J. T. Baker Company, Phillipsburg, N. J., under the trade name of "Hydralo."

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(9) Drummond and Morton, *Biochem. J.*, **23**, 785 (1929).

(10) Lathbury, *ibid.*, **28**, 2254 (1934).

(11) Strain, *J. Biol. Chem.*, **105**, 523 (1934).

Silica.—The silica used was Holmes' chalky silica gel prepared in the Severance Laboratory.

"Hyflo Super Cel."—A siliceous earth with practically no adsorbent qualities, purchased from Johns-Manville, Cleveland.

Nitrogen.—Compressed gas, from the Ohio Chemical Co., Cleveland, containing less than 0.05% oxygen. This trace of oxygen was removed by passing the gas through alkaline pyrogallol.

Methods

Our columns were set up according to the diagram in Fig. 2. The tip of the column tube was tightly plugged with glass wool and the entire system was then filled with nitrogen. A thin mixture of activated carbon and pentane, well shaken, was then poured into the column and allowed to settle. While the level of the liquid fell to the upper level of the column of carbon the tube was tapped with a block of wood to dislodge gas bubbles. A pentane solution of the concentrate was then carefully added and allowed to filter down through the carbon with the aid of slight suction at B, while nitrogen entered the top of the column at A. After all the solution of concentrate had entered the carbon, pentane was carefully added through the separatory funnel and allowed to wash the concentrate down through the carbon. Fractions of the filtrate of from 50 to 150 cc. each were collected. Upon changing receivers, stopcocks B and C at the bottom were closed (cutting off suction), B was opened to admit nitrogen to the partially evacuated receiver before removal, and a clean nitrogen-filled bottle was connected.

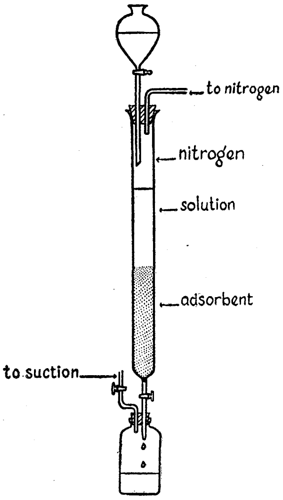

Fig. 2.—Column for selective adsorption.

Only slight suction can be used, otherwise the powdered adsorbent packs too tightly for effective filtration. To aid in hastening the filtration through magnesia columns we used a heat-treated siliceous earth, "Hyflo Super Cel," mixed in equal part by weight with the magnesia as suggested by Strain in his work on carotenes. This siliceous earth is a poor adsorbent but aids in more uniform packing of the magnesia and in more rapid filtration. Both powders were activated together (after thorough mixing) in order to remove any moisture or oxygen present.

Our usual practice was to filter about 6 g. of concentrate, contained in 50 cc. of pentane solution, through a column of carbon 2.5 cm. in diameter and 23 cm. high (about 40 g. of carbon). The filtrate from a column of this size contained from 1 to 40 mg. per cc.

Summary

1. Cholesterol and some other impurities were frozen out of a pentane solution of the nonsaponifiable portion of halibut-liver oil; the resulting solution was then fractionated by Tswett adsorption columns with an improved technique. Using a column of a specially prepared oxygen-free carbon followed by treatment with a column of a new type magnesia a concentrate of vitamin A at least 40% more potent than any previously recorded was obtained.

2. Lovibond tintometer readings were checked biologically and spectrographically in the Parke–Davis laboratories and elsewhere.

3. The most potent concentrate had a blue value of at least 140,000.

OBERLIN, OHIO RECEIVED JULY 16, 1935

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Mercuration of Ethylenes and Reactions of the Methoxy Mercurials

BY GEORGE F. WRIGHT[1]

Introduction

When an unsaturated compound is treated with mercuric acetate in alcohol solution, the elements of methoxymercuric acetate combine with the ethylene. The nature of the product has been the subject of controversy for some years and the evidence has been well summarized by Adams, Roman and Sperry.[2] These authors as well as others[3,4] have rejected Manchot's hypothesis[5] that such mercurials are molecular compounds of the type $RCH{=}CHR'\cdot R''OHgX$ (I) and they have preferred the second of two mechanisms of formation which designate the reaction as ordinary addition to a double bond. More recent work has substantiated the structure for the mercurials as III rather than I. Marvel and co-workers,[6] by separating disastereomers with different rotations from the mercuration of optically active cinnamic esters, have shown that

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[1] National Research Fellow in Chemistry.

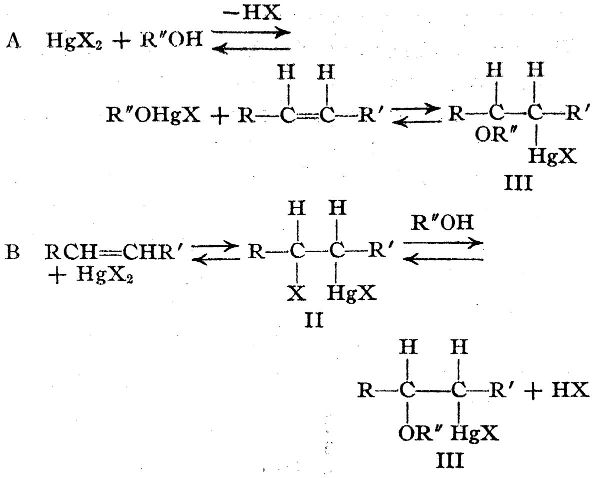
[2] Adams, Roman and Sperry, THIS JOURNAL, **44**, 1781 (1922).

[3] Mills and Adams, *ibid.*, **45**, 1842 (1923).

[4] Middleton, *ibid.*, **45**, 2763 (1923).

[5] Manchot, *Ann.*, **420**, 174 (1920); *ibid.*, **421**, 316, 331 (1921).

[6] Sandborn and Marvel, THIS JOURNAL, **48**, 1409 (1926); Griffith and Marvel, *ibid.*, **53**, 789 (1931).



asymmetric centers are actually produced in the synthesis. Likewise the instability of the mercurials finds a parallel in the analogous organomagnesium compounds,[7] which exhibit the same tendency to decompose into the unsaturated compound and the alkoxy metal salt.

This communication is concerned with further proof for the existence of structure III as well as a critical study of its mode of formation. To this end the methoxymercurials have been prepared from *cis* and *trans* methyl cinnamate, isostilbene, styrene, propenylbenzene, cyclohexene and 1-phenylbutadiene-1,3. In general their properties are identical with those of analogous mercurials already known. Specifically the rates of formation as well as the type differences intrinsic in the ethylenes used indicate that the first of the alternative mechanisms suggested by Adams, Roman and Sperry actually takes place. This disposes of an obnoxious feature of mechanism B, namely, the formation of the ether III from the ester II at a carbon atom which would not be expected to enhance the tendency toward this limited reaction. This tendency should be greater when such a carbon atom is surrounded with increased unsaturation; the greater ease of mercuration found with styrene and cyclohexene as compared with methyl cinnamate and isostilbene suggest that this etherification is at least not the controlling step in the reaction.

Furthermore, a kinetic study of *cis* methyl cinnamate mercuration at varied concentrations indicates that the reaction is second order. The results are complicated by the existence of a measurable equilibrium, demonstrated in the cases of methyl α-acetoxymercuri-β-methoxy-β-phenylpropionate and α-acetoxymercuri-β-methoxy-β-phenylethane; nevertheless, the agreement among the second order constants leaves little doubt that the rate-controlling reaction is bimolecular. Such an order militates against mechanism B, where the etherification involved in the second step should be pseudo-unimolecular, especially in the higher dilutions.

The question arises whether the formation of II in the first step of mechanism B might not control the rate and thus explain the second order constants. It is undeniable that addition products of unhydrolyzed mercuric salts to ethylenes do exist,[8] either as type II or as the molecular compound $RCH{=}CHR'\cdot HgX_2$ (IV). However, Hugel and Hibou have observed that addition compounds of type II are formed in a few minutes. With the exception of the styrene reaction, none of the methoxy mercurials (Type III) is formed so rapidly. Furthermore, if formation of II were the rate-controlling step the choice of alcohol used as reactant should have relatively little effect upon the reaction velocity whereas, in point of fact, the mercuration proceeds slowly in water but is much more rapid in methanol, although progressively slower when higher alcohols are employed.[9] It is, then, unlikely that the second order constants are a result of the reactions involving mechanism B.

Mechanism A is supported by several innovations in the reaction. First, the addition of a small amount of nitrate ion markedly accelerates the process. This would be expected if hydrolysis of mercuric salt were a prerequisite to formation of III.[10] Second, the addition of sodium methylate (necessarily toward the end of the reaction to avoid precipitation of mercuric oxide) soon carries the reaction to completion. This latter modification, to be sure, does not differentiate between mechanisms A and B. Its action becomes more understandable when addition of an equivalent of acetic acid to a methanol solution of the acetoxymercurial is found not to shift the equilibrium. Likewise when cyclohexene is treated with methoxymercuric chloride, prepared by interaction of equivalent amounts of sodium methylate and mercuric chloride, the product, 1-chloromercuri-2-methoxycyclohexane,

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[7] Tallman, THIS JOURNAL, **56**, 126 (1934).

[8] Hugel and Hibou, *Chimie et Industrie*, Special No., 296 (Feb., 1929) [*C. A.*, **23**, 3898 (1929)].

[9] Schoeller, Schrauth and Struensee, *Ber.*, **43**, 695 (1910).

[10] Mellor, "Inorganic and Theoretical Chemistry," Longmans, Green and Company, New York City, 1923, Vol. IV, p. 991.

is difficult to explain on any basis other than mechanism A. Unfortunately for a good case, the formation of intermediates like type II or IV can also be demonstrated. Thus, if styrene in an inert solvent is treated with mercuric acetate for some hours and the solvent and excess of styrene are removed, the residue when treated with methanol is converted to α-acetoxymercuri-β-methoxy-β-phenylethane. When this method is applied to cyclohexene the mercurial does not form. Although the reaction with styrene may be misleading because of difficulty in extracting the excess of reactant, the significant yield indicates that the intermediate does form. There is, however, no good reason to assume that the styrene intermediate reacts *per se* rather than in its dissociation fragments, styrene and mercuric acetate.

There is, of course, the possibility that in methanol solution methoxymercuric acetate exists as methoxy and acetomercury ions which add at random to the double bond. This should give rise to a mixture of diastereomers, whereas each mercurial actually produced is a chemical individual. Furthermore, when *cis* and *trans* methyl cinnamates are mercurated the isomeric racemic forms are obtained, respectively. On the basis of random addition the pure compounds obtained would not be expected. The fact that methyl *cis* cinnamate reacts about three times as fast as the *trans* isomer,[11] as shown by the relative half-lives (Fig. 1), likewise indicates that the addition proceeds by way of the undissociated methoxymercuric acetate, for the space configuration should offer but little hindrance to the ions. In the case of the geoisomeric stilbenes this is even more apparent since the *trans* stilbene does not react at all, although a good yield of mercurial is obtained from the *cis* isomer (isostilbene). It is in keeping with this concept that nitrate ion (assumed only to promote alcoholysis) does not cause *trans* stilbene to mercurate.

On the basis of this evidence it is believed that formation of the α-methoxy mercurials proceeds *via* mechanism A, as a result of the tendency of mercuric salts to hydrolyze or alcoholize in an appropriate medium.

Since the methoxy mercurials are stable toward aqueous alkali, it has been customary to consider the mercuration complete when this reagent no longer precipitates mercuric oxide. This test has been found to be unreliable and quite misleading. The disappearance of mercuric ion may coincide, as in the case of the rapid reaction with styrene, with completion of the formation of III, but in the greater number of cases the reaction is not finished when the mercuric ion disappears. This discrepancy between removal of mercuric ion and the end of the reaction is illustrated in Fig. 1, the notation Hg indicating the time at which no mercuric ion is detectable. Such a test is evidently not an absolute criterion of completion of reaction.

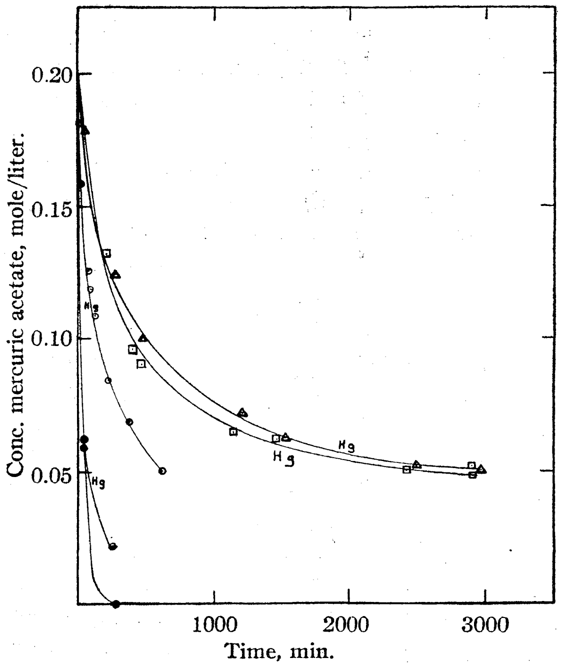

Fig. 1.—△, Isostilbene; □, *trans* methylcinnamate; ○, *cis* methylcinnamate; ◒, *trans* methylcinnamate + nitrate ion; ●, isostilbene + nitrate ion.

Reports concerning the instability of these mercurials have not been exaggerated. In addition to the ease of acid splitting, they decompose thermally to regenerate the unsaturated compounds. This has been shown in the case of *meso* and *dl* methyl α-chloromercuri-β-methoxy-β-phenylpropionate, the decomposition temperatures being 159 and 170°, respectively. In both cases *trans* methyl cinnamate is the sole product.

When methyl α-acetoxymercuri-β-methoxy-β-phenylpropionate is treated with alcoholic ammonium sulfide, the acetoxymercuri group is replaced by hydrogen and methyl β-methoxy-β-phenylpropionate is produced.[12] It has been

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[11] This is in agreement with selective mercuration of the cinnamic acids, Biilmann, *Ber.*, **35**, 2571 (1902).

[12] Schoeller, Schrauth and Struensee, *ibid.*, **44**, 1432 (1911).

found that hydrogen sulfide in alcoholic pyridine, also aqueous sodium thiosulfate, is equally efficient in this transformation. The reaction appears to be limited to acids and esters, since every other mercurial tried yielded only the parent ethylene. In the case of the styrene mercurial, using sodium thiosulfate there was evidence for the transient existence of either the thiosulfate mercurial[3] or the *bis*-mercurial but the intermediate could not be isolated and styrene was the only product.

The positions assumed by the elements of methoxy mercuric acetate upon addition to a double bond are known with certainty in *dl* methyl α-acetoxymercuri-β-methoxy-β-phenylpropionate. The *meso* form derived from methyl *cis* cinnamate was shown to have a similar structure by conversion with sodium thiosulfate to β-methoxy-β-phenylpropionic acid. Since this method failed with every other mercurial, the structures of the styrene and propenylbenzene mercurials were ascertained by bromination and subsequent elimination of hydrogen bromide with sodium methylate. The resulting α,β-unsaturated ethers were hydrolyzed to acetophenone and propiophenone. As a reliable structure proof, such a method is obviously dependent on the mechanism of bromination of these dissociable mercurials.

Bromination of these acetoxymercurials was found to proceed stepwise. The first equivalent of bromine formed the bromomercuri compound (apparently with liberation of peracetyl bromide), while the second equivalent severed the C–Hg bond to form the bromo derivative. In like manner, bromocyanogen, although incapable of breaking the C–Hg link, does react to give the bromomercurial. As another case in point, the first equivalent of acetyl chloride reacts with methyl α-acetoxymercuri-β-methoxy-β-phenylpropionate to form the chloromercuri compound; an excess of this reagent produces methyl *trans* cinnamate.

The mercuration of 1-phenylbutadiene-1,3 proceeds stepwise and, on the basis of insecure ozonization data, the first addend enters the 3,4-positions. All attempts to establish the positions of the methoxy and mercuri groups proved fruitless. Only one of these attempts is worthy of mention. When the 3,4-[methoxychloromercuri]-1-phenylbutene-1 was reduced with one equivalent of hydrogen, using the Adams catalyst, the products were 1-phenylbutadiene-1,3 and 1-phenylbutane; the reduction proceeded as if the addend were not present.

The 1-chloromercuri-2-methoxycyclohexane initially produced from cyclohexene has been designated as the labile form, inasmuch as long refluxing in ethanol converts it to a lower melting isomer, the stable form.

The author takes this opportunity to thank Professor E. P. Kohler for the suggestions offered during the course of this work. He is also indebted to Dr. P. D. Bartlett for aid in interpreting the kinetic data.

Experimental

Titration with Potassium Thiocyanate.—When 0.001 mole of *trans* methyl α-acetoxymercuri-β-methoxy-β-phenylpropionate was dissolved in 5 cc. of methanol and this solution thrown into 100 cc. of water, titration with standard alkali, using phenolphthalein as the indicator, showed an equivalence of one. The addition of ferric nitrate dispersed the pink color; subsequent titration with standard potassium thiocyanate showed a mercury equivalence of 0.525. This indicated a dissociation[13] of 5% since the organomercurial consumes only half of the thiocyanate required for a mercuric salt. The percentage of dissociation was unaffected by addition of 0.0005 mole of acetic acid.

A similar titration with α-acetoxymercuri-β-methoxy-β-phenylethane consumed one equivalent of alkali and one mercury equivalent of thiocyanate. Since it was evident that the thiocyanate was decomposing this mercurial, the water solution, prior to titration, was extracted twice with 5-cc. portions of chloroform (per 0.001 mole of mercurial). The water solution now contained only inorganic mercury since salts of mercury are almost insoluble in chloroform, although the organomercurials are extremely soluble in this extractant. Titration of this solution with thiocyanate showed that 0.072 equivalent of mercuric salt remained after extraction; the styrene mercurial was 7.2% dissociated.

Trans methyl α-acetoxymercuri-β-methoxy-β-phenylpropionate was again titrated using the chloroform extraction method and the compound was found to be 2.5% dissociated. This latter figure is probably more accurate than the 5% value because the endpoint is very ephemeral when much of the organomercurial is present.

Using this method of following the mercury concentration, solutions of 0.01 mole of mercuric acetate and 0.01 mole of the unsaturated compound in methanol were made up to the desired volume and the reaction was maintained at 25 ± 2°. Samples were withdrawn at intervals, diluted with 100 cc. of water, and titrated within three minutes. Since the mercuration in water is much slower than in methanol, this error is of no significance. The rate of reaction with styrene was much too fast to be measured but at its completion 8% of the mercuric acetate remained. This checks closely with the value (7.2%) obtained for the dissociation of the mercurial in pure methanol. The reac-

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(13) Dissociation in this sense means reversion to methoxymercuric acetate and the unsaturated compound.

tion with cyclohexene was somewhat slower but the titration (even with the chloroform extracted solution) was very erratic and at best it indicated that the acceleration due to added sodium methylate was approximately that observed in the actual preparation of the mercurial.

A series of such determinations with *cis* methyl cinnamate at concentration of 0.4, 0.2 and 0.1 molar gave a second order constant varying from 0.041 to 0.032 within the first half-life of the reaction. The second order constant for the reaction with isostilbene varied from 0.011 to 0.006, while that for *trans* methyl cinnamate was about 0.012. When the mercuration of this latter compound (at 0.2 molar) was three-fourths completed (twenty-nine hundred minutes), upon addition of 0.05 mole of sodium methylate, further titration showed the equilibrium was attained in ten minutes. The effect of prior addition of 0.05 g. of concentrated nitric acid to the 0.2 molar mercuric acetate solutions used in the *trans* methyl cinnamate and isostilbene reactions is shown in Fig. 1.

Mercuration of *trans* Methyl Cinnamate.[9]—To a solution of 3.18 g. (0.01 mole) of mercuric acetate in 25 cc. of methanol was added 0.05 g. of concentrated nitric acid, followed by 1.94 g. (0.012 mole) of methyl cinnamate. After seventy-five minutes at 25° a test portion gave no precipitate with 10% sodium hydroxide and the product began to crystallize in the reaction mixture. In a similar run, but using no nitric acid, about thirty-six hours must elapse before these conditions prevail, although the reaction is complete in eight hours when carried out at 50°. The acetoxymercuri compound was immediately filtered off (wt. 1.11 g., m. p. 142°) and the filtrate treated with dilute sodium chloride solution to yield 2.70 g. of methyl α-chloromercuri-β-methoxy-β-phenylpropionate, m. p. 134°. The total yield is 88% as compared with 84% in the analogous run using no nitric acid.

When the acetoxymercuri compound is treated with one equivalent of acetyl chloride in chloroform or acetone, the chloromercuri compound results. An excess of acetyl chloride regenerates *trans* methyl cinnamate. The chloromercuri compound is recovered unchanged from twelve hours of refluxing in ethyl acetate.

Mercuration of *cis* Methyl Cinnamate.—A solution of 1.78 g. (0.011 mole) of *cis*-methyl cinnamate[14] (m. p. −3°) and 3.18 g. (0.01 mole) of mercuric acetate in 25 cc. of methanol was filtered after nine hours and the filtrate treated with 2% sodium chloride solution. The precipitated methyl α-chloromercuri-β-methoxy-β-phenylpropionate was crystallized from ethanol to melt at 141° and weighed 2.07 g. (50%). A mixed melting point with the diastereomer obtained from *trans* methyl cinnamate (m. p. 134°) was lowered 20°.

Anal. Calcd. for $C_{11}H_{13}O_3HgCl$: C, 30.77; H, 3.05. Found: C, 31.10; H, 3.13.

When either of the diastereomers was decomposed thermally under 25 mm. pressure the distillate (*ca.* 50% of theoretical) was entirely *trans* methyl cinnamate. Under these conditions the *cis* mercurial decomposed at 157°; the *trans* decomposed at 170°. When the *cis* mercurial is refluxed for eight hours in ethyl acetate there is no tendency toward isomerization; the mercurial is recovered unchanged.

β-Methoxy-β-phenylpropionic Acid.—To a 10% sodium thiosulfate solution was added 4.52 g. (0.01 mole) of *trans* methyl α-acetoxymercuri-β-methoxy-β-phenylpropionate. After ten minutes of agitation ether was added and the reaction set aside for twelve hours. The ether layer was separated. The aqueous layer was filtered to remove a black precipitate and the filtrate carefully acidified with 10% hydrochloric acid. The acid which slowly separated melted at 102°. It was combined with the acid of similar melting point obtained by saponification of the separated ether layer with 10% sodium hydroxide solution. Total yield was 1.09 g. or 60.5%. A similar treatment of the *cis* mercurial yields the identical acid, as does the reaction between sodium thiosulfate and anhydro α-hydroxymercuri-β-methoxy-β-phenylpropionic acid.

α - Chloromercuri - β - methoxy - α,β - diphenylethane.—After three days at room temperature a solution of 12.72 g. (0.04 mole) of mercuric acetate and 6.3 g. of isostilbene (b. p. 102° (2 mm.)) in 100 cc. of methanol was stirred while 2% aqueous sodium chloride was added slowly. The solid was filtered off and crystallized from ethanol to melt at 141°. It weighed 11.18 g. or 64% yield. Recrystallization from ethanol raised this melting point to 143°. When the reaction was refluxed the time was decreased to one-third. Addition of 0.05 g. of *concd.* nitric acid decreased the reaction time to four hours at room temperature. *Trans* stilbene could not be mercurated under any of these conditions.

Anal. Calcd. for $C_{15}H_{15}OHgCl$: C, 40.27; H, 3.38. Found: C, 40.35; H, 3.55.

Every attempt to regenerate pure isostilbene or to form α,β-diphenylethyl methyl ether failed. Treatment of the mercurial with hydrogen sulfide in alcoholic ammonia or alcoholic pyridine reaction with sodium thiosulfate, steam distillation from aqueous hydrochloric acid, oxalic acid or potassium iodide all yielded an equilibrium mixture of the isomeric stilbenes.

α-Acetoxymercuri-β-methoxy-β-phenylethane.—To a suspension of 159 g. (0.5 mole) of mercuric acetate in 1 liter of methanol was added 52 g. (0.5 mole) of styrene. The mercuric salt dissolved immediately; a test portion gave no mercuric oxide with 10% aqueous sodium hydroxide. A solution of 20 g. (0.5 mole) of sodium hydroxide in 25 cc. of water was added; following this treatment 800 cc. of methanol was distilled off. The residue was filtered and the filtrate evaporated *in vacuo.* The residue was extracted with 50 cc. of boiling benzene to remove sodium acetate and the resulting solution diluted with 1600 cc. of boiling petroleum ether (b. p. 60–70°). After a slow crystallization 117 g. (60%) of product melting at 64–65° was filtered off. The evaporated filtrate yielded 12 g. of impure product. Recrystallization from the mixed solvent raised the melting point to 70°.

Anal. Calcd. for $C_{11}H_{14}O_3Hg$: C, 33.42; H, 3.57. Found: C, 33.65; H, 3.78.

The mercurial was unchanged by twelve hours reflux with *t*-amyl alcohol. It reverted to styrene in boiling acetic anhydride but this reagent is without effect at 25°. Acetyl chloride (in acetone or chloroform), methylmagne-

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[14] I am indebted to Professor G. B. Kistiakowsky for generously supplying the *cis* methyl cinnamate and the isostilbene used in this investigation.

sium bromide[15] or sodium thiosulfate solution (in part) only served to regenerate styrene.

α - Benzoxymercuri - β - methoxy - β - phenylethane.—A solution of 3.18 g. (0.01 mole) of mercuric acetate in 25 cc. of methanol was treated with 1.09 g. (0.011 mole) of styrene. Eight cc. of 10% aqueous sodium hydroxide (0.02 mole) was added, followed by 1.22 g. (0.01 mole) of benzoic acid. After filtration the solution was diluted with water. The crystalline precipitate weighed 3.73 g. (82%) and melted at 79°. It was crystallized from 110 cc. of petroleum ether (b. p. 60–70°) to melt at 80°. The compound was unchanged by eight hours of refluxing in toluene.

Anal. Calcd. for $C_{16}H_{16}O_3Hg$: C, 42.01; H, 3.53. Found: C, 41.73; H, 3.53.

α - Bromomercuri - β - methoxy - β - phenylethane was obtained almost quantitatively by treating the acetoxymercuri compound either with an excess of aqueous potassium bromide or with one equivalent of bromine in methanol solution at 0°. It was likewise obtained in 50% yield by treating a solution of the acetoxymercuri compound in either methanol or chloroform with two equivalents of bromocyanogen. It was crystallized from ethanol to melt at 63°.

Anal. Calcd. for $C_9H_{11}OHgBr$: C, 26.03; H, 2.67. Found: C, 26.10; H, 2.67.

Intermediate in Styrene Mercuration.—The existence of the intermediate in this reaction was demonstrated by adding 3.18 g. (0.01 mole) of mercuric acetate to a solution of 1.09 g. (0.011 mole) of styrene in 10 cc. of dioxane. After several days of intermittent shaking the reaction was filtered and the filtrate evaporated under 2 mm. pressure on a water-bath at 30°. The gummy residue was washed four times with 25-cc. portions of petroleum ether (b. p. 20–40°) and was then covered with 10 cc. of methanol. After twenty-four hours the methanol was removed *in vacuo* and the residue treated with dilute aqueous potassium bromide. The precipitate was crystallized from ethanol to give a 26% yield of the bromomercurial, melting point 63°, identified by mixed melting point.

β-Methoxy-β-phenylethyl Bromide.—Following the prescribed procedure,[4,16] a 70% yield of this compound, b. p. 84–86° (3 mm.), was obtained from the bromomercurial. The reaction is slower in chloroform solution; the mercuric bromide precipitates and the resulting solution must be washed with sodium sulfite to remove hypobromite, but the product is identical.

α-Methoxy-α-phenylethylene was obtained in 45% yield (b. p. 86–89° (18 mm.)) by refluxing this bromo compound with an excess of sodium methylate solution. It was identified by hydrolysis with 2.5% aqueous sulfuric acid to acetophenone, authenticated by mixed melting point.

β - Chloromercuri - α - methoxy - α - phenylpropane.—A solution of 15.9 g. (0.05 mole) of mercuric acetate in 125 cc. of methanol was treated with 6.89 g. (0.058 mole) of phenylpropene-2 (b. p. 57.5–58° (10 mm.)). Within four hours a test portion gave no mercuric oxide with 10% aqueous sodium hydroxide. At the end of eighteen hours 0.05 mole of sodium methylate solution was added. Twenty-four hours later the reaction was filtered and the solvent removed *in vacuo*. The residue was shaken with 2% aqueous sodium chloride. After an hour the aqueous layer was decanted and the gummy residue extracted with 100 cc. of boiling ethanol. Six days elapsed before crystal clusters formed which were filtered off and crystallized from ethanol to melt at 95–95.5°, weight 4 g. or 21%.

Anal. Calcd. for $C_{10}H_{13}OHgCl$: C, 31.17; H, 3.40. Found: C, 31.00; H, 3.40.

Since the mother liquors were not amenable to further crystallization the solvent was removed *in vacuo* and the residue was dissolved in 50 cc. of chloroform followed by 4.8 g. (0.03 mole) of bromine. After twenty-four hours the colorless solution was decanted from mercuric salt and washed with iced sodium sulfite solution, then with water and finally dried with anhydrous sodium sulfate. Following evaporation of the solvent the residue was distilled under 14 mm. pressure. The distillate, b. p. 107–125°, wt. 2.24 g., was refluxed for five hours with 0.05 mole of sodium methylate solution. The methanol was removed by evaporation, the residual oil being taken up in ether, washed to neutrality with water, dried with anhydrous sodium sulfate and distilled *in toto*. The distillate was hydrolyzed with alcoholic hydrochloric acid[17] and the semicarbazone prepared directly from this solution. This derivative contained an alkali insoluble impurity which was crystallized from methanol to melt at 183°. However, the great part of the product was precipitated by neutralizing the alkaline solution and was crystallized from ethanol to melt at 173–174°. A mixed melting point with propiophenone semicarbazone was not lowered.

β-Bromo-α-methoxy-α-phenylpropane was prepared from 0.01 mole of the pure β-chloromercuri-α-methoxy-α-phenylpropane and 0.02 mole of bromine in chloroform solution essentially as described above. The product boiling at 122–125° weighed 1.35 g. (92%), $n^{26}D$ 1.5412.

α-Methoxy-α-phenylpropene was prepared from this bromo compound, by the procedure already described, in 31% yield as an oil, b. p. 96–97° (19 mm.), $n^{26}D$ 1.5347. It was identified by hydrolysis with alcoholic hydrochloric acid; the semicarbazone prepared from this solution showed no depression in melting point when mixed with propiophenone semicarbazone.

Labile 1-Chloromercuri-2-methoxycyclohexane.—A solution of 9.84 g. (0.12 mole) of cyclohexene in 250 cc. of methanol was treated with 3.8 g. (0.1 mole) of mercuric acetate. A test portion removed immediately upon solution of the mercuric salt gave no mercuric oxide with 10% aqueous sodium hydroxide. After thirty-six hours the mercurous salt was filtered off and the filtrate evaporated *in vacuo*. Alternatively if, after a reaction period of ninety minutes, 0.1 mole of sodium methylate solution is added, the reaction can be worked up shortly afterward and the solvent can be removed at atmospheric pressure. The residue was suspended in water and 10% aqueous sodium chloride was added. When the precipitated oil solidified after occasional agitation, it was filtered off. This crude product, wt. 33 g., m. p. 109°, was crystallized from ethanol to weigh 26 g. (75%) and melted at 114–115°. Further purification from a solution of 150 cc. of benzene and 30 cc.

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[15] Middleton, THIS JOURNAL, **45**, 2763 (1923).

[16] Kohler, *ibid.*, **52**, 3728 (1930).

[17] Lauer and Spielman, *ibid.*, **53**, 1533 (1931).

of petroleum ether (b. p. 30–60°) did not raise the melting point.

Anal. Calcd. for $C_7H_{13}OHgCl$: C, 24.07; H, 3.75. Found: C, 23.97; H, 3.92.

Stable 1 - Chloromercuri - 2 - methoxycyclohexane.—When the labile mercurial is refluxed for fifteen hours in ethanol, an isomer, m. p. 86°, crystallizes almost quantitatively from the filtered solution. The melting point is not raised by further crystallization from ethanol.

Anal. Calcd. for $C_{17}H_{13}OHgCl$: C, 24.07; H, 3.75. Found: C, 24.06; H, 3.79.

Intermediates in Cyclohexene Mercuration.—To a solution of 2.7 g. (0.01 mole) of mercuric chloride in methanol was added a solution of 0.23 g. of sodium in 10 cc. of methanol. To the suspension of white precipitate was added 0.98 g. (0.012 mole) of cyclohexene. After twenty-four hours the white precipitate was filtered off; it contained no cyclohexene mercurial and rapidly became yellow in presence of moisture. The filtrate was concentrated *in vacuo* and the residue treated with dilute aqueous sodium chloride. The precipitate was crystallized from ethanol to weigh 0.15 g. (4%). It was 1-chloromercuri-2-methoxycyclohexane, m. p. 114–115°, identified by mixed melting point.

When 0.02 mole of sodium methylate was used under otherwise identical conditions the yield of mercurial was 5%.

Demonstration of the type of intermediate encountered with styrene (*vide supra*) could not be reproduced when 0.01 mole of mercuric acetate was dissolved (with comparative ease) in 5 cc. of cyclohexene. After twenty-four hours the excess of cyclohexene was removed at 30° under 25 mm. pressure and the oily residue extracted five times with 25-cc. portions of petroleum ether (b. p. 20–40°) The washed residue was treated with dilute sodium chloride solution. No chloromercurial could be isolated from the precipitate.

1-Lactomercuri-2-methoxycyclohexene.—Mercuric lactate was prepared by treating a solution of 31.8 g. (0.3 mole) of 85% lactic acid in 200 cc. of water with 21.6 g. (0.1 mole) of red mercuric oxide. After two days with occasional shaking the solution was filtered and the solvent removed *in vacuo*. The residue was diluted with 100 cc. of ethanol. Next day the granular solid was filtered off and washed with alcohol; it weighed 17 g., after drying over sulfuric acid, and melted at 144° with decomposition. Evaporation of the alcoholic filtrate in a current of air yielded successive fractions of impure salt.

To a suspension of 3.78 g. (0.01 mole) of this salt in 25 cc. of methanol was added 0.98 g. (0.012 mole) of cyclohexene. After two days 4 cc. of 10% aqueous sodium hydroxide was added, the solution filtered and the solvent removed *in vacuo*. The residue was extracted with 80 cc. of boiling petroleum ether (b. p. 90–120°). The compound crystallizing therefrom weighed 1.74 g. (43%) and melted at 91–92°. It was recrystallized from the same solvent for analysis (m. p. 92°).

Anal. Calcd. for $C_{10}H_{18}O_4Hg$: C, 29.81; H, 4.51. Found: C, 29.44; H, 4.61.

Chloromercurimethoxyphenylbutene.—To a solution of 3.18 g. (0.01 mole) of mercuric acetate in 25 cc. of methanol was added 1.56 g. (0.012 mole) of freshly distilled phenyl butadiene. After five minutes a test portion gave no precipitate of mercuric oxide with 10% aqueous sodium hydroxide. After four hours the reaction was filtered to remove mercurous salt and 10% aqueous sodium chloride was added slowly to the filtrate. The oil which precipitated soon solidified and was filtered, washed twice with water and twice with petroleum ether. The yield of product melting at 89° was 3.35 g. (85%). It was crystallized from 25 cc. of ethanol to melt at 92°.

Anal. Calcd. for $C_{11}H_{13}OHgCl$: C, 33.25; H, 3.30. Found: C, 33.52; H, 3.37.

Following an identical procedure bromomercurimethoxyphenylbutene was obtained by substituting a solution of potassium bromide. The yield was 4 g. (91%) melting at 75–76°. This was crystallized from 35 cc. of ethanol to melt at 76°.

Anal. Calcd. for $C_{11}H_{13}OHgBr$: C, 29.90; H, 2.97 Found: C, 29.57; H, 2.97.

Ozonization of Chloromercurimethoxyphenylbutene.—A solution of 3.97 g. (0.01 mole) of the mercurial was dissolved in 12 cc. of dry chloroform. This solution was ozonized at 0° for five hours. The solvent was removed in a stream of dry, oxygen-free nitrogen. After adding 10 cc. of water the nitrogen stream was continued for two days; the outlet tube bubbled through a solution of phenylhydrazine hydrochloride. The benzaldehyde phenylhydrazone thus formed (70%) melted at 148–150° and after purification was identified by mixed melting point. A test portion taken from the aqueous suspension of decomposed ozonide at this time gave no mercuric oxide with 10% sodium hydroxide. The aqueous layer was decanted off and the residue washed thoroughly with ether. This residue was then covered with 10 cc. of 5:8 aqueous hydrochloric acid and the passage of nitrogen was resumed but no odor of acrolein could be detected, nor was phenylpyrazoline found in the absorption tube. After twenty-four hours the acid layer when treated with sodium hydroxide precipitated mercuric oxide. The remainder of the decomposed ozonide was found to be chiefly mercurous chloride.

Diacetoxymercuridimethoxyphenylbutane.—To a solution of 6.36 g. (0.02 mole) of mercuric acetate in 55 cc. of methanol was added 1.43 g. (0.011 mole) of phenylbutadiene (b. p. 86° (11 mm.)). After two hours a test portion gave no precipitate with 10% aqueous sodium hydroxide. Twelve hours later 40 cc. of methanol was distilled off and the residue filtered and chilled to 10°. The crystalline product weighed 7.62 g. (35%) and melted at 142–145°. Crystallization from a mixture of 25 cc. of benzene and 35 cc. of petroleum ether (b. p. 60–70°) raised the melting point to 149° with little loss of material.

Anal. Calcd. for $C_{16}H_{22}O_6Hg_2$: C, 27.00; H, 3.12; Hg, 56.40. Found: C, 26.53; H, 3.18; Hg, 56.43.

This procedure was varied by using a 33% excess of mercuric acetate and, subsequent to the twelve-hour reaction period, adding sodium methylate solution until appearance of the first permanent yellow coloration. The reaction after a day was worked up as before to give a 60% yield based on the phenylbutadiene.

Dichloromercuridimethoxyphenylbutane.—A solution of 0.4 g. (0.001 mole) of chloromercurimethoxyphenylbutene in 5 cc. of methanol was treated with 0.32 g. (0.001 mole) of mercuric acetate. The latter dissolved immediately but test portions gave a precipitate with 10% aqueous sodium hydroxide for twelve hours. After thirty-six hours a solution of 10% sodium chloride was added. The precipitated solid melted roughly at 100°. After washing with hot ethanol it melted at 180° and weighed 0.16 g. The compound can be obtained more easily by treating the diacetoxymercuridimethoxyphenylbutane in methanol with exactly two equivalents of dilute hydrochloric acid. The compound crystallizes slowly from acetone.

Anal. Calcd. for $C_{12}H_{16}O_2Hg_2Cl_2$: C, 21.68; H, 2.43. Found: C, 21.60; H, 2.52.

Summary

1. The rate of mercuration of ethylenes has been found to depend on a bimolecular reaction.

2. Some *cis* ethylenes mercurate more rapidly than the *trans* isomers.

3. An alternative mechanism is suggested to explain the mercuration.

CAMBRIDGE, MASS. RECEIVED APRIL 5, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, VASSAR COLLEGE]

The Reaction between 2,3-Dimethyl-1,4-naphthoquinone and Phenylmagnesium Bromide.[1] I

BY H. MARJORIE CRAWFORD

Numerous studies have been made of the reactions between quinones and Grignard reagents. Only in the cases of anthraquinone[2] and phenanthraquinone[3] were the reactions clean-cut and the yields good. The mono- or di-addition product resulted, depending on the relative amounts of reactants.

If there was a possibility of a 1,4 addition to a conjugated system besides the addition to the carbonyl group, the reactions were complicated, many different products resulted and tars and oils formed the main products of the reaction. Bamberger[4] studied the reaction of methylmagnesium iodide on *p*-xyloquinone and identified six solid products which accounted for only one-fourth of the quinone used. Another fourth was reduced to the hydroquinone, and amorphous solids and oils remained. Franssen,[5] using α-naphthoquinone, isolated a di-addition product in 25% yields, but obtained colored amorphous products, reduction products and tars. Thinking that these complex results might have been due to hydrogen atoms attached to the quinone nucleus, Smith and Crawford[6] studied the reaction between a fully substituted quinone (duroquinone) and phenylmagnesium bromide and found that in this case also the reaction was very complex. The main product of the reaction was an oil (80%) and from the other 20% eight solids were separated and identified. 1,2- and 1,4-addition occurred as well as reduction and the formation of double compounds of the quinhydrone type.

Discussion of the Reaction and Products

In the present work, 2,3-dimethyl-1,4-naphthoquinone was chosen because it appeared to be intermediate in structure between duroquinone, which gave complex results, and anthraquinone which gave clean-cut results. However, it seems that as long as any 1,4-conjugated system is open the reaction is complicated, even though one side of the quinone is blocked by a benzene ring. The predicted mono- and di-addition products were obtained as well as double compounds, reduction products and dehydration products.

Three types of reaction products were formed and will be discussed separately, although all were formed at the same time. If one or one and a half moles of phenylmagnesium bromide was used per mole of the quinone, mono- and di-addition products were formed. If two moles of phenylmagnesium bromide were used per mole of quinone, di-addition products predominated.

A. Reduction Products.—The reduction of quinones by Grignard reagents is quite general and, regardless of procedure, reduction products

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[1] Presented in part at the New York meeting of the American Chemical Society in April, 1935.

[2] (a) Haller and Guyot, *Compt. rend.*, **138**, 327 and 1251 (1904); (b) Guyot and Staehling, *Bull. soc. chim.*, **33**, 1104 and 1144 (1905); (c) Haller and Comtesse, *Compt. rend.*, **150**, 1290 (1910); (d) Clarke and Carleton, THIS JOURNAL, **33**, 1966 (1911).

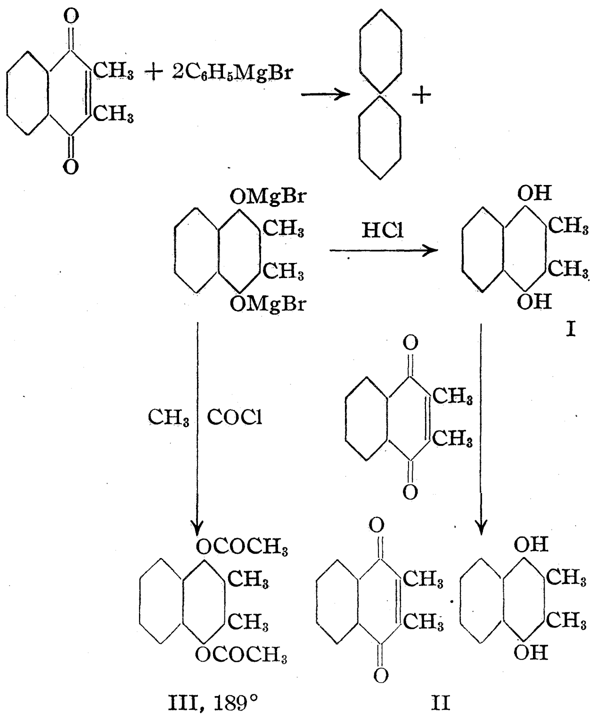
[3] (a) Werner and Grob, *Ber.*, **37**, 2887 (1904); (b) Zincke and Tropp, *Ann.*, **362**, 242 (1908); (c) Bachmann and Chu, THIS JOURNAL, **57**, 1095 (1935).

[4] Bamberger, *Ann.*, **384**, 272 (1911).

[5] Franssen, *Bull. soc. chim.*, **37**, 902 (1925); **45**, 1030 (1929).

[6] Smith and Crawford, THIS JOURNAL, **50**, 869 (1928).

were obtained corresponding to about 10% of the quinone.

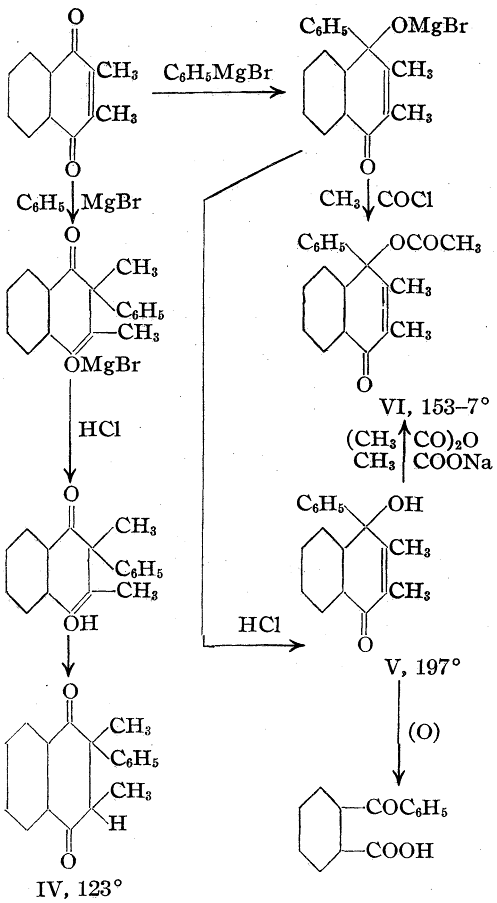


The diacetate of the hydroquinone (III) was obtained when the green reaction mixture was decomposed by acetyl chloride. The hydroquinone (I) was formed when the reaction mixture was decomposed by ice and hydrochloric acid. It was isolated as the quinhydrone (II), a black solid.

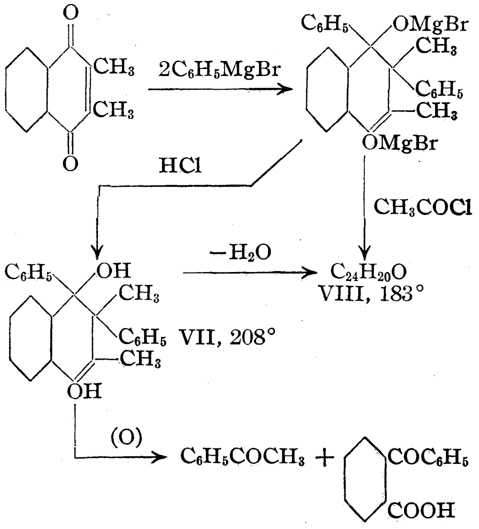
B. Mono-addition Products.—One molecule of phenylmagnesium bromide may react with one molecule of the quinone to give either a 1,2 or a 1,4 addition product (see next diagram).

The 123° compound (IV) was obtained in small amounts in two runs. Oxidation to give acetophenone indicates a 1,4 addition. The keto structure is more probable than the enol first formed, for the Grignard machine[7] shows no active hydrogen.

The 197° compound (V) had one active hydrogen and one carbonyl group (Grignard machine), and on oxidation gave *o*-benzoylbenzoic acid. The 197° compound was obtained in all reactions, and accounts for about one-fourth of the solid products isolated. The corresponding 153–157° acetate (VI) was obtained once when the reaction mixture was decomposed by acetyl chloride.



C. Di-addition Products.—The main solid product in most reactions was the 208° compound (VII)



Its structure was established by analyses, by the fact that the Grignard machine showed two active hydrogens and no carbonyl group, and by oxidation to acetophenone and *o*-benzoylbenzoic acid.

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[7] Kohler and co-workers, THIS JOURNAL, **49**, 3181 (1927); **52**, 3736 (1930).

The nature of the 183° compound (VIII) is under investigation. It corresponds to a di-addition product minus one molecule of water, and is obtained by treating the metallic addition product with acetyl chloride, or from the 208° compound by reagents which suggest a pinacol rearrangement.

Another di-addition product (IX) melting at 203° was obtained in very small amounts (less than 0.5 g.). It was isolated from the reaction mixture in the form of a double compound (X) containing two molecules of quinone to one molecule of the 203° compound.

$$\underset{\text{IX, 203°}}{C_{24}H_{22}O_2} + 2C_{12}H_{10}O_2 \rightleftarrows \underset{\text{X, 137°}}{C_{24}H_{22}O_2 \cdot 2C_{12}H_{10}O_2}$$

There is also a dehydration product, $C_{24}H_{20}O$, (XI) related in some way to the 203° compound (IX). These products are being further investigated.

Total yields of solid products from 348 g. of quinone (1.87 mole) and 3.5 moles of phenylmagnesium bromide: quinone and quinhydrone, 65 g.; 208° compound, 40 g.; 197° compound, 20 g.; 123° compound, 2.4 g.; 137° compound, 14 g.

Total yields of solid products from 55.8 g. of quinone (0.3 mole) and 0.55 mole of phenylmagnesium bromide when the reaction mixture was decomposed by excess acetyl chloride: quinone, 7.6 g.; 153° acetate, 0.22 g.; 189° diacetate, 7.9 g.; 183° compound, 1.1 g.

Experimental Part

All combustions were carried out using the semi-micro method of Lauer and Dobrovolny.[8] Molecular weight determinations were made by the lowering of the freezing point of benzene, or by the Rast method using camphor as the solvent.

Preparation of the 2,3-Dimethyl-1,4-naphthoquinone.—The quinone was prepared from 2,3-dimethylnaphthalene according to the method of Kruber[9] in 41–48% yields, m. p. 125–127°. Variations in the procedure, including lower temperatures and the use of a stirrer, did not affect the yield. Glacial acetic acid was the best solvent for recrystallization.

The Reaction between 2,3-Dimethyl-1,4-naphthoquinone and Phenylmagnesium Bromide.—Reactions carried out as nearly alike as possible gave different results, and for this reason the quinone was divided into small amounts and the reaction products worked up separately. One, one and a half or two moles of phenylmagnesium bromide were used per mole of quinone.

A freshly prepared Grignard solution containing approximately 0.1 mole of phenylmagnesium bromide per 100 cc. was added slowly to a suspension of 18.6 g. (0.1 mole) of 2,3-dimethyl-1,4-naphthoquinone in ether. The solid addition product was bright green. The mixtures were allowed to stand overnight before decomposing with ice and hydrochloric acid. The water layer, colored bright purple by quinhydrone, was extracted with ether. The ether solutions, after evaporating to about 50 cc., were diluted to 100 cc. with diisopropyl ether. Crops of solid obtained on standing were filtered off and washed with diisopropyl ether. Similar crops were combined for crystallization. In every case a dark oil was the main product.

In three cases the first green magnesium addition products, after standing for four hours, were decomposed with excess acetyl chloride and allowed to stand overnight, then treated with ice and hydrochloric acid. The yields in these cases were small and the acetates hard to isolate. The main product was the diacetate of the hydroquinone. The 153–157° acetate (VI) and the 183° compound (VIII) were obtained in small amounts.

Diphenyl could always be obtained by steam distillation of the oils, or from the ether filtrate if the original green magnesium compound was removed by filtration.

In one case the quinone was added to the Grignard reagent and the green precipitate first formed dissolved to give a yellowish brown solution. The yield of solids was low.

The Hydroquinone, I.—The hydroquinone was isolated in practically every reaction as the black quinhydrone.

It was also prepared from the quinone by reduction with boiling 80% acetic acid and excess zinc dust. The solution turned dark red at first, but in twenty minutes was practically colorless. A white precipitate formed as soon as the filtered solution cooled, but all attempts to filter, wash and dry it, even in an atmosphere of nitrogen, resulted in color changes from white through pink, lavender and purple, to black. The melting point is around 135–140° but no very definite results could be obtained due to its extreme ease of oxidation.

The Quinhydrone, II, m. p. 136–140°.—This substance was obtained in most of the reactions. It could be recrystallized from alcohol or ether and separated from the dark red solution as glistening black leaflets. Considerable oxidation to quinone occurred unless the recrystallization was carried out rapidly.

Anal. Calcd. for $C_{24}H_{22}O_4$: C, 76.97; H, 5.93. Found: C, 76.21, 76.87; H, 5.93, 6.17.

The compound dissociates in solution and while the quinone is very soluble in benzene, the hydroquinone is not so soluble. This gave a high result for the molecular weight, 224 instead of 187.

Diacetate of the Hydroquinone, III, m. p. 189–189.5°.—This diacetate was formed when the solid magnesium addition product was treated with acetyl chloride. It was also made by boiling the quinone with acetic anhydride and zinc dust, and from the impure hydroquinone by treatment with phenylmagnesium bromide followed by acetyl chloride. It is white when pure, and is soluble in chloroform but only slightly soluble in alcohol and benzene.

Anal. Calcd. for $C_{16}H_{16}O_4$ (272.1): C, 70.55; H, 5.92.

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[8] Lauer and Dobrovolny, *Mikrochem. Pregl Festschr.*, 243 (1929).

[9] Kruber, *Ber.*, **62**, 3044 (1929).

Found: C, 70.22, 70.20, 70.15; H, 5.92, 5.74, 5.71; mol. wt. (camphor), 284.4.

1,4 - Dioxo - 2,3 - dimethyl - 2 - phenyltetrahydronaphthalene, IV, m. p. 123°.—This mono-addition product was obtained in very small yields in two runs: 2.4 g. from 348 g. of quinone. It is a white solid, quite soluble in alcohol, ether and benzene. Half a gram was boiled for five hours with 2 g. of potassium dichromate in 15 cc. of acetic acid. An ether extract of the neutralized oxidation mixture was treated with semicarbazide, and gave acetophenonesemicarbazone.

Anal. Calcd. for $C_{18}H_{16}O_2$ (264.1): C, 81.78; H, 6.11. Found: C, 81.19, 81.04; H, 6.07, 5.99; mol. wt. (benzene), 257.3, 256.4.

1-Oxy-4-oxo-2,3-dimethyl-1-phenyldihydronaphthalene, V, m. p. 197–197.5°.—This compound is formed in practically all reactions. It is a white solid soluble in pyridine, 1,4-dioxane, chloroform and ether, but only slightly soluble in alcohol and benzene, and practically insoluble in diisopropyl ether. A mixture of chloroform and alcohol was best for crystallization. Phosphorus tribromide in bromoform solution gave a red brown oil. A solution of 1 g. of the 197° compound and 0.7 g. of hydroxylamine hydrochloride in 50 cc. of pyridine heated on the steam-bath for twelve hours gave 0.95 g. of the starting material unchanged.

Anal. Calcd. for $C_{18}H_{16}O_2$ (264.1): C, 81.78; H, 6.11. Found: C, 81.57, 81.68, 81.65; H, 6.20, 6.17, 6.24; mol. wt. (camphor), 265.6, 280.3.

The Grignard machine showed 1.12 moles of methane liberated and 1.86 moles of methylmagnesium iodide reacting per mole of 197° compound.

Oxidation.—One gram of the 197° compound and 3 g. of potassium dichromate in 25 cc. of glacial acetic acid were boiled for six hours. The mixture was then diluted with 100 cc. of water, neutralized with sodium carbonate and extracted with ether. An ether extract of the acidified water layer gave *o*-benzoylbenzoic acid melting at 126–128°.

Treatment of the 197° compound with sodium followed by acetyl chloride, and heating with acetyl chloride alone failed to give the acetate.

Acetate of 1-Oxy-4-oxo-2,3-dimethyl-1-phenyldihydronaphthalene, VI, m. p. 153–157°.—A mixture of 1.6 g. of the 197° compound, 2 g. of fused sodium acetate and 30 cc. of freshly distilled acetic anhydride was boiled for four hours. After cooling, water was added to dissolve the sodium acetate, the layers were separated and the water layer discarded. After the addition of alcohol and the evaporation of the solvents, 0.73 g. of the very soluble acetate separated.

This acetate was also obtained once (0.22 g.) when the original green metallic addition product was decomposed by acetyl chloride. It is very soluble in alcohol, ether, ethyl acetate and diisopropyl ether, and crystallizes in needles.

Anal. Calcd. for $C_{20}H_{18}O_3$: C, 78.39; H, 5.92. Found: C, 78.53, 77.90, 78.15; H, 5.80, 5.98, 6.00.

1,4 - Dioxy - 2,3 - dimethyl - 1,2 - diphenyldihydronaphthalene, VII, m. p. 208–209°.—This compound was formed in larger amounts than any of the other addition products. It is a white solid, soluble in ethyl acetate, pyridine, 1,4-dioxane and chloroform, but only slightly soluble in alcohol, benzene and ethers (diethyl, diisopropyl and diisoamyl). The best solvents for recrystallization are ethyl acetate or a mixture of alcohol and chloroform. From the reaction mixture the 208° compound and the 197° compound (V) often separate together as an apparently homogeneous material melting at 175°. Separation could be effected by dissolving the 175° material in boiling chloroform, then adding diisopropyl ether. The first solid separating was mainly the 197° compound. The middle fractions melted at 175°, and the final fractions were mainly the 208° compound.

Anal. Calcd. for $C_{24}H_{22}O_2$ (342.2): C, 84.17; H, 6.48. Found: C, 83.93, 84.04, 83.86; H, 6.56, 6.55, 6.51; mol. wt. (camphor), 347.8.

The Grignard machine showed 1.6, 1.7, 1.8 moles of methane per mole of the 208° compound. The gas was shown to be methane by analysis. The slight solubility of the 208° compound in solvents inert to the methylmagnesium iodide prevented further reaction.

Oxidation.—Two grams of the 208° compound and 6 g. of potassium dichromate in 50 cc. of glacial acetic acid were heated under reflux for five hours, then cooled and diluted with 200 cc. of water. The solution was neutralized with potassium hydroxide and extracted with ether. The ether solution, on treatment with semicarbazide, gave acetophenonesemicarbazone. The water solution was acidified with sulfuric acid and extracted with ether. The white solid, melting 126–128° was shown to be *o*-benzoylbenzoic acid by conversion to anthraquinone and mixed melting point with a known sample of anthraquinone.

Potassium permanganate in acetone failed to oxidize the 208° compound. When 1 g. of the 208° compound was heated for twelve hours on the steam-bath with hydroxylamine hydrochloride in pyridine solution, 0.63 g. was recovered unchanged, and 0.5 g. of an oil remained.

In an attempt to make the acetate by adding acetyl chloride to the magnesium derivative resulting from the reaction of the 208° compound with Grignard reagent, a white solid was obtained which melted at 183° (VIII). Treatment of the 208° compound with phosphorus tribromide in bromoform solution gave the same 183° compound. Heating 1 g. of the 208° compound on the steam-bath for six hours with zinc chloride and hydrochloric acid in benzene, or heating 1 g. for an hour with 0.5 g. of iodine in 50 cc. of acetic acid gave practically quantitative conversion to the 183° compound. This latter method was the procedure followed by Bachmann and Chu[3c] in rearranging their 9,10-diaryldihydrophenanthrenediols to diarylphenanthrones. Heating the 208° compound with 20% sulfuric acid for one half hour caused no loss of water.

$C_{24}H_{20}O$, VIII, m. p. 183°.—This compound results when the 208° compound loses a molecule of water. It was also formed when the original green reaction mixture was treated with acetyl chloride. After separating the diacetate of the hydroquinone, the remaining oils were distilled under reduced pressure. The fraction boiling 250–270° (15 mm.) finally gave 1.1 g. of the 183° compound from 70.4 g. of oil.

This compound is very soluble in alcohol, ether and benzene and separates in shining white leaflets. Heating 0.5 g. of the 183° compound with 20 cc. of constant boiling hydrobromic acid for three hours gave 0.4 g. of unchanged material. The starting material was recovered unchanged after heating on the steam-bath for seven hours with hydroxylamine. After heating 1 g. for five hours with potassium dichromate at the boiling point of acetic acid, 0.75 g. of the 183° compound was recovered unchanged.

Anal. Calcd. for $C_{24}H_{20}O$ (324.2): C, 88.84; H, 6.22. Found: C, 88.81, 88.87; H, 6.42, 6.22; mol. wt. (benzene), 315.1, 329.1.

The Grignard machine showed no active hydrogen, but 1.05 mole of methylmagnesium iodide reacted per mole of the 183° compound.

$C_{24}H_{22}O_2$, **IX**, m. p. 203–204°.—This white di-addition product was very soluble in benzene and alcohol, and was obtained from the reaction mixture in the form of a double compound (X) with two molecules of quinone. The clear crystals first obtained soon became opaque and sticky even in a desiccator. Less than 0.5 g. was available for study and the oxidation of 0.2 g. of this was inconclusive, so no structure can be assigned at this time.

Anal. Calcd. for $C_{24}H_{22}O_2$ (342.2): C, 84.17; H, 6.48. Found: C, 84.86, 83.75, 83.70; H, 6.66, 6.44, 6.46; mol. wt. (benzene), 338.8.

$C_{24}H_{22}O_2 \cdot 2C_{12}H_{10}O_2$, **X**, m. p. 137–138°.—The thick prisms of this yellow compound separated from various reaction mixtures and could be recrystallized from diisopropyl ether. Recrystallization from alcohol gave first quinone, then 137° compound, and finally the very soluble white di-addition product (IX). When the white compound (IX) and quinone were recrystallized together from alcohol, the yellow 137° compound was formed. The quinone could also be separated from the white compound by steam distillation.

Anal. Calcd. for $C_{24}H_{22}O_2 \cdot 2C_{12}H_{10}O_2$ ([342 + 2(186)]/3 = 238): C, 80.63; H, 5.93. Found: C, 79.66, 79.56; H, 5.96, 5.80; mol. wt. (benzene), 226.2.

$C_{24}H_{20}O$, **XI**, m. p. 124°.—This dehydration product is related in some way to the 203° compound (IX), and was obtained only once (2.15 g.) out of fifteen runs. The structure is still under investigation. Oxidation with potassium dichromate gave acetophenone and *o*-benzoylbenzoic acid.

Anal. Calcd. for $C_{24}H_{20}O$ (324.2): C, 88.84; H, 6.22. Found: C, 88.98, 88.64; H, 6.22, 6.40; mol. wt. (benzene), 316.5, 314.9.

The Grignard machine showed no active hydrogen, but 0.7 mole of methylmagnesium iodide reacted per mole of the 124° compound.

The author wishes to thank Lillian G. Hoagland, formerly instructor at Vassar College, for much preliminary work on other methods of preparing the quinone, and for the preparation of the hydroquinone and its diacetate.

Summary

1. Whenever a 1,4-conjugated system in a quinone is open to attack by a Grignard reagent the reaction is complex and the yields of solids low.

2. A study of the reaction between 2,3-dimethyl-1,4-naphthoquinone and phenylmagnesium bromide shows that several reactions take place at the same time and the quinone acts more like duroquinone than like anthraquinone.

3. Eleven new compounds, products of this reaction and their derivatives, are described and structures are proposed for seven of them. About 70% of the reaction product is a dark oil.

4. The study of the dehydration products is being continued.

POUGHKEEPSIE, N. Y. RECEIVED JULY 12, 1935

NOTES

The Decomposition Voltage of Grignard Reagents in Ether Solution

By Elliot Q. Adams

Evans, Lee and Lee[1] have found decomposition voltages of Grignard reagents ranging from 0.86 volt for allylmagnesium bromide, to 2.17 volts for phenylmagnesium bromide. If the *differences* in the decomposition voltages of the saturated aliphatic derivatives produced by the introduction of one methyl group are taken, it is

$$\begin{array}{llllll}
\alpha_1 & -0.66 & \alpha_2 & -0.21 & \alpha_3 & -0.10 \\
 & & & -0.18 & & \\
\beta_1 & +0.14 & & & & \\
 & +0.17 & & & & \\
\gamma_1 & -0.10 \text{ (Evans, Lee and Lee)} & & & &
\end{array}$$

$$\begin{array}{lll}
\Delta pK_A/pK_{A(\text{subst.})}\alpha & = & -0.68 \\
\beta \quad \text{(Derick)} & = & -0.19 \\
\gamma & = & -0.06 \\
\delta & = & -0.02
\end{array}$$

α_1, α_2, α_3 represent the changes *in volts* in the decomposition potential of Grignard reagents in ether solution, produced by replacing, respectively, the first, second, and third α-hydrogen by methyl; β_1 and γ_1 represent similarly the changes *in volts* produced by the first methyl group in, respectively, the β and γ positions. α, β, γ and δ are the changes in Derick's function[3] produced by substituting chlorine for, respectively, the α-, β-, γ- or δ-hydrogens in butyric or valeric acid, or their chlorinated derivatives.

found that successive substitutions in the alpha position produce diminishing decreases in the decomposition potential, and that the effect of substitution in the beta position is opposite in sign to that of alpha or gamma substitution. Conant[2] has found that irreversible oxidation–reduction potentials are represented by equations similar in form to those for oxidation–reduction equilibrium potentials. Derick[3] has pointed out that the relative effects of substituents on the logarithms of the ionization constants of organic acids ($\Delta pK_A/pK_{A(\text{substituted})}$ in present-day notation) are reduced approximately 3-fold by each additional carbon atom between the carboxyl and the substituent, without change in sign. The results of Evans, Lee and Lee agree within the error of measurement with the series

$$-0.63{:}\mp 0.21{:}-0.07 = 9{:}\pm 3{:}1$$

that is, 3-fold reduction in the effect of successive alpha replacements, as well as with increasing distance from the MgBr radical. In the latter case, there is also an alternation in sign of the effect.

The results for phenyl- and allylmagnesium bromides indicate an effect of unsaturation alternating in sign, and less for the more distant double bond, in qualitative agreement with the rule for methyl groups.

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[1] W. V. Evans, F. H. Lee and C. H. Lee, This Journal, **57**, 489–490 (1935).

[2] J. B. Conant and M. F. Pratt, *ibid.* **48**, 3178–3192 (1926).

[3] C. G. Derick, *ibid.* **33**, 1182 (1911). The approximate numerical agreement between Evans, Lee and Lee's results in volts, and Derick's is, of course, a coincidence. Since pK_A for unsubstituted aliphatic acids is of the order of 5 and with a single strongly negative α-substituent becomes about 3, the unit of Derick's function for singly substituted acids will range from 3 to 5 pK units. (1 volt $\simeq$ 17 pK units.) The form of Derick's function provides for a diminishing effect on pK_A with successive substitutions, but the decrease even in the case of α-substitution is not as great as that shown in the results of Evans, Lee and Lee. Since the acid hydrogen in substituted acetic acids is separated by a carbon and an oxygen atom from the α-carbon of the chain, while in the Grignard reagents the magnesium atom is directly attached, a factor of the order of 9 is to be expected. There is, to be sure, no reason to expect the effect of a methyl group on the irreversible breaking of the bonding of magnesium to carbon in ether solution to be identical with the effect of chlorine on the equilibrium of the bonding of hydrogen to oxygen in aqueous solution.

Incandescent Lamp Department
General Electric Company
Nela Park
Cleveland, Ohio

Received July 22, 1935

Some Acyl Derivatives of *o*-Anisidine

By Lawrence H. Amundsen and C. B. Pollard

We have prepared a number of acyl derivatives of *o*-anisidine, the majority of which have not been described in the literature. The monoacyl derivatives were prepared by the action of the corresponding acyl chlorides upon 2 molecular proportions of *o*-anisidine.[1]

The diacyl derivatives were prepared by boiling a toluene solution of *o*-anisidine with 2.5 molecular proportions of acyl chlorides under reflux for twelve to eighteen hours. The dibenzoyl derivative precipitated upon cooling the solution and the dipropionyl derivative was obtained by evaporation of the toluene.

The first six compounds are very soluble in most organic solvents but only moderately soluble in pentane, hexane, etc. The next four compounds are very soluble in chloroform, dioxane and acetone, fairly soluble in alcohol, slightly

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[1] Mühlhäuser, *Ann.*, **207**, 235 (1881); *Ber.*, **13**, 919 (1880).

TABLE I

ACYL DERIVATIVES OF *o*-ANISIDINE

Acyl groups	Solvent used in crystn.	Yield, %	M. p., °C.	Formula	Nitrogen % Calcd.	Nitrogen % Found
Propionyl	Ether[a]	73	33.5–34.5	$C_{10}H_{13}NO_2$	7.82	7.80
Butyryl	Ether[a]	78	24.5–25.5	$C_{11}H_{15}NO_2$	7.25	7.11
Valeryl	Ether[a]	91	25.5–26.5	$C_{12}H_{17}NO_2$	6.76	6.45
Isovaleryl	Ether[a]	94	49–49.5	$C_{12}H_{17}NO_2$	6.76	6.59
Caproyl	Ether[a]	61	33–33.5	$C_{13}H_{19}NO_2$	6.33	6.38
Heptanoyl	Pet. ether	67	42–43	$C_{14}H_{21}NO_2$	5.96	5.73
Phenylacetyl[b]	Dilute alc.	88	82.5–83			
Hydrocinnamyl	Isopropyl ether or benzene and heptane	100	59.5–60	$C_{16}H_{17}NO_2$	5.49	5.50
m-Bromobenzoyl		86	112.5–113	$C_{14}H_{12}BrNO_2$	4.58	4.59
					Br, 26.11	25.60
p-Anisoyl		100	96.5–97.5	$C_{15}H_{15}NO_3$	5.45	5.42
Benzoyl[c]			66–67			
Acetyl[d]			85–85.5			
Dibenzoyl	Alc. or toluene	60	149.5–150	$C_{21}H_{17}NO_3$	4.23	4.25
Dipropionyl	Hexane	85	62.5–63.5	$C_{13}H_{17}NO_3$	5.96	5.98

[a] By cooling with solid carbon dioxide.

[b] Aggarwal, Das and Rây[2] prepared this compound from *o*-anisidine and phenylacetic acid and reported a melting point of 84°.

[c] Prepared by Mühlhäuser,[1] who reported a melting point of 59.5°.

[d] Mühlhäuser[1] reported a melting point of 78°. Our melting point agrees with the one given in Mulliken's "Identification of Pure Organic Compounds," Vol. II, p. 151.

soluble in ether, and almost insoluble in hexane. *o*-Dibenzoylanisidine is difficultly soluble in toluene and alcohol but readily soluble in chloroform. *o*-Dipropionylanisidine is soluble in practically all organic solvents.

One additional compound was prepared during this investigation. Its properties are given below.

***o*-Benzoylmethylaminophenyl Benzoate.**—This compound was prepared by the Schotten–Baumann method in 40% yield. It was crystallized from alcohol. It is soluble in dioxane, acetone, chloroform and benzene; somewhat soluble in alcohol and ether; and almost insoluble in petroleum solvents, m. p. 114–115°.

Anal. Calcd. for $C_{21}H_{17}NO_3$: N, 4.25. Found: N, 4.12.

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(2) Aggarwal, Das and Rây, *J. Ind. Chem. Soc.*, **6**, 717 (1929).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF FLORIDA
GAINESVILLE, FLORIDA

RECEIVED JULY 19, 1935

Addition of Methyl Alcohol to Dialkylacetylenes

BY G. F. HENNION AND J. A. NIEUWLAND

The many well-known reactions of acetylene and its homologs with hydroxylated compounds (alcohols, carboxylic acids, etc.) are characterized by the fact that they proceed quite readily in an appropriate acid medium in the presence of a small amount of a suitable mercuric salt. The mechanism of this catalysis has engaged our attention for some time. There is little doubt but what the reaction of an acetylene with methyl alcohol, for example, produces first a vinyl ether which in turn immediately adds a second molecule of alcohol to form the ketal or acetal. There is evidence to indicate that the mercuric salts function only in the first of these reactions.

In attempting to determine whether the catalytic mercuric salt forms an intermediate with the acetylene by addition or substitution (or both) we have succeeded in adding methyl alcohol to two dialkylacetylenes in the usual way.[1] This indicates quite clearly that an intermediate of the mercury acetylide type is not essential to the mechanism of catalysis.

Preparation of 2-Octyne.—This compound was obtained by the action of methyl iodide on sodium amylacetylide in liquid ammonia: b. p. 132–136°; d^{32} 0.751; $n^{32}{}_D$ 1.4227.

Reaction of 2-Octyne with Methyl Alcohol.—The catalyst was prepared by heating together momentarily 3 g. of red mercuric oxide, 1 ml. of $(C_2H_5)_2O{\cdot}BF_3$, 0.5 g. of trichloroacetic acid, and 3 ml. of methyl alcohol. The reaction was carried out and the product purified as previously described.[1] From 55 g. of 2-octyne there was obtained 48 g. of 3,3-dimethoxyoctane: yield, 55%; b. p. 90–92° at 26 mm.; d^{25} 0.8552; $n^{25}{}_D$ 1.4171; MR calcd. 51.67, found 51.22.

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(1) Hennion, Killian, *et al.*, THIS JOURNAL, **56**, 1130 (1934), and subsequent papers.

Anal. Calcd. for $C_{10}H_{22}O_2$: C, 68.89; H, 12.73. Found: C, 69.00; H, 12.79.

Hydrolysis of a 1-ml. sample yielded a ketone which was in turn converted to the semicarbazone. The latter melted at 112–113° which agrees with the value of 112° given by Pickard and Kenyon[2] for the semicarbazone of 3-octanone.

Reaction of Methoxy-4-butyne-2 with Methyl Alcohol.—A sample of this acetylene[3] was obtained through the courtesy of Dr. Wallace H. Carothers of E. I. du Pont de Nemours & Company to whom our sincere thanks are extended.

The catalyst was prepared as described above and the reaction carried out in the usual way. Forty-two grams of the acetylene yielded 42 g. of 2,2,4-trimethoxybutane, b. p. 67–69° at 30 mm.; yield, 57%. This compound has been obtained previously from vinylacetylene.[4]

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[2] Pickard and Kenyon, *J. Chem. Soc.*, **103**, 1936 (1913).

[3] Jacobson, Dykstra and Carothers, THIS JOURNAL, **56**, 1169 (1934).

[4] Killian, Hennion and Nieuwland, *ibid.*, **56**, 1786 (1934).

CONTRIBUTION FROM THE
CHEMICAL LABORATORIES OF THE
UNIVERSITY OF NOTRE DAME
NOTRE DAME, INDIANA

RECEIVED FEBRUARY 28, 1935

p-Bromophenacyl Formate, a Solid Derivative of Formic Acid

BY CHARLES D. HURD AND ROBERT E. CHRIST

It was found by Judefind and Reid[1] that many aliphatic acids could be identified easily as their *p*-bromophenacyl esters. These solid esters made excellent derivatives for the acids. According to these authors, however, formic acid gave negative results. In contrast to this statement, we have found that formic acid behaves regularly. The preparation of *p*-bromophenacyl formate is a simple matter and the compound makes an admirable derivative. It melts at 140°.

One gram of sodium formate (solid) was dissolved in 5 cc. of water and 10 cc. of 95% alcohol. Then 1 g. of *p*-bromophenacyl bromide was added. The solution was boiled until nearly all the solvent had disappeared. More alcohol was added and it was boiled another half hour until the solvent had nearly disappeared. Finally, the product was dissolved in dilute alcohol and then cooled. The crystalline product was filtered and recrystallized from dilute alcohol. A total of 0.38 g. of product was obtained which possessed a melting point of 140°.

Equally good results were obtained by refluxing instead of boiling away the solvents. Then, the first amount of alcohol is sufficient.

Anal. Subs., 0.2027; AgBr, 0.1551. Calcd. for $C_9H_7O_3Br$: Br, 32.89. Found: Br, 32.56.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

RECEIVED JULY 26, 1935

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[1] Judefind and Reid, THIS JOURNAL, **42**, 1052 (1920).

Optical Rotation Study of the New Orally Effective Principle of Ergot

BY E. C. KLEIDERER

Commercial production of the orally effective principle recently isolated from ergot has provided an adequate source for an intensive study of its properties.

The free base, called ergotocin by Kharasch and Legault, was crystallized from benzene and dried *in vacuo* for about eight hours. It melted at 157–158° (corr., bath at 150° when sample was introduced). The maleate salt was prepared from the crystalline base, and dried *in vacuo*.

The initial specific rotations of the free base in various solvents are given below. All rotations in this investigation were made in a one-decimeter tube at 28° unless otherwise stated. Due to the slight solubility of the base in cold chloroform and benzene, the rotations in these solvents were taken in a Landolt heating chamber.

TABLE I

Solvent	Wt. and vol. of solvent	α_D	$[\alpha]_D$
Distilled water	0.0276 g. in 10 cc.	+0.21°	+76.1°
Abs. methyl alcohol	.0485 g. in 15 cc. tube, 2 dm.	+ .26°	+40.2°
Cyclohexanol	.00659 g. in 1 cc. (micro)	+ .21°	+31.6°
Chloroform	.0179 g. in 10 cc.	− .08° at 50°	−44.7° at 50°
Benzene	.0164 g. in 10 cc.	− .10° at 75°	−61.0° at 75°

The rotation of the methyl alcoholic solution of the free base on standing at room temperature became more dextro as shown in Table II, while no change was observed on a water solution of the free base after standing at room temperature for one hundred hours.

TABLE II

Time, hr.	Initial	17	30	71.5	95.5
$[\alpha]^{28}_D$	+40.2°	+48.0°	+53.1°	+59.6°	+61.8°

The methyl alcohol was evaporated from the sample which had stood ninety-five and one-half hours, the residue recrystallized from benzene and the dried (*in vacuo*) product dissolved in water giving $[\alpha]^{28}\text{D}$ +95.4°. The melting point of the initial sample was 157–158° (dec.) and of the sample obtained from the 95.5-hour solution was 160–161° (dec.).

By the isolated rabbit uterus method,[1] the physiologic activity of the base obtained from the 95.5-hour sample was about 90% of that of the initial sample.

Initial rotations of the maleate salt of the new base were as follows.

TABLE III

Solvent	Wt. and vol. of solution	$\alpha^{28}\text{D}$	$[\alpha]^{28}\text{D}$
Distilled water	0.1042 g. in 10 cc.	+0.48°	+46.2°
Abs. methyl alcohol	.1017 g. in 25 cc.	+ .308°	+37.9°

Rotations were again made on these same solutions after standing at room temperature for forty-eight hours, and were found to be as follows: on the water solution $\alpha^{28}\text{D}$ +0.56°, $[\alpha]^{28}\text{D}$ +53.7°; on the methyl alcohol $\alpha^{28}\text{D}$ +0.20°, $[\alpha]^{28}\text{D}$ 24.6°. The forty-eight-hour methyl alcohol solution was evaporated *in vacuo* to dryness at room temperature, water was added to bring the solution up to the original methyl alcohol volume. The rotation was $\alpha^{28}\text{D}$ 0.214°, $[\alpha]^{28}\text{D}$ 52.9°. The physiologic activity of these forty-eight-hour samples as determined by the isolated rabbit uterus method was approximately the same as that of an initial sample.

The explanation of these results is not clear at present; evidently some change is occurring in the molecule which affects the optical rotation, but which does not greatly affect the physiologic activity. Changes of rotation have been noted in the cases of ergotinine and ergotamine which have been ascribed to a change into ergotoxine in the former case and into ergotaminine in the latter case. This explanation does not appear to be a logical one for the changes occurring here, since the physiologic activity seems to be practically unchanged and since the product obtained from a solution of the salt of the new base in methyl alcohol and the product obtained from a solution in water appear to be the same.

The author wishes to express his thanks to Dr. K. K. Chen and to Mr. E. E. Swanson of the Lilly Research Laboratories for their aid in determining the physiologic potency.

THE LILLY RESEARCH LABORATORIES
INDIANAPOLIS, INDIANA

RECEIVED JULY 24, 1935

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[1] Davis, Adair, Chen and Swanson, *J. Pharmacol.*, **54**, 398 (1935); Swanson, Hargreaves and Chen, *J. Am. Pharm. Assoc.*, in press.

An Improved Method of Extraction

BY CHARLES A. MARLIES AND VICTOR K. LA MER

In an investigation on the acid and salt catalysis of nitramide,[1] NH_2NO_2, a novel method of extraction was employed in the final stage of the preparation of this interesting compound. In the customary method[2] the compound is extracted from its aqueous solution, some forty extractions with ether being necessary on account of the exceedingly unfavorable distribution ratio. The improvement consists of immersing the flask containing the nitramide solution and supernatant ether layer into a "dry ice" freezing mixture and swirling until the water layer solidifies completely. The nitramide passes into the ether layer which is decanted through a filter. Complete extraction was achieved by repeating the process three times. The yield obtained on evaporation of the four combined ether extracts was 80%, whereas the maximum yield by the previous method was but 25%, in agreement with the experience of Brönsted's laboratory.[3]

The low yields by the previous[2] method are probably due to decomposition during the prolonged evaporation of the large volume of ether. Nitramide is an extremely unstable substance and the catalytic action resulting from the concentration of the ever-present impurities (including water) during the evaporation probably causes considerable loss by decomposition.

This method of freezing the solvent during extraction should prove generally useful not only in cases where the distribution ratio is unfavorable but also to remove small amounts of material from large volumes of solution, provided, of course, that solid solution is not an important complication.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK, N. Y.

RECEIVED JUNE 3, 1935

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[1] Marlies and La Mer, THIS JOURNAL, **57**, 1812 (1935).

[2] Thiele and Lachman, *Ann.*, **288**, 267 (1895).

[3] Brönsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924); and a later private communication.

COMMUNICATIONS TO THE EDITOR

DIMENSIONS OF SOAP MOLECULES AS SUPPOSEDLY DEDUCED FROM SURFACE TENSION MEASUREMENTS

Sir:

The surface tension measurements of Du Noüy [*Phil. Mag.*, [6] **48**, 664 (1924)] as carried out with the ring method were recently reproduced by Washburn and Berry [This Journal, **57**, 975 (1935)] using the capillary rise method for sodium palmitate solutions. The equilibrium surface tension–concentration curve shows three minima and the same number of maxima.

According to the Gibbs theorem for these concentrations no adsorption at all takes place. Instead, the interpretation of Du Noüy as now repeated by Washburn and Berry introduces the hypothesis that the minima are due to condensed films on the water surface, but differing in orientation corresponding to the three dimensions of the adsorbed molecule. No other confirmation for the validity of this view has been available.

However, the assumptions on which the theory of Du Noüy is based—besides contradicting the thermodynamics of Gibbs—are also objectionable. First, the acceptance of the supposition that the adsorbed quantities are proportional to the concentrations is quite untenable. Second, in calculating the surface tensions the possible influence of the angle of contact was completely disregarded, because it was tacitly taken for granted that perfect wetting always occurred.

This point, alone, seems to lead to a very plausible explanation of the experiments, if they are compared with the wonderful results of Miss Blodgett [This Journal, **57**, 1007 (1935)], who proved the existence of polymolecular soap films of alternating orientation as adsorbed on glass and other solids, when in contact with the solutions. The same phenomenon, unfortunately, is to be expected at the platinum ring of Du Noüy as well as at the walls of the glass tubes.

As Miss Blodgett showed, the first layer of molecules is always fixed with the active groups toward the adsorbent, whereas the paraffin groups are directed toward the solution. Therefore, with increasing concentration the glass or platinum is covered at first with a film of paraffin character which, as is well known, repels water. But the second layer may be orientated in the opposite direction, causing a decrease of the angle of contact. Consequently the apparent surface tension rises, unless a new paraffin surface is deposited.

The author in collaboration with E. J. Better applied the bubble pressure method, as being independent of the angle of contact, for the measurement of oleate solutions. Only one minimum was found, and that at a higher concentration than any of the minima of Du Noüy.

Stanford University, Calif. Hans M. Cassel

Received August 21, 1935

THE RELATIONSHIP OF ERGOTOCIN TO ERGOMETRINE

Sir:

Dudley and Moir [*Brit. Med. J.*, i, 520 (1935)] recently described the isolation from ergot of an alkaloid, chemically and pharmacologically different from any of the then known alkaloids of ergot, which they named ergometrine.

Although there were strong grounds for believing that ergotocin [Kharasch and Legault, This Journal, **57**, 956 (1935)] was identical with ergometrine, Kharasch and Legault have not adopted this view, but have suggested that the two substances may be different [*e. g.*, *Lancet*, i, 1243 (1935)]. They have now published a formula, $C_{21}H_{27}O_3N_3$, for ergotocin [This Journal, **57**, 1140 (1935)], while analyses of ergometrine and its salts now very accessible [Dudley, *Pharm. J.*, iv, **80**, 709 (1935)] indicate the formula $C_{19}H_{23}O_2N_3$, which is still being critically examined. [Further work on this substance since this "Communication" was dispatched (July 11, 1935) affords convincing evidence that this formula is correct.]

Ergometrine: *Anal.* Calcd. for $C_{19}H_{23}O_2N_3$: C, 70.15; H, 7.08; N, 12.92. Found: C, 70.0; H, 6.96; N, 12.91.

Ergometrine Hydrobromide. *Anal.* Calcd. for $C_{19}H_{23}O_2N_3 \cdot HBr$: C, 56.15; H, 5.91; N, 10.35; Br, 19.71. Found: C, 56.24; H, 6.19; N, 10.71; Br, 19.76.

Ergometrine Hydrochloride. *Anal.* Calcd. for $C_{19}H_{23}O_2N_3 \cdot HCl$: C, 63.08; H, 6.64; N, 11.62; Cl, 9.82. Found: C, 63.1; H, 6.81; N, 11.29; Cl, 9.54.

Ergometrine Oxalate: *Anal.* Calcd. for $C_{19}H_{23}O_2N_3 \cdot$

$H_2C_2O_4$: C, 60.73; H, 6.02; N, 10.12. Found: C, 60.58; H, 5.98; N, 10.18.

Taken by themselves these formulas would seem to support Kharasch and Legault's contention, but all other available evidence points to the identity of the substances. It is therefore probable that the apparent difference in elementary composition is not real, and that further analyses of ergotocin and its salts may yet lead to the establishment of its complete identity with ergometrine.

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H. W. DUDLEY

RECEIVED JULY 22, 1935

THE SYNTHESIS OF BIS-2,2'-(1,3-DIPHENYLINDENOL-3)

Sir:

In connection with attempts to synthesize rubrene we have prepared bis-2,2'-(1,3-diphenylindenol-3) by the following series of reactions

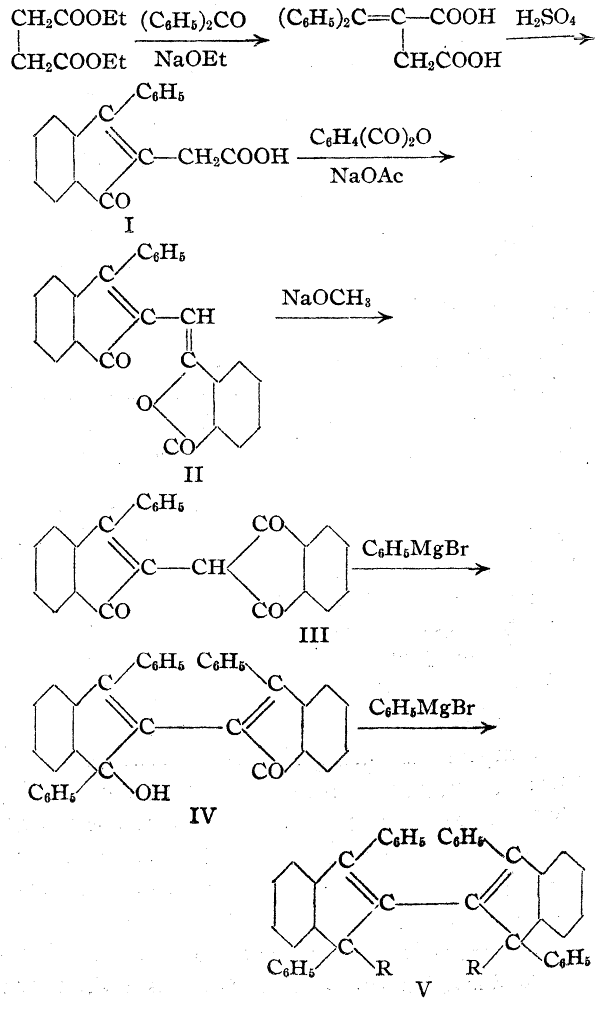


TABLE I

PROPERTIES OF COMPOUNDS INVOLVED

Compound	M. p., °C.	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
I	166–167	$C_{17}H_{12}O_3$	[a]			
II	173.5–174	$C_{24}H_{14}O_3$	82.2	4.0	81.9	4.3
III	190.5–191.5	$C_{24}H_{14}O_3$	82.2	4.0	82.0	3.9
IV	244–245	$C_{36}H_{24}O_2$	88.5	4.9	88.0	4.8
V, R = OH	292	$C_{42}H_{30}O_2$	89.0	5.3	89.0	5.5
V, R = Cl	237–242	$C_{42}H_{28}Cl_2$	83.6	4.6	83.6	4.6

[a] Stobbe and Vieweg, *Ber.*, **35**, 1728 (1902).

The product is identical with the one obtained by a different method by Eck and Marvel [THIS JOURNAL **57**, 1898 (1935)].

TABLE II

PROPERTIES OF BIS-2,2'-(1,3-DIPHENYLINDENE) DERIVATIVES

Compound	Source	M. p., °C.[c]	Mixed m. p., °C.[d]
V, R = OH	[a]	293	291
	[b]	292	
V, R = Cl	[a]	240–245	237–242
	[b]	237–242	

[a] Eck and Marvel. [b] Koelsch and Richter. [c] Melting involves decomposition, and the temperature at which it occurs depends to some extent on the stage of subdivision of the compound and on the rate of heating. [d] We are indebted to Professor Marvel for the melting points reported here.

Like these authors we have found the derived dichloride to be unreactive toward metals (zinc or mercury). The dichloride, however, appears to give an alkali derivative with 40% sodium amalgam and we hope to make use of this reaction in converting it into the di-radical.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINN.
C. F. KOELSCH
H. J. RICHTER

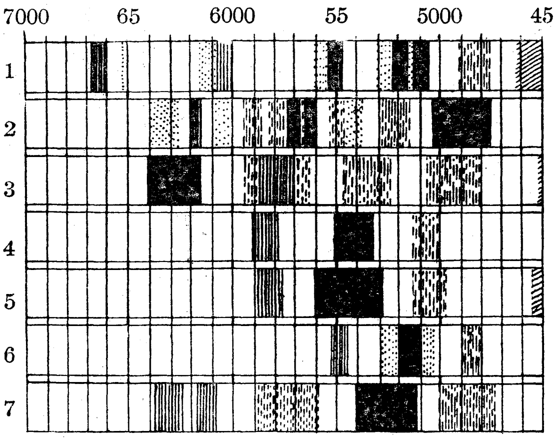
RECEIVED SEPTEMBER 18, 1935

FORMATION OF PORPHYRINS FROM PYRROLE AND ALDEHYDES

Sir:

Porphyrin formation was observed under the following conditions: pyrrole, C. P., was dissolved in a solution of gaseous acetaldehyde (I) or formaldehyde (II) in methanol (saturated in the cold), and the reaction mixture was either (a) kept at room temperature for several weeks, or (b) heated under reflux for fifteen to twenty-five hours, or (c) heated in a sealed tube to 85–90° for ten to twenty hours in a water-bath.

The reaction mixture was then subjected to vacuum distillation to remove the methanol and the aldehyde; the oily residue was taken up in warm pyridine, transferred into ether and the ether solution was fractionated with hydrochloric acid. The results are indicated in a somewhat abbreviated form in the chart of the absorption spectra.



Absorption spectra.

(1) Porphyrin from reaction I (pyrrole + acetaldehyde) in ether. (2) Porphyrin from reaction II (pyrrole + formaldehyde) in ether. (3) Porphyrin from reaction I in 0.05% hydrochloric acid. (4) Porphyrin from reaction II in 3.0% hydrochloric acid. (5) Copper complex salt of porphyrin from reaction I in ether. (6) Copper complex salt of porphyrin from reaction II in ether. (7) 3% hydrochloric acid fraction from the reaction pyrrole + furfuraldehyde in ether.

The main fraction in case I enters 0.5% hydrochloric acid and has a hydrochloric acid number of 0.075. The main fraction in case II enters 3% hydrochloric acid, its hydrochloric acid number is 3.3. The porphyrin from I crystallized in rhomb-shaped crystals, the one from II in platelets. The corresponding copper complex salts and hemins were prepared.

The yield increased upon addition of pyridine to the original solution, or when suitable agents (*e. g.*, $CaCO_3$ + MgO, $PbCrO_4$) were added; the resulting porphyrins were different from the ones mentioned above when the reaction was performed in presence of PbO_2.

Further studies are in progress to secure information on the structure of the porphyrins formed, and to determine the applicability of the reaction to other aldehydes; a comprehensive report of the research will soon be published. From theoretical considerations and in the light of numerous porphyrin syntheses by H. Fischer [*Ann.* since 1926; H. Fischer and H. Orth, "Die Chemie des Pyrrols," Leipzig, 1934 and 1935], the main porphyrin formed from acetaldehyde and pyrrole seems to be α,β,γ,δ-tetramethylporphin. The reaction between formaldehyde and pyrrole apparently leads to porphin, the as yet hypothetical tetracyclic parent ring system of the porphyrins, and hence, also the fundamental structure in the physiologically important pigments, hemin and chlorophyll.

C. F. KETTERING FOUNDATION PAUL ROTHEMUND
FOR THE STUDY OF CHLOROPHYLL
AND PHOTOSYNTHESIS
ANTIOCH COLLEGE
YELLOW SPRINGS, OHIO

RECEIVED AUGUST 23, 1935

CONTRIBUTION TO THE KNOWLEDGE OF THE TESTICULAR HORMONE

Sir:

The communication of E. S. Wallis and E. Fernholz [THIS JOURNAL, **57,** 1511 (1935), received July 15] occasions the present note. In an article accepted on June 1 and published in the number of *Helv. Chim. Acta* [**18,** 986 (1935)] which appeared on July 1, we described the preparation of androstene-3,17-dione (I) and suggested the probability that the testicular hormone (not then isolated) is identical either with this diketone or with androstene-3-one-17-ol (II).

At our request, Dr. E. Tschopp in Basel began the investigation of this hypothesis by submitting (I) to the usual tests on capons and castrated rats. The details of his study, which were communicated to the League of Nations committee in London (July 15–17), will be published elsewhere; they are summarized in the table.

Substance investigated	Capon unit	Seminal vesicle wt. in mg. after 20 days[a] 50 γ daily	100 γ daily	200 γ daily
(I) Androstene-3,17-dione	100 γ	25	51	285
(III) Androstane-3,17-dione	100 γ	16	27	51
(IV) Androstane-3,17-diol	15 γ	14	25	40
(V) Androsterone	60 γ	11	14	17

[a] The control animals had a seminal vesicle weight of about 6 mg.

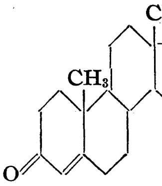
Compared in terms of capon units, (I) is five times as effective on seminal vesicle growth as (V), on the basis of the 50 γ daily dose; on the basis of the 200 γ daily dose, however, (I) is 25 times as effective as (V). The corresponding activity ratios for (IV) and (I) are 1:12 and 1:50, respectively.

This constituted the first description of the physiological activity of a substance of known constitution which exhibits the relationship between rat-tests and capon-test potency characteristic of testicular extracts. The natural expectation that this observation would prove significant in the elucidation of the constitution of the testicular hormone was fulfilled with surprising promptitude.

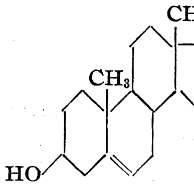
Laqueur, *et al.* [*Z. physiol. Chem.*, **233**, 281 (1935), appearing on June 7] described the isolation of a testicular hormone of unknown constitution (m. p. 154°), with a capon activity of about 10 γ, which was called testosterone (VI). Although (VI) showed the characteristic difference in capon-test and rat-test effectiveness, the published figures do not permit a rigorous comparison with (I).

At London, Laqueur expressed the opinion, based on chemical evidence, that (VI) is an isoandrosterone. The physiological activity of (I) suggested further investigation of (VI) and we have recently learned by private communication from Prof. Laqueur that (VI) yields (I) upon oxidation. Therefore it appears highly probable that formula (II) is that of testosterone (VI).

In pursuance of the program outlined in our paper (*loc. cit.*) we reduced androstene-3-ol-17-one (VII) with sodium and alcohol to androstene-3,17-diol (VIII), m. p. 175–178° corr. Utilizing the greater reactivity of the 3-substituent we partially oxidized the dibromide of (VIII) to produce (II) upon subsequent debromination. We also partially saponified the diacetate of (VIII) to produce the 17-monoacetate, which, upon oxidation of its dibromide and debromination, should yield the acetate of (II).



(I)



(VIII)

Further details will be published elsewhere, and we hope that the previous announcement of our research program (*loc. cit.*), together with the work initiated before the isolation of testosterone, may serve as a reservation of this project.

Footnote (*Sept. 7*).—At the time this note was written the author was unaware that testosterone (androstene-3-one-17-ol) had already been synthesized in his laboratory in Zürich by his assistants. The substance was made by partially saponifying the unsaturated diol diacetate and oxidation of the monoacetate dibromide.

GEORGE HERBERT JONES LABORATORY L. RUZICKA
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

RECEIVED AUGUST 20, 1935

EXPERIMENTS ON THE CONSTITUTION AND PREPARATION OF THE TESTICULAR HORMONE

Sir:

In the preceding Communication of L. Ruzicka it is evident from the dates given that the publication of his experiments on the preparation of androstendione-3,17 antedates the publication of our experiments on the preparation of this same compound. However, we would like to state that the particular issue of the *Helv. Chim. Acta* to which reference is made was not received in our library until August 8, three days after the publication of our experiments, and that a sample of dehydroandrosterone prepared by our method (received by THIS JOURNAL, June 4) was sent to Professor Butenandt on May 20. We were unaware, therefore, of Professor Ruzicka's experiments, and our suggestion as to the constitution of the testicular hormone and our experiments on its preparation were made independently. At the time of the appearance of his article in the *Helv. Chim. Acta* we were engaged in the preparation of 17-hydroxy-androsten-one-3, and we had succeeded in preparing androstendiol (m. p. 175°), and its diacetate (m. p. 159°) by the reduction of our synthetically prepared dehydroandrosterone when the above Communication reached us. In view of Professor Ruzicka's Communication, and of his request that this project be reserved we are discontinuing our work in this particular direction.

FRICK CHEMICAL LABORATORY EVERETT S. WALLIS
PRINCETON UNIVERSITY E. FERNHOLZ
PRINCETON, N. J.

RECEIVED SEPTEMBER 23, 1935

THE PREPARATION OF β-CHLOROVINYLARSINE SULFIDE

Sir:

β-Chlorovinylarsine sulfide was first described by Lewis and Stiegler [THIS JOURNAL, **47**, 2546 (1925)] as a clear, amber-colored plastic mass insoluble in the usual solvents other than carbon disulfide and possessing an extraordinarily irritating and noxious odor.

We have succeeded in obtaining this substance, β-chlorovinylarsine sulfide, in a crystalline condition by the following procedure. Hydrogen sulfide was conducted for two hours through a solution of 45 g. of β-chlorovinyldichloroarsine (b. p. 78° at 12 mm.) in 50 cc. of alcohol. The solution became noticeably warmer and a yellow viscous oil gradually separated out. After two hours separation ceased and this was taken as the end of the reaction. The resulting product was an amber-yellow viscous oil which adhered to the walls of the flask. The alcoholic solution was poured off, the oil washed repeatedly with alcohol and then dissolved with warming in carbon disulfide. After cooling and distilling off part of the solvent, the substance separated in crystalline form. In order to obtain a more complete separation an equal volume of benzene may be added to the solution; yield 20 g. or 51% of the theoretical. After recrystallization from benzene and drying in a vacuum desiccator, the melting point was 114°.

Anal. Calcd. for C_2H_2ClSAs: As, 44.49; Cl, 21.05; S, 19.03. Found: As, 44.55; Cl, 21.06; S, 19.27.

β-Chlorovinylarsine sulfide crystallizes in cubes, possesses a pale yellow color and a weak, not unpleasant, odor; is easily soluble in carbon disulfide, less so in benzene and ether and insoluble in water. Under the influence of sunlight the substance acquires an orange color.

MOSCOW, U. S. S. R. S. L. WARSCHAWSKI

RECEIVED JULY 17, 1935

THE ISOLATION OF CROTYL AND METHYLVINYLCARBINYL BROMIDES

Sir:

The composition of bromide mixtures arising from the action of hydrogen bromide and phosphorus tribromide on crotyl alcohol or methylvinylcarbinol has been the subject of much discussion. Some claim that pure products [Charon, *Ann. chim. phys.*, [7] **17,** 216 (1899); Prévost, *Ann. chim.*, **10,** 113 (1928); Claisen and Tietze, *Ber.*, **59B,** 2344 (1926); Juvala, *Ber.*, **63B,** 1989 (1930)] are obtained from alcohols of this type while others report the formation of mixtures of bromides but have not separated them [Baudrenghien, *Bull soc. chim. Belg.*, **31,** 160 (1922); Meisenheimer and Link, *Ann.*, **479,** 211 (1930); Young and Prater, This Journal, **54,** 404 (1932); Gredy and Piaux, *Bull. soc. chim.*, [5] **1,** 1481 (1934)]. The bromides obtained in this Laboratory have always been mixtures. We have recently separated these mixtures into the primary (crotyl bromide) and secondary (methylvinylcarbinyl bromide) isomers by fractional distillation at 0°. The properties are $n^{23}\text{D}$ 1.4805 and 1.4612; $d^{25}{}_4$ 1.3335 and 1.2998; b. p. 49° and 31.0° at 93 mm., >107° and 86.5° at 760 mm., and +2.0° at 5 mm. and −2.0° at 14 mm. for the primary and secondary isomers, respectively. Mixtures of these bromides may be analyzed from density or refractive index measurements since these properties are linear functions of the composition.

Both of the pure bromides rearranged to an equilibrium mixture of 14% secondary and 86% primary in a few days at room temperature, in less than one hour at 75° and in less than five minutes at 100°. If a mixture of the bromides is subjected to slow distillation at atmospheric pressure through a 100-cm. packed column, almost pure secondary bromide is obtained as a distillate. Equilibrium is so rapidly established in the boiler that the secondary bromide is replaced as fast as it is removed from the top of the column.

It is now evident that the bromides reported by Juvala, Baudrenghien and Gredy and Piaux having $n^{23}\text{D}$ 1.4750 to 1.4759 contained from 24–29% of secondary bromide. Their compositions were dependent on the method of distillation and had nothing to do with the method of preparation. The bromides used by Gredy and Piaux must have gone to equilibrium after the refractive index was taken and before the Raman spectra were measured, since their analysis of 90% primary and 10% secondary is qualitatively in agreement with the equilibrium composition and not with the composition calculated from the refractive index.

In the light of these developments, crotyl alcohol and methylvinylcarbinol are being converted into bromide mixtures by various reagents under conditions designed to avoid rearrangement of the product. The composition of these mixtures will be reported in the near future.

DEPARTMENT OF CHEMISTRY WILLIAM G. YOUNG
UNIVERSITY OF CALIFORNIA AT LOS ANGELES
LOS ANGELES, CALIFORNIA SAUL WINSTEIN

RECEIVED AUGUST 12, 1935

NEW BOOKS

Annual Review of Biochemistry. Vol. IV. Edited by JAMES MURRAY LUCK, Stanford University. Annual Review of Biochemistry, Ltd., Stanford University P. O., California, 1935. vii + 639 pp. Illustrated. 15.5 × 23 cm. Price, $5.00.

The fourth volume in this series of annual reviews introduces two new sections on choline and allied substances by J. H. Gaddum, and on growth substances in plants by K. V. Thimann. The biochemistry of malignant disease as reviewed by Barbara E. Holmes differs somewhat from the discussion of malignant tissue prepared by E. Boyland a year ago.

Several new reviewers contributed to this volume, including M. H. Jacobs, on permeability; R. Sonderhoff, on biological oxidations and reductions; J. B. Sumner, on enzymes; Sir J. C. Irvine and G. J. Robertson, on the chemistry of the carbohydrates and the glycosides; E. Chargaff, on the chemistry of the acyclic constituents of natural fats and oils; E. J. Cohn, on the chemistry of the proteins and amino acids; C. Artom, on fat metabolism; B. A. Houssay, V. Deulofeu, and A. D. Marenzi, on the hormones; P. Eggleton, on the chemistry of muscle; R. Kuhn, on plant pigments; and F. C. Steward, on the mineral nutrition of plants.

In addition to these reviews, the volume also includes the following: The chemistry and metabolism of the compounds of sulfur, by H. B. Lewis; the chemistry and metabolism of nucleic acids, purines and pyrimidines, by L. R. Cerecedo; carbohydrate metabolism, by C. F. and G. T. Cori; the metabolism of amino acids and proteins, by Y. Kotake; the metabolism of creatine and creatinine, by W. C. Rose; detoxication mechanisms, by B. Harrow and C. P. Sherwin; vitamins, by L. J. Harris; nutrition, by S. Brody; the metabolism of brain and nerve, by E. G. Holmes; chemical embryology, by J. Needham; the alkaloids, by R. Robinson; immunochemistry, by M. Heidelberger; the chemistry of bacteria, by M. Stephenson. About a dozen sections or subjects that were reviewed in Volume III are omitted from the current volume, these being subjects that apparently are being covered in this series every other year or thereabouts. In fact it appears to be the policy of the editors to alternate certain subjects and the current volume covers subjects that were included two years ago but were not included in Volume III.

Comments made by the reviewer a year ago respecting Vol. III apply equally well to the recent issue of Vol. IV. The surveys are concise, and critical, and must be very serviceable to the workers in this expansive field of biochemistry. Thimann's review of growth substances in plants, covering, as it does, contributions dating back ten years, constitutes a welcomed addition to the book. Not only has he discussed cell elongation and root formation in the higher plants, but he has included a consideration of growth substances for fungi, and yeast (bios) as well.

It appears to the reviewer that errors have been made in the diagrammatic formulas of tachysterol and the compound intermediate between it and calciferol on page 364. The two double bonds in the ring system are not represented here as conjugated, despite the fact that the text immediately above described them as such, and they were so represented by Rosenheim and King in their paper to which reference is made in the bibliography appended to this chapter.

C. H. BAILEY

The Principles of Quantum Mechanics. By P. A. M. DIRAC. Second edition. Oxford University Press, 114 Fifth Ave., New York, 1935. xi + 300 pp. 16 × 24 cm. Price, $6.00.

This is a book intended for those who are interested in deepening their understanding of the essential significance of quantum mechanics, rather than in the actual solution of problems. The list of topics treated contains few that will not be already familiar to the reader; the method of approach, however, is wholly different from those usually followed.

To the exposition of this method of approach, the first six of the thirteen chapters are devoted. The author's aim is to find statements of the laws of nature which shall be as far as possible free from quantities depending upon arbitrary frames of reference or particular states of mind of the observer. Where such quantities do enter, they must merely illustrate fundamental relations, the latter remaining invariant under all possible transformations of the special terms in which they are stated. This guiding principle is developed in terms of the theory of vectors according to which the mathematical relations of directed quantities can be formulated without the introduction of any particular coördinate system or set of reference vectors, although this is required for the solution of any particular problem. In the present application, the vectors are imagined as existing in a space of infinite number of dimensions. Any particular vector corresponds to a particular state of knowledge of the observer concerning the state of the system under discussion, such as that each particular "observable" (energy, angular momentum, etc.) has a certain probability of having each of its possible values. "Eigenstates" are those for which one or more observables certainly have particular "eigenvalues," and the corresponding vectors, forming a complete orthogonal set, may conveniently serve as coördinate axes in terms of which other vectors may be expressed numerically. Owing to the characteristic impossibility of assigning definite values to several observables simultaneously, the eigenstates and the reference frames corresponding to different observables do not in general coincide. The squares of the coefficients with which the eigenvectors of a given observable must be taken in order to produce by vectorial addition any given vector (as an eigenvector of another observable) are equal to the probabilities that a measurement of the given observable, performed upon the system in the given state, will yield as result the several corresponding eigenvalues.

In order to determine these coefficients, and to discuss other relations between the vectors, it is necessary to introduce tensors, which correspond to observable quantities. When expressed in terms of a given coördinate system, the tensors take the form of the familiar matrices of ordinary presentations of quantum mechanics. The customary processes of matrix multiplication thus appear as simply special methods of representing operations of combining tensors and vectors, whose real meaning (similar to the scalar product of two vectors) is quite independent of any particular system of axes, and which therefore are well suited for stating fundamental laws.

The picture so far is limited to a particular instant of time, and is therefore not properly relativistic. This is a defect which it has not been possible to remedy. The next few chapters are devoted to a study of the way in which the vectors change with the time, giving an account of the motions occurring in the system. An alternative presentation regards the vectors as stationary, but referred to moving axes; the tensors corresponding to observables then become functions of the time. On this basis is developed the theory of simple problems such as motion in a central field, perturbations, collision effects, etc., the final results being those already well-known.

The last three chapters, on Radiation, Relativistic Electron and Field Theory, are devoted to subjects in which the author himself has done much of the pioneer work, and will be valuable as a convenient unified presentation of the essential material.

The book is carefully worked out and well-written. Naturally, it is extremely arduous reading for anyone not accustomed to the formalism and abstractness of modern physical theory, but in the opinion of the reviewer the effort expended upon it will be richly rewarded.

ALBERT SPRAGUE COOLIDGE

Étude Thermodynamique de la Tension Superficielle. (A Thermodynamic Study of Surface Tension.) By RAYMOND DEFAY. Preface by Th. DeDonder. Gauthier-Villars et Cie., Éditeurs, 55 Quai des Grands-Augustins, Paris, France, 1934. xi + 372 pp. 16 × 24 cm. Price, fr. 30.

This volume coördinates the work of the author on surface tension published 1929 to 1934 and contains the material of his doctorate thesis. In the first part of the work he takes up from the beginning the thermodynamic problem of capillary and adsorption phenomena, using the approach of DeDonder, which postpones the assumption of equilibrium to a later point in the reasoning than in the treatment of Gibbs and thus enables the presentation of certain results more general than those of Gibbs. The equilibrium assumptions which the reviewer has noted as being thus postponed are those relating to phase equilibrium and to equilibrium with respect to chemical reactions.

In his logical development he rejects the hypothesis that the surface phase is autonomous, *i. e.*, that its thermodynamic properties can be expressed by functional relations containing only variables appropriate to the surface phase itself. This is of consequence only when there is not equilibrium; for when the hypothesis of "localization of equilibrium" is admitted—that any portion of a system in equilibrium constitutes itself a system in equilibrium—the usual results for equilibrium are obtained.

The reviewer does not agree with a remark (page 77) that this latter hypothesis is introduced by Gibbs when he writes his equation 476, but considers it explicitly introduced in the beginning when Gibbs states that in case of equilibrium the criteria must be satisfied in *all possible variations.*

Defay introduces the radius of curvature into his equations by means of the relation $p'' - p' = \sigma/(R_1 + R_2)$, which is assumed from mechanics. He places the dividing surface always within the region of discontinuity, insisting that the location of this dividing surface is not arbitrary (page 99). His treatment here is very clear. Yet his remarks on Gibbs and his followers seem not entirely adequate, and Gibbs' statements on page 234 seem ignored: (1) that the position of the quantity σ, considered as a tension, is in the surface of tension and, strictly speaking, nowhere else; (2) that the value of σ is independent of the position of the dividing surface, when this is plane; and (3) that the positions which he will consider will not vary from the surface of tension sufficiently to make this distinction of any practical importance. Defay has a right to his own development and this is in several respects simpler than that of Gibbs. The gain here is accompanied, however, by a loss—Defay is not able to derive the Gibbs equation for the so-called adsorption isotherm and does not discuss it.

Under the heading "Catalysis at a Distance," Defay shows the theoretical possibility (depending on the non-autonomy of the surface phase) that a surface may act as a catalyst without any exchange of mass and that surface catalysis can affect the affinity of a reaction.

The phase rule is extended to systems containing surface phases (in both parts of the book) and is often applied in the treatment. Various thermodynamic theorems are generalized to take account of the presence of surface phases and the possibility that equilibrium is not reached.

It is pointed out (page 17) that the surface tension is not necessarily equal (when there is adsorption) to the superficial free energy per unit area.

The second part of the work is so written as not to require preliminary study of the first part. It is entitled "The Extrema [maxima or minima] of Surface Tension and the Indifference of Capillary Systems" and deals mostly with the azeotropic properties of such systems. The conditions of equilibrium of systems containing surfaces which meet *along edges* are discussed, but without consideration of the effects of gravity. The rule of Antonoff 1907 is traced to Poisson 1831 and it is shown that (in a system uninfluenced by gravity) this rule is inconsistent with the presence of edges between coexistent surface phases. Theorems of Duhem, of Saurel, and of Gibbs and Konovalow are generalized.

The book is clearly written by an author obviously competent in mathematics and the theory of thermodynamics. The symbols chosen will give little or no difficulty to readers of Gibbs. There is no index, but the table of contents is unusually effective as it contains over 150 headings.

L. J. GILLESPIE

Physique Moléculaire. Matière et Énergie. (**Molecular Physics. Matter and Energy.**) By VICTOR HENRI, Professor at the University of Liége. Hermann et Cie., Éditeurs, 6 Rue de la Sorbonne, Paris, France, 1933. v + 436 pp. 16 × 24.5 cm. Price, fr. 110.

The ten chapters of the book are entitled: Discontinuity of matter, Determination of the number of molecules, The chemical elements, X-ray spectra, Atomic numbers, Periodic System, Radioactive elements, Isotopes, Disintegration and synthesis of elements, Space properties of the elements, Kinetic theory of gases, Atomic structure.

Inspired by an early attachment to the Leibnizian monadology, the gifted author has burst the walls of his own specialty and tried to write in one moderate-sized volume a compact yet penetrating account of nearly all those aspects of modern molecular and atomic physics which are of special significance for chemistry. Henri's own early studies (1908) of the Brownian movement in rubber latex gave him an interest in molecular theory and the determination of N which make the first chapter (on the discontinuous structure of matter) unusually excellent. In the chapter on the chemical elements (p. 61) he espouses a lost cause when he tries to limit the word "element" to a single atomic species.

The later chapters contain good discussions of ionization and resonance potentials and their significance for the periodic system. The Bohr theory is discussed in some detail, but modern quantum ideas are hardly mentioned. The spatial properties of atoms and ions receive some attention.

The book was surprisingly up to date when it was published two years ago, but has already fallen somewhat behind the rush of new developments in its field. It contains a large number of very useful literature references, but is marred by careless proof reading, particularly of English names. Some random examples are thalium, Lokyer, isote for isotope, Stockes, Bridgeman for Bridgman, John Tydall. On p. 355 and elsewhere Davisson and Germer's discovery is credited to Davisson and Kunsman.

NORRIS F. HALL

The Chemistry of Organic Compounds. A Year's Course in Organic Chemistry. By JAMES BRYANT CONANT, Professor of Chemistry, Harvard University. The Macmillan Company, 60 Fifth Avenue, New York, 1933. x + 623 pp. 14.5 × 22.5 cm. Price, $4.00.

The present text, designed for a full year course in organic chemistry, and an appropriate expansion of the author's excellent "Brief Introductory Course," has much to recommend it. It is concisely and logically written; it adapts itself admirably to classroom usage; and it gives a true appreciation of the scientific method.

The author has made use of the electron theory of valency with excellent discrimination, employing it in cases where it is generally regarded as of value to the organic chemist, and avoiding it when it would make for confusion in the minds of elementary students.

There is material beyond the scope of the usual course, but this is of particular advantage for the instruction of the honors type of student, to whom, in most institutions, special reading is given.

In short, then, this text is a very notable addition to the group of the few worthwhile texts of its degree of difficulty in organic chemistry.

ARTHUR J. HILL

A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Volume XIV. **Fe** (Part III), **Co.** By J. W. MELLOR, D.Sc., F.R.S. Longmans, Green and Co., 114 Fifth Avenue, New York City. viii + 892 pp. 277 figs. 15.5 × 25 cm. Price, $20.00.

The first part (416 pages) of this volume concludes the section on iron, recounting the physical and chemical properties of the salts of iron. The remainder of the volume (some 476 pages) is devoted to the element cobalt and its compounds.

The treatment throughout is analogous to, and maintains the same high quality as, that of previous volumes.

There remain but two volumes of this monumental handbook to appear: Volume XV, covering nickel and the elements of the platinum group other than platinum itself, and Volume XVI, covering platinum and containing the General Index for the whole Treatise. The publisher states that both of these volumes are in the press.

ARTHUR B. LAMB

Annual Tables of Constants A. T. C. and Numerical Data Chemical, Physical, Biological and Technological, published under the patronage of the International Union of Chemistry. Volume X (1930). McGraw-Hill Book Co., Inc., 330 West 42d St., New York, 1935. Two parts, about 1800 pages. Price (for subscribers) cloth, $20.00.

In the Introduction to this Volume X (1930) of the Annual Tables, Dr. Marie, Editor-in-Chief, states:

"When Volume IX was published in 1931, we hoped that the period of the difficulties which we had to overcome was at last over and that we should be able to take up again the publication of annual Volumes. This hope, however, was not fulfilled. The financial means which we thought we could rely upon have been reduced to such an extent that we were compelled to suspend the printing of the Annual Tables. The general economic crisis is responsible for this situation. Consequently, we had to postpone the publication of Volume X, which brings to a close our 2nd series and of the Index to this series.

"We hope that this work will be completed in the course of 1935. We further hope to be able, at the same time, to start with the publication of the data of the years 1931 to 1934 in Volume XI, which is to be the first of our 3d series."

This volume follows the same method and exhibits the same excellence that have characterized the earlier volumes. Dr. Marie and his collaborators deserve both our gratitude and our congratulations in having kept alive this important branch of scientific documentation during a prolonged and world-wide period of depression.

It also should not be forgotten by those who have difficulty with the French language that all texts in the Annual Tables of Constants are given in both French and English.

ARTHUR B. LAMB

An Introduction to Quantum Theory. By G. TEMPLE, F.R.S., Ph.D., D.Sc., Imperial College of Science and Technology, London. D. Van Nostrand Company, Inc., New York, 1934. 196 pp. 14 × 22 cm.

This book covers the topics usual to an elementary text on quantum mechanics, including a discussion of both the wave equation and matrix mechanics, with a few elementary applications; finally the relativistic theory of the electron is presented. The treatment is based squarely on classical mechanics and relativity, and the relation between these older branches of physics and the quantum mechanics is constantly brought out and emphasized. For this reason the book will be useful to those who are interested in the fundamental aspects of the subject. It may also be recommended to beginners in quantum mechanics who are thoroughly grounded in classical physics, though it seems likely that on account of its rather abstract and formal style it will not appeal to chemists as much as some of the other books on the subject now available.

O. K. RICE

Atomic Structure and Spectral Lines. By ARNOLD SOMMERFELD. Translated from the Fifth German Edition by HENRY L. BROSE, M.A., D.Phil., D.Sc., Lancashire-Spencer Professor of Physics, University College, Nottingham. Volume I. E. P. Dutton and Company, Inc., 286–302 Fourth Avenue, New York, 1934. xi + 675 pp. 151 fig. 14.5 × 22.5 cm. Price, $10.80.

In the development of quantum theory since the advent of the Bohr atom in 1913, there has probably been no one book which has been first and last of as great value and influence as the various editions of Sommerfeld's "Atomic Structure and Spectral Lines." In this connection we may well quote what the translator (Brose) says of Professor Sommerfeld: "He has earned the gratitude of physicists throughout the world for carrying out so successfully the monumental task of a comprehensive and lucid exposition of modern atomic physics." The volume in question is such a well-known one that a review of its contents seems scarcely necessary, except to remark on how it differs from the earlier editions. Like the earlier ones, it does not utilize the methods of quantum mechanics, except for occasional quotation of results. Instead the presentation of the new mechanics is deferred to a promised second volume, which will be an amplification of Sommerfeld's well-known and excellent "Wellenmechanische Erganzungsband" (translated under the title "Wave Mechanics"). Of course this plan keeps the procedure in the first volume from being too mathematical, and there is a great deal to be said in favor of the author's statement that "it is possible to understand the new theory only by building it up from the old." Still there are many cases where the situation is really more lucid and intelligible if the new analysis has first been developed.

As compared with earlier editions, sections have been added on the Pauli principle, hyperfine structure, complex spectra, and other subjects. In the discussion of helium, one misses the dramatic quotation from Faust "Hier stock'ich schon; wer hilft mir weiter fort?" found in earlier editions. The dilemma of the helium atom has been explained away by the new quantum mechanics, and the words of Faust are no longer necessary. However, the revision is not sufficiently drastic and recent that the volume can be classed as up-to-date, particularly as regards references to the literature. It is, for instance, somewhat startling to learn that the most recent experimental determinations of the hydrogen fine structure are those of G. Hansen in 1925. Actually a whole bibliography could be given of later papers. It is now, we believe, generally conceded that the old theory of Fues and Wentzel of "partially penetrating orbits" discussed in section 5 of Chap. VII is not the true explanation of the anomalous behavior of the principal series of mercury, but that rather the latter is due to a perturbation effect, as proposed by Shenstone and Russell in 1932, and so on.

A major reason why the volume is not more modern is that whereas the German edition was written in 1931, the English translation did not appear until 1934, without any attempt to collate with publications in the intervening period (except for a translator's addendum of five papers largely on nuclear structure).

J. H. VAN VLECK

Alkaloidhaltige Genussmittel, Gewürze, Kochsalz. (Alkaloid-Containing Luxuries, Condiments, Cookery Salt.) By E. BAMES, A. BEYTHIEN, C. GRIEBEL, H. HOLTHÖFER, P. KOENIG, R. STROHECKER, K. TÄUFEL, J. TILLMANS. Bömer–Juckenack–Tillmans, "Handbuch der Lebensmittelchemie," Vol. VI. Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany, 1934. ix + 604 pp. 344 figs. 17.5 × 25.5 cm. Price, RM. 76; bound, RM. 79.60.

This is volume six of a series of eight volumes of a Handbook of Food Chemistry which are not appearing in numerical order. Volume one—a general introduction to the series—was reviewed in THIS JOURNAL [**56,** 1429 (1934)] by C. A. Browne. This volume is divided into six principal sections and an appendix, each by a separate compiler: I, Coffee, coffee substitutes and adulterants (Täufel); II, tea, tea substitutes, maté and cola (Strohecker); III, cocoa and chocolate (Beythien); IV, tobacco (Koenig); V, condiments (Griebel); VI, cooking salt (Strohecker); and the supplement which gives a very brief digest of the laws and regulations under which the products are sold in various countries (Holthöfer–Bames). Under coffee (for example), the compiler (Dr. Täufel) describes the botanical and geographical sources of the product, its varieties and physical properties and gives methods for the determination of the principal chemical constituents such as ash, water-soluble extract, caffeine, nitrogenous substances, etc. The composition of unroasted and roasted coffee and the changes which take place in roasting are discussed at considerable length. Several brands of "caffeine-free" coffees are named and the methods for preparing them are described in a general way. The chapter on the microscopical characteristics of coffee and its substitutes is by Griebel, although most of the drawings are taken from Moeller rather than from the author's publications. The other sections of the work are treated in a similar manner. The references to German writings on all of the topics are very complete but the authors have made almost no use of the literature in English. It is difficult for the reviewer to understand how it was possible to compile a work of this character and omit nearly all references to American or English contributors. For example, the Power–Chesnut method for determining caffeine, which was published in 1919, and which has been adopted by the Association of Official Agricultural Chemists, is not mentioned. Instead, other less reliable methods are given. Again, the Self and Rankin method for the determination of theobromine and theophylline, which has been known for several years and is official now in the British Pharmacopoeia, is not considered.

Six methods for determining volatile oils in such materials as cinnamon and cloves are given but no editorial opinion is expressed as to which is considered best. The Clevenger method, which has attained such wide recognition in this country because of its relative simplicity and broad applications, is overlooked. Even where the original papers on other topics are in English, such as Schmitt's researches on the assay of theophylline, the compiler refers only to abstracts in German. The reviewer did not observe a single reference to any method adopted by the Association of Official Agricultural Chemists and noted but few references to papers published in its Journal. The volume includes a workable index. Throughout the work there is neglect to discuss critically the merits of the several methods for the determination of a given substance where more than one procedure is given. From the standpoint of the analyst this is the most conspicuous fault in the volume. Because of its lack of critical judgments and because of its general ignoration of the chemical literature of the world (except German) this volume of the work will not be as serviceable to American chemists as it would otherwise have been. It is hoped that these defects will be remedied in future editions.

L. E. Warren

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August 15, 1935–September 15, 1935

J. J. Carlberg. "Bestämning av *p*H-Värdet I Utspädda Bikarbonatlösningar vid Olika CO_2-Tryck." Helsingfors University, Helsingfors, Finland. 79 pp.

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G. H. Cartledge and H. M. Woodburn. "Laboratory Exercises in Inorganic Chemistry." Ginn and Company, 15 Ashburton Place, Boston, Mass. 149 pp. $1.00.

H. Jermain Creighton. "Principles and Applications of Electrochemistry. Vol. I. Principles." Third edition. John Wiley and Sons, Inc., 440 Fourth Ave., New York. 502 pp. $4.00.

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"Gmelins Handbuch der anorganischen Chemie. System-Nummer 53, Molybdän." Verlag Chemie, Corneliusstrasse 3, Berlin W 9, Germany. 393 pp. RM. 64.

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[CONTRIBUTION FROM THE LABORATORY OF THE DEPARTMENT OF AGRICULTURAL AND BIOLOGICAL CHEMISTRY, THE PENNSYLVANIA STATE COLLEGE]

Ricinus Lipase, its Nature and Specificity[1]

BY HERBERT E. LONGENECKER[2] AND D. E. HALEY

The lipolytic principle of the castor bean (*Ricinus communis*) has engaged the attention of many research workers since its presence was first proved in 1890 almost simultaneously by Green[3] and Sigmund.[4] However, a review of the available literature on the active substance, Ricinus lipase, has failed to reveal any general concordance of experimental results. Haley and Lyman's discovery[5] that with oils optimum conditions for activity were obtained only within narrow limits of hydrogen ion concentration, about *p*H 4.7–4.8, made it necessary to repeat most of the previous work.

The object of the present investigation was to prepare a highly active, dry and stable preparation of Ricinus lipase from resting castor seeds and to study the nature of its action and its relative specificity in the hydrolysis of various vegetable and animal oils. These studies were undertaken to elucidate the mode of action of Ricinus lipase and to contribute to the knowledge of enzyme action in general.

Experimental

A. Preparation of Lipase Material.—Ricinus lipase was prepared from large size castor beans[6] by hulling and macerating them, extracting the fat as completely as possible with low boiling petroleum ether (20–40°), and finally drying, pulverizing and sifting the finished product through a 60-mesh sieve. This is a modification of the method given by Haley and Lyman.[5] Other methods for the preparation of Ricinus lipase have been reviewed by Longenecker.[7] Most of them are less suitable.

B. Estimation of Activity.—In all experiments reported here, a standard procedure was adopted for the determination of lipolytic activity: 1.00 gram of oil was weighed into five-cc. hard-glass bottles and two drops of toluene added to prevent bacterial action. To this was added a weighed quantity of enzyme material and its activator, tenth normal acetic acid. The *p*H of the resulting mixture was 4.8. It was emulsified by vigorous shaking for three minutes. Digestion was carried on at a temperature of 37°. To prevent loss of any of the digestion materials, the bottles were stoppered with paraffined corks. The results reported represent averages of triplicate determinations. "Blanks" always accompanied the samples.

After a definite time of incubation, the reaction mixture was placed in 50 cc. of hot 95% alcohol and the free fatty acids in the digestion mixture were titrated with 0.1 *N* alkali using phenolphthalein as the indicator. The starting time for each experiment was that time when acetic acid was added to the digestion mixture; the final time, when the reaction mixture was placed in the alcohol. It was found by preliminary experiments that no hydrolysis took place until after addition of the acid and that hydrolysis was completely inhibited in the amount of alcohol used in the titration.

Titration results are of little value, *per se*, in studies of the relative specificity of lipolytic catalysis of oils although several workers have reported their findings in this way. A more significant expression is the percentage of oil hydrolyzed or the number of moles of triglyceride hy-

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(1) Presented before the Division of Biological Chemistry at the 90th meeting of the American Chemical Society, San Francisco, California, August 19–23, 1935.

(2) Submitted in partial fulfilment of the requirements for the degree of Master of Science at The Pennsylvania State College.

(3) Green, *Proc. Roy. Soc.* (London), **48B**, 370 (1890).

(4) Sigmund, *Monatsh.*, **11**, 272 (1890).

(5) Haley and Lyman, THIS JOURNAL, **43**, 2664 (1921).

(6) Courtesy of The Baker Castor Oil Co., Newark, N. J.

(7) Longenecker, M. S. Thesis, The Pennsylvania State College, 1934.

drolyzed. For the calculation of the percentage hydrolysis, the formulas suggested by Sudborough, Watson and Varma and Wilson and Merrill[8] have been used as a basis. The difference between the volume of alkali required for the sample and that required for the blank is a measure of the fatty acids resulting from the direct cleavage of glycerides due to the action of the lipase; the ester number is a measure of the total fatty acids in glyceride combination. To obtain the percentage hydrolysis, the following formula has been used

$$\frac{\text{cc. } 0.1\ N \text{ alkali (sample)} - \text{cc. } 0.1\ N \text{ alkali (blank)}}{\text{Saponification no.}^{a} - \text{Free fatty acid no.}^{a}} = \%\ \text{hydrolysis}$$

[a] Expressed in cc. of 0.1 N alkali.

C. Activity of Old and New Preparations.—The ability of Ricinus lipase to retain its activity over a long period was demonstrated in the following experiment in which the activity of a sample similarly prepared by one of us in 1924 was compared with that of a freshly prepared sample: 1.00 gram of olive oil and 0.6 cc. of 0.1 N acetic acid were used; the amount of enzyme material was varied; one set of samples (A) was shaken for three minutes at the start, then allowed to stand for twenty-four hours at 29–30°; another set of samples (B) was shaken continuously by machine for fourteen hours then allowed to stand for ten hours at 29–30°. The results are given in Table I.

TABLE I

COMPARISON OF ACTIVITIES OF TEN-YEAR OLD AND NEW PREPARATIONS

Treatment	Percentage ten-year old sample 0.050 g.	0.100 g.	Hydrolysis new sample 0.050 g.	0.100 g.
A	6.79	17.82	77.83	86.00
B	14.03	49.36	85.43	86.70

TABLE II

TYPICAL RATE OF REACTION AND THE EFFECT OF TEMPERATURE AND SHAKING

In each experiment, 1.00 g. of olive oil, 0.6 cc. of 0.1 N acetic acid, 0.100 g. of lipase material and two drops of toluene were shaken together and incubated at 37–38°. A, shaken for three minutes at the start. B, shaken for three minutes at the start, let stand for thirty minutes and shaken again for two minutes. C, same as A except that temperature was 27–28°.

Time of digestion	Percentage hydrolysis A	B	C
5 min.	11.02	...	...
10 min.	19.35	...	25.88
15 min.	31.91	...	...
20 min.	38.33	...	44.70
30 min.	39.22	...	...
40 min.	50.63	...	55.88
45 min.	...	57.93	...
50 min.	51.91	...	...
60 min.	59.60	66.39	59.66
2 hrs.	65.37	74.85	67.80
3 hrs.	71.14	79.34	71.90
5 hrs.	72.42	80.50	...
10 hrs.	74.21	...	...
24 hrs.	77.80	77.42	...

D. Rate of Hydrolysis of Olive Oil.—Olive oil was selected as a substrate to demonstrate, first, typical rates of reaction and second, some of the factors influencing it. In Table II, data are given which express (A) a normal rate of reaction, (B) the effect of shaking the digestion mixture after the reaction has proceeded for thirty minutes and (C) the effect of temperature.

E. Relative Specificity of Ricinus Lipase Action.—A study of the rates of hydrolysis of various members of a general group of substances should yield information as to the relative specificity or affinity of an enzyme for a particular substrate. A variety of oils of vegetable and animal origin were selected for specificity studies. Rates of hydrolysis of these oils are found in Table III.

Discussion

In analyzing and interpreting these results the nature of the active material must be considered. "Ricinus lipase" has been used here to represent the hulled, fat-free, resting castor seeds. Proteins, carbohydrates and salts originally present have not been removed from the final product.

It is significant that a ten-year old preparation retained a fairly high activity compared with a fresh sample. Enzymatic activity is known to decrease considerably in short periods, especially when the enzymic material is in solution. Dry preparations are usually more stable. So far as the authors can ascertain, however, there is no report in the literature showing the retention of activity of any enzyme preparation over a period of ten years.

One condition that appears to be a *sine qua non* factor for Ricinus lipase activity is the colloidal state. One may assume that an emulsion arises in a heterogeneous system such as the digestion mixture of oil, enzyme and dilute acid. Sudan III and conductivity tests indicated in this work that it is of the water-in-oil type under the experimental conditions. This type of emulsion was favorable for the action of Ricinus lipase. In fact, there is every reason to believe that the enzyme is not as active in an emulsion of the opposite type.

The production of a suitable emulsion was aided decidedly by shaking the digestion mixture. Shaking by hand for three minutes ensured that approximately the same degree of emulsification was obtained at the beginning of each experiment. Once formed, however, the emulsion was not stable. It tended to separate into layers of water and oil within one-half hour, when the rate of hydrolysis began to decrease. Shaking the digestion mixture at this point restored the emul-

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(8) Sudborough, Watson and Varma, *J. Indian Inst. Sci.*, **2**, 241 (1919); Wilson and Merrill, *J. Am. Leather Chem. Assocn.*, **1** (1926).

TABLE III

RATES OF HYDROLYSIS OF VARIOUS OILS OF VEGETABLE AND ANIMAL ORIGIN

In each experiment, 1.00 g. of oil, 0.100 g. of lipase material, two drops of toluene and 0.6 cc. of 0.1 *N* acetic acid were shaken together for three minutes at the start, then let stand at 37–38°.

	Percentage hydrolysis								
	Minutes					Hours			
Oil	15	30	45	60	120	3	5	10	24
Castor	33.33	47.48	59.15	59.15	72.70	83.30	...	...	...
Coconut	30.67	43.26	48.96	50.73	54.27	59.58	61.37	65.81	67.05
Corn	35.37	53.86	60.74	67.16	71.64	72.09	81.79	87.01	90.75
Cottonseed	36.96	52.90	62.75	63.33	72.61	71.30	83.33	86.52	87.25
Fish	17.66	22.24	26.81	27.33	31.48	33.24	36.06	37.00	41.67
Linseed	21.44	34.25	38.78	42.88	52.48	56.61	71.12	72.59	72.90
Neat's-foot	28.93	32.43	43.11	47.96	57.86	63.69	68.31	69.33	70.68
Olive	31.91	39.22	50.63	59.60	65.31	71.14	72.42	74.21	77.80
Peach kernel	24.36	33.35	47.57	52.20	57.57	61.20	65.54	70.18	69.60
Peanut	37.55	55.86	63.55	67.40	77.73	83.70	94.40	97.24	...
Rape	39.52	48.36	54.95	62.02	71.49	69.89	77.44	81.14	83.45
Sperm	10.18	13.71	16.83	20.36	18.28	18.89	23.68	19.53	23.47
Soybean	17.66	35.05	53.13	61.30	77.64	73.99	84.35	84.94	89.17
Whale	16.77	25.33	26.26	28.98	32.82	35.14	37.67	41.81	41.71

sion and with it there was an increased rate and extent of reaction in a given time, as is seen in Table II.

A higher percentage of hydrolysis in cases where a lower temperature was used, as shown also in Table II, can be correlated with the stability of the emulsion. In each case it was observed that the tendency for the emulsion to break was much less at the lower temperature.

That Ricinus lipase exhibits a differential rate of attack for various oils appears obvious from Table III. Previous investigators have reported similar experiments and results.[9-13] In the majority of cases, it has been emphasized that the Ricinus lipase exhibited a relative specificity for those glycerides of high molecular weight. The results above seem to offer support for this argument, with a few exceptions. Thus, for the various oils used, listed in the order of decreasing percentage hydrolysis, the mean molecular weights are:

Oils	Mean mol. wt.	Oils	Mean mol. wt.
Peanut	870	Linseed	786
Castor	921	Neat's-foot	995
Corn	895	Peach kernel	785
Cottonseed	870	Coconut	589
Soybean	869	Whale	590
Rape	956	Fish	616
Olive	765		

However, if another line of reasoning be adopted, this apparent specificity disappears almost entirely. When the number of moles of glyceride hydrolyzed after a given time is considered, no relative specificity of Ricinus lipase is observed. The results are all of the same order of magnitude and the probability that any individual variations are due to an actual difference in specificity is very low indeed.

Summary and Conclusions

A dry, stable and highly active preparation of Ricinus lipase has been obtained from hulled castor beans by extracting the fat with low boiling petroleum ether, pulverizing and sifting the residue of the bean through a 60-mesh sieve. The activity of this fresh preparation was compared with that of one ten years old. Considerable activity was obtained with the latter.

A water-in-oil emulsion appears to be desirable for Ricinus lipase action. The formation of this emulsion was aided by shaking and by lower temperatures of incubation.

Rates of hydrolysis of a variety of oils of vegetable and animal origin were obtained for studies on the nature of action and specificity of Ricinus lipase. Under the experimental conditions, Ricinus lipase catalyzed the hydrolysis of the following oils, listed in order of decreasing percentage hydrolysis after a given time: peanut, castor, corn, cottonseed, soybean, rape, olive, linseed, neat's-foot, peach kernel, coconut, whale, fish and sperm. An analysis of the data on the basis of the number of moles hydrolyzed revealed that the lipase showed no specificity in its attack on glyceride molecules containing carbon chains of different length.

STATE COLLEGE, PENNA.

RECEIVED JUNE 17, 1935

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(9) Connstein, *Ergebnisse der Physiol.*, **3**, 194 (1904).

(10) Tanaka, *J. Coll. Eng.* (*Imp. Univ. Tokyo*), **5**, 25, 152 (1912).

(11) Takamiya, *J. Agr. Chem. Soc.* (Japan), **5**, 595 (1929).

(12) Falk, THIS JOURNAL, **35**, 616 (1913).

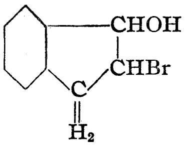
(13) Sudborough and Watson, *J. Indian Inst. Sci.*, **5**, 119 (1922).

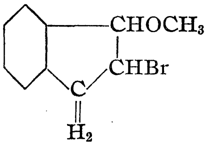
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Some Bromine Derivatives of Indene and Indane[1]

BY H. D. PORTER AND C. M. SUTER

It was shown by Courtot[2] and co-workers that the well-known indene bromohydrin has structure I since on oxidation it gives 2-bromo-1-indanone. Von Braun and Weissbach[3] therefore logically assumed that the methoxybromoindane obtained from indene dibromide and methanol had structure II. On the other hand, Jacobi[4] has presented evidence indicating that the alkoxybromoindanes prepared in this manner correspond to III.


I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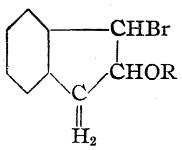
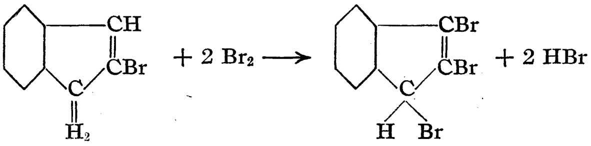

III

The present investigation was undertaken to explain this apparent contradiction and amplify the available information concerning other bromine derivatives of indene and indane.

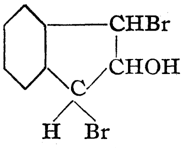
Indene bromohydrin, either upon pyrolysis at 150–160° or by dehydration with phosphorus pentoxide, is converted into 2-bromoindene, m. p. 38–39°. The structure of this compound was confirmed by reaction with sodium ethoxide and hydrolysis of the resulting ethoxyindene to 2-indanone by the action of dilute acid. Thermal decomposition of indene dibromide likewise gives 2-bromoindene although the yield is somewhat lower. Jacobi[4] reported that the compound formed in this reaction was 1-bromoindene. Apparently unknown to Jacobi, 1-bromoindene had been prepared previously[5] by the action of cyanogen bromide upon indenylmagnesium bromide and has quite different properties from the 2-bromoindene obtained from indene dibromide. As evidence for the structure he proposed, Jacobi found that the Grignard reagent of the bromoindene gave indene-1-carboxylic acid. It would not be surprising to obtain this acid from 2-bromoindene because of the activity of the methylene hydrogens in indene toward Grignard reagents.[6] However, upon repeating Jacobi's experiment numerous times, the only product isolated was a low yield of indene-2-carboxylic acid.[7]

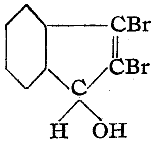
2-Bromoindene is inert toward boiling aqueous alkali or potassium formate in methanol. It adds hydrogen bromide in glacial acetic acid to give indene dibromide, identified by hydrolysis to the bromohydrin. Various attempts to alter the manner in which addition occurred by a change of solvent and the presence of hydroquinone or benzoyl peroxide[8] were unsuccessful.

Bromine reacts readily with 2-bromoindene in carbon tetrachloride at room temperature with evolution of hydrogen bromide. The product obtained is apparently 1,2,3-tribromoindene as it contains only one hydrolyzable bromine and upon oxidation gives phthalic acid.


IV V

The exact mechanism of the bromination is uncertain. The "tribromoindane" obtained by Jacobi[4] from his supposed 1-bromoindene is probably V. 1,2,3-Tribromoindane had been prepared considerably earlier[5] by addition of bromine to 1-bromoindene. It is a solid melting at 133–134° while Jacobi's product was described as an oil. Jacobi's 1,3-dibromo-2-hydroxyindane (m. p. 90°), VI, is unexplained as the VII obtained in this investigation did not crystallize. 1,2,3-Tribromoindane, obtained from indene dibromide and bromine,[9] was found to be unexpectedly inert toward hydrolysis and no hydroxydibromoindane could be isolated for comparison with Jacobi's product.


VI


VII

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[1] Presented before the Organic Division of the American Chemical Society at the New York Meeting, April, 1935.

[2] Courtot, Fayet and Parant, *Compt. rend.*, **186**, 371 (1928).

[3] Von Braun and Weissbach, *Ber.*, **63B**, 3052 (1930).

[4] Jacobi, *J. prakt. Chem.*, **129**, 55 (1931).

[5] Grignard, Bellet and Courtot, *Ann. chim.*, **4**, 28 (1915).

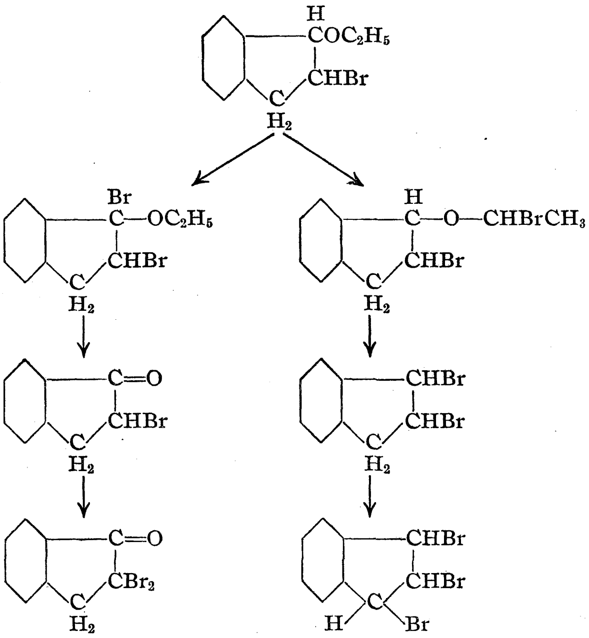
[6] Grignard and Courtot, *Compt. rend.*, **152**, 272 (1911).

[7] Perkin and Révay, *Ber.*, **26**, 2254 (1893); *J. Chem. Soc.*, **65**, 228 (1894).

[8] Kharasch and Mayo, THIS JOURNAL, **55**, 2468 (1933).

[9] R. Meyer and W. Meyer, *Ber.*, **51**, 1571 (1918).

Refluxing indene dibromide with ethyl alcohol gives a mixture containing 1-ethoxy-2-bromoindane, 2-bromoindene and indene dibromide. The pure ethoxy compound is obtainable by adding pyridine to the mixture to carry the alcoholysis to completion or by removal of the unchanged indene dibromide by hydrolysis to the bromohydrin or glycol. Jacobi's 3-bromoindene[4] was apparently a mixture of indene dibromide and ethoxybromoindane. It was noted in one preparation of the ethoxy compound that calcium chloride which was accidentally introduced into the mixture greatly increased the amount of 2-bromoindene formed. Here sodium carbonate was added to hydrolyze the unchanged indene dibromide.

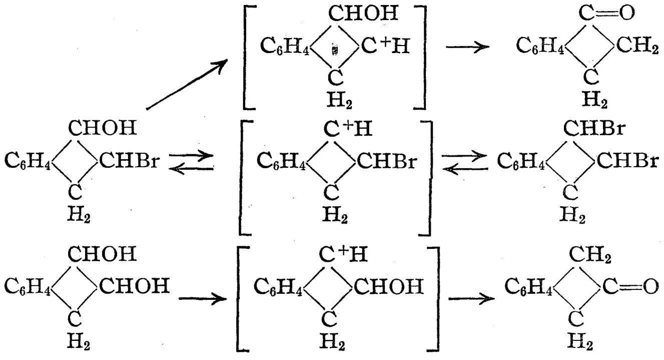


The structure of the ethoxybromoindane was established by converting it into 1-indanone through reaction with sodamide in liquid ammonia followed by acid hydrolysis of the enol ether.

The bromine in 1-ethoxy-2-bromoindane is quite unreactive, prolonged heating with aqueous sodium hydroxide or potassium acetate in glacial acetic acid having little effect. Bromination in boiling carbon tetrachloride gave a mixture of 2,2-dibromo-1-indanone and 1,2,3-tribromoindane. The formation of these products is explainable upon the basis of the behavior of α-chloro ethers toward heat.[10] The reaction probably proceeds by the steps indicated above.

Trans indene glycol was obtained in 60–70% yields by hydrolysis of indene bromohydrin with aqueous sodium carbonate. This yield is twice that obtained by the hydrolysis method of Weissgerber[11] and the procedure is much simpler than the one involving the preparation and hydrolysis of indene diacetate.[11,12] Conversion of the glycol and of indene oxide[12] to 2-indanone by boiling with dilute acid has been reported by several investigators.[11,12,13] In the present work it was found that both indene bromohydrin and 1-ethoxy-2-bromoindane under similar treatment yield 1-indanone. Since indene bromohydrin was found to be readily obtainable from a drip oil fraction containing less than 50% indene, both indanones are now readily accessible.

The formation of 1-indanone from indene bromohydrin has considerable bearing upon the validity of the mechanism advanced by Whitmore[14] to explain aldehyde and ketone formation from the hydrolysis of dibromides. According to this mechanism the hydrolysis of indene dibromide or treatment of indene bromohydrin with dilute acid should produce 2-indanone, whereas actually none of this results. As long as the bromine atom remains attached to carbon atom 2 the hydrogen joined to this carbon is apparently immobilized. This is not the case for the corresponding hydrogen in indene glycol. These reactions may be formulated thus



By analogy it seems likely that in the conversion of an aliphatic dibromide containing a tertiary bromine to an aldehyde or ketone the formation of the glycol precedes that of the carbonyl compound.

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(10) Straus and Heinze, *Ann.*, **493**, 191 (1932).

(11) Weissgerber, *Ber.*, **44**, 1436 (1911).

(12) Böeseken and Van Loon, *Proc. Acad. Sci. Amsterdam*, **20**, 1181 (1918).

(13) Heusler and Schieffer, *Ber.*, **32**, 28 (1899); Walters, *J. Soc. Chem. Ind.*, **46**, 150 (1927).

(14) Whitmore, THIS JOURNAL, **54**, 3280 (1932); Evers, Rothrock, Woodburn, Stahly and Whitmore, *ibid.*, **55**, 1136 (1933).

Practically all of the indene dibromide employed in this investigation was prepared from indene bromohydrin and hydrobromic acid. This dibromide was found to be identical with that obtained directly from indene. In view of the recent work of Bartlett[15] upon the *cis* and *trans* cyclohexene chlorohydrins, it is probably that indene bromohydrin is the *trans* isomer as it yields indene oxide with great ease. Correspondingly, the indene chlorohydrin obtained in larger amount by the hydrolysis of indene dichloride[2] would be the *trans* isomer. The fact that 1-indanone was obtained as the final product in the action of sodium methoxide upon the other (*cis*) indene chlorohydrin tends to confirm these structures.

Experimental

Indene Bromohydrin.—Bromine water was added in successive 2-liter quantities to 165 g. of a crude indene, b. p. 176–182°, obtained by the fractionation of drip oil or crude solvent naphtha[16] and the mixture stirred vigorously. The spent bromine water was siphoned off before addition of the next portion. When no more bromine reacted the pasty product was filtered and washed with benzene. The yield was 95 g. or 31%, assuming the starting material to be 100% indene. The product thus prepared melted at 126–128°. Similar preparations employing pure indene have been described previously.[17]

Preparation of 2-Bromoindene.—(1) A solution of 22 g. of indene bromohydrin in 150 cc. of carbon tetrachloride was refluxed with 7 g. of phosphorus pentoxide for two hours. The solution was decanted from the phosphoric acid and distilled. The fraction distilling at 123–124° (22 mm.) solidified on cooling and after recrystallizing from methanol melted at 38–39°. The yield was 11 g. or 55% of the theoretical amount.

(2) Heating 10.5 g. of indene bromohydrin in a small flask in an oil-bath at 155–160° for two hours gave 4 g. of crude 2-bromoindene, b. p. 123–128° (17 mm.). A better method was as follows. A mixture containing 25 g. of indene bromohydrin and 40 cc. of bromobenzene, b. p. 156°, was distilled very slowly, additional bromobenzene being added at the same rate through a dropping funnel. The end of the reaction was indicated by the absence of water in the distillate. Distillation of the residue gave 10.2 g. or 45% of the theoretical amount of product, boiling at 125–127° (23 mm.), which solidified upon standing. Recrystallization gave the pure 2-bromoindene, m. p. 38–39°.

Anal. Calcd. for C_9H_7Br: Br, 41.02. Found: Br, 40.9.

2-Indanone from 2-Bromoindene.—Two grams of 2-bromoindene was added to 10 cc. of 100% ethyl alcohol in which 0.5 g. of sodium had been dissolved. The mixture was refluxed for three hours, poured into excess 10% sulfuric acid and steam distilled. After removal of the alcohol a small amount of an oil came over. Upon crystallization from petroleum ether this melted at 57–58°. This was identified as 2-indanone[18] by conversion to the oxime, m. p. 152°.

Refluxing 2-bromoindene with 2 *N* sodium hydroxide for two hours gave negative results, as did refluxing with potassium formate in methanol for sixteen hours.

Indene-2-carboxylic Acid.—Four grams of 2-bromoindene was treated with 0.5 g. of magnesium in 25 cc. of dry ether. The reaction was started by using a few drops of an ethylmagnesium bromide solution. After refluxing for two hours the solution was cooled and carbon dioxide introduced. After working up the product in the usual manner there was obtained 0.5 g. of indene-2-carboxylic acid,[7] m. p. 228–229°. The only other product noted was indene. Various modifications of this procedure gave substantially the same results.

2-Bromoindene and Hydrogen Bromide.—A solution containing 0.5 g. of 2-bromoindene in 5 cc. of 37% hydrogen bromide in glacial acetic acid was allowed to stand for a day. The oil obtained, n^{25}_D 1.6285, gave upon refluxing in an acetone–water mixture for two hours and cooling, crystals of indene bromohydrin, m. p. 128°. This result was not affected by the addition of a small amount of either benzoyl peroxide or hydroquinone to the acetic acid solution.

The reaction between hydrogen bromide and 2-bromoindene in benzene in the presence of benzoyl peroxide was incomplete after two days. The only reaction product found was again indene dibromide. When the benzoyl peroxide was replaced by hydroquinone the 2-bromoindene remained practically unchanged after two days. Warming the reaction mixture on the steam-bath, however, again gave a trace of indene dibromide.

Bromination of 2-Bromoindene.—To 7.4 g. of 2-bromoindene dissolved in carbon tetrachloride was added bromine in the same solvent until the color persisted. During the course of the reaction hydrogen bromide was evolved copiously. The solution was washed with aqueous sodium bisulfite, dried, and the solvent allowed to evaporate. The product was an oil, n^{25}_D 1.6615, d^{25} 2.12. It could not be distilled but judging by its analysis and behavior it was a pure substance. The yield was 13 g. or 97% of the theoretical amount.

Anal. Calcd. for $C_9H_5Br_3$: Br, 68.05. Found: Br, 67.8.

Oxidation with aqueous potassium permanganate gave phthalic acid, m. p. 184–186°, which upon heating above its melting point gave the anhydride, m. p. 128°.

Hydrolysis of 1,2,3-Tribromoindene.—The tribromoindene decomposed to a tar when treated with aqueous alkali. Hydrolysis by boiling in acetone–water solution over calcium carbonate followed by steam distillation gave a few drops of an oil, n^{22}_D 1.6350, which analyzed for a dibromoindenol.

Anal. Calcd. for $C_9H_6OBr_2$: Br, 55.3. Found: Br, 54.9.

Indene Dibromide from Indene Bromohydrin.—A mixture of 38 g. of indene bromohydrin and 130 cc. of

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[15] Bartlett, This Journal, **57**, 224 (1935).

[16] This material was supplied through the courtesy of Mr. R. B. Harper, Vice-President, and Mr. E. F. Pohlmann, Chief Testing Engineer, of the Peoples Gas Light and Coke Company of Chicago, to whom we wish to express our appreciation.

[17] Pope and Read, *J. Chem. Soc.*, **99**, 2071 (1911); **101**, 760 (1912).

[18] Schad, *Ber.*, **26**, 222 (1893), first prepared this compound.

47% hydrobromic acid was stirred on the steam-bath for three hours. The oily layer was separated, dried with calcium chloride and distilled at 1 mm. The main fraction, b. p. 100–105°, was indene dibromide, n^{25}_{D} 1.6290, d^{25}_{4} 1.747. The yield was 31 g. or 61% of the theoretical amount. The product distilling at 77–100° (1 mm.), which came over as a forerun, solidified upon cooling and proved to be 2-bromoindene, m. p. 38–39°. Some difficulty was encountered at first in inducing the indene dibromide to crystallize. Satisfactory results were finally obtained by cooling its petroleum ether solution to a low temperature. The product, m. p. 32°, was found to be identical with that obtained from indene. No other dibromide could be isolated.

Pyrolysis of Indene Dibromide.—(1) Upon heating 25.6 g. of indene dibromide in a flask in an oil-bath at 200–210° for one hour hydrogen bromide was evolved and the residue distilled at 113–115° (13 mm.). It solidified upon cooling and after recrystallization from alcohol melted at 38–39°. A mixed melting point with 2-bromoindene gave the same value. The yield was 3.3 g. or 16% of the theoretical amount.

(2) Refluxing 19 g. of indene dibromide in 30 cc. of dry tetralin (b. p. 205–210°) as long as hydrogen bromide was evolved (four hours) gave 4.8 g. or 36% of the theoretical amount of 2-bromoindene.

Preparation of 1-Ethoxy-2-bromoindane.—(1) A mixture of 40 cc. of 100% ethyl alcohol and 20 g. of indene dibromide was refluxed for four hours. During the third hour a total of 6.5 g. of pyridine was added slowly. Water was then added and the oily layer separated, washed, dried and distilled. There was obtained 6.7 g. of product, b. p. 144–148° (19 mm.), which is 38% of the theoretical amount. A portion, b. p. 147–148° (19 mm.), n^{25}_{D} 1.5515, d^{25}_{4} 1.344, was analyzed.

Anal. Calcd. for $C_{11}H_{13}OBr$: Br, 33.15. Found: Br, 33.2.

In similar experiments in which pyridine was not added the product always contained unchanged dibromide, besides a trace of 2-bromoindene.

(2) In another experiment, after refluxing 40 g. of indene dibromide with 105 cc. of alcohol containing about 5 g. of calcium chloride for five and one-half hours, 20 cc. of water and enough saturated sodium carbonate solution were added to make the mixture alkaline. This was then stirred on the steam-bath for four hours. More water was added and the product separated and dried. There was obtained 13.4 g. of material, b. p. 143.5–144.5° (17 mm.), which is 38% of the theoretical amount. A forerun of 9 g. of 2-bromoindene, b. p. 132–136°, was also recovered.

Proof of Structure of 1-Ethoxy-2-bromoindane.—A solution of sodamide in liquid ammonia was prepared by treating 0.24 g. of sodium with 50 cc. of the solvent in the presence of a trace of ferric oxide. To this solution was added 2.5 g. of the ethoxy compound. The residue remaining after the gradual evaporation of the ammonia was extracted with ether and the oil thus obtained was steam distilled from 10% sulfuric acid. From the oil in the distillate there was obtained through treatment with hydroxylamine hydrochloride and sodium acetate in methanol followed by dilution with water, crystals of 1-indanone oxime,[19] m. p. 143–144°. This was identified by a mixed m. p. with an authentic sample.

Bromination of 1-Ethoxy-2-bromoindane.—A boiling solution of 2.5 g. of the ethoxy compound in 25 cc. of carbon tetrachloride was treated with bromine as long as reaction occurred. The solvent was removed and the residue recrystallized from petroleum ether. This was a mixture, m. p. 100–106°, in which two types of crystals were evident. Those with a needle-like appearance were separated mechanically and after recrystallization from methanol melted at 133–134°. A mixed melting point indicated the substance to be 1,2,3-tribromoindane.[9] Fractional crystallization of the original mixture from ether or ether–benzene gave rhombic crystals likewise melting at 133–134°. These were found to be 2,2-dibromo-1-indanone[19] through comparison with a sample of this substance prepared from 1-indanone.

Preparation of Trans Indene Glycol.—The following procedure was found to be more convenient than those in the literature.[11,12] A mixture of 350 cc. of saturated aqueous sodium carbonate and 17 g. of indene bromohydrin was stirred on the steam-bath for three hours. After cooling, the mixture was filtered and the product treated with hot water to separate the glycol from an insoluble tarry material. Cooling the water solution gave 6.8 g. of *trans* indene glycol, m. p. 159°, which is 60% of the theoretical amount. The water-insoluble material (4.7 g.) upon treatment with methanol left a residue which melted above 285°. Treatment of 1-indanone with aqueous sodium carbonate gave a similar product while the glycol was unaffected by long heating with the carbonate. It seems probable that 1-indanone is the precursor of this by-product.

Preparation of 1-Indanone.—A mixture of 400 cc. of 7% (by volume) sulfuric acid and 20 g. of indene bromohydrin was refluxed for ten hours. Steam distillation gave an oil, b. p. 117–118° (15 mm.), which solidified upon cooling and melted at 42° after crystallizing from petroleum ether. The yield was 10 g. or 80.6% of the theoretical amount. The oxime melted at 145–146°.

Preparation of 2-Indanone.—Refluxing 4 g. of *trans* indene glycol with 7% (by volume) sulfuric acid for one hour gave 2.5 g. or 71% of 2-indanone, m. p. 58–59°.

1-Indanone from 1-Ethoxy-2-bromoindane.—A mixture of 20 cc. of 10% (by volume) sulfuric acid and 1.1 g. of the ethoxy compound was refluxed for eight hours. Steam distillation gave 0.32 g. or 53% of an oil, identified as 1-indanone by conversion to the oxime, m. p. 143–144°.

Summary

1. 2-Bromoindene has been obtained by pyrolysis or dehydration of indene bromohydrin, pyrolysis of indene dibromide and as a by-product in other reactions. Its structure is evident from its mode of preparation and its reactions.

2. Reaction of indene dibromide with ethyl alcohol gives 1-ethoxy-2-bromoindane. Various reactions of this compound have been investigated.

3. The action of dilute sulfuric acid upon in-

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(19) Kipping, *J. Chem. Soc.*, **65**, 480 (1894).

dene bromohydrin produces 1-indanone in high yields. The mechanism of this reaction and its bearing upon the theory of aldehyde and ketone formation from aliphatic dibromides has been discussed.

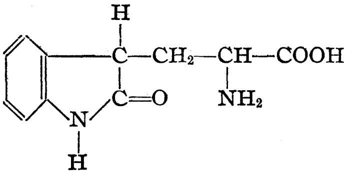
EVANSTON, ILLINOIS RECEIVED JULY 11, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DEPAUW UNIVERSITY]

Studies in the Indole Series. VI. On the Synthesis of Oxytryptophan and Further Studies of 3-Alkylation of Oxindoles[1]

BY PERCY L. JULIAN, JOSEF PIKL AND FRANK E. WANTZ

The program of investigation into the chemistry of oxindoles, undertaken some time ago in this Laboratory, centered largely in its first phase around 1,3-dimethyloxindoles since these offered convenient starting material for the synthesis of physostigmine.[2] The ease with which these 1,3-dialkyloxindoles underwent alkylation in the 3-position, led us to attempt the synthesis of oxytryptophan (I) by way of condensation reactions similar to those recently communicated.

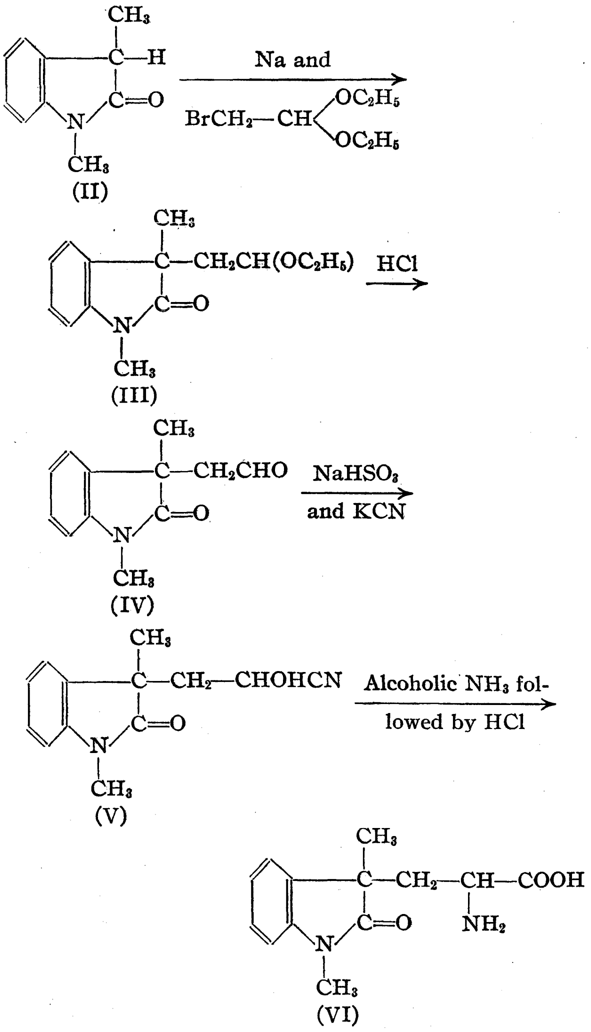


(I)

Much attention has been directed recently to this amino acid (I) since it has been indicated by Kotake[3] to be the first transformation product in the intermediary metabolism of tryptophan in the animal organism. Moreover, proof of the conversion of tryptophan into oxytryptophan, which might occur through certain oxidases, would probably explain the origin of many natural products containing the indole nucleus, among these physostigmine.[4]

In order to eliminate complications which might arise from possible enolizations of the hydrogen atoms in positions 1 and 3 of ordinary oxindole (VII), we decided to test out our proposed condensations, for introduction of the grouping —CH_2—$CH(NH_2)COOH$ into the 3-position of oxindoles, on 1,3-dimethyloxindole (II), with which we were quite familiar.

This paper reports the successful synthesis of the expected dimethyloxytryptophan (VI). 1,3-Dimethyloxindole was condensed with bromoacetal, the product (III) hydrolyzed and the aldehyde (IV) converted by way of the well-known Strecker synthesis into the amino acid (VI).



Attempts to carry out the same reactions with oxindole (VII) failed of their purpose, the initial condensation with bromoacetal presenting difficulties. That this is probably not due to enoli-

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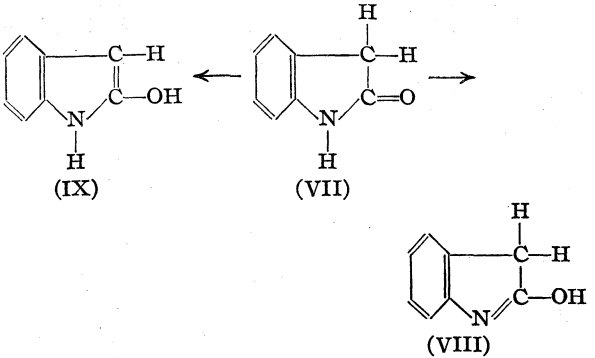
[1] Abstracted in large part from the senior research of Frank E. Wantz at DePauw University, 1934–1935.

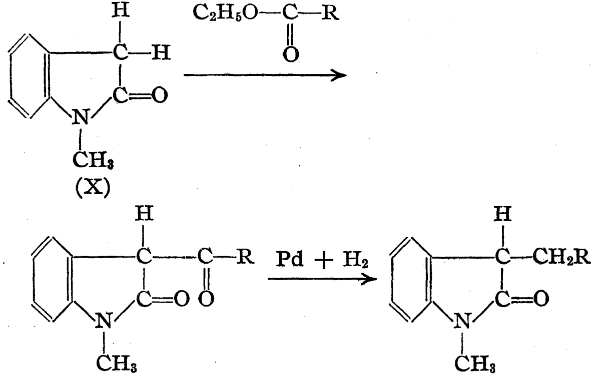
[2] Julian, Pikl and Boggess, THIS JOURNAL, **56**, 1797 (1934); Julian and Pikl, *ibid.*, **57**, 539, 563, 755 (1935).

[3] Kotake, *Z. physiol. Chem.*, **195**, 158–166 (1931).

[4] Julian and Pikl, THIS JOURNAL, **57**, 755 (1935).

zation of (VII) in the sense represented by formula (VIII) rather than (IX) is indicated by the results obtained with (VII) in the Grignard machine. It gives two moles of gas and consumes two moles of reagent.


(IX) (VII) (VIII)


(X) (XI) (XII)

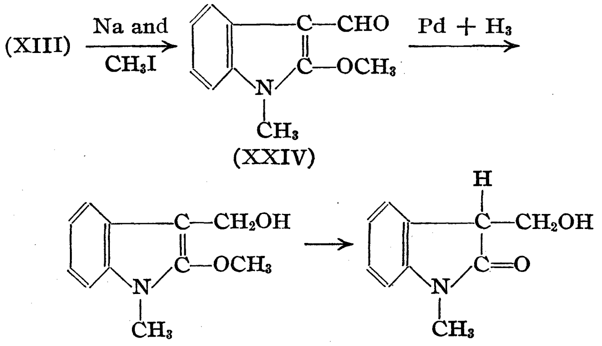
Condensation even of 1-methyloxindole (X) with bromoacetal could not be smoothly effected, despite numerous attempts.

We were therefore compelled to work out an entirely different procedure for smooth 3-alkylation of oxindoles not bearing an alkyl group in the 3-position, and the initial results with 1-methyloxindole (X) are communicated in this paper.

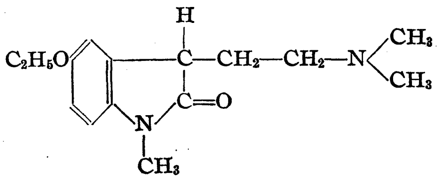
This new procedure makes use of 3-acyloxindoles (XI) which we have been able to obtain quite readily and in excellent yield through condensation of the oxindole (X) with esters. These 3-acyloxindoles, though readily cleaved by acids or bases, are cleanly hydrogenated catalytically to the corresponding 3-alkyl derivatives (XII). Table (I) shows the 3-acyloxindoles we have employed, together with the corresponding reduction products.

Compounds (XVIII) and (XIX), resulting, respectively, from condensation of the oxindole (X) with malonic ester and reduction of the product secured, are of particular interest to us in our attempts to synthesize oxytryptophan, for they point to possible successful outcome of this synthesis through condensation of oxindole with phthalimido-malonic ester, reduction of the resulting acyl derivative and hydrolytic cleavage to the amino acid (I). The results of this study will be reported in a later communication.

That the enolic hydrogen atom in position 3 of the acyloxindoles is responsible for the ease with which catalytic reduction takes place is suggested by the failure to reduce 1,3-dimethyl-3-acetyloxindole (XVII) by the same procedure. This latter substance was prepared by treating the sodium salt of (XV), suspended in acetone, with methyl iodide. It is interesting to note that 1-methyl-3-formyloxindole, methylated by this same procedure, gave an O-methyl derivative (XXIV),[5] which rapidly took up hydrogen when reduced catalytically to yield (XXV), a substance which is apparently readily hydrolyzed to the oxindole alcohol (XXVI). This compound is interesting in that it is the anhydride of *o*-methylamino-tropic acid.


(XXIV) (XXV) (XXVI)

The substances (XXI) and (XXIII) were included in this study because of their close resemblance to bufotenine (XXVII), one of the toad secretions.


(XXIII)

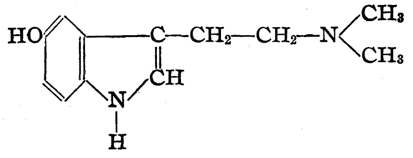

(XXVII)
Bufotenine

TABLE I

Acyl products on first line
Reduction products, second line

3-Acyloxindole	Reduction product	M. p. or b. p., °C.	Analyses, % Calcd. C	Calcd. H	Found C	Found H
1-Methyl-3-formyloxindole[5] (XIII)	1,3-Dimethyloxindole[5] (XIV)					
1-Methyl-3-acetyloxindole (XV)	1-Methyl-3-ethyloxindole (XVI)	109	69.80	5.87	69.69	6.00
	(Tribromo product analyzed)	169	32.03	2.43	31.74	2.68
1,3-Dimethyl-3-acetyl-oxindole (XVII)	....	79	70.90	6.45	71.07	6.70
1-Methyl-3-carboethoxy-acetyl-oxindole (XVIII)	β-1-Methyloxindolyl-propionic ester (XIX)	67	64.34	5.79	64.34	5.88
		Liq. b. p. 160 (1 mm.)	67.99	6.92	67.60	7.17
1-Methyl-3-dimethylaminoacetyl-oxindole (XX)	1-Methyl-3-β-dimethylamino-ethyloxindole (XXI)	219	67.20	6.94	67.25	7.15
	(Picrate analyzed) m. p. 168°	Liq. b. p. 185 (16 mm.)	50.98	4.74	51.05	4.86
1-Methyl-5-ethoxy-3-β-dimethyl-aminoacetyloxindole (XXII)	1-Methyl-5-ethoxy-3-β-dimethylaminoethyloxindole	196	65.17	7.31	65.00	7.53
	(XXIII). Picrate analyzed, m. p. 157°	Liq. b. p. 221 (17 mm.)	51.30	5.13	51.30	5.40
1-Methyl-2-methoxy-3-formyl-indole[5] (XXIV)	1-Methyl-2-methoxy-indolyl-carbinol (XXV)	...	...	..	...	..
		62	69.11	6.81	69.39	7.19

It has been pointed out by Jensen and Chen[6] that bufotenine has remarkable effect upon the blood pressure. Dr. Jensen (Laboratory for Endocrine Research, Johns Hopkins Medical School) has kindly undertaken investigation of (XXI) and (XXIII) for action similar to that of bufotenine in raising the blood pressure.

The authors are grateful for a grant from the Rosenwald Fund, which is defraying some of the expenses of this and other investigations. They also wish to renew their expressions of appreciation to Dean W. M. Blanchard, Head of the Department, for his untiring labor in making this research program possible.

Experimental Part

A. Synthesis of β-1,3-Dimethyloxindolylalanine (VI)

1,3-Dimethyloxindolylacetal (III).—To a cooled solution of 6.9 g. of sodium in 90 cc. of absolute alcohol, a mixture of 49 g. of 1,3-dimethyloxindole and 55 g. of bromoacetal was added. After heating on the water-bath (gently at first) for one hour under reflux, the mixture was poured into water, taken up with ether, the ethereal extract washed with water and distilled. At 11 mm., 56 g. of material boiling at 170–185° was collected. For analysis the portion boiling at 182.5–183.5° (11 mm.) was collected.

Anal. Calcd. for $C_{16}H_{23}O_3N$: C, 69.26; H, 8.36. Found: C, 69.65; H, 8.33.

1,3-Dimethyloxindolylacetaldehyde (IV).—43.2 grams of the acetal (III) was covered with 300 cc. of 5% hydrochloric acid and shaken frequently. Solution occurs after about two hours. Allowed to stand overnight, it was then made alkaline with a generous excess of sodium carbonate and extracted with ether. The ethereal extract on distillation gave a quantitative yield of aldehyde (IV), b. p. 177–178° (12 mm.).

Anal. Calcd. for $C_{12}H_{13}O_2N$: C, 70.93; H, 6.40. Found: C, 70.66; H, 6.80.

The semicarbazone, prepared in the usual manner, melts at 206°, recrystallized from dilute alcohol.

Anal. Calcd. for $C_{13}H_{16}O_2N_4$: C, 59.98; H, 6.19. Found: C, 59.82; H, 6.42.

1,3-Dimethyloxindolylacetaldehydecyanhydrin (V).—To a well-stirred mixture of 64 g. of aldehyde (IV), 35 g. of sodium bisulfite, 50 cc. of water and 100 cc. of ether, a mixture of 25 g. of potassium cyanide and 30 cc. of water was added. The beautifully crystalline cyanhydrin which separated was filtered and washed generously with water and then a little ether; yield 50 g.; recrystallized from ether–petroleum ether, m. p. 142°.

Anal. Calcd. for $C_{13}H_{14}O_2N_2$: C, 67.82; H, 6.09. Found: C, 67.80; H, 6.33.

β-1,3-Dimethyloxindolylalanine (VI).—Twenty grams of cyanhydrin (V) was warmed for seven hours at about 60° with 16 cc. of 12% absolute alcoholic ammonia. The reaction product was poured into 50 cc. of 10% hydrochloric acid, whereby all went into solution. When sufficient water was added to bring the acid concentration down to about 3%, a precipitate was formed which was removed by shaking with ether. The aqueous solution was evaporated on the water-bath almost to dryness, and 10 cc. of concentrated hydrochloric acid added. This mixture was then heated on the water-bath for eight hours, after which the whole mass was taken up in 300 cc. of alcohol and alcoholic ammonia added until no more precipitate formed. The precipitate, consisting mainly of ammonium chloride, was filtered off, and ether added to the filtrate to precipitate the amino acid; 10.5 g. of product was obtained. After several recrystallizations from

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[5] Julian, Pikl and Boggess, THIS JOURNAL, **56**, 1797 (1934).

[6] Jensen and Chen, *Ber.*, **65**, 1310 (1932).

80% alcohol it was fairly pure, m. p. 188° with decomposition, colorless, thin rhombic flakes. It still contained traces of ammonium chloride, very difficult to remove by this procedure.

Anal. Calcd. for $C_{13}H_{16}O_3N_2$: C, 62.88; H, 6.49. Found: C, 62.26; H, 6.60.

Heated above its melting point in a sublimation tube in vacuum, the acid loses carbon dioxide and pure 1,3-dimethyloxindolylethylamine[7] distils over, yielding a picrate, m. p. 186°, identical with that described in an earlier communication.

B. Preparation and Catalytic Reduction of 3-Acyloxindoles

Preparation of the 3-Acyloxindoles.—The general procedure was to add a mixture of 1 mole of oxindole (X) and 1.2 moles of ester to a 10% solution of sodium ethylate containing 1.3 moles of sodium. In most cases the sodium salt separated, was filtered off and decomposed with dilute hydrochloric acid.

In the case of the condensation of (X) with malonic ester the procedure above gave a difficultly soluble substance, m. p. 225°, doubtless the trimolecular condensation product. When from two to three moles of ester was employed and the oxindole dropped into the mixture of ethylate and ester, the product consisted almost entirely of the dimolecular condensation product, m. p. 67°, recrystallized from ether–petroleum ether.

The isolation of the condensation product between oxindole and dimethylaminoacetic ester called for further modification of the procedure since this product behaves like an amino acid. The sodium salt of the condensation product was decomposed with excess 10% hydrochloric acid in the cold, then sodium bicarbonate was added rapidly and the free amine extracted with chloroform. The chloroform extract was concentrated and upon addition of ether to the hot solution the acyl amines (XX) and (XXII) snowed out. Recrystallized from chloroform and ether.

For preparation of (XXII) two new oxindoles were prepared, which have not hitherto been described, namely, 1-methyl-5-hydroxyoxindole and 1-methyl-5-ethoxy-oxindole. These were prepared from chloroacetyl chloride and N-methylphenetidine in the same manner as described for the 3-methyl analog.[8] 1-Methyl-5-hydroxy-oxindole melts at 187° recrystallized from alcohol.

Anal. Calcd. for $C_9H_9O_2N$: C, 66.23; H, 5.56. Found: C, 66.20; H, 5.55.

1-Methyl-5-ethoxy-oxindole melts at 92°, recrystallized from ether–petroleum ether.

Anal. Calcd. for $C_{11}H_{13}O_2N$: C, 69.07; H, 6.86. Found: C, 68.76; H, 7.14.

Catalytic Reduction of the 3-Acyloxindoles.—For the first four and the last acyl oxindole listed in Table I, the procedure was to dissolve the oxindole in alcohol and reduce at about 1.5 atmospheres' pressure with from 0.05 to 0.1 its weight of Adams palladium oxide catalyst. The product after filtration was extracted with ether, the ether solution washed with sodium hydroxide to remove unchanged material and distilled. The yields were from 50 to 70% of the theoretical.

The acyloxindoles (XX) and (XXII) (Table I) were suspended in ten times their weight of absolute alcohol, about one-tenth this quantity of glacial acetic acid was added, and about 0.2 as much catalyst as oxindole employed. It was necessary to heat the mixture in the hydrogenation vessel to about 50° and maintain this temperature for reduction to proceed smoothly. The products were filtered, the alcohol removed in vacuum, the residue taken up in 3% hydrochloric acid and separated from an appreciable quantity of non-basic material by extraction with ether. The aqueous solution was made alkaline with sodium hydroxide, extracted with ether, and the ethereal extracts distilled under diminished pressure.

Summary

1. 1,3-Dimethyloxindole is smoothly condensed with bromoacetal, in presence of sodium ethylate, to yield 1,3-dimethyloxindolylacetal. The aldehyde resulting from hydrolysis yields by the Strecker synthesis the expected dimethyloxytryptophan.

2. Condensation of oxindole and 1-methyloxindole with bromoacetal by the same procedure could not be effected.

3. Several 3-acyloxindoles have been easily reduced catalytically to 3-alkyloxindoles, and it is hoped to employ the appropriate acyloxindole for the synthesis of oxytryptophan.

4. Substances related to bufotenine have been prepared by catalytic reduction of the appropriate acyloxindoles, particularly the ethyl ether of 1-methyl-2-oxybufotenine.

GREENCASTLE, INDIANA

RECEIVED JULY 19, 1935

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[7] Julian and Pikl, THIS JOURNAL, **57**, 539 (1935).

[8] Julian and Pikl, *ibid.*, **57**, 563 (1935).

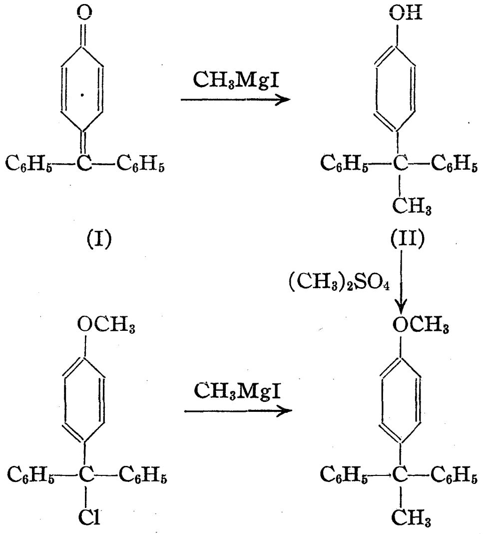
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DEPAUW UNIVERSITY]

The Action of the Grignard Reagent on Certain Fuchsones[1]

BY PERCY L. JULIAN AND WILLIAM J. GIST

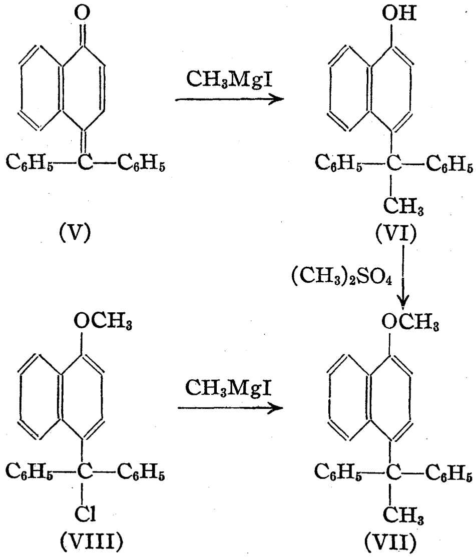
The only conclusively proven case of 1,6-addition of the Grignard reagent to a conjugated system of multiple linkages is the recently reported reaction between this reagent and methylene anthrone.[2] Of the three other cases found in the literature[3] only that one reported by Baeyer and Villiger deserves further attention, since the two cases recorded by Nakanishi have been reinvestigated and shown not to represent 1,6-addition.[2,4]

Baeyer and Villiger suggest without proof that the reaction product which they secure on treating fuchsone (I) with methylmagnesium iodide has the constitution (II). It is, if their assumption is correct, a product formed by 1,6-addition to a conjugated system similar to that found in methylene anthrone.



In connection with an investigation of the hindrance to 1,6-addition offered by various groupings, we have reëxamined the reaction studied by Baeyer and Villiger. To prove the constitution of the phenol (II) we methylated it in the usual manner with methyl sulfate. The product should have the constitution (III). The only other attractive possibility of synthesizing a compound like (III) arises out of Gomberg's observation[4a] that triphenylchloromethane reacts with methylmagnesium iodide, giving 1,1,1-triphenylethane in 70% yield. Accordingly, we treated the triaryl halide (IV) with methylmagnesium iodide, and secured a product identical with (III) obtained by methylating the addition product of Baeyer and Villiger. Their assumption was therefore a good one and the reaction is another case of 1,6-addition.

We have extended this study to include naphthofuchsone (V) and anthrafuchsone (IX). To the former methylmagnesium iodide adds 1,6 as in the case of fuchsone, but in much poorer yield. The constitution of the addition product has been proved in similar fashion, the triaryl halide (VIII) reacting smoothly with methylmagnesium iodide, yielding (VII).



With anthrafuchsone (IX) no trace of 1,6-addition could be detected, and the substance secured is the 1,2-addition product (X), the constitution of which has been proved by oxidation with chromic acid to anthraquinone and benzophenone.

Inasmuch as the completely arylated analogs of (II)—methyl group replaced by aryl residue—are among the easiest substances to prepare[5] it

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[1] Abstracted from the senior research of William J. Gist at DePauw University, 1934–1935.

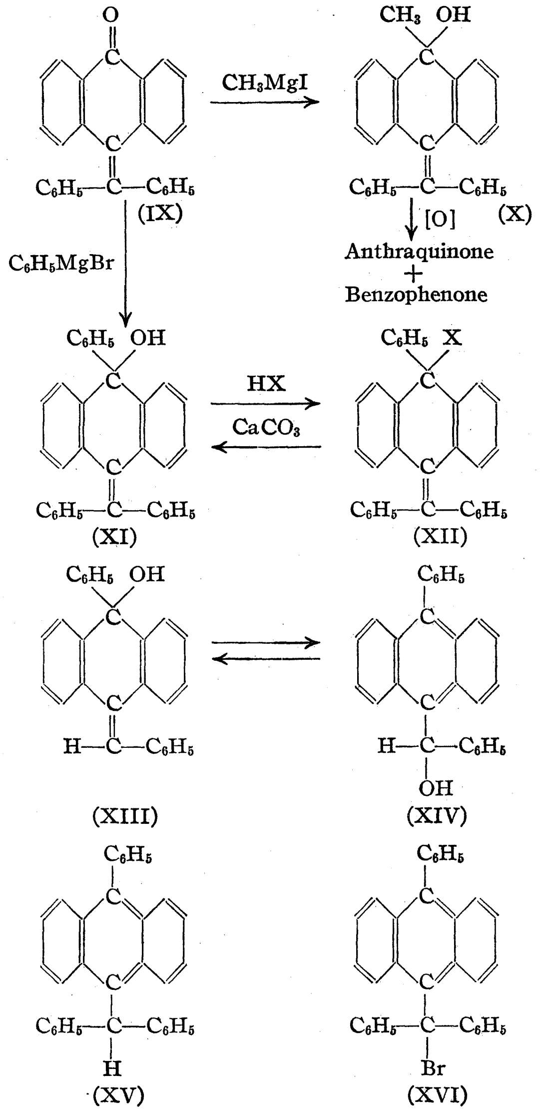
[2] (a) Julian and Magnani, THIS JOURNAL, **56**, 2174 (1934); (b) Julian and Cole, *ibid.*, **57**, 1607 (1935).

[3] Baeyer and Villiger, *Ber.*, **36**, 2793 (1903); Nakanishi, *Proc. Imp. Acad. Tokyo*, **9**, 394–397 (1933).

[4] Allen and Overbaugh, THIS JOURNAL, **57**, 740 (1935).

[4a] Gomberg and Cone, *Ber.*, **39**, 2964 (1906).

[5] Gomberg and Kamm, THIS JOURNAL, **39**, 2014 (1917).



seemed probable that phenylmagnesium bromide would likewise add 1,6 to fuchsone and to naphofuchsone. Despite numerous attempts, however, none of the readily crystallizing oxytetraarylmethanes could be isolated, only intractable gums resulting. Even on methylating these gums we could distil none of the pure methyl ethers from the products. The action of phenylmagnesium bromide on fuchsone and naphthofuchsone, therefore, is in marked contrast to that of methylmagnesium iodide on these substances, and if any amount of the 1,6-addition product is formed, it is present in such small quantities that the isolation of it is extremely difficult. One is reminded of the observation of Kohler[6] that "in most cases in which both 1,2- and 1,4-addition occur, the relative quantity of 1,4-addition product is always larger with alkyl than with arylmagnesium compounds." Our results indicate a similar conclusion with respect to 1,6-addition of aryl and alkyl magnesium derivatives.

Phenylmagnesium bromide reacts readily with anthrafuchsone (IX), the product being the 1,2-addition compound (XI).[7] This compound interested us because of the similarity in structure to another substance (XIII) on which we recently reported,[2a] and which we found to rearrange readily into the isomer (XIV). The new dihydroanthranol (XI), subjected to the same treatment, underwent no rearrangement and was recovered unchanged. In the earlier paper dealing with compound (XIII) we expressed the belief that certain steric influences might conceivably render the dihydroanthracene modification the more stable of the two, although generally the tendency to pass over into the modification containing the anthracene structure is so marked that least provocation effects this rearrangement. The additional phenyl group attached to the ω-carbon atom of (XI) seems to offer the necessary hindrance to rearrangement and it is the stable modification, while in the case of (XIII) and (XIV), the latter is certainly the more stable isomer, and no treatment could reconvert it into (XIII), although evidence for equilibrium between the two forms in solution could be adduced.

All attempts at replacement of the hydroxyl group in compound (XIII) led to derivatives having the structure corresponding to (XIV) and gave back (XIV) on hydrolysis. When the hydroxyl group in (XI) was replaced by halogen, and the resulting halide warmed for half an hour with moist calcium carbonate in acetone, the original carbinol was recovered. This is not satisfactory evidence that the halides have the structure (XII) since rearrangement might have occurred in the course of reconversion into carbinol. Moreover, solutions of both chloride and bromide (XII) are distinctly fluorescent, indicating that these might have the anthracene structure (XVI). To gain more light on this we prepared, according to Bergmann,[7] a substance to which he ascribes the formula (XV). From our experience with brominating phenylbenzylanthracene,[2a] we should secure (XVI) on brominating (XV). We did get a bromo compound, but one entirely different from our bromo derivative (XII). Hydrolysis of it

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[6] Kohler and Nygaard, THIS JOURNAL, **52**, 4132 (1930).

[7] Bergmann, *Ber.*, **63**, 1041 (1930).

with calcium carbonate yielded none of our carbinol (XI). Whether Bergmann's compound (XV) has actually the structure assigned we have not investigated, for when we found that it and its bromo derivative had no relationship to our substances, further work with it was discontinued.

The authors acknowledge gratefully a generous grant from the Rosenwald Fund and likewise the assistance and unstinted support of their first teacher of chemistry, Dean W. M. Blanchard, Head of the Department.

Experimental Part

1,1-Diphenyl-1-*p*-anisylethane (III)

(a) **From Fuchsone.**—Five grams of fuchsone, which we find is most conveniently prepared in large quantity according to the method of Bistrzycki,[8] was treated in the usual manner with 3 moles of methylmagnesium iodide. The crude product obtained on working up the Grignard was methylated in 10% sodium hydroxide solution with methyl sulfate. After destroying excess alkylating agent with alkali, the product was poured into water, extracted with ether, the ethereal solution washed and distilled. At 0.1 mm. and with air-bath temperature of 196°, 3.5 g. of a greenish-blue liquid distilled. Recrystallized from ether–petroleum ether it melted at 77°.

Anal. Calcd. for $C_{21}H_{20}O$: C, 87.50; H, 6.94. Found: C, 87.41; H, 7.23.

(b) **From Diphenyl-*p*-anisylchloromethane (IV).**—Five grams of the chloromethane (IV) was treated with 3 moles of methylmagnesium iodide, worked up on the usual way and distilled. The product, which came over at the same temperature as recorded above, melted at 77° and was identical in all respects with (III) secured from fuchsone.

Preparation of Naphthofuchsone (V).—The preparation described in the literature[9] we found to be troublesome and result in poor yields. The same type of procedure employed in the preparation of fuchsone, however, gave excellent results. The methyl ether of benzoyl α-naphthol was prepared according to the method employed by Scholl and Seer[10] for the ethyl ether, all heating avoided during the Friedel–Crafts reaction. We had little success with the method suggested by Fierz-David and Jaccard.[11] Our product, however, melted at 83° and was identical with that described by these authors.

Diphenyl-4-methoxynaphthylcarbinol, which resulted from the action of phenylmagnesium bromide on the methyl ether of benzoyl-α-naphthol, seems not to have been described heretofore. It melts at 162°, recrystallized from ether–petroleum ether.

Anal. Calcd. for $C_{24}H_{20}O_2$: C, 84.66; H, 5.93. Found: C, 84.59; H, 5.83.

The chloride (VIII), m. p. 151°, could not be isolated readily by passing hydrogen chloride into the ether solution of the carbinol. It was obtained on treating the carbinol with thionyl chloride. Conversion into the fuchsone (V) was effected by heating at 180–200° until evolution of methyl chloride was complete. Our fuchsone was identical with that described in the literature.[9]

1,1-Diphenyl-1,4-methoxynaphthylethane (VII), secured from naphthofuchsone (V) as well as from the chloride (VIII) described above, distilled at 220–230° (temperature of air-bath) and 0.1 mm., and melted at 144°, recrystallized from ether–petroleum ether.

Anal. Calcd. for $C_{25}H_{22}O$: C, 88.70; H, 6.56. Found: C, 88.68; H, 6.78.

9-Methyl-10-benzhydrylidene-9,10-dihydroanthranol-9 (X).—Obtained by the action of methylmagnesium iodide on anthrafuchsone, this substance melted at 223°, recrystallized from ether–petroleum ether.

Anal. Calcd. for $C_{28}H_{22}O$: C, 89.79; H, 5.93. Found: C, 89.68; H, 6.04.

On oxidation with chromic acid in glacial acetic acid solution it yielded anthraquinone and benzophenone. In the Grignard machine it gave one mole of gas and consumed one mole of reagent.

9-Phenyl-10-benzhydrylidene-9,10-dihydroanthranol-9 (XI) has already been described by Bergmann. On passing dry hydrogen chloride into an ethereal solution, the tertiary halide (XII) slowly crystallized out. Recrystallized from chloroform and ether, it melted at 220° with decomposition, beginning to turn dark at 185°.

Anal. Calcd. for $C_{33}H_{23}Cl$: C, 87.09; H, 5.10. Found: C, 86.78; H, 5.39.

When a benzene solution of the chloride is shaken with molecular silver it gives a deep reddish-brown solution, the color of which is almost completely discharged by passing in atmospheric oxygen. The peroxide, however, could not be induced to crystallize. Petroleum ether threw out an amorphous powder.

The bromide prepared as was the chloride melted at 165° with decomposition, while a bromo derivative of Bergmann's hydrocarbon (XV) melted at 143° and mixed melting point showed strong depression. When the 143° bromo derivative was hydrolyzed with moist calcium carbonate in acetone, only low melting material having no resemblance to the carbinol (XI) was secured.

Summary

1. The reaction between fuchsone and methylmagnesium iodide is another case of 1,6-addition. α-Naphthofuchsone behaves like fuchsone toward this reagent. None of the 1,6-addition products could be isolated from the reaction of these fuchsones with phenylmagnesium bromide.

2. 10-Benzhydrylidene-9-phenyl-9,10-dihydroanthranol-9 is stable and does not rearrange into its isomer with the anthracene structure. Its halogen derivatives likewise have apparently the dihydroanthracene structure.

GREENCASTLE, INDIANA RECEIVED JULY 29, 1935

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[8] Bistrzycki and Herbst, *Ber.*, **36**, 2335 (1903).

[9] Mazurkiewicz and Bistrzycki, *ibid.*, **45**, 1436 (1912).

[10] Seer and Scholl, *Ann.*, **398**, 85 (1913).

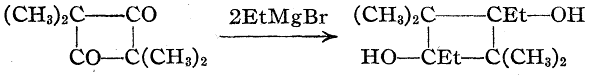
[11] Fierz-David and Jaccard, *Helv. Chim. Acta*, **11**, 1042–1046 (1928).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Reaction of Ketenes with Grignard Reagents

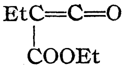
BY CHARLES D. HURD, RALPH N. JONES AND F. H. BLUNCK

Diphenylketene and phenylmagnesium bromide react[1] to produce a derivative of triphenylvinyl alcohol. With ketene[2] itself, the course of the Grignard reaction has not been established because of the vigor and complexity of the process. Toward the dimer of dimethylketene, ethylmagnesium bromide[3] adds to give the cyclic glycol in high yields



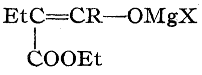
$$\begin{array}{l}(CH_3)_2C-CO \\ \quad\; | \qquad | \\ \quad\; CO-C(CH_3)_2\end{array} \xrightarrow{2EtMgBr} \begin{array}{l}(CH_3)_2C-CEt-OH \\ \qquad\quad | \qquad | \\ HO-CEt-C(CH_3)_2\end{array}$$

The present paper extends the Grignard reaction to ethyl ethylketenecarboxylate, (A), and its dimer (K).



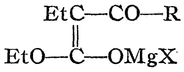
$$\begin{array}{l}EtC{=}C{=}O \\ | \\ COOEt\end{array}$$

(A)



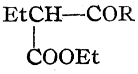
$$\begin{array}{l}EtC{=}CR-OMgX \\ | \\ COOEt\end{array}$$

(B)



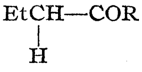
$$\begin{array}{r}EtC-CO-R \\ \| \\ EtO-C-OMgX\end{array}$$

(C)



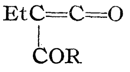
$$\begin{array}{l}EtCH-COR \\ | \\ COOEt\end{array}$$

(D)



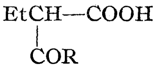
$$\begin{array}{l}EtCH-COR \\ | \\ H\end{array}$$

(E)



$$\begin{array}{l}EtC{=}C{=}O \\ | \\ COR\end{array}$$

(F)



$$\begin{array}{l}EtCH-COOH \\ | \\ COR\end{array}$$

(G)

Three types of addition should be considered, namely, at the ketene carbonyl, at the ester carbonyl, or 1,4-addition at the C=C—COOEt group. Since the ester group is known[4] to be more sluggish toward Grignards than the aldehyde group the first type should be favored instead of the second but no such basis of comparison is available for the third.

Addition of a Grignard reagent according to type 1 would produce (B), type 2 would produce (F), and type 3 would produce (C). On simple hydrolysis, both B and C would yield the β-keto ester (D), whereas F would yield the ketone E via G. If the reaction went via D, therefore, type 2 would be eliminated.

No satisfactory means of distinguishing between types 1 and 3 was found but the great reactivity of ketene, CH_2CO, toward Grignard reagents makes it appear reasonable that type 1 should be favored. Also, since $>C\begin{smallmatrix}OR \\ OMgX\end{smallmatrix}$ is an unstable configuration, (C) may decompose spontaneously to (F), in which case no (D) would arise.

That (C) may be a stable intermediate is apparent because some unsaturated esters (such as $PhCH{=}CPhCO_2CH_3$ and $PhCH{=}CHCO_2C_6H_5$) react with phenylmagnesium bromide to give saturated esters[5] ($Ph_2CHCHPhCOOCH_3$ and $Ph_2CHCH_2COOC_6H_5$, respectively), evidently by intermediates related to (C).

When phenyl- or ethylmagnesium bromides were added to (A), the esters (D) were formed: ethyl α-benzoylbutyrate and ethyl α-propionylbutyrate. Hydrolysis of these esters yielded the ketones (E), namely, phenyl *n*-propyl ketone and ethyl propyl ketone.

When (A) was added to the phenylmagnesium bromide (*i. e.*, the Grignard in excess) phenyl α-ethyl-β,β-diphenylvinyl ketone (J) was one of the reaction products. These steps account for its presence:

$$(A) \longrightarrow (B) \xrightarrow{PhMgBr}$$

$$\underset{(H)}{(PhCOCEt{=}CPhOMgX)} \xrightarrow[H_2O]{PhMgBr} \underset{(J)}{Ph_2C{=}CEt-COPh}$$

This normal type of addition of the Grignard reagent to (H) in producing (J) would probably not have occurred if 1,1-dibenzoylpropane, which would come from (H) by hydrolysis, were taken instead with the Grignard reagent. The analogous case is that of 1,1-dibenzoylethane, which gave[6] no phenyl α-methyl-β,β-diphenylvinyl ketone but yielded (with PhMgBr) propiophenone and triphenylcarbinol.

The structure of (J) is supported by its behavior on ozonization. The products were those predicted, namely, benzophenone, benzoic acid and propionic acid.

In one run with ethylmagnesium bromide the addition product (B) was pyrolyzed instead of hydrolyzed. No evidence for the allene ester, $CH_3CH{=}C{=}CEtCOOEt$, was found. This ester would be anticipated if HOMgBr were detached from (B). Instead, ethyl bromide was evolved in quantity, together with an unidentified, unsaturated liquid boiling at 100–110°. In view of the

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(1) Gilman and Heckert, THIS JOURNAL, **42**, 1010 (1920).

(2) Hurd, Sweet and Thomas, *ibid.*, **55**, 335 (1933).

(3) Wedekind and Miller, *Ber.*, **44**, 3285 (1911).

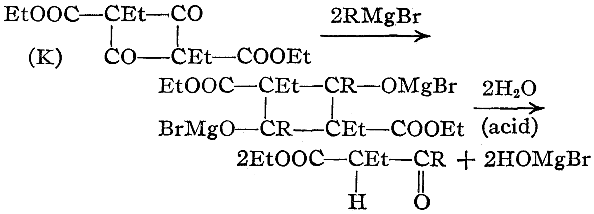
(4) Adams and Noller, THIS JOURNAL, **48**, 1074 (1926); Entemann and Johnson, *ibid.*, **55**, 2900 (1933).

(5) Kohler and Heritage, *Am. Chem. J.*, **33**, 153 (1905); **34**, 568 (1905).

(6) Kohler and Erickson, THIS JOURNAL, **53**, 2306 (1931).

non-production of the desired allene ester, this reaction was not studied further.

Phenyl- and ethylmagnesium bromides were also treated with the dimer (K) of the ketene. As with the ketene, a vigorous reaction resulted and the reaction products were β-keto esters (D) which, on hydrolysis, yielded ketones (E). Here again, practically no reaction occurred at the ester carbonyl. These steps appear probable



$$\begin{array}{l}\mathrm{EtOOC{-}CEt{-}CO}\\ \mathrm{(K)\quad CO{-}CEt{-}COOEt}\end{array} \xrightarrow{\mathrm{2RMgBr}} \begin{array}{l}\mathrm{EtOOC{-}CEt{-}CR{-}OMgBr}\\ \mathrm{BrMgO{-}CR{-}CEt{-}COOEt}\end{array} \xrightarrow[\mathrm{(acid)}]{2H_2O} \mathrm{2EtOOC{-}\underset{H}{CEt}{-}\underset{O}{CR}} + \mathrm{2HOMgBr}$$

The facile, hydrolytic rupture of the C–C bonds in the cyclobutane nucleus is noteworthy, but the reaction of (K) with aniline at 100°, whereby ethyl ethylmalonanilate, $\mathrm{EtO_2CCHEtCONHPh}$, is formed,[7] is somewhat analogous. The findings differ in kind from those of Wedekind and Miller[8] who reported direct addition of RMgX to the cyclobutanedione, but resemble those of Kohler and Erickson[6] who reported a C–C split with certain β-diketones.

Direct dehydration of ethyl hydrogen ethylmalonate proved to be an effective means of synthesis: $\mathrm{EtOOCCHEtCOOH} + P_2O_5 \longrightarrow \mathrm{EtOOCCEt{=}C{=}O} + 2HPO_3$. This saves three steps in the older procedure[9] which also started with ethyl hydrogen ethylmalonate.

Ethyl hydrogen ethylmalonate was synthesized from ethyl ethylmalonate. A method of synthesizing the latter from ethyl sulfate was developed. The older procedure employed ethyl bromide.

Experimental Part

Ethyl Ethylmalonate, $\mathrm{EtCH(COOEt)_2}$

From Ethyl Bromide.[9]—A 62% yield was obtained by the ethyl bromide method in a 3-mole run. This method is economical because the sodium bromide which separates is so readily recoverable.

Careful fractional distillation was required in the purification. Unused ethyl malonate was collected at 88–91° (12 mm.), only 10° below that of the desired homolog. A 60-cm. Vigreux column was employed. The ethyl ethylmalonate taken possessed these constants: b. p. 96–99° (12 mm.), d^{20}_4 1.005, n^{20}_D 1.4171. The density is a convenient criterion of purity for the d^{20}_4 value for ethyl malonate is 1.054. In order to demonstrate the absence of ethylmalonate in the ethyl ethylmalonate used, some of the ester was hydrolyzed to ethylmalonic acid and the latter pyrolyzed to butyric acid. Duclaux values on this material were correct for pure butyric acid.

From Ethyl Sulfate.—In a 2-liter, three-necked, round-bottomed flask which is fitted with a mechanical stirrer, dropping funnel and reflux condenser, 29 g. (1.25 moles) of sodium was dissolved in 300 cc. of absolute alcohol. While still warm (60–75°), 200 g. (1.25 moles) of technical ethyl malonate was added slowly to it. To this solution, which was well stirred, was added 155 g. (1 mole) of ethyl sulfate without cooling. The addition should be fast enough to keep the alcohol boiling, but under control. The time for the addition was 25 minutes, after which the solution was refluxed for one hour on a hot plate. The alcohol was then distilled off and the residual solution heated for one hour at 160–165°, and for three hours at 145–150°. After cooling, water was added to the residue, the ester layer removed, washed with dilute alkali, then with water and dried with calcium chloride. On vacuum distillation, the ethyl ethylmalonate was collected at 100–103° (14 mm.); yield, 200 g. (1.07 moles). This is an 86% yield based on the ethyl malonate or a 54% yield based on the ethyl sulfate (assuming the reaction $\mathrm{Et_2SO_4} + \mathrm{2CH_2(COOEt)_2} + 2\mathrm{Na} \longrightarrow \mathrm{2EtCH(COOEt)_2} + \mathrm{Na_2SO_4}$). No better yield of ethyl ethylmalonate was obtained when 2 moles each of ethyl malonate and sodium were taken instead of 1.25 moles, even when the hot reaction period was extended to twenty hours.

When exactly molar quantities of the three reactants were taken and refluxed in alcohol for two to three hours (without subsequent heating at 145–165°) the yield was 0.80–0.88 mole. This is an 80–88% yield based on the ethyl malonate or a 40–44% yield based as above on the ethyl sulfate.

Synthesis of other Reagents.—Staudinger and Bereza's[9] directions were followed and confirmed for the syntheses of ethyl hydrogen ethylmalonate,[10] its acid chloride (α-carbethoxybutyryl chloride),[11] and α-bromo-α-carbethoxybutyryl chloride. The reported yields in the conversion of the last substance into ethyl diethylcyclobutanedicarboxylate (K) and its depolymerization into (A) were 61 and 80%, respectively, whereas our experience was 50 and 15–30%.

Ethyl Ethylketenecarboxylate from Ethyl Hydrogen Ethylmalonate.—One hundred grams of dried sand and 50 g. of phosphorus pentoxide were mixed in a liter flask which was placed in an oil-bath at 180–200°. The flask was connected to an upright condenser containing water at 75–85°, hot enough to force over the ketene, but cool enough to keep back impurities. Another cold water condenser and a receiver held at −78° were used to condense the ketene. The system was evacuated to 15 mm. and 30 g. of the acid was added rapidly through an attached dropping funnel. In this process the effort was made to cover the entire surface of the dehydrating mixture. Nine grams (34%) of distillate accumulated in thirty minutes. This, on redistillation, gave 6 g. (23%) of the

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[7] Staudinger and Bereza, *Ber.*, **42**, 4916 (1909).

[8] Wedekind and Miller, *ibid.*, **44**, 3285 (1911).

[9] Staudinger and Bereza, *ibid.*, **42**, 4909 (1909).

[10] The use of 95% alcohol for the alcoholic potassium hydroxide also gave satisfactory results.

[11] In this synthesis, it was found more convenient to add the acid to the phosphorus pentachloride than *vice versa*.

ketene. b. p. 45–55° at 11–12 mm. The ketene was kept at −78° to retard polymerization effects.

Distillation of the residue gave a small fraction at 89–91° (11 mm.), n^{23}D 1.4171 which was ethyl ethylmalonate. At a still higher temperature a small fraction of butyric acid was collected, evidently a decomposition product of ethylmalonic acid. The butyric acid was identified by its odor, solubility in water and Duclaux constants. Although most of the ethyl hydrogen ethylmalonate underwent dehydration, a small, concurrent disproportionation was also encountered.

The ketene (0.5 g.) reacted with pure aniline to produce ethyl ethylmalonanilate (yield, 0.8 g.) as stated by Staudinger and Bereza[9] but no reaction was found between the ketene and β-naphthylamine (in benzene).

Reactions with Grignard Reagents

Phenylmagnesium Bromide and (A). First Experiment.—Twenty-five cc. of absolute ether (distilled from a Grignard preparation) and 8.5 g. (0.06 mole) of the ketene were mixed. Then 0.06 mole of phenylmagnesium bromide was dropped into it. Following the vigorous reaction, the solution was refluxed for one-half hour, then stirred with dilute sulfuric acid. The ether layer was removed, washed with dilute sodium carbonate and dried over calcium chloride and distilled. Vacuum distillation (11 mm.) of the residue gave these fractions: (1) 70–120°, 3 g.; (2) 120–170°, 7 g. Redistillation of the 3 g. fraction revealed no constant-boiling material. It distilled between 90–120° (11 mm.). The 7-g. fraction was chiefly ethyl α-benzoylbutyrate.[12] Six grams of it was collected at 159–162° (11 mm.). Its identity was established as follows: (1) its saponification number was 215 (calcd. 210); (2) it was refluxed for 2.5 hours with a 5% solution of potassium hydroxide, then ether extracted, the extract dried and the ether removed. The 2 g. of residue contained some diphenyl but it was largely phenyl *n*-propyl ketone. It gave a semicarbazone, m. p. 184–185° after one crystallization. The recorded value[13] is 188°.

Second Experiment.—In this run, 0.077 mole (11 g.) of the ketene was dropped into a solution of 0.2 mole of phenylmagnesium bromide. By adding the ketene rather than the Grignard reagent, the latter was in great excess throughout.

The reaction product was hydrolyzed with cold, dilute acid. After separation and removal of ether the residue was distilled at 15 mm. There was 0.3 g. of diphenyl and 5.0 g. of liquid collected between 100–140°. The residue from the distillation was taken up in alcohol. On cooling, 2.5 g. of white crystals, m. p. 126–127°, separated. Five cc. of liquid, presumably ethyl α-benzoylbutyrate, was left on evaporation of the alcohol.

A small quantity of the same crystalline material was obtained by interaction of α-bromo-α-carbethoxybutyryl chloride (8 g.) and the Grignard reagent from 13 g. of bromobenzene. Only 0.1 g. was isolated when the former was added to the latter. The reverse type of addition, which should have given better yields, was not tried.

The crystalline material was phenyl α-ethyl-β,β-diphenylvinyl ketone (J). It was non-volatile in steam. It was unaffected by acetic anhydride and did not undergo hydrolysis by refluxing with dilute sulfuric acid or concd. sodium hydroxide solutions. A mixed melting point determination with triphenylcarbinol showed a depression to 109–115°, which showed the virtual absence of the latter.

Anal. Calcd. for $C_{23}H_{20}O$: C, 88.4; H, 6.45. Found: C, 87.7, 87.6; H, 6.28, 6.44.

Ozonolysis of (J).—The sample (1.85 g.) was dissolved in 80 cc. of carbon tetrachloride and 5.4 liters of ozonized oxygen was passed through. The ozonide was insoluble. Eighty cc. of water was added and the mixture distilled until all the carbon tetrachloride and much of the water had been removed. The residue contained about 0.5 g. of benzophenone, present as a yellow oil. When treated with hydroxylamine, 0.6 g. of benzophenone oxime, m. p. 143°, was formed.

The carbon tetrachloride layer was separated from the distillate and evaporated. The oily residue was taken up in hot water. On cooling, 0.7 g. of benzoic acid separated, m. p. 121°. No attempt was made to determine the propionic acid content of the carbon tetrachloride layer.

The water layer was neutralized with 49.10 cc. of 0.053 *N* sodium hydroxide, then evaporated to a volume of 5 cc. Ten cc. of alcohol and 0.5 g. of *p*-bromophenacyl bromide were added and the mixture refluxed for one hour. On cooling, the more insoluble *p*-bromophenacyl benzoate, m. p. and mixed m. p. 118° (yield, 0.3 g.), separated. By concentrating the filtrate, crystals were obtained which melted about 39°. After two recrystallizations, the melting point was raised to 59°, which is characteristic of *p*-bromophenacyl propionate.

Phenylmagnesium Bromide and the Dimer of (A).—When phenylmagnesium bromide solution was dropped into an ice-cold solution of 25 g. of (K) in 50 cc. of absolute ether, a vigorous reaction occurred until nearly the calculated quantity had been introduced. Then the mixture was refluxed for an hour and worked up as in the preceding "first experiment." On distillation at 30 mm., these fractions were obtained (°C., g.): 107–111, 7; 115–120, 8; 120–130, 3; 150–165, 5; 170–175, 15; some residue. The first two fractions appeared to be a mixture of the ketene and its dimer (A and K). Similar material was produced in the distillation of the dimer (K) to produce (A). Thus, distillation of 50 g. of (K) at 25 mm. gave: 50–100°, 20 g. of (A); 109–112°, 13 g.; 125–127°, 2 g.; 140–150°, 5 g.; some residue. The 107–120° portions from both experiments, on alkaline hydrolysis, yielded ethylmalonic acid of neutral equivalent 67 and m. p. 100–105°. (Values, if pure, would be 66 and 112°, respectively.) Carbon dioxide was detached (as shown by lime water test) from this acid by pyrolysis and the butyric acid residue yielded *p*-bromophenacyl butyrate of m. p. 59–60° (literature, 62°) with *p*-bromophenacyl bromide.

The 15-g. fraction (b. p. (30 mm.) 170–175°) was chiefly ethyl α-benzoylbutyrate. Six grams of it gave rise to 4 g. of phenyl *n*-propyl ketone, b. p. 200–210°; semicarbazone, m. p. 185–186°.

Ethylmagnesium Bromide and (A). First Experiment.—The calculated quantity of ethylmagnesium bromide in dry ether was added dropwise with stirring into 4 g. of the ketene (also in ether and cooled by ice). An-

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[12] Hope and Perkin, *J. Chem. Soc.*, **95**, 2047 (1909).

[13] Sorge, *Ber.*, **35**, 1074 (1902).

other 4-g. portion of the ketene was added to the solution and the process repeated till 17.5 g. of the ketene had been used. Then the mixture was refluxed for a half hour, cooled and mixed with ice and dilute sulfuric acid. The ether layer was removed, washed with water, with 5% sodium carbonate solution and dried with calcium chloride. There was 15 g. of residue after removal of the ether. Most of it distilled at 97–100° (18 mm.) but there were higher (100–110°) and lower boiling fractions. The latter, which was collected at 65–70° (40 mm.) and which weighed about 1 g. possessed a mol. wt. of 147–156. The quantity at hand was insufficient for definite characterization.

The mol. wt. of the 97–100° (18 mm.) fraction was 162, 172 (calcd. for $C_9H_{16}O_3$, 172). This material was largely ethyl α-propionylbutyrate. In another similar run (from 5 g. of the ketene) the product was hydrolyzed by stirring with dilute alkali until dissolved and then acidified with 50% sulfuric acid. Ethyl propyl ketone was extracted from it with ether and characterized as the semicarbazone. The latter melted at 107–108° after two crystallizations from water. Michael[14] lists 111° as the m. p. for this semicarbazone.

Second Experiment.—Twenty-two grams (0.15 mole) of the redistilled ketene (b. p. 50–53° (11 mm.)) in 10- and 12-g. portions was treated as before with 0.16 mole of ethylmagnesium bromide. After the half-hour period of refluxing, the ether was distilled away and the temperature of the oil-bath progressively raised to 200°. A drop of paraffin lessened the tendency of the residue to foam. A distillate was obtained near 200°. The temperature was increased to 300° and finally a free flame was used. The 6 g. of liquid obtained was redistilled into two fractions: (1) 37–45°, 3 g.; (2) 45–110°, 2 g. The mol. wt. determination, high bromine content, and b. p. of fraction (1) confirmed its identity as ethyl bromide. Over half of fraction (2), on redistillation, boiled at 100–110°. The substance was unsaturated and 0.0034 mole of it (0.4265 g.) absorbed 0.0032 mole of bromine solution, indicative of one double bond. The mol. wt. values found were 113.7 and 117.4.

Ethylmagnesium Bromide and the Dimer of (A).—Fifteen grams of the dimer, diluted with 50 cc. of dry ether, was taken. Into it (ice cold) was dropped the calculated amount of ethylmagnesium bromide. The reaction mixture was worked up as with the ketene. These fractions were obtained at 12 mm.: 95–97°, 5 g.; 97–145°, 2 g.; 145–155°, 2 g.

The identity of the higher boiling fractions was not established but the 95–97° fraction was ethyl α-propionylbutyrate, the same as from the ketene itself. Hydrolysis yielded ethyl propyl ketone as before; semicarbazone, m. p. 108.5–109°.

Summary

Ethyl ethylketenecarboxylate was prepared by direct dehydration of ethyl hydrogen ethylmalonate with phosphorus pentoxide. The behavior was studied of this ketene and its dimer toward phenyl- and ethylmagnesium bromides. Addition was found to occur preferentially at the ketene carbonyl, giving β-keto esters. No allene type was produced when the addition product of the ketene and ethylmagnesium bromide was pyrolyzed. Instead, ethyl bromide and an unsaturated compound were formed.

Ethyl malonate was converted to ethyl ethylmalonate by the use of ethyl sulfate and sodium ethoxide.

EVANSTON, ILLINOIS RECEIVED JUNE 24, 1935

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[14] Michael, THIS JOURNAL, **41**, 393 (1919).

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

The Reaction between Ethylene and Chlorine in the Presence of Chlorine Acceptors. The Photochlorination of Ethylene

BY T. D. STEWART AND BERNHARDT WEIDENBAUM

This work was instigated by the concept of the reaction between ethylene and chlorine being a chain reaction, similar to the photochemical formation of benzene hexachloride from benzene and chlorine, which has been shown to have a quantum efficiency of the order of 100. That these two reactions have a common intermediate was shown by Stewart and Hanson[1] when they found that ethylene passed into a solution of chlorine in benzene in the dark yielded benzene hexachloride, in the ratio of about ten moles of chlorine reacting with benzene for each one reacting with ethylene, or an induction factor of ten.[2]

These photochlorinations are now commonly considered to involve chlorine atoms or possibly the complex Cl_3, with no clear way as yet of distinguishing their relative importance.[3] The chlorinations of hydrogen and of saturated hydrocarbons involve the same variables.

The Photochlorination of Gaseous Ethylene.—To ascertain that this addition reaction, normally

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[1] Stewart and Hanson, THIS JOURNAL, **53**, 1121 (1931).

[2] Two years ago, Mr. Harold Pitt, in this Laboratory, succeeded occasionally in obtaining an induction factor of 70–100. Rigid exclusion of oxygen and low partial pressures of ethylene permitted the longer benzene–chlorine chains.

[3] Dickinson and Carrico, THIS JOURNAL, **56**, 1478 (1934).

slow in the gas phase, proceeds without complication as a photochemical reaction, a mixture of chlorine and ethylene gases, each at a pressure of ten centimeters of sulfuric acid, was illuminated by light of approximately 4360 Å.

Preparation of Materials.—Chlorine was prepared by heating a tube of copper chloride which was sealed in the line. Ethylene was prepared from the dibromide with zinc, scrubbed with 95% alcohol, dried over calcium chloride and phosphorus pentoxide and condensed in liquid air. The first portion upon evaporation was discarded, the rest stored under pressure in a bulb sealed to the line. There was rigid exclusion of water and oxygen in the line. Electrolytic hydrogen passed over hot copper and through a liquid air trap was used.

The light source was a 500-watt tungsten lamp, about 46 cm. from the 130-cc. reaction flask. Two Zeiss monochromator filters were used; calibrated screens varied the light intensity. Evacuation was achieved with a mercury diffusion pump. The partial pressure of each gas was measured on a sulfuric acid manometer, which also served to follow the reaction rate.

In every experiment the reaction flask was first "cleaned up" by exploding a mixture of hydrogen and chlorine in it, and then evacuating to a pressure less than 10^{-5} mm. of mercury. The criterion of cleanliness was the absence of appreciable induction period upon explosion.

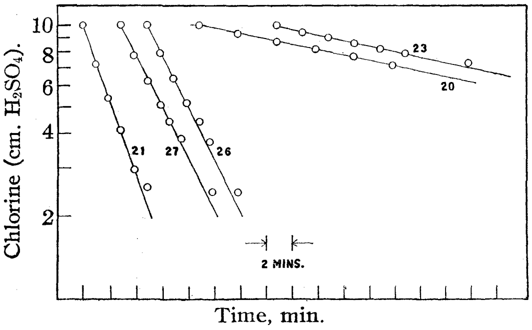

Fig. 1.—The photochemical addition of chlorine and ethylene gases.

If the pressure of chlorine is plotted against time on semi-logarithmic paper, a linear relationship is found to exist during the early part of the reaction. As the reaction proceeds, deviation from linearity is observed; this is caused probably by a concurrent reaction, such as the chlorination of the addition product. In Fig. 1 the results of a few experiments, in which the initial pressure of the reactants is kept constant and the light intensity varied, are plotted. Table I gives a summary of the initial rates as a function of the intensity of the incident light; the rates are given in arbitrary units and were obtained from the slopes of the curves.

TABLE I

EFFECT OF LIGHT INTENSITY UPON THE RATE OF ADDITION OF ETHYLENE AND CHLORINE

Experiment number	Light intensity	Rate
2-21	1	3.39
2-26	0.67	2.31
2-27	.67	2.31
2-28	.47	1.63
2-29	.47	1.62
2-18	.379	1.24
2-22	.372	1.23
2-19	.148	0.54
2-24	.148	.54
2-20	.059	.25
2-23	.059	.25

These data are plotted in Fig. 2, from which it is apparent that a linear relationship exists between the incident light intensity and the initial rate of the reaction. The rate law may then be expressed

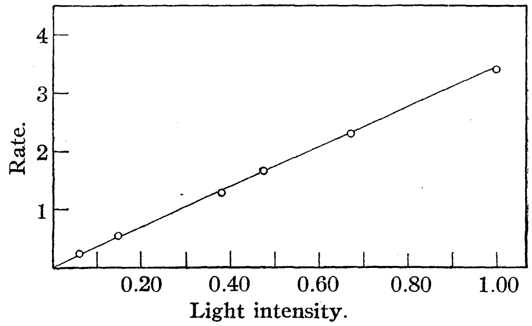

Fig. 2.—Effect of light intensity.

$$\frac{-d(Cl_2)}{dt} = kI_{\text{abs.}} = KI_0(Cl)_2$$

Although the quantum yield was not measured, there is little doubt that it is very large, since explosions of these gases are obtained when illuminated under the proper conditions.

It is possible to derive this rate law on the basis of several mechanisms, in each of which one chain-continuing intermediate (Cl or Cl_3) reacts much more rapidly with ethylene than in any other way, to form another intermediate which may either continue the chain or terminate the chain at the walls. For instance

$$Cl_2 + h\nu \longrightarrow Cl + Cl \qquad (1)$$

$$Cl + Cl_2 \longrightarrow Cl_3 \qquad (2)$$

$$Cl_3 + C_2H_4 \longrightarrow C_2H_4Cl_3 \qquad (3)$$

$$C_2H_4Cl_3 \longrightarrow C_2H_4Cl_2 + Cl \qquad (4)$$
$$C_2H_4Cl_3 + W \longrightarrow C_2H_4Cl_2 + {}^1/_2Cl_2 \qquad (5)$$

or

$$Cl_2 + h\nu \longrightarrow Cl + Cl \qquad (1)$$
$$Cl + C_2H_4 \longrightarrow C_2H_4Cl \qquad (2)$$
$$C_2H_4Cl + Cl_2 \longrightarrow C_2H_4Cl_3 \qquad (3)$$
$$C_2H_4Cl_3 \longrightarrow C_2H_4Cl_2 + Cl \qquad (4)$$
$$C_2H_4Cl_3 + W \longrightarrow C_2H_4Cl_2 + {}^1/_2Cl_2 \qquad (5)$$

The rate determining step in each case is equation (4), and either mechanism yields the experimental rate law. In any case it is evident that ethylene must have a very high collision efficiency with the intermediate, in order that within wide limits its concentration should not affect the rate.[4]

The Reaction of Chlorine in a Mixture of Ethylene and Hydrogen.—This reaction was measured in the apparatus just described. Before each experiment the walls were "cleaned up" as usual. The reaction with ethylene could be followed by the manometer at room temperature; that with the hydrogen was measured by taking a manometer reading with the vessel in a liquid air-bath whose temperature was measured with a gold resistance thermometer.

Table II gives some of the data obtained. Some experiments of identical results are omitted, as well as measurements taken at intermediate time intervals. The table headings are self-explanatory, except that the manometer reading is arbitrary and differences only are significant. The initial partial pressures are measured; final ones are calculated from the manometer readings on the assumption of a simple addition reaction to ethylene, and in experiments 2–9 and 2–11, from measured loss of hydrogen.

In the dark reaction no detectable reaction with hydrogen occurred during the ethylene–chlorine reaction. Even in the presence of light, a hydrogen–ethylene ratio of 9.64/1 permitted only 10.7% of the total chlorine reacting to react with the hydrogen, or a reactivity in favor of the ethylene of about 81-fold. If this be interpreted solely in terms of the difference in the heats of activation of the two reactions, since the heat of activation of the photochemical hydrogen-chlorine reaction is 6000 calories, that for the ethylene–chlorine photochemical reaction is less than 1400 calories.

TABLE II

THE REACTION IN MIXTURES OF ETHYLENE, CHLORINE AND HYDROGEN

Expt.	Partial pressures, cm. Chlorine	Hydrogen	Ethylene	Manometer reading	Time, min.	Temp., °K.
		Part A. Dark reaction				
2–1	47.48	27.95	16.40	102.5	0	298
	...	...	...	18.95	0	83.79
	45.78	27.95	14.70	100.8	15	298
	...	...	...	18.95	15	83.88
	ca. 31.0	*ca.* 27.0	0	86.0	α[a]	298
	...	...	...	18.65	α[a]	83.91
2–2	32.95	19.35	11.70	73.2	0	298
	...	...	...	16.0	0	83.61
	21.25	19.35	0	61.5	1080	298
	...	...	...	16.0	1080	83.81
		Part B. Illuminated by 500-watt lamp				
2–5	26.9	20.1	17.9	75.1	0	294.5
	...	...	...	6.45	0	83.81
	14.2	20.1	15.2	62.4	45	294.5
	...	...	...	6.45	45	83.90
2–9	10.0	92.5	9.6	125.5	0	294.0
	...	...	...	38.3	0	82.73
	1.66	91.61	2.15	118.05	50	294.0
	...	...	...	38.05	50	82.73
2–11	11.4	92.55	0	115.9	0	294.0
	...	...	...	38.65	0	83.63
	0	81.15	...	115.9	50	294.0
	...	...	...	35.40	50	83.81

[a] To complete the reaction the 500-watt lamp was held close to the reaction vessel until perceptible change in the manometer ceased. The total pressure drop, 16.5 cm., was practically equal to the original ethylene pressure.

The Ethylene–Chlorine Reaction in Ethylene Chloride and in Pentane as Solvents.—Commercial ethylene chloride was refluxed over both calcium chloride and phosphorus pentoxide for several hours each, and distilled into dried bottles at 83.4–83.6°. The purifications of the *n*-pentane,[5] ethylene and chlorine have been described.[6] Carbon tetrachloride was refluxed for twelve hours with chlorine and iodine, washed with alkali, acid and water successively, dried with calcium chloride and refluxed over phosphorus pentoxide for six hours. It was distilled at 76.6° into carefully dried bottles.

Procedure.—Stock solutions of the olefin and chlorine in the solvents concerned were kept at 0° in an ice-bath. The reaction vessel, which usually was a 125-cc. glass-stoppered Erlenmeyer flask, was also immersed in an ice-bath. A known amount of each solution was pipetted into

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(4) It is estimated that if chlorine and ethylene, each at a pressure of 0.001 of an atmosphere, were illuminated in a 130-cc. cylindrical reaction vessel, the rate of disappearance of chlorine atoms by reaction with ethylene should be nearly equal to the rate at which they combine at the wall.

(5) The refractive index of the carefully purified pentane was measured in a Pulfrich refractometer, referred to air at 20°.

$n^{20}{}_D$ 1.35750 $n^{20}{}_\alpha$ 1.35572
$n^{20}{}_\beta$ 1.36187 $n^{15}{}_\alpha$ 1.35854

(6) Stewart and Weidenbaum, THIS JOURNAL, **57**, 1702 (1935).

the reaction flask; as a rule the olefin was added first and then the chlorine. After the reaction had proceeded for the time interval desired, it was "quenched" by adding an aqueous solution of potassium iodide. The iodine liberated was determined by titration with sodium thiosulfate of suitable strength, using the method suggested by Liebhafsky.[7] The amount of hydrogen chloride produced, which was a measure of the induced substitution reaction, was obtained then by titrating the contents of the reaction flask with sodium hydroxide of suitable strength; brom cresol green was used as the indicator for this titration because of the distinctness of the end-point in spite of the two phases being present.

The stock solution of olefin was analyzed by adding a known amount of a solution of bromine in carbon tetrachloride, which was approximately twice the amount that would be required by the sample of olefin used. The mixture was kept in the dark for two hours at 0°. At the end of this time the uncombined bromine was determined by adding an aqueous solution of potassium iodide and titrating with sodium thiosulfate.

Experimental Results.—A large number of experiments using ethylene dichloride as the solvent for the reaction between chlorine and ethylene were performed with various changes in the experimental conditions. These included various ratios of the concentration of chlorine to that of ethylene over a range of 0.5 to 2, different treatment of the reaction vessel, such as burning it out in order to clean up the walls, variation of the temperature from 0 to 25°, and changes in the order of mixing the reactants.

When the concentration of each reactant was 0.05 *M* or larger, the reaction proceeded too rapidly to allow a study of its kinetics to be made. The induction factor was never greater than 0.1; here the induction factor is given by the ratio of the number of moles of hydrogen chloride produced to the number of moles of chlorine that are used by the olefin in the addition reaction.

Pentane was next used as the solvent. Here again the reaction was exceedingly rapid, being over 95% complete in fifteen seconds, but an induction factor as large as 2.8 was observed. Some typical results are given in Table III.

The members of the last two pairs of experiments differed only in the order in which the reagents were added.

TABLE III

THE CHLORINATION OF PENTANE INDUCED BY ETHYLENE

Time, seconds	Concentration × 10^3 Chlorine	Concentration × 10^3 Ethylene	Induction factor
30	8.6	25.0	2.8
30	16.0	6.7	0.85
30	3.8	13.0	2.3
30	3.5	18.7	2.6
60	1.33	1.85	1.5
60	3.64	0.93	0.7
60	3.64	0.93	0.6
60	0.57	1.85	1.9
60	0.57	1.85	1.9

It is seen that from 35.5 to 73.6% of the reacting chlorine produces hydrogen chloride. Moreover, if at a given initial chlorine concentration the initial ethylene concentration is increased, more substitution occurs (items 3, 4, 6 and 7); conversely a relative increase in the chlorine concentration decreases substitution (items 5 and 8). The substitution is probably upon the pentane, as the use of ethylene dichloride as a solvent for the same reactants produced but about 10% substitution at a maximum; pentane and chlorine alone do not react in the time allowed.

The question arises as to whether the intermediate in this induced substitution of pentane is the same molecule as the intermediate in its photochemical chlorination. Chlorine atom may be an intermediate in both the chain reaction of addition to ethylene and the chain reaction of substitution upon pentane, but as in the case of the hydrogen–chlorine reaction, ethylene should be an efficient inhibitor for the pentane–chlorine reaction. Increasing ethylene should decrease, not increase, the substitution if chlorine atoms were responsible. It would appear then, that some derivative of ethylene is the intermediate in the substitution reaction. If chlorine atom were competed for by both ethylene and chlorine, and if of the two products C_2H_4Cl promoted substitution and Cl_3 promoted addition, the facts could be qualitatively accounted for. We may then write

(1a) $Cl + Cl_2 \longrightarrow Cl_3$
(1b) $Cl + C_2H_4 \longrightarrow C_2H_4Cl$
(2) $C_2H_4 + Cl_3 \longrightarrow C_2H_4Cl_3 \longrightarrow C_2H_4Cl_2 + Cl \ldots$
(3a) $C_2H_4Cl + Cl_2 \longrightarrow C_2H_4Cl_3 \longrightarrow C_2H_4Cl_2 + Cl \ldots$
(3b) $C_2H_4Cl + C_5H_{12} \longrightarrow C_2H_4 + C_5H_{11} + HCl$
(4) $C_5H_{11} + Cl_2 \longrightarrow C_5H_{11}Cl + Cl \ldots$

with appropriate chain breaking steps. While the data do not permit a quantitative test of this mechanism, it may be interesting to derive an

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(7) Liebhafsky, THIS JOURNAL, **53**, 165 (1931).

expression based upon it, for the instantaneous values of the induction factor as functions of the relative concentrations of reagents and of the various specific reaction rate constants. Assuming that the source of chlorine atoms is thermal decomposition and that any possible substitution due to the reaction

$$Cl + C_5H_{12} \longrightarrow C_5H_{11} + HCl$$

is slow compared to reaction (3b) above, and assuming as a chain terminating reaction

$$C_2H_4Cl_3 + W \longrightarrow C_2H_4Cl_2 + {}^1/_2Cl_2$$

we may write

$$\text{Induction factor} = \frac{d(HCl)}{dt} \Big/ \frac{d(C_2H_4Cl_2)}{dt} = K_{1b}K_{3b} \times \frac{(C_2H_4)}{(Cl_2)} \times \frac{(C_5H_{12})}{K_{1a}K_{3b}(C_5H_{12}) + K_{1a}K_{3a}(Cl_2) + K_{1b}K_{3a}(C_2H_4)}$$

The subscripts relate the specific reaction rate constants to the equations above. It is seen that should by accident the competitive reactions 1a, 1b and 3a, 3b, be equal in rate, so that $K_{1a} = K_{1b}$ and $K_{3a} = K_{3b}$, the expression reduces to

$$\text{I. F.} = (C_2H_4)/(Cl_2)$$

since here (C_5H_{12}) is large compared to (C_2H_4) or (Cl_2). Similarly, if ethylene be in large excess, or excessively reactive, causing only equations (3a) and (3b) to operate as competitive, it reduces to

$$\text{I. F.} = K_{3b}(C_5H_{12})/K_{3a}(Cl_2)$$

It should be stressed that the induction factors measured are integrated values over wide ranges of relative concentrations of reagents.

A very rapidly reacting ethylene should produce more substitution (reaction 1b being favored) than a slowly reacting one. The compound to be substituted must be very reactive, favoring reaction 3b over reaction 3a; ethylene chloride as solvent is perhaps for this reason less attacked than pentane. It is thus seen that ethylene does inhibit the normal chain of pentane chlorination; if it did not, conditions would be found where the induction factor approximated the quantum efficiency factor in the photochemical reaction. Experience with the induced benzene–chlorine addition lends credence to this expectation. But in addition to this inhibition, a new path is furnished for the substitution reaction, favored by excess of ethylene. Further evidence of this interpretation will be presented in a succeeding paper.[8]

Summary

1. The photochlorination of gaseous ethylene proceeds at a rate proportional to the chlorine concentration at constant light intensity, and independent of the ethylene concentration.

2. Practically no hydrogen reacts in a mixture of hydrogen, chlorine and ethylene, either in the dark or when illuminated, while the ethylene–chlorine reaction goes to completion.

3. The ethylene–chlorine reaction in ethylene dichloride solution is very rapid, and involves less than 10% of the chlorine in substitution; while in pentane solution from 37 to 73% of the chlorine substitutes, and the amount of the substitution is increased by an increase in the ethylene/chlorine ratio.

BERKELEY, CALIF. RECEIVED JULY 22, 1935

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[8] Stewart and Smith, THIS JOURNAL, **52**, 2869 (1930), found that excess chlorine, when reacting with ethylene on surfaces coated with the reaction products, served to decrease the reaction rate and *increase* substitution. They obtained a maximum induction factor of unity, much higher than is found here in homogeneous solution. The difference in behavior is very real; one possible reconciliation is as follows. The series of reactions given above still holds, but the intermediate $C_2H_4Cl_3$ may react at the wall, not alone to produce Cl_2 as is often assumed for a chain breaking step, but also to give hydrogen chloride and products which no longer propagate a chain. Thus excess chlorine, winning in the competition for chlorine atom, might give an intermediate with ethylene which decomposed homogeneously one way, but at a surface differently. This could be true particularly on a surface which did not catalyze the chlorine–ethylene addition, since such a surface might also not catalyze recombination of chlorine atoms and thereby would give opportunity for the type of decomposition leading to substitution.

[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF HARVARD UNIVERSITY]

The Viscosity of Solutions of Salts in Methanol

BY GRINNELL JONES AND HOLMES J. FORNWALT

Introduction

Grüneisen[1] long ago showed experimentally that, although the viscosity–concentration curves for aqueous solutions of salts are approximately linear, nevertheless they exhibit systematic deviation from the simple linear relationship at low concentrations. The first plausible explanation of this "Grüneisen Effect" was offered by Jones and Dole,[2] who ascribed it to an increase in viscosity due to the electrical attraction between the ions. The increment of the viscosity due to this cause varies as the square root of the concentration and, therefore, becomes relatively more important at low concentrations in comparison with other effects which vary linearly with the concentration. Jones and Dole, Jones and Talley, and Wolfenden[3] and his associates have demonstrated that the equation $\eta = 1 + A\sqrt{c} \pm Bc$ is valid for aqueous solutions of many salts up to 0.2 N or above.

Falkenhagen and Dole, and Falkenhagen and Vernon[4] have deduced from the Debye theory of interionic attraction a complicated but explicit expression for the coefficient A of the square root term as a function of the mobilities and valences of the ions, the dielectric constant and viscosity of the solvent, the temperature and the usual universal constants which appear in the equations of the interionic attraction theory. Jones and Talley, and Wolfenden and his associates, have found a gratifying agreement between the values of A found experimentally for aqueous solutions of several salts and those computed by the equation of Falkenhagen and Vernon.

Finally Onsager and Fuoss[5] have proposed a generalized expression for the properties of solutions as a function of the concentration which in the case of viscosity would give the equation $\eta = 1 + A\sqrt{c} + Bc + Dc \log c + \ldots$ for the variation of the viscosity with the concentration, but without discussing the agreement of this equation with the available data.

The recent advances summarized above make it desirable to test the validity of these new relationships when applied to non-aqueous solutions. Methanol was chosen as the solvent to be studied because the dielectric constant is substantially lower than that of water and therefore the equation of Falkenhagen predicts a larger value of the coefficient A than for water solutions. This in turn means that the "Grüneisen Effect" should be more pronounced. Moreover, methanol has sufficient solvent power for many salts and gives solutions having a conductivity comparable with that of aqueous solutions and, therefore, the ionization must be substantial and the interionic attraction theory applicable.

Another object of this investigation was to obtain viscosity data to be used in the interpretation of conductance data on methanol solutions which were being determined simultaneously in this Laboratory.

Earlier investigations of the viscosity of solutions of salts in methanol have been made by Ewart and Raikes,[6] Tower,[7] and Harry C. Jones and E. C. Bingham.[8]

Experimental

Preliminary trials showed that the addition of water to methanol increases the viscosity at the rate of about 4% for each per cent. of water added. It was, therefore, evident that great care must be taken to purify the alcohol and to prevent the absorption of water from the air during the preparation and manipulation of the solutions.

The methanol used was a synthetic product made by the Commercial Solvents Company. A letter from the company stated that it contained no ethyl alcohol, less than 0.03% acetone and less than 0.2% water. It was purified by treatment with magnesium methylate in accordance with the method of Lund and Bjerrum,[9] followed by fractional distillation through a column 75 cm. long. The middle fraction consisting of about three liters of methanol boiling within about 0.04° of the true boiling point of

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[1] E. Grüneisen, *Wiss. Abh. phys.-techn. Reichsanstalt*, **4**, 151, 237 (1905).

[2] Grinnell Jones and Malcolm Dole, THIS JOURNAL, **51**, 2950 (1929).

[3] W. E. Joy and J. H. Wolfenden, *Nature*, **126**, 994 (1930); *Proc. Roy. Soc.* (London), **A134**, 413 (1931); Grinnell Jones and S. K. Talley, THIS JOURNAL, **55**, 624, 4124 (1933); W. M. Cox and J. H. Wolfenden, *Proc. Roy. Soc.* (London), **A145**, 475 (1934); V. D. Laurence and J. H. Wolfenden, *J. Chem. Soc.* 1144 (1934).

[4] H. Falkenhagen and M. Dole, *Z. physik. Chem.*, **B6**, 159 (1929); *Physik. Z.*, **30**, 611 (1929); H. Falkenhagen, *ibid.*, **32**, 365, 745 (1931); H. Falkenhagen and E. L. Vernon, *ibid.*, **33**, 140 (1932); *Phil. Mag.*, [7] **14**, 537 (1932).

[5] L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

[6] F. K. Ewart and H. R. Raikes, *J. Chem. Soc.*, 1907 (1926).

[7] O. F. Tower, THIS JOURNAL, **38**, 833 (1916).

[8] H. C. Jones and E. C. Bingham, *Am. Chem. J.*, **34**, 536 (1905)

[9] H. Lund and J. Bjerrum, *Ber.*, **64B**, 210 (1931).

64.65°, as given by Timmermans and Hennaut-Roland,[10] was collected in storage reservoirs with suitable protection from the moisture in the air. These reservoirs were provided with standardized interchangeable ground glass connections with the flasks used to make the solutions. During the progress of the work it was discovered that the methanol contained a trace of ammonia. Therefore, in the later part of this work the methanol after purification as described above was distilled again from solid anhydrous copper sulfate, as recommended by Hartley and Raikes,[11] although the results were not influenced significantly by the change in procedure. The average density at 25° of the seventeen batches whose density was determined was 0.786545 g. per milliliter. The maximum difference between the density of any batch and the mean was only 0.00001.

The four salts used in this investigation were the chloride, bromide, and iodide of potassium, and ammonium chloride. All were carefully purified and dried and are believed to have contained no impurity in significant amounts. The salts were weighed out and solutions of the desired concentration prepared with suitable precautions to prevent absorption of moisture from the air during the preparation of the solutions and subsequent transfer to the pycnometers and viscometers. All concentrations are expressed in gram molecules per liter of solution at 25°. The viscometric technique was the same as that already described in earlier papers from this Laboratory.[12] Kinetic energy corrections have been applied to the data. Two different quartz viscometers having periods of 623 and 539 seconds with water at 25° were used. Duplicate runs on the same filling rarely differed by more than 0.02 second. The variations caused by removing the viscometer from the thermostat, cleaning and drying it and replacing the solution did not exceed 0.05 second, and were usually less than this. The viscosities given in the tables are relative to that of pure methanol at the same temperature. The viscosity of the solution, η, was always compared with that of the same sample of methanol which was used to prepare the solution. The comparative measurements on the solution and on pure methanol were always made on the same day in the same instrument and with every care to maintain all conditions which might affect the results (temperature, mounting, timing mechanism, etc.) as nearly constant as possible. The relative viscosities given are, therefore, believed to have been determined more precisely than the absolute viscosity of methanol is known.

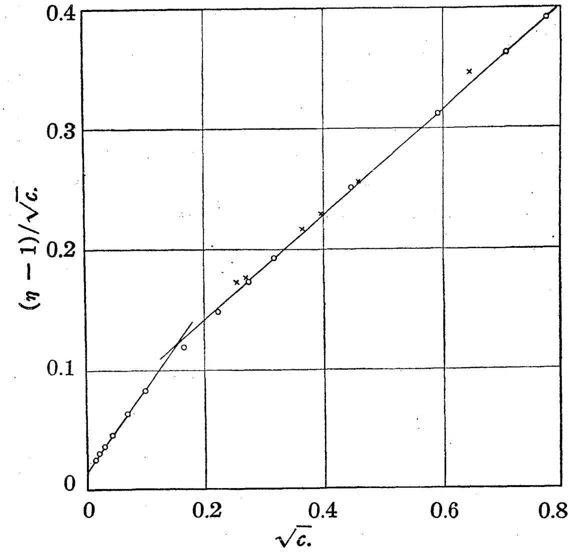

Fig. 1.—Test of the Jones and Dole equation: ○, Jones and Fornwalt; ×, Ewart and Raikes.

Potassium Iodide.—The results on potassium iodide solutions are shown in Table I and in Figs. 1 and 2. The density of potassium iodide solutions in methanol at 25° can be expressed by an equation of the form suggested by Root;[13] $d^{25}{}_4 = 0.786545 + 0.148096c - 0.007833c^{3/2}$; with an average deviation between our observed values and those computed by this equation of only 0.0021%.

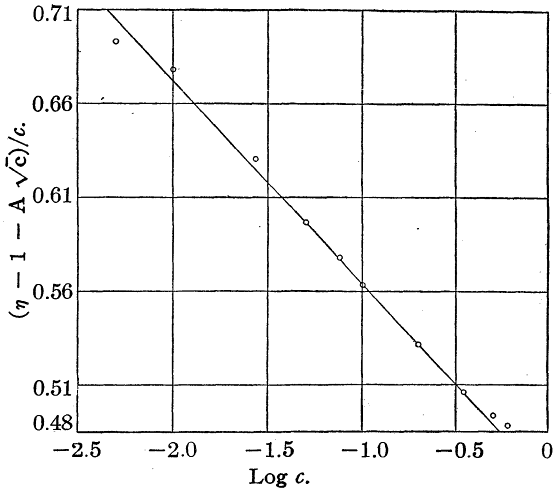

Fig. 2.—Test of the Onsager and Fuoss equation.

If the viscosity–concentration curves were linear the quantity $(\eta - 1)/c$ should be a constant, but column four shows that this quantity diminishes rapidly with increasing concentration at low concentrations but that, unlike most aqueous solutions, $(\eta - 1)/c$ does not pass through a minimum within the range of concentrations studied, which extends almost to saturation. The "Grüneisen Effect" is more pronounced in this case than for aqueous solutions. The Jones and Dole equation was then tested by plotting $(\eta - 1)/\sqrt{c}$ against $\sqrt{c}$ which gave a straight line up to and including $c = 0.01$. The coefficients A and B were then determined by the method of least squares using the data up to $c = 0.01$; giving η

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(10) J. Timmermans and Hennaut-Roland, *J. chim. phys.*, **27**, 412 (1930).

(11) H. Hartley and H. R. Raikes, *J. Chem. Soc.*, **127**, 524 (1925).

(12) Grinnell Jones and S. K. Talley, THIS JOURNAL, **55**, 624 (1933); *Physics*, **4**, 215 (1933).

(13) W. C. Root, THIS JOURNAL, **55**, 850 (1933).

$= 1 + 0.0159\sqrt{c} + 0.6747c$. As will be seen from Table I this equation agrees with the data up to $c = 0.01$ with an average deviation of only 0.002% but fails badly above this concentration. This same plot shows that the points from $c = 0.05$ to $c = 0.6$, inclusive, are also on a different straight line whose equation is $\eta = 1 + 0.05546\sqrt{c} + 0.43362c$ with an average deviation of 0.05%. The data were also used to test the Onsager and Fuoss equation: $\eta = 1 + A\sqrt{c} + Bc + Dc \log c$ by plotting $(\eta - 1 - A\sqrt{c})/c$ against $\log c$, which should give a straight line if the Onsager and Fuoss equation is valid and if the proper numerical value of A has already been chosen. Using the value $A = 0.0159$ already determined, an approximation to a straight line was found for the middle range of concentration (see Fig. 2). The two highest concentrations ($c = 0.5$ and $c = 0.6$) are clearly out of line. The deviations at the dilute end, although apparently large, are not significant because this method of plotting is extremely sensitive at the dilute end to experimental errors or to the value of A chosen. The method of least squares was then used to determine all of the coefficients in the Onsager and Fuoss equation using the data up to $c = 0.35$. The result was

TABLE I

RELATIVE VISCOSITY AND DENSITY OF POTASSIUM IODIDE SOLUTIONS IN METHANOL AT 25°

Concentration c	Density d^{25}_4	Relative viscosity η observed	$(\eta - 1)/c$	Jones and Dole equation η Comp.	Jones and Dole equation $\Delta\eta \times 10^5$	Onsager and Fuoss equation η Comp.	Onsager and Fuoss equation $\Delta\eta \times 10^5$
0.0002504	0.786573	1.00040	1.60	1.00042	− 2	1.00044	− 4
.0005010	.786621	1.00069	1.38	1.00069	0	1.00076	− 7
.0010001	.786687	1.00115	1.15	1.00118	− 3	1.00128	− 13
.0020035	.786846	1.00206	1.03	1.00206	0	1.00220	− 14
.0050017	.787281	1.00457	0.91	1.00450	+ 7	1.00462	− 5
.0100232	.788032	1.00833	.83	1.00836	− 3	1.00828	+ 5
.0271490	.790538	1.01962	.722	1.02094	− 132	1.01947	+ 15
.0499222	.793891	1.03316	.664	1.03724	− 408	1.03312	+ 4
.0752514	.797520	1.04752	.632	1.05513	− 761	1.04749	+ 3
.100245	.801198	1.06107	.609	1.07267	− 1160	1.06113	− 6
.199325	.815356	1.11215	.563	1.14158	− 2943	1.11222	− 7
.348769	.836530	1.18420	.528	1.24470	− 6050	1.18417	+ 3
.501918	.858108	1.25651	.511	1.34991	− 9340	1.25420	+231
.603193	.872214	1.30385	.504	1.41932	−11547	1.29909	+476

Root equation: $d^{25}_4 = 0.786545 + 0.148096c - 0.007833c^{3/2}$.
Jones and Dole equation: $\eta = 1 + 0.0159\sqrt{c} + 0.6747c$.
Onsager and Fuoss equation: $\eta = 1 + 0.01575\sqrt{c} + 0.45174c - 0.10847c \log c$.

TABLE II

RELATIVE VISCOSITY AND DENSITY OF AMMONIUM CHLORIDE SOLUTIONS IN METHANOL AT 25°

Concentration c	Density d^{25}_4	Relative viscosity η observed	$(\eta - 1)/c$	Jones and Dole equation η Comp.	Jones and Dole equation $\Delta\eta \times 10^5$	Onsager and Fuoss equation η Comp.	Onsager and Fuoss equation $\Delta\eta \times 10^5$
0.0005015	0.786556	1.00078	1.56	1.00074	+ 4	1.00085	− 7
.0007966	.786578	1.00102	1.28	1.00104	− 2	1.00118	−16
.0009928	.786598	1.00113	1.14	1.00123	− 10	1.00138	−25
.0019827	.786621	1.00212	1.07	1.00213	− 1	1.00231	−19
.0049911	.786738	1.00467	0.936	1.00459	+ 8	1.00475	− 8
.0079583	.786839	1.00696	.875	1.00689	+ 7	1.00692	+ 4
.0099441	.786950	1.00832	.837	1.00840	− 8	1.00831	+ 1
.0149778	.787122	1.01166	.778	1.01214	− 48	1.01168	− 2
.0200046	.787317	1.01476	.738	1.01581	− 105	1.01490	−14
.0300215	.787676	1.02102	.700	1.02302	− 200	1.02105	− 3
.0400008	.788064	1.02707	.677	1.03010	− 303	1.02693	+14
.0499413	.788405	1.03298	.660	1.03710	− 412	1.03262	+36
.0700415	.789126	1.04386	.626	1.05114	− 728	1.04377	+ 9
.100215	.790195	1.05990	.598	1.07204	−1214	1.05986	+ 4
.199413	.793589	1.10932	.548	1.13998	−3066	1.10974	−42
.351163	.798518	1.18134	.516	1.24296	−6162	1.18118	+16

Root equation: $d^{25}_4 = 0.786545 + 0.039225c - 0.008672c^{3/2}$.
Jones and Dole equation: $\eta = 1 + 0.0183\sqrt{c} + 0.6610c$.
Onsager and Fuoss equation: $\eta = 1 + 0.02129\sqrt{c} + 0.43823c - 0.09196c \log c$.

TABLE III

RELATIVE VISCOSITY AND DENSITY OF POTASSIUM BROMIDE SOLUTIONS IN METHANOL AT 25°

Concentration c	Density d^{25}_4	Relative viscosity η observed	$(\eta - 1)/c$	Jones and Dole equation η Comp.	Jones and Dole equation $\Delta\eta \times 10^5$	Onsager and Fuoss equation η Comp.	Onsager and Fuoss equation $\Delta\eta \times 10^6$
0.0004104	(0.786589)	1.00058	1.41	1.00059	− 1	1.00064	− 6
.0005038	.786608	1.00067	1.33	1.00069	− 2	1.00075	− 8
.0010044	.786657	1.00116	1.15	1.00119	− 3	1.00129	−13
.0020020	.786775	1.00216	1.08	1.00212	+ 4	1.00224	− 8
.0050194	.787079	1.00473	0.942	1.00472	+ 1	1.00483	−10
.0100141	.787636	1.00882	.881	1.00883	− 1	1.00871	+11
.0149908	.788174	1.01257	.839	1.01283	− 26	1.01235	+22
.0300121	.789793	1.02265	.755	1.02466	− 201	1.02264	+ 1
.0500105	.791920	1.03548	.709	1.04017	− 469	1.03548	0
.0800065	.795098	1.05363	.670	1.06319	− 956	1.05373	−10
.100011	.797237	1.06527	.653	1.07846	−1319	1.06548	−21
.118905	.799295	1.07649	.643	1.09284	−1635	1.07630	+19

$d^{25}_4 = 0.786545 + 0.107068c$.

Jones and Dole equation: $\eta = 1 + 0.0142\sqrt{c} + 0.7396c$.

Onsager and Fuoss equation: $\eta = 1 + 0.01325\sqrt{c} + 0.48758c - 0.12504c \log c$.

TABLE IV

RELATIVE VISCOSITY AND DENSITY OF POTASSIUM CHLORIDE SOLUTIONS IN METHANOL AT 25°

Concentration c	Density d^{25}_4	Relative viscosity η observed	$(\eta - 1)/c$	Jones and Dole equation η Comp.	Jones and Dole equation $\Delta\eta \times 10^5$	Onsager and Fuoss equation η Comp.	Onsager and Fuoss equation $\Delta\eta \times 10^5$
0.0004786	0.786563	1.00068	1.42	1.00070	− 2	1.00064	+4
.0010431	.786615	1.00126	1.21	1.00128	− 2	1.00126	0
.0019996	.786676	1.00224	1.12	1.00220	+ 4	1.00222	+2
.0048375	.786884	1.00474	0.978	1.00475	+ 1	1.00482	−8
.0099940	.787233	1.00914	.915	1.00914	0	1.00912	+2
.0199816	.787914	1.01676	.839	1.01739	− 63	1.01671	+5
.0299878	.788589	1.02376	.792	1.02551	−175	1.02378	−2
.0350097	.788918	1.02716	.775	1.02956	−240	1.02719	−3
.0400159	.789246	1.03055	.763	1.03357	−302	1.03053	+2

$d^{25}_4 = 0.786545 + 0.067895c$.

Jones and Dole equation: $\eta = 1 + 0.0151\sqrt{c} + 0.7635c$.

Onsager and Fuoss equation: $\eta = 1 + 0.00367\sqrt{c} + 0.43974c - 0.21803c \log c$.

$\eta = 1 + 0.01575\sqrt{c} + 0.45174c - 0.10874c \log c$. The values computed from the equation are shown in the last two columns of Table I. As will be seen, this equation is better between $c = 0.027$ and $c = 0.35$ than any other equation known to us, but gives low results at $c = 0.5$ and $c = 0.6$ and is not as good as the Jones and Dole equation at $c = 0.01$ and below *if the constants are chosen to fit the data over the entire range up to* $c = 0.35$.

Ammonium Chloride.—Taking up the salts studied in order of decreasing solubility we find that ammonium chloride presents a picture very similar to potassium iodide. The density can be expressed by the Root equation with an average deviation of less than 0.001%; $d^{25}_4 = 0.786545 + 0.039225c - 0.008672c^{3/2}$. Again it was found that the Jones and Dole equation, $\eta = 1 + 0.0183\sqrt{c} + 0.6610c$ holds up to $c = 0.01$ but not above. The Onsager and Fuoss equation $\eta = 1 + 0.02129\sqrt{c} + 0.43823c - 0.09196c \log c$, is the best between $c = 0.01$ and $c = 0.35$, but not as good as the Jones and Dole equation for the more dilute solutions. The "Grüneisen Effect" is similar to potassium iodide solutions but slightly more pronounced.

Potassium Bromide and Potassium Chloride.—Owing to their limited solubility these salts do not give as severe and useful tests of the equations in which we are interested as the other salts studied. The densities of the solutions of both of these salts can be expressed as a linear function of the concentration (see Tables III and IV) with an average deviation of less than 0.002%. All four salts show the "Grüneisen Effect" in a similar degree. Again we find that the Jones and Dole equation is valid up to $c = 0.01$ but not above, and that the Onsager and Fuoss equation is better than the Jones and Dole equation for solutions more concentrated than $c = 0.01$.

General Discussion

Earlier investigations cited above have shown that the Jones and Dole equation is valid for aqueous solutions of salts which diminish the viscosity of water up to about 0.2 normal and to a considerably higher concentration for some salts which increase the viscosity. On the other hand, for these methanol solutions the Jones and Dole equation is valid only up to 0.01 normal.

All four of these salts give aqueous solutions which within certain ranges of concentration and of temperature, have a viscosity less than that of the pure solvent but none of them diminishes the viscosity of methanol at 25°. No salt has yet been found to have this effect in methanol solution. The B term in the Jones and Dole equation is positive for all methanol solutions that have yet been studied, but is negative for many salts in water solutions.

Falkenhagen and Vernon have used the Debye theory of interionic attraction to derive an expression for the coefficient of the square root term which for uni-univalent salts reduces to

$$A = \frac{1.45}{\eta_0\sqrt{2DT}}\left[\frac{l_1 + l_2}{4l_1l_2} - \frac{(l_1 - l_2)^2}{(3 + 2\sqrt{2})l_1l_2(l_1 + l_2)}\right]$$

where η_0 and D are the absolute viscosity and dielectric constant of the solvent, T is the absolute temperature, and l_1 and l_2 are the equivalent conductances of the ions present; and the factor 1.45 is computed from universal constants. The values of A for the four salts have been computed by this equation using: $\eta_0 = 0.00542$ (a preliminary value from our own measurements, details to be published later); $D = 31.5$ (after Åkerlöf[14]); and the following values for the equivalent conductances of the ions; K^+, 53.8; Cl^-, 51.3; Br^-, 55.5; I^-, 61.0; NH_4^+, 59.0 (after Hartley and Raikes, and Ulich[15]).

The results are shown in Table V and compared with the values of A obtained directly from our experimental data by the use of the Jones and Dole equation and the Onsager and Fuoss equation. The agreement is sufficiently close to show that Falkenhagen's theory is correct in its fundamentals even if it may require some modification or elaboration in detail. Of special significance is the comparison of these results in methanol solutions with the investigations on aqueous solutions referred to above. For aqueous solutions A has a value of 0.005 (more or less for various salts), whereas an inspection of the Falkenhagen and Vernon equation shows that the lower value of η_0 and D for methanol in comparison with water should make A about threefold larger. This is confirmed by our experimental data.

TABLE V

COMPARISON OF THE THEORETICAL AND EXPERIMENTAL VALUES OF THE COEFFICIENT OF THE SQUARE ROOT TERM A

Salt	Theoretical Falkenhagen	Experimental Jones and Dole	Experimental Onsager and Fuoss
KCl	0.0173	0.0151	0.0037
KBr	.0165	.0142	.0133
KI	.0158	.0159	.0158
NH_4Cl	.0165	.0183	.0213

Summary

1. The absolute density and relative viscosity at 25° of many solutions of potassium chloride, potassium bromide, potassium iodide and ammonium chloride in methanol have been measured covering a range of concentration from extreme dilution nearly to saturation.

2. The density of solutions of these salts in methanol may be expressed by an equation of the form suggested by Root for aqueous solutions.

3. Although all of these salts may cause a decrease in viscosity when dissolved in water, none of them shows this effect when dissolved in methanol.

4. All of these solutions show the "Grüneisen Effect" strongly.

5. The data are used to test the validity of several equations for the viscosity as a function of the concentration.

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[14] C. Åkerlöf, THIS JOURNAL, **54**, 4125 (1932).

[15] G. S. Hartley and H. R. Raikes, *Trans. Faraday Soc.*, **23**, 394 (1927); H. Ulich, *ibid.*, **23**, 390 (1927).

[CONTRIBUTION FROM THE LABORATORY OF PLANT NUTRITION, UNIVERSITY OF CALIFORNIA]

The Structure of Sodium Sulfuric Acid Ester of Galactan from Irideae Laminarioides (Rhodophyceae)

BY W. Z. HASSID

In a previous paper[1] the writer reported the isolation of a new carbohydrate from a red alga, *Irideae laminarioides*, which proved to be a sodium sulfuric acid ester of galactan. A tentative formula was proposed for this compound.

In the following work the compound has been subjected to a series of chemical processes, whereby the structure and the linkages involved between its groupings were studied.

Experimental

Acetylation of the Sodium Sulfuric Acid Ester of Galactan.—Haworth's method for acetylation of inulin[2] was followed with some modifications. Three grams of the finely powdered sodium sulfuric acid ester of galactan, prepared from *Irideae laminarioides* was stirred with 5 cc. of pyridine at 80° for half an hour. After cooling to room temperature, 30 cc. of acetic anhydride was slowly added with thorough mixing of the ingredients. After several hours 15 cc. of acetic acid was also added to the mixture. The substance did not, however, dissolve as in the case of acetylated inulin prepared by Haworth. This preparation was tested for its acetyl content at three or four day intervals, and it was observed that its acetyl value was gradually rising. After about two weeks, the acetyl value became constant and corresponded to two hydroxyl groups per one molecule of galactose.

For the acetyl determination the following method was used. About 20 cc. of 0.1 *N* sodium hydroxide was added to 0.1 g. of the acetylated substance in a flask and after standing for several hours was titrated with 0.1 *N* hydrochloric acid.

Duplicate determinations on 0.1 g. of material required 5.5 cc. of 0.1 *N* hydrochloric acid. The acetyl value was found to be 23.6%. Calculated acetyl content for two acetyl groups in $C_{10}H_{13}O_{10}SNa$ was 24.7%.

The hydrogen atoms of two hydroxyl groups in the compound were replaced by acetyl groups. The addition of 0.1 *N* sodium hydroxide regenerated the two hydroxyl groups using up an equivalent amount of alkali. The ethereal sulfate group was not saponified under these conditions.

Preparation of Galactan.—The ethereal sulfate group could be hydrolyzed off the compound either by acid or alkali.

(a) The acid hydrolysis was accomplished in the following manner. Thirty grams of the original material was hydrolyzed with 600 cc. of 0.5 *N* sulfuric acid under a reflux condenser for five hours at a temperature of 65–70°. The solution was then cooled and neutralized with barium hydroxide. The barium sulfate precipitate was filtered off and washed. The filtrate was concentrated under reduced pressure to a thick sirup and poured into an excess of 95% alcohol. The galactan precipitated as an amorphous white mass. It was dried at 50° in a vacuum oven. The yield was about 13 g. Its specific rotation (*c*, 0.4) in water, $[\alpha]_D$ was +82.2. Its reducing value, after hydrolysis of the substance with 2% sulfuric acid at 105–110° for seven hours and neutralization of the acid with barium hydroxide, was 95.8%.

(b) The alkali hydrolysis was accomplished as follows. Five grams of the original substance was placed in a flask containing 100 cc. of water and 5 g. of barium hydroxide. The mixture was heated under a reflux condenser at 70°. As the hydrolysis progressed, the sulfate ion precipitated by the barium as barium sulfate could be seen forming and settling at the bottom of the flask. The barium sulfate precipitate was then filtered off, a little hot saturated barium hydroxide added to the filtrate, and the mixture again heated under the reflux condenser at the same temperature. This operation was repeated a few times until no more barium sulfate precipitate could be seen forming. The solution was then cooled and the excess of hydroxide neutralized with dilute sulfuric acid. The precipitate was filtered off and washed, the filtrate concentrated and the galactan precipitated out from 95% alcohol. It was then dried in the vacuum oven at 50°. Its specific rotation (*c*, 0.4) in water, $[\alpha]_D$ was +78.0°.

The reducing value after hydrolysis with 2% sulfuric acid at 105–110° for seven hours and neutralization of the acid was 86.3%. This low reducing value is probably due to the incomplete removal of the sulfuric acid group or destruction of some of the carbohydrate by the alkali.

Methylation of the Sodium Sulfuric Acid Ester of Galactan.—Seventeen grams of the substance was methylated by the procedure described by Haworth and Learner[3] for methylation of inulin. A methylated sirup was obtained. After the addition of 30 cc. of absolute alcohol, and upon standing, a white amorphous mass was precipitated. The solid was filtered off, washed with absolute alcohol, and dried at 50°.

The methoxy content of the methylated substance was determined by Dore's method[4] with the following modification. The water in one of the two U-tubes of the apparatus was replaced by a 5% solution of cadmium sulfate. This was done in order to take care of the sulfur present in the compound which in the presence of hydrogen iodide is reduced to hydrogen sulfide and precipitated by the silver as silver sulfide. By introducing cadmium sulfate, the hydrogen sulfide was decomposed and trapped as cadmium sulfide.

A methoxy determination was made on the methylated substance. It was found to be 14.8%.

This partially methylated substance was subjected twice

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[1] W. Z. Hassid, THIS JOURNAL, **55**, 4163 (1933).

[2] W. N. Haworth, *Helv. Chim. Acta*, **15**, 609 (1932).

[3] W. N. Haworth and A. Learner, *J. Chem. Soc.*, 619 (1928).

[4] W. H. Dore, *J. Ind. Eng. Chem.*, **12**, 472 (1920).

to further methylation with Purdie's reagents. Its methoxy content was raised to 20.0%.

A third methylation with the Purdie reagents did not increase the methoxy content. The substance was, apparently, completely methylated. The results obtained agreed well with the calculated value for two methoxy groups in the compound $C_8H_{13}O_8SNa$, 21.23%.

The specific rotation (*c*, 0.8) in chloroform, $[\alpha]_D$ of this methylated compound was +17.2.

Hydrolysis of the Methylated Compound and Preparation of Dimethylmethylgalactoside.—Six grams of the methylated substance was hydrolyzed with 300 cc. of 2% sulfuric acid under a reflux condenser at a temperature of 105–110° for seven hours. The solution was cooled and nearly neutralized with barium hydroxide and completely neutralized with silver carbonate. The precipitate was filtered off and extracted four times with 100-cc. portions of chloroform. The chloroform extracts were dried with anhydrous sodium sulfate. The sodium sulfate was filtered off and after evaporating the chloroform under reduced pressure, a sirup was obtained, which did not crystallize after standing for several days. This sirup reduced Fehling's solution and did not precipitate barium sulfate on the addition of barium chloride after boiling a small amount with hydrochloric acid.

This showed that the methylated polysaccharide was hydrolyzed to a methylated monosaccharide, and that the sulfuric acid group was split off.

The methylated monosaccharide was then converted into its glycoside by boiling with 75 cc. of methyl alcohol containing 2 g. of hydrogen chloride under a reflux condenser for eight hours. The acid was then neutralized with silver carbonate and the filtered solution was evaporated to a sirup which was extracted with benzene and evaporated again. The sirup distilled at 90° and 0.1 mm. pressure. This sirup was taken up in a little petroleum ether and left standing in the cold with occasional stirring. In the course of a few days the sirup gave a crystalline substance, which did not reduce Fehling's solution, and apparently was dimethylmethylgalactoside.

Its methoxy content was 39.0%; calculated OCH_3 content for dimethylmethylgalactoside, $C_6H_{18}O_6$ was 41.8%; $[\alpha]_D$ (*c*, 0.8) in water was +97.2.

Preparation of Trimethylgalactan.—Twenty-five grams of galactan prepared by the acid hydrolysis, was methylated by the method of West and Holden.[5] A methylated sirup was obtained, which, upon the addition of a little petroleum ether and stirring, set to a mass of crystals. The crystals were filtered off and dried at 40°. The specific rotation of this substance (*c*, 0.8) in water $[\alpha]_D$ was +32.4. Its methoxy content was 44.5%. The calculated value for OCH_3 content in trimethylgalactan $C_9H_{16}O_5$ was 45.6%.

Preparation of Trimethylgalactose from the Methylated Galactan.—Eighteen grams of the methylated galactan was hydrolyzed with 400 cc. of 2 *N* hydrochloric acid in a distilling flask for an hour under a reflux condenser, using a boiling water-bath. The solution was cooled, saturated with sodium sulfate and extracted four times with 150-cc. portions of chloroform. The combined chloroform extracts were dried with sodium sulfate. Five grams of carboraffin was added and filtered on a dry talc filter, prepared on a small Büchner funnel. The solution was then transferred into a distilling flask, and the chloroform distilled off under reduced pressure. The remaining sirup was then distilled under 0.1 mm. pressure. About 12 g. of the sirup distilled over at 94°. An attempt to crystallize this sirup failed.

The sirup reduced Fehling's solution, and its specific rotation (*c*, 0.8) in water, $[\alpha]_D$ was +129.0. Its methoxy content was 40.9%. The calculated value for three OCH_3 groups, trimethylgalactose in $C_6H_{18}O_6$ was 41.8%.

An attempt to prepare an osazone from this trimethylgalactose failed. This fact shows that the hydroxyl on the second carbon atom must be occupied by one of the methoxy groups.

Oxidation and Esterification of the Trimethylgalactose.—The degradative oxidation of this compound was carried out in two stages, involving first the oxidation to the lactone by bromine water, and second, its conversion into a dibasic acid. This mode of procedure in stages possesses the advantage that the final product is homogeneous, whereas this is not the case when the methylated sugar is oxidized directly with nitric acid.

Ten grams of the sirup was placed in a glass-stoppered flask to which 8 cc. of bromine and 50 cc. of water were added. The contents of the flask were placed at a temperature of 30° for seven hours with frequent shaking. At the end of that time the oxidation was not complete, as it gave a positive test with Fehling's solution. After keeping the flask at the same temperature for about seventy-two hours with occasional shaking, the solution was devoid of action toward Fehling's solution. The excess of the bromine was removed by aëration and this was followed by treatment of the solution with litharge and finally with silver oxide until neutral to litmus. The filtrate was saturated with hydrogen sulfide, again filtered, and the solution evaporated to a sirup. This sirup was extracted several times with anhydrous ether; the ether was evaporated, and a sirup was obtained.

The sirup obtained from the oxidation with bromine weighing about 7 g. was treated with 56 cc. of concentrated nitric acid and warmed for half an hour at 50–60°, whereupon oxidation commenced. The temperature was gradually raised to 90°, and so maintained for five hours. At the end of that time the reaction ceased and the solution was transferred to a distilling flask and diluted with water. The nitric acid was removed by distillation under diminished pressure with frequent additions of water. The residue was dried at 80° in the vacuum oven overnight.

This sirup was esterified by boiling with 100 cc. of methyl alcohol containing 3 g. of hydrogen chloride under a reflux condenser for eight hours. The acid was neutralized with silver carbonate and the filtered solution was evaporated to a sirup. The small quantity of mineral matter was removed by extracting the sirup in benzene and then evaporating the solution. The sirup distilled at 0.1 mm. pressure and 95°. Its specific rotation (*c*, 0.8) in water, $[\alpha]_D$ was +41.1°. Its methoxy content OCH_3, was 51.1%; calculated for $C_9H_{16}O_7$, dimethylarabodimethoxyglutarate was 52.5%.

Isolation of a Dimethoxyhydroxyglutaric Acid from the Esterified Substance.—About 4 g. of the sirup, dimethyl-

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[5] E. S. West and R. F. Holden, THIS JOURNAL, **56**, 930 (1934).

arabodimethoxyglutarate, was hydrolyzed with 50 cc. of 2% hydrochloric acid at 90° for two hours. The acid was neutralized with silver carbonate, the solution filtered and evaporated under diminished pressure, extracted with chloroform and the chloroform again distilled off.

The sirup was then distilled at 0.1 mm. pressure. The water-bath was replaced by an oil-bath as the sirup did not distil at 100°. A small amount (not enough to analyze) distilled over at 115°. The temperature was raised but no more of the sirup would distil over. The residue was then examined for its methoxy content and this was found to be 31.1%.

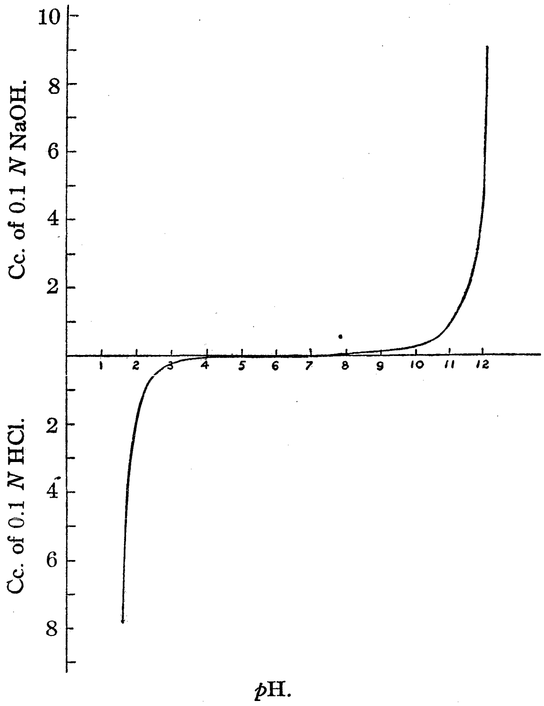

Fig. 1.—Titration curve of sodium sulfuric acid ester of galactan.

0.0921 gram of the sirup, on heating with 0.1 *N* sodium hydroxide and titrating with 0.1 *N* hydrochloric acid, required 9.3 cc. of 0.1 *N* sodium hydroxide for its neutralization. The undistilled residue was apparently dimethoxyhydroxyglutaric acid. The calculated value for the methoxy content of dimethoxyhydroxyglutaric acid, $C_7H_{12}O_7$, was 29.8% and its titration value for 0.0921 g. is 8.8 cc. of 0.1 *N* sodium hydroxide. This suggests that part of the acid is in the form of its lactone which would account for the high results obtained.

Evidence to Show that the Sodium Sulfuric Acid Ester of Galactan is a Salt of a Strong Acid.—The *p*H of a 1% solution of the acid previously obtained (1) was 3.6. On further continuation of the electrodialysis, the *p*H could be reduced to 2.86.

0.3 gram of this acid was titrated with 0.1 *N* sodium hydroxide. The amount required was 0.82 cc. The theoretical value for the titration of 0.3 g. was 1.24 cc. The titration, therefore, showed this acid to be of a greater equivalent weight than the theoretical one. The theoretical value of one equivalent weight of the acid $[(C_6H_9O_4)OSO_2OH]$ being 242, the calculated value from the titration was 366.

On further experimentation with this acid, it was found that part of the sulfur group was hydrolyzed off during the process of dialysis. It was noticed that by adding a solution of barium chloride to the anode compartment of the dialysis apparatus, a precipitate of barium sulfate was formed. This showed that some of the sulfate was hydrolyzed off the compound and moved through the membrane to the positive electrode. This accounts for the apparent high equivalent weight.

A 1% solution of the neutral salt itself (*p*H 6.8) was then taken and a titration curve was run by adding 0.1 *N* acid and 0.1 *N* alkali. A curve typical of that of a salt of a strong acid was obtained as shown in Fig. 1.

The specific conductance at 25° of various concentrations of the salt of the compound was then determined by using an electrical conductivity apparatus with the following results.

Solution, %	Specific conductance at 25°
2.0	2.53×10^{-3}
1.0	1.43×10^{-3}
0.5	6.88×10^{-4}
.25	3.68×10^{-4}
.125	1.84×10^{-4}

A 2% solution of sodium sulfuric acid ester of galactan, the specific conductance of which is 2.53×10^{-3} reciprocal ohms at 25°, is equivalent to 0.076 *N*. If we compare this with the specific conductance of 0.02 *N* potassium chloride, which is 2.77×10^{-3} reciprocal ohms at the same temperature, we find that the specific conductance of the salt is about 25% of that of the potassium chloride. The low specific conductance of the salt may be due to the fact that the solution of the compound in question is highly viscous and colloidal, and its large negative ion is probably highly hydrated and has a low mobility.

The neutrality of the compound, the shape of its titration curve and its specific conductance show that the sodium sulfuric acid ester of galactan is a salt of a strong acid.

Determination of Molecular Weight of the Sodium Sulfuric Acid Ester of Galactan.—The molecular weight of this compound was determined cryoscopically, the semimicrochemical method of Rieche[6] being used.

The rise in temperature when 30 mg. was dissolved in 5 cc. of water was 0.004°.

From the formula $M = 1000\ (C \times S)/S' \times \Delta$, where M is molecular weight, C is boiling point constant of water, S is weight of substance, S' is weight of solvent, Δ is rise in temperature, the value of the molecular weight of the substance was calculated as 780.

Considering that this substance is a sodium salt of a strong acid, the above value should be multiplied by two; thus, the approximate molecular weight becomes 1560. If we divide this value by the weight of one unit in the compound $[(C_6H_9O_4)OSO_2ONa]_n$ which is 264, the value n becomes 5.91. The data seem to indicate that there are approximately 6 units per one molecule of the compound. We can therefore, write the empirical formula for this compound as $[(C_6H_9O_4)OSO_2ONa]_n$, where n is approximately 6.

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[6] A. Rieche, *Ber.*, **59**, 2186 (1926).

Discussion

The empirical formula for the sodium sulfuric acid ester of galactan was established from the analytical data as $[(C_6H_9O_4)OSO_2ONa]_n$.[1] The analytical data shown in the experimental work also indicate that this non-reducing polysaccharide consists entirely of galactose units and sodium ethereal sulfate groups and that there is one unit of galactose for each ethereal sulfate group.

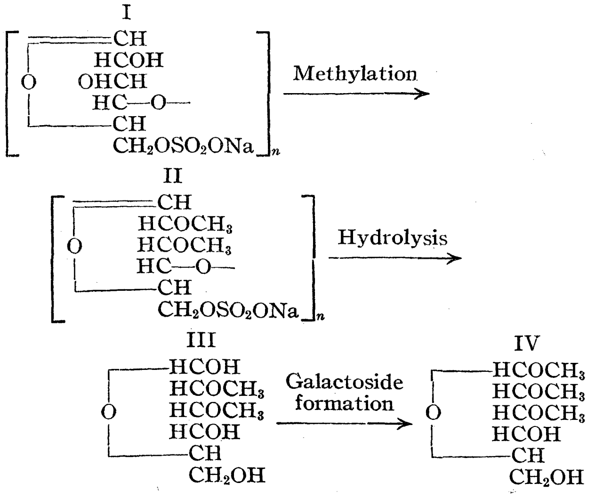
Two questions arise: (1) how are these galactose units linked together in the polysaccharide and (2) what position does the ethereal sulfate group occupy?

It is evident that the terminal carbon atom is tied up in a galactosidal linkage between the individual galactose units, from the fact that the substance is non-reducing. On complete methylation of the original compound two methoxy groups could be substituted for the same number of hydroxyls. That there are two free hydroxyl groups in one unit of galactose is confirmed by the fact that by acetylation of the compound two acetyl groups could be introduced into it.

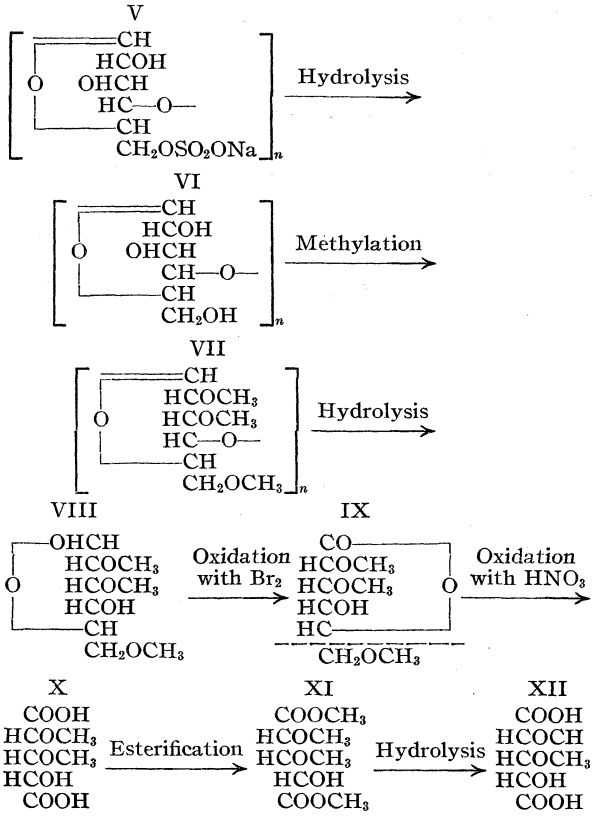
Acid hydrolysis of the methylated compound resulted in a reducing dimethylgalactose. The linkages holding together the galactose units, apparently, were broken with simultaneous splitting off of the ethereal sulfate group.

When the dimethylgalactose was boiled with methyl alcohol containing 3% hydrochloric acid, dimethylmethylgalactoside was obtained.

The above series of changes can be expressed by the equations



On hydrolyzing off the ethereal sulfate group of the original compound (V), galactan was obtained (VI). Upon methylation and subsequent hydrolysis of the trimethylgalactan (VII), trimethylgalactose was obtained (XIII). Oxidation with bromine, then with nitric acid and subsequent esterification, resulted in a dimethylarabodimethoxyglutarate. On hydrolysis of this dimethylarabodimethoxyglutarate, dimethoxyhydroxyglutaric acid was obtained.



It is evident that one of the methyl groups in the trimethylgalactose (VIII) is on the primary alcohol group, because, after splitting off the sixth carbon atom of the substance by oxidation with nitric acid, dimethoxyhydroxyglutaric acid was obtained, a substance with only two methyl groups.

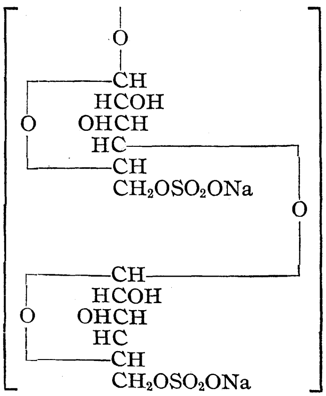
This shows that there could be no 1,6 linkage between the individual units in the original compound (V), because if we assume this to be true, the ethereal sulfate group could not have been attached to the sixth carbon atom, and should have occupied any other one of the five positions of carbon atom groups in the galactose unit. After hydrolyzing off the ethereal sulfate group and methylating the compound, a trimethylgalactan would have resulted, which had no methyl group on the sixth carbon atom. On hydrolysis of the compound and subsequent oxidation with nitric acid, a trimethoxyglutaric acid would have been obtained instead of a dimethoxyhydroxyglutaric acid (XII) as was the case. This, therefore, eliminates the possibility of 1,6 linkage.

The linkage between both of the first carbon atoms of the individual units is excluded, because a trimethylgalactan would have been obtained in (II) instead of a dimethylgalactan, and a tetramethylgalactan in (VII) instead of a trimethylgalactan.

The linkage between the first and second carbon atoms is eliminated on the basis that no osazone could be obtained from a trimethylgalactose (VIII). If there were a 1,2 linkage in the polysaccharide, a free hydroxyl should have resulted on the second carbon atom group on hydrolysis of the trimethylgalactan to the trimethylgalactose, and, consequently, the preparation of an osazone should have been possible.

The linkage of 1,5 between the units may also be eliminated, if we assume the usual amylene ring of the galactose itself. Since the four positions, 1,1, 1,2, 1,5 and 1,6 are eliminated, only the two possibilities, 1,3 and 1,4 remain. Since the 1,3 linkage has never been found, while the 1,4 is common in many disaccharides and polysaccharides, it is, therefore, reasonable to assume that the latter is more probable.

Presumably the ethereal sulfate group exists as a side chain formed by replacement of an hydroxyl group. The position of this ethereal sulfate group is uncertain. However, from consideration in a previous paper[1] this group is assigned to the sixth C atom as the most probable position. Further studies are being undertaken in attempt to establish this point.



In accordance with these considerations, the arrangement shown is tentatively proposed, indicating the linkage between two units.

The molecular weight determination indicates that the polysaccharide is made up of approximately six of these building units, perhaps similarly arranged.

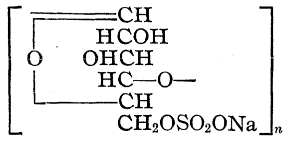
The writer wishes to express his indebtedness to Mr. W. H. Dore under whose general direction this work was carried out. The many valuable suggestions received materially aided the progress of the work.

Summary

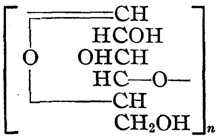
1. The sodium sulfuric acid ester of galactan isolated from *Irideae laminarioides* indicates that it is a salt of a strong acid. This is shown from the titration curve of the substance and also its conductivity data.

2. When the sodium sulfuric acid ester of galactan was subjected to electrodialysis, the sodium was removed and the substance initially neutral became acid, *p*H of about 3. This resulting substance, apparently, was sulfuric acid ester of galactan. It could not be obtained in pure form because the sodium could not be entirely dialyzed out and also because part of the sulfuric acid group was split off in the process of dialysis.

3. A tentative structural formula shown is proposed for the substance in which *n* seems to be approximately 6.



4. The sulfuric acid group in this compound was removed by hydrolysis and a polysaccharide was thus obtained which, in the chemical sense, is a pure galactan.



This is, apparently, the first time that a homogeneous galactan, consisting entirely of galactose units, was obtained from a plant.

BERKELEY, CALIFORNIA RECEIVED JUNE 14, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MANITOBA, WINNIPEG]

The Viscosity of Liquid Phosphorus

BY ALAN NEWTON CAMPBELL AND SIDNEY KATZ

This work was undertaken, firstly as an application of Smits' theory of allotropy and, secondly, to evaluate a physical constant which had not been determined at the time this work was commenced (September, 1934). Smits[1] draws attention to the abnormally low viscosity of liquid phosphorus in the neighborhood of the melting point of the α-white (ordinary yellow) form. The viscosity is abnormally low in the sense that the molten form is supercooled by 550° with respect to the stable violet form, and Tammann[2] has shown that there is usually a sudden and large increase of viscosity with increasing supercooling. Smits, however, quotes no figures and presumably his statement is based on visual observation of the mobility of phosphorus.

The first part of our work consisted in raising molten phosphorus to a fairly high temperature in the viscometer, chilling as rapidly as possible to the solid state and determining the viscosity just above the melting point. Such treatment has been found slightly to alter the melting point of substances, even in the absence of intensive drying, and might be expected to show an effect on the viscosity, particularly if the internal equilibrium is one between simple and associated molecules. On the latter assumption the viscosity of a rapidly chilled liquid would be less than normal, since there would be a deficiency of polymerized particles.

Toward the conclusion of this work, an abstract was received of work on the viscosity of phosphorus carried out by Dobinski[3] in the previous year. His measurements give the viscosity of phosphorus over the temperature range, 17.5–79.9°. As the original paper[4] is somewhat inaccessible, we reproduce his figures here.

DATA OF DOBINSKI

Temp., °C.	Viscosity in poises	Temp., °C.	Viscosity in poises
17.5	0.02515	47.75	0.01648
21.5	.02342	48.1	.01640
25.15	.02197	49.6	.01612
27.95	.02094	50.5	.01595
31.2	.02021	53.65	.01549
34.15	.01929	60.2	.01446
37.5	.01849	65.6	.01377
43.2	.01728	69.7	.01323
45.05	.01695	74.8	.01260
46.4	.01671	79.9	.01209
47.05	.01659		

Dobinski plotted his results in accordance with the formula of Andrade[5] and, as the graph changes slope at low temperatures, he concluded that association becomes appreciable below 49°. He observed visual indications of an internal equilibrium but he did not investigate the equilibrium shift by chilling experiments.

Experimental

An Ostwald viscometer of the ordinary type was used in this work. The plan of procedure in all cases consisted in maintaining the temperature of the phosphorus at some initial temperature until internal equilibrium was presumably established. The viscometer was then plunged in ice water to "freeze" the equilibrium, and then placed in a thermostat just above the normal melting point. Times of flow were then read in rapid succession until a steady value was reached, or until experimental difficulties, such as the appearance of particles of a solid form, made further readings impossible.

The phosphorus used in these experiments had been in stock for many years and it is not possible to state its origin. It had been kept in a subdued light, and was only superficially coated with a more stable form. It was purified by the method of Cohen and Olie[6] and then stored under water in a dark cupboard. A fresh preparation was made every ten days.

To displace the liquid phosphorus in manipulation and purification, either nitrogen or carbon dioxide was used. To remove the residual oxygen and moisture, the gases passed through hot copper turnings, pyrogallol solution, spiral water condensers, sulfuric acid bubblers, calcium chloride towers and phosphorus pentoxide towers.

The thermostat used in the viscosity determinations had a variation of ±0.02° over the range 20–40°. From 40 to 60° the temperature variation was greater, about ±0.05°. For heating bath in the experiments on shift of internal equilibrium a glycerol bath was used, and this had no temperature regulation, the temperature being kept approximately constant by adjusting the heating flame.

It is well known that white phosphorus is photosensitive; the rate of transformation to more stable forms is greatly enhanced when the phosphorus is illuminated. To minimize this effect direct light was excluded from the labora-

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(1) Smits, "Theory of Allotropy," p. 233.

(2) Tammann, *Z. physik. Chem.*, **28**, 17 (1899).

(3) Dobinski, *Sci. Abstracts, A*, Jan. 25, 1935, abs. no. 137.

(4) Dobinski, *Acad. Polonaise Sci. et Lettres*, Ser. A., p. 103, March–April, 1934.

(5) Andrade, *Nature*, **128**, 835 (1930).

(6) Cohen and Olie, *Chem. Weekbl.*, **6**, 821 (1909).

tory. Operations were carried out in a fume-cupboard whose walls were covered with black paper. The heating bulb of the thermostat was also covered with black paint. Observations were made by means of a ruby-colored photographic light.

The viscometers were of a 5-cc. lower bulb capacity and had a water run time of about eighty seconds or more at room temperature. The stems were calibrated for five different volumes as shown in Fig. 1. A complete series of run times was taken for each of the five volumes over the temperature range in which the phosphorus was to be investigated. As standardizing liquid water was used for the range 20 to 80°. The water used was laboratory distilled water, redistilled from potassium hydroxide and potassium permanganate through a block tin condenser; it was collected and stored in a silica flask. For standardization at the higher temperatures, monobromobenzene was used. It was purified by dehydration over calcium chloride and redistilling the fraction with the correct boiling point being collected. After the conclusion of a series of runs with phosphorus, the apparatus was dismembered, and the viscometer restandardized. No appreciable variation was ever observed.

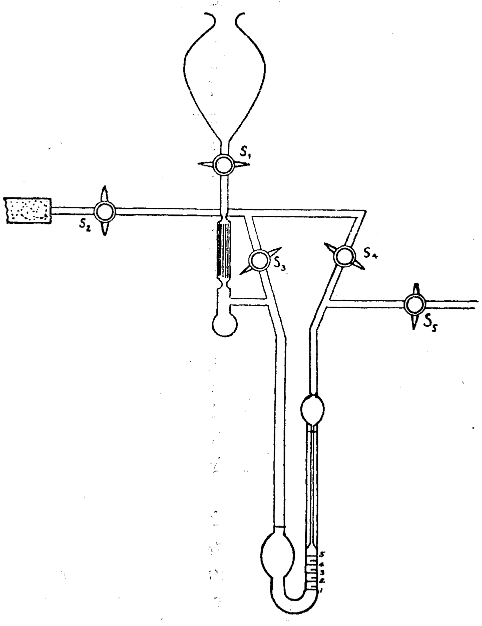

Fig. 1.

The very simple apparatus of Fig. 1 was used. The viscometer proper was wired to a wooden mount, to which were attached small spirit levels. The preliminary work had shown that molten phosphorus rapidly develops a thin yellowish scum,[7] and eventually particles of the stable violet form. As soon as particles commenced to deposit on the walls the apparatus had to be cleaned. Hence, after a day's running the apparatus was completely dismembered and the viscometer cleaned. After rebuilding, the apparatus was again cleaned. It was then thoroughly flushed for at least two hours with nitrogen or carbon dioxide.

The mode of operation was as follows. The reservoir of the apparatus was half filled with hot water and a few cc. of the purified liquid phosphorus then forced into it. The apparatus was full of inert gas and stopcocks, S_2, S_3, S_4 and S_5, being open, inert gas was streaming through the apparatus. Stopcock S_1 was then cautiously opened and phosphorus allowed to enter the capillary filled tube, drop by drop. The capillaries served to filter off any scum which might be formed at the phosphorus–water interface. The small round bulb below was intended to trap any impurities heavier than liquid phosphorus, but none were detected. The phosphorus was then allowed to run very slowly into the viscometer till the large lower bulb was approximately full. S_1 was closed and the phosphorus in the upper part of the system frozen by chilling the upper tube. From this point on work was performed as rapidly as possible to obtain the maximum number of runs before the accumulation of red phosphorus rendered the readings unreliable. By opening and closing suitable cocks, the phosphorus was brought to the level, O, in the bulb of the viscometer and the volume read from the level attained in the calibrated limb. Application of pressure then drove the phosphorus through the capillary of the viscometer, to the graduation mark above the bulb. With stopcocks S_1, S_2, and S_5 closed, and S_3 and S_4 open, the phosphorus was then under uniform gas pressure in both limbs.

Our first experiments dealt with the effect of rapid chilling from a high temperature on the viscosity at a fixed temperature. The viscometer and its contents were kept in the high temperature glycerol bath for from one-half to one hour. It was removed and plunged into ice water to "freeze" the equilibrium. It was then immersed in the thermostat which was set at a temperature slightly above the melting point of α-white phosphorus. Run times were taken in rapid succession as soon as the phosphorus was sufficiently liquid. At the same time, the time interval from the moment of placing the viscometer in the thermostat to the beginning of each run was noted. The results of a set of determinations are given below. In several cases, runs were begun before the phosphorus in the lower bulb had completely melted. The presence of unmelted phosphorus during a run is indicated by an (x). Data for runs so marked are, of course, meaningless. The thermostat temperature was 45.0°.

It is apparent that chilling from 80° has produced no effect on the viscosity. Considering the 100 and 120° figures, and discounting the asterisked figures, where unmelted phosphorus was present, there is some indication of a decrease in run-time with time. One would expect, however, if the pseudo-components of phosphorus stand in the relation of simple and associated molecules that chilling from a high temperature

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(7) Mellor, "Comprehensive Treatise on Inorganic Chemistry," Longmans, Green and Co., New York City, Vol. VIII, p. 747.

TABLE II

EFFECT OF SUDDEN CHILLING ON VISCOSITY OF PHOSPHORUS

Run	Total time, min.	Run time, sec.	Run	Total time, min.	Run time, sec.
A. Viscometer No. 1. Heated to 80° for 60 minutes					
1	6	106.5	3	14	106.3
2	9.5	106.4	4	18.5	106.6
B. Viscometer No. 1. Heated to 100° for 30 minutes					
x1	13	110.8	8	32.5	103.4
x2	15.5	107.0	9	37.5	103.3
x3	18.5	106.0	10	40.5	103.9
4	21	104.9	11	42.5	103.4
5	23.5	103.8	12	45.0	103.4
6	26.5	104.0	13	47.0	103.4
7	29.5	103.8			
C. Viscometer No. 1. Heated to 120° for 30 minutes					
1	10.5	104.7	3	17.0	103.8
2	14	104.3	4	19	103.8
D. Viscometer No. 1. Heated to 120° for 30 minutes					
x1	5.5	103.9	5	31	104.3
x2	9	104.4	6	34	104.3
x3	13	104.5	7	36	104.4
4	28.5	104.4			

would give rise to a solid, and eventually to a melt, abnormally high in simple molecules, and therefore having a viscosity lower, not higher, than normal. The only conclusion we feel justified in drawing is that the effect, if it be real, is very slight; in other words, the internal equilibrium in liquid phosphorus is very rapidly established.

The normal viscosities of phosphorus were determined in the same way, except, of course, that the prior heating and chilling were omitted. At 140°, in spite of the rapidity of working, the viscometer became badly clogged with red phosphorus in a very short time, but below this temperature no difficulty was experienced from this cause. In the supercooled region, little difficulty due to solidification was experienced above 25°. At 25° spontaneous crystallization occurred once, and at 20° three or four times. It is well known that the velocity of crystallization of phosphorus is very great[8] and once nuclei are developed, crystallization is almost instantaneous. By slowing the stirrer somewhat to minimize vibration, a satisfactory set of readings was obtained at 20°. The effect of shock on initiating spontaneous crystallization has been demonstrated.[9] Attempts at 17.5° invariably resulted in solidification half way through the runs, and it was found impossible to supercool to 15° without spontaneous crystallization occurring immediately.

Calculations and Results

In the determination of the viscosity of phosphorus about two hundred runs were made.

The density and viscosity of water were obtained from the "International Critical Tables." The figures of Meyer and Mylius[10] were used for the density and viscosity of bromobenzene. The data for the density of phosphorus were taken from a paper by Pisati and De Franchis and from Dobinski.[11] The former made dilatometric measurements over the range 20–280°. Dobinski developed an empirical formula

$$D = 1.76705 - 0.0009222(t - 20)$$

which shows good agreement with the figures of Pisati and De Franchis, especially up to about 60°. The density figures of both Pisati and De Franchis and of Dobinski were used in a series of preliminary calculations of viscosity. Determinations to four figures, of which only three are probably significant, gave the same results for both sets of densities.

The data for the standardizing fluid were determined at very nearly the same temperature as the corresponding phosphorus run. The greatest difference was at 48°, where the nearest water determination was at 50°. In order that the volume of standardizing fluid and of phosphorus might be the same, time of flow of standardizing fluid was determined for each volume graduation of the viscometer. Where the value of phosphorus did not exactly coincide with a calibrated volume, half-interval interpolation was employed. It was found that intervals of less than half a scale division gave rise to variations less than the working limits of the stopwatch.

Dobinski plotted the logarithm (Napierian) of viscosity against the reciprocal of the absolute temperature, in accordance with the method of Andrade (*loc. cit.*) and, as he obtained a change of slope toward lower temperatures, he deduced that association was setting in. We, therefore, repeated our determinations twice, over the range of 25 to 60°, where the highest accuracy is obtainable, using fresh preparations, fresh apparatus

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(8) Gernez, *Compt. rend.*, **95**, 1278 (1882); **97**, 1298, 1366, 1433 (1883).

(9) Young and Van Sicklen, THIS JOURNAL, **35**, 1067 (1913).

(10) Meyer and Mylius, *Z. physik. Chem.*, **95**, 349 (1920).

(11) Pisati and De Franchis, *Gazz. chim. ital.*, **4**, 497 (1874); Dobinski, *Z. Physik*, **83**, 129 (1933).

TABLE III

THE ABSOLUTE VISCOSITY OF PHOSPHORUS

Temperature °C.	Temperature variation °C., ±	n poise	Log$_{10}n$
	1st Series		
20.0	0.02	0.0231	−1.6366
24.9	.02	.0221	−1.6562
29.9	.02	.0202	−1.6562
35.5	.02	.0190	−1.7222
40.05	.04	.0177	−1.7513
42.05	.04	.0173	−1.7612
44.1	.04	.0169	−1.7734
44.6	.05	.0167	−1.7762
45.1	.05	.0167	−1.7783
45.2	.05	.0167	−1.7783
46.1	.05	.0165	−1.7825
47.1	.05	.0163	−1.7889
48.1	.05	.0168	−1.7951
49.1	.05	.0158	−1.8005
50.1	.05	.0157	−1.8049
60.3	.05	.0132	−1.8794
70.35	.1	.0124	−1.9083
80.55	.1	.0114	−1.9423
90.85	.5	.0104	−1.9834
100.9	.5	.0095	−2.0214
120.0	.5	.0080	−2.0953
140.0	1.0	.0071	−2.1481
	Second and Third Series		
25.1		0.0218	−1.6617
30.2		.0205	−1.6897
35.2		.0191	−1.7183
40.25		.0179	−1.7467
45.3		.0169	−1.7719
50.3		.0160	−1.7959
55.4		.0153	−1.8176
60.5		.0145	−1.8392

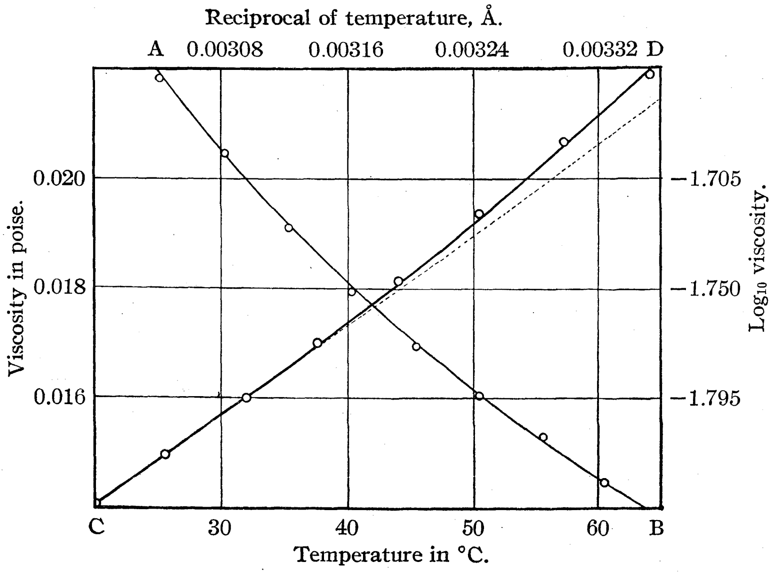

Fig. 2.—Curve AB, temperature–viscosity; Curve CD, reciprocal of temperature—log of viscosity.

and fresh calibrations. The two sets of observations were practically identical. They were therefore averaged and these results are appended to our previous results in Table III. Viscosities are given to three significant places. The common logarithms of the viscosities and the variation in temperature of the thermostat, as measured with a Beckmann thermometer, are also given. The repeat figures differ very slightly from our previous figures, with the exception of the figure for 60°, which the plot of our earlier figures showed to be discordant.

In Fig. 2, (a) viscosity is plotted against temperature for the range 25 to 60°; (b) the logarithm (common) of the viscosity is plotted against the reciprocal of absolute temperature, between the same temperature limits.

Discussion

There is no evidence of a change of viscosity when heated phosphorus is suddenly chilled, under our experimental conditions. There are logically four explanations of this, of unequal probability.

1. Smits' theory is incorrect.

2. The equilibrium displacement on cooling is so rapid that it is complete before solidification takes place. This is in agreement with Smits' own belief. He comments on the rapidity with which the inner equilibrium of liquid phosphorus is established just above the melting point of the α-white form.[12] We were not able to apply the anti-catalytic effect of intensive drying.

3. The temperature–composition curve of the inner equilibrium of liquid phosphorus is practically vertical, that is, the temperature change of internal equilibrium is too small to be detectable.

4. The shifting internal equilibrium does not reflect itself in viscosity change. In other words, the pseudo-components are isomers and not polymers.

Considering the viscosity figures as such, it is apparent that the agreement with Dobinski's figures is good, being well within 1%, below 60°. Above this temperature, the error probably increases with rising temperature, but it cannot be great, since, when all our figures,

[12] "Theory of Allotropy," p. 233.

including the figure for 140° and eliminating our first figure for 60°, which is obviously discrepant, are plotted against temperature, a smooth curve is obtained. Dobinski's figures do not extend above 80°. When our figures are plotted by the method of Andrade, the same change in slope is observed as with Dobinski's figures. If, therefore, Andrade's theory is sound, so is Dobinski's deduction, *viz.*, association of liquid phosphorus becomes appreciable below about 45°. If this is so, possibilities 3 and 4 (above) are ruled out. It is very probable that 2 contains the real explanation of our failure to observe positive results.

Summary

1. Experiments have been carried out on the effect of rapid chilling on the viscosity of phosphorus.

2. The viscosity of liquid phosphorus has been determined between the temperature limits 20–140°. The agreement with the prior figures of Dobinski (range 17.5–79.9°) is very good. As most of our work was carried out in ignorance of the very recent work of Dobinski, it appears that the viscosity of phosphorus is now known with a satisfactory degree of accuracy, at least over the temperature range common to both.

3. Association becomes appreciable in liquid phosphorus below 45°. The bearing of this and of the chilling experiments on Smits' theory is discussed.

WINNIPEG, CANADA RECEIVED JUNE 24, 1935

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 487]

The Potentials of Cells in Liquid Ammonia Solutions. The Thermodynamic Constants of the Ammino Cadmium Chlorides and of Cadmium Chloride

BY CLIFFORD S. GARNER, EMERSON W. GREEN AND DON M. YOST

Introduction

The present investigation was undertaken to determine the suitability of the cadmium amalgam–hexammino cadmium chloride half-cell as a reference electrode for electromotive force measurements in liquid ammonia, and to evaluate the thermodynamic constants of the ammino cadmium chlorides and cadmium chloride.

For the purpose of establishing an electromotive series in the ammonia system it is desirable to refer all half-cells to some half-cell whose potential is taken arbitrarily as zero. Such a half-cell in the aqueous system is the hydrogen electrode. The same half-cell is here adopted for the liquid ammonia system in which the ammonium ion corresponds to the hydrogen ion of the aqueous system.

In this paper are presented the results of measurements on cells of the type Zn(amalg., N_2), $ZnCl_2 \cdot 6NH_3(s)$, NH_4Cl(in $NH_3(l)$, f.), $CdCl_2 \cdot 6NH_3(s)$, Cd(amalg., N_1) together with the thermodynamic constants for the ammino cadmium chlorides and cadmium chloride. Provisional values of known potentials in terms of the standard hydrogen half-cell in liquid ammonia are also presented.

Preparation of Materials and Experimental Procedure

Ammonia.—The gas from a tank was passed over solid potassium hydroxide, condensed into a trap containing metallic sodium, and then fractionated over into an auxiliary vessel.

Mercury.—Mercury was repeatedly sprayed through nitric acid, and washed and dried. It was then redistilled five times in a current of air.

Zinc.—C. P. zinc sticks were scraped free from an oxide coating, placed in a sectioned Pyrex tube and distilled in four fractions in a current of pure dry hydrogen. It was then stored in weighing bottles filled with hydrogen.

Cadmium.—C. P. cadmium sticks were purified and stored in the same manner as for zinc.

Hydrogen.—The gas from a tank was passed through platinized asbestos at 350° to remove oxygen, and then through anhydrous phosphorus pentoxide to dry it.

Zinc Chloride.—Analytical reagent zinc chloride was fused, and immediately upon solidifying it was placed on the zinc amalgam in the cell. A stream of pure hydrogen was passed through the cell during this operation.

Cadmium Chloride.—A nearly saturated solution of recrystallized cadmium chloride (C. P.) was prepared containing a very small amount of hydrochloric acid to prevent hydrolysis. The solution was placed in a desiccator containing sulfuric acid, and the crystals resulting were filtered, pressed dry, and then placed in a flask. The flask was evacuated and at the same time heated to nearly the melting point of the cadmium chloride. Portions of the purified cadmium chloride were then placed on the cad-

TABLE I

RESULTS OF THE ELECTROMOTIVE FORCE MEASUREMENTS

Temp., °C.	Mole fraction Cd, N_1	Cd(amalg. N_1) = Cd(s) E_1, volt	Mole fraction Zn, N_2	Zn(s) = Zn(amalg. N_2) E_2, volt	Formality[a] NH_4Cl, f	E. m. f. observed E, volt	Standard potential E^0, volt
25.00	0.0008234	−0.1132	0.01751	0.0140	0.20	0.4593	0.3601
	.0008234	− .1132	.01751	.0140	.089	.4599	.3607
	.01086	− .0801	.02739	.0087	.28	.4314	.3600
	.0008099	− .1136	.03328	.0066	.22	.4675	.3605
	.0008099	− .1136	.03328	.0066	.045	.4675	.3605
	.05020	− .0568	.03328	.0066	.25	.4111	.3609
	.05020	− .0568	.03328	.0066	.25	.4112	.3610
	.05020	− .0568	.03328	.0066	.089	.4107	.3605
	.05020	− .0568	.03328	.0066	.086	.4107	.3605
						Mean	.3605
3.20	.05020		.03328		.086	.3933	
35.00	.05020		.03328		.086	.4179	

[a] By formality is meant the number of formula weights per thousand grams of solvent.

mium amalgam in the cell. This last operation was carried out in an atmosphere of pure hydrogen.

Ammonium Chloride.—Analytical reagent ammonium chloride was recrystallized several times from water, and after subliming it was stored in a vacuum desiccator.

The Amalgams.—Purified mercury was distilled over into a receiver and a weighed piece of metal added in an atmosphere of hydrogen. The receiver was then partially evacuated, sealed off, and placed in a shaking device for about twenty hours. The receiver with contents was then weighed, the tip was broken off in a stream of hydrogen and the amalgam poured into a hydrogen-filled vessel provided with a number of side tubes. Equal portions were allowed to flow into the small side tubes which were then sealed off under hydrogen at atmospheric pressure. The empty receiver was weighed after these operations had been completed. It was found necessary to evacuate and bake thoroughly all apparatus coming in contact with the amalgams to prevent formation of oxides. The amalgams were always clean and bright.

The cell used was essentially the same as that described by Elliott and Yost.[6] A Leeds and Northrup Type K potentiometer was used in connection with a sensitive null galvanometer for making the electromotive force measurements. The standard cell was carefully calibrated against a new laboratory standard.

Results of the Experiments

Since no data were available on the solubility of cadmium chloride in liquid ammonia, a single rough determination was made using a modified method based on that of Hunt and Boncyk.[1] The value obtained was 0.0011 mole of $CdCl_2$, as such, per 1000 g. of liquid ammonia at 25.0°, but due to the inadequacy of the method for very slightly soluble salts, this is to be regarded as an upper limit. It is probable that the true solubility is not greater than about one-half of this value. The solid phase was $CdCl_2 \cdot 6NH_3$. This follows from the results of Biltz and Mau,[2] on the equilibrium pressures of ammonia above the solid decammino and hexammino cadmium chlorides.

In Table I are presented the results of the electromotive force measurements made on the cell

$$\text{Zn(amalg., } N_2\text{), } ZnCl_2 \cdot 6NH_3\text{(s), } NH_4Cl \text{ (in } NH_3\text{(l), f.), } CdCl_2 \cdot 6NH_3\text{(s), Cd(amalg., } N_1\text{)} \quad (1)$$

for which the reaction is

$$\text{Zn(amalg., } N_2\text{)} + CdCl_2 \cdot 6NH_3\text{(s)} = ZnCl_2 \cdot 6NH_3\text{(s)} + \text{Cd(amalg., } N_1\text{)} \quad (2)$$

The activities of cadmium in its amalgams have not been calculated, but the electromotive forces of cells at 25.0° in which the following reactions take place are known.

$$\text{Zn(amalg. satd. with pure Zn)} = \text{Zn(amalg., } N_2\text{)}^3 \quad (3)$$

$$\text{Cd(2 phase)} = \text{Cd(amalg., } N_1\text{)}^4 \ (4), \text{ and Cd(2 phase)} = \text{Cd(s)}^5 \quad (5)$$

In the table E_1 is the electromotive force of the cell whose reaction is

$$\text{Cd(amalg., } N_1\text{)} = \text{Cd(s)} \quad (6)$$

and E_2 is that for the cell whose reaction is

$$\text{Zn(s)} = \text{Zn(amalg., } N_2\text{)} \quad (7)$$

It is assumed here that the electromotive force of the cell Zn(s) = Zn(saturated amalgam) is zero. In the last column of Table I are presented the values calculated from the relation $E^0 = E_{\text{obsd.}} + E_1 + E_2$, for the standard potential E^0 of the cell

$$\text{Zn(s), } ZnCl_2 \cdot 6NH_3\text{(s), } NH_4Cl \text{ (in } NH_3\text{(l), f.), } CdCl_2 \cdot 6NH_3 \text{ (s), Cd(s)} \quad (8)$$

for which the reaction is

$$\text{Zn(s)} + CdCl_2 \cdot 6NH_3\text{(s)} = ZnCl_2 \cdot 6NH_3\text{(s)} + \text{Cd(s)} \quad (9)$$

and the total pressure is the vapor pressure of the liquid ammonia solution at 25°.

Each cell required between four and five hours to attain equilibrium, after which time the elec-

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(1) Hunt and Boncyk, THIS JOURNAL, **55**, 3528 (1933).

(2) Biltz and Mau, *Z. anorg. allgem. Chem.*, **148**, 170 (1925).

(3) Pearce and Eversole, *J. Phys. Chem.*, **32**, 209 (1928).

(4) Teeter, THIS JOURNAL, **53**, 3927 (1931).

(5) Parks and La Mer, *ibid.*, **56**, 90 (1934).

tromotive force was constant to 0.1 millivolt or better for days. The cadmium electrode was always positive.

From the results of the measurements of the cell, it appears that the cadmium amalgam–hexammino cadmium chloride half-cell can be used to advantage as a reference electrode in liquid ammonia. Inasmuch as hexammino cadmium chloride is less soluble in liquid ammonia at 25° than thallous chloride, and since cadmium amalgams do not oxidize as readily as thallium amalgams, it would seem that this half-cell is superior to the thallium amalgam–thallous chloride half-cell.

Thermodynamic Constants of the Ammino Cadmium Chlorides and Cadmium Chloride.—The standard free energy increase accompanying reaction (9) was calculated from the relation $\Delta F^0 = -NE^0F$ to be $-16{,}637$ cal. The free energy of formation of $ZnCl_2 \cdot 6NH_3(s)$ at 25° is $-142{,}290$ cal.[6,7] and hence the free energy of formation of $CdCl_2 \cdot 6NH_3(s)$ at 25° is $-125{,}650$ cal.

The increase in heat content accompanying reaction (9) is -8060 cal., and it was calculated from the temperature coefficient of one of the cells $+0.000756$ volt/deg., and the partial molal heats of solution of zinc[3] and cadmium[4] in their amalgams. The heat of formation of $ZnCl_2 \cdot 6NH_3(s)$ at 25° is 250,840 cal.,[6] and consequently the heat of formation of $CdCl_2 \cdot 6NH_3(s)$ at 25° is 242,780 cal. This is a more reliable value than that given in the "International Critical Tables," namely, 237,000 cal.

From the results of other investigators, taken in connection with the above, the calculation of the free energies and heat contents of the other four ammoniated cadmium chlorides and cadmium chloride itself is possible. From the data of Biltz and Mau[2] the following equations have been derived.

$$CdCl_2 \cdot 10NH_3(s) = CdCl_2 \cdot 6NH_3(s) + 4NH_3(g) \qquad \Delta F^0_{298.2} = -6660 \text{ cal.} \quad \Delta H = 32{,}200 \text{ cal.} \tag{10}$$

$$CdCl_2 \cdot 6NH_3(s) = CdCl_2 \cdot 4NH_3(s) + 2NH_3(g) \qquad \Delta F^0_{298.2} = 2300 \text{ cal.} \quad \Delta H = 19{,}580 \text{ cal.} \tag{11}$$

$$CdCl_2.4NH_3(s) = CdCl_2 \cdot 2NH_3(s) + 2NH_3(g) \qquad \Delta F^0_{298.2} = 2350 \text{ cal.} \quad \Delta H = 32{,}660 \text{ cal.} \tag{12}$$

$$CdCl_2 \cdot 2NH_3(s) = CdCl_2 \cdot NH_3(s) + NH_3(g) \qquad \Delta F^0_{298.2} = 5681 \text{ cal.} \quad \Delta H = 10{,}800 \text{ cal.} \tag{13}$$

$$CdCl_2 \cdot NH_3(s) = CdCl_2(s) + NH_3(g) \qquad \Delta F^0_{298.2} = 10{,}700 \text{ cal.} \quad \Delta H = 23{,}510 \text{ cal.} \tag{14}$$

From these data, combined with those from the cell measurements, the thermodynamic constants of all the ammino cadmium chlorides and cadmium chloride have been computed, and are presented in Table II. In making the calculations, the free energy of formation of ammonia gas at 25° was taken as -3910 cal.[8] and its heat of formation as 10,940 cal.[9] The standard virtual entropies at 25° of cadmium,[8] chlorine,[10] nitrogen,[11] and hydrogen[12] are 11.80, 53.31, 45.79 and 31.23 cal./deg., respectively. The free energy and heat content values are referred to the elements in their standard states of 25° and one atmosphere. These free energy, heat content and entropy values for $CdCl_2(s)$ agree well with those obtained independently by Ishikawa, Kimura and Murooka,[13] namely $\Delta F^0_{298.2} = -81{,}857$ cal., $\Delta H_{298.2} = -92{,}149$ cal., and $S^0_{298.2} = 31.2$ cal./deg.

TABLE II

THE THERMODYNAMIC CONSTANTS OF THE AMMINO CADMIUM CHLORIDES AND CADMIUM CHLORIDE AT 25°

Substance	$\Delta F^0_{298.2}$, cal.	$\Delta H^0_{298.2}$, cal.	$S^0_{298.2}$, cal./deg.
$CdCl_2 \cdot 10NH_3(s)$	$-134{,}633$	$-318{,}741$	145.1
$CdCl_2 \cdot 6NH_3(s)$	$-125{,}653$	$-242{,}781$	90.8
$CdCl_2 \cdot 4NH_3(s)$	$-115{,}533$	$-201{,}321$	56.4
$CdCl_2 \cdot 2NH_3(s)$	$-105{,}363$	$-146{,}781$	65.7
$CdCl_2 \cdot NH_3(s)$	$-95{,}772$	$-125{,}041$	36.7
$CdCl_2(s)$	$-81{,}162$	$-90{,}591$	33.5

$S^0_{298.2}$ is the standard virtual entropy.

The Evaluation of the Standard Electrode Potentials Referred to the Standard Hydrogen Electrode.—In a former paper[6] were described briefly the attempts to measure the potential of the thallium amalgam–thallous chloride half-cell against a hydrogen half-cell in liquid ammonia. Due to experimental difficulties a completely satisfactory result was not obtained. It is now possible to calculate a value for the potential of the cell whose reaction is

$$Tl(s) + NH_4^+(a = 1, \text{in } NH_3(l)) + Cl^-(a = 1, \text{in } NH_3(l)) \qquad TlCl(s) + {}^1/_2H_2(g, 1 \text{ atm.}) + NH_3(l) \tag{15}$$

The standard free energies for all the substances entering into this reaction are known except that for ammonium chloride. Hunt and Larsen have determined the solubility of ammonium chloride in liquid ammonia as well as the vapor pressures of

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[6] Elliott and Yost, THIS JOURNAL, **56**, 1057 (1934).

[7] For corrections see *ibid.*, **56**, 2797 (1934).

[8] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, pp. 273, 464, 608.

[9] "International Critical Tables," Vol. V, p. 178.

[10] Giauque and Overstreet, THIS JOURNAL, **54**, 1731 (1932).

[11] Giauque and Clayton, *ibid.*, **55**, 4875 (1933).

[12] Giauque, *ibid.*, **52**, 4816 (1930).

[13] Ishikawa, Kimura and Murooka, *Bull. Inst. Phys. Chem. Research* (Tokyo), **9**, 744 (1930), through *Chem. Abs.*, **25**, 3552 (1924).

ammonia above its solutions over a large range of concentrations.[14] These data permit the calculation of provisional values for the activities of the ammonium chloride by the graphical methods described by Lewis and Randall.[8] In Table III are presented the results of the calculations.[15] The lowest concentration at which Hunt and Larsen worked is 0.4 f, and for more accurate activity coefficients it is necessary to go to still lower concentrations.

TABLE III

ACTIVITY COEFFICIENTS OF AMMONIUM CHLORIDE IN LIQUID AMMONIA SOLUTIONS AT 25°

Formality, f, of NH_4Cl	Activity coefficient $\gamma = a_{NH_4Cl}/f$
1	0.25
5	.079
10	.068
15	.079
20	.17
24.4 (satd.)	.31

If the provisional values for the activity coefficients given in the table are accepted, and if it is also assumed that the solid phase present in the experiments of Hunt and Larsen is $NH_4Cl(s)$ and not $NH_4Cl{\cdot}3NH_3(2)$[16] then there results

$$\begin{aligned} NH_4Cl(s) &= NH_4Cl(a = 1, \text{ in } NH_3(l)) \\ \Delta F^0_{298.2} &= -1210 \text{ cal.} \end{aligned} \qquad (16)$$

The standard free energy of formation of NH_4Cl (s) at 25° is −47,810 cal.[17] The corresponding value for $NH_4Cl(a=1, \text{ in } NH_3(l))$ is therefore −49,020 cal. Taking −44,164 cal. as the standard free energy of formation of $TlCl(s)$[8] and −2620 cal. as that for liquid ammonia,[8] at 25°, we now have for reaction (15), $\Delta F^0_{298.2} = 2236$ cal., and $E^0_{298.2} = -0.10(00)$ volt. The experimental value becomes, when the differences between the concentrations used in the cell measured and those given for equation (15) are taken into account $E^0_{298.2} = -0.15$ volt. The agreement is satisfactory.

In Table IV are given the standard electrode potentials of three known half-cells referred to the standard hydrogen electrode in liquid ammonia as zero. The value for the half-cell involving zinc was derived from the measurements of Elliott and Yost[6] on the cell Zn(amalg.)-$ZnCl_2{\cdot}6NH_3(s)$, $NH_4Cl(\text{in } NH_3(l))$, $TlCl(s)$, Tl-(amalg.), and that for cadmium comes from the results presented above. These values are, of course, to be regarded as provisional.

TABLE IV

STANDARD ELECTRODE POTENTIALS IN LIQUID AMMONIA AT 25°

Half-cell reaction	$E^0_{298.2}$, volt
$Tl(s) + Cl^-(\text{liq. } NH_3) = TlCl(s) + E^-$	−0.10(00)
$Zn(s) + 2Cl^-(\text{liq. } NH_3) + 6NH_3(l) =$ $ZnCl_2{\cdot}6NH_3(s) + 2E^-$	+ .7293
$Cd(s) + 2Cl^-(\text{liq. } NH_3) + 6NH_3(l) =$ $CdCl_3{\cdot}6NH_3(s) + 2E^-$	+ .3688

When the solubilities and the activities of the solid substances are known it will, of course, be possible to estimate the molal electrode potentials.

Summary

In liquid ammonia solutions of ammonium chloride at 25° the potentials of the cell Zn(amalg., N_2), $ZnCl_2{\cdot}6NH_3(s)$, $NH_4Cl(\text{in } NH_3(l)$, f., $CdCl_2{\cdot}6NH_3(s)$, Cd(amalg., N_1) have been measured at several concentrations of the dissolved substances. The cell gives accurately reproducible and reversible e. m. f.'s. When zinc and cadmium are present as pure metals $E^0_{298.2} = 0.3605$ volt.

From the e. m. f. and the temperature coefficient of the cell, together with the results of other investigators, the standard free energies, heat contents and virtual entropies of the solid ammino cadmium chlorides and cadmium chloride were calculated and are presented in Table II.

Provisional values for the activity coefficients of ammonium chloride in liquid ammonia at 25° were calculated and the results, combined with free energy data, were used to evaluate the standard electrode potentials of three known half-cells with reference to the standard hydrogen electrode in liquid ammonia.

PASADENA, CALIF.

RECEIVED JULY 8, 1935

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[14] Hunt and Larsen, *J. Phys. Chem.*, **38**, 801 (1934).

[15] After the present paper was submitted, an article by Larsen and Hunt, *J. Phys. Chem.*, **39**, 877 (1935), has appeared in which relative mean activity coefficients of ammonium chloride are given. Their values are not applicable to the type of calculation made here.

[16] No proof is given by Hunt and Larsen in their paper that the solid phase is $NH_4Cl(s)$. In a private communication Dr. Hunt states that the solid phase does consist of NH_4Cl. Moreover, an extrapolation of the equilibrium pressure data of Troust ("I. C. T.," Vol. VII, p. 240) for the reaction $NH_4Cl{\cdot}3NH_3(s) = NH_4Cl(s) + 3NH_3(g)$ gave 6.5 atm. for the pressure of $NH_3(g)$. The vapor pressure of ammonia above a saturated solution of NH_4Cl is 4.13 atm. This confirms the supposition that the solid phase is NH_4Cl.

[17] "International Critical Tables," Vol. VII, p. 240.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Accommodation Coefficient of Hydrogen on Iron

BY H. H. ROWLEY AND W. V. EVANS

Introduction

The concept of the accommodation coefficient as a measure of the completeness of heat exchange between a gas and a solid body was introduced by Knudsen[1] and has since been studied experimentally by numerous investigators. It was found that the accommodation coefficient is dependent not only on the nature of the gas but also to a large extent upon the condition of the solid surface.

Most of the previous experiments concerned the accommodation coefficient of light gases, such as helium and hydrogen, on the surfaces of heavy metals like platinum and tungsten. Earlier work[2] showed that the accommodation coefficient of hydrogen on a platinum surface freed from ordinary contamination was 0.22 at room temperature and that with decreasing temperature it rose to a value of 0.37 at 110°K. A similar rise was noted by Blodgett and Langmuir[3] for hydrogen on a tungsten surface. This negative temperature coefficient is contrary to the results obtained for helium[4] and to certain theoretical expectations.[5] The anomaly was explained by the presence of two types of adsorption layers: at room temperature the hydrogen was atomically adsorbed (active adsorption) giving rise to a more firm, rigid (smoother) surface and thus a lower accommodation coefficient; at the temperature of liquid air, the more loosely bound, molecular adsorption prevailed and the resulting rougher surface favored better heat exchange and consequently a higher accommodation coefficient.

The present work was undertaken to determine whether this rise was characteristic for hydrogen and also to determine whether a metal of lighter mass had any appreciable effect on the value of the accommodation coefficient. To determine this, the heat exchange of hydrogen at an iron surface was determined over a temperature range from 120–450°K. The method used was essentially the measurement of the amount of heat given up by an electrically heated wire at relatively low pressures of hydrogen.

Experimental

Apparatus.—The apparatus was practically the same as that used previously in determining the heat exchange of hydrogen on a platinum surface.[2] The cell consisted of a fine iron wire (over 99.9% pure) with a measured diameter of 0.0128 cm. stretched along the axis of a vertical Pyrex glass tube 1 cm. in diameter and about 23 cm. in length. The ends of the iron wire were silver soldered to 0.03-mm. tungsten leads which in turn were sealed through the glass. The lower lead-in wire was sealed through the side of the cell about 3 cm. from the bottom and the lower portion of the iron wire formed into a loop from which was suspended a glass weight filled with mercury. This weight not only served to keep the wire centered in the tube but also to take up the slack when the wire was heated and prevent its touching the walls and becoming contaminated.

The cell was sealed to a regular vacuum system containing a manometer, McLeod gage, hydrogen reservoir, mercury diffusion pump, Hy-vac oil pump, appropriate freezing-out traps and phosphorus pentoxide tubes. The hydrogen used was obtained by the electrolysis of dilute sodium hydroxide solution followed by diffusion of the hydrogen into the reservoir through an electrically heated palladium tube.

In order to eliminate the cooling effect of the tungsten leads, the resistance of the iron wire was not measured directly but the potential drop on the wire was determined between two potential leads of 0.05-mm. platinum wire firmly wrapped about the iron wire and connected to a Leeds and Northrup type K potentiometer through two extra tungsten leads sealed into the sides of the cell. The section of wire between the potential leads was 6.21 cm. in length and located in the middle of the wire as far removed from the lead in wires as possible.

The current passing through the wire was determined by means of an accurate milliammeter placed in the circuit. The temperature–resistance curve was determined by letting pure hydrogen at a pressure of 10–20 mm. into the cell which was immersed in a liquid bath at the proper temperature and passing a small current through the wire, sufficient to give an accurate potential reading but not enough to heat the wire above the temperature of the bath. Separate experiments showed that even with thirty milliamperes flowing, there was no appreciable rise of temperature. Twenty milliamperes was the current used for all calibrations.

Condition of the Wire.—The wire was carefully cleaned and placed in position, care being taken not to touch the wire with the fingers after cleaning. When the cell was constructed and sealed to the apparatus, the wire was

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[1] M. Knudsen, *Ann. Physik*, **34**, 593 (1911).

[2] H. H. Rowley and K. F. Bonhoeffer, *Z. physik. Chem.*, **B21**, 84 (1933).

[3] K. Blodgett and I. Langmuir, *Phys. Rev.*, **40**, 78 (1932).

[4] J. K. Roberts, *Proc. Roy. Soc.* (London), **A129**, 146 (1930); **A135**, 492 (1932).

[5] C. Zener, *Phys. Rev.*, **37**, 556 (1931); **40**, 335 (1932); Jackson and Mott, *Proc. Roy. Soc.* (London), **A137**, 703 (1932); Jackson and Howarth, *ibid.*, **A142**, 447 (1933).

further cleaned by alternately heating in hydrogen and in vacuum at a temperature of not over 900°K., a treatment which should reduce any oxide formed and remove the resulting water. This cleaning process was repeated at frequent intervals throughout the course of experiments. This was the condition of the wire during most of the experiments and a wire so treated is referred to as a "normally" clean wire. The glass cell, freezing-out traps and connecting tubes were also baked out in electric ovens and frequently torched with a Bunsen flame in order to remove adsorbed and occluded gases that might affect the results.

Some later experiments were performed in which the wire was glowed for considerable time in vacuum just before the measurements in an effort to dislodge the adsorbed hydrogen layer which was believed to be present under the above conditions. It was found that after heating, the resistance of the wire at the bath temperature changed—sometimes considerably. At first, it was believed that this change was due to strains in the wire caused by uneven annealing and an attempt was made to relieve these by glowing at about 900–1000°K. in hydrogen for a period of several hours. This treatment did not seem to correct the difficulty. A separate series of experiments seemed to indicate very clearly that this change in resistance was not due to absorbed hydrogen, which is in agreement with work of Sieverts.[6] Inasmuch as the glowing wire reached a temperature of 1000–1200°K., the change in resistance was probably due to incomplete changes in the internal structure of the iron which is known to exist in at least three modifications, α-, β-, γ-iron and which have different resistances. This incomplete change caused different parts of the wire to have different resistances and hence when the wire was heated in vacuum (to avoid any possible Busch effect[7]) it glowed unevenly. This uneven heating might be due to variations in the diameter of the wire,[8] but since the dark places in the wire showing varying resistances shifted, this could not be the answer.

However, numerous calibrations of the temperature–resistance curve over the temperature range used for the experiments showed all these curves to have essentially the same slope, so that by determining the resistance of the wire at the temperature of the bath for each experiment, the temperature–resistance curve for that run could be found, even though the resistance of the wire at 274°K. varied from 0.110 ohm/cm. to 0.082 ohm/cm. Due to this irregularity, the temperature of the wire as read from the calibration curve was the average temperature of the section measured.

Calculation of the Accommodation Coefficient.—The method of calculation was the same as that used for determining the accommodation coefficient of hydrogen on platinum[2] and evolved the following formula

$$\alpha = \frac{\sqrt{2mk/\pi} \times 10^7}{dk\ 1332} \times \frac{W_c \sqrt{T_a}}{(\beta + {}^1/_2)p(T - T_a)}$$

where m is mass of molecule (3.32×10^{-24} g. for hydrogen), k is the Boltzmann constant (1.371×10^{-16} ergs/deg.), d is the diameter of wire (0.0128 cm.), p is pressure in mm., T is temperature of the wire, T_a is temperature of the incident gas molecules. Since, at the pressures used, the mean free path of the hydrogen molecules equals or exceeds the radius of the cell, the temperature of the incident molecules can be taken as equal to the temperature of the cell walls or the bath temperature. W_c is the energy loss per second from the wire in watts/cm. and is calculated from the potential drop along 6.21 cm. of the wire and the current flowing. βk is the specific heat at constant volume per molecule expressed in ergs/deg. K. When hydrogen is cooled to low temperatures, the specific heat approaches that of an ideal monatomic gas and β has the value 1.5 at 45°K.; at higher temperatures, the specific heat increases to values characteristic of diatomic gases and $\beta = 2.44$ at 273°K.[9] The values of β used when T_a was below 273°K. were those for the average temperature of the wire and the bath. Though β changes rather rapidly in this temperature range it was believed to be a better approximation of the true value than the value at either the wire or the bath temperature. It might be noted here that substitution of the other values did not materially change the type of curve obtained.

The pressure was measured with a McLeod gage, the mercury vapor being kept from the cell by means of liquid air or solid carbon dioxide–acetone traps. Since the measurements were never at room temperature, there is, according to Knudsen,[10] a pressure difference between the cell and the McLeod. In the pressure range used in these experiments where the quotient (diameter of connecting tube d)/(mean free path)λ has a value between 1.5 and 6, the following empirical formula holds according to Roberts[4]

$$p_1 - p_2 = (\lambda_0 \times 10^4/7.28\ d)\ (T_1 - T_2)$$

where λ_0 is the mean free path at 273°K. and 760 mm. and taken as 1.8×10^{-5} cm. for hydrogen. The pressures were corrected with this formula for all bath temperatures.

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(6) A. Sieverts, *Intern. Z. Metallog.*, **3**, 37 (1913).

(7) H. Busch, *Ann. Physik*, **64**, 401 (1921); A. Farkas and H. H. Rowley, *Z. physik. Chem.*, **B22**, 335 (1933). This effect is frequently noted when a fine wire is heated in a gas at low pressures. Under certain conditions, the even temperature distribution along a wire becomes suddenly unstable and the wire takes on an uneven temperature; some sections may be glowing while others are at room temperature, though the average temperature of the entire wire may not change appreciably from its previous value.

(8) Actual measurements of sections of the wire taken at random failed to show any marked deviation from 0.0128 cm.

(9) "International Critical Tables."

(10) M. Knudsen, *Ann. Physik*, **31**, 205 (1910); O. Reynolds *Phil. Trans.*, **170**, 727 (1879).

Experimental Procedure and Data

Surface of Wire "Normally" Clean.—After treating the wire and getting it in a "normally" clean condition, the cell was completely immersed in a constant temperature bath. Five different bath temperatures were used during the experiments: liquid air at 88°K., acetone–solid carbon dioxide at 195°K., ice water at 273°K., petroleum oil bath at 325 and 373°K. Pure hydrogen was let into the apparatus at a pressure of about 0.025 mm. of mercury and accurately measured with the McLeod gage. A known current from a six-volt storage battery was then passed through the cell and the potential drop along the wire measured. From these data the resistance and hence the temperature of the wire could be found. About five minutes was allowed for the cell to come to thermal equilibrium. Four or five measurements were made during each trial, the temperature of the wire ranging from 30 to 100° above that of the bath. Typical data for the various bath temperatures are given in Table I.

In a separate series of experiments, the heat lost from the wire by metallic conduction and radiation was determined for each bath by evacuating the cell and recording the energy necessary to bring the wire to a temperature 30–100° above that of the bath. Values from these curves were always subtracted from the total energy input in order to determine the amount of heat actually carried away from the wire by the gas molecules. Check determinations at various times indicated that this correction factor was constant for any one bath and wire temperature.

TABLE I

ACCOMMODATION COEFFICIENT OF HYDROGEN ON A "NORMALLY" CLEAN IRON WIRE

Press., mm.	T, °K. wire	Watts/cm.	β	α
		Bath temp., 88°K.		
0.0230	119	0.001316	1.76	0.555
.0230	122	.001509	1.77	.580
.0230	130	.001785	1.79	.550
.0223	133	.001810	1.81	.530
.0230	137.5	.002073	1.84	.530
.0230	147	.002418	1.86	.515
.0223	152	.002487	1.87	.500
.0230	157.5	.002810	1.88	.505
.0230	171.5	.003310	1.93	.485
.0223	181.5	.003480	1.96	.465
.0230	190.5	.004006	1.98	.465
.0230	205	.004509	2.03	.450
.0223	215.5	.004621	2.06	.435
		Bath temp., 195°K.		
0.0175	229	0.000679	2.31	0.410
.0175	236.5	.000818	2.32	.405
.0200	237	.000884	2.32	.380
.0175	243.5	.000932	2.33	.395
.0200	247.5	.001096	2.33	.375
.0175	250.5	.001052	2.34	.385
.0175	259	.001197	2.35	.380
.0200	262	.001377	2.35	.365
.0175	270.5	.001381	2.37	.370
.0200	274	.001597	2.37	.360
.0175	282	.001586	2.38	.365
		Bath temp., 273°K.		
0.0240	317	0.000416	2.47	0.315
.0250	320	.000883	2.47	.305
.0250	325	.000995	2.47	.310
.0240	328.5	.000985	2.47	.300
.0250	330	.001091	2.47	.310
.0250	335	.001174	2.47	.305
.0240	339	.001187	2.47	.305
.0250	340	.001306	2.47	.315
.0250	347.5	.001413	2.47	.305
.0240	349.5	.001370	2.47	.300
.0240	356.5	.001509	2.47	.305
.0250	357.5	.001619	2.47	.310
		Bath temp., 325°K.		
0.0245	358.5	0.000582	2.48	0.310
.0225	362.5	.000603	2.48	.315
.0245	367.5	.000742	2.48	.315
.0225	371.5	.000741	2.48	.310
.0245	377	.000886	2.48	.305
.0245	383	.001006	2.48	.310
.0225	390	.001005	2.48	.300
		Bath temp., 373°K.		
0.0240	416.5	0.000707	2.49	0.320
.0235	418	.000694	2.49	.310
.0240	424	.000802	2.49	.310
.0235	424.5	.000791	2.49	.305
.0235	431.5	.000905	2.49	.310
.0240	432	.000912	2.49	.305
.0240	439	.001005	2.49	.300
.0235	439	.001008	2.49	.305
.0240	446.5	.001115	2.49	.295

Attempts to Obtain Bare Surface.—It appears quite certain that the "normally" clean surface is actually covered with adsorbed hydrogen. Patterning after the work of Roberts[4] and Mann,[11] a similar technique was employed in attempting to obtain an iron surface free from adsorbed hydrogen. The wire which had been cleaned of ordinary contamination in the usual way, was glowed at 1000–1100°K. for varying periods of time in vacuum. The temperature of the wire was quickly lowered to a value about 80° above that of the bath and the time noted. Pure hydrogen at the proper pressure was introduced as soon as possible (within one minute) after re-

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(11) W. B. Mann, *Proc. Roy. Soc.* (London), **A146**, 776 (1934).

ducing the current and readings taken at frequent intervals for twenty to thirty minutes. It was found that after about thirty minutes of glowing in vacuum the values of the accommodation coefficient dropped appreciably, giving 0.35 at 180°K. and 0.18 at 351°K. Further half-hour periods of heating at 1000–1100°K. failed to lower these values.

In an attempt to lower the values still further, the wire was heated to 1000–1100°K. in a vacuum for twelve hours. During this heating the resistance of the wire changed markedly as noted above. Using the same technique as before, the accommodation coefficient was found to be 0.21 at 346°K. and failed to change by further fifteen minute periods of heating in vacuum. The slightly higher value obtained might well be due to a change of surface caused by prolonged glowing.

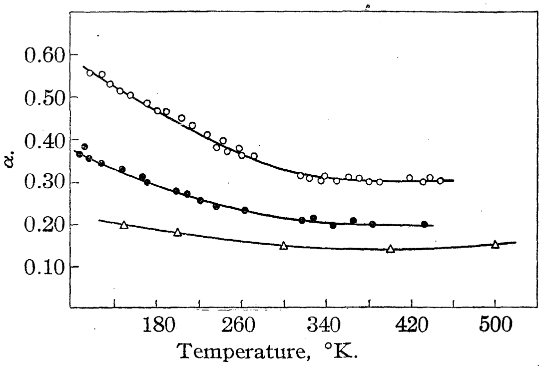

Fig. 1.—Change of accommodation coefficient with temperature: ○, iron wire saturated with hydrogen; ●, platinum wire recently glowed; △, tungsten wire specially cleaned.

Some runs were also made in which the wire was heated in hydrogen. In a typical experiment it was found that according to the measurements of the first few minutes, the accommodation coefficient rose quite rapidly. It is interesting to note that in some cases after this first sharp rise the values remained fairly constant for twenty to thirty minutes though showing a definite tendency to increase. In certain other cases, the increase was more rapid though nowhere near as great as during the first few minutes as shown in Table II. Upon letting the wire stand in contact with hydrogen at room temperature for several hours, the regular value of 0.31 was always obtained.

Table II

Increase of Accommodation Coefficient with Time

Bath temperature, 273°K.

Minutes	1	2	3	6	17
α	0.172	0.196	0.209	0.210	0.211
Minutes	1	2	3	4	6
α	0.130	0.205	0.228	0.236	0.238
Minutes	10	15	30	60	
α	0.245	0.250	0.263	0.278	

Discussion of Results

The values of the accommodation coefficient obtained for a "normally" clean iron wire follow quite closely those of hydrogen on a platinum surface, rising considerably as the temperature of the wire is decreased. The relatively higher values obtained with iron might be due to the smaller mass of the iron, since according to the theory of Baule[12] the energy exchange by collision between gas molecules and surface atoms of a solid body is more complete the smaller the difference in mass between the colliding particles. However, it seems more probable that the higher value is due to adsorbed layers on the surface. This is further substantiated by the fact that shortly after glowing the iron wire, the values of the accommodation coefficient are practically the same as those for a platinum surface which had been similarly treated.

With respect to the increasing accommodation coefficient with decreasing temperature, it is interesting to compare three different sets of values obtained at low temperatures. In Fig. 1 are plotted the values for a "normally" clean iron wire, a platinum wire that had been recently glowed[2] and a tungsten wire with which special pains had been taken to obtain a perfectly clean surface.[3] It is significant that in all cases there is a decided upward trend below 350°K., being greatest in the case of the iron and least in the case of tungsten. Recent work of Gregory[13] with platinum surface also shows a definite rise from 500 to 300°K. though not as great as that obtained at lower temperatures. This general rise in all cases would tend to substantiate the suggestion made in the previous paper[2] that two types of adsorption are causing this effect. According to certain theoretical considerations,[5] if the condition of the surface remains unaltered, the accommodation coefficient should decrease with decreasing temperature. That this is the case above approximately 500°K. appears to be shown by work of Blodgett and Langmuir[3] and others. In this range it might be assumed that the hydrogen was atomically adsorbed. Below

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[12] B. Baule, *Ann. Physik*, **44**, 145 (1914).

[13] H. S. Gregory, *Proc. Roy. Soc.* (London), **A149**, 35 (1935).

this range, a second type of adsorption begins to take place, possibly a molecular adsorption on top of the atomic adsorption. This second type, being more loosely bound, would form a rougher surface and hence bring about a better exchange of energy between the gas molecules and solid. For a range of about 150°, this increasingly rough surface would offset the drop in the accommodation coefficient due to decreasing temperature and give values more or less constant such as actually found between 350 and 500°K. As the temperature was lowered still further, this molecular adsorption would become predominant and cause an actual rise in the accommodation coefficient. If such is the case, the values should reach a maximum and then drop sharply. Since no supply of liquid hydrogen was available, it was impossible to test this experimentally. The more ready adsorption of hydrogen on iron might explain the steeper rise at low temperatures than that observed with platinum or tungsten.

It might appear that this rise at low temperatures was caused by applying the pressure correction when the bath was not at room temperature. When the bath was below room temperature this correction, which amounted to 0.005 mm. at liquid temperatures, was subtracted from the pressure as read on the McLeod. This would tend to cause a rise in the calculated values. However, even if this correction were ignored, which we did not feel justified in doing, the curve still showed a decided upward trend giving values of 0.41 at 150°K.

It would appear that in all cases, even with the tungsten surface which had been carefully cleaned, there was adsorbed hydrogen on the wire to a greater or less extent. The value of 0.31 might be taken as the accommodation coefficient of hydrogen on a bright iron surface saturated with hydrogen at 350°K. It is interesting to compare values of the accommodation coefficient of hydrogen on various surfaces in this temperature range as shown in Table III. In all the cases chosen, the condition of the surface might be termed "normally" clean, *i. e.*, no special attempt had been made to get rid of adsorbed hydrogen. Considering the wide difference in the substances used and also the noticeable effect of rough surfaces, it is surprising to find the values of the accommodation coefficient so nearly the same. This fact seems to indicate that in all cases the solid surface was covered with adsorbed hydrogen and that the heat exchange was between hydrogen gas molecules and an adsorbed hydrogen surface. When a special technique is used to remove this hydrogen layer, lower values are always obtained, *i. e.*, 0.11 for platinum,[11] 0.14 for tungsten,[3] 0.18 for iron, but it is believed that even in these cases there is some adsorbed hydrogen. Langmuir[3] and others also postulated adsorbed layers in these cases.

TABLE III

ACCOMMODATION COEFFICIENT OF HYDROGEN ON VARIOUS SURFACES

Investigator	Surface	Temp. of surf. °K.	α
Knudsen[14]	Platinum	273	0.315
Knudsen[1]	Platinum	273	.26
Soddy and Berry[15]	Platinum	335	.25
Gregory[13]	Platinum	389	.25
Rowley and Bonhoeffer[2]	Platinum	350	.21
Soddy and Berry[15]	Palladium	(335)	(0.25)
Blodgett and Langmuir[3]	Tungsten	400	.22
Hughes and Bevan[16]	Nickel	437	.25
Chapman and Hall[17]	Silver	373	.25
Knudsen[1]	Glass	300(?)	.26
Rowley and Evans	Iron	350	.31

In the experiments where an attempt was made to dislodge this adsorbed hydrogen from the iron surface, the rapid rise of values during the first few minutes (see Table II) might be construed to mean a very rapid adsorption during the first few minutes such as Mann found on platinum.[11] Though this may be true, it appears certain that the wire and cell were not at thermal equilibrium much under three or four minutes after glowing the wire. Since the correct calculation of the accommodation coefficient by this method depends upon thermal equilibrium, values taken before this time have no great significance.

Summary

1. The accommodation coefficient of hydrogen on a bright iron surface saturated with hydrogen has been determined for the temperature range 120–450°K. and found to be 0.31 at the higher temperatures and rising steadily below 350°K. to 0.55 at 120°K.

2. This rise with decreasing temperature has been compared to similar results obtained with platinum and tungsten surfaces and discussed

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(14) M. Knudsen, *Ann. Physik*, **6**, 129 (1930).

(15) F. Soddy and A. J. Berry, *Proc. Roy. Soc.* (London), **A83**, 254 (1910); *ibid.*, **A84**, 576 (1911).

(16) D. R. Hughes and R. C. Bevan, *ibid.*, **A117**, 101 (1928).

(17) D. L. Chapman and W. K. Hall, *ibid.*, **A124**, 578 (1929).

on the basis of two distinct types of adsorbed hydrogen.

3. Comparison of the accommodation coefficients obtained by numerous investigators on different surfaces leads to the conclusion that the exchange of energy between hydrogen gas molecules and an adsorbed layer of hydrogen was measured in each case.

4. An attempt to remove this adsorbed layer lowered the accommodation coefficient from 0.31 to 0.18 at 350°K.

EVANSTON, ILLINOIS

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Some Fluorinated Chlorobenzenes[1]

BY HAROLD SIMMONS BOOTH, HOWARD M. ELSEY[2] AND PAUL E. BURCHFIELD[3]

A survey of the literature revealed descriptions of the preparation of only ortho[4] and para-chlorofluorobenzene.[5] In order to complete the series of monochlorofluorobenzenes the preparation of meta-chlorofluorobenzene from meta-chloroaniline was undertaken.

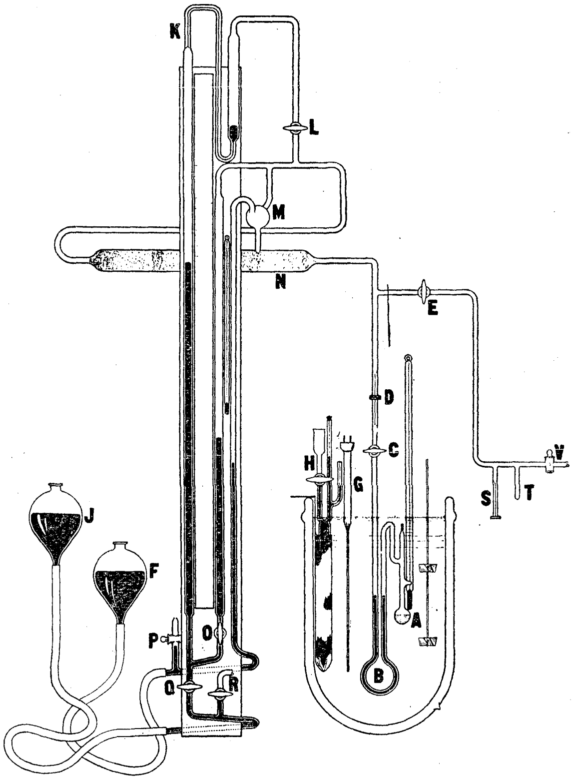

Fig. 1.

De Crauw[6] reported the preparation of 2,4,5-trichlorofluorobenzene from meta-fluoroaniline by several steps. De Crauw stated that a fluorine atom cannot be introduced into the benzene ring ortho to chlorine. The preparation of 2,4,6-trichlorofluorobenzene was attempted in order to extend the knowledge of this class of compounds and to discover whether or not the Balz and Schiemann reaction would effect the introduction of fluorine ortho to chlorine. In addition 2,4,6-trichlorofluorobenzene was successfully prepared from 2,4,6-trichloroaniline.

Experimental

Method of Determining Vapor Pressures

The apparatus for the determination of vapor pressure used in this research consisted of a modified "static isoteniscope,"[7] a suitable thermostat equipped with automatic and manual heat controls, and a modified Germann barometer,[8] shown in Fig. 1.

For the measurement of vapor pressure, a carefully purified sample was introduced into the bulb (A) the volume of which was approximately 2 cc. One arm of the bulb was connected to one side of the short U-manometer (B), the other arm was sealed to a tube (T) connected to a Hyvac pump. The second side of the U-manometer was provided with a stopcock (C) and a flat joint (D) and could also be connected by means of the flat joints (D) and (S) to the Hyvac pump. Both sides of the U-manometer were simultaneously evacuated for some time, and the mercury was carefully heated to its boiling point under the reduced pressure so that residual gases entrapped by the mercury were driven out.

When the mercury cooled, a small part of the sample was condensed on it in (B) and redistilled off in order to completely wash out any residual permanent gases in the sample chamber. The tube (T) connecting the sample bulb to the vacuum system was sealed off while the liquid in A was cooled in liquid air, and the other side of the small manometer was closed by means of stopcock (C).

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[1] From a portion of a thesis submitted by **Paul E. Burchfield** to the Graduate School, Western Reserve **University, June**, 1934, in partial fulfilment of the degree of Doctor of **Philosophy**.

[2] Manager of Chemical Division, Westinghouse Research Laboratories, East Pittsburgh, Pa.

[3] Holder of the Westinghouse Fellowship in Chemistry, 1932–1934.

[4] Rinkes, *Chem. Weekblad*, **11**, 360, 952 (1914).

[5] Wallach and Heusler, *Ann.*, **243**, 219 (1888); Swarts, *Rec. trav. chim.*, **35**, 131 (1915).

[6] De Crauw, *ibid.*, **48**, 1061 (1929).

[7] A. Smith and A. W. C. Menzies, THIS JOURNAL, **32**, 1412 (1910).

[8] A. F. O. Germann, *ibid.*, **36**, 2456 (1914).

The system was introduced into a clear mineral oil bath, contained in a 4-liter Dewar vessel, to such a depth that the space containing the sample was completely immersed. By means of the flat joint (D), the short manometer was connected to the manometer on which the vapor pressures were read.

The temperature was measured on a thermometer graduated to 0.1°. The thermometer, calibrated by the Reichsanstalt, was checked in this Laboratory against a precision platinum resistance thermometer and was found to be correct. The ice point was checked before each period of use. The necessary stem corrections were calculated and were added to the observed reading.

When the vapor pressure of the compound was to be measured, stopcock (C) was opened, and the mercury in the U-manometer (B) was brought to the same level by varying the pressure in the space connecting the large and small manometers by means of an air inlet (V) and a leveling bulb (F). The tube (N) was filled with barium oxide so that only dry air would come in contact with the mercury in the large manometer. When the mercury in (B) reached the same level the pressure was read on the large manometer at successive time intervals at constant temperature by a reading telescope until no change was observed in several observations. The observed pressure was corrected for the vapor pressure of mercury, and the necessary correction was applied to convert the observed pressure reading to the equivalent pressure at 0°, on the basis of a glass scale.

The boiling points of the compounds described below were read from the temperature–vapor pressure curves plotted on a large scale.

***m*-Chlorofluorobenzene.**—*m*-Chlorofluorobenzene was prepared from *m*-chloroaniline by the method of Balz and Schiemann.[9] The yield of *m*-chlorofluorobenzene was 60% calculated from the weight of chloroaniline used: b. p. 127.6° at 760 mm. (corr.); m. p. below −78°; d_{25} 1.221; $n^{27.0}{}_D$ 1.4911.

Analysis.—Chlorine was determined by the method of Chablay[10] as modified by Vaughn and Nieuwland.[11]

Anal. Calcd. for C_6H_4FCl: Cl, 27.17. Found: Cl, 27.15, 27.20.

Qualitative tests revealed the presence of fluorine.

Vapor pressure of *m*-chlorofluorobenzene and temperature are related by the equation $\log P$ (mm.) = $(-2342.4/T) - 2.4165 \log T + 15.017$. The average deviation of the calculated values from the observed values is ±1 mm.

2,4,6-Trichlorofluorobenzene was prepared from 2,4,6-trichloroaniline by the method of Balz and Schiemann.[9]

Twenty-four grams of trichloroaniline was added to 40 cc. of concd. hydrochloric acid. A concentrated solution of 8.4 g. of sodium nitrite was slowly added to the cold mixture. The diazonium solution was rapidly filtered to remove unreacted trichloroaniline, after which the diazonium fluoborate was precipitated by the addition of an excess of 45% fluoboric acid. After washing with alcohol and ether the salt was thoroughly dried at 70–80°. Efficient drying of the salt is necessary; otherwise the subsequent decomposition takes place with uncontrollable rapidity. The diazonium fluoborate was obtained in 75% yield.

The diazonium fluoborate was decomposed by heating in an evacuated system. Decomposition began at 187°, but it was necessary to heat to a considerably higher temperature to complete the decomposition. An appreciable quantity of tar was formed with each decomposition. From 13 g. of diazonium fluoborate 7 g. of crude trichlorofluorobenzene was obtained. The crude compound was washed successively with saturated sodium carbonate and 17% sodium hydroxide solutions, dried with barium oxide and repeatedly distilled under reduced pressure (10 mm.). Sixty grams of purified trichlorofluorobenzene was prepared in all: b. p. 208.4° at 760 mm. (corr.); m. p. 11.2°; d_{25} 1.530; $n^{27.2}{}_D$ 1.5429.

Anal. Calcd. for $C_6H_2Cl_3F$: Cl, 53.35. Found: Cl, 53.39, 53.22.

Qualitative tests revealed the presence of fluorine.

Vapor pressure of 2,4,6-trichlorofluorobenzene and temperature are related by the equation $\log P$ (mm.) = $-2452/T - 0.7316 \log T + 9.9389$.

The average deviation of the calculated values from the observed values is ±2.6 mm.

Instability of 2,4,6-Trichlorofluorobenzene.—The sample of 2,4,6-trichlorofluorobenzene on which the vapor pressures were run acquired a deep brown color after it was heated to 215.5°, which denoted thermal instability.

TABLE I

VAPOR PRESSURES OF *m*-C_6H_4ClF		VAPOR PRESSURES OF 2,4,6-$C_6H_2Cl_3F$	
T, °C.	Press., mm.	*T*, °C.	Press., mm.
0.0	4.0	25.1	2.0
16.2	10.0	71.8	11.0
24.2	15.0	92.0	21.8
41.3	34.0	120.1	63.3
54.3	61.0	132.7	92.3
69.1	112.0	143.5	132.3
83.0	187.0	154.5	185.9
90.6	246.0	165.1	256.8
102.5	366.5	183.0	411.2
116.1	549.5	192.5	534.1
120.2	618.0	201.8	656.0
124.1	690.5	206.4	729.5
128.7	786.0	211.5	815.6
129.6	805.5	215.5	899.0

Summary

1. The preparation and properties of *m*-chlorofluorobenzene have been described.

2. 2,4,6-Trichlorofluorobenzene has been synthesized and the physical properties have been measured.

3. It has been demonstrated that a fluorine atom may be introduced ortho to chlorine in the benzene ring by means of the Balz and Schiemann procedure.

4. An improved precision technique for the determination of the vapor pressures of liquids has been devised.

CLEVELAND, OHIO RECEIVED APRIL 1, 1935

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[9] Balz and Schiemann, *Ber.*, **60B**, 1186 (1927).

[10] Chablay, *Ann. chim.*, [9] **1**, 469 (1914).

[11] Vaughn and Nieuwland, *Ind. Eng. Chem.*, *Anal. Ed.*, **3**, 274 (1931).

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Benzotrifluoride and its Halogenated Derivatives[1]

BY HAROLD SIMMONS BOOTH, HOWARD M. ELSEY[2] AND PAUL E. BURCHFIELD[3]

The purpose of this paper is to describe an improved method for the preparation of benzotrifluoride, the preparation and study of the isomeric monofluoro- and monochlorobenzotrifluorides, 3,4-dichlorobenzotrifluoride, and two mixtures of more fully chlorinated derivatives.

Wertyporoch[4] prepared the more or less impure monochlorobenzotrifluorides and small amounts of the dichloro derivative by the direct action of chlorine on benzotrifluoride in the presence of antimony pentachloride.

Since the investigation described in this paper was completed, Aelony[5] published a description of the preparation and properties of *m*-fluorobenzotrifluoride. The properties as described agree closely with our findings with the exception of the index of refraction.

Determination of Physical Properties.—Vapor pressures (Table I) were determined as described by Booth, Elsey and Burchfield.[6] The boiling points were read from the temperature–vapor pressure curves plotted on a large scale. The latent heats of vaporization were calculated from the Rankine and Clausius–Clapeyron equations. Melting points were determined as described by Booth and Stillwell.[7]

TABLE I

VAPOR PRESSURES OF BENZOTRIFLUORIDE AND ITS HALOGENATED DERIVATIVES

T, °C.	Press., mm. $C_6H_5CF_3$	*T*, °C.	Press., mm. *m*-$C_6H_4FCF_3$
0.0	8.5	0.0	9.0
27.7	43.5	15.0	22.5
34.4	60.0	20.7	30.5
41.3	82.5	35.6	65.5
50.2	122.5	41.2	84.5
57.5	165.5	50.5	127.0
64.9	220.5	55.4	155.0
70.0	268.5	65.4	230.5
75.8	326.0	71.0	284.5
80.7	385.0	80.8	400.0
91.3	542.0	91.3	567.5
96.3	632.5	96.8	670.0
100.5	720.0	100.2	745.5
103.5	789.6	103.5	822.5
107.2	877.0	105.4	868.5
	o-$C_6H_4ClCF_3$		*m*-$C_6H_4ClCF_3$
19.6	3.5	20.7	6.5
28.4	6.0	26.9	9.5
35.6	9.5	33.2	14.0
42.8	13.5	41.8	20.5
51.3	20.5	57.3	43.5
65.2	39.0	71.1	79.5
78.6	67.5	83.8	131.0
86.6	93.0	90.7	169.5
93.5	120.5	103.4	264.5
124.0	333.5	110.2	329.0
131.7	422.5	121.9	473.5
139.1	522.5	128.5	574.5
145.8	631.0	133.5	662.5
153.4	774.0	137.3	738.0
157.7	868.5	141.6	831.5
	p-$C_6H_4FCF_3$		*p*-$C_6H_4ClCF_3$
13.4	22.0	19.3	5.0
16.4	26.5	27.1	9.0
21.1	33.5	33.5	12.0
25.7	41.0	45.6	22.5
30.3	50.5	51.2	31.0
35.7	65.0	63.5	55.0
40.6	81.5	77.9	100.5
55.6	150.5	97.0	206.5
61.4	188.0	103.4	257.5
71.0	270.0	116.1	387.5
81.2	384.5	121.9	462.5
91.9	542.5	128.5	562.5
96.6	631.0	133.5	646.5
102.3	749.0	139.8	770.5
107.1	865.5	143.5	851.5
	3,4-$C_6H_3Cl_2CF_3$		3,4-$C_6H_3Cl_2CF_3$
24.6	2.0	113.9	124.5
35.1	4.0	130.1	216.0
44.2	6.0	146.1	358.0
52.1	9.0	154.8	462.0
59.8	12.5	169.9	694.0
71.8	22.0	174.3	774.5
81.5	35.0	179.8	888.5
99.7	73.0		

Analyses.—The compounds described in this paper were analyzed for hydrogen and carbon by the combustion method. The volatilized sample was led with an excess of oxygen over cerium nitrate and copper oxide followed by molecular silver on asbestos and lead chromate, the two latter reagents serving to remove completely free

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[1] From a portion of a thesis submitted by Paul E. Burchfield to the Graduate School of Western Reserve University, June, 1934, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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[3] Holder of the Westinghouse Fellowship in Chemistry, 1932–1934.

[4] Wertyporoch, *Ann.*, **493**, 153–165 (1932).

[5] Aelony, THIS JOURNAL, **56**, 2063 (1934).

[6] Booth, Elsey and Burchfield, *ibid.*, **57**, 2064 (1935).

[7] Booth and Stillwell, *ibid.*, **56**, 1532 (1934).

or combined fluorine. The resulting water and carbon dioxide were absorbed in a Fischer absorption bottle filled with calcium chloride and a Gomberg type absorber filled with 50% potassium hydroxide solution. The results of the analyses are given in Table II.

Experimental Part

(a) **Benzotrifluoride.**—Benzotrifluoride was prepared by the action on benzotrichloride of an excess of sublimed antimony trifluoride instead of the ratios recommended by Swarts[8] and by Aelony.[5] The reaction was initiated and carried to completion as quickly as possible and the product was distilled from the reaction vessel as fast as it was formed since antimony salts, etc., greatly decrease the yield of benzotrifluoride by the production of resinous products.

The distillate was washed successively with 6 *N* hydrochloric acid, sodium bicarbonate and 20% sodium hydroxide solutions, dried by shaking with barium oxide and twice distilled at a high reflux ratio through an insulated, electrically-heated column 2.5 cm. in diameter and 110 cm. high packed with jack-chain and surmounted by a Vigreux condenser.

(b) *o*-**Fluorobenzotrifluoride.**—An attempt was made to prepare *o*-fluorobenzotrifluoride by chlorinating *o*-fluorotoluene to *o*-fluorobenzotrichloride and fluorinating the side chain with sublimed antimony trifluoride.

Accordingly, one mole (110 g.) of *o*-fluorotoluene from the Eastman Kodak Co. was chlorinated until the system gained 95 g. The compound chlorinated very slowly, and phosphorus pentachloride as a catalyst does not increase the speed or the extent of chlorination. Fractionation yielded a liquid boiling at 215–223°, which supposedly was *o*-fluorobenzotrichloride.

Fluorination of the above liquid produced volumes of hydrogen fluoride, a large quantity of resin, but only a few grams of a compound boiling between 114 and 116°. The products of several fluorinations were combined, purified and fractionated. Approximately 10 cc. of a liquid was obtained which boiled at 113.8–114.3° at 740.6 mm., and which resembled benzotrifluoride in odor and physical properties. It was thought that the compound was *o*-fluorobenzotrifluoride.

Anal. Calcd. for $C_6H_4FCF_3$: C, 51.21; H, 3.45. Found: C, 47.1; H, 2.42.

These analyses revealed that the compound was not *o*-fluorobenzotrifluoride. Since the yields were so small this was probably some secondary decomposition product.

(c) *m*-**Fluorobenzotrifluoride.**—*m*-Fluorobenzotrifluoride ($C_6H_4FCF_3$) was prepared by the following reactions: benzotrifluoride was nitrated, the nitro group was reduced to an amino group[9] and the amino group was replaced by a fluorine atom by the method of Balz and Schiemann.[10]

m-Nitrobenzotrifluoride was prepared in 96% yield using a nitrating mixture composed of one part fuming nitric (sp. gr. 1.5) and 1.5 parts of concentrated sulfuric acids.

One mole (191 g.) of *m*-nitrobenzotrifluoride was reduced with tin and concd. hydrochloric acid with a yield of 154 g. of *m*-aminobenzotrifluoride corresponding to 95%.

A solution of the diazonium salt was prepared by the addition of a saturated solution containing 15 g. of sodium nitrite to 32 g. of *m*-aminobenzotrifluoride and 40 cc. of concentrated hydrochloric acid. The addition of an excess of fluoboric acid precipitated the diazonium fluoborate. There was obtained 46 g. of the salt corresponding to 87% yield. The decomposition taking place below 140° was effected by gentle heat. There remained in the flask a small amount of a slightly brown residue which was probably sodium fluoborate. From 166 g. of diazonium fluoborate 86 g. of fluorobenzotrifluoride was recovered—a yield of 82% calculated from the weight of the salt decomposed. The compound was chemically and physically purified in the usual manner.

(d) *p*-**Fluorobenzotrifluoride.**—One hundred and thirty grams of *p*-fluorotoluene[11] was chlorinated in the usual manner with phosphorus pentachloride as a catalyst. After eighteen hours of chlorination, the reaction stopped and the products were fractionated. There was obtained 220 g. of *p*-fluorobenzotrichloride ($C_6H_4FCCl_3$) which boiled at 212–213° (uncorr.) at 741.6 mm.; a yield of 76%.

Two hundred and twenty grams of *p*-fluorobenzotrichloride ($C_6H_4FCCl_3$) was converted into 130 g. of *p*-fluorobenzotrifluoride ($C_6H_4FCF_3$) in the usual manner by means of antimony trifluoride. This yield corresponded to 73%. After purification the compound had a boiling point range of 0.3°.

(e) *o*-**Chlorobenzotrifluoride.**—*o*-Chlorobenzotrifluoride was prepared from *o*-toluidine by replacing the amino group by chlorine, chlorinating and subsequently fluorinating the side chain.

One hundred and seventy-five grams of *o*-chlorotoluene[12] and 5 g. of phosphorus pentachloride were introduced into a suitable flask. A slow stream of chlorine was led into the flask, the contents of which were maintained at the boiling point throughout the chlorination. This treatment resulted in the formation of much tarry matter, but with small yield of the desired product. It was thought that possibly phosphorus pentachloride at the elevated temperatures may have caused the formation of the decomposition products.

Accordingly, 170 g. of *o*-chlorotoluene was chlorinated at 160–190° without a catalyst, with the formation of only traces of tarry products. Chlorination took place much less readily in the case of *o*-chlorotoluene compared with that of the para isomer.

Two hundred grams of *o*-chlorobenzotrichloride was obtained, corresponding to a yield of 64%.

Two hundred grams of *o*-chlorobenzotrichloride was mixed with 190 g. (excess) of sublimed antimony trifluoride. The mixture was heated rapidly until reaction set in. The product weighed 124 g. after washing several times with 6 *N* hydrochloric acid, corresponding to a yield of 85%, on the basis of *o*-chlorobenzotrichloride. After purifying and drying in the usual manner, the *o*-chlorobenzotrifluoride boiled at 148.2–148.7° (uncorr.) at 741 mm.

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(8) Swarts, *Bull. acad. roy. sci. Belg.*, **113**, 241 (1913); **35**, 375 (1898); *Rec. trav. chim.*, **35**, 155 (1915); **33**, 263, 299 (1914).

(9) Beilstein and Kurbatow, *Ann.*, **176**, 29 (1875).

(10) Balz and Schiemann, *Ber.*, **60**, 1186 (1927).

(11) G. Schiemann, *ibid.*, **62**, 1794 (1929).

(12) Gattermann, *ibid.*, **23**, 1218 (1890).

(f) ***m*-Chlorobenzotrifluoride.**—The starting compound for the preparation of *m*-chlorobenzotrifluoride was *m*-aminobenzotrifluoride, the preparation of which was previously described.

The amino group was replaced by a chlorine atom by the method of Sandmeyer.[13] One hundred and thirty-eight grams of *m*-aminobenzotrifluoride was mixed with 200 cc. of concentrated hydrochloric acid in 180 cc. of water. The amine was diazotized by the addition of a concentrated solution of sodium nitrite which contained 60 g. of the salt. The diazotized solution was slowly poured into 400 cc. of boiling, 10% cuprous chloride solution. The resulting mixture was distilled with steam and the water–oil distillate was extracted with ether. The *m*-chlorobenzotrifluoride–ether solution was dried with anhydrous calcium chloride and was fractionated. There was obtained 110 g. of product which boiled between 136–140°, corresponding to a yield of 70%. The product was agitated with a saturated solution of sodium carbonate, dried by refluxing with barium oxide for five hours and was distilled through a column filled with glass beads.

(g) ***p*-Chlorobenzotrifluoride.**—In order to prepare *p*-chlorobenzotrifluoride it was necessary to prepare *p*-chlorotoluene, chlorinate the side chain to *p*-chlorobenzotrichloride, and replace the chlorine atoms in the side chain by fluorine atoms by means of antimony trifluoride.

p-Chlorotoluene was prepared by the Gattermann[12] method. One mole of *p*-chlorotoluene was introduced into a 500-cc. flask provided with conical ground glass joints for a chlorine inlet and a reflux condenser. Five grams of phosphorus pentachloride was added to serve as a catalyst for the chlorination of the side chain. The contents of the flask were heated to boiling and were maintained at the boiling point during the chlorination. A slow stream of dry chlorine was led into the liquid until the weight of the system gained 105 g. The chlorination process required ten hours. The product was fractionally distilled, and a yield of 215 g. of *p*-chlorobenzotrichloride (93%) boiling between 248–250° was obtained.

Two hundred and fifteen grams of *p*-chlorobenzotrichloride was mixed with 200 g. (excess) of sublimed antimony trifluoride and the mixture was heated rapidly to initiate the reaction. The reaction proceeded smoothly and rapidly. The product was washed several times with 6 *N* hydrochloric acid, followed by several washings with water. The compound thus treated weighed 148 g., a yield of 95% calculated on the basis of the weight of *p*-chlorobenzotrichloride used.

(h) **3,4-Dichlorobenzotrifluoride.**—The preparation of 3,4-dichlorobenzotrifluoride was carried out in a manner similar to that whereby the monochloro derivatives of benzotrifluoride were obtained. The starting compound was *p*-toluidine which was successively converted into 3,4-dichlorotoluene, 3,4-dichlorobenzotrichloride and 3,4-dichlorobenzotrifluoride. The preparation of 3,4-dichlorotoluene was carried out as described by Cohen and Dakin.[14]

The side chain of the above compound chlorinated readily at 160–190° without a catalyst. The chlorinated product was not distilled, but was fluorinated without further purification. The compound was fluorinated with resublimed antimony trifluoride with a yield of 59% of the desired product calculated on the basis of the dichlorotoluene used. The crude 3,4-dichlorobenzotrifluoride was purified in the usual manner. The final product had a boiling point range of 0.5°.

(i) **Exhaustive Chlorination of Benzotrifluoride.**—Two hundred grams of benzotrifluoride and several pieces of iron gauze were introduced into a flask provided with a reflux condenser. The temperature of the contents of the flask was maintained at 60–70° by means of a water-bath.

Volumes of hydrogen chloride were liberated when dry chlorine was bubbled through the mixture. After the system had gained 60–70 g. in weight the reaction slowed considerably. The temperature was then raised to 100°, with a noticeable increase in the speed of the reaction. The chlorination was continued for twenty-five hours until the system had gained 97 g.

The first distillation of the chlorinated product revealed a boiling point of 180–230°, with only 10–15 g. of a higher boiling liquid remaining in the distilling flask. The distillate had a dark brown color, which color changed to a light yellow when water was added. The compound was agitated with concentrated hydrochloric acid to remove traces of aluminum chloride or iron chloride, carefully washed with saturated sodium carbonate solution, 20% sodium hydroxide solution, followed by several treatments with distilled water. The clear yellow liquid was dried with calcium chloride and fractionated. The small amount of residue from this fractionation was liquid at 0° but partially solidified at −15°. The first fractionation gave a clear colorless liquid, boiling between 180 and 220° and melting below −15°.

From a comparison of the boiling points of the *o*-, *m*- and *p*-monochlorobenzotrifluorides and the 3,4-dichlorobenzotrifluoride, one would surmise that this mixture consists of dichlorobenzotrifluorides and trichlorobenzotrifluorides.

To introduce more chlorine into the ring, the contents of the flask were heated over a direct flame, below the boiling point of the contents but to such a temperature that crystals of ferric chloride formed in the flask, while a stream of dry chlorine was simultaneously led in. It was surprising to note that practically no decomposition products were formed by this drastic treatment. After purification in the usual manner the mixture boiled between 230 and 260° and crystals appeared if it cooled to 15°. On the basis of previous experience it seems reasonable to assume that this mixture consists of the isomeric tri- and tetrachlorobenzotrifluorides.

Discussion of Results

The physical properties of the compounds prepared and studied in this research are listed with their analyses in Table II.

The introduction of chlorine into the benzotrifluoride ring raises the boiling point of the original compound 35–37° for each chlorine atom replacing an atom of hydrogen, except in the case of the ortho compound where the elevation of the boiling point is decidedly higher. Practically the same elevation is noted when chlorine is introduced into the benzotrichloride ring, and the same inconsistency with the ortho chloro compound. These facts are shown in Table III.

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(13) Sandmeyer, *Ber.*, **17**, 1633, 2650 (1884).

(14) Cohen and Dakin, *J. Chem. Soc.*, **81**, 1336 (1902).

TABLE II

SUMMARY OF PROPERTIES OF NEW AROMATIC FLUORIDES

Compound	B. p., °C.	M. p., °C.	Refractive index n_D	Refractive index °C.	Sp. gr., 25°C.	ΔH cal./mole at b. p.
$C_6H_5CF_3$	102.3	−29.05[a]				8,110
m-$C_6H_4FCF_3$	100.9	−81.5	1.3980	25	1.289	8,250
p-$C_6H_4FCF_3$	102.8	−41.7	1.3996	22	1.293	8,450
o-$C_6H_4ClCF_3$	152.8	− 7.4 to −7.6	1.4544	22	1.364	9,445
m-$C_6H_4ClCF_3$	138.4	−55.4	1.4466	21.2	1.336	9,165
p-$C_6H_4ClCF_3$	139.3	−34.0	1.4469	21.0	1.334	8,985
3,4-$C_6H_3Cl_2CF_3$	173.5	−12.3 to −12.5	1.4736	22.0	1.478	10,310

[a] Value obtained by F. Swarts.

Compound	Constants of Rankine equation *A*	*B*	*C*	Average deviation of calcd. values from obsd. values, mm.	Analyses, % Calcd. C	Calcd. H	Found C	Found H
$C_6H_5CF_3$	−2777.4	−6.166	26.153	±1.0	...	..	...	..
m-$C_6H_4FCF_3$	−2718.8	−5.589	24.575	±0.5	51.20	2.45	51.29	2.39
p-$C_6H_4FCF_3$	−1741.9	0.650	5.841	±0.8	51.20	2.45	51.40	2.45
o-$C_6H_4ClCF_3$	−2410.0	−1.752	13.149	±1.0	46.54	2.23	46.60	2.25
m-$C_6H_4ClCF_3$	−2698.0	−3.887	19.600	±0.7	46.54	2.23	46.32	2.30
p-$C_6H_4ClCF_3$	−3431.0	−8.193	32.627	±1.2	46.54	2.23	46.34	2.28
3,4-$C_6H_3Cl_2CF_3$	−2587.3	−1.719	13.229	±1.2	39.08	1.41	39.55	1.52

TABLE III

BOILING POINTS OF BENZOTRIFLUORIDE, BENZOTRICHLORIDE AND HALOGENATED DERIVATIVES

Parent compound	B. p., °C.	Chlorine derivative	B. p., °C.	Increase in b. p., °C.
$C_6H_5CF_3$	102.3	*o*-$C_6H_4ClCF_3$	152.8	50.3
		m-$C_6H_4ClCF_3$	138.4	36.1
		p-$C_6H_4ClCF_3$	139.3	37.0
		3,4-$C_6H_2Cl_2CF_3$	173.5	2(35.6)
$C_6H_5CCl_3$	212–213	*o*-$C_6H_4ClCCl_3$	260	47–48
		m-$C_6H_4ClCCl_3$	247–250	35–38
		p-$C_6H_4ClCCl_3$	248–250	36–38

The melting points of the compounds prepared in this investigation are in line with the generalization that the introduction of fluorine in place of hydrogen in the benzene ring lowers the melting point of the original compound. It should be noted that the chlorinated benzotrifluorides, with the exception of the ortho compound, have lower melting points than even the analogous chlorine derivatives of toluene, *o*-, *m*- and *p*-chlorotoluene, which melt at −34, −47.8 and 6.5 to 7.5°, respectively.

The latent heats of vaporization are in accordance with the values usually found in non-associated liquids of similar boiling points.

Summary

1. It was found that the best yields of benzotrifluoride were obtained when an excess of antimony trifluoride was distilled with benzotrichloride.

2. The preparation and properties of *p*-fluorobenzotrifluoride, *o*-, *m*- and *p*-chlorobenzotrifluoride and 3,4-dichlorobenzotrifluoride have been described.

3. The vapor pressures of benzotrifluoride, *m*- and *p*-fluorobenzotrifluoride, *o*-, *m*- and *p*-chlorobenzotrifluoride and 3,4-dichlorobenzotrifluoride were measured over temperature ranges.

4. The preparation and boiling point of *p*-fluorobenzotrichloride (unanalyzed) was described.

5. Two exhaustively chlorinated mixtures of benzotrifluoride were prepared.

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Fluorination of Halogeno Methyl Ethers. I. Fluorination of Trichlorodimethyl Ether

BY HAROLD SIMMONS BOOTH AND PAUL E. BURCHFIELD[1]

This paper describes an investigation of the fluorination of, and the fluorinated products of, trichlorodimethyl ether.

Experimental

Monochlorodimethyl ether was prepared essentially as described by C. Friedel.[2] Continuous streams of chlorine and dimethyl ether were introduced into a reaction tube, in which a sufficient excess of dimethyl ether necessary to prevent flashing was maintained. Monochlorodimethyl ether was further chlorinated according to the method of A. de Sonay,[3] with the formation of dichloro-, trichloro-, and tetrachlorodimethyl ethers. The chlorinated products were readily separated by fractional distillation.

Fluorination of Trichlorodimethyl Ether

One-half mole (75 g.) of trichlorodimethyl ether (b. p. 130.6 corr., 748 mm.) was refluxed for two hours with 100 g. (excess) of sublimed anhydrous antimony fluoride only. There was obtained, after washing with water and drying with barium oxide, 50 g. of a mixture boiling between 30 and 55.3°. The components of the fluorinated mixture were separated by fractional distillation in a modified Dufton column and the mixture was shown to consist of two volatile liquids, difluoromonochloro- and trifluorodimethyl ether.

Analyses

Difluoromonochlorodimethyl ether: Calcd. for $C_2F_2ClH_3O$: mol. wt., 116.4; C, 20.6; H, 2.59; Cl, 30.5. Found: mol. wt. (Victor Meyer), 119.0; C, 20.47; H, 2.46; Cl (Carius), 30.7.

Trifluorodimethyl ether: Calcd. for $C_2F_3H_3O$: mol. wt., 100.0; C, 23.9; H, 3.0. Found: mol. wt. (Victor Meyer), 102.7; C, 23.85; H, 2.96.

Qualitative tests revealed the presence of fluorine in each of the above compounds.

Physical Properties

The physical properties of the compounds reported in this paper were determined as described by Booth, Elsey and Burchfield,[4] and are found in Table I.

TABLE I

PHYSICAL PROPERTIES OF $C_2F_2ClH_3O$ AND $C_2F_3H_3O$

Compound	B. p., °C. (corr.)	M. p., °C.	ΔH at b. p. Calcd.	Sp. gr. 25°C.
$C_2F_2ClH_3O$	55.3	−105.1	7650	1.370
$C_2F_3H_3O$	30.1	− 96.2	6990	1.328

Constants of the Rankine Equation

	A	B	C	Av. deviation of calcd. values from obsd. values—mm.
$C_2F_2ClH_3O$	−1649	0.1686	7.479	±1.6
$C_2F_3H_3O$	−2405	−6.661	27.344	±1.2

These compounds have a very faint odor somewhat resembling chloroform. They do not fume in air, but slowly hydrolyze in water.

Attempted Preparation of Monofluorodichlorodimethyl Ether

Rapid reaction of trichlorodimethyl ether with antimony fluoride and calcium fluoride, respectively, gave no indication of a fluorinated compound boiling above 55.3° in either case. In this fact, that a monofluoro compound could not be made and that antimony fluoride would fluorinate it without a catalyst, trichlorodimethyl ether resembles benzotrichloride, which until now has been the only organic chloride in the literature with this behavior. It would be interesting to see whether trichloromethyl phenyl ether would behave in the same way.

Summary

The fluorination of trichlorodimethyl ether by anhydrous sublimed antimony fluoride without a catalyst yields a mixture of difluoromonochlorodimethyl ether, m. p. −105.1° and b. p. +55.3°, and trifluorodimethyl ether, m. p. −96.2° and b. p. +30.1°. These compounds are only slowly hydrolyzed in water.

CLEVELAND, OHIO RECEIVED AUGUST 16, 1935

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[1] Holder of the Westinghouse Fellowship in Chemistry, 1932–1934.

[2] Friedel, *Compt. rend.*, **84**, 247 (1877).

[3] A. de Sonay, *Bull. Acad. Roy. Belg.*, **26**, 629 (1893).

[4] Booth, Elsey and Burchfield, THIS JOURNAL, **57**, 2066 (1935).

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, NEW YORK CITY]

Transitions in Camphor and Chemically Related Compounds. I. Dipole Rotation in Crystalline Solids

BY W. A. YAGER AND S. O. MORGAN

The measurement of the dielectric constant may often provide a means of determining both the structure of molecules and the physical changes which take place in the material as it undergoes a phase change, either from liquid to solid or from one solid form to another. This paper points out how dielectric studies on certain solids have disclosed phase changes not heretofore known and how these phase changes contribute to our knowledge of dielectric behavior. In a companion paper[1] it is pointed out that the dielectric evidence of phase changes in these solids is confirmed by density and specific heat measurements and the nature of these changes is discussed in more detail.

The dielectric constant ϵ of a pure polar liquid which freezes sharply usually decreases abruptly, upon solidification, to a value equal to the square of the optical refractive index. For most organic materials this refraction value of ϵ is between 2 and 3. In nitrobenzene, an example of this class of material, which has been measured by several investigators,[2,3] ϵ decreases from 36 to 3 at the melting point, as a result of the inability of the polar nitrobenzene molecules to orient in the solid. The ability to orient is determined by the magnitude of the inner friction, which in normal crystalline solids becomes so high immediately on solidifying that orientation is impossible even at very low frequencies. Therefore in this class of materials the change from high to low ϵ is usually independent of frequency. In certain crystalline solids such as ice[4,5] and in some materials having water of crystallization,[6] as well as in substances such as glycerol[7] which solidify to glasses instead of crystallizing, the inner friction in the solid is still low enough to permit orientation at low frequencies. In these cases anomalous dispersion is always observed. Other crystalline solids are known in which the inner friction is so low that orientation is possible even at high radio frequencies. In these materials the dielectric constant characteristic of the liquid does not decrease to the refraction value at the freezing point but does so, without dispersion, at a lower temperature where a solid–solid transition occurs.

The significance of this behavior was made apparent by the work of Pauling[8] on the rotational motion of molecules in crystalline solids. As was pointed out by Pauling, the distinction between the two solid forms may be recognized, in the case of polar materials, by dielectric measurements. This fact has served both to explain the dielectric behavior of some crystalline materials and to provide a useful tool for the investigation of phase changes in solids. Since there are no very satisfactory criteria of the moments of inertia and intermolecular forces involved in the rotation of complex organic molecules, a convenient starting point for this dielectric investigation has been polar materials known to have solid–solid transitions. The work of Wallerant[9] on the crystal structure and Bridgman[10] on phase changes has shown that camphor is polymorphic. This paper discusses the interpretation of phase changes in camphor and some related compounds by means of dielectric measurements.

Experimental Details.—The experimental work to be described consists of measurements of the variation of dielectric constant and conductivity of camphor and some related compounds with frequency and temperature. The frequency range was from 1 to 100 kc. and the temperature range from liquid air temperature to somewhat above the melting points. Direct capacitance and conductance measurements were made with a capacitance bridge described by Shackelton and Ferguson.[11]

The original measurements on camphor in parallel plate and cylindrical condensers gave values of ϵ which were consistently about half those of corresponding measurements on pressed disks, due presumably to unusually great con-

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(1) White and Morgan, THIS JOURNAL, **57**, 2078 (1935).

(2) Smyth and Hitchcock, *ibid.*, **54**, 4631 (1932).

(3) Sun and Williams, *Trans. Am. Electrochem. Soc.*, **65**, 121 (1934).

(4) Errera, *J. Phys.*, [6] **5**, 304 (1924).

(5) Murphy, *Trans. Am. Electrochem. Soc.*, **65**, 133 (1934).

(6) Errera and Sack, *Trans. Faraday Soc.*, **30**, 687 (1934).

(7) Morgan, *Trans. Electrochem. Soc.*, **65**, 109 (1934).

(8) Pauling, *Phys. Rev.*, **36**, 430 (1930).

(9) Wallerant, *Compt. rend.*, **158**, 597 (1914).

(10) Bridgman, *Proc. Am. Acad. Arts Sci.*, **52**, 91 (1916).

(11) Shackelton and Ferguson, *Bell System Tech. J.*, **7**, 70 (1928).

traction on cooling from the liquid state, although precautions were taken to solidify the material as uniformly as possible. That the dielectric constant obtained for pressed disks of camphor was not due to any change produced by pressing was shown by a number of experiments on sheets pressed at different pressures, and by the fact that the high value was also obtained on a section cut from a cast specimen of the material. The dielectric data presented here are for pressed disks, except for camphoric anhydride, which pressed with such difficulty that recourse to melting the material into a cylindrical condenser was necessary.

Homogeneous disks 1.0 to 1.3 mm. thick and reasonably free from entrapped air were prepared by pressing the materials under 7.5 to 30 tons ram pressure in a 4.4 cm. circular mold. Tin foil disks were placed between the material and the plungers to facilitate removal from the mold and also to ensure good electrical contact between electrodes and dielectric. Two disks of each material, with tin-foil electrodes in place, were clamped one on top of the other between two brass disks 10 mm. thick and 6.35 cm. in diameter, by an arrangement of pins and springs as shown in Fig. 1. The object of the springs was to provide constant clamping pressure upon the disks of the dielectric so as to minimize void formation on cooling. The brass plates constituted the ground electrodes and the tin foil between the disks of dielectric the high tension electrode, which was connected to the bridge by a shielded lead insulated from the brass plates. The error due to edge effects in this arrangement was found to be negligible.

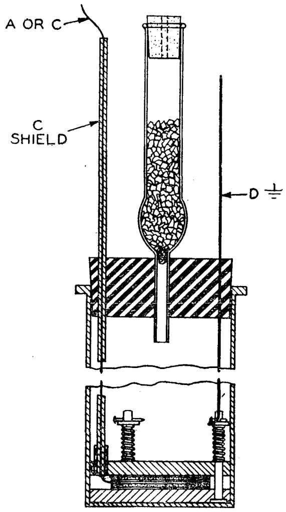

Fig. 1.—Arrangement of condenser for direct capacitance and conductance measurements on pressed disks of dielectric.

The cylindrical condenser employed for the measurements on camphoric anhydride is shown diagrammatically in Fig. 2. It was so designed that, by making direct capacitance and conductance measurements, all fixed and stray capacitances and conductances were eliminated.

The usual procedure in making preliminary measurements at low temperatures was to place the condenser containing the specimen in a Dewar flask, cool with liquid air, then remove the liquid air and allow the sample to warm up slowly. Capacitance and conductance were measured at 1 and 100 kc. alternately as the system warmed up, no attempt being made to hold the temperature constant. For bornyl chloride and *d*-camphor drifting measurements only were made with ascending temperatures. For the other materials measurements were made at constant temperature with both increasing and decreasing temperatures, the specimen being equilibrated in a simple liquid air thermostat. Good agreement was obtained between the values with a drifting temperature and those equilibrated at fixed temperatures. For measurements above room temperature an oil thermostat was used for the pressed disks and an aluminum block thermostat for measurements with the cylindrical condenser.

Materials.—The *d*-camphor was a refined commercial gum camphor which was recrystallized twice from absolute alcohol, dried and resublimed.

The *dl*-camphor was refined synthetic camphor from the du Pont Company and was used without further purification. A sample of refined synthetic camphor from the Eastman Kodak Company gave identical results and a sample of this camphor, which was recrystallized twice from alcohol and then resublimed, also gave the same dielectric constant, though slightly different dielectric loss.

Borneol and isoborneol from Fritzsche Brothers were measured as received.

d-Camphoric anhydride from Eastman Kodak Company was measured as received.

Eastman Kodak Company pinene hydrochloride (bornyl chloride)[12] was recrystallized from absolute alcohol and dried over calcium chloride.

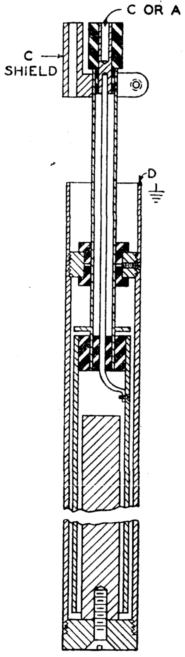

Fig. 2.—Cylindrical condenser for direct capacitance and conductance measurements on liquids or solids.

Experimental Results and Discussion

The temperature dependence of the dielectric constant of *d*-camphor is shown graphically in Fig. 3 for low temperatures. With descending temperature (Curve A) ϵ was found to increase to a maximum value of 14.9 at $-37°$. The temperature was maintained constant at $-37°$ for at least two hours, but ϵ retained its high value with no indication of falling off. On lowering the temperature a degree or two, however, ϵ decreased abruptly to a value of 2.82, which remained constant to liquid air temperature. With ascending temperature (Curve B) the same value of ϵ, independent of temperature, was observed up to $-32°$. At this temperature it increased rapidly to a maximum of 12.4 at $-25°$ and subsequently decreased with further increase in temperature. Within the experimental error the 1 and 100 kc. dielectric constants fall on the

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[12] According to Brooks, "Non-Benzenoid Hydrocarbons," p. 438, what is commonly called pinene hydrochloride, m. p. 127°, is bornyl chloride.

same curves with no evidence of an anomalous dispersion even in the transition interval. The conductance, which is a more sensitive test for anomalous dispersion, was low so that changes could not be followed through the transition interval due to inability to balance the bridge, because of the rapidly changing capacity. It can be safely said, however, that the variation in conductance, if any, was extremely small. The dielectric constant at 18 megacycles, measured at room temperature, was also found to agree with the value at lower frequencies. It appears, therefore, that the relaxation time of the polarization which accounts for the value of ϵ above the transition is less than 9×10^{-9} seconds at room temperature.

The fact that the transition occurred at −37° on cooling, but at −32° on heating, can probably be attributed to an overstepping of the transition point in both directions as is often observed in solid–solid transitions.[13] The curve a-b of Fig. 3 was obtained by continuing the measurements which gave curve B from the point b, going first in the direction of descending and then in the direction of ascending temperature. The points all fall on the same curve, showing that after completion of the change to the high temperature form there is no hysteresis above the transition temperature.

The abrupt change in dielectric constant of *d*-camphor at the transition is accompanied by a large change in heat content, as revealed by heating and cooling curves. The first break in the heating curve occurred at −32° and the second at −27°, checking remarkably well the range determined from the dielectric data. On cooling, the transformation began at −37° and was practically complete at −40°, again in good agreement with the dielectric data.

In 1914, Wallerant,[9] studying the crystallography of *d*-camphor, found that if it is made to crystallize by fusion it assumes four different states. Upon first solidifying the crystals are cubic, transforming into rhombohedral at 97°. Small crystals, also rhombohedral, then develop on these large crystals and are to be considered the stable form as an inverse transformation never takes place at any temperature. Since these new crystals are produced by crystalline supercooling, the transformation takes place near 90° instead of 97°. Finally at −28° these crystals are again transformed into very birefringent crystals which are also rhombohedral. Bridgman[10] found that *d*-camphor is polymorphic with six possible solid phases depending upon the temperature and pressure. At atmospheric pressure a solid–solid transition was found at 87°, and another in the neighborhood of −40°. The dielectric data for camphor serve to define the lower of these phase changes more clearly than the earlier work, but tell very little about the change near 90°.

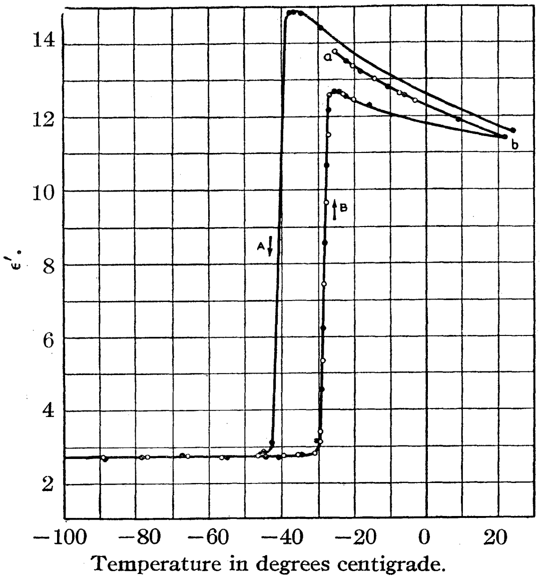

Fig. 3.—Dielectric constant of *d*-camphor as a function of temperature: Curve A, descending temperature; Curve B, ascending temperature. ○, 1 kc.; ●, 100 kc.

The temperature dependence of the dielectric constant of *d*-camphor at temperatures including the melting point and the transition in the neighborhood of 90° is shown in Fig. 4. A cylindrical condenser was employed for the measurements in the liquid state, and the disk condenser for the measurements in the solid state up to 168°. At these temperatures the vapor pressure of the camphor is so high as to cause excessive evaporation at the edges of the disks. To cover the range between 168° and the melting point (177.6°), the cylindrical condenser was again used, precautions being taken to solidify the material from the bottom up. The data up to 168° and above the melting point are shown as solid lines in the figure, and that of the intermediate region as dashed lines, there being some uncertainty as to the absolute values in this region.

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[13] Findlay, "The Phase Rule and Its Applications," Longmans, Green and Co., New York City, 1923, p. 27.

The dielectric constant of solid *d*-camphor was observed to decrease with increasing temperature in a manner very similar to that of polar liquids, where the decrease is supposedly due to decreasing density and greater hindrance to dipole orientation. Up to approximately 75° ϵ is practically independent of frequency (between 1 and 100 kc.) and the dielectric loss may be accounted for entirely by direct current conductance. Between 90 and 100°, where the rhombohedral crystals should be transformed to cubic crystals, there is still no discontinuity in the higher frequency curves but the 1 kc. curve shows a slight break.

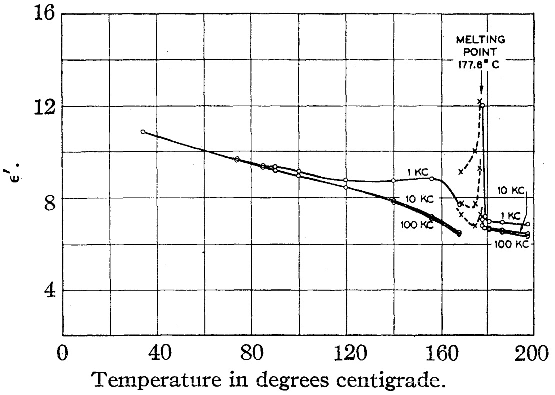

Fig. 4.—Dielectric constant of *d*-camphor as a function of temperature and frequency above room temperature.

The fact that ϵ at the higher frequencies decreases more rapidly as the melting point is approached than at lower temperatures, is probably due to the decrease in area of the test specimen as a result of evaporation. The 1 kc. value, although subject to the same percentage error, increases to a maximum at approximately 156° and then decreases rapidly. This maximum indicates the presence of an anomalous dispersion which, however, does not appear to be present at 10 and 100 kc. The conductivity data are too uncertain to assist in analyzing this behavior. In the neighborhood of the melting point there are two regions of anomalous behavior both of which are probably the result of interfacial polarizations due either to impurities or to the formation of two layers. The lower may be due to solid–air layers produced by contraction of the solid and the upper to the coexistence of a liquid and solid phase near the melting point.

Impurities present might give rise to a liquid phase just below the melting point but failure to attain temperature equilibrium is a more probable cause. As the system is allowed to cool gradually, a solid layer will form on the outer electrode giving in effect a two layer dielectric composed of a solid layer in series with a liquid layer. As cooling proceeds, the solid layer will increase in thickness at the expense of the liquid layer until the entire mass between the electrodes has solidified. The dielectric constants of the liquid and solid phases are essentially the same but the conductivity, γ, of the solid phase is less than that of the liquid phase so that the necessary condition for the existence of a Maxwell–Wagner interfacial polarization, namely, that $\epsilon_1\gamma_2 - \epsilon_2\gamma_1$ be either greater or less than but not equal to zero, is fulfilled. Furthermore, the conductivity is of the right order for the anomalous dispersion to occur in the frequency range of these measurements. It can be shown from the equations for a two-layer dielectric, that a behavior analogous to that observed may be obtained if the ratio of the thickness of the solid layer to the total electrode separation be allowed to increase progressively from 0 to 1. The reverse procedure of gradually heating the system through the melting point will give precisely the same results.

Apart from the uncertainties in the values near the melting point, the data indicate clearly that there is no appreciable change in value of ϵ for camphor on solidifying. They indicate that the same polarization which exists in the liquid state also is present in the solid. The melting point, usually supposed to represent the place where the molecules align themselves into a crystal pattern, does not introduce any appreciable interference with the ability of the molecules to orient. The restraint to rotation sets in at the transition point some 215° lower.

There is no evidence to indicate that any difference should have been expected between the dielectric properties of the natural *d*-camphor and the synthetic *dl*-camphor. Figure 5 shows that the two are very similar, though not identical. The transition for *dl*-camphor is displaced to lower temperatures, and ϵ undergoes but half the sharp drop shown by *d*-camphor at the transition. ϵ then decreases more gradually with descending temperature through a region of anomalous dispersion before finally reaching the state corresponding to the refraction polarization at −180°. There apparently is no temperature hysteresis in the region of anomalous dispersion as the data for ascending and descending temperatures fall on the same curves, but at higher temperatures a slight hysteresis appears, which is probably associated with the transition as in the case of *d*-camphor. The dielectric loss factor, ϵ', is shown for the region of anomalous dispersion below the transition temperature. At higher temperatures ϵ'' was too small to be significant.

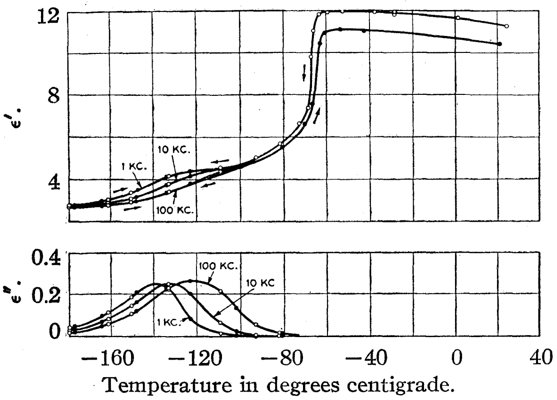

Fig. 5.—Dielectric constant and dielectric loss factor of *dl*-camphor as a function of temperature and frequency below room temperature; ●, ascending temperature; ○, descending temperature.

The anomalous dispersion below the transition was at first thought to be due to the presence of impurities. However, no systematic variation in ϵ'' with degree of purification was found. For a purified sample, which was recrystallized twice from absolute alcohol and then sublimed, ϵ'' was reduced somewhat in magnitude but by no means eliminated. The loss factor of a sample which, in addition to being recrystallized twice from absolute alcohol was recrystallized once from hexane, and subsequently sublimed, was higher than that of the unpurified sample and was shifted to somewhat higher temperatures. It appears that this dispersion below the transition is not entirely due to the presence of impurities in the usual sense of the term.

Heating and cooling curves for *dl*-camphor show breaks which are much less pronounced than those of *d*-camphor, in accord with the more gradual falling off of the dielectric constant in passing through the transition. From these data the transition interval appears to be between −65.7 and −66.7° on cooling and between −65.4 and −64.4° on heating, in fair agreement with the dielectric data.

A point of considerable interest is that the transition of *dl*-camphor occurs at a considerably lower temperature than that of *d*-camphor. Unpublished work in this Laboratory indicates that the transition of *d*-camphor is displaced to lower temperatures when it is one component of a solid solution, whereas its transition temperature is unaffected when it is one component of a eutectic mixture. This is in agreement with the usually observed behavior of transitions in metals. Whether or not the transition temperature is altered when it forms a compound with another material has not been determined. However, it appears that *dl*-camphor is either a racemic compound or a pseudo-racemic mixed crystal and[13] (p. 177) not a racemic mixture.

The dielectric data for samples of borneol and isoborneol are presented in Fig. 6. The data indicate a dielectric transition in borneol with a change in ϵ from 3.02 at 70° to 3.67 at 75°. The transition is less critical to temperature than those of the camphors as evidenced by the gradual increase in ϵ with temperature both above and below the transition proper. It is interesting to note that no temperature hysteresis was found in this case. There is also no evidence of an anomalous dispersion, between 1 and 100 kc., over the range of temperature shown, including the transition interval. Furthermore, ϵ'' and d. c. conductivity remained very low, even up to 100°.

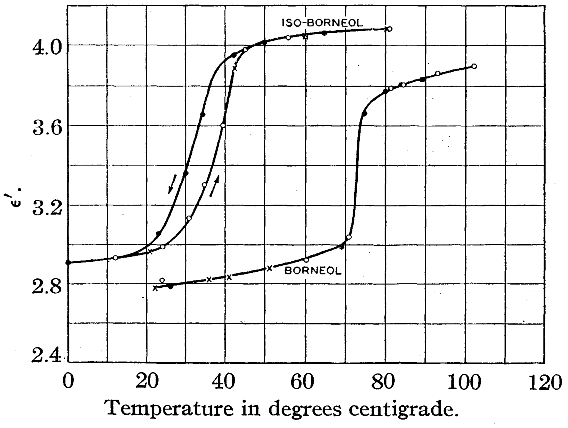

Fig. 6.—Dielectric constant of borneol and isoborneol as a function of temperature: x, ascending temperature—first run; ○, ascending temperature—second run; ●, descending run.

The data for isoborneol indicate a dielectric transition in which ϵ increases from 2.9 at 12° to 4.0 at 46° with a pronounced temperature hysteresis through this interval. There is no anomalous dispersion, between 1 and 100 kc., over the temperature range shown. In isoborneol also ϵ'' and the d. c. conductivity remain low, even up to 80°.

No transitions corresponding to those observed in borneol and isoborneol have been reported in the literature. As is shown elsewhere,[1] a change of volume accompanies this transition in both materials.

The fact that the dielectric constants of borneol and isoborneol decrease below their transition points to values somewhat higher than the refraction values (2.5 to 2.6) leads to further low temperature study of these materials. In both cases a second decrease of ϵ to the refraction value, and showing anomalous dispersion, was observed between about -50 and $-100°$. A similar small decrease of ϵ with a dispersion has also been observed in this Laboratory in other solids, particularly those having OH or OCH_3 groups. Since this change occurs at very nearly the same temperature in widely different compounds containing these groups it is believed that this is evidence of group rotation.

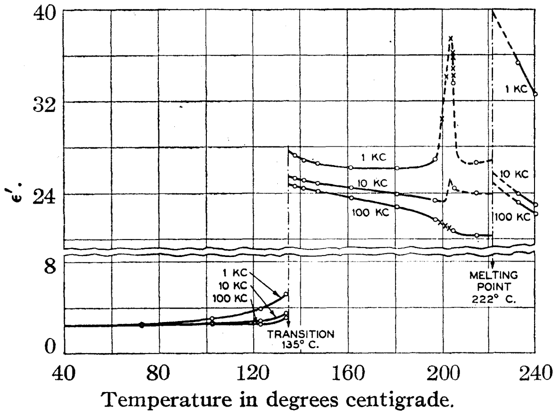

Fig. 7.—Dielectric constant of *d*-camphoric anhydride as a function of temperature and frequency.

The dielectric constant data for *d*-camphoric anhydride are presented in Fig. 7. They reveal a dielectric transition at 135°, at which ϵ suddenly increases, with no evidence of an anomalous dispersion, from a value of 3.2 to 24.8 at 100 kc., and to somewhat higher values at lower frequencies. Above 135° the dielectric constant at 1, 10 and 100 kc. shows the typical decrease with temperature characteristic of polar liquids, but between 190 and 210° some anomalous results are obtained. The 1-kc. dielectric constant increases rapidly to a maximum and then decreases again with equal rapidity. This anomalous behavior was much less pronounced at 10 kc. and apparently absent at 100 kc. The relative spacing of the 1, 10 and 100 kc. curves between 205° and the melting point suggests an anomalous dispersion. The d. c. conductivity in this range is so large as to mask the accompanying dielectric absorption so that the loss factor cannot be used to confirm the existence of the anomalous dispersion. At the melting point the dielectric constant increases somewhat, with no evidence of an anomalous dispersion, and exhibits the typical decrease with increasing temperature in the liquid state. There is, however, marked evidence of electrolytic polarization. The peculiar behavior of the dielectric constant some 20° below the melting point is similar to that observed for *d*-camphor about the same distance below the melting point. As in the case of camphor also, the change of ϵ at the melting point is so small compared to that at the transition as to indicate that dipole orientation is taking place in the solid, between the melting and transition temperatures.

The temperature dependence of the conductivity of *d*-camphoric anhydride is illustrated in Fig. 8. A discontinuity in the 1, 10 and 100 kc. curves is observed at both the transition and melting points, the conductivity increasing suddenly by a factor of approximately 10 in each case. However, the d. c. conductivity, measured with a microammeter after a one-minute application of 50 volts, apparently shows no discontinuity at the transition point. It seems, therefore, that the ionic conductivity which increases exponentially with temperature is essentially unaffected by the solid–solid transition. Above the melting point the conductivity is predominantly ionic and hence independent of frequency.

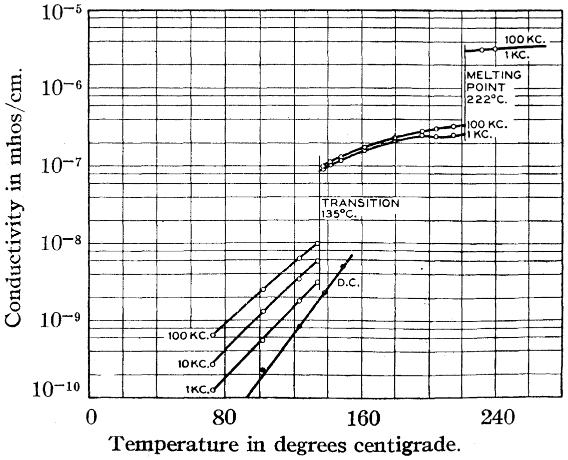

Fig. 8.—Conductivity of *d*-camphoric anhydride as a function of temperature and frequency.

The dielectric data for bornyl chloride are reproduced in Fig. 9. This behavior closely resembles that of *dl*-camphor, in that ϵ drops suddenly at the transition only part way to its refraction value and then passes through a region of anomalous dispersion with further decrease in temperature. ϵ'' curves of the same type as for *dl*-camphor are also obtained. The dispersion in bornyl chloride was very much altered by purification, a result contrary to that for *dl*-camphor. The unpurified sample showed an anomalous dispersion starting so close to the transition as to mask it.

The anomalous dispersion observed immediately below the transitions for *dl*-camphor and bornyl chloride probably arises from the restricted rotation of dipoles in the solid. Several causes of this restricted rotation suggest themselves. The initial decrease of ϵ without dispersion suggests that it may result from the separation of the material into two or more components, one of which has an inner friction of the correct magnitude to produce dispersion. Alternatively, it may be that following the transition of a part of the material to the low temperature form the resultant inner friction becomes large enough to restrict the rotation of the remainder. It must also be considered that the dispersion may be due to an interfacial polarization resulting from the existence of more than one solid phase. Since the free-ion conductivity of the solid phases is very low this explanation requires that there be a polarization conductivity of considerable magnitude. There appears to be little doubt that the high dielectric constants above the transition temperatures are a result of orientation of dipoles and that the inner friction opposing rotation is small compared to that below the transitions. The absence of an anomalous dispersion immediately above the transition temperature in the camphor compounds may be regarded as evidence of the sharpness of the change from the high temperature form, having low inner friction forces, to the low temperature form, where inner friction forces are too large to permit rotation.

The type of dielectric behavior described in this paper fits very closely into the picture provided by Pauling's theory. From consideration of the thermal properties, Pauling predicted that the polar hydrogen halides would have high dielectric constants in the solid state, the values and their temperature variation being those predicted by the Debye theory. Experimental study has confirmed this prediction.[14,15] In addition to hydrogen chloride, bromide and iodide this dielectric behavior has been reported for hydrogen sulfide, dimethyl sulfate and methyl alcohol.[16] All of these materials are known to show specific heat changes at their transition points, these changes, in fact, being used as an indication of expected dielectric constant change. The heat capacity measurements on the materials studied in this work, as far as they have been made, also show that a change of specific heat accompanies the solid–solid transitions.

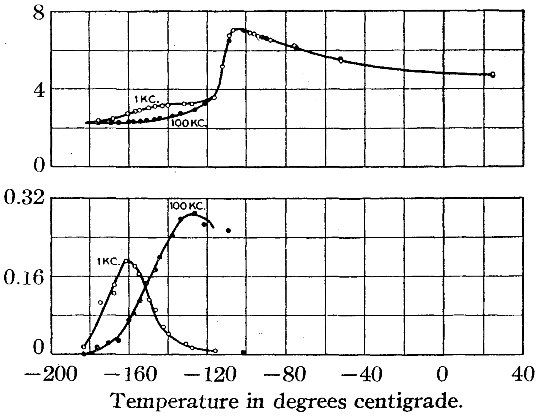

Fig. 9.—Dielectric constant and dielectric loss factor of bornyl chloride as a function of temperature and frequency.

The dielectric behavior of camphor and related compounds differs from that of many other crystalline solids, such as ice, for example, in the effect of frequency. In ice there is an anomalous dispersion at all temperatures below the freezing point. This has been observed by several experimenters.[2,4,5,17,18] Furthermore there is no discontinuity in the specific heat or density of ice which would lead to the prediction that the dielectric constant should change suddenly. It is to be expected that the gradual decrease in heat capacity and density would necessitate a gradual increase of the forces opposing dipole rotation and hence that anomalous dispersion should result.

The phase diagram of ice suggests the possibility that if the dielectric constant were studied with decreasing temperature at high pressure, a discontinuity might be expected at the temperature where a change from phase I to phase II takes place. This assumes that phase I is a high and

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(14) Cone, Denison and Kemp, THIS JOURNAL, **53**, 1278 (1931).

(15) Smyth and Hitchcock, *ibid.*, **55**, 1830 (1933).

(16) Hitchcock and Smyth, *ibid.*, **55**, 1296 (1933).

(17) Wintsch, *Helv. phys. acta*, **5**, 126 (1932).

(18) Oplatka, *ibid.*, **6**, 198 (1933).

phase II a low dielectric constant form, which seems probable.

The molar polarization of these materials likewise undergoes a change at the transition point and is a linear function of $1/T$ in the range between the transition and melting temperatures. This is in agreement with the prediction of the Debye dipole theory but nevertheless is of doubtful significance except as qualitative evidence that a dipole polarization is present in these solids. Qualitative evidence that dipole rotation is contributing to the dielectric constant is also given by the correlation between the magnitude of ϵ and the dipole moment. No values are available for the moment of camphoric anhydride but it is safe to predict that it is the highest of this group of materials, probably between 4 and 5 *D*. The moment of camphor, 2.7 *D*, is higher than either bornyl chloride or borneol, as is its dielectric constant.

Summary

A study of the dielectric properties of *d*-camphor, *dl*-camphor, *d*-camphoric anhydride, borneol, isoborneol and bornyl chloride has shown that these materials undergo solid–solid transitions. These transitions have not been previously reported in the literature, except for *d*-camphor. Above the transition the value of the dielectric constant of the solid is that normally expected of the polar material in the liquid state. Below the transition the dielectric constant has a low value, approximately equal to the square of the optical refractive index. This dielectric behavior is explained by the rotation of dipoles in the solid.

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[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, NEW YORK CITY]

Transitions in Camphor and Chemically Related Compounds. II. Vibration of Atomic Groups

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Introduction

In 1914 Wallerant[1] observed at −28° a transition of *d*-camphor from rhombohedral crystals of slight birefringence to similar crystals of pronounced birefringence, upon cooling. P. W. Bridgman[2] studied this transition at higher temperatures and pressures, and designated the solid phases stable above and below it as phase II and phase III, respectively.

Linus Pauling[3] has shown that some crystalline transitions accompanied by thermal phenomena may be explained by assuming that molecules or atomic groups begin to rotate at the transition when the crystal is heated. The possibility that a rise of molecular rotation is responsible for transitions occurring in crystals of complex organic molecules, as well as in the simple molecular lattices studied by Pauling, was the original subject of this investigation.[4] Activity was centered on the above-mentioned transition in *d*-camphor, at which dielectric constant undergoes a change similar to that predicted by Pauling for the transitions in crystals composed of simpler polar molecules.[5]

The molecule of *d*-camphor is so much more complex than that of hydrogen, which Pauling studied, that a mathematical discussion of the possibility of its rotation in the crystal would not be very informative. However, Pauling's theory suggests three lines of attack which should help to determine experimentally the mechanism responsible for the transition in *d*-camphor.

1. Heat capacity measurements through the transition should yield information as to any increase in mobility of units whose motion is restrained below the transition.

2. Specific volume and thermal expansion measurements should reveal any general loosening up of structure such as may accompany increased mobility of its units.

3. Dielectric measurements, interpreted in the light of the Debye[6] theory, should give some information as to the specific type of motion involved, and particularly as to whether the motion is rotational or translational.

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(1) Wallerant, *Compt. rend.*, **158**, 597 (1914).

(2) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **52**, 91 (1916).

(3) Linus Pauling, *Phys. Rev.*, **36**, 430 (1930).

(4) Yager and Morgan, THIS JOURNAL, **57**, 2071 (1935).

(5) Morgan, Yager and White, *ibid.*, **55**, 2171 (1933).

(6) Debye, "Polar Molecules," Chemical Catalog Co., New York City, 1929.

Experimental Work

Thermal Measurements.—A modified Nernst vacuum calorimeter, modeled on that described by Southard and Andrews,[7] but greatly simplified, was used in this work. Measurements were made by the continuous heating method of Deese.[8] A large lag of temperature of the sample behind that of the container, to which the thermocouples were attached, undoubtedly resulted. Neither this error nor that of calibration of the container was important in work where the significant data are the increase of heat capacity at the transition and the heat of transition. However, the heat capacity of Schering–Kahlbaum calorimetric naphthalene as determined in this calorimeter at intervals between −180 and 0° was found to differ from the values of Southard and Andrews[7] by no more than 5%, being always lower than their more accurate measurements. The direction of the error agrees with that found by Deese.[8] It was concluded that despite its simplicity this calorimeter was capable of determining the increase of heat capacity and the heat of transition of *d*-camphor with the accuracy required.

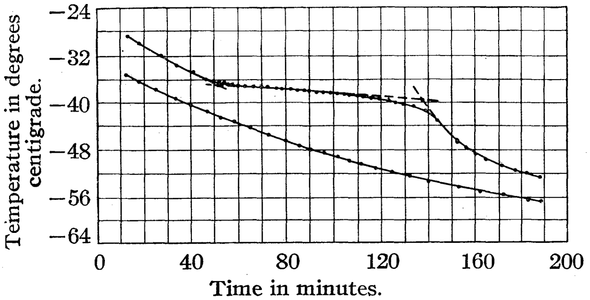

Fig. 1.—Cooling curve of *d*-camphor through the transition. The upper curve represents the temperature of the sample; the lower, that of the bath.

The *d*-camphor used in these measurements was purified as described by Yager and Morgan.[4]

Table I records the values of heat capacity found from the tangents of continuous heating curves taken at various temperatures and heating rates and for each phase of the *d*-camphor.

TABLE I

	t, °C.	V	C_p(cal./°C./mole)
Phase III	−56	1.86	39
	−49	1.86	42
	−40	1.86	40
	−31	1.86	40
		Average	40
Phase II	−30	1.57	58
	−28	1.39	59
	−16	1.86	58
	−14	1.86	58
		Average	58

The rate of heat input is proportional to the square of the applied voltage, which is listed in the third column of the table. The data show an increase of molar heat capacity of about 18 calories per degree accompanying the transition from phase III to phase II. The possibility that the high values observed in phase II are merely due to a further contribution of the heat of transition to the apparent specific heat is reduced by two considerations.

1. The heat capacity of phase II is relatively independent of temperature between −30 and −14°.

2. The value at −30° was obtained after cooling the sample only to −32°, where because of temperature hysteresis[4] the transition had not yet started. The cooling curve of the same sample shows in Fig. 1 that the transition does not begin above −36°. These data were not subject to temperature lag inasmuch as they were obtained with the thermocouple embedded in the sample.

The heat of transition was determined from continuous heating curves such as that illustrated in Fig. 2, where heat was applied to a sample of 6.871 g. of camphor at the rate of 0.1549 watt. The heat of transition was found from the time AB to be 1780 calories per mole. Two other measurements yielded the respective values of 1850 and 1950 for this quantity, whose best value was therefore taken to be 1860 calories per mole.

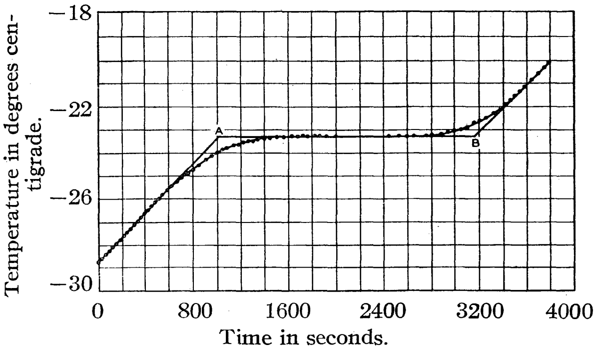

Fig. 2.—Calorimeter heating curve of *d*-camphor through the transition.

It will be noticed in Fig. 2 that the temperature of the transition as recorded thermally is about −23°, where Wallerant,[1] Bridgman,[2] and Yager and Morgan[4] place it between −28 and −40°. The difference is believed to be a rough measure of the temperature lag involved in making a continuous measurement in this calorimeter. Figure 3 shows, however, that the heat of transition thus determined falls on the same curve as those determined by the application of the Clapeyron–Clausius equation to Bridgman's data,[2] where the temperature of the transition is increased by the application of high pressures. This is regarded as evidence of the general accuracy of these thermal measurements.

Specific Volume.—A gas expansion volume meter similar in principle to that described by MacGee[9] was used to measure the specific volume of *d*-camphor through the transition. The apparatus differed from that of MacGee in that no mercury was allowed to enter the reference volumes, which were maintained at equal temperatures by means of a constant temperature bath. This modification was made necessary by the desirability of obtaining data below the freezing point of mercury. The random error of observation greatly exceeded errors from all other sources, being about ±0.5%.

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(7) Southard and Andrews, *J. Franklin Inst.*, **209**, 349 (1930).

(8) Deese, THIS JOURNAL, **53**, 3676 (1931).

(9) MacGee, *J. Am. Ceram. Soc.*, **9**, 817 (1926).

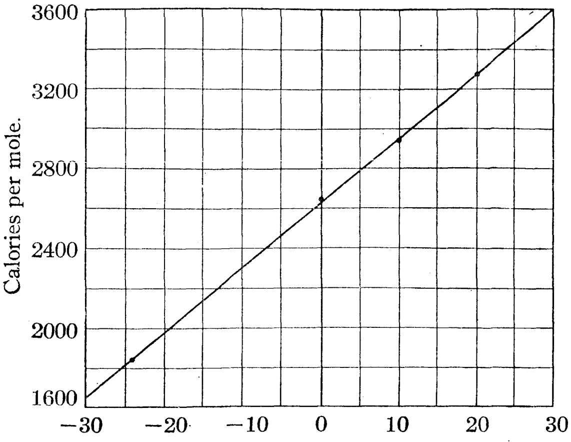

Fig. 3.—Heat of transition of *d*-camphor as a function of temperature.

The data thus obtained are represented in Fig. 4, and show a decrease of about 7% in the specific volume of *d*-camphor between −37 and −41°. The dielectric data are included for comparison. No temperature hysteresis of specific volume, analogous to those observed by thermal and dielectric measurements, could be detected. The discrepancy has not been satisfactorily explained, since equivalent precautions for obtaining thermal equilibrium were taken in the two series of measurements.

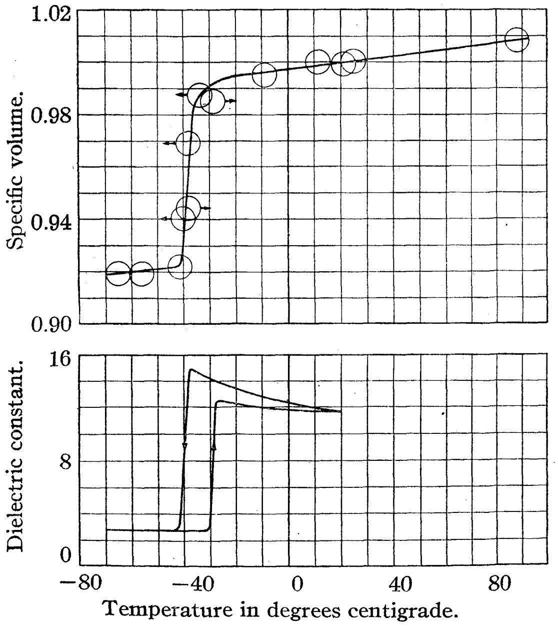

Fig. 4.—Specific volume of *d*-camphor compared with its dielectric constant.

Since dielectric measurements[4] had shown several closely related compounds to undergo dielectric transitions similar to that of *d*-camphor, the specific volume of these materials was measured in the hope of revealing a corresponding similarity in the behavior of this property. Figure 5 shows that a similar volume transition of about 4% is found in *dl*-camphor between −55 and −80°. Figures 6 and 7 portray data obtained for borneol and isoborneol by the much more sensitive method of observing the rise with temperature of a mercury meniscus in the calibrated capillary outlet of a dilatometer in whose bulb the sample had been solidified so as to be as free as possible from voids into which the mercury could not enter. Specific volume undergoes a small change at each of these transitions. The temperature hysteresis of dielectric constant observed in isoborneol[4] is reproduced by the specific volume data.

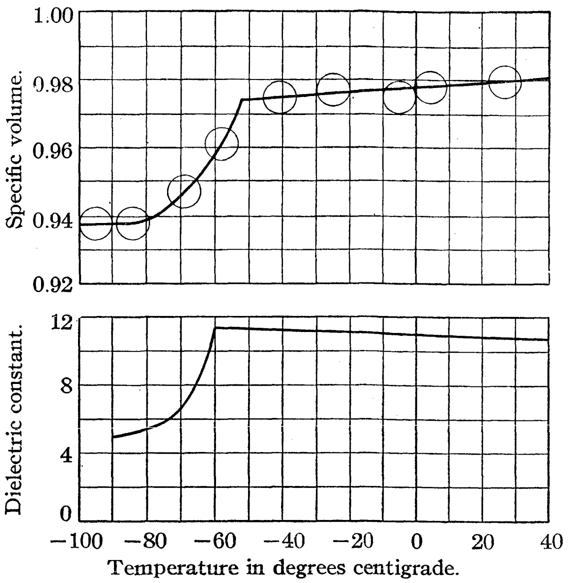

Fig. 5.—Comparison of specific volume and dielectric constant of *dl*-camphor.

Dielectric Measurements.—In seeking data on thermal transitions similar to that observed in *d*-camphor, it was found that in cyclohexanol there is a heat absorption of 1960 cal./mole and an increase of about five calories in C_p at a transition occurring at −10°.[10] Since these thermal data resemble those obtained for *d*-camphor, a corresponding similarity in dielectric properties was sought by measuring the variation of dielectric constant through this transition. Both cylindrical and parallel plate condensers were used to make grounded capacity measurements, which were in substantial agreement.

The results are shown for cyclohexanol in Fig. 8. Dielectric constant is, within the error of measurement, continuous through the melting point (+18°). It is possible to supercool phase I of the cyclohexanol far below the transition temperature;[10] below −25° an anomalous dispersion similar to that observed in supercooled liquids and involving nearly the whole polarization is observed. After the transformation to phase II, which occurred anywhere between −40 and −62°, heating failed to reverse the process until a temperature of about −25° was reached. Repeated distillation and drying of the cyclohexanol, which raised the melting point from 12 to 18°, and the boiling point to 161.0°, failed to change the upper temperature limit of this transition by any measurable amount. It is nevertheless thought to be essentially the

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[10] Kelley, THIS JOURNAL, **51**, 1400 (1929).

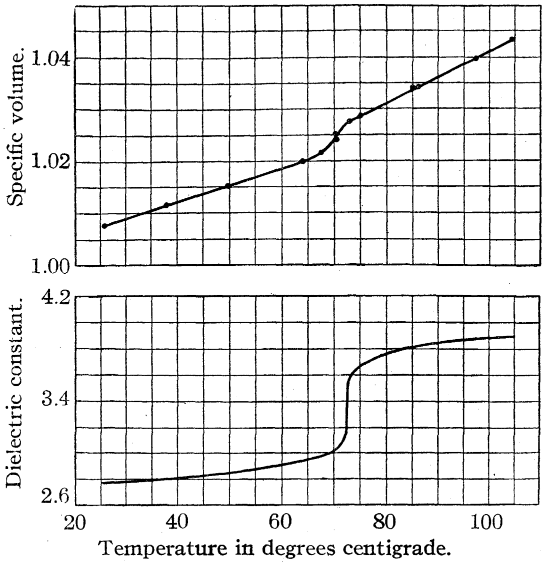

Fig. 6.—Specific volume and dielectric constant of borneol.

transition which Kelley[10] observed at −10°, especially considering the relative impurity of the samples as measured here; the melting point of the pure material is 24°, and its boiling point, 161.1°.

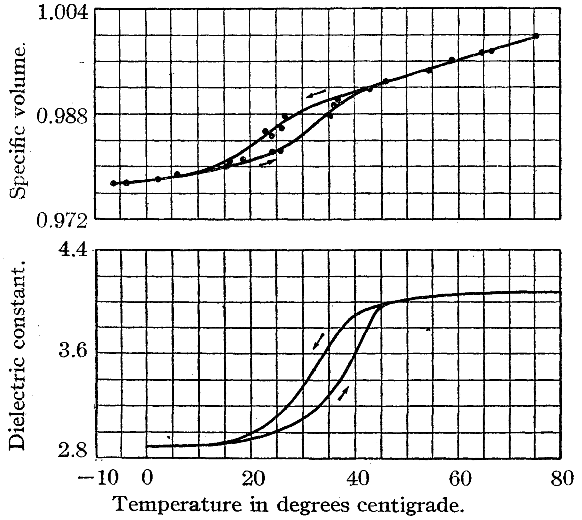

Fig. 7.—Specific volume and dielectric constant of isoborneol.

Measurements were also made on dilute solutions of the same sample of *d*-camphor in purified petroleum hexane, in order to calculate the dipole moment and atomic polarization of the *d*-camphor molecule according to the Debye theory.[6] Dielectric constant, density, and refractive index of each solution were measured by the method and with the equipment described by Morgan and Lowry.[11] Extrapolation of the refractive index measurements to low frequencies with respect to the optical showed the *d*-camphor to have as expected a molar refraction of 44.4 cc.

Density and dielectric constant data interpolated at 10° intervals from the experimental curves are plotted against concentration in Figs. 9 and 10. It is obvious that both variables are linear functions of concentration within the error of measurement. Thus it is possible accurately to calculate molar polarization of *d*-camphor at infinite dilution by the method of Hedestrand.[12] Such a calculation yields the curve of molar polarization against the reciprocal of absolute temperature shown in Fig. 11.

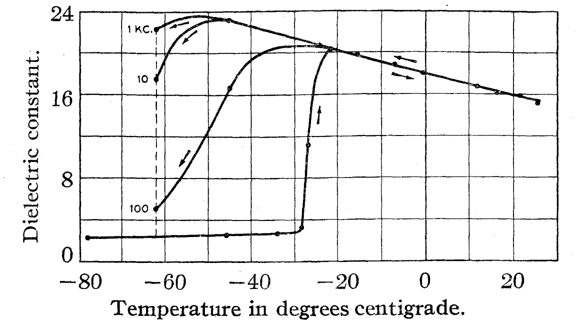

Fig. 8.—Dielectric constant of cyclohexanol as a function of temperature and frequency. The melting point of this sample is 18°.

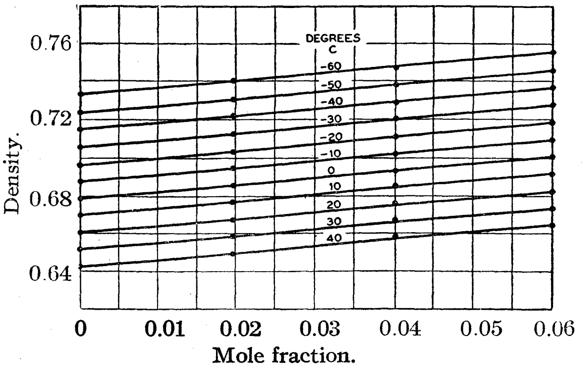

Fig. 9.—Density of solutions of *d*-camphor in petroleum hexane at various concentrations and temperatures.

Discussion of Results

From the theoretical point of view the significant increase of heat capacity at the transition in *d*-camphor is that at constant volume rather than the value experimentally determined at constant pressure. There are no compressibility data available for making the correction from C_p to C_v for the two phases of *d*-camphor. Andrews[13] has proposed the following approximation for this correction for organic lattices

$$C_p - C_v = 0.0214(T/T_M)\, C^2 \text{ (Molecule)}$$

where $C_p - C_v$ is expressed in calories per mole, C (Molecule) is the heat capacity at constant volume due only to translational and rotational

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[11] Morgan and Lowry, *J. Phys. Chem.*, **34**, 2385 (1930).

[12] Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929).

[13] Andrews, *Chem. Rev.*, **5**, 533 (1928).

oscillations of the unit molecules, T_M is the melting point of the crystal, and T is its absolute temperature. Assuming C (Molecule) as calculated by Andrews[13] for benzene to be roughly typical of all organic lattices whose molecules are of similar complexity, this quantity should reach its classical value of about 12 calories in the crystal of *d*-camphor at some temperature between −170 and −120°. If then T_M is the same in both phases of *d*-camphor, $C_p - C_v$ does not increase at the transition, and the change of C_v should essentially correspond with that of C_p, being about 18 calories.

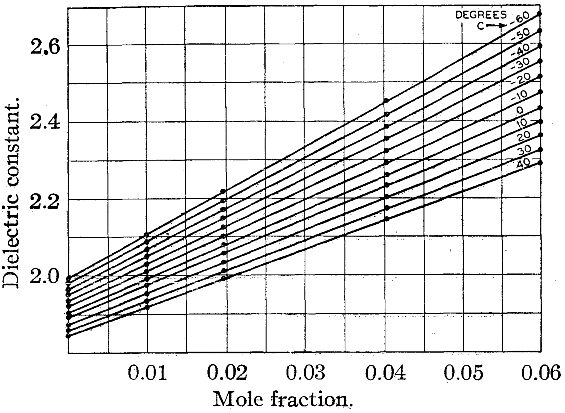

Fig. 10.—Dielectric constant of solutions of *d*-camphor in petroleum hexane at various concentrations and temperatures.

If the molecules of *d*-camphor are subject to a rotational oscillation capable, as inferred from Andrews' calculation for benzene, of absorbing heat above −120° at the classical rate of about six calories per degree per mole, the transition of this oscillation alone to free rotation should involve a decrease of specific heat, because of the loss of potential energy degrees of freedom. Even the transitions at much lower temperatures which are specified by Pauling[3] as involving molecular rotation are found to be characterized by only a very small increase of heat capacity. For example, the thermal transitions occurring at −174.6° in hydrogen chloride,[14] at −183.2° in hydrogen bromide,[15] at −207° in hydrogen iodide,[16] and −169° in hydrogen sulfide[17] all show a net increase of heat capacity of less than 1.5 calories per mole. Frenkel and his colleagues[18] have calculated that in hydrogen chloride the heat capacity should decline 1.32 calories per mole at the transition after correcting the observed values to constant volume. Each of the above-mentioned transitions involves so great an increase of dielectric constant over that normally observed in crystals that the rise of simple molecular rotation seems to be the best explanation.[19,20,21] It is therefore concluded that if C_v for *d*-camphor increases at the transition similarly to C_p, as has been assumed, the magnitude of this increase indicates that some change other than a simple rise of molecular rotation is occurring.

The observed heat of transition, 1860 calories per mole, also appears to be rather too large to be explained by the rise of molecular rotation alone. It is true that a three-dimensional molecule rotating in the crystal with so low an energy that its average potential and kinetic energy terms were nearly equal would have in the classical theory a total energy of $3RT$, which would be about 1500 calories per mole in *d*-camphor at 250 Å. However, all of this energy would have to be absorbed at the transition to explain the observed absorption of heat. This in turn would imply that below the transition temperature the rotational oscillation of the molecule is almost completely restrained. There is no reason to believe that this is true; Andrews' work[13] referred to above indicates that in the benzene crystal energy is absorbed by the degrees of freedom of rotational oscillation at the classical rate at tem-

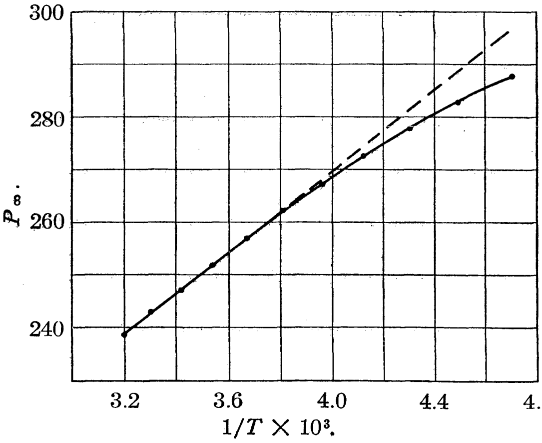

Fig. 11.—Molar polarization of *d*-camphor at infinite dilution as a function of reciprocal temperature (uncorrected).

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(14) Giauque and Wiebe, This Journal, **50**, 101 (1928).

(15) Giauque and Wiebe, *ibid.*, **50**, 2193 (1928).

(16) Giauque and Wiebe, *ibid.*, **51**, 1441 (1929).

(17) Clusius, *Z. Elektrochem.*, **39**, 598 (1933).

(18) Frenkel, Tode and Ismailow, *Acta Phys. U. R. S. S.*, **1**, 97 (1934).

(19) Cone, Denison and Kemp, This Journal, **53**, 1278 (1931).

(20) Smyth and Hitchcock, *ibid.*, **55**, 1830 (1933).

(21) Kemp and Denison, *ibid.*, **55**, 251 (1933).

peratures far below 250 Å. It therefore seems unlikely that the heat of transition can be completely accounted for by a rise of rotation of rigid molecules.

In terms of the current theory there is reason to believe that the rotation of so large and polar a molecule as *d*-camphor would not ordinarily be expected. Pauling's theory[3] shows that molecular rotation is unlikely where potential energy of restraint of molecular orientation and molecular moment of inertia are large. For a polar molecule Frenkel and his co-workers[18] state the potential energy to be

$$V = \mu E(1 - \cos \vartheta)$$

where μ is the dipole moment, at angle ϑ with the field E due to surrounding molecules. While nothing is known about E in the camphor crystal, μ is sufficiently large (at least 2.7 D) to indicate that the maximum value of V is not unusually small. On the other hand, the moments of inertia of the *d*-camphor molecule are far larger than those of the molecules which Pauling found able to rotate in the crystal. Mr. L. A. MacColl of these Laboratories has calculated the three moments of inertia of the camphor molecule from the accepted three-dimensional model, and finds the values 690, 600 and 510, all multiplied by 10^{-40} g. sq. cm. The moment of inertia of camphor about any axis of rotation is thus about 250 times as great as that of hydrogen chloride; molecular rotation in the crystal should therefore be considerably more difficult for the rigid *d*-camphor molecule than for hydrogen chloride, as far as the theory goes.

In general, any increase of C_v, at temperatures above 150 Å. and in crystals whose units are complex organic molecules, is due to atomic or group vibration within the molecule. When the heat capacity of such a crystal increases by about 50% it seems reasonable to ascribe most of that change to an abrupt increase of vibration of atoms or atomic groups. This should be particularly true when the molecule involved is completely saturated at all carbon to carbon bonds. Raman data show that vibration is more easily excited about single than about double bonds.[22] It is therefore proposed that unusually vigorous vibration of atoms or atomic groups arises in the molecule of crystalline *d*-camphor at the transition temperature.

If an increase of intramolecular vibration were the only significant mechanical feature of the transition in the *d*-camphor crystal, a certain increase of dielectric constant due to atomic polarization might be expected at the transition temperature, and a further large increase of dielectric constant due to free rotation of polar *d*-camphor molecules would be expected at the melting point of the crystal. Furthermore, the value of the atomic polarization would not in general be expected to decrease with increasing temperature.

Reference to the experimentally determined dielectric constant data for solid *d*-camphor[4] shows that neither of the above conditions is met. Dielectric constant rises sharply at the transition, subsequently declines rapidly with increasing temperature, and proves to be larger 20° below the melting point than immediately above it. These data lead Yager and Morgan to the conclusion that the dielectric properties of *d*-camphor in phase II are best explained by the assumption that the molecules rotate in the crystal lattice to much the same extent that they do in the liquid. Similarly, the dielectric constant of cyclohexanol, whose transition also seems to involve the rise of atomic vibration, changes so little at the melting point as to suggest that the rotation of polar molecules which is known to typify its liquid phase must continue below the freezing point.

The thermal data, dielectric measurements and Pauling's theory of molecular rotation in crystals may be reconciled by the following picture. As the crystal of *d*-camphor is heated through −30° the very marked increase of atomic vibration against reduced restoring forces suggested by the thermal data occurs rather generally throughout the crystal at the transition temperature. The accompanying reduction of the directional forces within the crystal should be large, as evidenced by a heat of transition larger than that of the fusion of *dl*-camphor[23] and by the 8% increase of specific volume. This reduction of internal forces together with the increased molecular pliability which should accompany the increased vibrational freedom would greatly reduce the magnitude of Pauling's potential hump $2V_0$, and permit the complex camphor molecules to rotate in the manner suggested by Pauling where molecules of more rigid structure might not be able to do so. This is of course only a rough

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[22] See, *e. g.*, Andrews, *Phys. Rev.*, **36**, 531, 545 (1930).

[23] Frandsen, *Bur. Standards J. Research*, **7**, 477 (1931).

working hypothesis, as a detailed mathematical consideration of such a picture would become extremely involved. It seems to be useful, however, when the solution measurements are examined in the light of its implications.

Figure 11 shows that the measured molar polarization of *d*-camphor in dilute solution varies with temperature above $-10°$ ($(1/T) \times 10^3 = 3.81$) as predicted by the Debye theory, according to which

$$P = P_e + P_a + B/T$$

P_e the electronic polarization or molar refraction and P_a the atomic polarization are assumed to be independent of temperature, while the polarization of the rotating dipoles is a linear function of the reciprocal temperature, with tangent B related to the dipole moment μ by the expression

$$\mu = 0.0127\sqrt{B} \text{ Debye units}$$

From the tangent observed above $-10°$ the dipole moment is found to be 2.51 Debye units and from the intercept at $T = \infty$ the sum of P_e and P_a is found to be 113.3 cc. Since P_e is 44.4 cc., the value of P_a in the temperature range -10 to $+40°$ turns out to be 69 cc.

Jenkins[24] has recently shown that dilute solution measurements yield spuriously high values of atomic polarization unless the effect of temperature on the dielectric constant of the solvent is taken into account. At any given temperature the polarization of *d*-camphor calculated from the data of Figs. 10 and 11 is found to obey a modified form of Müller's[25] empirical formula for its variation with dielectric constant of the medium

$$P = A - B(\epsilon - 1)^2$$

where P is observed total polarization of *d*-camphor in solution and ϵ is dielectric constant of the solution. The constant A is taken to be the value of the solute polarization after correcting for all effect of the solvent. Within experimental error B was found to be independent of temperature in the case of *d*-camphor, having the mean value 20.78. Using this value of B, the accurately determined polarizations of Fig. 11 were then corrected for the effect of the dielectric constant of the solvent by finding the respective values of A in equation (2). The results thus obtained are shown in the second column of Table II; the nature of the P *vs.* $1/T$ curve is unchanged, although the part above $-10°$ which is linear shows a dipole moment of 2.69 D and an atomic polarization of about 69.6 cc. for the *d*-camphor molecule.

TABLE II

T, Å.	P	$P_0 = 43{,}600/T$	P_e	$P_a = P - P_0 - P_e$
313	253.3	139.3	44.5	69.5
303	258.2	143.9		69.8
293	262.8	148.8		69.5
283	268.3	154.1		69.7
273	273.9	159.7		69.7
263	279.9	165.8		69.6
253	285.5	172.3		68.7
243	291.5	179.4		67.6
233	297.1	187.1		65.5
223	302.7	195.5		62.7
213	308.5	204.7		59.3

This atomic polarization is very much higher than any reported in the reliable literature,[26] and would be regarded with extreme suspicion if there were no corollary evidence of unusual atomic vibration in the camphor molecule. The hypothesis proposed above for the mechanism of the crystalline transition, however, would require even freer atomic group vibration in the molecule when in the liquid state than when in the crystal lattice, since the restraints of the crystal forces on this vibration are eliminated in the former case. Van Vleck[27] has concluded that atomic polarization is negligible in stable diatomic molecules, but not necessarily so in those which are polyatomic. For a diatomic molecule he finds the contributions of atomic polarization to the total dielectric constant to be inversely proportional to the square of the natural frequency of the vibration involved. Applying this relation to the polyatomic camphor molecule, it is evident that an unusually large atomic polarization is required by our hypothesis that the intramolecular vibration is opposed by small restoring forces and therefore has an unusually low natural frequency.

Below $-10°$ this interpretation of the polarization data agrees with our picture in that the total polarization begins to decline below the value to be expected if the number of atomic groups engaged in unusual vibrations, and hence total atomic polarization, remained constant. The rate of decline of atomic polarization with temperature may be estimated by assuming that in this temperature range dipole moment remains

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[24] Jenkins, *Trans. Faraday Soc.*, **30**, 739 (1934).

[25] Müller, *ibid.*, **30**, 729 (1934).

[26] Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., New York, 1931, pp. 163–168.

[27] Van Vleck, "Electric and Magnetic Susceptibilities," Oxford Press, 1932, p. 51.

constant, as seems reasonable, since in the *d*-camphor molecule the effect of any atomic vibration on the time mean square of dipole moment would presumably be of the second order. Table II shows that the rate of decline of atomic polarization thus calculated is, as would be expected, less than that of the transition in the crystal, and seems to indicate that the maximum rate of this decline will occur below −100°. In a similar way the transition of *d*-camphor in *dl*-camphor[4] occurs at a lower temperature and over a broader range of temperatures than in pure *d*-camphor.

Donle and Volkert[28] and Wolf[29] agree in calculating a dipole moment of about 2.95 Debye units for camphor; the former investigators find a total polarization at 22° of about 234 cc. At 22° Fig. 11 shows a total polarization of 248 cc. for *d*-camphor. These values are in fairly good agreement, and the discrepancy between the accepted value of 2.95 Debye units for the dipole moment of camphor and the value of 2.69 presented here for *d*-camphor is mainly due to the large value calculated for P_a in the latter case. The older data were all obtained at single temperatures, no attempt being made to measure atomic polarization.

It is obvious that without independent evidence of great atomic vibration in *d*-camphor, the above interpretation of the polarization data would not be necessary, and that even with the corollary evidence it should be accepted with considerable caution until verified by measurements of the temperature variation of polarization of other compounds undergoing a similar crystalline transition, such as borneol,[4] isoborneol,[4] cyclohexanol and cyclohexanone.

The thermal and dielectric data indicate that the transition observed in cyclohexanol is due to the same mechanism as is the transition in *d*-camphor. Data to be published in the near future show similar dielectric transitions occurring in solid cyclohexene, cyclohexanone and chlorocylohexane. Now it is well known that there is possible in the cyclohexane ring a type of atomic group vibration which involves large amplitudes and large energy absorption, and which furthermore cannot occur in the benzene ring. Mohr's[30] modification of Sachse's[31] theory of strainless carbon rings predicted that the *cis*-form of the basic cyclohexane ring should be pliable and subject to large linear and rotational vibration of the methylene groups, while the *trans* form should be rigid. The possible amplitude of vibration of groups 2, 4 and 6 with respect to the plane of groups 1, 3 and 5 in the *cis* form of the ring is illustrated in Fig. 12. Henriquez[32] has shown mathematically that these vibrations may occur without bending or stretching any carbon valences which are directed away from each other at tetrahedral angles. It would therefore be expected that such a vibration would be possible in polar cyclohexane derivatives of the *cis* form, and would involve immensely greater displacements than would vibrations of equal energy but opposed by the elastic restoring forces of the valence bonds. A pliable polar molecule of this type should be unusually subject to deformation in an electric field, and hence should exhibit a large atomic polarization independent of temperature. This vibration would apparently account for part of the value of 1.6 found by O. Hassel[33] for the moment of 1,4-cyclohexadione.

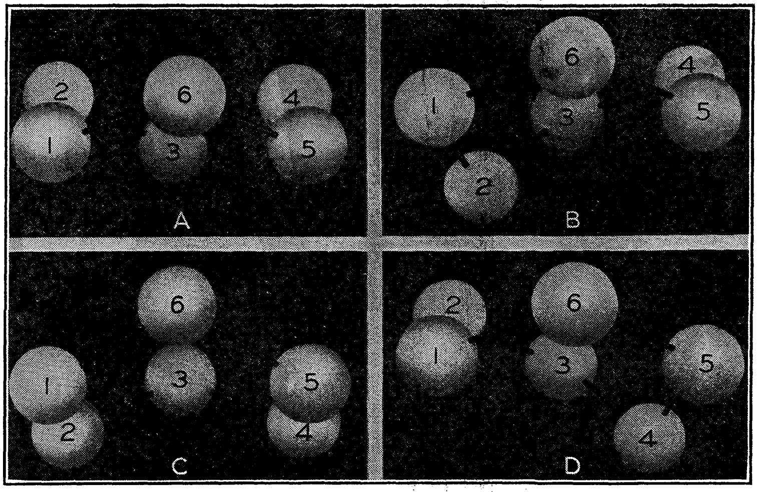

Fig. 12.—Strainless forms of the cyclohexane ring: A, the relatively rigid *trans* form; B, the pliable *cis* form obtained from A when atomic group No. 2 assimilates sufficient energy to change its position as indicated; C and D, further examples of the infinite series of equally probable configurations of the *cis* form.

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(28) Donle and Volkert, *Z. physik. Chem.*, [B] **8**, 60 (1930).

(29) Wolf, *Physik. Z.*, **31**, 227 (1930).

(30) Mohr, *J. prakt. Chem.*, [II] **98**, 315 (1918).

(31) Sachse, *Ber.*, **23**, 1363 (1890).

(32) Henriquez, *Kon. Akad. Weten. Amst.*, **37**, 532 (1934).

(33) O. Hassel, *Trans. Faraday Soc.*, **30**, 874 (1934).

The appearance of this vibration only above a transition in the cyclohexane derivatives would be explained if at low temperatures the *trans* form (Fig. 12) of the cyclohexane ring were the more stable. With rising temperature vibration of increasing amplitude might be expected to attain sufficient energy to carry some carbon over the potential hump between it and the pliable *cis* position. The difficulty of exciting atomic group vibrations should then decrease abruptly by a large factor, in line with the reduction of the Einstein parameter Θ. Absorption of energy and increased heat capacity would result. In a crystal the effect might spread from one molecule to another very rapidly, in the manner suggested by Pauling[3] for rotational transitions, because of the relaxation of crystal forces which might be expected to accompany a great reduction of the rigidity of the molecule, and an expansion of its "average volume." The same reduction of crystal forces should greatly facilitate the molecular rotation which is also believed to rise at the transition temperature.

An alternative possibility is that, even if the *cis* form were stable at the lowest temperatures, dipole forces, London forces and steric hindrance might prevent pliable rotation and vibration until a transition temperature was reached.

The accepted model of the *d*-camphor molecule is not pliable in the same sense as the cyclohexane ring, and hence gives very little indication of being subject to the type of extremely low frequency vibration required by our hypothesis. It is possible that the mechanical model does not reveal all types of vibration actually present in the molecule. However, the model does show that camphor contains a cyclohexane *cis* ring, whose tendency to pliable vibration would be elastically opposed only by the two bonds in the "bridge" of the molecule.

Summary

1. A rise of about 18 cal./°C./mole in the specific heat of *d*-camphor at the transition at −30° is observed and is explained by assuming that unusually energetic intramolecular vibration arises at the transition temperature.

2. The rise of molecular rotation at the transition which is evidenced by the dielectric data of Morgan and Yager is qualitatively explained in terms of Pauling's theory of molecular rotation in crystals, by assuming that the forces opposing this rotation are greatly diminished by a transition which reduces the rigidity of the molecules.

3. The behavior of total polarization of *d*-camphor in dilute solution is explained by assuming that at room temperature dipole moment is smaller and atomic polarization much larger than formerly supposed, and that the latter polarization begins to decline with temperature below −10° when the transition to the more rigid molecules begins.

4. Transitions very similar to that occurring in *d*-camphor are observed in crystals of derivatives of cyclohexane, whose carbon ring is supposed to be very pliable in the *cis* form and relatively rigid in the *trans* form. These transitions appear to be due to transformations from the rigid to the pliable forms of the molecules of which the crystals are composed.

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A Quantum Mechanical Discussion of Orientation of Substituents in Aromatic Molecules

BY G. W. WHELAND AND LINUS PAULING

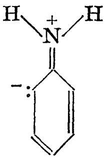
Introduction

When a substituent is introduced directly into an aromatic molecule, it may enter into certain of the available positions more readily than into others. This phenomenon of *orientation* has been exhaustively studied, and empirical rules have been found which describe the experimental results fairly satisfactorily. In a monosubstituted benzene C_6H_5R, for example, the introduction of a second substituent is governed by the nature of the atom or group, R, already present. Thus, for R = F, Cl, Br, I, OH, NH_2, and so on, the further substitution takes place largely in the ortho and para positions, while for R = COOH, CHO, NO_2, $(CH_3)_3N^+$, SO_3H, and so on, the substitution takes place largely in the meta position. Most ortho–para directing substituents, with the exception of fluorine, chlorine and bromine, activate the molecule so that the second substitution takes place more easily than in benzene itself. The meta directing substituents, on the other hand, produce deactivation. For other aromatic molecules similar rules have been found: in naphthalene substitution takes place largely at the α-position; in furan, pyrrole, and thiophene it takes place at the α-position; in pyridine it takes place at the β-position; and so on. In all the cases named except the last the molecule is more reactive than benzene.

Several qualitative theories have been proposed to explain the phenomenon of orientation, but of these we shall mention only a single one, which has been developed during the last fifteen years. This theory, which has achieved a considerable measure of success, and which we believe to be essentially correct, presents the following picture of the process of directed substitution. For definiteness we shall consider a mono-substituted benzene, since this is the type of molecule which has been most carefully studied from both the experimental and the theoretical standpoints. In the molecule C_6H_5R, with R attached to carbon atom 1, the electron distribution may be such as to place an excess or a deficiency of electrons on the various carbon atoms 2–6. Moreover, the electron distribution may be changed somewhat on the approach of a group R′ to one of the carbon atoms ("polarization" of the molecule by the group). We assume that *the rate of substitution of R′ for hydrogen on the* i*th carbon atom increases with increase in the negative charge of the* i*th carbon atom when the group R′ approaches it.* We thus take into consideration, in addition to the permanent charge distribution, the changes in it caused by the approaching group.

There are two principal ways in which the charge distribution is affected by the substituent R. The first, called the *inductive effect,* results when the electron affinity of this group is appreciably larger, or smaller, than that of the hydrogen atom which it replaces. Thus, for example, if its electron affinity is larger, it will attract to itself a larger proportion of the electrons which form the bond between it and the carbon atom. This carbon atom will accordingly be left with a small positive charge, compared with the others, and its own electron affinity will be correspondingly increased. Consequently, it will tend to appropriate some of the electrons belonging to its neighbors, and so on around the ring. The net effect is, then, a transference of negative electricity from the ring to the substituent R. In an analogous manner, if R has a smaller electron affinity than the hydrogen atom which it replaces, it will give up negative electricity to the ring. In order to obtain agreement with experiment, it is necessary to assume that the *o*- and *p*-positions are affected by this redistribution of charge to approximately equal extents, and that the *m*-positions remain nearly unaffected. This is at variance with the simple classical picture, which predicts the order ortho > meta > para, but it finds its explanation in the quantum mechanical treatment given later.

The second way in which the substituent R affects the charge distribution of the molecule is called the *resonance effect* (or sometimes the *tautomeric* or *electromeric effect*). This results when the molecule resonates among several electronic structures. For example, for aniline the structures



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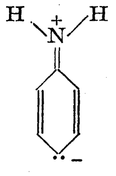

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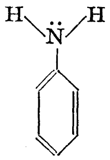
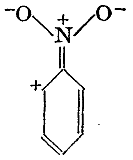


contribute to the normal state of the molecule, and for nitrobenzene



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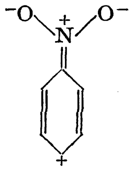

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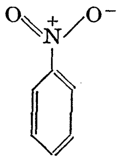
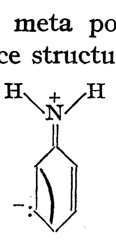


In the first molecule the resonance produces an increased concentration of electrons on the *o* and *p* carbon atoms, and in the second it produces a decreased concentration. As with the inductive effect, the meta positions remain nearly unaffected, since structures of the type



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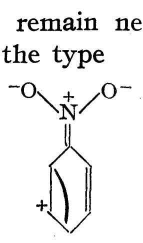

make relatively small contributions to the state of the molecule.

Some examples will illustrate the application of the theory to particular molecules. In toluene, the observed direction of the dipole moment shows that electrons have been transferred from the methyl group to the ring. Hence substitution takes place readily, particularly at the *o*- and *p*-positions, which have the greatest excess of electrons.

In nitrobenzene the nitro group has a large electron affinity, and accordingly draws electrons away from the ring. The resonance effect works in the same direction, and, as a result, all positions have a deficiency of electrons. The meta positions are least affected, and the substitution takes place there with difficulty. In aniline, the inductive effect and the resonance effect oppose each other, but the latter wins out, and very easy *o-p* substitution takes place.

These ideas have arisen through the combined efforts of a large number of different workers, among whom may be mentioned Fry, Stieglitz, Lapworth, Lewis, Lucas, Lowry, Robinson, and especially Ingold. For details the reader is referred to the excellent review articles of the last named author.[1]

With the development of a detailed quantum mechanical theory of the structure of aromatic molecules, it has become possible to attack the problem of orientation quantitatively. An attempt to do this was made by Hückel,[2] who showed that a polarizing substituent in benzene induces alternating charges in the ring. He limited his calculations, however, to the inductive effect, and neglected the resonance effect as well as the polarization of the molecule by the attacking group. As a result of these over-simplifications, he was led to make incorrect physical and chemical assumptions in order to obtain a rough correlation between his calculations and experiment. Thus, he assumed that "negative" groups, such as Cl, NH_2, and so on, increase the electron affinity of the attached carbon atom, while "positive" groups, such as NO_2, SO_3H, and so on, decrease its electron affinity. (Actually, all of the groups named tend to draw electrons away from the attached carbon atom, as far as the inductive effect alone is concerned, and hence to increase its electron affinity.) With this assumption, he then showed by a perturbation calculation that the negative groups induce positive charges on the *o*- and *p*-positions, while the positive groups induce negative charges there. This can be reconciled with the facts of orientation only if the ease of substitution is assumed to increase with increase of *positive* charge at the point of attack.

This is the exact opposite of the rule stated above, and appears to be in definite disagreement with other chemical evidence.[2] It is, furthermore, incapable of giving a consistent picture even of the process of orientation, as the following examples will show. (1) The observed direction of the dipole moment of toluene shows that electrons have been transferred from the methyl group to the ring. The methyl group is accordingly a positive one, in the sense of the foregoing discussion, and consequently should direct meta. Actually it directs ortho–para. (2) In pyridine the electron affinity of the nitrogen atom is larger than that of the carbon atoms. Consequently the charge distribution is the same as in benzene with a very strongly negative substituent. Substitution should accordingly take place in the α and γ positions (analogous to *o* and *p*) with great ease, but actually it takes place in the β position (analogous to *m*) with considerable difficulty.

The error in Hückel's treatment lies not in the quantum mechanical calculations themselves, which are correct as far as they go, but in the over-simplification of the problem and in the incorrect interpretation of the results. Consequently it has seemed desirable to us to make the necessary extensions and corrections in order to see if the theory can lead to a consistent picture. In the following discussion we have found it necessary to consider all of the different factors mentioned heretofore: the resonance effect, the inductive effect, and the effect of polarization by the attacking group. The inclusion of these several effects in the theory has led to the introduction of a number of more or less arbitrary parameters, and has thus tended to remove significance from the agreement with experiment which is achieved. We feel, however, that the effects included are all justified empirically and must be considered in any satisfactory theory, and that the values used for the arbitrary parameters are reasonable. The results communicated in this paper show that the quantum mechanical theory of the structure of aromatic molecules can account for the phenomenon of directed substitution in a reasonable way.

Outline of the Method

There are two principal methods available for the quantum mechanical treatment of molecular structure, the valence bond method and the molecular orbital method. In this paper we shall make use of the latter, since it is simpler in form and is more easily adapted to quantitative calculations.[3] We accordingly consider each electron

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(1) C. K. Ingold, *Ann. Rep.*, **23**, 129 (1926); *Rec. trav. chim.*, **48**, 797 (1929); *J. Chem. Soc.*, 1120 (1933); *Chem. Rev.*, **15**, 225 (1934).

(2) E. Hückel, *Z. Physik*, **72**, 310 (1931). For criticism of this work from the chemical side see A. Lapworth and R. Robinson, *Nature*, **129**, 278 (1932); **130**, 273 (1932); see also E. Hückel and W. Hückel, *ibid.*, **129**, 937 (1932).

(3) For purely qualitative arguments, on the other hand, the former is quite convenient. The description of the theory up to this point has been, in fact, merely a statement of the qualitative conclusions of the valence bond theory.

to be moving essentially alone in a self-consistent field, which is produced by the nuclei and by all the electrons other than itself, and we approximate the individual one-electron wave functions, φ_j, by means of linear combinations of the orbitals, ψ_k, belonging to the different atoms.

$$\varphi_j = \sum\nolimits_k a_{jk}\,\psi_k \qquad (1)$$

In systems of the type under consideration the aromatic rings lie in a single plane. Consequently the atomic s and p orbitals, ψ_k, to which the present discussion will be limited, can be divided into two classes, depending upon whether they are symmetric or antisymmetric with respect to reflection in this plane. Since orbitals from one of these classes do not combine with orbitals from the other, each of the summations of Eq. 1 needs to be extended only over the members of a single class. Electrons will of course be assigned to molecular orbitals, φ_j, of both types, but it will be sufficient for our purposes to consider only the ones which are formed from the antisymmetric atomic orbitals—the $[p]_h$ orbitals in Hückel's nomenclature. In energy calculations this is a legitimate simplification, since it affects merely the arbitrarily chosen zero point of energy, but in the present treatment it requires further justification, since we are now interested in the charge distribution. There is, however, considerable experimental evidence to show that π bonds, such as are formed by the $[p]_h$ orbitals, are much more polarizable than σ bonds, such as are formed by the symmetric orbitals. This is in accord with their smaller binding energy, and also with the fact that orientation phenomena are not common in saturated systems. Consequently we shall assume that the inclusion of the polarization of the symmetric orbitals would result in only a negligibly small correction.

We return now to those molecular orbitals, φ_j, of Eq. 1 which are expressed in terms of the $[p]_h$ functions. The variation method shows that the best values of the coefficients a_{jk} are those which satisfy the equations

$$\sum\nolimits_{k=1}^{l} a_{jk}\,(H_{mk} - \Delta_{mk}\,W_j) = 0,\ j, m = 1,2,\ldots,l \qquad (2)$$

where l is the total number of $[p]_h$ functions (one for each atom present, except the hydrogens);

$$H_{mk} = \int \psi_m^*\,H\psi_k\,d\tau \qquad \Delta_{mk} = \int \psi_m^*\,\psi_k\,d\tau$$

and W_j is the energy of an electron occupying the molecular orbital φ_j.

For each value of j there is a set of equations, but the different sets are all identical except for the replacement of the subscript j by some other, say j'. The condition for the solubility of this set of equations is that their determinants vanish. The l roots of this secular equation, $W = W_j$ $(j = 1,2,\ldots,l)$ give the energies of the l molecular orbitals. We then assign two electrons (one with positive and one with negative spin) to the lowest root, two more to the next lowest root, and so on until all have been used up. The values of W_j found in this manner are then substituted back into the Equations 2, from which the ratios of the values of the coefficients a_{jk} can be derived. The absolute magnitudes of the coefficients are determined by the normalization condition, $\int \varphi_j^*\,\varphi_j d\tau = 1$.

$$|H_{mk} - \Delta_{mk}\,W| = \begin{vmatrix} H_{11} - \Delta_{11}W & H_{12} - \Delta_{12}W & \cdots & H_{1l} - \Delta_{1l}W \\ H_{21} - \Delta_{21}W & H_{22} - \Delta_{22}W & \cdots & H_{2l} - \Delta_{2l}W \\ \cdots & \cdots & \cdots & \cdots \\ H_{l1} - \Delta_{l1}W & H_{l2} - \Delta_{l2}W & \cdots & H_{ll} - \Delta_{ll}W \end{vmatrix} = 0 \qquad (3)$$

An electron occupying the molecular orbital φ_j will spend a fraction of its time given by the expression $|a_{jk}|^2$ in the atomic orbital ψ_k. Consequently the total average charge on atom k will be

$$C_k = e\sum\nolimits_j |a_{jk}|^2 \qquad (4)$$

where the summation is extended over all occupied orbitals φ_j (the orbital being counted twice if occupied twice),[4] and e represents the charge of the electron.

As usual in these calculations, we make the following assumptions in regard to the magnitudes of the integrals H_{mk} and Δ_{mk}.

$$\begin{aligned} H_{kk} &= q + \delta_k\beta \\ H_{mk} &= \beta,\ \text{if } \psi_m \text{ and } \psi_k \text{ are on adjacent atoms,} \\ &= 0,\ \text{otherwise, for } m \neq k \\ \Delta_{kk} &= 1 \\ \Delta_{mk} &= 0,\ \text{for } m \neq k \end{aligned}$$

Here q represents the coulomb energy of an electron occupying a definite $[p]_h$ orbital in unsubstituted benzene; its value has been estimated to be about -2.7 v. e. = -60 kcal./mole.[5] β is a *resonance integral* between adjacent orbitals; its value has been estimated to be about -0.85 v. e. = -20 kcal./mole.[5] δ_k is a constant, the purpose of which is to allow for the different electron affinities of the different atoms. For $\delta_k > 0$, the

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(4) Strictly speaking, the complete eigenfunction for the molecule should be made antisymmetric before the charge densities at the various positions are calculated. It is easily shown, however, that this further refinement in the treatment does not alter the results obtained.

(5) G. W. Wheland, *J. Chem. Phys.*, **2**, 474 (1934).

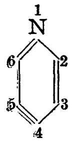
atom k has a larger, and for $\delta_k < 0$, a smaller electron affinity than a carbon atom in unsubstituted benzene.

We have attempted to estimate values of the δ's for the different kinds of atoms with which we will deal later, but we have not been able to arrive at any very consistent figures. Our procedure was to determine the values which would bring the calculated resonance energies into agreement with the empirical ones. The figures obtained in this way averaged about +4 for oxygen and +2 for nitrogen, and accordingly were of the correct sign, and of a reasonable order of magnitude, but the spread in both cases was quite large. Moreover, it is questionable if δ values obtained from energy calculations can be applied directly to calculations of charge distribution, when the method of treatment is as rough as the present. Accordingly we shall not choose a definite set of δ's which we shall use throughout, but instead shall allow the values to vary within fairly wide limits, in order to see the effect of such a variation upon the calculated polarization. Very fortunately it turns out that the decisive factor in most cases is not the magnitude of δ but its sign, which can be predicted with almost complete assurance.

Our method of calculation is now quite straightforward. We account for the permanent polarization resulting from the inductive effect by introducing suitable δ's upon the proper atoms; we account for that resulting from the resonance effect by explicitly including in the treatment all the $[p]_h$ orbitals of the problem, and not merely those on the atoms of the ring; and finally we account for the polarizing effect of the reacting group by introducing a small δ at the point of attack. For the sake of simplicity, we shall first treat only the permanent polarization, and then later consider the polarizability at the different positions.

Application to the Calculation of the Permanent Polarization

Pyridine.—We shall begin the discussion with pyridine rather than with a substituted benzene, since it offers a particularly simple example, in which only the inductive effect is operative. We number the atoms in order, beginning with nitrogen. Then δ_1, which takes into account the electron affinity of the nitrogen atom, will be positive in sign, and of the order of magnitude of perhaps 2; $\delta_2 = \delta_6$ will also be positive in sign as a result of induction, but will be much smaller in magnitude than δ_1; the remaining δ's can be considered negligibly small. The secular equation is then



$$\begin{vmatrix} x+\delta_1 & 1 & 0 & 0 & 0 & 1 \\ 1 & x+\delta_2 & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x+\delta_6 \end{vmatrix} = 0$$

where, for simplicity in writing, we have divided each row by β and set $(q-W)/\beta = x$. We cannot solve this equation rigorously unless we put into it definite numerical values for δ_1 and δ_2 $(=\delta_6)$. The perturbation theory, however, gives a method by which we can expand both the solutions, W_j, and the eigenfunctions, φ_j, in rising powers of the δ's. If we carry the procedure only as far as the first order, we obtain linear expressions which represent approximately the variation of the different quantities of interest for small values of the δ's. The unperturbed secular equation, which is obtained by setting $\delta_1 = \delta_2 = \delta_6 = 0$, is just the same as the one which arises in the treatment of benzene. Its roots are

$$W_j^0 = q + 2\beta \cos (2\pi j/6)$$
$$j = 1,2, \ldots, 6$$

and the corresponding wave functions are

$$\varphi_j^0 = \frac{1}{\sqrt{6}} \sum_{k=1}^{6} e^{(2\pi i/6)jk}\, \psi_k \qquad i = 1,2, \ldots, 6 \tag{5}$$

The familiar equations of the first order perturbation theory now show that the corresponding perturbed quantities are

$$\left.\begin{aligned} W_j &= \int \varphi_j^{0*} H \varphi_j^0\, d\tau = W_j^0 + \int \varphi_j^{0*} H' \varphi_j^0\, d\tau \\ \varphi_j &= \varphi_j^0 + \sum_k{}' \frac{\int \varphi_k^{0*} H' \varphi_j\, d\tau}{W_j^0 - W_k^0} \varphi_k^0 \end{aligned}\right\} \tag{6}$$

where H' is the part of the complete Hamiltonian operator which refers to the perturbation, such that

$$\left.\begin{aligned} \int \psi_k^* H' \psi_l\, d\tau &= \delta_1\beta \text{ if } k = l = 1 \\ &= \delta_2\beta \text{ if } k = l = 2 \text{ or } 6 \\ &= 0 \quad \text{otherwise} \end{aligned}\right\} \tag{7}$$

and the prime on the summation sign indicates that the term with $k = j$ is omitted. When Eqs. 5 and 7 are inserted in Eq. 6 and use is made of Eq. 4, the following results are obtained.

$$C_N = C_1 = \left(1 + \frac{43}{108}\delta_1 - \frac{17}{54}\delta_2\right)e$$

$$C_\alpha = C_2 = C_6 = \left(1 - \frac{17}{108}\,\delta_1 + \frac{22}{54}\,\delta_2\right) e$$
$$C_\beta = C_3 = C_5 = \left(1 + \frac{1}{108}\,\delta_1 - \frac{14}{54}\,\delta_2\right) e$$
$$C_\gamma = C_4 = \left(1 - \frac{11}{108}\,\delta_1 + \frac{1}{54}\,\delta_2\right) e$$

(neglecting terms in δ_1^2, $\delta_1\delta_2$ and δ_2^2). These figures differ somewhat from the corresponding ones given by Hückel,[2] because he put $\delta_2 = 0$ and also, in applying the perturbation treatment, he made use of a rather different procedure which so complicated the calculations that he did not carry them through completely.

If, now, δ_2 lies within the limits $^1/_{28}\,\delta_1 < \delta_2 < ^1/_4\,\delta_1$, which seem quite reasonable, the over-all effect of the perturbation is a transference of negative electricity from the various carbon atoms to the nitrogen atom at position 1, with the consequence, in accordance with the rule formulated above, that the molecule is deactivated so that substitution is more difficult than in benzene; and furthermore the α and γ positions (2 and 6, and 4, respectively) are most affected by this transference of electricity, so that substitution will take place at the β positions (3 and 5), which have the smallest deficiency of electrons. Both of these conclusions are borne out by experiment.

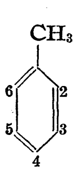
This calculation and its comparison with experiment hence provide us with a rough idea as to the magnitude of the inductive effect from atom to atom, as given by the ratio δ_2/δ_1. If this ratio were greater than $^1/_4$ the effect of δ_2 would overcome that of δ_1 and pyridine would substitute in the α and γ positions, whereas if it were less than $^1/_{28}$ substitution would occur in the β positions more readily than in benzene. A value of about $^1/_{10}$ for δ_2/δ_1 seems reasonable to us from a consideration of the electronic phenomena involved.

In order to see how accurate this perturbation treatment actually is, we have substituted numerical values for the δ's directly into the secular equation, and then solved it rigorously by numerical methods. The calculations are not given in detail, since they are quite straightforward and proceed along well-known lines. The results are shown in Table I.

TABLE I

δ_1	1	2	3	2
$\delta_2 = \delta_6$	0	0	0	0.2
$C_N = C_1$	1.37e	1.62e	1.79e	1.59e
$C_\alpha = C_2 = C_6$	0.85	0.76	0.71	0.83
$C_\beta = C_3 = C_5$	1.01	1.01	1.01	.96
$C_\gamma = C_4$	0.91	0.84	0.79	.82

It is seen that for $\delta_1 = 1$ the perturbation treatment is still fairly accurate, but that for larger values it is only qualitatively satisfactory. In any case, however, if we assume that the ease of substitution increases with increased negative charge at the point of attack, the calculations are in very good agreement with experiment; if, on the other hand, we follow Hückel in making the opposite assumption, the calculations can be reconciled with experiment only by making δ_1 negative, which seems highly improbable in view of the fact that the nuclear charge of nitrogen is greater than that of carbon.



Toluene.—The toluene molecule is complicated in that it contains atomic orbitals (in the methyl group) which are neither symmetric nor antisymmetric with respect to reflection in the plane of the ring. However, since it seems very unlikely that there will be any appreciable resonance between the methyl group and the ring, we are able to avoid the difficulty by formally replacing the substituent by a small δ value on the adjacent carbon atom. The dipole moment of the molecule requires that this δ be negative in sign. It is also presumably small enough so that the same perturbation treatment as was employed in the case of pyridine will represent a good approximation.[6] The results are then just the same as those given in Eq. 8, except that C_α, C_β, and C_γ are to be replaced by C_{ortho}, C_{meta}, and C_{para}, respectively, in order to be in accord with the customary nomenclature. Here, as before, all the the δ's except δ_1 and δ_2 can be set equal to zero. Since δ_1 is negative, we see, neglecting δ_2, that the ortho and para positions have excess negative charges, in agreement with the experimental result that substitution takes place there very readily. This result is not changed by the consideration of δ_2 so long as the ratio δ_2/δ_1 is less than $^1/_4$.

Phenyltrimethylammonium Ion, $N^+(CH_3)_3$-C_6H_5.—In this ion, as in toluene, we ignore the electrons involved in bonds from nitrogen to the attached groups, and consider only the inductive effect. The positive charge on the nitrogen atom increases its electron affinity to a value still greater than that for neutral nitrogen, so that we

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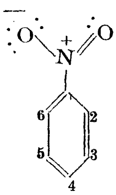
(6) For larger δ values, the results for toluene can be read off at once from those for pyridine (Table I); reversing the sign of the δ's in a given secular equation of the present type merely reverses the direction of the induced polarization, and leaves its magnitude unchanged.

introduce in the above expressions (for toluene) a large positive value for δ_1 (and a small value for δ_2). This leads to greatly decreased values of C for ortho and para carbon atoms, with smaller decrease for meta, and in consequence to meta directed substitution, in agreement with experiment.



Nitrobenzene.—In the treatment of nitrobenzene we must consider nine $[p]_h$ orbitals and ten electrons, including an unshared pair on the negative oxygen atom in the indicated structure and one electron for each of the remaining atoms. We assume the resonance integral β to have the same value for O-N and N-C as for C-C. The results of the calculation are given in Table II, the next to the last column of which corresponds to the δ values which seem reasonable to us. It is seen that all positions are deactivated, the deactivation occurring least at the meta positions, where substitution should take place. These conclusions are in agreement with experiment.

TABLE II

δ_O	0	0	4	4	4
δ_N (δ_C)	0	2	2	2	0.8
δ_1	0	0	0	0.2	0
C_O	1.50e	1.24e	1.95e	1.94e	1.92e
C_N (C_C)	1.00	1.53	1.37	1.32	0.68
C_1	1.00	0.96	0.62	0.70	.95
$C_{\text{ortho}} = C_2 = C_6$	1.00	1.01	.79	.79	.85
$C_{\text{meta}} = C_3 = C_5$	1.00	1.00	.95	.95	1.00
$C_{\text{para}} = C_4$	1.00	1.01	.63	.61	0.83

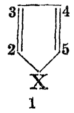
Benzoic Acid, C_6H_5COOH.—The treatment of benzoic acid is the same as for nitrobenzene except for the δ values. The results for $\delta_O = 4$ and δ_C (of the carboxyl group) $= 0.8$ are given in the last column of Table II; it is seen that the carboxyl group, like the nitro group, is meta directing, in agreement with experiment. The calculation, however, indicates a rather too small deactivation of the meta position. This effect appears only in the third decimal place of C_{meta}, and is consequently not shown in the table.

Benzaldehyde, C_6H_5CHO, **Acetophenone,** $C_6H_5COCH_3$, **and Benzonitrile,** C_6H_5CN.—The results obtained for these molecules by considering eight $[p]_h$ orbitals and eight electrons are given in Table III.

It is seen that the aldehyde, ketone and nitrile groups are all meta directing, in agreement with experiment.

TABLE III

δ_O (δ_N)	0	2	2	4	4
δ_C	0	0	0.2	0	0.4
$C_O(C_N)$	1.00e	1.76e	1.75e	1.92e	1.92e
C_C	1.00	0.49	0.55	0.41	0.56
C_1	1.00	1.03	1.02	1.02	.98
$C_{\text{ortho}} = C_2 = C_6$	1.00	0.90	0.89	0.88	.85
$C_{\text{meta}} = C_3 = C_5$	1.00	1.00	1.00	1.00	1.00
$C_{\text{para}} = C_4$	1.00	0.91	0.90	0.87	0.85

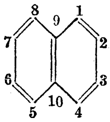


(X = O, S, NH)

Furan, Thiophene, Pyrrole.—The calculations for this case, with five orbitals and six electrons, show that when $\delta_2 (= \delta_5)$ (on the α carbon atoms) is neglected the β positions (3 and 4) are more strongly activated than the α. When, however, these δ's are given a reasonable magnitude, greater than $^1/_{25}\ \delta_1$, the situation is reversed, and the α positions are found to be the more strongly activated, as is demanded by experiment. Some calculated charge values are given in Table IV.

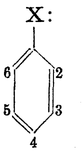
TABLE IV

δ_1	0.5	2.9	4	4	2	3
$\delta_2 = \delta_5$	0	0.29	0	0.5	0.25	0.375
$C_X = C_1$	1.38e	1.80e	1.88e	1.87e	1.69e	1.81e
$C_\alpha = C_2 = C_5$	1.14	1.08	0.98	1.13	1.10	1.13
$C_\beta = C_3 = C_4$	1.18	1.02	1.08	0.93	1.06	0.96



Naphthalene.—Naphthalene offers the first example of a molecule in which a consideration of the permanent polarization alone does not lead to the correct answer. Since this is a hydrocarbon, we might expect that no δ values would be necessary. In this case, however, the charge on each atom is found to be exactly 1.00e, so that substitution would take place at the α and β positions (1, 4, 5, 8 and 2, 3, 6, 7, respectively) with equal ease. If we attempt to avoid this difficulty by putting a δ upon the 9 and 10 carbon atoms, we find that its sign must be negative in order to produce an excess of electrons on the α positions. This seems unreasonable, however, since these carbon atoms carry no hydrogens, and would consequently be expected to have a larger rather than a smaller electron affinity than the others. We shall see later that a possible explanation of this discrepancy can be found by a consideration of the polarizing effect of the attacking group.

Aniline, Phenol, Fluorobenzene, etc.—The treatment of this group of molecules, involving seven $[p]_h$ orbitals and eight electrons, is comparatively unsatisfactory, in consequence of the fact that in them the inductive and the resonance effects work in opposite directions. In order to be able to predict which of the two will win out in any specific example, we need to have fairly accurate numerical values of the different δ's to be introduced in each case. In the absence of such information, the best we can do is to carry through a number of calculations, in order to see if any reasonable sets of values lead to agreement with experiment. The results are given in Table V.

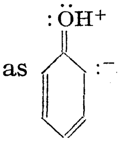
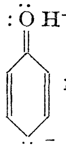


($X = NH_2$, OH, F, etc.)

TABLE V

δ_X	0	2	4	6	2	4	6
δ_1	0	0	0	0	0.25	0.4	0.5
C_X	1.57e	1.91e	1.96e	1.98e	1.91e	1.97e	1.98e
C_1	1.00	0.93	0.95	0.95	1.02	1.10	1.15
$C_{\text{ortho}} = C_2 = C_6$	1.14	1.06	1.04	1.02	1.02	0.97	0.95
$C_{\text{meta}} = C_3 = C_5$	1.00	1.00	1.00	1.00	1.00	1.00	1.00
$C_{\text{para}} = C_4$	1.14	1.05	1.02	1.02	1.02	0.98	0.96

It will be seen that, as might be expected from purely qualitative considerations, the inductive effect, which deactivates the molecule and favors *m* orientation, is increased in importance with increase of the δ's, while the resonance effect, which activates the molecule and favors *o-p* orientation, is decreased in importance. This is in agreement with the fact that the *o-p* directing power of the halogens is in the order $F < Cl < Br < I$, which is the opposite of the order of electron affinities. On the other hand, it does not explain the marked difference between the halogens as a whole and the amino and hydroxyl groups—the former being relatively feeble in orienting power, and the latter being among the most powerful known. It also does not explain why the orders $NH_2 < PH_2 < AsH_2$ and $OH < SH$, which would be expected from analogy, are not correct.

It is possible that the explanation of these discrepancies is to be found in the fact that the resonance integral, β, may vary with the row and group of the periodic table. Such a variation must almost certainly exist, but it can be taken into account only with difficulty. Furthermore, the introduction of the large number of additional arbitrary parameters would deprive the whole procedure of much of its significance. A second possible explanation is that, with phenol for example, resonance with such structures as  and  may make relatively important contributions to the state of the molecule. The inclusion in the theory of such effects also would be difficult and would result in a further decrease in the significance of the treatment. Instead of resorting to such heroic measures to force the calculations into agreement with experiment, we prefer to let the matter stand as a possible weakness of the theory. It would not be surprising if our rough treatment should fall down in evaluating the relative importance of two opposed effects which differ so greatly in nature.

A further difficulty in the case of fluoro-, chloro- and bromobenzenes is that with them apparently no choice of the δ values seems to be reconcilable with the observed order of ease of substitution at the various positions: unsubstituted benzene > para > ortho > meta. Both the inductive and the resonance effects are seen to leave the charge on the *m*-position practically unchanged, and approximately equal to 1.00e, while the observed order demands a considerably smaller value. As in the case of naphthalene, however, we shall find later that this discrepancy can apparently be explained by taking into account the polarization of the molecule by the attacking group.

Polarization by the Attacking Group

The calculations so far have been concerned with the "permanent" charge distribution which the molecule would have when isolated, and which would be observed in its dipole moment. The factor that actually determines the orientation of the entering group, however, is the charge distribution at the instant of attack, which differs from the permanent charge distribution in consequence of polarization by the entering group. In most cases it is not necessary to take this latter effect into account explicitly, since it represents only a small correction. However, in certain cases it is apparently of decisive importance.[7]

In order to investigate the relative ease of substitution at the ith carbon atom, we shall introduce a small δ_i upon that atom, in addition

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[7] This was suggested originally by Ingold, *cf.* Ref. 1.

to any other δ's that may be required by the permanent polarization. This δ_i will presumably be positive in sign in all cases, since the customary reacting groups are "electron-seeking" and will accordingly tend to increase by induction the electron affinity of the near-by carbon atom.

In benzene itself the charge at the point of attack will be not 1.00*e*, as has been assumed heretofore, but $(1.00 + (43/108)\delta_i)e$. (Since δ_i is small, the results of the perturbation treatment can be applied directly.) In other molecules the ease of reaction at the *i*th carbon atom will then be greater than that of benzene if the charge at that point is greater than $(1.00 + (43/108)\delta_i)e$, and conversely.

Let us apply these considerations to pyridine. If we set $\delta_N = \delta_1 = 2$, $\delta_\alpha = \delta_2 = \delta_6 = 0.2$, and $\delta_i = 0.2$, we obtain the results given in Table VI. As might be expected, the polarizability of the molecule at the various positions is practically constant, and is very nearly the same as that of benzene. Consequently the orientation is not affected by considering the polarization by the approaching group. This state of affairs can be expected to hold whenever the permanent polarization produces marked differences, as here, between the different positions.

TABLE VI

POLARIZABILITY OF PYRIDINE

i[a]	Charge at *i*th atom			Charge in benzene
	$\delta_i = 0$	$\delta_i = 0.2$	Difference	$(1.00 + \frac{43}{108}0.2)e$
2	0.831*e*	0.920*e*	0.089*e*	1.080*e*
3	.960	1.038	.078	1.080
4	.825	0.905	.080	1.080

[a] For the numbering of the different atoms see the diagrams given previously.

In naphthalene, on the other hand, the permanent polarization leaves all atoms with the same or very nearly the same charge, and as a result any small difference in polarizability has an opportunity to make its effect felt. The results of perturbation treatments are given in Table VII. With $\delta_i > 0$ the α position is activated, and substitution would take place there readily, as is demanded by experiment.

TABLE VII

POLARIZABILITY OF NAPHTHALENE

i	Charge on *i*th atom	Charge in benzene
1	$(1.00 + 0.44\delta_i)e$	$(1.00 + 0.40\delta_i)e$
2	$(1.00 + .40\delta_i)e$	$(1.00 + .40\delta_i)e$

In the halogen benzenes the ortho and para positions are found to be more polarizable than the meta, as is shown in Table VIII.

TABLE VIII

POLARIZABILITY OF $C_6H_5\ddot{X}$

$\delta_X = 4.0$, $\delta_1 = 0.4$

i	Charge at *i*th atom			Charge in benzene
	$\delta_i = 0$	$\delta_i = 0.2$	Difference	
2	0.975*e*	1.055*e*	0.080*e*	1.080*e*
3	1.002	1.069	.067	1.080
4	0.984	1.064	.080	1.080

With the particular choice of the δ's used in the calculation the observed order[8] unsubstituted benzene > para > ortho > meta is not obtained, but agreement can be achieved by a suitable readjustment of the parameter values. If, with δ_X held fixed and equal to 4, the charges at the different positions are assumed to be linearly dependent upon δ_1 and δ_i (as is the case when these quantities are sufficiently small), the results of Table VIII can be expressed as

$$\begin{aligned}\text{Charge on } 2 &= (1.036 - 0.152\delta_1 + 0.402\delta_i)e\\ \text{Charge on } 3 &= (0.998 + 0.009\delta_1 + 0.339\delta_i)e\\ \text{Charge on } 4 &= (1.024 - 0.099\delta_1 + 0.400\delta_i)e\end{aligned}$$

If we use the particular values $\delta_1 = 0.3$, $\delta_i = 0.2$ (any of several other sets would do as well), we find

$$\begin{aligned}\text{Charge on } 2 &= 1.071e\\ \text{Charge on } 3 &= 1.069e\\ \text{Charge on } 4 &= 1.074e\end{aligned}$$

These figures are now in agreement with the observed order given above. While it is doubtful if much significance can be attached to parameter values obtained in such an arbitrary and *ad hoc* manner, it is nevertheless gratifying to observe that the ones found are not unreasonable.

Conclusion

By introducing reasonable values (about 2 for nitrogen, 4 for oxygen) for the electron affinity parameter relative to carbon, δ, and for the induced electron affinity for adjacent atoms ($\delta_2/\delta_1 \simeq {}^1/_{10}$), we have shown that the calculated permanent charge distributions for pyridine, toluene, phenyltrimethylammonium ion, nitrobenzene, benzoic acid, benzaldehyde, acetophenone, benzonitrile, furan, thiophene, pyrrole, aniline, and phenol can be satisfactorily correlated qualitatively with the observed positions and rates of substitution. For naphthalene and the halogen benzenes this calculation does not lead to results

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[8] Iodobenzene substitutes more easily than benzene. In this case, however, δ_X is comparatively small, and the discrepancy does not exist.

in complete qualitative agreement with experiment; agreement is obtained, however, by the consideration of the effect of polarization of the molecule by the attacking group. Because of the presence of several adjustable parameters, this treatment cannot be considered as a pure quantum mechanical theory of directed substitution in aromatic molecules. However, the various effects which we have considered are certainly real, and there is no reason to doubt that they act in the directions calculated, and are of the general order of magnitude assumed; the parameters introduced are not completely arbitrary in value, because they are related to definite and fairly well understood atomic and molecular quantities. Furthermore, in the cases in which only one effect is important, as in pyridine, or in which all effects act in the same direction, as in nitrobenzene, the calculations lead to completely unambiguous conclusions, which are dependent to only a small degree upon the particular parameter values chosen. We accordingly feel that the degree of success realized in these quantitative considerations provides strong support for the underlying ideas as to the nature of the effects involved.

Summary

Using the method of molecular orbitals, a quantitative discussion of the charge distribution in aromatic molecules undergoing substitution reactions is carried out, taking into consideration the inductive effect, the resonance effect, and the polarizing effect of the attacking group. It is shown that, with reasonable values for the parameters involved, the calculated charge distributions for pyridine, toluene, phenyltrimethylammonium ion, nitrobenzene, benzoic acid, benzaldehyde, acetophenone, benzonitrile, furan, thiophene, pyrrole, aniline, phenol, naphthalene, and the halogen benzenes are in qualitative agreement with the experimental results regarding position and rate of substitution, the auxiliary hypothesis being made that the rate of substitution of the group R′ for hydrogen on the *i*th carbon atom increases with increase in the negative charge of the *i*th carbon atom when the group R′ is in position to react.

PASADENA, CALIFORNIA RECEIVED JULY 26, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Dibenzofuran. VII. Derivatives of Tetrahydrodibenzofuran

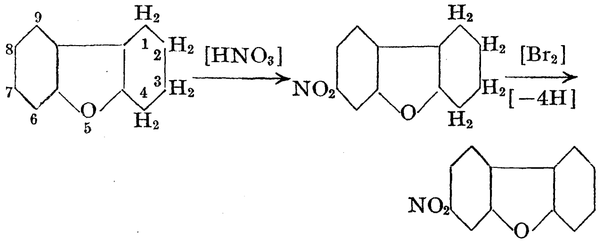
BY HENRY GILMAN, E. W. SMITH AND L. C. CHENEY

Introduction

The presence of a reduced dibenzofuran nucleus in morphine suggested an examination of nuclearly substituted reduced dibenzofurans. From the results of the present study on 1,2,3,4-tetrahydrodibenzofuran it appears (1) that the orientation of the parent dibenzofuran cycle is essentially unlike that of 1,2,3,4-tetrahydrodibenzofuran; (2) that the position assigned to the nitro group in nitro-1,2,3,4-tetrahydrodibenzofuran is incorrect; and (3) that the nuclear substituted *hexa*hydrodibenzofurans are in reality substituted *tetra*hydrodibenzofurans.

Nuclear substitution of dibenzofuran strikingly illustrates that the rule of conservation of the substitution type is not inviolate, and that the position assumed by substituents is significantly dependent on the kind of entering group. For example, with dibenzofuran, halogenation, sulfonation and the Friedel–Crafts reaction involve the 2-position; nitration involves predominantly the 3-position with only a small amount of 2-nitro compound being formed; and metalation (the replacement of hydrogen attached to carbon by a metal) takes place in the 4-position. With 1,2,-3,4-tetrahydrodibenzofuran, sulfonation, the Friedel–Crafts reaction and nitration involve the 7-(or 3′-)position; whereas metalation proceeds as with dibenzofuran to give a 6-(or 4′-) organometallic compound. Bromination may be difficult because bromine is at this time a reagent of choice for dehydrogenation of tetrahydrodibenzofurans to dibenzofurans.

The position of the nitro group in nitro-1,2,3,4-tetrahydrodibenzofuran was established as follows



Ebel[1] nitrated tetrahydrodibenzofuran and assumed that the nitro group was in the 8-position. Von Braun[2] assumed that his nitration product was 8-nitro-*hexa*hydibenzofuran. Through the kindness of Professor von Braun it was possible to show that a sample of his nitro compound was in reality the 7-nitro-1,2,3,4-*tetra*hydrodibenzofuran. The 8-position assigned to nuclear substituents by these earlier workers was predicated on the reasonable assumption of a *para*-orienting effect of oxygen.

The constitution of the sulfonation product as 1,2,3,4-tetrahydrodibenzofuran-7-sulfonic acid was established by the following sequence of reactions:

$$\begin{tikzcd}
C_{12}H_{12}O \text{ (tetrahydrodibenzofuran)} \arrow[d] & C_{12}H_8O \text{ (dibenzofuran)} \arrow[d] \\
7\text{-}(SO_3H)(C_{12}H_{11}O) \arrow[dd] & 3\text{-}(NO_2)(C_{12}H_7O) \arrow[d] \\
 & 3\text{-}(NH_2)(R) \arrow[d] \\
7\text{-}(SO_2Cl)(C_{12}H_{11}O) \arrow[d] & 3\text{-}(N_2X)(R) \arrow[d] \\
7\text{-}(SO_2NH_2)(C_{12}H_{11}O) \arrow[dd] & 3\text{-}(SO_2H)(R) \arrow[d] \\
 & 3\text{-}(SO_3H)(R) \arrow[d] \\
7\text{-(or 3-)}(SO_2NH_2)(C_{12}H_7O) & 3\text{-}(SO_2Cl)(R) \arrow[l]
\end{tikzcd}$$

A related procedure was used to identify the acetyl compound obtained by a Friedel–Crafts reaction:

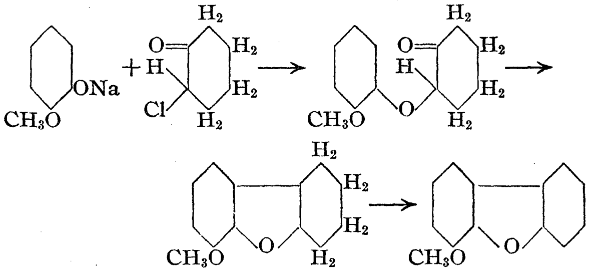
$$7\text{-}(CH_3CO)(C_{12}H_{11}O) \xrightarrow{I_2 + NaOH} 7\text{-}(CO_2H)(C_{12}H_{11}O) \xrightarrow[Br_2]{-4H} 7\text{- (or 3-)}(CO_2H)(C_{12}H_7O)$$

The 7-acetyl-1,2,3,4-*tetra*hydrodibenzofuran was shown to be identical with a supposed 8-acetyl-*hexa*hydrodibenzofuran.[2]

Metalation of *tetra*hydrodibenzofuran by means of phenyl-lithium or *p*-tolyl-lithium or *n*-butylsodium replaced a 6-hydrogen.

$$C_{12}H_{12}O \longrightarrow (C_{12}H_{11}O)(\text{Li or Na}) \xrightarrow{CO_2} (C_{12}H_{11}O)(CO_2H) \xrightarrow[Br_2]{-4H} 6\text{-(or 4-)}C_{12}H_7O(CO_2H)$$

The structure of 6-methoxy-1,2,3,4-tetrahydrodibenzofuran, prepared by the following interesting ring closure synthesis,[1] has been definitely established by dehydrogenation to 4-methoxydibenzofuran which in turn was made available by the recent unequivocal synthesis involving the metalation of dibenzofuran.[3]



An account of some reduction products of dibenzofuran is contained in the Experimental Part.

The pharmacological action of the several compounds will be reported by Dr. A. W. Dox and co-workers.

Experimental Part

1,2,3,4-Tetrahydrodibenzofuran.—The tetrahydrodibenzofuran used in all of the procedures, except when otherwise noted, was prepared according to the directions of Hönigschmid.[4] In a typical preparation 50 g. of dibenzofuran was reduced with 60 g. of sodium, a total of 400 cc. of absolute ethanol being used. The product was purified by distillation at atmospheric pressure, b. p. 270° (740 mm.), followed by a second distillation at reduced pressure, b. p. 145° (15 mm.), 135° (9 mm.), n^{20}_D 1.5795, sp. g.$^{20}_{20}$ 1.0938.

The reduction of 50 g. of dibenzofuran with 20 g. of sodium in boiling ethanol gave 25.7 g. of product distilling between 265–273° (740 mm.), and 15.4 g. boiling at 273–275° (740 mm.). Chilling the second fraction in an ice-salt bath yielded 3.6 g. of crystalline product which melted at 40–45° after one crystallization from ethanol. Several crystallizations from petroleum ether raised the melting point to 80° and this compound was shown to be dibenzofuran.

Nitration of Tetrahydrodibenzofuran.—Nitration by the method of Ebel[1] gave a nitro compound which melted at 124–125° when crystallized from ethanol. The material used was prepared both by ring closure and sodium–ethanol reduction. The compound was identical with the supposed 8-nitrohexahydrodibenzofuran[2] (mixed melting point). This substantiates Ebel's[1] surmise that his nitrotetrahydro compound was probably the same as von Braun's nitrohexahydro compound.

Anal. Calcd. for $C_{12}H_{11}O_3N$: C, 66.33; H, 5.11. Found: C, 66.02; H, 5.23.

A solution of 2.2 g. (0.01 mole) of the nitrotetrahydrodibenzofuran and 3.2 g. (0.02 mole) of bromine in 40 cc. of

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(1) Ebel, *Helv. Chim. Acta*, **12**, 3 (1929).

(2) Von Braun, *Ber.*, **55**, 3761 (1922).

(3) Gilman and Young, THIS JOURNAL, **57**, 1121 (1935).

(4) Hönigschmid, *Monatsh.*, **22**, 561 (1901), and **23**, 829 (1902).

glacial acetic acid was allowed to stand for fifteen hours at room temperature and then refluxed for one-half hour. On cooling, 0.75 g. or a 35% yield of 3-nitrodibenzofuran precipitated (mixed melting point).

The amine and the picrate of the amine prepared by reduction of 7-nitro-1,2,3,4-tetrahydrodibenzofuran were found by Mr. W. H. Kirkpatrick to have the same melting points as the reported amino-hexahydrodibenzofuran and its picrate, respectively.[2] However, the 7-acetamino-1,2,3,4-tetrahydrodibenzofuran was found to melt at 146° and not at 123°, which is the melting point reported for the acetamino-hexahydrodibenzofuran.[2] It is possible that the latter substance, for which no analysis was reported, is a mixture of mono-acetamino and di-acetamino compounds (acylation having introduced two acetyl groups).

Anal. Calcd. for $C_{14}H_{15}O_2N$: N, 6.11. Found: N, 6.31.

Friedel–Crafts Reaction.—The acetylation of tetrahydrodibenzofuran with acetyl chloride and aluminum chloride in carbon disulfide by Mr. J. A. V. Turck yielded an acetyltetrahydrodibenzofuran. The use of acetic anhydride and stannic chloride in benzene proved to be a better choice of reagents and gave the same product. Twenty and four-tenths grams (0.2 mole) of acetic anhydride was added dropwise with stirring to a solution of 34.4 g. (0.2 mole) of tetrahydrodibenzofuran and 104.4 g. (0.4 mole) of anhydrous stannic chloride in 150 cc. of dry benzene. At the conclusion of the addition the mixture was refluxed gently for ten hours and then hydrolyzed with cracked ice. The mixture was extracted with ether, the ether–benzene extract washed with 10% sodium hydroxide and then with water, and, finally, dried over anhydrous calcium chloride. The solvents were removed and the residue fractionated at reduced pressure. The fraction boiling at 200–217° (15 mm.) weighed 28.3 g., or a 66% yield. The solidified product crystallized from petroleum ether as colorless needles, m. p. 66–67°, b. p. 210° (15 mm.). A mixed melting point with an authentic sample of acetylhexahydrodibenzofuran[2] kindly supplied by Professor von Braun, and melting at 66–67°, showed no depression.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.46; H, 6.59. Found: C, 78.46 and 78.44; H, 6.25 and 6.74.

Dibenzofuran was also isolated from the reaction product.

The acetyl derivative supplied by Professor von Braun was also analyzed.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.46; H, 6.59. Calcd. for $C_{14}H_{16}O_2$: C, 77.73; H, 7.46. Found: C, 78.14; H, 6.64.

An aqueous solution of iodine in potassium iodide was added in small portions with shaking to a solution of 4 g. of acetyltetrahydrodibenzofuran in 100 cc. of dioxane and 40 cc. of 10% sodium hydroxide solution in accordance with Fuson's procedure. When the iodine color persisted at 60° for one minute, excess sodium hydroxide was added and the solution cooled. The supernatant liquid was decanted from the iodoform and acidified with sulfuric acid. The resulting precipitate was filtered and then washed. A 2.3 g. or 57% yield of 1,2,3,4-tetrahydrodibenzofuran-7-carboxylic acid was obtained which melted at 247–248° after crystallization from ethanol or glacial acetic acid. *Neutral equivalent:* calcd., 216.1; found, 213 and 213.

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.19; H, 5.60. Found: C, 72.07 and 71.90; H, 5.64 and 5.61.

Diazomethane was used to prepare the methyl ester, which melted at 72.5–73.5° after crystallization from dilute methanol.

One and six-tenths grams (0.01 mole) of bromine was added to a suspension of 1.08 g. (0.005 mole) of the above tetrahydrodibenzofuran-7-carboxylic acid in 25 cc. of glacial acetic acid at room temperature and the resulting solution was allowed to stand for ten hours. The solution was refluxed strongly until the evolution of hydrogen bromide ceased, and then cooled. A quantitative yield of dibenzofuran-3-carboxylic acid was obtained which melted at 271.5–272° after crystallization from glacial acetic acid. A mixed melting point with authentic dibenzofuran-3-carboxylic acid, m. p. 271.5–272°, showed no depression.

Diazomethane was used to convert the acid to the methyl ester which melted at 138.5° after crystallization from petroleum ether. A mixed melting point with authentic methyl dibenzofuran-3-carboxylate showed no depression. The methyl ester was prepared by the action of diazomethane on dibenzofuran-3-carboxylic acid, and melted at 138° after crystallization from petroleum ether.

Anal. Calcd. for $C_{14}H_{10}O_3$: C, 74.31; H, 4.46. Found: C, 74.31 and 74.67; H, 4.85 and 4.93.

Sulfonation of Tetrahydrodibenzofuran.—To a well-stirred solution of 34.4 g. (0.2 mole) of tetrahydrodibenzofuran in 100 cc. of carbon tetrachloride was added dropwise 23.4 g. (0.2 mole) of chlorosulfonic acid. The temperature was kept at 10°. At the conclusion of the addition the reaction was stirred for one hour at 0° and at room temperature for three hours. The reaction product was decomposed with cracked ice and the carbon tetrachloride layer separated. The aqueous layer was neutralized in the usual manner with barium carbonate and the slightly soluble barium sulfonate extracted with hot water. Concentration and cooling of the aqueous extract yielded 23.3 g. or a 36.3% yield of barium 1,2,3,4-tetrahydrodibenzofuran-7-sulfonate. The salt was crystallized several times from water prior to analysis.

Anal. Calcd. for $(C_{12}H_{11}O_4S)_2Ba$: Ba, 21.48. Found: Ba, 21.30 and 21.68.

On the basis of the formation of isomers in nuclear substitution reactions of partially reduced related systems, it is not at all unlikely that isomers may have formed in nuclear substitution reactions of 1,2,3,4-tetrahydrodibenzofuran.

Tetrahydrodibenzofuransulfonamide.—An intimate mixture of 21.5 g. (0.0785 mole) of crude sodium tetrahydrodibenzofuransulfonate and 12.3 g. (0.08 mole) of phosphorus oxychloride was allowed to stand for twenty-four hours at room temperature and then heated for one and one-half hours at 100–110°. The pasty reaction product was decomposed with cold concentrated ammonium hydroxide. The solid product was digested with fresh ammonium hydroxide and filtered to give a yield of 77%. The colorless flat plates melted at 207.5–208.5° after crystallization from ethanol and 60% acetic acid.

Anal. Calcd. for $C_{12}H_{13}O_3NS$: C, 57.33; H, 5.21. Found: C, 57.09; H, 4.92.

Dehydrogenation of Tetrahydrodibenzofuransulfonamide.—A solution of 1.28 g. (0.008 mole) of bromine and 1 g. (0.004 mole) of 1,2,3,4-tetrahydrodibenzofuran-7-sulfonamide in 25 cc. of glacial acetic acid was allowed to stand at room temperature for two days and then refluxed until the evolution of hydrogen bromide ceased. The chilled solution precipitated 0.55 g. of dibenzofuran-3-sulfonamide, which gave compact colorless crystals melting at 241–243° after crystallization from 60% acetic acid. A 10% yield of the same product was obtained when 1 g. of tetrahydrodibenzofuransulfonamide and 2 g. of sulfur was heated at 240–275° until evolution of hydrogen sulfide ceased. The product was extracted with and crystallized from 60% acetic acid. A mixed melting point of this compound with the authentic dibenzofuran-3-sulfonamide as prepared by the following sequence of reactions was not depressed.

Dibenzofuran-3-sulfonamide.—A solution of 4.4 g. of sodium nitrite in 20 cc. of water was added slowly to a suspension of 10 g. of 3-aminodibenzofuran in a solution of 40 cc. of concd. sulfuric acid in 150 cc. of water at 0°. The reaction mixture was stirred for one hour at 0° and allowed to stand at room temperature for twelve hours. The diazonium sulfate was saturated with sulfur dioxide at $-5°$, and then 40 g. of copper powder added in portions with vigorous stirring, the temperature being maintained at $-5°$. The resulting sludge was filtered off when the reaction was complete and both filtrate and precipitate were thoroughly extracted with ether. The ether extract, containing the sulfinic acid, was extracted several times with 6 *N* potassium hydroxide. The potassium sulfinate was immediately oxidized with permanganate in the usual manner to the potassium sulfonate which separated from the filtrate of the oxidation solution upon concentration and cooling. The yield of dry product was 10.2 g. or 65.3%, and the free acid was prepared by the acidification of an aqueous solution of this salt. Dibenzofuran-3-sulfonic acid sinters without melting; it was crystallized several times from water and oven-dried prior to analysis.

Anal. Calcd. for $C_{12}H_8O_4S$: S, 12.92. Found: S, 12.58 and 12.67.

An intimate mixture of 2.4 g. of potassium dibenzofuran-3-sulfonate and 5 g. of phosphorus pentachloride generated a considerable amount of heat and soon liquefied. The liquid was poured upon cracked ice, and the resulting precipitate melted at 148.5° after crystallization from benzene and petroleum ether.

Anal. Calcd. for $C_{12}H_7O_3ClS$: C, 54.02; H, 2.65. Found: C, 54.41; H, 2.91.

An ether solution of dibenzofuran-3-sulfonyl chloride was saturated with ammonia gas to yield dibenzofuran-3-sulfonamide melting at 241–242° after crystallization from 60% acetic acid.

Anal. Calcd. for $C_{12}H_9O_3NS$: C, 58.27; H, 3.67. Found: C, 57.87; H, 3.61.

Metalation of Tetrahydrodibenzofuran.—In this reaction it was necessary to use pure tetrahydrodibenzofuran prepared by ring closure.[1] Tetrahydrodibenzofuran prepared by the sodium–alcohol reduction of dibenzofuran contains sufficient impurity to cause the formation of 4-dibenzofurancarboxylic acid, which made isolation of the tetrahydrodibenzofurancarboxylic acid difficult. In a typical preparation, 0.5 mole of phenyl-lithium was prepared in the customary manner[5] from 7.6 g. of lithium, 78.5 g. (0.5 mole) of bromobenzene and 300 cc. of anhydrous ether. This preparation, after removal of the excess lithium, was gently refluxed with a solution of 86.0 g. (0.5 mole) of tetrahydrodibenzofuran in 200 cc. of anhydrous ether for fifteen hours. Carbonation was effected by slowly pouring the cooled reaction product on 500 g. of pulverized solid carbon dioxide. The mixture was allowed to stand overnight and was then extracted with two liters of water made alkaline with sodium hydroxide. Steam distillation of the ether layer resulted in the recovery of 41.4 g. of tetrahydrodibenzofuran. Acidification of the aqueous alkaline extract after decolorization with Norite yielded 18.1 g. of a resinous material. Crystallization of this product from ethyl acetate yielded 2.7 g. of crude 1,2,3,4-tetrahydrodibenzofuran-6-carboxylic acid which melted at 197° after further crystallization from the same solvent. This is a 4.8% yield based on the tetrahydrodibenzofuran used. *Neutral equivalent:* Calcd., 216.1; found, 216.8.

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.19; H, 5.60. Found: C, 71.92; H, 5.75.

The use of *p*-tolyl-lithium and *n*-butylsodium as metalating agents yields the same product, but in smaller yields. Metalations of substituted dibenzofurans will be reported later. Depending on the kind and position of substituents, it is possible to metalate in positions other than 4 and 6.

Dehydrogenation of 1,2,3,4-Tetrahydrodibenzofuran-6-carboxylic Acid.—A solution of 0.4 g. (0.00185 mole) of tetrahydrodibenzofurancarboxylic acid and 0.65 g. (0.004 mole) of bromine in 10 cc. glacial acetic acid was allowed to stand overnight at room temperature and then refluxed until the evolution of hydrogen bromide ceased. The solution was diluted to 250 cc., made alkaline with sodium hydroxide, decolorized with Norite and acidified. Dibenzofuran-4-carboxylic acid melting at 207–208° was obtained after crystallization of the resulting precipitate from ethanol. A mixed melting point with authentic dibenzofuran-4-carboxylic acid showed no depression.

In this connection, it is interesting to observe that the reduction of dibenzofuran-4-carboxylic acid by sodium and absolute ethanol gives a reduced acid which appears to be 1,2,3,4-tetrahydrodibenzofuran-4-carboxylic acid. The exact structure of this compound together with others prepared by reduction of substituted dibenzofurans will be described in a forthcoming article. This tetrahydro acid melts at 168° after crystallization from dilute acetone from which the acid separates as large silvery plates. *Neutral equivalent:* Calcd., 216.1; found, 216.3.

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.19; H, 5.60. Found: C, 71.89 and 72.42; H, 5.66 and 5.67.

Dehydrogenation of 1,2,3,4-Tetrahydro-6-methoxydibenzofuran.—An intimate mixture of 0.25 g. of the methoxytetrahydro compound[1] and 0.3 g. of sulfur was heated up to 275° until the evolution of hydrogen sulfide

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(5) Gilman, Zoellner and Selby, THIS JOURNAL, **54**, 1957 (1932).

ceased. The solid melt was extracted with hot petroleum ether and the solvent evaporated to dryness. The residue was extracted with cold absolute ethanol and the extract concentrated to yield 4-methoxydibenzofuran[3] (mixed melting point).

Reduced Dibenzofurans.—There appears to be some confusion concerning variously reduced dibenzofurans. The 1,2,3,4-tetrahydrodibenzofuran was first prepared by Hönigschmid[4] by reduction of dibenzofuran with sodium in boiling ethyl or amyl alcohol. Extensive treatment with sodium and amyl alcohol did not yield a more completely reduced product, and when a lesser amount of sodium was used Hönigschmid isolated a compound melting at 43° which he assumed to be dihydrodibenzofuran. We repeated the work and obtained the same product melting at about 43°. However, several crystallizations from ethanol and petroleum ether raised the melting point to 80° and the compound as obtained was shown to be dibenzofuran.

The tetrahydrodibenzofuran has also been prepared by reduction of dibenzofuran with sodium and cyclohexanol.[6]

An entirely different procedure was used by Ebel,[1] who synthesized the tetrahydrodibenzofuran by a ring-closure reaction using 2-chlorocyclohexanone and sodium phenolate. This reaction together with oxidation of the tetrahydro compound to δ-(o-hydroxybenzoyl)-valeric acid leaves no doubt as to the constitution of the compound.

The hexahydrodibenzofuran of von Braun[2] was prepared by the catalytic reduction of o-biphenol. Ebel[1] introduced two atoms of hydrogen into tetrahydrodibenzofuran, using platinum–palladium black as a catalyst, and obtained a compound whose analysis and boiling point agreed with that of von Braun's hexahydrodibenzofuran.

We have found, however, that the picrates obtained from von Braun's hexahydrodibenzofuran, from Ebel's reduction product of the tetrahydrodibenzofuran and from the tetrahydrodibenzofurans prepared both by Ebel's and Hönigschmid's methods are identical, on the basis of mixed melting points.

The picrates were all prepared in the same manner and melted at 97–98° after crystallization from ethanol.[7] There were significant differences in yields of the picrates prepared from the variously reduced dibenzofurans. Incidentally, it might be added that the picrate prepared from von Braun's hexahydrodibenzofuran was decomposed by steam distillation of a suspension in sodium carbonate solution to yield a compound distilling at 145° (15 mm.) and having an index of refraction (1.5795 at 20°) identical with that observed with the tetrahydrodibenzofuran prepared by sodium reduction.

A dodecahydrodibenzofuran was described recently.[8] Mr. C. W. Bradley prepared this perhydrodibenzofuran by catalytic reduction of dibenzofuran at moderate temperatures and pressures using noble metal catalysts: b. p. 258–259° (740 mm.) and 108–110° (7 mm.); n^{20}_{D} 1.5023; sp. g. $^{20}_{20}$ 1.0312.

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.93; H, 11.19. Found: C, 80.37; H, 11.19.

An experiment by him to introduce 4 or 6 atoms of hydrogen by this method gave a product from which only dibenzofuran and perhydrodibenzofuran have so far been isolated. Mention should be made of the fact that hydrogenation of 2-hydroxydibenzofuran by Mr. Bradley also gave perhydrodibenzofuran.

The reduced dibenzofurans have been oxidized, von Braun obtaining δ-(o-hydroxybenzoyl)-valeric acid from his hexahydrodibenzofuran and chromic acid, and Ebel obtaining the same acid by ozonization of tetrahydrodibenzofuran. Mr. Bradley got a 16.7% yield of the acid by ozonizing the hexahydrodibenzofuran obtained in accordance with Ebel's directions for the reduction of tetrahydrodibenzofuran, an 87% yield of the same acid on ozonization under corresponding conditions of 1,2,3,4-tetrahydrodibenzofuran, and ozonization of the perhydrodibenzofuran gave an as yet unidentified product which is partly soluble in alkali.

From present evidence, there is no doubt concerning the existence of tetrahydrodibenzofuran and the perhydrodibenzofuran. No dihydrodibenzofuran has been definitely established.[7] The hexahydrodibenzofuran presents a different problem. This compound may be known as a parent type, but it seems quite clear that nuclear substitution reactions of it produce tetrahydro derivatives. The removal of two hydrogens from the hexahydro is not surprising with reagents like bromine, nitric acid, ozone and aluminum chloride. Possibly the picric acid also behaves as an oxidizing agent, and if so this would account for the apparent identity of the picrates prepared from the tetra- and hexahydrodibenzofurans.

The authors gratefully acknowledge the assistance of Mr. H. Oatfield with part of the sulfonation experiments and of Mr. W. Hoehn with some of the analyses.

Summary

A study has been made of variously substituted reduced dibenzofurans.

Metalation and nitration of 1,2,3,4-tetrahydrodibenzofuran involve the same relative positions observed with dibenzofuran. However, sulfonation and acetylation take place in the 7-(or 3′-) position, rather than in the 8-(or 2′-) position as in the case with dibenzofuran.

Some substituted *hexa*hydrodibenzofurans reported earlier have been shown to be substituted *tetra*hydrodibenzofurans, the substituents being in the 7- and not in the 8-position as assumed previously.

AMES, IOWA RECEIVED JULY 19, 1935

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[6] Mayer and Krieger, *Ber.*, **55**, 1659 (1922). Cullinane and Padfield [*J. Chem. Soc.*, 1131 (1935)] have just reported the preparation of the tetrahydro compound in 97% yield by reduction of dibenzofuran using platinum black as a catalyst.

[7] Both Ebel and Hönigschmid report the picrate as melting at 91°. Also Cullinane and Padfield [*J. Chem. Soc.*, 1131 (1935)] have just reported a melting point of 91°.

[8] Stenger, German Patent 566,782 [*C. A.*, **27**, 2459 (1933)].

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

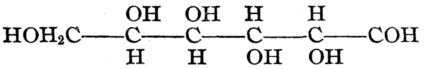
Crystalline *d*-Alpha-Galaheptose and Some of its Derivatives[1]

BY RAYMOND M. HANN, ALICE T. MERRILL AND C. S. HUDSON

In his pioneer studies of the two galaheptoses possible by addition of hydrocyanic acid to *d*-galactose, Fischer[2] isolated the *d*-[β-galaheptose] in crystalline condition, but was unsuccessful in his attempts to crystallize the isomeric *d*-[α-galaheptose]. He did, however, reduce the sirupy sugar with sodium amalgam and obtained the crystalline alcohol, *d*-[α-galaheptitol]. While Fischer recorded the rotation of this substance, it remained for Peirce[3] to point out that it is the antipode of *d*-[α-mannoheptitol] (perseitol), thus proving the configurations of the galaheptoses and the mannoheptoses.

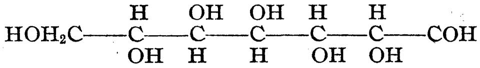
Recently the *d*-[α-galaheptose][4] has been obtained in crystalline condition as the monohydrate. The study of its derivatives has indicated that they crystallize with considerable difficulty, which was not unexpected because of the close similarity in configuration of the sugar to *l*-mannose. Incidental to the preparation of the lactone of *d*-[α-galaheptonic] acid, confirmation of the early work of Maquenne[5] and Kiliani[6] upon the isolation of crystalline *d*-[α-galaheptonic] acid has been obtained and a study of its rotational behavior has been made.

The data now at hand permit a good comparison of the properties of two aldoses which have very similar configurations, *l*-mannose and *d*-[α-galaheptose].



$$HOH_2C-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-COH$$

l-Mannose



$$HOH_2C-\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-COH$$

d-Alpha-galaheptose

Because of the paucity of data in the *l*-mannose series the comparisons will be made upon substances of the *d*-mannose series, which are opposite in sign of rotation. On the plausible hypothesis that the physical and chemical properties (though not the biological) of an aldose and most of its derivatives are conditioned in first measure by the space configurations of carbons one to five inclusive, it is to be expected that *l*-mannose and *d*-[α-galaheptose] will be especially similar sugars. This inference is fully borne out by the facts now at hand. Considering first those properties which are the same for the *d*- and *l*-forms of a given sugar, it is noted that mannose is characterized by a readily crystallizable phenylhydrazone of unusually low solubility; the same applies to the phenylhydrazone of the heptose in question, as indeed was noted by Fischer before the configurations of the galaheptoses were established. Mannose is also peculiar among aldoses in that the equilibrium between its α and β stable methyl glycosides in acidified methyl alcohol is usually far toward its α form; the same is now found to hold for its heptose analog, though because of conventions of nomenclature, this heptoside is to be named the β-form.[7] Other paralleling characteristics which have been observed in the two series are the sparing solubilities of the amides and phenylhydrazides as well as the ease of crystallization of the

TABLE I

SIMILARITY OF SPECIFIC ROTATIONS ($[\alpha]^{20}_D$) OF SUBSTANCES IN THE MANNOSE AND ALPHA-GALAHEPTOSE SERIES

		d-Mannose series		*d*-Alpha-gala-heptose series
Sugar, (initial)	(α)	+34	(β)	−26
(final)		+14.6		−15.3
Sodium salt of aldonic acid		− 8.8[8]		+ 9.6
γ-Lactone		+51.8[9]		−52.3[2]
Aldonic acid phenylhydrazide		− 8.1[10]		+ 8.5[10]
Aldonic acid amide		−17.3[11]		+14.3[11]
Methyl glycoside	(α)	+79.2[12]	(β)	−70.2
Methyl glycoside acetate		+49.1[13]		−20.4
Benzyl mercaptal		−32.9[14]		+30.3

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(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

(2) Fischer, *Ann.*, **288**, 144 (1895).

(3) Peirce, *J. Biol. Chem.*, **23**, 327 (1915).

(4) Hann, Merrill and Hudson, THIS JOURNAL, **56**, 1644 (1934).

(5) Maquenne, *Compt. rend.*, **106**, 286 (1888).

(6) Kiliani, *Ber.*, **21**, 915 (1888).

(7) The designation of *d*- and *l*- is made according to the configuration of the asymmetric carbon atom nearest the end of the sugar structure away from the carbonyl group (the Rosanoff nomenclature) and the designation α and β for isomeric substances of like structure in a given sugar series is in turn dependent, first upon this *d*- and *l*-classification, and second, upon the sign of rotation of carbon atom one.

(8) Levene and Meyer, *J. Biol. Chem.*, **26**, 355 (1916).

(9) Hedenburg, THIS JOURNAL, **37**, 345 (1915).

(10) Hudson, *ibid.*, **39**, 462 (1917).

(11) Hudson and Komatsu, *ibid.*, **41**, 1141 (1919).

(12) Fischer and Beensch, *Ber.*, **29**, 2927 (1896).

(13) Dale, THIS JOURNAL, **46**, 1048 (1924).

(14) Pacsu and v. Kary, *Ber.*, **62**, 2811 (1929).

γ-lactones in relatively pure condition, for the monobasic acids derived from the two aldoses.

In regard to optical properties, the data of Table I show a striking similarity in magnitude and full agreement in sign for substances of the two series. For reasons previously stated the values for mannose are taken from its *d*-series and hence for comparison the sign should be reversed.

The close similarity of properties in these particular sugar series is not limited to this pair but seems to be generally true, as can be readily verified by comparing known data,[15] and it appears to be of considerable practical value in furnishing a guide for preparative work and for studies of structure and configuration.

We express our appreciation to Dr. Reid Milner and Mrs. Mildred S. Sherman of the Fertilizer Investigations Laboratory, U. S. Department of Agriculture, for performing the micro analyses in connection with this work.

Experimental

Crude *d*-(α-Galaheptonic) Amide from *d*-Galactose.—To a solution of 500 g. of galactose in 750 cc. of water held at 0° in an ice–salt bath, 10 drops of concd. ammonia and 140 cc. of liquid hydrocyanic acid were added and the tightly stoppered flask allowed to stand in the ice box for two or three days, during which time the mixture set to a paste through crystallization of α-galaheptonic amide. It was thinned with 100 cc. of ice water, filtered on a large Büchner funnel and washed with three 50-cc. portions of ice water, dried for several hours at room temperature and finally in an oven at 60°. The yield varies according to the time necessary to obtain a satisfactory crystallization. In twenty-three experiments the lowest yield was 242 g. and the highest 355 g., an average yield of 47.5% being obtained. A considerable amount of α-galaheptonic lactone may be recovered from the filtrates by converting the soluble amides in solution to a mixture of α- and β-galaheptonic phenylhydrazides, separating by crystallization, and decomposing with copper sulfate as previously described.[16]

_d_-(α-Galaheptonic) Lactone from Crude _d_-(α-Galaheptonic) Amide.—A suspension of 500 g. of finely powdered amide in a solution of 300 g. of barium hydroxide octahydrate in 1000 cc. of water was boiled briskly under the hood for seven hours, water being added from time to time to replace that lost by evaporation. The barium was roughly precipitated with about 320 cc. of 6 *N* sulfuric acid and thereafter the solution balanced until free of barium and sulfate ions. The filtered solution was concentrated to a thick sirup and heated for six to eight hours on the steam-bath, 250 cc. of methyl alcohol was stirred in and upon standing overnight it crystallized to a solid mass; yield 380 g. (82.2%). The lactone can be conveniently recrystallized by dissolving 400 g. of crude lactone in 160 cc. of hot water, adding 1600 cc. of hot 95% alcohol and filtering through a preheated funnel. Overnight a yield of 285 g. of lactone (71.2%) showing a specific rotation[17] of −49.2° in water separates, and additional material may be recovered from the filtrate for further purification. One additional recrystallization from 3 parts of 90% alcohol yields the pure lactone, rotating −52.3° in water, in agreement with Fischer's[2] value.

_d_-(α-Galaheptonic Acid).—Under milder conditions of transformation the amide yields α-galaheptonic acid. A solution containing 138 g. of amide, 100 g. of barium hydroxide octahydrate and 500 cc. of water was boiled under reduced pressure at 60–70°, keeping the volume approximately constant by addition of water until ammonia could no longer be detected in the distillate. Sufficient 6 *N* sulfuric acid was added to the slightly warm solution to precipitate the barium exactly and upon filtering and cooling, a small amount of α-galaheptonic acid crystallized. The filtrate was concentrated *in vacuo* to 200 cc. and the main portion of the acid removed after cooling. The total yield of acid was 57.2 g. (41.3%). The mother liquor was heated in a shallow dish on the steam-bath for two days and yielded 33.5 g. of α-galaheptonic lactone.

α-Galaheptonic acid crystallizes from 100 parts of 95% alcohol in brilliant colorless leaflets melting at 143 to 147° (corr.) depending upon the rate of heating. A 5-g. sample heated under vacuum for one hour in a glycerol bath at 155–160° readily gave off water and the resulting melt, upon treatment with 10 cc. of methyl alcohol, deposited 2.8 g. of crystals. Examination of the recrystallized product showed it to be a mixture of needles and prisms, indicating a mixture of lactones. Confirmatory evidence was obtained on successive recrystallizations, the specific rotation decreasing in the order from −56.3, −54.2, −53.1 to −52.2° with disappearance of the needle form and separation of pure γ-*d*-[α-galaheptonic] lactone. Fresh solutions of the acid titrate immediately as an acid and upon standing they show the characteristic acid–lactone titration behavior. These solutions exhibit mutarotation and after the first twenty minutes closely follow a unimolecular course. Table II records the log of a typical rotation.

TABLE II

MUTAROTATION OF *d*-[α-GALAHEPTONIC] ACID IN WATER

Concentration 0.3431 g. in 25 cc.; tube length 2 dm.; $T = 20 \pm 0.5°$.

Time, min.	5	15	30	60	120	180
$[\alpha]^{20}_{D}$	+2.5	+2.3	+1.0	−0.6	−4.0	−6.9
Time, min.	240	360	720	72 hrs.	10 days	
$[\alpha]^{20}_{D}$	−8.8	−13.2	−19.5	−28.3	−28.3	

Anal. Acid titration: 0.1281 g. neutralized 5.65 cc. 0.1 *N* NaOH. Calcd., 5.67 cc. Calcd. for $C_7H_{14}O_8$: C, 37.2; H, 6.2. Found: C, 37.1; H, 6.3.

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[15] A good example is the ease with which the ketose, sedoheptose, now known to be *d*-altroheptulose, passes in acid solution to a non-reducing anhydro form by a balanced reaction, which was unique in the sugar group until the recent discovery that *d*-altrose, of closely similar configuration, behaves in like manner [Richtmyer and Hudson, THIS JOURNAL, **57**, 1716 (1935)].

[16] Hann and Hudson, *ibid.*, **56**, 957 (1934).

[17] Throughout the article the rotations are specific rotations at 20° for sodium light.

d-(*α*-**Galaheptose**).—Forty-five grams of *α*-galaheptonic lactone was reduced in cold acid solution in the usual manner with 2000 g. of 2.5% sodium amalgam. Following removal of the sodium sulfate, the solution was freed of the sodium salt of *α*-galaheptonic acid by concentrating to a sirup and treating repeatedly with methyl alcohol. In one case treatment of this sirup with phenylhydrazine yielded 31.4 g. of hydrazone and 7.1 g. of osazone, equivalent to 38.5 g. of galaheptose, whereas the theoretical yield would have been 45.4 g. of sugar. The salt-free sirup was placed in a calcium chloride desiccator and treated repeatedly with small amounts of methyl alcohol; it finally crystallized as a monohydrate after about four months. The yield averaged about 25 g. The sugar may be recrystallized in a yield of 80% by solution in one-half part of water and addition of 5 parts of 95% alcohol, separating in glistening prisms melting at 77–78° (corr.) to a colorless sirup. The course of its mutarotation (Table III) is not unimolecular. The final specific rotation of the sugar, considered as anhydrous ($C_7H_{14}O_7$), is −15.3° and the initial rotation is approximately −26°.

TABLE III

MUTAROTATION OF *β*-*d*-[*α*-GALAHEPTOSE] MONOHYDRATE IN WATER

Concentration 1.1560 g. in 10 cc. solution; tube length 1 dm.; $T = 20 \pm 0.5°$

Time after making solution, min.	$[\alpha]^{20}_D$	Time, min.	$k_1 + k_2$
2.4	−22.5	0	...
3.4	21.9	1	0.032
5.3	21.1	2.9	.027
6.3	21.0	3.9	.022
7.3	20.7	5.9	.018
15.4	18.9	13.0	.019
20.5	18.1	18.1	.018
25.4	17.4	23.0	.018
30.4	16.9	28.0	.017
35.4	16.5	33.0	.017
40.2	16.2	37.8	.016
55.1	15.3	52.7	.016
70.1	14.8	67.7	.016
93.1	14.4	90.7	.016
190.1	14.1 (equilibrium)	187.7	...
72 hrs. (final)	14.1	∞	...

Anal. Iodimetric Titration: 0.0519 g. consumed 4.56 cc. 0.1 *N* iodine equivalent to 0.0479 g. of heptose (92.3%): H_2O, 0.2632 g. lost 0.0214 g. (8.13%) on heating seven hours at 110° in Abderhalden drier. Calcd. for $C_7H_{14}O_7 \cdot H_2O$: C, 36.82; H, 7.07; sugar, 92.1; H_2O, 7.90. Found: C, 36.98; H, 7.13; sugar, 92.3; H_2O, 8.13.

Sodium *d*-[*α*-**Galaheptonate**].—This salt was obtained from the reduced solution following separation of the sodium sulfate by treatment of the sirup resulting upon vacuum concentration, with anhydrous methyl alcohol. It crystallized in clusters of glistening prisms showing a specific rotation of +9.7° in water. Recrystallized from one part of water by addition of one volume of methyl alcohol it rotated +9.5° (0.5265 g. in 10 cc. water in a 1-dm. tube rotated 0.50° to the right). Analysis showed it to be a monohydrate.

Anal. Calcd. for $C_7H_{13}O_8Na \cdot H_2O$: Na, 8.6; H_2O, 6.8. Found: Na, 8.6; H_2O, 6.7.

β-**Methyl** *d*-[*α*-**Galaheptoside**].—Ten grams of *α*-galaheptose monohydrate was refluxed for one hour with 100 cc. of methyl alcohol containing 1.5% of dry hydrochloric acid gas, when all reducing power disappeared. The solution was treated with 15 g. of dry silver carbonate and the halogen-free filtrate concentrated to a sirup and treated with about 20 cc. of ethyl alcohol, which induced crystallization readily. The substance was recrystallized from three parts of absolute alcohol; it separated in brilliant prisms rotating −70.1° in water. Upon recrystallization a rotation of −70.2° (0.2708 g. in 10 cc. of water in a 1-dm. tube rotated 1.90° to the left) was found. The compound melts at 132° (corr.); yield 6.4 g. (65%). The rate of hydrolysis in 0.05 *N* hydrochloric acid at 100° was 0.0004 (expressed in minutes and decimal logarithms), proving the glycoside to be of the stable type.

Anal. Calcd. for $C_8H_{16}O_7$: C, 42.83; H, 7.20. Found: C, 42.72; H, 7.19.

The substance is designated as the *β*-methyl glycoside because it is more negative in rotation than the *β*-form of the sugar, which belongs to the *d*-series. It has already been explained[7] how the accepted conventions of nomenclature led to this naming whereas the method of preparation and properties of the substance show it to be the analog of *α*-methyl *d*-mannoside. Likewise the crystalline form of *d*-*α*-galaheptose, for which the conventional naming is *β*, is the analog of the crystalline *α*-form of mannose.

Pentaacetyl *β*-**Methyl** *d*-[*α*-**Galaheptoside**].—Five and one-tenth grams of methyl-*α*-galaheptoside was dissolved in 30 cc. of pyridine and acetylated by adding an equal volume of acetic anhydride and allowing to stand overnight at room temperature. The solution was poured upon cracked ice and the gummy precipitate which formed was extracted with carbon tetrachloride and the dried extract concentrated to a sirup. It failed to crystallize by the usual procedure, but was finally obtained in crystalline condition by successive treatments with small amounts of absolute alcohol over a period of two months, yield 7.9 g. (80%). The compound may be recrystallized from two parts of 95% alcohol and separates in glistening plates. The specific rotation of −20.4° (0.2354 g. in 10 cc. of chloroform in a 1-dm. tube rotates 0.48° to the left) did not change appreciably upon recrystallization. The compound melts at 108° (corr.) to a colorless oil.

Anal. Calcd. for $C_{18}H_{26}O_{12}$: C, 49.74; H, 6.04. Found: C, 49.61; H, 6.11.

β-**Ethyl** *d*-[*α*-**Galaheptoside**].—This compound was prepared in an analogous manner to the methyl homolog and was obtained in a yield of 7.0 g. (67%). It was recrystallized from three parts of absolute alcohol as thin glistening plates, melting at 138° and showing a specific rotation of −65.4° (0.2310 g. in 10 cc. of water in a 1-dm. tube rotated 1.51° to the left), unchanged by recrystallization.

Anal. Calcd. for $C_9H_{18}O_7$: C, 45.35; H, 7.62. Found: C, 45.28; H, 7.70.

Pentaacetyl *β*-**Ethyl** *d*-[*α*-**Galaheptoside**].—This acetylated glycoside was obtained in a yield of 9.6 g. (85%) when 6.0 g. of the ethyl glycoside was acetylated with pyridine and acetic anhydride. It crystallized from five parts of 50% alcohol in long colorless needles melting at 92° (corr.) to a colorless oil. Its specific rotation was −24.9° (0.3570 g. in 10 cc. of chloroform in a 1-dm. tube rotated 0.89° to the left) after recrystallization to constancy.

Anal. Calcd. for $C_{19}H_{28}O_{12}$: C, 50.87; H, 6.30. Found: C, 50.81; H, 6.37.

d-[*α*-**Galaheptose] Benzyl Mercaptal.**—A solution of 5 g. of *α*-galaheptose monohydrate in 10 cc. of concd. hydrochloric acid was shaken with 10 cc. of benzyl mercaptan for ten minutes, when it set to a paste. After standing overnight at room temperature the solid was filtered, washed with 95% alcohol and dried, yield, quantitative. The mercaptal may be recrystallized readily from 75 parts of 95% alcohol, separating in small glistening plates, melting at 191° (corr.) and rotating +30.3° in pyridine (0.2212 g. in 10 cc. in a 1-dm. tube rotated 0.67° to the right).

Anal. Calcd. for $C_{21}H_{28}O_6S_2$: S, 14.56. Found: S, 14.50.

Hexaacetyl *d*-[*α*-**Galaheptose] Benzyl Mercaptal.**—A solution of 5 g. of mercaptal in 25 cc. of pyridine was treated with 25 cc. of acetic anhydride, allowed to stand overnight at room temperature and the acetate precipitated by pouring the solution over crushed ice. The compound crystallizes from 10 parts of 95% alcohol in clusters of elongated, very thin terminated plates, melting at 120° (corr.) and rotates −10.6° (0.2633 g. in 10 cc. in a 1-dm. tube rotated 0.28° to the left) in chloroform.

Anal. Calcd. for $C_{33}H_{40}O_{12}S_2$: S, 9.26. Found: S, 9.14.

Hexabenzoyl *d*-[*α*-**Galaheptose] Benzyl Mercaptal.**—A solution of 3 g. of mercaptal in 25 cc. of pyridine was treated dropwise with 11.5 g. of benzoyl chloride. The mixture became warm, developed a red color and soon became a mush of glistening crystals. The next day the mass was poured upon crushed ice, stirred and a red crystalline meal gradually formed. This was filtered off and recrystallized from 100 parts of 95% alcohol, the benzoate separating in clusters of colorless small prisms. The pure substance melts at 129° (corr.) and rotates −48.1° in chloroform (0.2950 g. in 10 cc. in a 1-dm. tube rotated 1.42° to the left).

Anal. Calcd. for $C_{63}H_{52}O_{12}S_2$: S, 6.02. Found: S, 6.03.

Summary

1. *d*-[*α*-Galaheptose] has been obtained in crystalline condition as the monohydrate of its beta form.

2. The rotational behavior of solutions of crystalline *d*-[*α*-galaheptonic] acid has been studied.

3. Methyl and ethyl glycosides of [*d*-*α*-galaheptose] and their acetates have been obtained in pure condition.

4. The benzyl mercaptal, its acetate and benzoate have been prepared and described.

5. Attention has been called to the parallelism of physical and chemical properties, as well as rotational behavior, of substances of configurationally related structure in the sugar group, as illustrated from substances of the mannose and *α*-galaheptose series.

WASHINGTON, D. C. RECEIVED JULY 8, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Determination of Ionization by Ultraviolet Spectrophotometry: Its Validity and its Application to the Measurement of the Strength of Very Weak Bases[1]

BY LEO A. FLEXSER,[2] LOUIS P. HAMMETT AND ANDREW DINGWALL

It has been amply demonstrated that most organic oxygen compounds are bases of the same kind as ammonia or aniline, but of a much less pronounced basicity.[3] Quantitative knowledge of the strength of these very weak bases is practically non-existent,[4] yet is of crucial importance for the understanding and interpretation of the phenomena of acid catalysis. One of the most promising methods for obtaining these data[4] involves the measurement of the extent of ionization of the base (that is to say, the extent of conversion of the base B to the cation or conjugate acid BH^+) in mixtures of sulfuric acid and water. Such measurements of extent of ionization have previously been made by the method of visual colorimetry;[5] we have now made the rather obvious extension[4] to spectrophotometry in the ultraviolet for cases where there is no visible change in color.

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(1) This article is based upon the dissertation submitted by Leo A. Flexser to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, May, 1935. The material was presented at the New York meeting of the American Chemical Society, April, 1935. A preliminary Communication appeared in THIS JOURNAL, **56**, 2010 (1934).

(2) University Fellow in Chemistry, 1934–1935.

(3) (a) Hantzsch, *Z. physik. Chem.*, **61**, 257 (1908); (b) *ibid.*, **65**, 41 (1908); (c) Hammett and Deyrup, THIS JOURNAL, **55**, 1900 (1933).

(4) Hammett, *Chem. Rev.*, **13**, 61 (1933).

(5) (a) Hammett and Deyrup, THIS JOURNAL, **54**, 2721 (1932); (b) Hammett and Paul, *ibid.*, **56**, 827 (1934); (c) Hammett, *Chem. Rev.*, **16**, 67 (1935).

The simple fact that most organic acids and bases have absorption spectra which differ materially from those exhibited by the corresponding anions or cations has been so beclouded in the discussions of indicator theory that there has even been room to doubt the possibility of determining ionization by measurements of the absorption spectra of simple acids and bases. The method has indeed been successfully applied by Stenström and co-workers[6] to the measurement of the ionization of phenol, but they reported the method inapplicable to the ionization of benzoic acid, and no one else seems to have considered even the possibility of such measurements. Before attempting the determination of unknown constants we have therefore first verified the method on the constants in dilute aqueous solution of benzoic acid, dinitrophenol and aniline, which are known from more familiar methods of measurement.

Experimental

Apparatus.—All apparatus was calibrated either directly or indirectly against apparatus certified by the Bureau of Standards.

The absorption spectra were determined with a Hilger quartz sectorphotometer[7] and E-316 spectrograph using as a source of light a 25,000-volt condensed spark between tungsten electrodes in air. The ultraviolet spectrum down to 2000 Ångström units could be recorded on a single 10.2 by 25.4 cm. photographic plate. The wave length scale was calibrated by means of a copper arc and found to be correct within the error of visually determining match points, *i. e.*, better than 5 Å. throughout the ultraviolet and better than 10 Å. between 4000 and 5000 Å.

Moving pictures taken of the original photometer while the sectors were rotating showed that erratic slipping took place between the belts and the rotating sector disks. This was eliminated by cutting gears into the disks, and meshing them with one another. The upper and lower sectors could both be varied and were used on alternate exposures so that any error arising from initially imperfect matching of the upper and lower halves of the spectrum was automatically canceled out. The angular apertures of the sectors were measured and found to be correct within 5% up to sector settings of $-\log T = 1.3$. The sectors were never used above settings of 1.2 and since most settings were taken in half-unit steps on the less crowded portions of the scale between 0 and 1.0, it is probable that the error is in the neighborhood of 3%. The spark stand, photometer, and spectrograph were mounted on a heavy iron casting, which gave such stability that the instruments would keep their relative positions for several months.

As a check on the set-up, the percentage transmission of a piece of blue glass was measured and compared with the results obtained by the Bureau of Standards for the same piece of glass by an entirely different method, results herewith.

Wave length, Å.	% Transmission Obsd.	Bureau report
5200	80.0	80.6
5600	55.0	58.0
6000	34.0	34.5
6400	17.7	18.0

The agreement is surprisingly good considering the various sources of error inherent in the method.[8]

Two quartz cells were used, one to contain the solvent and the other the solution. The solvent cell was placed in front of the upper sector, the solution cell in front of the lower sector and settings of $-\log T = 0$, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90, 1.0 and 1.2 were taken on the upper sector. The cells were then interchanged and settings of 0.05, 0.15, 0.25, 0.35, 0.45, 0.55, 0.65, 0.75, 0.85, 0.95 and 1.1 taken on the lower sector. A blank setting of 0 on both sectors with the cells removed was taken at the beginning and end of each plate as a check on the instrumental adjustment.

Although several types of cells were used, the most satisfactory were made by clamping two clear fused quartz circular disks to a fused quartz cylinder in a metal holder. The cylinder had a side-arm fitted with a ground silica stopper by which it could be filled and emptied without removal from the holder. The disks were 21 mm. in diameter and 1.5 mm. thick. The cylinder was 1.00 cm. long and had an outer diameter of 20 mm. The faces of the disks and the edges of the cylinder were polished optically plane and parallel. The fit was so good that no leakage was perceptible over a period of several hours. The cell holders could be securely mounted in the photometer by means of spring clips.

Considerable difficulty was encountered at the beginning of this investigation because of the fact that the more concentrated sulfuric acid solutions after standing in the cells for about an hour would begin to absorb ultraviolet light very strongly. The trouble was finally traced to the use of crystalline quartz disks. When fused quartz disks were substituted, the sulfuric acid solutions could be kept indefinitely in the cells without any change occurring. The crystalline quartz appeared to be of excellent quality, was very clear, and transmitted ultraviolet light down to the limit of sensitivity of the photographic plate, about 2000 Å., and the source of the difficulty is unknown. A soft glass cylinder also caused similar difficulty.

Materials.—The materials were of the highest commercially available purity (C. P. or C. P. analyzed grade).

Sulfuric acid solutions were prepared by dilution of the 95% acid. Analyses of weighed samples by titration with sodium hydroxide agreed to better than two parts per thousand. After standing for over a year in No-Solvit and in flint glass bottles, they were still transparent to ultraviolet light and showed no change in concentration greater than the error of analysis. One hundred per cent. sulfuric acid transparent to ultraviolet light was obtained by distilling sulfur trioxide from 60% fuming acid into the

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(6) (a) Stenström and Reinhard, *J. Phys. Chem.*, **29**, 1477 (1925); (b) Stenström and Goldsmith, *ibid.*, **30**, 1683 (1926).

(7) Twyman and Allsopp, "The Practice of Spectrophotometry," Adam Hilger, Ltd., London, 1934.

(8) For a discussion see Gibson, McNicholas, Tyndall, Frehafer and Mathewson, *Scientific Papers of the Bureau of Standards*, No. 440, **18**, 121 (1922).

95% acid in an all-glass apparatus. Benzoic acid and acid potassium phthalate were standard samples from the Bureau of Standards. 2,4-Dinitrophenol was twice crystallized from water after treatment with norite (m. p. 111°). Aniline sulfate was twice crystallized from approximately 1 *N* sulfuric acid after treatment with norite. *p*-Nitrobenzoic acid was twice crystallized from alcohol with one norite treatment, dissolved in 95% sulfuric acid and reprecipitated with ice, then slowly sublimed (m. p. 242°). After each step in the purification the absorption spectrum in 0.1 *M* hydrochloric acid was determined. It remained unchanged throughout the process. Phenylacetic acid was recrystallized from water several times (m. p. 77°). The acidimetric titers of these acids and of the aniline sulfate were found to be correct within two parts per thousand. Anthraquinone was crystallized from glacial acetic acid after treatment with norite; dissolved in 95% sulfuric acid and reprecipitated with ice, then crystallized again from acetic acid. Another sample was crystallized from benzene, then from alcohol, precipitated from 95% sulfuric acid, again crystallized from alcohol and finally crystallized from glacial acetic acid. Both products had identical absorption spectra in 95% sulfuric acid, and the spectrum of the second sample was not changed by the last crystallization.

The late Professor J. L. R. Morgan generously provided a sample of acetophenone which had been very carefully purified in the work of Morgan and Lammert,[9] and which had been kept in a paraffin sealed bottle in a dark closet since 1924. During this time its melting point had dropped from 19.65 to 18.9°. It contained a small amount of absorbing impurity because the spectrum in 95% sulfuric acid of the liquid residue remaining after some 98% had been slowly frozen out differed from that of the original sample. It was purified by twenty-five fractional freezings. These were carried out by slowly freezing (over a period of eight hours) all but 1 cc. of an originally 100-cc. sample, pouring off the liquid, and discarding it. The sample was preserved and the operations were carried out in the exclusion of daylight. The final sample had a melting point of 19.65 ± 0.02°, further fractional freezing had no effect on the melting point, and the spectrum of a small unfrozen residue was identical with that of the whole sample. The sample was carefully protected from moisture and light and its freezing point remained unchanged over a period of about a month.

Method

An approximately 0.002 *M* solution of the substance whose absorption spectrum was to be determined was made up by weighing out the calculated amount of solute and adding 50 cc. of solvent. Absorption spectra of this solution and of successive two or three fold dilutions of it were taken until the complete character of the absorption was brought out. This required from three to six plates. In the case of phenylacetic acid and aniline, a more concentrated original solution had to be made up because of the weak absorption of these substances. In all cases the plates were taken on the same day that the solutions were made up and usually within four hours. All measurements were made at room temperature, about 22 ± 5°.

The plates, which were the Eastman 33 type, were developed with a contrast developer, fixed with Eastman Acid Fixer, washed and dried. They were then mounted over an opal glass in an illuminated stand and match points were visually determined and recorded. The sector setting then gave immediately the value of the logarithm of the transmission T, and from this the extinction coefficient k for this wave length was obtained by Beer's law

$$k = -\log T/cl \qquad (1)$$

where c is concentration in moles per liter and l is the length (in this case 1.00 cm.) in centimeters of the path traversed by the light through the solution. The extinction coefficients were then plotted against wave length on semilogarithmic paper. Since at least twenty points were obtained from each plate, each absorption spectrum thus contained at least sixty points, in a fairly even logarithmic distribution. (See curve 8 in Fig. 4 where the experimental points are plotted.)

Inasmuch as some errors were likely to be introduced in the manipulative details of preparing the solutions in addition to the instrumental error of the apparatus itself, the error in the extinction coefficients is probably about 5%, and more often than not is less than this.

If Beer's law holds, the absorption spectrum from one solution should overlap and run smoothly into the absorption spectrum of its next dilution. This was always found to be the case within the experimental error. In those cases where dilution might change the amount of ionization and thereby result in failure of Beer's law, a buffer solution was used as the solvent in order to prevent this.

The calculation of acid or base strength was made as follows. If a solute exists in two forms, say B and BH^+, so that the total concentration c is equal to the sum of the concentrations of these two forms

$$c = c_B + c_{BH^+} \qquad (2)$$

and if, as seems generally to be the case, each substance absorbs independently of the presence of the other, then[7]

$$-\log T = (k_B c_B + k_{BH^+} c_{BH^+})l \qquad (3)$$

and it follows from equations (1), (2) and (3) that

$$(c_{BH^+})/(c_B) = (k - k_B)/(k_{BH^+} - k) \qquad (4)$$

In a dilute aqueous solution, k_B may be determined by reducing the acidity to the point where the concentration of BH^+ is vanishingly small; k_{BH^+} similarly by increasing the acidity. Knowing these, a measurement of k in some solution of intermediate acidity permits the calculation of c_{BH^+}/c_B and from this, if the *p*H of the solution is known, of the ionization constant of the base. The modifications of the above considerations necessary if the ionization constant of a weak acid HA which ionizes to H^+ and A^- is to be measured are obvious. In the measurement of the strengths of very weak bases in strong sulfuric acid solutions, certain complications, which will be discussed later, arise from the fact that the change of acidity involves necessarily a significant change in the nature of the medium with a concomitant change in the absorption spectrum.

Measurements in Dilute Aqueous Solution

The Acid Strength of Benzoic Acid.—The absorption of benzoic acid was determined in the

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[9] Morgan and Lammert, THIS JOURNAL, **46**, 881 (1924).

following solvents: (1) 0.1 *N* sulfuric acid; (2) a buffer containing 0.10 *M* sodium acetate and 0.35 *M* acetic acid (this solvent is transparent in most of the range of wave lengths available); (3) 0.1 *M* sodium hydroxide. The results are plotted in Fig. 1, and the extinction coefficients are given in Table I.

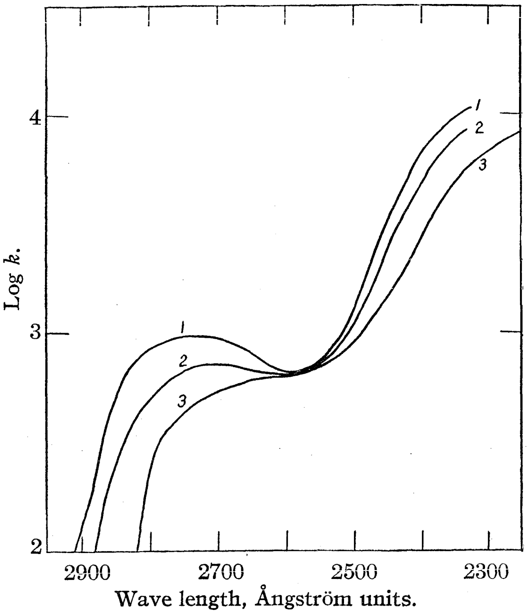

Fig. 1.—Ionization of benzoic acid as an acid: Curve 1, 0.1 *N* H_2SO_4; Curve 2, buffer; Curve 3, 0.1 *N* NaOH.

TABLE I

BENZOIC ACID

Wave length, Å.	Extinction coefficients in 0.1 *N* H_2SO_4	0.1 *M* NaOH	Buffer	pK
2857	450	50	225	4.11
2791	840	300	540	4.13
2727	950	475	680	4.10
2667	820	575	680	4.09
2609	675	620	640	..
2553	740	700	720	..
2500	1350	900	1050	3.92
2449	3050	1400	2350	4.35
2400	6450	2300	4500	4.27
2353	9200	4800	7200	4.30
			Average	4.16 ± 0.11

The logarithmic ionization constant pK was calculated by the equation

$$pK_{\text{HB}} = pK_{\text{HA}} + \log c_{\text{A}^-}/c_{\text{HA}} - \log (k - k_{\text{HB}})/(k_{\text{B}^-} - k) \quad (5)$$

derived from substitution of equation (4) in the equation

$$pK_{\text{HB}} = pK_{\text{HA}} + \log c_{\text{A}^-}/c_{\text{HA}} - \log c_{\text{B}^-}/c_{\text{HB}} \quad (6)$$

which is an obvious combination and transformation of the equilibrium expressions for the ionization of acetic and benzoic acids. The subscript A refers to acetate and the subscript B to benzoate. For the calculations values of k_{HB} were taken from curve 1, those of k_{B^-} from curve 3, and those of k from curve 2. The value of pK_{HA} was taken as 4.76.[10] This equation assumes that the quantity $f_{\text{A}^-}f_{\text{HB}}/f_{\text{HA}}f_{\text{B}^-}$ is unchanged by a transfer from infinite dilution to an ionic strength of 0.1. Within the precision of this assumption, therefore, the pK_{HB} obtained is the value in terms of activities referred to infinite dilution in water as the standard state

$$pK_{\text{HB}} = -\log a_{\text{H}^+}a_{\text{B}^-}/a_{\text{HB}} \quad (7)$$

Table I gives the values of pK thus obtained at various wave lengths, omitting those in the neighborhood of the isobestic point, the point where all three curves meet.[11] The average value of 4.16 thus obtained is in satisfactory agreement with the value of 4.20 found in the recent measurements by the conductivity method of Brockman and Kilpatrick[12] and of Saxton and Meier.[13]

The conclusion of Stenström and co-workers[6] that ultraviolet colorimetry cannot be applied to the measurement of the ionization of benzoic acid was apparently due to the limitations of their measurements. They did not determine the complete absorption spectra of benzoic acid but instead measured the wave lengths at which benzoic acid has an extinction coefficient of 800 (log k = 2.9). They thereby determined three points of the curve for benzoate ion and three for molecular benzoic acid. Four of these six points happen to fall on the isobestic point where of course no change takes place. The other two points are not in agreement with our measurements.

The Acid Strength of 2,4-Dinitrophenol.—The absorption spectra were determined in the

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[10] (a) Harned and Ehlers, THIS JOURNAL, **55**, 652 (1933); (b) MacInnes and Shedlovsky, *ibid.*, **54**, 1429 (1932).

[11] The existence or non-existence of an isobestic point is a matter of considerable significance in studies of this sort. Suppose a given solute exists in two forms or reaction products (such as a base B and a cation BH^+) each of which possesses a characteristic absorption which is constant for a series of solutions. If both of the forms have equal extinction coefficients at some wave length, if, that is, the absorption curves of the two pure individuals intersect, then all of the solutions must likewise have the same coefficient at this wave length, because they contain only various mixtures of these individuals. The absorption curves of all the solutions, therefore, will pass through this intersection. Conversely, if two absorption curves intersect at a point which is not common to all the other curves, then it must be true either that more than two forms or reaction products of the solute must be present, or else that the change in conditions, for instance, in acidity, which produces the variation in proportion of the two forms also changes their specific absorption by what we have called a medium effect. See Clark, "The Determination of Hydrogen Ions," Baltimore, Md., 1928, pp. 153–154.

[12] Brockman and Kilpatrick, THIS JOURNAL, **56**, 1483 (1934).

[13] Saxton and Meier, *ibid.*, **56**, 1919 (1934).

following solvents: (1) 0.1 *M* sodium hydroxide; (2) a buffer containing 0.55 *M* acetic acid and 0.10 *M* sodium acetate; (3) 0.1 *M* hydrochloric acid. The results are shown in Fig. 2 and Table II. In this case the absorption of the anion extends well into the visible, and this part of the spectrum as well as the ultraviolet is included. The average value of $pK = 4.10$ agrees excellently with the value of 4.09 obtained by von Halban and Kortum[14] and with the earlier conductivity results quoted in the Landolt–Börnstein "Tabellen."

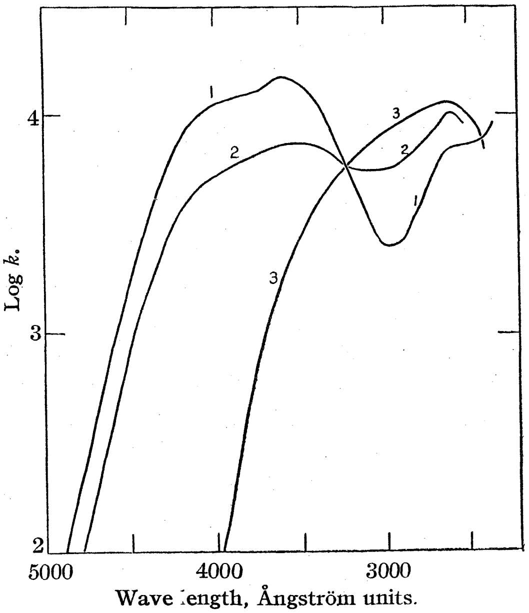

Fig. 2.—Ionization of 2,4-dinitrophenol as an acid: Curve 1, 0.1 *N* NaOH; Curve 2, buffer; Curve 3, 0.1 *N* HCl.

TABLE II

2,4-DINITROPHENOL

Wave length, Å.	Extinction coefficients in 0.1 *M* HCl	0.1 *M* NaOH	Buffer	pK
4615	0	750	300	4.20
4444	0	2500	1100	4.12
4286	0	5800	2500	4.14
4138	0	8800	3950	4.11
4000	0	10800	4900	4.10
3871	250	11700	5500	4.09
3750	630	12500	6500	4.03
3636	1,600	14500	7300	4.12
3529	2,450	14000	8000	4.05
3429	3,600	11800	7700	4.02
3333	4,800	9000	6800	4.06
3243	5,700	6500	6100	4.02
3158	6,700	4450	5700	4.12
3077	7,400	3250	5400	4.05
3000	8,000	2500	5500	4.10
2927	8,500	2400	5700	4.09
2857	9,000	3050	6300	4.10
2791	9,600	3800	7100	4.14
2727	10,200	4650	7900	4.17
2667	11,000	6000	8900	4.16
2609	11,200	6900	10000	4.43[a]
2553	10,900	7200	9100	4.04
			Average	4.10
				± 0.04

[a] Omitted from average.

The Base Strength of Aniline.—The absorption spectra of aniline were determined in the following solvents: (1) 0.1 *M* sodium hydroxide; (2) a buffer solution containing 0.080 *M* acetic

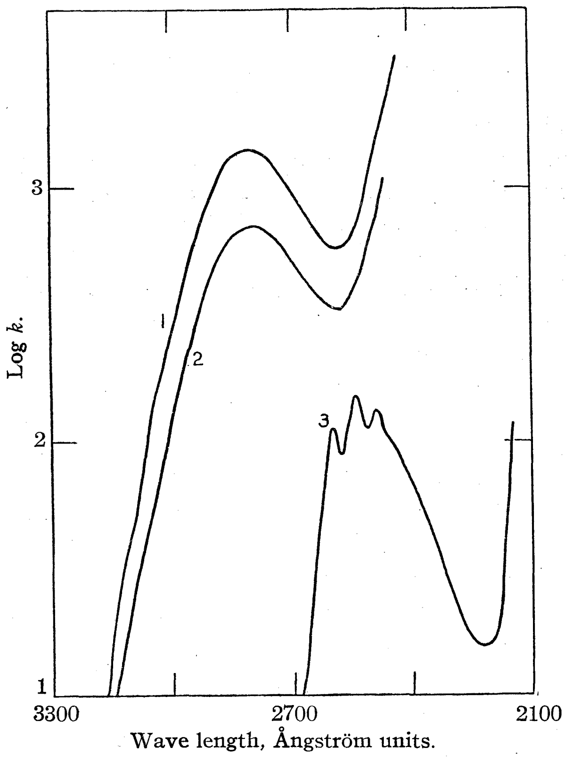

Fig. 3.—Ionization of aniline as a base: Curve 1, 0.1 *M* NaOH; Curve 2, buffer; Curve 3, 0.1 *M* H_2SO_4.

TABLE III

ANILINE

Wave length, Å.	Extinction coefficients in 0.1 *M* H_2SO_4	0.1 *M* NaOH	Buffer	pK'
3077	0	63	36	4.51
3000	0	275	130	4.68
2927	0	710	340	4.67
2857	0	1300	620	4.67
2791	0	1480	710	4.67
2727	0	1200	600	4.63
2667	14	810	440	4.57
2609	88	590	345	4.61
2553	120	630	375	4.63
2500	113	1250	630	4.71
			Average	4.64 ± 0.05

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(14) Von Halban and Kortum, *Z. Elektrochem.*, **40**, 502 (1934).

acid and 0.10 *M* sodium acetate; (3) 0.1 *M* sulfuric acid. For convenience the solutions were prepared from anilinium sulfate rather than from aniline. The results are shown in Fig. 3 and Table III.

In computing the base strength from these curves, it is not possible to correct for salt effects as simply as in the case of the acids because the activity coefficient terms do not cancel out. The base strength of aniline is defined by

$$\begin{aligned} pK'_A &= -\log a_{H^+}a_A/a_{AH^+} \\ &= pH - \log f_A/f_{AH^+} - \log c_A/c_{AH^+} \qquad (8) \\ &= pH - \log f_A/f_{AH^+} - \log (k - k_{AH^+})/(k_A - k) \qquad (9) \end{aligned}$$

The *p*H of the buffer was calculated from the tables of A. A. Green[15] and found to be 4.75. The activity coefficient term was computed from the formula based on the Debye–Hückel theory.

$$-\log f_A/f_{AH^+} = +\log f_{AH^+} = 0.5\sqrt{\mu}/(1 + \sqrt{\mu}) \qquad (10)$$

This gives a value of $\log f_{AH^+} = -0.12$, for the ionic strength of 0.1 which prevailed.

The average value of pK' obtained is in excellent agreement with the value of 4.66 given in the Landolt–Börnstein "Tabellen" and based upon hydrolysis measurements by both conductivity and indicator methods.

Some Cases of Small Change in Absorption.—It should not be concluded that spectrophotometry in the quartz ultraviolet is a perfectly general method for the determination of ionization. Thus the change in ultraviolet absorption when phenylacetic acid ionizes to phenylacetate ion is appreciable[16] but too small to permit a useful estimate of acid strength. Similarly, the conversion of *p*-nitrobenzoic acid to *p*-nitrobenzoate ion also results in only a small change in this part of the ultraviolet absorption (see Fig. 8). However, our results, together with data in the literature, tend toward the conclusion that with the majority of organic substances ionization results in a change in ultraviolet absorption above 2000 Å. and that ultraviolet spectrophotometry in the range accessible to an ordinary quartz spectrograph is a very general method for measuring ionization.

The Strengths of Some Very Weak Bases

Acetophenone.—Acetophenone has been shown to behave as a monobasic strong electrolyte when it is dissolved in pure sulfuric acid.[3a] The substance is therefore capable of undergoing the reaction

$$C_6H_5COCH_3 + H_2SO_4 = C_6H_5COH^+CH_3 + HSO_4^- \qquad (I)$$

For such a weak base, the work of Hammett and Deyrup[5] carried out by the methods of visual colorimetry lead one to expect the following changes in light absorption with varying concentration of sulfuric acid–water mixtures. Within a relatively narrow range of concentrations there will be a large change in absorption accompanying the ionization represented by equation I. Outside this range there will be a smaller change in absorption due not to a chemical reaction but to the gradual variation in the nature of the medium in which the substance $C_6H_5COCH_3$ or the substance $C_6H_5COH^+CH_3$ is dissolved. The absorption spectra of acetophenone shown in Fig. 4 and Table IV agree entirely with this prediction. There is only a small change in absorption, consisting essentially in a shift toward longer wave lengths in the range from 0 to 55% sulfuric acid (Curves 1 and 2). The same thing is true in the region above 86% sulfuric acid (Curves 8 and 9). In the intermediate region (Curves 2 to 8) there is a much more rapid change which is no longer of the nature of a lateral shift. It is rather of a sort which can hardly be attributed to any other cause than the presence in the solution in varying amounts of two substances, one of which has an absorption much like curve 2, the other one similar to curve 8. The composite nature of the intermediate curves is particularly apparent in curves 4 and 5.

The qualitative picture, that ionization according to equation I takes place in the region from 55 to 86% sulfuric acid, while only a medium effect—a slow lateral shift in the absorption curves—occurs at higher and lower concentrations, seems very well established. The quantitative treatment is more difficult because the same medium effect must be expected to exist also in the region of ionization. That it is present is demonstrated by the failure to obtain a true isobestic point.[11]

In order to calculate the base strength we use the values (taken from large scale plots) of the acidity function H_0 which have been obtained in previous work.[5] This acidity function has been shown[5] to be uniquely determined in these solutions by the equation

$$H_0 = pK'_B - \log c_{BH^+}/c_B \qquad (11)$$

where B is any base and

$$pK'_B \equiv -\log \frac{a_{H^+}a_B}{a_{BH^+}} \qquad (12)$$

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[15] A. A. Green, This Journal, **55**, 2331 (1933).

[16] Ley and Hünecke, *Ber.*, **59**, 521 (1926).

TABLE IV

EXTINCTION COEFFICIENTS OF ACETOPHENONE IN $H_2SO_4 + H_2O$ MIXTURES

Wave length, Å.	% H_2SO_4									
	0.0	50.03	55.0	65.15	70.45	73.65	77.66	80.40	85.96	95.99
3700	0	0	0	0	0	0	0	120	175	300
3600	0	0	0	0	0	130	240	360	530	850
3500	0	0	0	60	175	325	580	840	1120	1500
3400	0	0	0	110	370	650	1100	1400	1750	2100
3300	0	0	0	200	670	960	1480	1820	2080	2400
3200	55	90	95	380	890	1300	1850	2250	2600	2900
3100	105	220	300	770	1550	2200	3200	4100	5400	7200
3000	310	680	840	1800	3700	5800	9400	12300	15400	20500
2900	900	1350	1590	3400	6600	10000	13900	17200	19900	20500
2800	1150	1800	2260	4750	7800	10500	12700	13300	13700	12000
2700	1400	3000	3800	6500	8400	9000	8700	8200	6500	4600
2600	4300	7700	8400	10000	9000	7700	5800	4200	2600	1500
2500	11000	11500	11700	10100	7500	5800	3350	2000	900	400
2400	11000	9000	8600	6200	4300	3000	1650	830	375	200
2300	5700	4100	3800	2400	1800	1200	680	500	420	380

is the measure of the strength of the base in terms of activities. By combination of equations (11) and (4) we obtain

$$pK'_B = H_0 - \log (k - k_{BH^+})/(k_B - k) \qquad (13)$$

which is of course closely analogous to equation (9). Because of the medium effect, however, pure non-ionized acetophenone must have a different absorption in say 70% sulfuric acid from that which it possesses in water or even in 50% acid. We cannot, therefore, use the extinction coefficient of acetophenone in water solution as the value of k_B, nor can we use the coefficient in 100% sulfuric acid as the value of k_{BH^+}, even though we know that it is practically non-ionized in the former solvent and practically all ionized in the latter.

We have used two methods of correcting for this medium effect error, both dependent upon the assumption that the medium effect consists essentially in a lateral shift of the spectrum within the range of ionization as it does without this range. The first method was evolved from the following considerations. Suppose that in the neighborhood of some wave length at which the pK' is to be calculated, the reference curve for ionized acetophenone is very steep while the reference curve for non-ionized acetophenone is more or less flat. Now if the medium effect is causing the curves to shift, the reference curve for ionized acetophenone will be in great error because of its steepness, whereas the extinction coefficients of the curve for non-ionized acetophenone will be only slightly affected because of the flatness of the curve in the neighborhood of the wave length under consideration. Thus in calculating the pK' by means of formula (13), the error will be due primarily to the large error in k_{BH^+} resulting from the medium effect. There will, therefore, be considerable advantage if the pK' is calculated from experimental values of k and k_B alone in this range of wave lengths. There will be a similar advantage in using only k and k_{BH^+} in a range of wave lengths where the curve for ionized acetophenone is flat and that for the non-ionized compound is steep.

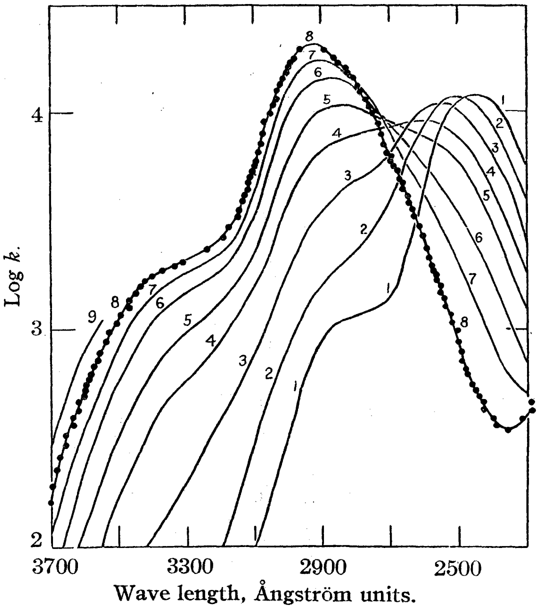

Fig. 4.—Ionization of acetophenone as a base: Curve 1, solvent is water; other curves sulfuric acid—2, 55%; 3, 65.15%; 4, 70.45%; 5, 73.65%; 6, 77.66%; 7, 80.40%; 8, 85.96%; 9, 95.99%.

For purposes of this calculation we transform equation (13) to the form

$$\text{antilog } (-pK'_{\text{B}}) \equiv K = \text{antilog } (-\text{H}_0) \times (k - k_{\text{BH}^+})/(k_{\text{B}} - k)$$

or

$$K = h_0\,(k - k_{\text{BH}^+})/(k_{\text{B}} - k) \qquad (14)$$

where

$$h_0 \equiv \text{antilog } (-H_0) \qquad (15)$$

Formula (14) may be put into two forms

$$K + k_{\text{BH}^+}[h_0/(k_{\text{B}} - k)] - h_0 k/(k_{\text{B}} - k) = 0 \qquad (16)$$

$$1/K + k_{\text{B}}[1/h_0(k_{\text{BH}^+} - k)] - k/h_0(k_{\text{BH}^+} - k) = 0 \qquad (17)$$

Both of these equations are of the form

$$a + bx - y = 0 \qquad (18)$$

where x and y are known quantities and a and b may be calculated, if two sets of values for x and y are known. If more than two sets of values of x and y are known, it is of course best to use a least squares solution. Formula (16) is to be used when the reference curve for non-ionized acetophenone is the flatter and formula (17) at those wave lengths at which the curve for ionized acetophenone is flatter. At those wave lengths where both curves are equally flat, formula (13) should give satisfactory values.

The reference curves for the ionized and for the non-ionized substance should obviously be taken as near the range of ionization as possible, yet sufficiently removed so that the substance is present essentially in one form, ionized or non-ionized only. To make this choice we have used the following procedure: a rough value of pK' was calculated using reference curves well outside the region of ionization. Using this approximate value, a calculation was made of the range of sulfuric acid concentration in which ionization of acetophenone would be less than 5% and greater than 95%. An appropriate safety factor was then allowed to take care of the error in the pK'. In this way, 55% sulfuric acid was chosen as the reference solvent for non-ionized acetophenone, and 86% sulfuric acid as the reference solvent for completely ionized acetophenone.

In deciding which reference curve is the flatter, the plot of log k against the wave length is misleading because of its logarithmic nature. Accordingly, the curves were replotted using k instead of log k as ordinate. Inspection of these curves revealed which reference curve and, therefore, which equation should be used for each wave length. The equations so chosen are listed in Table V which contains the results of the calculation.

TABLE V

$-pK'$ VALUES OF ACETOPHENONE COMPUTED BY LEAST SQUARES

Wave length, Å.	Equation	% H_2SO_4 65.15	70.45	73.65	77.66	80.40	Average	Deviation
3500	16	6.10	6.27	6.32	6.34	6.17	6.25	0.08
3400	16	6.04	6.13	6.18	6.16	6.10	6.13	.04
3300	13	5.87	5.92	6.07	6.09	6.03	6.00	.08
3200	13	5.79	5.93	6.03	6.11	6.09	5.99	.10
3100	16	5.80	5.97	6.08	6.12	5.88	5.99	.10
3000	16	6.01	6.16	6.23	6.23	6.09	6.15	.08
2900	13	5.86	6.03	6.07	6.17	6.12	6.05	.08
2800	16?	5.46	5.64	5.61	5.52	5.57	5.56[a]	.06
2700	..	..	..	..	..	..	..	..
2600	17?	6.31	6.30	6.30	6.33	6.30	6.31[a]	.01
2500	17	6.00	5.89	5.98	5.99	5.97	5.96	.03
2400	17	5.80	5.77	5.82	5.86	5.73	5.79	.04
2300	17	5.58	5.74	5.69	5.57	5.42	5.58[a]	.09
						Average	6.03	±.10

[a] Omitted from final average.

The second method of calculation depends upon the principle that all of the absorption curves due to mixtures in varying proportions of two substances (in this case the base and the cation) must intersect in a single point if any two intersect and if there is no medium effect.[11] If the medium effect represents a shift in wave length only, without change in shape or height of the bands, it should be possible to compensate for its effect by shifting all of the absorption curves laterally to produce a single intersection, an isobestic point, somewhere in the middle of the ionization region. Inspection of the curves of Fig. 4 shows that Curves 4 and 5 are very close to what would be expected for approximately 50% ionization. We have, therefore, shifted the curves for other solvents laterally so that they all pass through the intersection of these two

TABLE VI

$-pK'$ VALUES FOR ACETOPHENONE BY ISOBESTIC POINT METHOD

Wave length, Å.	% H_2SO_4 65.15	70.45	73.65	77.66	80.40	Average	Deviation
3600	..	..	6.05	6.32	5.98	6.12	0.14
3500	..	6.07	6.05	6.18	6.06	6.09	.04
3400	5.87	6.01	6.02	6.13	5.91	5.99	.08
3300	5.94	6.02	6.03	6.10	5.93	6.00	.06
3200	5.74	5.89	5.92	6.01	5.79	5.87	.08
3100	5.67[a]	4.86[a]	5.65[a]	5.82[a]	..	5.50[a]	.32
3000	5.69[a]	5.85[a]	5.66[a]	5.63[a]	..	5.71[a]	.07
2900	5.83	6.02	6.03	6.15	6.04	6.01	.08
2800	5.77	5.96	6.04	6.12	6.22	6.02	.13
2700	..	5.89	6.06	6.23	..	6.06	.11
2600	..	6.06	6.00	6.06	5.78	5.98	.10
2500	5.85	5.99	5.99	6.04	5.80	5.93	.09
2400	..	6.32	6.08	6.21	6.08	6.17	.09
Average	5.83	6.02	6.03	6.14	5.96	6.02	
Deviation	0.05	0.08	0.03	0.07	0.12	0.08	

[a] Omitted from average.

curves and have then calculated the pK' of acetophenone from these shifted curves. The results are given in Table VI.

The average values of pK' obtained by the two methods agree excellently. Furthermore, both methods show only a random variation of pK' with wave length. (This is most decidedly not the case if no account is taken of the medium effect.) All in all, it seems probable that this quantity, which has never before been measured in even the most approximate fashion, is now known within at least 0.1 unit.

A solution of acetophenone in 0.1 *M* aqueous hydrochloric acid would therefore be converted to the cation $C_6H_5COH^+CH_3$ to the extent of only one part in ten million. This is of course a figure of interest for the interpretation of such acid-catalyzed reactions of acetophenone as the bromination. The base acetophenone is nearly 10^{10} weaker than aniline; compared with nitrogen bases it is intermediate in strength between 2,4-dinitroaniline and 6-bromo-2,4-dinitroaniline, but is still over a thousand times stronger than 2,4,6-trinitroaniline; compared with other oxygen bases, its strength lies between that of β-benzoylnaphthalene and that of *p*-benzoyldiphenyl, and it is only about 0.4 logarithmic unit weaker than the familiar "halochromic" ketone benzalacetophenone.

Some Considerations about Indicators.—A medium effect was recognized in the colorimetric work in sulfuric acid–water mixtures of Hammett and Deyrup[5a] where it appeared as a variation in color intensity. There was no visible change in color quality which would have rendered a colorimetric match impossible. Yet the lateral shifts of the whole absorption curve toward longer wave lengths to which we now apply the same term, might, at first sight, be expected to result much more in a change in color quality than one in intensity. The explanation of the apparent contradiction derives from certain properties of human vision combined with the fact that the indicators studied were all of the colorless–yellow type. Their colorimetric behavior depends, therefore, upon the absorption by the yellow form of frequencies in the violet. In this range the human eye has little if any sense of color quality and it apprehends a shift in the absorption curve simply as a change in intensity without a concomitant change in color quality.[17] Thus the medium effect does not interfere with obtaining a colorimetric match, and all that need be corrected for is the change in intensity, which is not too difficult.

If, however, the indicator changed from colorless to let us say, blue, an evaluation of the medium effect would be very difficult because a small shift in the absorption spectrum due to the medium effect would not only change the intensity of the absorbed light but also its color, and it would be impossible to obtain a match in the colorimeter. This result has some application to colorimetric measurements in dilute aqueous solution, where medium effects due to changes in ionic strength or other variations in composition are larger than is sometimes appreciated. The nitrophenol indicators of Michaelis avoid color matching difficulties in this way, because they change from colorless to strong yellow.

An example of the difficulties which may result from the medium effect may be found in the work of Baker.[18] His work on the basic properties of organic oxygen compounds is of the greatest significance and interest, but he appears to have been misled by a medium effect in respect to the range of acidity in which acetophenone ionizes. He considered that the ionization occurs in the region in which the pale yellow color possessed by acetophenone in concentrated sulfuric acid is developing. Now in Fig. 4 the curves have been so drawn that an intercept on the ordinate of 3700 Å. corresponds to a visible yellow color in a solution containing a few thousandths molar acetophenone. It will be seen that the color does not appear until the acetophenone is practically completely converted to the ion and that the deepening of the yellow color with increasing concentration of sulfuric acid is due solely to the shift resulting from the medium effect. The change in absorption due to ionization occurs entirely in the ultraviolet.

Benzoic Acid.—This substance is also known to be a strong monoacid base in 100% sulfuric acid.[3] The absorption spectra were determined in sulfuric acid–water mixtures from 0.5 to 100% sulfuric acid. Some of the curves are given in Fig. 5. Only a medium effect shift to higher wave lengths appears between 0.5 and 70.20% sulfuric acid (Curves 1 and 2) and the large change corresponding to the basic ionization occurs between 70.20 and 95.65% sulfuric acid (Curves 3 to 5,

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(17) Gibson and Tyndall, *Bureau of Standards Scientific Paper* No. 475 (1923).

(18) Baker, *J. Chem. Soc.*, 307 (1931).

TABLE VII

EXTINCTION COEFFICIENTS OF BENZOIC ACID IN $H_2SO_4 + H_2O$ MIXTURES

Extinction coefficients for 0.5% = 0.1 N H_2SO_4 are in Table I

Wave length, Å.	% H_2SO_4 70.20	76.11	77.66	80.40	81.84	83.46	85.69	90.52	95.65	100.0
3243	0	0	25	50	75	85	120	220	310	360
3158	0	60	100	185	260	340	500	790	970	1130
3077	15	170	250	450	600	790	1025	1440	1600	1800
3000	120	360	470	750	960	1150	1450	1840	1950	2040
2927	390	710	800	1120	1270	1420	1625	1920	1950	1900
2857	910	1125	1180	1340	1450	1600	1665	1890	1930	1950
2791	1150	1330	1360	1500	1580	1780	1900	2500	2760	2840
2727	1130	1500	1600	2100	2550	3200	4100	6100	7880	8560
2667	1060	2060	2700	4080	5500	6800	8800	12350	14050	15600
2609	1400	3200	4100	6320	8150	9700	12100	15350	16050	17700
2553	2550	5000	6050	8250	9850	11000	12160	14750	14800	14350
2500	5100	7700	8500	9650	10650	11400	11200	12350	11600	10400
2449	8450	10300	10450	10000	10300	10750	9500	8850	7800	7000
2400	10700	10900	10800	9650	9200	8800	7500	5900	4750	4150
2353	11000	10500	9750	8200	7600	6800	5480	3900	2720	2130
2308	9700	8650	7800	6500	5800	4850	3600	2440	1660	1180
2264	7450	6400	5500	4400	3800	3080	2200	1350	870	560
2222	5600	4200	3800	2850	2300	2000	1300	800	455	300
2182	3450	2600	2400	1750	1520	1250	880	615	405	320

inclusive). Above 95.65% sulfuric acid there is again a shift corresponding to the medium effect. Curves 3 and 4 for the solvents 81.84 and 83.46% sulfuric acid correspond approximately to half ionization. The extinction coefficients for the various solvents are given in Table VII.

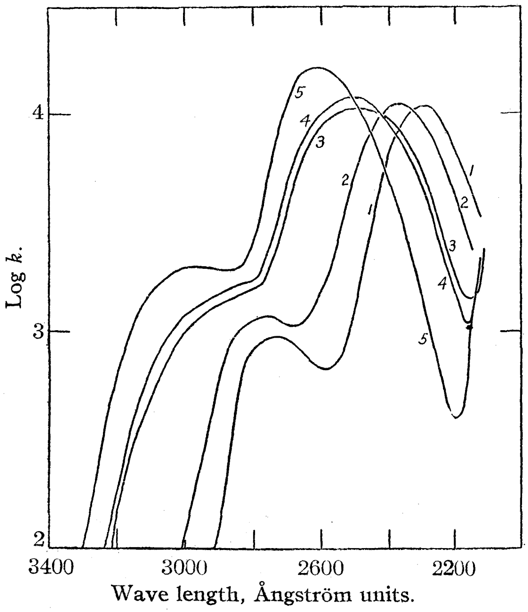

Fig. 5.—Ionization of benzoic acid as a base in sulfuric acid: Curve 1, 0.5% (0.1 N); 2, 70.20%; 3, 81.84%; 4, 83.46%; 5, 95.65%.

The pK' values computed by the least squares method (or by equation (13) where both reference curves are flat) are contained in Table VIII. The concentration of ion was assumed to be negligible in 70.20% acid, and the ionization was taken as essentially complete in 95.65% acid. Values were also computed by the second method, shifting the curves laterally so that they all passed through the intersection of Curves 3 and 4 at a wave length of 2430 Å. and an extinction coefficient of 10,000. This gave a value of -7.11 ± 0.10 from the data on 83.46% acid and -7.09 ± 0.04 from those on 81.84% acid. These are in fair agreement with the average of -7.26 ob-

TABLE VIII

$-pK'$ VALUES OF BENZOIC ACID COMPUTED BY LEAST SQUARES

Wave length, Å.	Equation	Average-pK' for seven solvents	Deviation
3243	16	7.56	0.12
3158	16	7.51	.08
3077	16	7.33	.08
3000	13	7.17	.08
2927	17	7.01	.15
2857	17	7.11	.07
2791	16	7.31	.22
2727	16	7.59	.07
2667	16	7.40	.06
2609	13	7.16	.09
2353	17	7.33	.10
2308	17	7.22	.07
2264	17	7.11	.08
2222	17	7.09	.07
2182	17	7.07	.06
		Average, 7.26 ± 0.16	

tained by the least squares method, which should be considered the more reliable.

The base benzoic acid is from 1 to 1.5 logarithmic units weaker than the various phenyl ketones previously studied. The wide spread between the first and second acidity constants of the cation $C_6H_5C(OH)_2^+$ is worthy of note but not unexpected in view of the small distance between the two hydrogens. The acidity of a solution in which benzoic acid is half ionized to benzoate ion must be increased about 11.5 logarithmic units in order to convert it to a half ionized base.

Anthraquinone.—The base strength has previously been determined by the colorimetric method.[5a,b] Absorption curves are given in Fig. 6 and extinction coefficients in Table IX. The solubility in aqueous sulfuric acid of less than 85% concentration is so small that the determination of a reference absorption spectrum for the non-ionized base is impracticable. The pK' values must, therefore, be calculated from equation (17), which can be applied without serious error only in regions where the curve for BH^+ is flat. This limits us in this case to the region around 4000 Å. From the absorption at 100 Å. intervals between 4400 and 3900 we obtain an average pK' of -8.18 ± 0.19, which agrees well with the value of -8.15 from visual colorimetry.

TABLE IX

EXTINCTION COEFFICIENTS OF ANTHRAQUINONE IN $H_2SO_4 + H_2O$ MIXTURES

Wave length, Å.	% H_2SO_4 85.96	89.27	90.52	92.97	95.99	100.0
4500	1080	1750	1900	2300	3000	4250
4400	1700	3100	3500	4300	5200	6400
4300	2600	4700	5300	6200	7400	8300
4200	3550	5400	6000	7500	8800	9500
4100	4150	5750	6300	8200	9400	9900
4000	4800	5950	6500	8100	9300	9700
3900	5300	6000	6550	7300	8600	8800
3800	5600	6000	6300	6500	7300	7500
3700	5600	5800	5900	5800	6000	5600
3600	5200	5000	4800	4500	4400	3900
3500	4500	3850	3750	3100	2800	2600
3400	3600	2750	2500	2150	1800	1750
3300	2500	1900	1700	1600	1300	1300
3200	2800	2900	3000	3200	4000	4400
3100	6600	9200	9900	11200	12500	12700
3000	7500	8800	9000	9300	9800	9400
2900	10500	8200	7600	6500	5550	5400
2800	9500	7000	6700	6400	5800	5600
2700	23000	29000	35000	35000	39000	39000
2600	45000	37000	35000	32000	29000	26000
2500	21000	18000	17000	16000	15000	14000

The low precision is due, at least in part, to the low dispersion of the spectrograph used in this range of wave lengths.

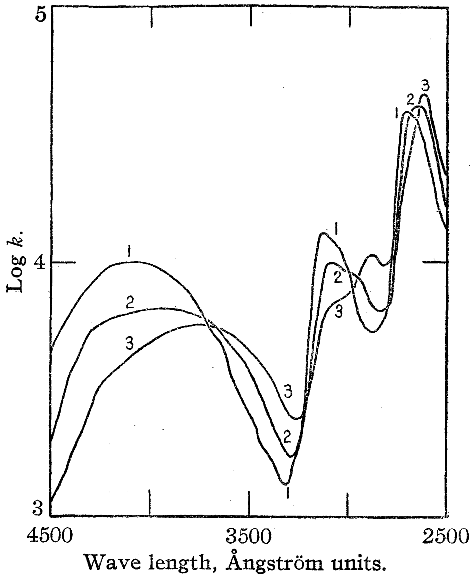

Fig. 6.—Ionization of anthraquinone as a base in sulfuric acid as solvent: Curve 1, 100.0%; 2, 90.52%; 3, 85.96%.

Phenylacetic Acid.—In spite of the fact that there is very little change in absorption when phenylacetic acid ionizes to phenylacetate ion,[16] there is a fairly large change when this acid gains rather than loses a hydrogen ion. Results of absorption measurements are shown in Fig. 7 and Table X.

TABLE X

EXTINCTION COEFFICIENTS OF PHENYLACETIC ACID IN $H_2SO_4 + H_2O$ MIXTURES

Wave length, Å.	% H_2SO_4 70.20	76.11	81.84	85.69	90.52
2800	0	0	10	26	68
2750	0	0	26	65	160
2700	22	30	69	130	260
2650	90	95	150	240	400
2600	138	142	225	350	500
2550	165	183	260	400	600
2500	140	178	290	460	700
2450	117	168	330	550	840
2400	126	205	405	640	950
2350	200	320	560	770	1130
2300	405	520	770	1000	1290
2250	720	850	1050	1270	1550
2200	1300	1430	1650	1600	1840

Above 90% sulfuric acid, the absorption changes rapidly with time, probably as a result of sulfonation. Thus the spectrum of a solution in 95.99% acid taken within an hour after prepa ration was similar in shape to curve 3 in Fig. 7 but displaced upward. The spectrum after three hours is shown in Curve 4. At 90% sulfuric acid or less the rate of this change is negligible. It is, therefore, impracticable to determine the absorption of the completely ionized form, and the pK' must be calculated from measurements on the non-ionized base and on partially ionized mixtures, using equation (16). The average value obtained from wave lengths of 2350, 2400, 2450, 2500 and 2550 Å., in the region in which the curve for the non-ionized base is flat, is -7.59 ± 0.13.

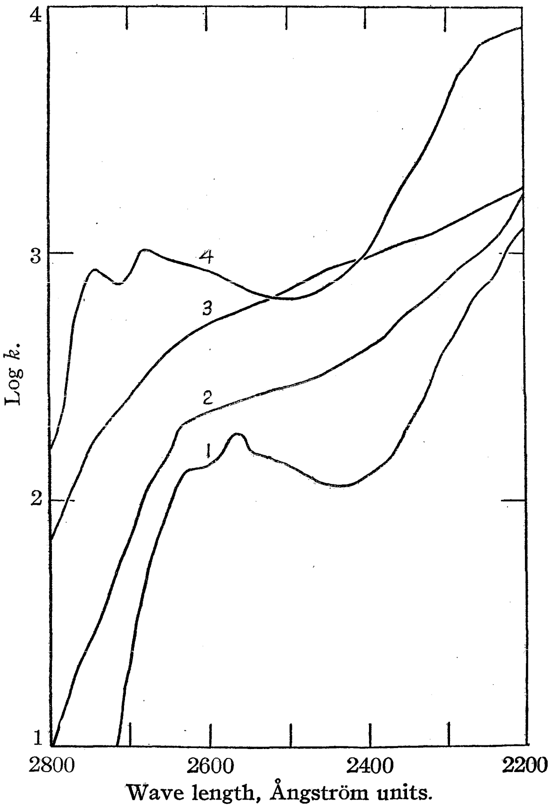

Fig. 7.—Ionization of phenylacetic acid as a base in sulfuric acid: Curve 1, 70.20%; 2, 81.84%; 3, 90.52%; 4, 95.99% (stood three hours).

It will be noted that base strength does not go inversely as acid strength. Phenylacetic acid is both a slightly weaker acid and a slightly weaker base than benzoic acid.

Although the base strengths of benzoic and phenylacetic acids are very nearly the same, the reaction rates of their acid catalyzed esterifications are very different.[19] Thus the esterification of phenylacetic acid with absolute ethyl alcohol in the presence of catalyzing hydrochloric acid is almost a hundred times faster than the corresponding esterification of benzoic acid.

It has not infrequently been implied in discussions of the acid catalysis of esterification that the rate should be uniquely determined by the base strength of the acid being esterified. This is evidently not the case.

***p*-Nitrobenzoic Acid.**—We have already pointed out that the change in ultraviolet absorption attending the ionization of this substance into *p*-nitrobenzoate ion is too small to permit measurement of the acid strength by this method (see Fig. 8). The ionization as a base also takes place with very little change in ultraviolet absorption. (It is completely ionized in 100% sulfuric acid.[3]) In fact the whole change in absorption from 0.1 *M* sodium hydroxide to 95.65% sulfuric acid might reasonably be attributed to medium effect alone. There is no obvious reason why this should be the case.

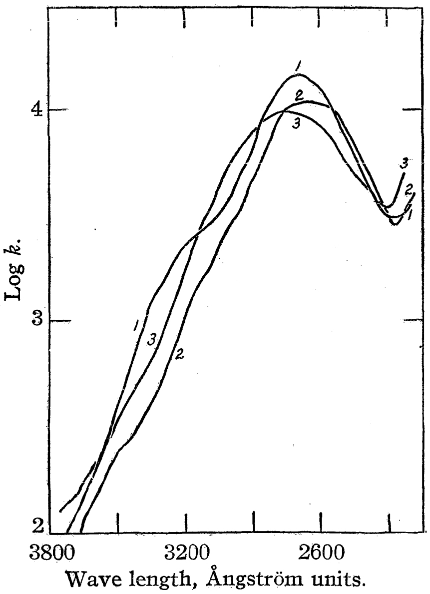

Fig. 8.—*p*-Nitrobenzoic acid: Curve 1, 95.65% H_2SO_4; Curve 2, 0.1 *M* HCl; Curve 3, 0.1 *M* NaOH.

We wish to acknowledge the kindness of Professors H. T. Beans and H. C. Urey, who made available for us apparatus which was indispensable for this work.

Summary

1. The ultraviolet absorption spectra in various solvents have been determined of benzoic acid, 2,4-dinitrophenol, aniline, acetophenone,

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[19] Goldschmidt, *Ber.*, **28**, 3218 (1895).

anthraquinone, phenylacetic acid and *p*-nitrobenzoic acid.

2. The validity of ultraviolet spectrophotometry as a method of measuring ionization has been demonstrated for a carboxylic acid and a phenol, and for an oxygen and a nitrogen base.

3. Mathematical methods have been devised for taking into account the effect of changing solvent in measuring the strength of very weak bases.

4. Criteria have been established for the choice of indicators to be used in changing media.

5. The strengths of the following very weak bases have been measured: acetophenone, benzoic acid and phenylacetic acid.

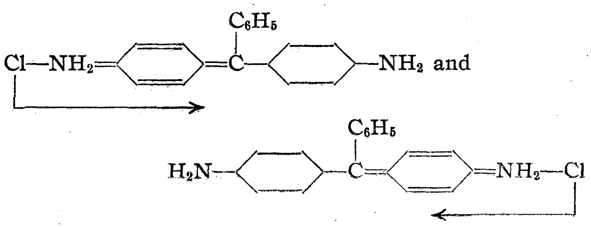
NEW YORK, N. Y. RECEIVED JULY 1, 1935

[CONTRIBUTION FROM EDWARD DAVIES CHEMICAL LABORATORIES, UNIVERSITY COLLEGE OF WALES]

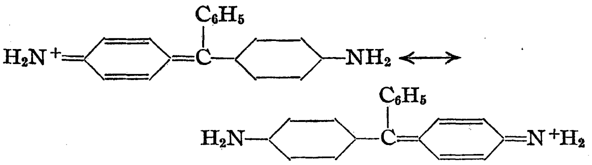
Auxochromes and Resonance

BY C. R. BURY

Baeyer[1] suggested that the color of the triphenylmethane dyes was due to the oscillation of an atom in the molecule. Döbner's violet (the hydrochloride of *p,p*-diaminotriphenylcarbinol) was considered to be in a state of oscillation between the two forms



Now that the distinction between electrovalent and covalent bonds is known, it is clear that the oscillation is purely structural

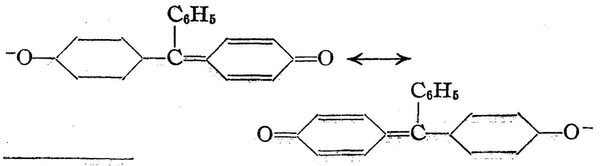


since change from one form to the other involves movement of electrons only, but no movement of atoms. Further, such an oscillation is to be expected: it is merely an example of resonance. Baeyer's hypothesis can be restated in terms of modern theory as follows. The intense absorption of light that characterizes dyes is due to an intimate association of a chromophore and of resonance in the molecule.

There is much indirect evidence that this hypothesis is true, not only for the triphenylmethane dyes, but also for most of the best investigated types of dyes. In particular, it gives some explanation of the function of an auxochrome. Willstätter and Piccard[2] called attention to the fact that certain simple compounds containing the quinonoid group were colorless, or very feebly colored: the development of color in these compounds depends on the introduction of certain substituent groups—auxochromes. In the light of the hypothesis put forward, the function of the auxochrome is to introduce the possibility of resonance. (Auxochromes also facilitate the attachment of the dye to the fabric, but this aspect is not considered further here.)

The hypothesis enables one to understand what groups can act as chromophores and what positions they must occupy. Thus, fuchsonimine $HN{=}C_6H_4{=}C{-}(C_6H_5)_2$ is colorless, though it contains the same chromophore as Döbner's violet. Introduction of an amino group in the *p*-position results in the development of color and the possibility of resonance. Other substituent groups are ineffective in producing color, though they may alter the shade of color of a dye that already contains an amino group. The amino group may be alkylated (—NR_2), but conversion to a trialkyl substituted group (—N^+R_3) renders resonance impossible and is found in practice to render it ineffective. The destruction of the color of methyl violet and similar dyes by excess concentrated acid can be attributed to the same change.

The color of the hydroxytriphenylmethane dyes is associated with a similar resonance, *e. g.*, the anion of benzaurin.



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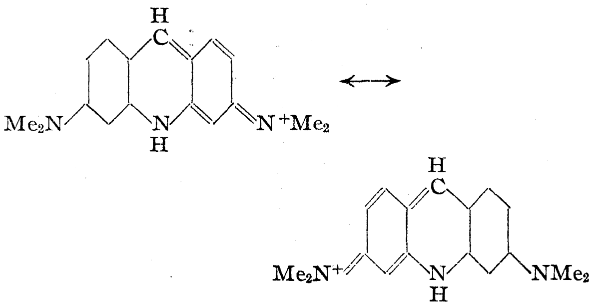
[1] Baeyer, *Ann.*, **354**, 152 (1907).

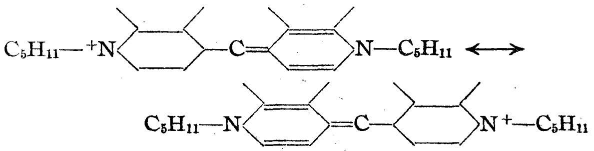
[2] Willstätter and Piccard, *Ber.*, **41**, 1458 (1908).

The hypothesis demands that the color of phenolphthalein in alkaline solution should be due to a dibasic ion, though most textbooks continue to attribute the color to a monobasic ion, which is adequate to explain the color on the usual theory, but is contrary to all experimental evidence.[3]

Resonance similar to that of the triphenylmethane dyes must also occur in the diphenylmethane dyes, the indamines, indophenols and auramines, and again in a group of dyes in which the two benzene nuclei are joined by a second bridge, such as the acridine, pyronine, azine, oxyazine and thiazine dyes. For instance, the colored cation of acridine orange can be represented.

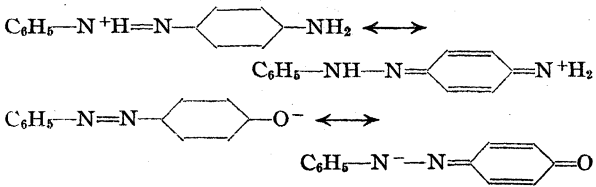


A closely related type of resonance is probable in the cyanines



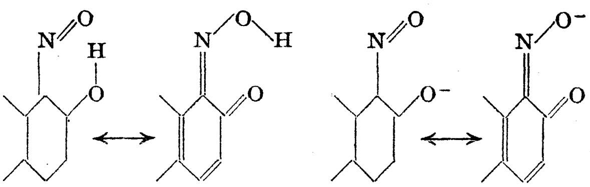
Mills and Ordish[4] have proposed tautomeric formulas, that are identical in principle with the resonance formulas of this paper, for the apocyanines.

Turning to a different type of dye, the azo dyes, it is well known that most molecules that contain the azo group are colored, but their color is feeble compared with that of the azo dyes; compare, for example, the color of methyl orange in alkaline solution with its color in acid. The resonance of this type of dye can be illustrated by formulas of the cation of aminoazobenzene and the anion of hydroxyazobenzene.

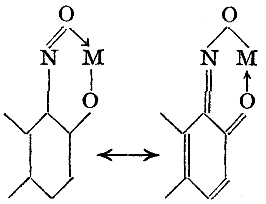


In support of these formulas is the fact that some syntheses and reactions of hydroxyazobenzenes suggest that they are really quinone phenylhydrazones. The change azo compound to hydrazone obviously occurs readily, but must be a slow reaction since it involves movement of a hydrogen atom. Change of the corresponding ions is, however, a purely structural change that involves no movement of atoms; the ions, therefore, may be expected to be in a state of resonance. Again, Hantzsch and Hilscher[5] have shown that the hydrogen ion introduced on formation of a salt of an aminoazobenzene is not attached to the amino group, but is probably in the position required by the above formula. Lastly, the hypothesis gives an explanation of the function of the auxochrome amino and hydroxy groups, and enables one to predict what substituent groups can act as chromophores, and what positions they must occupy. As with the triphenylmethane dyes, conversion of an amino group to a trialkylated group renders it ineffective.

A third important type of dye is the mordant or lake type, of which α-nitroso-β-napthol is a simple example. This type differs from previous examples in that the same resonance can persist in the neutral molecule I, in the ion II, and in the coördinate compound III which is the basis of the lakes.[6]

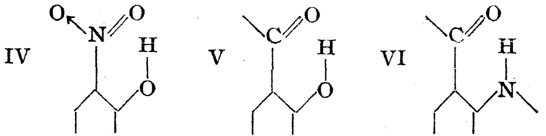


I II



III

Similar groups that can exhibit a similar resonance are IV, V and VI.



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(3) Green and Perkin, *J. Chem. Soc.*, **85**, 398 (1904); Green and King, *Ber.*, **40**, 3724 (1907); Meyer and Spengler, *ibid.*, **38**, 1318 (1905); Kober and Marshall, THIS JOURNAL, **33**, 59 (1911).

(4) Mills and Ordish, *J. Chem. Soc.*, 81 (1928).

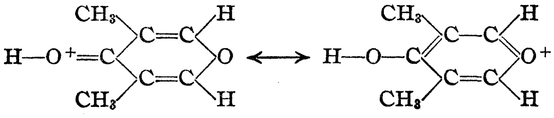
(5) Hantzsch and Hilscher, *Ber.*, **41**, 1171 (1908).

(6) Morgan and Smith, *J. Chem. Soc.*, **119**, 704 (1921).

The physical properties of such *o*-disubstituted benzene derivatives are abnormal[7] compared with those of the corresponding *m*- and *p*-derivatives in such a way as to indicate that the *o*-substituents unite to form a second ring, a behavior that can only be explained by resonance.[8] Again, *o*-quinone monoximes are indistinguishable from *o*-nitrosophenols. With similar *p*-substituted compounds, resonance is restricted to the ion. Thus *p*-nitrophenol gives an intensely colored ion in alkaline solution, but is colorless in acid and in the solid state, whereas *o*-nitrophenol is colored in all conditions. The nitro dyes contain group IV, and the two most important types of mordant dyes, the hydroxyanthraquinones and the flavones, contain group V.

Some of the vat dyes contain similar groups and may be expected to exhibit similar resonance. Thus, alizarin yellow (gallacetophenone), which is probably the simplest vat dye, contains group V, and the side chain derivatives of anthraquinone that are vat dyes, and indanthrene, contain group VI.

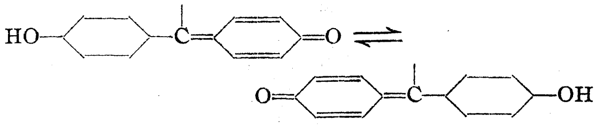
An interesting benzenoid–quinonoid type of resonance can occur in the dimethylpyronium ion.



This type of resonance was detected in dimethylpyrone by Sutton[9] from dipole measurements. The same grouping occurs in the flavones.

It is probable that more than one type of resonance is at work in the more complex dyes: thus two types of resonance have been postulated for the flavones. It is improbable, however, that resonance is extremely complex or the simple treatment applied above would be valueless. This implies that only resonance between states of nearly equal energy, or "complete" resonance, is effective in determining the structure that a molecule must have in order that it may be a dye.

There must, however, be more possibilities of resonance in the solid state than there are in solution. Thus, the change



involves movement of a hydrogen atom, and therefore cannot produce resonance. A similar change that does not involve movement of a hydrogen atom can, however, take place between suitably placed molecules in the solid state. This may account for the fact that rosolic acid is intensely colored in the solid state though it is colorless in neutral solution, but is given merely as an example of a phenomenon that must be expected frequently with dyes in the solid or in the colloidal state. Quinhydrone, the crystal structure of which has been elucidated by Foz and Palacios,[10] provides an example of exchange of hydrogen atoms between neighboring molecules in the solid state that involves no movement in space. The intense color of this compound may be attributed to the conjunction of resonance and of the chromophore in quinone.

The simple modes of resonance discussed above are sufficient to explain the phenomenon of auxochromes in the majority of the most thoroughly investigated dyes. Other probable modes can be devised for most other dyes the structure and reactions of which are known with any certainty; only the indigo dyes present any difficulty.

ABERYSTWYTH, WALES

RECEIVED AUGUST 8, 1935

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[7] Sidgwick and Callow, *J. Chem. Soc.*, **125**, 527 (1924).

[8] Sidgwick, *Ann. Reports*, **31**, 37 (1934).

[9] Sutton, *Trans. Faraday Soc.*, **30**, 789 (1934).

[10] Foz and Palacios, *Anal. soc. españ. fís. quím.*, **30**, 421 (1932).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

An Investigation of Certain Sapinic Acids Obtained from Various Species of Pine and Spruce

BY TORSTEN HASSELSTROM AND MARSTON TAYLOR BOGERT[1]

It has been observed frequently[2] that when the solid portion of the oleoresins of pine and spruce is subjected to fractional crystallization from anhydrous solvents at temperatures below 60°, there are obtained the so-called sapinic acids. These are resin acids of the molecular formula $C_{20}H_{30}O_2$, with melting points in the neighborhood of 142–144°, which are very sensitive to oxidation, and easily isomerized by heat or by mineral acids to an abietic acid.[2e,g,h,3]

In optical rotation, they vary greatly, not only as between different tree species, but even in the case of different trees of the same species (see Table I).

The sapinic acids of *Pinus maritima*,[4] and of *Pinus Palustris*,[5] have been separated into *d*-pimaric and "*levo*-pimaric" acids. The former is stable;[6] whereas the latter is quite unstable, for it is easily oxidized, and is isomerized by heat or by mineral acids to abietic acids.[2c,3,4a,7]

This labile acid, however, is not the true optical antipode of the well-known *d*-pimaric acid. In fact, the real *l*-pimaric acid apparently has not yet been described. It has for some time been the approved usage of investigators in the resin acid field, to classify as "pimaric" acids only those resin acids which yield pimanthrene when fused with sulfur or selenium; and as "abietic" acids, those which when similarly treated give retene.

Since this so-called "*levo*-pimaric" acid yields retene when fused with sulfur,[4b] it belongs to the abietic and not to the pimaric class of resin acids. The name "*levo*-pimaric," originally given to it by Vesterberg,[8] therefore should be replaced by one more in agreement with our present knowledge, and we suggest in its place the designation "*l*-sapietic" acid. This name we have coined to recall its occurrence in the original sapinic acids of the gum and its belonging to the abietic group.

TABLE I

The optical rotations on the crude gums were determined upon selected samples carefully dried between filter papers.

Oleoresin	$[\alpha]_D$	Sapinic acid, m. p., °C.	$[\alpha]$	Calculated composition of the sapinic acids $[\alpha]_D$ +79.3 *d*-Pimaric acid	$[\alpha]_D$ −280.4 *l*-Sapietic acid	Reference
Pinus palustris	−131.0	142–144.5	− 22.36	71.7	28.3	This paper
Pinus caribbea	− 31.96	142–144.5	− 47.01	64.9	35.1	This paper
Pinus taeda	− 74.50	141–143.5	− 69.38	58.8	41.2	This paper
Pinus serotina	− 56.42	142–143.5	−112.11	46.8	53.2	This paper
Pinus silvestris	.....	142–144	−105.3	49.0	51.0	Leskiewicz[2b]
Pinus silvestris	− 40.14	148.5–150.5	− 46.88	64.9	35.1	This paper
Pinus densiflora	.....	141	− 63.1	61.4	39.6	Suzuki[2d]
Picea excelsa	−126.6	137–139	− 35.2	68.2	31.8	Aschan[2f]
Picea excelsa	−111.5	140–144.5	− 93.33	48.0	52.0	This paper
Picea excelsa	−238	138–151	−278	1.0	99.0	Köhler[2c]
Picea excelsa	.....	142–143	−101.97	49.6	50.4	Nordström[3]

The crystals found by Köhler[2c] between the sapwood and the bark of *Picea excelsa* and which, therefore, had not been exposed to light and air, were probably fairly pure *l*-sapietic acid, containing relatively small amounts of *d*-pimaric acid. Köhler recorded their rotation as $[\alpha]^{20}_D$ −238° and, after four recrystallizations from methanol, as $[\alpha]^{20}_D$ −278°. Subsequent investigators have reported the rotation of the pure acid as $[\alpha]^{17}_D$ −279.4,[4b] −280.4,[9] and −274.5°.[5] Assuming

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[1] Presented in abstract before the Division of Organic Chemistry at the New York meeting of the American Chemical Society, April 23, 1935.

[2] (a) Klason and Köhler, *J. prakt. Chem.*, [2] **73**, 337 (1904); (b) Leskiewicz, *ibid.*, **81**, 403 (1910); (c) Köhler, *ibid.*, **85**, 534 (1912); (d) Suzuki, *J. Pharm. Japan*, **515**, 49 (1925); (e) Suzuki, *ibid.*, **524**, 888 (1925); (f) Aschan, *Naftenföreningar, Terpener och Kamferarter*, Helsingfors, **367** (1926); (g) Dupont and Dubourg, *Bull. Inst. Pin*, **31**, 581 (1926); (h) Nordström, *J. prakt. Chem.*, [2] **121**, 206 (1929); (i) Vocke, *Ann.*, **508**, 11 (1933).

[3] Nordström, *Finska Kem. Medd.*, No. 4 (1929).

[4] (a) Dupont, *Bull. soc. chim.*, [4] **29**, 718 (1921); (b) Ruzicka, Balaš and Vilim, *Helv. Chim. Acta*, **7**, 458 (1924).

[5] Palkin and Harris, THIS JOURNAL, **55**, 3677 (1933).

[6] (a) Vesterberg, *Ber.*, **18**, 3331 (1885); (b) *ibid.*, **19**, 2167 (1886); (c) *ibid.*, **20**, 3248 (1887); (d) *ibid.*, **38**, 4125 (1905); etc.

[7] (a) Fanica, *Bull. inst. pin*, **44**, 151 (1933); (b) *ibid.*, **45**, 181 (1933).

[8] Vesterberg, "Kemiska studier öfver några hartser," Diss., Upsala, 1890.

[9] Balaš, *Časopis Československeho Lekarnictva*, **7**, 320 (1927).

that the crude crystals contained only *l*-sapietic and *d*-pimaric acids, and taking Balas' figure[9] for the rotation of the latter ($[\alpha]_D + 79.3°$), their composition as calculated from Biot's relationship,[10] $-280.4x + (1-x)\ 79.3 = -238°$, would be approximately 88.2% of *l*-sapietic and 11.8% of *d*-pimaric acid.

It is the hypothesis of the authors that most of the so-called "sapinic acids" of the oleoresins of conifers are mainly isomorphous mixtures of *l*-sapietic and *d*-pimaric acids, the differences in optical rotation being due to the relative amount of *d*-pimaric present in the unoxidized and unisomerized acid mixture.

All of the sapinic acids examined by us, when hydrogenated in the presence of the Adams platinum oxide catalyst, yielded large quantities of dihydropimaric acid, which was easily isolated by virtue of its sparing solubility in methanol. Our experiments show that this is a satisfactory solvent for accomplishing the separation of a mixture of the dihydropimaric from the dihydroabietic type of acid.

Attempts to isolate dihydrosapietic acid,[4b,5] m. p. 144–146°, from the mother liquors were unsuccessful. There was obtained a low-melting acid mixture containing some dihydropimaric acid. As noted by previous investigators,[4a,5] catalytic hydrogenation even of pure *l*-sapietic acid yields a mixture of isomers difficult to separate.

As Palkin and Harris[5] have shown, and as we ourselves had observed in the course of some experiments carried out a year before the appearance of their paper, *d*-pimaric acid is readily identified by catalytic hydrogenation to its dihydro derivative.

The presence of *l*-sapietic in the original sapinic acid was established by refluxing the latter with glacial acetic acid, as described by Steele,[11] a treatment which isomerizes the *l*-sapietic to abietic, but leaves the *d*-pimaric acid unaltered. The solids obtained from the mother liquors of the abietic acid, when subjected to catalytic hydrogenation, yielded dihydropimaric acid in considerable amount.

It is generally recognized that the "abietic acids" constitute the major portion of ordinary colophony. Our demonstration of the occurrence of *d*-pimaric in the sapinic acids, indicates its presence also in rosins produced by the usual methods.

Acknowledgments.—For samples of oleoresins supplied, our thanks are due especially to Messrs. I. A. von Julin, Fiskars, Finland; William F. Allen, of Dr. Charles H. Herty's laboratory, Savannah, Ga.; and Edward A. Brennan, of the G. & A. Laboratories, Savannah, Ga.

Experimental

Preparation of the Sapinic Acids.—The semi-solid oleoresin, or the press-cake obtained therefrom by expressing, was dissolved in an anhydrous solvent (ethyl acetate), using approximately 1 part gum to 2–3 parts of solvent, at a temperature not exceeding 60°, and filtered from chips, bark, dirt, etc. The filtrate was concentrated to a sirup by evaporation under diminished pressure at a temperature below 60°, since above that temperature the *l*-sapietic acid begins to isomerize. This sirup was seeded with a few selected dry crystals of the sapinic acid obtained directly from the original gum and, on standing for from four to twelve hours, set to a semi-solid crystalline mass which was easily filtered. The crude sapinic acid so obtained was colorless. It was purified by successive crystallization from ethyl acetate, acetone and methanol.

The *Picea excelsa* oleoresin (from Finland) contained considerable oxidation products. These were removed by adding petroleum ether to the viscous ethyl acetate solution of the gum until no more dark colored precipitate separated. The filtrate from this precipitate was concentrated under reduced pressure at a temperature below 60°, and this process of purification was repeated thrice. The final sirup was then seeded and the crude product recrystallized as noted above.

Further details concerning the preparation of these sapinic acids and their properties, are given in Table II.

Hydrogenation of the Sapinic Acids.—To one part of sapinic acid in 20 of ethyl alcohol, there was added one-twentieth to one-tenth of a part of Adams platinum oxide catalyst and the hydrogenation was conducted at room temperature and a pressure of 7–25 lb. per sq. in. When approximately one mole of hydrogen per mole of acid had been absorbed, the hydrogenation was interrupted, the alcoholic solution concentrated to incipient crystallization and let stand for some time at room temperature. The separated solid was removed and crystallized from methanol until the product showed a m. p. of about 240°. Further crystallization to the m. p. of 249–250°, the figure given by Palkin and Harris[5] for pure dihydropimaric acid, was not undertaken since 240–241° has been generally accepted[12] as the m. p. of a practically pure acid.

From the mother liquors, by fractional crystallization, more dihydropimaric acid was recovered, but no constant melting product which could be identified as a dihydrosapietic acid.

The results of these hydrogenation experiments are presented in Table III.

By crystallization of a mixture of the oleoresins of *Pinus palustris* and *P. carribea*, Vocke[21] obtained a levo-

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(10) Biot, *Ann. chim. phys.*, [3] **59**, 206 (1860); etc.

(11) Steele, THIS JOURNAL, **44**, 1333 (1912).

(12) Tschugaeff and Tearu, *Ber.*, **46**, 1769 (1913).

TABLE II

SAPINIC ACIDS

	Pinus palustris	*Pinus caribbea*	*Pinus taeda*	*Pinus serotina*	*Pinus silvestris*	*Picea excelsa*
Initial subs.	Crude gum[a]	Crude gum[b]	Press-cake[c]	Press-cake[d]	Crude gum[e]	Crude gum[f]
Its rotation	$[\alpha]^{30}_{\mathrm{D}}$ −131	$[\alpha]^{33}_{\mathrm{D}}$ −31.96	$[\alpha]^{30}_{\mathrm{D}}$ −74.60	$[\alpha]^{27}_{\mathrm{D}}$ −56.42	$[\alpha]^{30}_{\mathrm{D}}$ 40.14	$[\alpha]^{31}_{\mathrm{D}}$ −111.5
Times crystallized	6	8	4	5	7	6
Solvents used	AcOEt, AcMe, MeOH	AcOEt, MeOH, AcMe	AcOEt, AcMe	AcOEt, AcMe	AcOEt, AcMe	AcOEt, AcMe
Oxid. products removed	No	No	No	No	No	Yes
Yield sapinic acid, 1st crystallization, g.	190	130	130	120	25	15
M. p. after 2d crystallization, °C.	137.5–139.5	134–137	139–141	134–137	135.5–137.5	134.5–137.5
M. p. after final crystallization (corr.), °C.	142–144.5	142–144.5	141.5–144	142–144	148.5–150.5	140–144.5
Final yield, g.	2	3	22	12	3.5	1.5
Final rotation	$[\alpha]^{33}_{\mathrm{D}}$ −22.36	$[\alpha]^{33}_{\mathrm{D}}$ −47.01	$[\alpha]^{30}_{\mathrm{D}}$ −69.38	$[\alpha]^{27}_{\mathrm{D}}$ −112.11	$[\alpha]_{\mathrm{D}}^{31}$ −46.88	$[\alpha]^{33}_{\mathrm{D}}$ −93.33
M. p. of solids from mother-liquor (corr.), °C.	140.5–142.5		140.5–142.5	139.5–143.5		
Their rotation	$[\alpha]^{33}_{\mathrm{D}}$ −31.08		$[\alpha]^{30}_{\mathrm{D}}$ −59.94	$[\alpha]^{27}_{\mathrm{D}}$ −92.37		

[a] From E. A. Brennan, Savannah, Ga.; May, 1932 = 400 g. [b] From E. A. Brennan, Savannah, Ga.; May, 1932 = 312 g. [c] From William F. Allen, Savannah, Ga.; Dec., 1934 = 320 g. [d] From William F. Allen, Savannah, Ga.; Dec., 1934, = 190 g. [e] From I. A. von Julin, Fiskars, Finland; July, 1932 = 50 g. [f] From I. A. von Julin, Fiskars, Finland; July, 1932 = 112 g.

TABLE III

HYDROGENATION OF SAPINIC ACIDS

		Pinus palustris	*Pinus caribbea*	*Pinus taeda*	*Picea serotina*	*Pinus silvestris*	*Picea excelsa*	Tschugaeff and Tearu[12]	Ruzicka and Balaš[14]	Palkin and Harris[5]
Initial subs., g.		5	5	10	10	3	1.5			
Yield crude acid m. p. <200°, g.		2.79	2.2	3.5	4.5	1.5	0.6			
M. p. (corr.) of dihydropimaric acid, °C.		241–242.5	241–242	241.5–242.5	239–241	239–240	198–203[a]	240–241	239–240	249–250
Rotation of acid M. p. <215°		$[\alpha]^{32}_{\mathrm{D}}$ +18.78	$[\alpha]^{33}_{\mathrm{D}}$ +14.01	$[\alpha]^{29}_{\mathrm{D}}$ +12.42	$[\alpha]^{29}_{\mathrm{D}}$ +19.98	$[\alpha]^{33}_{\mathrm{D}}$ +22.93		$[\alpha]_{\mathrm{D}}$ +19.43	$[\alpha]_{\mathrm{D}}$ +14.5	
Calcd. for $C_{20}H_{32}O_2$	%C = 78.88	78.57	78.91			78.66	78.30	78.74	79.05	78.87
	%H = 10.60	10.82	10.87			9.77	10.68	10.60	10.68	10.63
Dihydropimaric acid recovered from mother liquors		Yes	Yes	Not examined	Not examined	Yes	Not examined			

[a] The quantity of material available was insufficient for further recrystallization, but the presence of dihydropimaric acid seems evident from the analysis and from the fact that no dihydroabietic acid is known with a m. p. above 175°.[2e,2f,2g,5,13]

rotatory sapinic acid, m. p. 143°, which, on hydrogenation, yielded a dihydro acid. This latter was purified by crystallization from ethyl alcohol, in which it was but slightly soluble, and then melted at 195°. On further hydrogenation, there was obtained a tetrahydro acid (m. p. 173°, not sharp) which he assumed to be of abietic type. It is our belief that if Vocke had used methyl instead of ethyl alcohol for the purification of his dihydro acid, he would have discovered the presence therein of dihydropimaric acid.

Formation of Steele's Abietic Acid from Sapinic Acids.—A mixture of 10 g. of the sapinic acid with 10 cc. of glacial acetic acid was refluxed for four hours, then allowed to cool and left overnight at room temperature. The abietic acid which separated was purified by crystallization from alcohol.

The original acetic acid mother liquor was poured into water and the precipitated resin acid mixture removed and hydrogenated catalytically in alcoholic solution as described above. Dihydropimaric acid was thus secured, the mother liquors from which contained a low melting dihydro acid, which could not be obtained of constant melting point and was not identified. It may have been the dihydro Steele abietic acid described beyond.

The results of these experiments are given in Table IV.

TABLE IV

ACTION OF GLACIAL ACETIC ACID UPON SAPINIC ACIDS

Steele's abietic acid (m. p. 161–165°, $[\alpha]_{\mathrm{D}}$ −80°)	*Pinus taeda*	*Pinus serotina*
Yield of crude acid, g.	4.5	4.8
M. p. of purified acid, °C.	163.5–165.5	163.5–165.5
$[\alpha]_{\mathrm{D}}$	−79.89	−87.3
Hydrogenation of solids from mother liquor		
Total solids, g.	5.5	4.2
Yield of dihydropimaric acid m. <200°, g.	1.5	1.2
M. p. (corr.) of purified dihydropimaric acid, °C.	238.5–240.5	240.5–242.5
$[\alpha]_{\mathrm{D}}$	$[\alpha]^{27}_{\mathrm{D}}$ +18.67	$[\alpha]^{29}_{\mathrm{D}}$ + 12.50

Hydrogenation of Steele's Abietic Acid.—Steele's abietic acid was prepared from the press-cake from sulfate "black liquor" tall oil[15] and the crude product was crystallized fifteen times from methanol, acetone and ethyl acetate. After eleven crystallizations, the melting point remained constant at 164.5–165.5°; $[\alpha]^{32}_{\mathrm{D}}$ −53.9°.

Anal. Calcd. for $C_{20}H_{32}O_2$: C, 79.41; H, 10.01. Found: C, 79.25; H, 10.03.

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(13) (a) Johansson, *Arkiv f. kemi*, **6**, 19, 20 (1917); (b) Ruzicka and Meyer, *Helv. Chim. Acta*, **5**, 324 (1922).

(14) Ruzicka and Balaš, *Helv. Chim. Acta*, **6**, 677 (1923).

(15) Hasselstrom, U. S. Patent 1,986,817 (1934).

A solution of 3 g. of this acid in 50 cc. of alcohol was hydrogenated catalytically as described for the sapinic acids, interrupting the operation when one mole of hydrogen had been added (ten minutes). The product was worked up in the usual way, as in the case of the hydrogenated sapinic acids. The crude solid acid was crystallized first from methanol and then from acetone, six times in all. It formed colorless needles, m. p. about 154.5–157° (corr.), $[\alpha]^{32}_D$ +17.54°.

Anal. Calcd. for $C_{20}H_{32}O_2$: C, 78.88; H, 10.60. Found: C, 78.46; H, 10.50.

In view of the unsatisfactory melting point, it is unlikely that this is the pure dihydro derivative of Steele's abietic acid. More probably, it is a mixture of isomers.

Summary

1. The sapinic acids of *Pinus palustris*, *P. caribbea*, *P. taeda*, *P. serotina*, *P. silvestris* and *Picea excelsa*, consist chiefly of a mixture of *d*-pimaric and *l*-sapietic acids. This is in accord with the findings of Palkin and Harris[5] in the case of *P. palustris* and of Dupont,[4a] and Ruzicka, Balaš and Vilim[4b] for *P. maritima*.

2. The presence of the former is proved by the formation of dihydropimaric acid when the sapinic acids are hydrogenated catalytically; and, of the latter, by the fact that, when refluxed with glacial acetic acid, the sapinic acids yield Steele's abietic acid as one of the products.

3. The stability of *d*-pimaric acid and its existence in the sapinic acids explains its presence in ordinary colophony.[16]

[16] (a) Rimbach, *Ber. pharm. Ges.*, **6**, 61 (1896); (b) Hosking and McFadyen, *J. Soc. Chem. Ind.*, **53**, 195T (1934).

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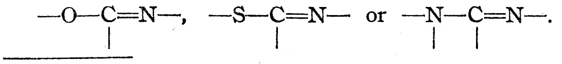
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

The Synthesis of Certain Phenylated Benzoxazoles and Derivatives[1]

BY VLADIMIR J. MIKESKA AND MARSTON TAYLOR BOGERT

The investigations of thiazole compounds conducted in these laboratories, especially on the connection between chemical constitution and tinctorial properties,[2] have made it seem worth while to carry out some similar studies in the closely related oxazole series.

The structural similarity between the oxazoles, thiazoles and imidazoles is paralleled by a close resemblance in methods of preparation and in properties of analogous compounds in the three series. Thus, in the basicity of their salts, the fluorescence of their solutions,[3] and odors, they are much alike. Auwers and Ernst,[4] who examined a large number of analogous compounds in the three groups in the helium region of the spectrum at 20°, found that their dispersion spectra corresponded closely, and that it seemed to make but little difference in the spectrum whether the grouping present in the cycle was



$-O-\underset{|}{C}=N-$, $-S-\underset{|}{C}=N-$ or $-\underset{|}{N}-\underset{|}{C}=N-$.

In all three series, the monocyclic types are most easily hydrolyzed, then the aliphatic 2-R derivatives of the benzo (dicyclic) type, the most stable derivatives being the 2-aryl compounds, like 2-phenylbenzoxazole. Of the three series, the oxazoles are most easily hydrolyzed,[5] even methylation breaking open the ring when 2-methylbenzoxazole is heated with methyl iodide.[6]

Clark[7] has carried out some interesting experiments on the opening of the cycle by the action of potassium hydroxide upon the methiodide.

Böttcher[8] was unable to effect ring closure by reduction of $CH_3COOC_6H_4NO_2$-(*o*), although this was accomplished easily by reduction of either C_6H_5-$COOC_6H_4NO_2$-(*o*) (2) or $C_6H_5COOC_{10}H_6NO_2$ (3).

For our attack upon the problem, the 2-R-5-phenyl and 2-R-7-phenylbenzoxazoles were used, because of the availability of the important industrial by-products *p*- and *o*-hydroxy diphenyls, from which they are easily synthesized. These syntheses are recorded in the present paper. The production of dyes from the phenylated benzoxazoles so obtained and a discussion of the tinctorial properties of these dyes, will form the subject of another communication.

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[1] Based upon the dissertation submitted by V. J. Mikeska, June, 1934, for the Ph.D. degree under the Faculty of Pure Science, Columbia University, New York, N. Y., to which dissertation the reader is referred for further experimental details and literature citations.—M. T. B.

[2] (a) Bogert and Bergeim, *Color Trade J.*, **15**, 63 (1924); (b) Bogert and Chertcoff, THIS JOURNAL, **46**, 2864 (1924); (c) Bogert and Allen, *Ind. Eng. Chem.*, **18**, 532 (1926); (d) Bogert and Allen, THIS JOURNAL, **49**, 1315 (1927).

[3] Henrich, *Ber.*, **54**, 2492 (1921).

[4] Auwers and Ernst, *Z. physik. Chem.*, **122**, 217 (1926).

[5] Skraup, *Ann.*, **419**, 33 (1919).

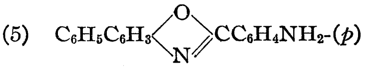
[6] Fischer, *J. prakt. Chem.*, [2] **73**, 436 (1906).

[7] Clark, *J. Chem. Soc.*, **129**, 232 (1926).

[8] Böttcher, *Ber.*, **16**, 629, 1933 (1883).

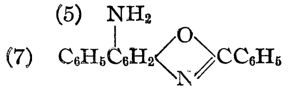
For the synthesis of the 5-phenyl derivatives, 3-nitro-4-hydroxydiphenyl was reduced to the corresponding amine and this in turn was condensed with *p*-nitrobenzoyl chloride to the 2-*p*-nitrophenyl-5-phenylbenzoxazole, reduction of which yielded the corresponding amino derivative (A).

For the preparation of the analogous 7-phenylbenzoxazoles, 3,5-dinitro-2-hydroxydiphenyl was converted first to the benzoate and this then reduced, with simultaneous cyclization, to the 2,7-diphenyl-5-aminobenzoxazole (B).



$$(5)\quad C_6H_5C_6H_3\langle{}^{O}_{N}\rangle CC_6H_4NH_2\text{-}(p)$$

(A)



$$(5)\ NH_2 \quad (7)\quad C_6H_5C_6H_2\langle{}^{O}_{N}\rangle CC_6H_5$$

(B)

Experimental

Raw Material.—In the manufacture of phenol by the fusion of sodium benzenesulfonate with sodium hydroxide and rectification of the crude product, there remain in the still residues certain higher boiling phenolic constituents, diphenylsulfone and other by-products. Through the courtesy of Weiss and Downs, Inc., of New York, and of The Bakelite Corporation of Bloomfield, N. J., we were provided with a supply of this crude still residue and also with a small quantity of a distillate composed mainly of a mixture of hydroxydiphenyls. To both of these firms we wish to express our thanks for their assistance. The crude still residue, which was our chief source material, was worked up as follows.

After adding an excess of dilute (about 10%) sodium hydroxide solution, the mixture was boiled and stirred vigorously for at least fifteen minutes, then diluted with about 2 volumes of cold water and filtered from the separated **diphenylsulfone** (I), which was purified by distillation under diminished pressure, crystallization of the distillate from alcohol and sublimation. The sublimed product melted at 128° (corr.), in agreement with the figure reported by Otto,[9] and this melting point was not altered when mixed with a sample of the pure sulfone, of the same melting point, prepared by the direct sulfonation of benzene as described by Mitscherlich.[10]

It was further identified by the production therefrom of a *dinitro derivative* (II), m. p. 197°, which figure agrees with that given by Gericke[11] for dinitrodiphenylsulfone.

The *o*- and *p*-hydroxydiphenyls were isolated from the alkaline filtrate from the diphenylsulfone.

When this filtrate was acidified with hydrochloric acid, both hydroxy derivatives were precipitated, as well as tarry material. On filtration, some of this tar ran through the filter in an emulsified or colloidal state, together with most of the phenol present. The precipitate of crude hydroxydiphenyls was washed, dried and distilled under reduced pressure (30 mm.), the distillation being continued until there was evidence of decomposition products coming over. The mixture of *o*- and *p*-hydroxydiphenyls so obtained was extracted with hot gasolene and the undissolved ***p*-hydroxydiphenyl** (III) was rectified. The distillate obtained in this rectification, when crystallized from alcohol, appeared in bunches of colorless minute silky needles or in flakes, both of which forms melted sharply at 164° (corr.). Raiford[12] reported the m. p. as 163°.

The product was further identified by the preparation therefrom of the following derivatives: *4-acetoxydiphenyl*, m. p. 88° (corr.), literature[12] m. p. 88°; *4-methoxy*, m. p. 89.5° (corr.), literature[13] m. p. 90°; *3-nitro-4-hydroxy*, m. p. 67° (corr.), literature[12] m. p. 66°; *3-amino-4-hydroxy*, m. p. 209° (corr.), literature[12] m. p. 208°.

The gasolene filtrate from the *p*-isomer was concentrated to one-fourth its volume or less and, as it cooled, the ***o*-hydroxydiphenyl** (IV) separated in colorless crystals which were purified by distillation at 30 mm. pressure. The fraction collected at about 190° was nearly pure *o*-hydroxydiphenyl. Crystallized from alcohol, it formed massive colorless glassy crystals, m. p. 67.5° (corr.), which coincides with the figure reported by Norris, Macintire and Corse.[14]

For further identification, the *3,5-dinitro derivative* prepared from this product melted at 204° (corr.), as compared with a m. p. of 203–204° recorded by Borsche and Scholten.[15]

Summarizing our results, the yields of the various products isolated from this particular still residue were approximately as follows: diphenylsulfone 33%, *p*-hydroxydiphenyl 10%, *o*-hydroxydiphenyl 11%; phenol, water, unidentified higher-boiling constituents, tar and loss 46%.

Derivatives of *p*-Hydroxydiphenyl

3-Nitro-4-hydroxydiphenyl Sulfonic Acid (V).—A solution of 20 g. of 3-nitro-4-hydroxydiphenyl (m. p. 67°, corr.) in 60 cc. of concentrated sulfuric acid was stirred for three hours at 70°. There resulted a water-soluble sulfo acid, whose barium salt gave a yellow solution, unless barium entered the phenolic group also, when a red precipitate separated. Excess of sulfuric acid was precipitated by titration with barium hydroxide solution, the appearance of the yellow barium sulfonate changing the color of the solution and giving a clear end-point. A slight excess of barium hydroxide was used. The mixture was heated, allowed to stand for twenty-four hours and filtered. The filtrate containing the barium sulfonate was then titrated with more barium hydroxide solution, giving a deep canary yellow solution. The end-point in this titration was the appearance of the red color, or red precipitate, due to the entrance of the barium into the phenolic group also. By concentration of the yellow solution, the barium sulfonate crystallized in bright canary-yellow flakes; yield, 80%.

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[9] Otto, *Ann.*, **136**, 160 (1865).

[10] Mitscherlich, *Ibid.*, **12**, 208 (1834).

[11] Gericke, *Ibid.*, **100**, 211 (1856).

[12] Raiford, THIS JOURNAL, **47**, 1456 (1925).

[13] Werner, *Ann.*, **322**, 167 (1902).

[14] Norris, Macintire and Corse, *Am. Chem. J.*, **29**, 123 (1903).

[15] Borsche and Scholten, *Ber.*, **50**, 600 (1917).

3-Nitrodiphenyl-4-*p*-toluene sulfonate (VI) was prepared by treating 5 g. of 3-nitro-4-hydroxydiphenyl with a solution of 5.2 g. of *p*-toluenesulfochloride in 5 g. of dimethylaniline and heating the mixture for a day at 100°. It was then acidified, the precipitate collected, dried, pulverized and extracted with 1% caustic alkali, to remove traces of unchanged initial materials. The residual ester was then purified by crystallization from alcohol and decolorization. The product formed bright yellow flakes, m. p. 114.8° (corr.); yield, 66%.

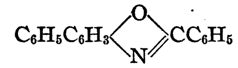
3-Nitrodiphenyl-4-*p*-nitrobenzoate (VII).—To a solution of 60 g. of 3-nitro-4-hydroxydiphenyl in 250 cc. of pyridine, there was added slowly, with stirring, 55 g. of well ground *p*-nitrobenzoyl chloride, keeping the temperature of the mixture below 25°. The reaction was completed in three hours and the mixture was poured into 400 cc. of 10% caustic alkali solution, let stand for an hour and filtered. Decolorized and crystallized from alcohol, the product appeared in colorless silky crystals, m. p. 169° (corr.); yield, 82%.

Reduced in glacial acetic acid solution by stannous chloride and hydrochloric acid, it yielded the 2-*p*-aminophenyl-5-phenylbenzoxazole.

3-Amino-4-hydroxydiphenyl was obtained by reduction of the corresponding nitro derivative, as reported by Raiford,[12] and formed minute colorless scales, m. p. 209° (corr.), in agreement with the literature;[12,16] yield, 65%.

3-(*p*-Nitrobenzoylamino)-4-hydroxydiphenyl (VIII).—In the synthesis of 2-*p*-nitrophenyl-5-phenylbenzoxazole from 3-amino-4-hydroxydiphenyl and *p*-nitrobenzoyl chloride (see beyond), the crude oxazole was extracted with warm normal sodium hydroxide, to remove by-products and unchanged initial materials. These alkali extracts were treated with a current of carbon dioxide, which precipitated the phenol and not the *p*-nitrobenzoic acid. This precipitate, when decolorized and crystallized from alcohol, gave the hydroxydiphenyl derivative in canary-yellow flakes, m. p. 249.3° (corr.); yield, 12%.

2,5-Diphenylbenzoxazole, (5)



$C_6H_5C_6H_3{<}\overset{O}{\underset{N}{}}{>}CC_6H_5$

(IX).—A mixture of 3 g. of finely ground 3-amino-4-hydroxydiphenyl with 5% more than the calculated quantity of benzoyl chloride was boiled for thirty minutes and then distilled. After removal of the excess benzoyl chloride, the benzoxazole distilled and congealed as it cooled. It was pulverized, digested for three hours with 2% sodium hydroxide to eliminate contaminants, washed thoroughly, decolorized and crystallized from alcohol, when it appeared in colorless silky flakes, m. p. 132.8° (corr.); yield, 1.5 g., **or** 35%.

2 - (*p* - Nitrophenyl) - 5 - phenylbenzoxazole (X).—An intimate mixture of 3.3 g. of 3-amino-4-hydroxydiphenyl with 4 g. of *p*-nitrobenzoyl chloride was heated for thirty minutes at 210°. The cooled melt was pulverized and extracted with warm normal sodium hydroxide, to remove by-products and unchanged initial material. The residue was washed thoroughly, dried and extracted repeatedly with small amounts of toluene. The crude oxazole recovered from these toluene extracts was decolorized and crystallized twice from glacial acetic acid, giving a colorless pulverulent solid, m. p. 288.8° (corr.); yield, 52%.

2 - (*p* - Aminophenyl) - 5 - phenylbenzoxazole (XI).—A solution of 8 g. of 3-nitrodiphenyl-4-*p*-nitrobenzoate in 200 cc. of glacial acetic acid at 100° was treated gradually with a solution of 60 g. of stannous chloride in 130 cc. of concentrated hydrochloric acid and the mixture was boiled for six hours. The complex tin salt which separated was removed, washed with water, dried, pulverized, and digested for six hours at 40° with normal sodium hydroxide, to decompose the tin complex and eliminate the tin. The crude oxazole when decolorized and crystallized from alcohol, formed pale yellowish needles, m. p. 174.2° (corr.); yield, 63%.

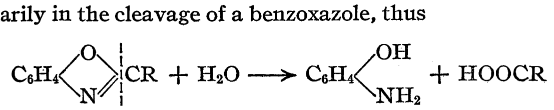
The same product was obtained by reduction of the 2-(*p*-nitrophenyl)-5-phenylbenzoxazole in a similar manner; yield, 75% (XII).

The alcohol solution of this compound exhibited a beautiful violet fluorescence, scarcely distinguishable from that produced by dehydrothio-*p*-toluidine.

2 - (*p* - Benzenediazochloride) - 5 - phenylbenzoxazole Hydrochloride (XIII).—The general method of Erdmann[17] was followed. A suspension of 1.5 g. of 2-*p*-aminophenyl-5-phenylbenzoxazole in 5 cc. of concentrated hydrochloric acid was cooled to 0–10° and diazotized by the gradual addition of the requisite amount of a 10% sodium nitrite solution. The mixture was allowed to stand (at room temperature) until a clear solution was secured, when it was diluted carefully until a precipitate appeared which was removed and dried. This diazochloride hydrochloride formed a yellow amorphous solid, m. p. 130.5° (corr.); yield, 42%. Boiled with dilute sulfuric acid, it gave the 2-*p*-hydroxyphenyl-5-phenylbenzoxazole.

2 - *p* - Aminophenyl - 5 - phenylbenzoxazole Disulfonic Acid (XIV).—A solution of 4 g. of 2-*p*-aminophenyl-5-phenyl-benzoxazole in 10 cc. of concentrated sulfuric acid was cooled to 20° and treated gradually with 15 cc. of fuming (60% free SO_3) sulfuric acid, maintaining the temperature below 55°, and protecting the solution from absorption of moisture by calcium chloride guard tubes. After stirring the mixture for twelve hours, it was cooled and poured upon ice. The colorless precipitate was removed, dissolved in dilute ammonium hydroxide, the solution filtered and the filtrate precipitated by acidification with hydrochloric acid. The precipitated sulfo acid was colorless and amorphous; yield, 80%.

When this disulfo acid was fused with caustic alkali, all of the products isolated were soluble in water but not in neutral organic solvents. Since this reaction results ordinarily in the cleavage of a benzoxazole, thus



$$C_6H_4{<}\overset{O}{\underset{N}{}}{>}\vdots CR + H_2O \longrightarrow C_6H_4{<}\begin{matrix}OH\\NH_2\end{matrix} + HOOCR$$

it follows that both cleavage products in the case of our disulfo acid carried a sulfonic acid group. *p*-Aminobenzoic acid dissolves quite readily in ether, but ether extraction of our products yielded nothing.

These results indicate that the original disulfo acid, like the corresponding thiazole compound,[18] carries one sul-

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[16] Bell and Kenyon, *J. Chem. Soc.*, **129**, 3044 (1926).

[17] Erdmann, *Ann.*, **247**, 328 (1888).

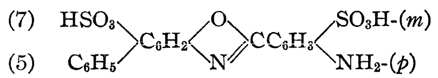
[18] Bogert and Snell, *Color Trade J.*, **14**, 109 (1924).

ANALYSES

		Calculated, %				Found, %			
		C	H	N	S	C	H	N	S
I	$C_{12}H_{10}O_2S$	66.02	4.62			66.03	4.64		
II	$C_{12}H_5O_6N_2S$	46.75	2.60	9.09		46.72	2.60	9.15	
III	$C_{12}H_{10}O$	84.70	5.90			84.70	5.88		
IV	$C_{12}H_{10}O$	84.70	5.90			84.68	5.93		
V	$C_{24}H_{16}O_{12}N_2Ba$			3.86				3.71	[a]
VI	$C_{19}H_{15}O_5NS$			3.79	8.67			3.36	8.75
VII	$C_{19}H_{12}O_6N_2$	62.63	3.29	7.69		62.79	3.16	7.28	
VIII	$C_{19}H_{14}O_4N_2$	68.26	4.27	8.38		68.62	4.32	8.01	
IX	$C_{19}H_{13}ON$	84.13	4.80	5.16		84.02	4.94	5.11	
X	$C_{19}H_{12}O_3N_2$	72.15	4.18	8.86		72.29	3.83	8.47	
XI	$C_{19}H_{14}ON_2$	79.70	4.92	9.55		79.80	5.14	9.55	
XII	$C_{19}H_{14}ON_2$	79.70	4.92			79.27	4.99		
XIII	$C_{19}H_{13}ON_3Cl_2$								[b]
XIV	$C_{19}H_{14}O_7N_2S_2$			6.37	14.13			6.27	14.31
XV	$C_{19}H_{13}O_2N$			4.87				4.69	
XVI	$C_{19}H_{12}O_6N_2$	62.63	3.29			62.91	3.28		
XVII	$C_{19}H_{14}ON_2$	79.70	4.92			79.39	4.60		
XVIII	$C_{19}H_{16}O_5N_2S$	59.34	4.19			58.92	4.05		

[a] Ba calcd., 19.00; found, 18.46. [b] Cl calcd., 19.20; found, 18.92.

fonic acid group on each of the two benzene nuclei, the most likely structure being the following.



2-*p*-**Hydroxyphenyl-5-phenylbenzoxazole** (XV).—When a solution of 2 g. of the diazo chloride (XIII) in a liter of 20% sulfuric acid was boiled for twelve hours and then cooled, this phenol separated. From alcohol, it crystallized in cream colored flakes, which were dried at 120° and then melted at 270° (corr.); yield, 65%. Its solution in concentrated sulfuric acid exhibited a sky-blue fluorescence. Under identical conditions, the corresponding amine gave a lighter violet blue fluorescence.

Derivatives of *o*-Hydroxydiphenyl

3,5-Dinitrodiphenyl-2-benzoate (XVI).—A solution of 10 g. of sodium 3,5-dinitrodiphenyl-2-phenolate[15] in acetone was stirred for two hours with an excess of benzoyl chloride. The precipitated benzoyl derivative was removed and a second crop obtained by the addition of water and ether to the filtrate. The combined precipitates, after thorough washing with water, alcohol and ether, were crystallized from alcohol and pale yellowish crystals obtained, which melted at 119.5° (corr.); yield, 65%.

2,7-Diphenyl-5-aminobenzoxazole (XVII) was obtained by reduction of the above benzoate in essentially the same way as the 2-*p*-aminophenyl-5-phenylbenzoxazole (XI) was prepared from the corresponding benzoate (VII). Decolorized and crystallized from alcohol, it formed pale yellowish needles, m. p. 220.8° (corr.); yield, 61%. Its alcoholic solutions exhibited a greenish fluorescence.

Sulfonic Acid (XVIII).—To a solution of 8 g. of the above oxazole (XVII) in 20 cc. of concentrated sulfuric acid at 20°, 40 cc. of fuming (50% free SO_3) sulfuric acid was added at such a rate that the temperature did not rise above 55°. After the initial reaction was over, the temperature of the solution was held at 55° until the sulfonation was complete (six hours). The mixture was then poured upon ice, the white precipitate collected, washed, dissolved in sodium carbonate solution, reprecipitated by hydrochloric acid, this solution and reprecipitation repeated. The product crystallized with one molecule of water and decomposed above 375°.

When fused with potassium hydroxide at 250–270° for ten minutes, the only product isolated and identified was benzoic acid. It seems probable, therefore, that the sulfo group was on the benzoxazole portion of the molecule.

Summary

1. From commercial phenol still residues, *p*- and *o*-hydroxydiphenyls have been isolated and converted into the new dye intermediates, 2-*p*-aminophenyl-5-phenylbenzoxazole, 2,7-diphenyl-5-aminobenzoxazole, and their sulfo acids.

2. A number of new intermediate and final products have been synthesized and their properties recorded.

NEW YORK, N. Y. RECEIVED AUGUST 19, 1935

[CONTRIBUTION FROM THE LABORATORY FOR PURE RESEARCH OF MERCK & CO., INC.]

Preparation and Properties of Acetyl Dextro- and Acetyl Levo-β-methylcholine Chloride

BY RANDOLPH T. MAJOR AND HOWARD T. BONNETT

Acetyl β-methylcholine chloride[1] has recently been shown to be a useful therapeutic agent.[2] It has been carefully studied pharmacologically and has been found to possess a strong muscarine-like action with none of the nicotine-like action observed with choline and many of its derivatives.[3]

An examination of the chemical formula of acetyl β-methylcholine chloride, $(CH_3)_3NClCH_2CH(CH_3)OCOCH_3$, reveals the fact that it contains one asymmetric carbon atom. Theoretically it should be possible to prepare two optically active forms of this compound. It is generally recognized that one of the optical isomers of a drug is usually much more active physiologically than the other.[4] In order to determine this in the case of acetyl β-methylcholine chloride the optical isomers of the compound have been prepared.

Dextro-dimethylaminoisopropanol was obtained by resolving the *dl* amine with bromocamphorsulfonic acid. Methyl iodide reacted with this to give dextro-β-methylcholine iodide from which acetyl dextro-β-methylcholine chloride was obtained by standard procedures.

Levo-dimethylaminoisopropanol was obtained by resolution of the *dl* amine with *d*-tartaric acid. Acetyl levo-β-methylcholine chloride was obtained by procedures similar to those indicated above for the dextro isomer.

PREPARATION AND PROPERTIES OF ACETYL DEXTRO AND ACETYL LEVO β-METHYLCHOLINE CHLORIDE

		β-Methylcholine iodide	β-Methylcholine	Acetyl-β-methylcholine chloride
Dextro form	M. p., °C.	176–177	165–167	200–201[a]
	[α]	+24.7	+38.8	+41.9
	N found, %	5.87 5.74	9.34 9.35	6.79 6.98
N calcd., %		5.71	9.12	7.16
Levo form	N found, %	5.39 5.53	9.45 9.25	7.04 6.89
	M. p., °C.	176.5–177.5	165–167	201–202[a]
	[α]	−24.7	−38.2	−41.3

[a] A mixed melting point of equal quantities of the *d*- and *l*-forms melted at 172–174°. Major and Cline [THIS JOURNAL, **54**, 247 (1932)] give 172–173° for *dl*-acetyl-β-methylcholine chloride.

Dr. Hans Molitor, Director of the Merck Institute for Therapeutic Research, has tested these compounds pharmacologically and reports that the muscarine-like action on the blood pressure of acetyl *l*-β-methylcholine chloride is one one-hundredth of that of acetyl *dl*-β-methylcholine chloride. The action of the former on isolated intestine was considerably less than the action of the latter. The muscarine-like action on the blood pressure of acetyl *d*-β-methylcholine chloride is somewhat greater than the action of the *dl* form. The action on isolated intestine is comparable to that of the *dl* form.

Experimental Part

Preparation of *d*-Dimethylaminoisopropanol.—Dimethylaminoisopropanol (b. p. 124–126°) was treated with a 5% excess of bromocamphor sulfonic acid in ethyl acetate solution. The salt was recrystallized from a mixture of 5 cc. of ethyl acetate and 1 cc. of absolute alcohol per gram of salt. Its rotation attained a value of +83.5° after five recrystallizations and was unchanged by additional recrystallizations. The amine was obtained from the salt by treating the latter with excess sodium hydroxide, extracting with ether, drying the ether solution with anhydrous potassium carbonate and distilling at atmospheric pressure; b. p. (770 mm.) 124.5–126°; $[\alpha]^{25}_D$ +17.1°.

Anal. Calcd. for $C_5H_{13}ON$: N, 13.59. Found: N, 13.61, 13.48.

Preparation of *l*-Dimethylaminoisopropanol.—Dimethylaminoisopropanol (b. p. 124–126°) was treated with 1.05 moles of *d*-tartaric acid in 95% alcohol solution. The salt was recrystallized from 6 cc. of 96% ethyl alcohol per gram of salt. A series of fifteen recrystallizations gave a salt having $[\alpha]^{25}_D$ −10.7°, the last four crystallizations changing the rotation from −10.3 to −10.7°. The amine was obtained from the salt as described above; b. p. 125°, $[\alpha]^{25}_D$ −14.8°.

Anal. Calcd. for $C_5H_{13}ON$: N, 13.59. Found: N, 13.00, 12.96.

Preparation of Acetyl *d*- and Acetyl *l*-β-Methylcholine Chlorides.—The methiodides of the optically active am-

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[1] Major and Cline, THIS JOURNAL, **54**, 242 (1932).

[2] Kovacs, *Am. J. Med. Sci.*, **188**, 32 (1934); Abbott, *ibid.*, **186**, 323 (1933); Starr, *ibid.*, **186**, 330 (1933).

[3] Simonart, *J. Pharmacol. Exptl. Therap.*, **46**, 157 (1932).

[4] Sollman, "A Manual of Pharmacology," W. B. Saunders & Co., Philadelphia, 1932, p. 364.

ines were prepared in the usual manner. They were recrystallized from hot absolute alcohol to which about 30% of acetone was added after solution, and were obtained as white non-hygroscopic crystals. The optically active β-methylcholine iodides were converted to the corresponding chlorides using silver chloride in alcohol according to standard procedures. The chlorides were recrystallized from butyl alcohol,[5] and were obtained as white hygroscopic crystals. The optically active β-methylcholine chlorides were acetylated according to the method of Major and Cline.[5] The acetyl esters thus obtained were white hygroscopic crystalline solids. The properties and analyses of the above-mentioned compounds are recorded in the table.

The authors wish to express their appreciation to Messrs. Douglass F. Hayman and Sol Adler for the analyses recorded in this paper.

Summary

1. *dl*-Dimethylaminoisopropanol has been resolved into its optically isomeric forms.

2. The dextro and levo isomers of β-methylcholine iodide, β-methylcholine chloride, and acetyl-β-methylcholine chloride have been prepared and characterized.

RAHWAY, N. J. RECEIVED JULY 9, 1935

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[5] Major and Cline, THIS JOURNAL, **54**, 247 (1932).

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

Potassium Thiocyanate as a Primary Standard Substance

BY I. M. KOLTHOFF AND J. J. LINGANE

Although potassium thiocyanate has long been used as a reagent in the classical Volhard method for the titration of silver, the use of the pure salt as a primary standard substance in argentimetry has been discouraged in the literature.[1]

The initial purpose of the present investigation was to investigate the possibility of preparing the pure salt for use as a standard substance. A secondary purpose was to determine the *accuracy* of the potentiometric and the Volhard methods for the titration of thiocyanate with silver, which has never been established, although the *precision* of the titration has been the subject of several studies.[2]

The second part of this work has led to the discovery of a hitherto unsuspected side reaction (or reactions) that takes place when thiocyanate is precipitated with silver.

Preparation of Pure Potassium Thiocyanate

Potassium thiocyanate from Kahlbaum and the reagent quality product of the Mallinckrodt Company have both been used in this study, and except for a considerable amount of hygroscopic water, the salts were found to be quite pure and suitable starting materials.

Samples of the salt were repeatedly recrystallized from water, ethanol and methanol. Recrystallization from the alcohols is somewhat simpler than from water, with respect to the manipulative details, but we have found that removal of chloride is incomplete on crystallization from alcohol and therefore it is preferable to recrystallize from water when the original salt contains appreciable amounts of chloride. The yield in either case is approximately 50%.

Other samples of the pure salt were prepared by fractional precipitation from a saturated ethanol solution by the addition of ether; four successive fractions were collected.

In all cases, the crystals were collected on a Büchner funnel without paper, the adhering mother liquor was removed by suction, and the products were dried in a desiccator at room temperature. The samples were then heated for an hour at 150° and were finally heated to 200° (m. p. 172°) and kept melted for ten to twenty minutes, to remove the last traces of solvent.

Experiments were made to determine whether chloride and ammonium thiocyanate can be removed completely from potassium thiocyanate by recrystallization from water or alcohol. A sample to which 1% of potassium chloride had been added still contained 0.6% after three recrystallizations from alcohol, but after three recrystallizations from water the final product contained less than 0.005% of chloride.

A sample to which 1% of ammonium thiocyanate had been added contained less than 0.005% of ammonia after three recrystallizations from alcohol or from water.

It was found occasionally that the salt became colored yellow on heating and melting. Systematic study showed that this yellow discoloration was only obtained when the salt was heated in an atmosphere that was slightly contaminated by acid vapors. The discoloration also takes place at room temperature when the dried salt is exposed for some time in an acid contaminated atmosphere. The yellow coloration was more frequently observed with products that had been recrystallized from alcohol, even though the atmosphere in which the salt was heated was entirely free from acid fumes.

The yellow coloration is probably due to the formation of isoperthiocyanic acid ($H_2C_2N_2S_3$) and isodithiocyanic acid

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[1] I. M. Kolthoff, "Die Massanalyse," 2 Aufl., Julius Springer, Berlin, 1931.

[2] *Cf.* I. M. Kolthoff and L. H. van Berk, *Z. anal. Chem.*, **70**, 369 (1927).

$(H_2C_2N_2S_2)$[3] or a mixture of these with the yellow oxidation products described by Offord.[4]

If reasonable care is taken to heat and melt the salt in a pure atmosphere, and to store the dried salt in glass-stoppered bottles in the dark, no trace of the yellow discoloration is formed. Samples prepared in this way are stable indefinitely. In direct sunlight the colorless crystals become yellow fairly quickly. Solutions of the pure salt in pure water are entirely stable, when protected from light. We have kept a solution of the pure salt for eleven months with no detectable change in titer.

Test for Impurities

Water (Alcohol).—Ten grams of the salt should not decrease in weight by more than 1 mg. (0.01%) when melted for ten minutes at 200°.

Chloride.—The test given by Murray[5] was found to be entirely satisfactory. One gram of the salt is dissolved in 50 cc. of water and 20 cc. of chloride-free concentrated nitric acid is added. The solution is heated for two to three hours at 90 to 95° under reflux, and after cooling and addition of a few drops of 0.5 *N* silver nitrate solution, no opalescence due to silver chloride should be observable.

Ammonia.—One gram of the salt is placed on a watch glass and 1 cc. of 4 *N* sodium hydroxide solution is added. The watch glass is covered with a second inverted one of the same size which has a strip of moistened litmus paper adhering to its under side. The presence of 0.001% of ammonia is easily detectable by a blue coloration of the litmus paper after the apparatus has stood for fifteen minutes. The products used by us contained less than 0.001% of ammonia.

Other Impurities.—Other tests given by Murray were found to be satisfactory.

The samples of potassium thiocyanate used in the titrations against silver were pure white, and tests showed that they were entirely free from heavy metals, alkaline earth metals, chloride, ammonia, sulfate, sulfur, cyanate and cyanide.

Drying of Potassium Thiocyanate and Hygroscopicity of the Dried Salt

Three 23-g. samples of potassium thiocyanate, which had been thrice recrystallized from water and dried for a week over phosphorus pentoxide at room temperature, were ground to a fine powder in an agate mortar and placed in large tared weighing bottles with well fitting stoppers. The samples were then subjected to the drying treatment described in Table I. The results with the three samples agreed within the limits of the possible error in weighing, and we therefore give only the data obtained with one sample for the sake of brevity.

TABLE I

LOSS IN WEIGHT OF POTASSIUM THIOCYANATE ON HEATING

Treatment	Wt. of salt, %	Total change in weight, g.
25 hrs. over P_2O_5 at room temp.	23.6163	(0.000)
45 hrs. over P_2O_5 at room temp.	23.6170	+ .003
1 hr. at 100–105°	23.6136	− .011
4 hrs. at 100–105°	23.6125	− .016
1 hr. at 150–155°	23.6083	− .032
3 hrs. at 150–155°	23.6072	− .038
5 hrs. at 150–155°	23.6069	− .039
10 min. at 200–210° (m. p. 172°)	23.6055	− .045
30 min. at 200–210°	23.6036	− .053
1 hr. at 200–210°	23.6065	− .041
1 hr. 40 min. at 200–210°	23.6087	− .032

It is evident from these experiments that no more than 0.02% of water is retained by the salt after heating for one to two hours at 150°. The last trace of water is removed by melting for a short time at 200°.

It will be observed that there was a slight, but definite, increase in weight on prolonged heating of the molten salt at 200°. This increase in weight is probably caused by a slow air oxidation and for this reason the melting period should not be unduly long.

Samples heated in the molten state for fifteen hours at 195° gained 0.05% in weight. Subsequent titration with pure silver solutions as described later showed that the effective strength of these samples was 0.04% less than samples which had been melted for only ten minutes at 200°.

Experiments were next made to determine the hygroscopicity of the dried salt. Twenty-three-gram samples of the solid melts from the drying experiments were crushed and ground to a fine powder in an agate mortar, and, after transferring to tared weighing bottles, they were redried at 150° to remove the water taken up during grinding (0.08%).

After standing for a week over deliquescent calcium chloride hexahydrate (relative humidity, 0.30), and for a week longer over deliquescent potassium carbonate dihydrate (r. h. 0.45), the weight of the dried samples remained unchanged. A sharp increase in weight, which increased rapidly with time, was found when the samples were placed over deliquescent sodium bromide dihydrate (r. h. 0.57). Therefore the dried salt is not hygroscopic at a relative humidity less than 45% but deliquesces rapidly at relative humidities greater than about 50%. This result is in accord with measurements of N. Schoorl (private communication), who found that the aqueous vapor pressure of a saturated potassium thiocyanate solution corresponds to a relative humidity of 0.50 at 13.5°.

Potentiometric Comparison of Potassium Thiocyanate against Silver.—We have studied the accuracy of this titration by direct comparison of pure potassium thiocyanate against pure silver.

Materials

Silver.—Pure silver was prepared according to the classical method of Richards and Wells[6] by reducing twice recrystallized silver nitrate with redistilled ammonia and pure formic acid. Several samples of the metal so obtained were further purified by melting into buttons on charcoal, and electrolyzing these buttons in the usual way.

Silver Nitrate.—Mallinckrodt reagent quality silver nitrate was twice recrystallized from nitric acid and after

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[3] H. N. Stokes and J. R. Cain, THIS JOURNAL, **29**, 443 (1907).

[4] H. R. Offord, *Ind. Eng. Chem., Anal. Ed.*, **7**, 93 (1935).

[5] Murray, "Standards and Tests for Reagent and C. P. Chemicals," D. Van Nostrand Company, New York City, 1927.

[6] T. W. Richards and R. C. Wells, THIS JOURNAL, **27**, 459 (1905).

drying at 110° the samples were melted for fifteen minutes at 225 to 250° in an electric oven, in platinum.

Water.—Twice distilled water was used for all standard solutions. All other materials used in this work were of a degree of purity consistent with the purposes for which they were used, as shown by appropriate tests.

Standard Solutions.—Standard solutions were prepared by weight, using a large Bunge balance which had a sensitivity of 1 mg. with a full load of two kilograms. Weighings below 200 g. were performed on an ordinary analytical balance. The set of weights used (10 mg. to 1000 g.) was carefully calibrated by the substitution method. Weighings were corrected to vacuum on the following density basis; weights 8.4, air 0.0012, potassium thiocyanate 1.91, silver nitrate 4.35 and silver 10.5 g. per cc.

The stock solutions were prepared and stored in specially constructed one-liter Erlenmeyer flasks, provided with finely ground glass stoppers carrying sealed-in delivery tubes similar to an ordinary wash bottle. The ends of the delivery tubes were closed with ground glass caps. These storage flasks were modeled after the storage bottles described by Lange and Schwartz.[7]

Potassium thiocyanate and neutral silver nitrate solutions were prepared from samples of the pure fused salts.

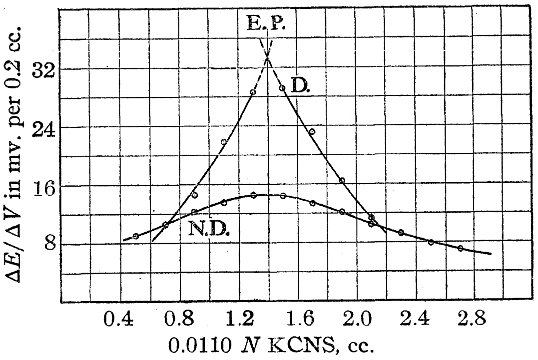

Fig. 1.—$\Delta E/\Delta V$ curves in region of equivalence point in final titrations of a digested and undigested precipitate: D., digested; N. D., not digested.

Acid silver solutions were prepared by dissolving carefully weighed buttons of the purified metal in an excess of 6 *N* nitric acid in a Kjeldahl flask. After diluting and heating to remove residual oxides of nitrogen, the solution was transferred to a previously weighed storage flask, diluted to *ca.* 800 cc. and weighed. The free acid concentration of these silver solutions (*ca.* 0.02 *N*) was determined by titrating suitable samples with standard sodium hydroxide, using brom cresol green indicator.

The standard stock solutions were approximately 0.2 molal. Twenty times diluted solutions (*ca.* 0.01 *N*) of each of the stock solutions were prepared using calibrated volumetric apparatus.

Apparatus and General Procedure of the Titrations

The usual potentiometric apparatus was used, allowing e. m. f. readings to ±0.1 mv. The silver electrodes were prepared by plating small platinum gauze electrodes (cylinders of 1 cm. diameter and 1 cm. in length) with silver from a potassium argenticyanide bath at low c. d. The saturated calomel and saturated mercurous sulfate reference electrodes were of the simple bottle type recommended by Müller.[8] The bridge tubes were of the inverted U-type, filled with a gel of saturated potassium sulfate in 3% agar.

The titrations were performed in very faint diffuse daylight in a room with closely drawn shades. As a further precaution against light decomposition, the 250-cc. titration beaker was placed in a closely fitting brown glass jar. Efficient mechanical stirring was employed in all measurements and titrations, using a small electric induction motor and a glass stirrer of the propeller type.

The general procedure of titration consisted in weighing out 40 to 50 g. of the stock silver solution into a small tared and stoppered flask directly from the storage flask (silver solutions cannot be dispensed from weight burets with greased stopcocks), transferring to a 250-cc. beaker and diluting to 125 cc., with or without the addition of nitric acid. The stock thiocyanate solution was then added from a weight buret over a period of three to five minutes, with constant stirring, until the measured e. m. f. indicated close approach to the equivalence point.

In some titrations it was desired to add the titrating solution very slowly over a period of fifteen to thirty minutes and for this purpose a special dropping funnel, without a stopcock, similar to the one described by Johnson[9] was used.

In some titrations a slight deficiency of potassium thiocyanate solution was added, and in others a slight excess was added. The titration was finally finished with the appropriate dilute solution (*ca.* 0.01 *N*), added from a 5-cc. microburet. The location of the equivalence point was found in the usual manner by calculating the point at which $\Delta E/\Delta V$ attained a maximum value.

The final titration was made very slowly, with care to obtain constant potential before adding successive increments of the dilute titrating solution. It required about one to one and a half hours for the final titration.

It was found that the titration could be made more quickly, and a more pronounced maximum in $\Delta E/\Delta V$ was obtained, when the mixture was heated to 70 to 90° for ten minutes after the addition of the stock thiocyanate solution, and cooled to room temperature again before the final titration. In this way the bulk of the precipitate is subjected to a drastic aging which causes a marked decrease in its adsorptive properties toward silver and thiocyanate ions.[7] In Fig. 1 the data of two final titrations in the region of the equivalence point have been plotted to illustrate this difference in the behavior of digested and undigested precipitates. In both cases the maximum in $\Delta E/\Delta V$ comes at the same place, but the break is more pronounced with digested precipitates.

Considerable time is required to obtain constant e. m. f. readings during the titration, especially with undigested precipitates. Constant potential was obtained more quickly when an excess of thiocyanate solution was added, and the final titration was made with the dilute silver solution, than when the reverse procedure was employed. Ad-

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(7) E. Lange and E. Schwartz, *Z. Elektrochem.*, **32**, 240 (1926).

(8) E. Müller, "Elektrometrische (Potentiometrische) Massanalyze," 5 Aufl., Theodor Steinkopff, Dresden, Germany, 1931.

(9) C. R. Johnson, *J. Phys. Chem.*, **37**, 923 (1933).

dition of barium nitrate as recommended by Müller[8] was not conducive to more rapid attainment of steady potential, the drift in potential, and the time required for the drift to decrease to a negligible magnitude, were practically the same as when no barium nitrate was present.

In order to show the precision of the comparisons the data of a typical titration are given in Table II.

TABLE II

DATA OF A TYPICAL TITRATION

52.476 grams of 0.17828 molar silver nitrate solution diluted to *ca.* 125 cc. and 1 cc. of concd. nitric acid added. 48.729 grams of 0.19131 molar potassium thiocyanate solution (salt recryst. once from alcohol) added from weight buret at room temperature. Mixture heated to 70 to 90°, digested ten minutes, and cooled to room temperature. Titration completed with 0.00955 M thiocyanate solution from microburet. Saturated mercurous sulfate reference electrode.

0.00955 N KCNS, cc.	E, volts	$\frac{\Delta E}{\Delta V}$	$\frac{\Delta^2 E}{\Delta V^2}$
0	+0.0800		
3.4	.1411		
3.6	.1558	147	
3.8	.1774	216	+68
4.0	.2058	284	−23
4.2	.2319	261	
4.4	.2519	200	

$V = 3.8 + 68/(68 + 23) \times 0.2 = 3.95$ cc. Correction to thiocyanate solution, +0.197 g. Total thiocyanate solution, 48.729 + 0.197 = 48.926 g. wt. $AgNO_3$ soln./wt. KCNS soln. = 52.476/48.926 = 1.0725 (calcd. 1.0731.) Effective strength of KCNS, 99.94%.

Five other titrations, using the same sample of potassium thiocyanate, yielded the following results, in terms of the effective strength of the salt: 99.96, 99.93, 99.90, 99.90 and 99.93%, or an average of 99.93% for the six titrations.

Products recrystallized two to five times from water and alcohol, and the samples obtained by fractional precipitation of a saturated alcohol solution of the salt with ether, were tested in a similar way.

The detailed results of these titrations are not given here but may be found in the thesis of the junior author.[10] It suffices here to state that the final average obtained with twelve different products corresponded to an effective strength of 99.92% for the potassium thiocyanate.

Titrations carried out in neutral solution at room temperature, and with varying concentration of nitric acid (0–0.5 N), indicated that the acidity did not influence the results. However, when the potassium thiocyanate was added to a hot (80–90°) neutral or acid (nitric) silver solution, the average effective strength of the potassium thiocyanate was 100.05%. When the hot silver solution was acidified with sulfuric acid (0.06 N) the effective strength of the potassium thiocyanate was several tenths of a per cent. too high.

The reverse order of precipitation was also used in several titrations in neutral and dilute nitric acid solution; *i. e.*, the silver nitrate solution was added to the thiocyanate solution. The results agreed with the data of the former experiments, which showed that the order of the precipitation is without influence in the titrations.

Titration to the Equivalence Potential.—Since the precision of this method is dependent on an exact knowledge of the equivalence potential, it is of prime importance to determine this value in an accurate way. A simple method has been proposed by Kolthoff[11] for determining the equivalence potential by titration. The method consists in performing a titration with very dilute solutions of known concentration, calculating an empirical equilibrium constant for the reaction from the titration data, and finally calculating the equivalence potential from the equilibrium constant. In this way the solubility product of silver thiocyanate in neutral 0.05 N potassium nitrate solution was found to be 3.2×10^{-12} at 24°, and the corresponding equivalence potential against the saturated mercurous sulfate electrode was +0.176 v., which agrees well with the value +0.175 v. found from the maximum in $\Delta E/\Delta V$. By a similar titration it was found that the equivalence potential in a solution 0.05 N in potassium nitrate and 0.032 N in nitric acid (which duplicates the conditions in the titrations described below) was +0.187 ± 0.002 v.

Titrations were performed by adding thiocyanate solution to a slight excess of silver solution, and finally adding dilute thiocyanate solution until the measured e. m. f. remained constant at +0.187 ± 0.002 v. for at least fifteen minutes. In four such titrations to the equivalence potential, the average effective strength of the potassium thiocyanate was found to be 99.92%. These results are in exact agreement with those obtained by locating the equivalence point from the maximum in $\Delta E/\Delta V$.

Titration by the Volhard Method.—Some titrations were made by the classical Volhard method employing ferric iron as indicator. The thiocyanate solution was added to a slight excess of silver solution and the excess was titrated back with the *dilute thiocyanate solution. The indicator* blank was found to be 0.10 cc. of 0.01 N thiocyanate, using 4 cc. of a saturated ferric alum solution as indicator, in a final volume of 200 cc., and this value was applied as a correction in the titrations. A comparison flask, containing the same amount of precipitate and ferric alum indicator with a slight excess of silver present, was used to assist in locating the color change. The end-point was taken when the yellowish-brown coloration persisted after a minute or two of vigorous shaking.

The results showed an effective strength for the potassium thiocyanate that varied between 100.01 and 100.05%, the average being 100.02%. These results, 0.10% higher than the potentiometric comparisons, indicate that adsorption equilibrium is not reached in the relatively rapid Volhard titration, and that an excess of silver is retained by the precipitate at the visual end-point. In the potentiometric titrations, which require more than an hour, the silver nitrate, co-precipitated by the precipitate, is given off during the time required to obtain constant e. m. f.

The correctness of this conclusion was verified by adding a slight known excess of silver nitrate to the suspension remaining after potentiometric titrations in which the pre-

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(10) J. J. Lingane, Senior Thesis, University of Minnesota, June, 1935.

(11) I. M. Kolthoff, *Rec. trav. chim.*, **47**, 397 (1928).

cipitate had been digested. The slight excess of silver was then titrated back with the dilute thiocyanate solution after the addition of 4 cc. of saturated ferric alum indicator. The effective strength of the potassium thiocyanate calculated from the results of two such titrations was only 0.01% higher in both cases than the value determined from the potentiometric end-point.

A Side Reaction During the Precipitation of Thiocyanate with Silver.—Although the methodical precision of the potentiometric titrations was better than 0.01%, the results frequently varied by as much as 0.05% under identical conditions of titration. Furthermore, the effective strength of the various preparations of potassium thiocyanate was consistently in the neighborhood of 99.92% instead of exactly 100.00%, although no impurities could be found in any of the products. These facts pointed to the occurrence of a side reaction (or reactions) accompanying the precipitation of silver thiocyanate.

When a hot, acid silver solution was precipitated with thiocyanate the effective strength of the thiocyanate was definitely greater than 100%. Further, when a hot, neutral silver solution was treated with thiocyanate, the precipitate was colored a light tan, even when the precipitation was made in the dark. From hot dilute sulfuric acid solution the precipitates were pure white, but the effective strength of the potassium thiocyanate was several tenths of a per cent. greater than 100%.

Some of the tan precipitates from hot neutral solution were washed with water and suspended in a weak acetic acid solution containing excess potassium iodide. A strong odor of hydrogen sulfide was observed and a test for hydrogen sulfide was obtained with a moistened lead acetate paper placed in the mouth of the flask.

It was thought that an air oxidation of thiocyanate might have been induced during the precipitation, but the results obtained in potentiometric titrations in an atmosphere of nitrogen were the same as in air, and tan colored precipitates were also obtained in the absence of air.

Another possibility was that silver, being a rather strong oxidizing agent under certain conditions, might oxidize a minute fraction of the thiocyanate with the formation of cyanide, or cyanate, and thionic acids. A test was developed which was capable of detecting as little as 0.01% of cyanide in the precipitate but no indication of the presence of cyanide was obtained.

It was thought that some cyanate might be formed according to the reaction

$$2\text{CNS}^- + \text{O} + 2\text{H}_2\text{O} \longrightarrow 2\text{CNO}^- + 2\text{S}^{=} + 4\text{H}^+ \quad (1)$$

with the simultaneous precipitation of the sulfide by silver or its oxidation to thionic acids or sulfate, depending on the conditions. Cyanic acid is a weak acid which decomposes very easily

$$\text{HCNO} + \text{H}^+ + \text{H}_2\text{O} \longrightarrow \text{NH}_4^+ + \text{CO}_2 \quad (2)$$

Thus, if cyanate were an intermediate product of the side reaction, ammonia should be present in the final solution. This was actually found to be true.

The traces of ammonia, formed under various conditions of precipitation of thiocyanate with silver, were determined in the supernatant solution by making alkaline with ammonia-free sodium hydroxide, distilling in an all-glass apparatus and collecting the distillate in 10 cc. of 0.001 *N* sulfuric acid. The amount of ammonia in the distillate was estimated colorimetrically with Nessler's reagent. Ammonia-free reagents were used. According to the procedure developed, 0.005 mg. of ammonia in 90 cc. of solution could be detected with certainty.

Table III

Formation of Ammonia During Precipitation of Silver Thiocyanate

1.75 g. of AgNO_3 in 100 cc. of water and 0.97 g. of KCNS in 75 cc. of water for each experiment. 1 cc. excess of 4 *N* NaOH added to 90 cc. of supernatant solution and distilled for 30 min. in current of pure air.

	Conditions of precipitation	NH_3 in 10 cc. of distillate, mg.
1	KCNS $\longrightarrow$ AgNO_3, 0.2 *N* in HNO_3, room temp.	0.03
2	As (1), except at 80–90°	.07
3	As (1), except both solutions boiled 2 min. before mixing, and boiled during precipitation	.04
4	As (1), except air displaced with NaHCO_3	.03
5	KCNS $\longrightarrow$ AgNO_3, neutral, room temp.	.03
6	KCNS $\longrightarrow$ AgNO_3, neutral, 80–90°	.05
7	As (5), except 0.5 g. of borax present	.03
8	As (7), except AgNO_3 $\longrightarrow$ KCNS	.02
9	KCNS $\longrightarrow$ AgNO_3, 0.2 *N* in H_2SO_4, room temp.	.03
10	As (9), except at 80–90°	.07

It will be observed that practically the same amount of ammonia was formed in the absence as in the presence of air. More ammonia was found when the precipitation was made in hot solution than when the precipitation was made at room temperature.

Discussion of Results

Although the end-point of the potentiometric titration can be found with a precision of better than 0.01%, the titration of silver with thiocyanate is not suited to work of a highly exact nature. As a result of the side reactions, the variations between duplicate titrations at room temperature may amount to as much as 0.05%, the average result corresponding to an effective strength of the potassium thiocyanate of 0.08% less than the theoretical.

The Volhard method of locating the end-point leads to the same result when the precipitate is digested with a slight excess of silver before the final titration. In the ordinary Volhard method at room temperature without digestion, the average effective strength of the potassium thiocyanate is 0.02% higher than the theoretical, and 0.10% greater than the effective strength found potentiometrically or after digestion, because 0.10% of the silver nitrate is still adsorbed or occluded by the precipitate at the end-point. The relatively good results obtained by the ordinary Volhard method are thus due to a compensation of errors.

Potassium thiocyanate may be recommended as a standard substance in work of ordinary accuracy.

Summary

1. Potassium thiocyanate is easily obtained in a pure state and is a suitable standard substance for work of ordinary accuracy (±0.1%).

2. During the precipitation of silver with thiocyanate, or the reverse, slight side reactions occur in which cyanic acid is an intermediate product decomposing to ammonia and carbon dioxide. When a hot neutral silver solution is precipitated with thiocyanate the precipitate is colored tan by silver sulfide. The side reactions also take place in the absence of oxygen.

3. As a result of the side reactions, the average effective strength of the potassium thiocyanate in the potentiometric titration with silver at room temperature is only 99.92%.

4. If titrated at 70 to 90° an effective strength slightly greater than 100% is found. If the precipitation is carried out in hot dilute sulfuric acid (0.06 *N*), the deviation is several tenths of a per cent. greater.

5. The ordinary Volhard titration at room temperature leads to an effective strength 0.10% greater than the potentiometric titration, due to occlusion of silver nitrate at the end-point. If the precipitate is digested just before the end-point, the Volhard method gives results practically identical with the potentiometric method.

6. The solubility product of silver thiocyanate at 24° in 0.05 *N* neutral potassium nitrate solution is equal to 3.2×10^{-12}.

MINNEAPOLIS, MINNESOTA RECEIVED JUNE 4, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Formation of Zirconeate Hydrosols and their Disintegration by Certain Neutral Salts

BY ARTHUR W. THOMAS AND HARRY S. OWENS

In a previous publication,[1] the *p*H raising action of neutral salts upon basic zirconium chloride (sometimes designated as "zirconium oxide") hydrosols was ascribed to the replacement of OH groups from the polyolated micelles by the anions of the added neutral salts. If the strongly coördinatively bound OH group can thus be displaced from the central metallic atom by added anions, one would expect other coördinatively bound groups also to be displaceable.

Increases in chloride ion activity of "oxide" hydrosols have been reported to result upon addition of neutral salts.[2] Inasmuch as the order of effectiveness of the anions of the salts in raising the chloride ion activity is in general similar to those reported from this Laboratory for displacing OH groups from the micelle, the writers submit this as evidence for the expected displacement of chlorido groups. Removal and replacement of aquo groups from the central metallic atom by

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[1] A. W. Thomas and H. S. Owens, THIS JOURNAL, **57**, 1825 (1935).

[2] (a) P. S. Wassiliev and A. J. Rabinowitch, *Kolloid Z.*, **56**, 305 (1931); (b) H. B. Weiser, *J. Phys. Chem.*, **35**, 1, 1368 (1931); (c) A. Lottermoser and T. Chang, *Kolloid Z.*, **65**, 62 (1933); (d) W. Pauli and E. Valkó, "Elektrochemie der Kolloide," Julius Springer, Vienna, 1929, p. 527.

added anions would likewise be expected. If so, then the positive charge of the micelle would be reduced and perhaps reversed.

The reversal of the sign of charge of cationic "metallic oxide" micelles by added electrolytes has been ascribed by some investigators to the adsorption of the added ions to the surface of the micelle. These investigators, reasoning from the physical point of view, base their arguments on *zeta* potential measurements such as those of Powis[3] with oil emulsions and of Kruyt[4] with glass–water interfaces. Their work has led to the following conclusion which is the main tenet of the adsorption advocates: "if the *zeta* potential is positive, it is influenced more by anions and the influence increases with the valency of the effective ions, unless the ion is strongly adsorbed."[5] Since the degree of adsorption of organic ions increases with valence and molecular complexity, one would not expect simple univalent organic anions to be as potent as divalent in reversing the charge of the cationic micelle. However, inasmuch as glycolate and lactate readily reverse the charge of basic zirconium chloride micelles while succinate or oxalate either do not or only under limited experimental conditions the weakness of the adsorption argument is apparent.

A chemical type of explanation has been suggested by Pauli,[6] who explains irregular series formation with "iron oxide" hydrosols by assuming that stable complex formers such as pyrophosphate or ferrocyanide react with the surface bound basic ferric chloride in the following way

$$\mathrm{Fe(OH)_2Cl + Na_4P_2O_7 \longrightarrow (FeP_2O_7)^-Na^+ + 2NaOH + NaCl}$$

while trivalent ions of the same type do not form negative particles since they can react to form neutral molecules[7]

$$\mathrm{Fe(OH)_2Cl + K_3Fe(CN)_6 \longrightarrow Fe[Fe(CN)_6] + 2KOH + KCl}$$

Further, he claims, with alkaline hydrolyzing salts like phosphates and citrates, the reversal always results with an excess of OH^- ion, whereas at lower concentrations the discharging by means of OH^- takes place with salts with high valence anions through the simultaneous action of the anion and OH^-. A model for this discharging and reversal reaction is

$$\mathrm{Fe(OH)_2Cl + KOH \longrightarrow Fe(OH)_3 + KCl}$$
$$\mathrm{Fe(OH)_3 + KOH \longrightarrow (Fe(OH)_4)^-K^+}$$

The charge on the sols can be due to ions varying in nature from $(Fe(OH)_4)^-$ to $(FeAnOH)^-$ in which "An" is a trivalent anion.

Inasmuch as the writers have in the case of basic zirconium chloride sols succeeded in reversing the micellar charge by the addition of certain acids, and addition of salts with anions of various valencies while maintaining the *p*H value below 7, the explanation by Pauli does not apply.

The writers have found that the anions listed in "Group A" of Table I reverse cationic basic zirconium chloride micelles to anionic zirconeate micelles while those in "Group B" do not.

TABLE I

Group A	Group B
Citrate[a]	Acetate
Glycolate[a]	β-Hydroxybutyrate
Lactate[a]	Chloride
Malate[a]	Ethoxyacetate
Mucate[a]	Ferricyanide
Pyruvate	Ferrocyanide
Tartrate[a]	Formate
Dihydrogen phosphate[b]	Fumarate
Pyrophosphate[b]	Glycine
	Maleinate
	Monochloroacetate
	Monohydrogen phosphate
	Oxalate
	Phosphate
	p-Hydroxyphenylglycine
	Propionate

[a] These salts were also found to peptize freshly prepared hydrated zirconium oxide to zirconeate hydrosols. The three salts in Group A not marked [a] were not tried. The salts in Group B would not, of course, be expected to peptize the oxide. [b] Provided medium was not too alkaline.

The conditions necessary for reversal of cationic to anionic micelles by added salts are: (1) ability of the salt anion to displace aquo groups from the cationic micelle, (2) the formation of a soluble anionic complex and (3) the equilibrium constant of the anionic complex must be near to or less than the solubility product of zirconyl hydroxide.

The first is essential to reversal of charge and inasmuch as the majority of anions in Group B possess known coördinative binding powers, they

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(3) F. Powis, *Z. physik. Chem.*, **89**, 91 (1914).

(4) H. R. Kruyt, "Colloids," John Wiley and Sons, Inc., 440 Fourth Ave., New York City, 1930, pp. 84–86.

(5) H. Freundlich, "Kapillarchemie," Akademische Verlagsgesellschaft m. b. H., Leipsig, 1930, Vol. I, p. 367.

(6) W. Pauli and H. Neurath, *Kolloid Z.*, **70**, 135 (1935); W. Pauli, *Trans. Faraday Soc.*, **31**, 11 (1935).

(7) Pauli and Neurath[6] state that because the stabilizing agent is distributed over the surface of the oxide micelle, it is impossible for the stabilizing agent to react with quadrivalent radicals to yield neutral complexes.

must be able to displace aquo groups. If they do displace a number sufficient to reverse the charge, their failure to repeptize the precipitated cationic basic zirconium complexes resulting upon their additon to the hydrosol means that the complexes either are insoluble or unstable, or both.

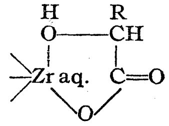
The anions in Group A must fulfill the conditions stated. The range of concentration in which charge reversal is effected is always very narrow. For example, the case of addition of potassium malate to Sol E[8] may be cited. At a malate concentration of 0.0035 *N* its micelles were positively charged, its *p*H was 4.65 and it was clear. At a malate concentration of 0.005 *N* it was a slightly turbid malato zirconeate hydrosol with a *p*H value of 7.40. Between these concentrations of malate the dispersed phase was all precipitated. Calculations show that more than 90% of the added malate was available to maintain equilibrium conditions and to react with the cationic micelle in some way other than displacement of OH groups. With the exception of the possible action of a small part of the malate in displacing chloride groups, part of the balance must have displaced aquo groups in order to confer the negative charge.

Inasmuch as hydrolysis (conversion of aquo to hydroxo groups) lowers the positive charge of basic metallic salt micelles, boiling of a sol (which process also favors olation and oxolation) should reduce the amount of added anion required to precipitate and reverse the charge of the micelles. A typical case may be cited. Sol E required (a) a concentration of 0.005 *N* potassium tartrate for precipitation and (b) 0.0088 *N* for conversion to tartrato zirconeate sol. After boiling under a reflux condenser for one hundred and ninety-two hours (a) = 0.0025 and (b) = 0.005.

The zirconeate sols formed by addition of the Group A (Table I) salts to basic zirconium chloride sols were very stable, being unaffected by addition of alkali (excepting phosphate and pyrophosphate) and it is significant that all are α-hydroxy compounds.[9] It is interesting in this connection to refer to the chemistry of crystalloidal zirconium compounds. De Boer[10] has shown that the ability of ions to form complex compounds with zirconium is in the following order: α-hydroxy organic salts[11] (in alkaline solution) $> OH > C_2O_4 > SO_4 > Cl$ (in acid solution) and Mandl[12] found a similar order: α-hydroxy organic salts $> C_2O_4 >$ maleinate $>$ saturated monobasic or dibasic organic acid salts.

The stability of metal–α-hydroxy complexes has for many years been ascribed to the ability of the α-hydroxy group to react with the metallic ion. There are two possible types of compounds (1) comparable to the β-diketone chelates[13] and (2) one in which the hydroxy group acts as an acid.[14]

These types would be formulated as follows.



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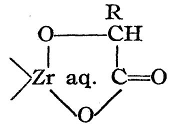

II

In "type I," negative micellar formation should be possible with radicals like monochloroacetate or ethoxyacetate, yet each of these acts like acetate when added to basic zirconium chloride sols. Evidently, ability of the α-substituted group to act as a donor of electrons to the metal has little effect on its ability of causing reversal of charge.

If "type II" illustrates the compound formed during chelation, then hydrogen ion should be liberated. An indication that such a reaction takes place is obtained from OH displacement experiments with salt mixtures, typical results of which are given in Table II. It is striking that mixtures of anions which do not reverse the charge of the micelles produced nearly the same *p*H values, while oxalate–lactate and oxalate–tartrate mixtures gave lower *p*H values. Chelation as illustrated by type II would account for the *p*H differences found and for the stability of the zirconeate hydrosols. Oxalate precipitates basic zirconium chloride sols without reversing the charge but subsequent addition of a salt of an α-hydroxy acid peptizes the precipitate to a complex zirconeate sol. Further, if sufficent α-hydroxy salt is first added to a basic zirconium chloride sol, subsequent addition of oxalate produces no precipitate. These behaviors are entirely in accord with the properties of crystalloidal zirco-

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(8) Sol E had a *p*H value of 3.50 (at the time of this experiment), its total Zr and total Cl contents were 126.2 and 11 milliequivalents per liter, respectively. Its micelles were cationic.

(9) The enol form of pyruvate exists in increasing concentration as the *p*H is raised.

(10) J. H. de Boer, *Z. anorg. allgem. Chem.*, **165**, 1 (1927); J. H. de Boer and H. Emmens, *Rec. trav. chim.*, **49**, 955 (1930).

(11) Irrespective of valence.

(12) A. Mandl, *Z. anorg. Chem.*, **37**, 252 (1903).

(13) N. V. Sidgwick, "The Electronic Theory of Valency," Oxford University Press, London, 1927, p. 233.

(14) L. Dede, "Komplexchemie," Walter de Gruyter and Co., Berlin, 1928, p. 97. See also articles by Pickering and by Work in *J. Chem. Soc.* from 1900 to date.

nium solutions where in almost every case α-hydroxy groups form more stable complexes than any other groups.

TABLE II

EFFECT OF ADDITION OF SALT MIXTURES TO SOL B[a]

(I)[b]	(II)[b]	pH
..	0.05 Oxalate	7.42
0.001 Tartrate	.05 Oxalate	7.23
.005 Tartrate	.05 Oxalate	7.01
.05 Tartrate	.05 Oxalate	6.86
.05 Lactate	.05 Oxalate	7.02
.05 Acetate	.05 Oxalate	7.34
.05 Sulfate	.05 Oxalate	7.34
.05 Oxalate	.05 Tartrate	6.88

[a] "B" was a basic zirconium chloride hydrosol, pH value = 3.22, total Zr and total Cl = 89.1 and 11.2 milliequivalents per liter, respectively. [b] (I) Solid potassium tartrate, acetate, sulfate or an 85% solution of potassium lactate was first added to the hydrosol. Then (II) a solution of potassium oxalate (or of tartrate) equal in volume to the hydrosol was added and the pH value of the mixture determined. The numbers in Columns I and II denote the normality of the salts in the resulting mixture of hydrosol and salt solution.

Ability to chelate does not necessarily mean that the anion will be capable of reversing the sign of the charge on the cationic sol particles, as illustrated by the case of glycine. This compound readily chelates with metallic ions in solution;[15] however, it affects basic zirconium chloride sols to but a slight extent. The authors were unable to precipitate a dilute sol containing cationic micelles with a large excess of glycine. Weitz and Conrad[16] report similar findings with glycine and aminobenzoic acids mixed with basic ferric chloride ("ferric oxide") hydrosols.

Deolation to the Crystalloidal State.—Since powerful coördinative binding ions weaken the ol linkage,[17] the α-hydroxy organic salts might be expected ultimately to effect disruption of ol bonds. According to the postulates from this Laboratory that "metallic oxide" hydrosols are polyolated structures, the salts mentioned should decompose an "oxide" sol to the crystalloid state. This postulate was tested in the following manner. To each of three portions of a basic zirconium chloride hydrosol was added, respectively, an equal volume of 0.1 N potassium citrate, tartrate and glycolate. The resulting zirconeate hydrosols were dialyzed in nitrocellulose bags against distilled water at room temperature. The diffusate contained zirconium (tested by the phosphate method) in each case but not in the instance of a control dialysis of the untreated basic zirconium chloride sol. As the dialysis continued the amount of zirconium diffusing decreased, but on further addition of the original salt solution to the dialysate more diffusible complexes were formed. These diffusions and additions of salt were continued until there was but a trace of zirconium left in the dialysate. With the potassium citrate the time of dialysis required to disintegrate the colloidal micelles was three hundred and fifty to four hundred hours,[18] with potassium tartrate four hundred to five hundred hours,[18] with potassium glycolate the time required was still longer. This order of ability to deolate the colloidal micelles, citrate > tartrate > glycolate, is the same as the tendency for these anions to become coördinatively bound with zirconium, as shown by titration experiments with basic zirconium chloride hydrosols.[1]

Zirconeate Hydrolysis of Low pH Value.—Basic zirconium chloride sols (Zr in the cationic micelle) which are of low pH value can be changed to zirconeate sols (Zr in the anionic micelle) by the careful addition of any of the following acids: citric, glycolic, lactic, oxalic, pyruvic,[19] sulfuric and tartaric. Zirconeate sols thus formed can exist only on account of the strong tendency of basic zirconium complexes to oxolate.[1] The oxo linkages are resistant to acids and thus render possible the existence of polynuclear complexes. The micelles are negatively charged because the anions of the acids named, strong coördinative binders, replace aquo groups from the central metallic atoms.

Acid zirconeate hydrosols may be prepared also by the action of acids (with powerful coördinative binding anions) upon hydrated zirconium dioxide. In studying the course of the peptization of such an oxide by tartaric acid, both positive and negative zirconium micelles arose in the same solution. This is so contrary to the accepted notions of colloid chemistry that a description of the experimental procedure is important.

A solution of $ZrOCl_2 \cdot 8H_2O$ was treated with ammonium hydroxide to complete precipitation of the zirconium. The precipitate was washed

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(15) E. Ferrell, J. M. Ridgion and H. L. Reilly, *J. Chem. Soc.*, 1440 (1934).

(16) E. Weitz and W. Conrad, *Kolloid-Z.*, **68**, 230 (1934).

(17) E. Stiasny, "Gerbereichemie (Chromgerbung)," Verlag von Theodor Steinkopff, Leipzig, 1931, p. 351; A. W. Thomas and R. D. Vartanian, THIS JOURNAL, **57**, 4 (1935).

(18) Dialysis times, of course, have no absolute significance; the times given here are of relative value only.

(19) Pyruvic acid acts very slowly.

at room temperature by means of centrifugal decantations until the supernatant liquid was free from chloride ion. It was then suction filtered and air dried at room temperature for twenty-four hours. Portions of this hydrated oxide equal to 1 g. of zirconium oxide were immediately[20] placed in 200-cc. portions of water to which the amounts of tartaric acid reported in Table III were added. Then, with the exception of the last stated case in Table III, the systems were rotated at 7 r. p. m. at 25 ± 0.2° for twenty-four hours. In the last stated case, the system was boiled under a reflux condenser for twenty-four hours. Then all were centrifuged to throw down the unpeptized oxide. The supernatant liquids which were turbid to reflected light while clear to transmitted light were subjected to the tests recorded in Table III.

TABLE III

PEPTIZATION OF A HYDRATED ZIRCONIUM OXIDE BY TARTARIC ACID

Tartaric acid, g.	Temp., °C.	Dispersed zirconium calcd. as milliequiv. ZrO_2 per liter	*p*H	Migration in electric field[a]
0.08	25	6	4.95	+ and −
.16	25	9	4.41	+ and −
.62	25	15	2.80	+ and −
.62	100[b]	112	2.27[c]	.....

[a] Migration of zirconium-containing micelles; + to cathode, − to anode. [b] In this instance, instead of agitating the system at 25°, it was boiled in a Pyrex glass reflux condenser apparatus for twenty-four hours. [c] In this case, the *p*H of the hydrosol was lower than of the original tartaric acid solution.

The startling fact shown in the table is the coexistence of cationic and anionic micelles. This fact was demonstrated by electrophoresis measurements upon the freshly prepared sols in a Coehn tube. The cationic micelle migrated faster than the anionic, thus indicating a greater charge density for the former. Probably none of the anionic micelles (tartrato zirconeate) would have been present were the systems allowed to stand for a longer time, as in the case of the peptization carried out at boiling temperature. The basic zirconium tartrate (cationic) micelles arise owing to the combination of H^+ ions with hydroxo groups of the hydrated oxide, forming aquo groups and thus conferring a positive charge upon the polynuclear complex. The tartrato zirconeate (anionic) micelles arise owing to the preponderant coördinative binding of tartrate ions over H^+ ions through displacement of aquo groups. The polynuclear zirconium or zirconeate complex would ultimately disintegrate to small particles if the complexes were not highly oxolated.

This is probably the first reported instance of the occurrence of positive and negative micelles in the same solution. The sols were rather dilute, however, and hence one can conclude that the solubility products of the sundry complex basic zirconium zirconeates present were not exceeded.

The subject of these acid dispersions of zirconeate micelles is being investigated further by one of us (H. S. O.).

Summary

Certain neutral salts convert basic zirconium (cationic) micelles to zirconeate (anionic) micelles while others do not. Certain neutral salts disintegrate basic zirconium ("zirconium oxide") micelles to the crystalloidal state. Zirconeate hydrosols of low *p*H value may be formed by the action of certain acids upon hydrated zirconium oxide. The possibility of the coexistence of positively and negatively charged micelles has been demonstrated. The polyolation and oxolation theory of the structure of "metallic oxide" hydrosol micelles proposed by this Laboratory renders possible the prediction and understanding of these behaviors.

NEW YORK, N. Y.

RECEIVED JULY 9, 1935

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[20] This hydrated zirconium oxide becomes refractory on aging, presumably due to oxolation. After forty-eight hours of standing at room temperature the amount peptizable by tartaric acid was decreased to about one-third of its former value. A specimen six months old was resistant to the action of boiling concentrated hydrochloric acid.

[CONTRIBUTION FROM THE LANKENAU HOSPITAL RESEARCH INSTITUTE]

Titrimetric Determination of Water and Alcohols by their Acid Catalyzed Reactions with Acetic Anhydride in Organic Media

BY GERRIT TOENNIES AND MARGARET ELLIOTT

The present work is an outgrowth of earlier observations on the acid catalyzed hydration of acetic anhydride in acetonitrile[1,2] and of a non-aqueous titration method[2] developed in this connection. For a review of the pertinent literature on the determination of water and alcohols reference is made to two papers by Smith and Bryant[3] which appeared while the present study was in progress. The method reported here is different in principle and scope from that of Smith and Bryant so that depending upon the nature of the analytical problem the one or the other will be preferable.

It was previously[2] shown that acetic anhydride can be titrated accurately in organic media by sodium methylate in methyl alcohol with thymol blue as an indicator according to

$$(CH_3CO)_2O + OCH_3^- \longrightarrow CH_3COOCH_3 + CH_3COO^- \quad (1)$$

while after hydration double the amount of methylate is consumed.

$$(CH_3CO)_2O + H_2O \longrightarrow 2CH_3COOH \quad (2)$$

$$2CH_3COOH + 2OCH_3^- \longrightarrow 2CH_3OH + 2CH_3COO^- \quad (3)$$

It was observed in this connection also that reaction (2) in dilute solution in acetonitrile is extremely slow, while in the presence of perchloric acid (0.1 M as cystine perchlorate) the reaction is complete in less than one hour. On account of certain disadvantages of perchloric acid (its liquid nature, uncertain degree of hydration and tendency to decompose with oxidation in the dehydrated state) in the present study 2,4-dinitrobenzenesulfonic acid was used as the acid catalyst. This acid was shown by Elgersma[4] to be comparable in acid strength with the strong mineral acids, it is easily obtained in a non-hygroscopic crystalline form with 2 molecules of water and it appears stable in a dehydrated solution. A concentration of this acid of the order of 10^{-3} M is sufficient catalytically to complete the above reaction (2) in organic media within from one hour to one day, depending on the nature of the medium. The reactions

$$(CH_3CO)_2O + ROH \longrightarrow CH_3COOR + CH_3COOH \quad (4)$$

($R = CH_3^-, C_2H_5^-$) were found to be accelerated to a similar degree, while the ester reaction

$$CH_3COOH + ROH \rightleftarrows CH_3COOR + H_2O \quad (5)$$

in both directions proved to be very slow under similar conditions compared with reactions (2) and (4). These circumstances permit determination of water by its acid catalyzed reaction with an excess of acetic anhydride according to equation (2), the molar amount of water present being equal to the increase in titration value compared with a blank, according to equations (1) and (2, 3). Alcohol can be determined by first letting reaction (4) go to completion in presence of excess anhydride and then decomposing the unused anhydride by excess water according to equation (2), while in a blank the same amount of anhydride is made to react directly with excess water. The difference between the two titrations is equal to the molar amount of alcohol present since each hydrolyzed molecule of anhydride consumes two equivalents of base while each alcoholized molecule consumes only one. Comparison of equations (1) and (4) will also show that in the water determination the presence of alcohol does not interfere since in the methylate titration acetic anhydride uses the same amount of base whether it has reacted with an alcohol previous to the titration or not.

The present investigation has been limited to establishing the principles and practicability and examining the accuracy and limits of sensitivity of the proposed method. The technique to be followed varies according to the problem at hand, and the examples given further on will enable the reader to adapt the method to his needs.

Experimental

Reagents.—2,4-Dinitrobenzenesulfonic acid was prepared according to Elgersma.[5] By dissolving 100 g. of the crude trihydrate in 440 cc. of acetonitrile and precipitating with 7.5 volumes of benzene the dihydrate was obtained in almost colorless crystals; equivalent weight by aqueous titration: found, 284.2, 283.8; calcd., 284.15.

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[1] G. Toennies and T. F. Lavine, *J. Biol. Chem.*, **100**, 474 (1933).

[2] T. F. Lavine and G. Toennies, *ibid.*, **101**, 727 (1933).

[3] D. M. Smith and W. M. D. Bryant, THIS JOURNAL, **57**, 61 and 841 (1935).

[4] J. N. Elgersma, *Rec. trav. chim.*, **48**, 770 (1929).

[5] J. N. Elgersma, *ibid.*, **48**, 752 (1929).

The yield is at least 50% in terms of initial chloro-2,4-dinitrobenzene. The dihydrate should not be stored in a closed container until acetonitrile has been very completely removed as the latter will react on standing with the crystal water with resulting odor of acetic acid.

$$CH_3CN + H_2O \longrightarrow CH_3COONH_4 \qquad (6)$$

$$CH_3COONH_4 + RSO_3H^{6} \longrightarrow RSO_3NH_4 + CH_3COOH \qquad (7)$$

A 0.1 *M* solution of the acid in dry acetonitrile (Merck Reagent) undergoes a slow change according to equations (6) and (7) (*cf.* also Ref. 2), but if kept at 0° can be used for several weeks.

A 1 *M* solution of acetic anhydride (Merck Reagent, about 95% $(CH_3CO)_2O$) in dry acetonitrile remains unchanged for months at room temperature.

A 1 *M* solution of water in acetonitrile is also stable for months.

A 0.1 *M* solution of sodium methylate in methyl alcohol (Merck Reagent) keeps a stable titer if it is set up in a closed titration system, protected against carbon dioxide and evaporation. Its absolute value is established by comparing it with standard sodium hydroxide in presence of an equal methanol concentration (about 15%) by titration against hydrochloric acid, using a (minor) correction for the effect of the methanol on the methyl red end-point. Regarding the standardization of sodium methylate *cf.* also Reference 2.

Thymol blue (Hynson, Westcott and Dunning) was used in a 0.125% methyl alcohol solution neutralized with 1 mole equivalent of sodium methylate solution. Approximately 10 drops per 20 cc. end-volume were used in the titrations.

General Technique.—The initial concentration of acetic anhydride preferably should be not higher than about 0.2 *M* in experiments extending over a few hours, or 0.04 *M* in experiments of one day or longer duration. After reaction with the water or alcohol present (including the crystal water of the catalyst and other water present in the blank) not less than 0.01 *M* acetic anhydride should be left. Also, in the alcohol determination the amount of water added to decompose the excess acetic anhydride is regulated so as to leave an unused excess of about 0.01–0.1 *M*. The sulfonic acid concentration of the test is made 0.002–0.004 *M*. Care must be taken to maintain a sufficiently high acetonitrile concentration to prevent crystallization of the sulfonic acid. In the case of ether 5% acetonitrile is sufficient with 0.004 *M* sulfonic acid, even though an opalescence may appear, on standing, while for benzene 10% acetonitrile is necessary.

Suitable amounts of acetic anhydride and sulfonic acid solution are combined immediately before the start of the experiment and equal amounts of the mixture are pipetted for tests and blanks. Glass-stoppered Erlenmeyer flasks, in case of the water determinations dried for several hours in high vacuum in the presence of calcium chloride, should be used. Suitable amounts of the liquid to be analyzed are added to the tests, and after sufficient time has elapsed both tests and blanks are titrated with the 0.1 *M* sodium methylate to a blue end-point. In the alcohol determination, after completion of the alcohol–acetic anhydride reaction excess water solution is added to tests and blanks and allowed to decompose the unused acetic anhydride before the titration is made. After adding to the solutions sufficient methylate to neutralize the sulfonic acid, thereby stopping the catalytic action, the solvent composition of all tests and the blanks is made the same by addition of the required amounts of the liquid used in the tests, and, after addition of indicator, the titration is finished. By this procedure perfect compensation[7] for medium effects on the end-point is obtained, and the absolute color of the end-point is immaterial as long as it is the same in blank and test.

Reaction Times.—No exact kinetic measurements were made in this study since it was realized that each analytical problem would present a different situation with regard to medium and concentration of reagents. It was established, however, that at ordinary temperatures a period of two hours is ample for the completion of the reactions of water, methyl and ethyl alcohol with acetic anhydride under the specified conditions in acetonitrile or a 4:1 mixture of benzene and acetonitrile, while in ether–acetonitrile (20:1 to 10:1) the reactions are approximately ten times slower. In presence of a catalyst concentration of the order of 10^{-2} *M* the water reaction in acetonitrile is complete in less than ten minutes, but as this concentration is, for reasons of solubility, too high for use in the presence of ether and similar solvents, catalyst concentrations about ten times lower were chosen throughout. Completeness of the reaction is made certain by running several tests with varying amounts of solution, varying excesses of acetic anhydride, or for different periods of time.

Practical Examples

Determination of Water. **(a) In Acetonitrile.**—Blanks: 0.045 millimol. RSO_3H + 1.25 mml. $(CH_3CO)_2O$ in

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[6] RSO_3H is used throughout as a symbol for 2,4-dinitrobenzenesulfonic acid.

[7] For maximal compensation the methyl alcohol content of blank and test should also be made equal at the end-point.

4 cc. acetonitrile. Tests: the same as the blank, + 5 cc. acetonitrile. Titration after four hours. Difference between tests and blanks (2 of each): 0.1555 ± 0.003 (average deviation from mean) mml. methylate. The same amounts of RSO_3H and $(CH_3CO)_2O$, 5 cc. and 10 cc. of acetonitrile. 2 blanks. Titration after twenty hours. Difference from blanks: for 5 cc. 0.156 ± 0.002, for 10 cc. 0.311 ± 0.002 mml. Result: the water content of the acetonitrile is 0.0311 ± 0.0003 *M*. Similar determination on another batch of acetonitrile gave (4 blanks, 1 test with 5 cc., 2 with 10 cc., reagents as before, three hours): 0.0143 ± 0.0005 *M* H_2O. The water concentration of the former acetonitrile was increased by 0.0206 *M;* found (4 blanks, 1 test with 10 cc.; 2 with 5 cc., reagents as before, three hours) 0.053 ± 0.001 *M;* calculated 0.052 *M.*

(b) In Ether.—For the determination of the minute residual water content of ether treated exhaustively with sodium the following technique was used: 0.225 mml. RSO_3H + 1.4 mml. $(CH_3CO)_2O$ in 5 cc. of acetonitrile, +50 cc. (2 blanks) and +100 cc. (2 tests) ether. Titration after twenty-four hours (1 pair) and after forty-eight hours (1 pair). Difference after twenty-four hours 0.040 mml., after forty-eight hours 0.035 mml. Result: the water content of the dried ether is 0.00075 ± 0.00005 *M*. The water concentration of the ether was increased by 0.00060 *M;* found by the same technique 0.0011, 0.0012 *M;* calculated 0.0013 *M*. A solution of water and alcohol in ether was made: 0.5644 *M* in water and 0.5241 *M* alcohol (0.2332 *M* C_2H_5OH + 0.2909 *M* CH_3OH). 0.045 mml. RSO_3H + 2.25 mml. $(CH_3CO)_2O$ in 10 cc. of acetonitrile, +4 cc. acetonitrile (blanks), and +5 cc. acetonitrile containing 1 cc. of the ether solution (tests). Titration after three hours (2 blanks and 2 tests): difference 0.567 ± 0.005 mml., after four hours (2 blanks and 2 tests): 0.568 ± 0.005 mml.; calculated 0.5644 mml.

Determination of Alcohols. (a) In Acetonitrile.—0.11 mml. RSO_3H + 2.1 mml. $(CH_3CO)_2O$ in 10 cc. of acetonitrile, +2 cc. 1 *M* H_2O in acetonitrile (4 blanks), and +25 cc. of acetonitrile (4 tests). After twenty minutes 2 cc. 1 *M* H_2O in acetonitrile were added to 2 tests and after an additional eighty minutes they were titrated together with two of the blanks. Blanks minus tests = 0.002 ± 0.005 mml. 2 cc. 1 *M* H_2O in acetonitrile was added to the other two tests after one hour's standing and they were titrated, together with two blanks, after an additional two hours. Blanks minus tests = −0.004 ± 0.004 mml. Results: less than 0.005 mml. of alcohol is present in 25 cc. of acetonitrile, *i. e.*, the alcohol concentration is less than 0.0002 *M*. A 0.00142 *M* solution of C_2H_5OH in acetonitrile was made. Analysis as above gave 0.035 ± 0.001 and 0.033 ± 0.005 mml.; found 0.0014 ± 0.0002 *M* alcohol; calculated 0.0014 *M*.

(b) In Ether.—The same dried ether that was used in the water determination was tested for alcohol as follows: 0.225 mml. RSO_3H + 1.8 mml. $(CH_3CO)_2O$ in 5 cc. of acetonitrile, +50 cc. (5 blanks), and +100 cc. (5 tests) ether. 2 blanks and 2 tests to which 2 cc. 1 *M* H_2O in acetonitrile was added after one day were titrated after another day (I). Of 3 blanks and 3 tests to which water solution was added after two days, one pair was titrated after one additional day (II) and two pairs after two days (III). Blank minus test = −0.004, −0.007 mml. (I); −0.010 mml. (II); −0.022, −0.015 mml. (III). The reaction with acetic anhydride of any alcohol should produce a positive difference between blanks and tests. A faint yellow discoloration observed during these protracted periods suggests that the slight tendency toward a difference in the opposite direction is caused by a minor polymerization or decomposition of the acetic anhydride. Tentatively the conclusion is drawn that the alcohol content of the ether is at the most 0.0001 *M*. A solution of 0.00058 *M* C_2H_5OH in this ether is made and analyzed in the same manner. Found after one + one day: +0.023, +0.028 mml., after two + two days: +0.017, +0.013 mml. By using the negative differences obtained in the previous experiment as corrections (−0.006 ± 0.002 mml. for one + one day and −0.019 ± 0.004 mml. for two + two days) one obtains 0.00061 ± 0.00006 *M* and 0.00068 ± 0.00010 *M*, or an average result of 0.00065 ± 0.0001 *M* alcohol; calculated 0.00058 *M*. The synthetic solution of water, methyl and ethyl alcohol mentioned above (under Determination of Water (b)) was analyzed for alcohol. 0.045 mml. RSO_3H + 2.26 mml. $(CH_3CO)_2O$ in 10 cc. of acetonitrile, +4 cc. of acetonitrile (4 blanks), and +5 cc. of acetonitrile containing 1 cc. of the ether solution (4 tests). Two cc. of 1 *M* H_2O in acetonitrile was added to two blanks at once and to two tests after thirty minutes. All were titrated after a total of two hours. Blanks minus tests = 0.526 ± 0.002 mml. Another 2 blanks and 2 tests, after addition of water after two and a half hours, were titrated after a total of six hours. Blanks minus tests = 0.524 ± 0.002 mml. Found 0.525 ± 0.003 mml.; calculated 0.524 mml.

Scope and Limitations.—The method seems primarily suited for the determination of small and moderate concentrations of water and alcohol in solvents that are inert against acetic anhydride and low concentrations of a strong acid, and that have no pronounced acidic or basic properties. As two extreme examples acetonitrile and ether, the one with an exceptionally high dielectric constant and the other with a low one, have been studied in detail. By proper modifications benzene (found 0.014 ± 0.001 *M* H_2O and less than 0.001 *M* alcohol; added C_2H_5OH 0.0602 *M*, found 0.0595 *M*) and chloroform (found 0.049 ± 0.002 *M* H_2O and 0.20 *M* alcohol) were studied.

The experiments show a maximum practical error of 0.010 mml. for a tested volume of 50 cc. equal to 0.0004% H_2O (by volume) and similarly for the alcohol determination a maximum error of 0.005 mml. for 50 cc. equal to 0.0004% C_2H_5OH or 0.0003% CH_3OH, while for tested volumes of 1 cc. the respective maximum errors encountered were 0.006% H_2O and 0.005% C_2H_5OH.

Substances that under the influence of acid split off water, such as for instance formic acid or acetone (mesityl oxide, phorone and mesitylene formation) should be expected to cause errors in the water determination. While these reactions prevent application of the method to the determination of water in acetone, acetone concentrations of the order of 0.1% or less cause only minor errors when the reaction medium is chiefly acetonitrile. In the water determination of acetonitrile (5 cc. of $RSO_3H - (CH_3CO)_2O$ mixture and 10 cc. of acetonitrile, titrated after three hours) to which 0.1 and 0.01% of acetone had been added, less than 1 mole per cent. of the added acetone reacted as water. In the case of the more protracted reaction in ether the error is more serious so that the presence of acetone should be excluded by specific tests. The fractions of the added acetone reacting as water were, with ether as the medium

Vol. % acetone added		1	0.1	0.01
Mol. % acetone reacted after	1 day	4.7	31	—
	2 days	5.2	37	85

In the case of the 1 and 0.1% acetone concentrations a yellow deposit was formed in the solutions and a very rapid fading of the blue titration end-point took place. It seems probable that the precipitation phenomenon contains the explanation for the inverse variation of the extent of the pseudo water reaction with the acetone concentration.

The question as to how far the respective reaction kinetics make the alcohol method practicable for higher alcohols, phenols, thiol compounds, etc., has not been covered in the present work, as the method is primarily intended for determining the purity of inert solvents with respect to their more common contaminants water and lower alcohols. For the same reason application to the water determination in alcohols has been left in abeyance for the present.

Thanks and appreciation are expressed to Merck and Company, Rahway, N. J., who generously supplied the acetonitrile used in this investigation.

Summary

The vigorous catalytic acceleration by strong acids in non-aqueous media, of the hydrolysis and alcoholysis of acetic anhydride is shown to be useful as a basis for the separate determination of water and alcohols in inert solvents. The error in concentrations of the order of one per cent. is less than ±1%. The lower limit of response is less than 0.001%.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Application of the Glass Electrode to Unbuffered Systems

BY SAMUEL B. ELLIS AND SAMUEL J. KIEHL

Introduction

In the realm of unbuffered or very weakly buffered systems the measurement of hydrogen-ion concentration or *p*H value becomes exceedingly difficult and involves considerable uncertainty. Most of the familiar methods of determining the *p*H value have been modified for use in such systems, but complete success can hardly be claimed for practical accurate measurement. For application of the hydrogen electrode to unbuffered systems reference may be made, among others, to the work of Beans and Hammett,[1] Kolthoff and Kameda,[2] and Hammett and Lorch.[3] Similar use of the quinhydrone electrode is described by Best.[4] Colorimetric methods have been discussed by numerous workers, among whom are Stern,[5] Acree and Fawcett,[6] and Kolthoff and Kameda.[2b]

The glass electrode with its obvious adaptability for use in unbuffered systems appears to have received definite attention only recently. Burton, Matheson and Acree,[7] who used a Thompson glass electrode, have given a brief account of some measurements on dilute buffers and distilled water. The development of glass electrode technique to its ultimate refinement has, however, been merely started and the field offers many possibilities for further research.

Accordingly, an extension of the use of the glass electrode and the development of methods whereby the accurate determination of the *p*H

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(1) Beans and Hammett, THIS JOURNAL, **47**, 1215 (1925).

(2) (a) Kolthoff and Kameda, *ibid.*, **51**, 2888 (1929); (b) **53**, 821 (1931).

(3) Hammett and Lorch, *ibid.*, **55**, 70 (1933).

(4) Best, *J. Phys. Chem.*, **34**, 1815 (1930).

(5) Stern, *J. Biol. Chem.*, **65**, 677 (1925).

(6) Acree and Fawcett, *Ind. Eng. Chem., Anal. Ed.*, **2**, 78 (1930).

(7) Burton, Matheson and Acree, *ibid.*, **6**, 79 (1934).

value may be made conveniently in the most difficult of unbuffered systems—highly purified water itself—were undertaken.

The Glass

The very soft glasses of low electrical resistance which have met with considerable favor for making glass electrodes have the serious disadvantage of being relatively soluble and of causing weakly buffered solutions with which they are in contact to become more alkaline, as the following experiment will illustrate. Three glass electrodes made of Corning 015[8] glass and of the type, to be described, were soaked in water for five weeks; then, under protection from atmospheric contamination, they were filled with distilled water and the *p*H value determined at intervals; at first the *p*H rose rapidly—approximately one *p*H unit per hour; even after twelve hours with a *p*H of 9, there was still a slow drift. In general the behavior of Corning 015 glass with unbuffered solutions was found to be quite erratic and unsatisfactory.

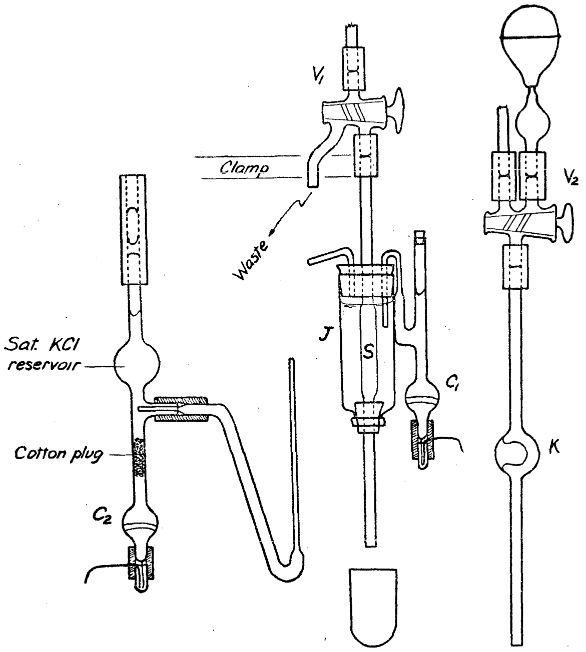

Fig. 1.—Glass electrode assembly.

From the standpoint of solubility, the ordinary soft (soda-lime) glass is much to be preferred to any of the special glasses. Electrodes made from it have much higher resistances, but a suitably designed electrical circuit will meet this difficulty.[9] Asymmetry potentials are also higher than those of Corning 015 glass, but in our experience they were just as constant—the important consideration. Again, ordinary soft glass does not agree with the hydrogen electrode over as wide a range as does Corning 015 glass. The work of Hughes,[10] of MacInnes and Dole,[8] of Sokolov and Passinski,[11] and of Lengyel and Blum,[12] in alkaline solutions indicate this. The matter of agreement with hydrogen electrode and the consistency of glass electrode measurements at extreme *p*H values and under varying conditions have not, however, been studied sufficiently to warrant the adoption of any particular glass to the exclusion of all others.

The measurements recorded in the work which follows were obtained by use of ordinary soft glass electrodes which had been carefully checked against the hydrogen electrode by use of phosphate and borate buffers over the *p*H range of 4 to 9.

Glass Electrode Assembly

The device used for measuring electromotive force was a sensitive vacuum tube potentiometer described by the authors elsewhere.[9]

The glass electrode, Fig. 1, was designed especially for convenient application to unbuffered solutions. The solution being measured is either sucked or siphoned into the tube, S, which drawn out thin in its central portion constitutes the glass membrane. This membrane of cylindrical shape is made by simultaneously blowing and drawing the central portion of an ordinary soft glass tube (6–7 mm. diameter). It is important and a little difficult to blow a sufficiently thin membrane. The required thinness however may be judged roughly by its flexibility when the membrane is depressed by a pointed instrument. Thicker membranes, even when their resistance is not exorbitant, are more likely to be erratic and unsatisfactory. The fixed portion of the system in the jacket surrounding the membrane is 0.1 *N* hydrochloric acid connected directly to a 0.1 *N* hydrochloric acid calomel cell C_1 of Hughes.[10] The liquid junction of the solution with a second calomel cell C_2 (saturated potassium chloride type) is effected either at the bottom of the tube S or at a point inside it, depending upon circumstances.

An easier method of forming the thin glass membrane is indicated by K of Fig. 1, which will be recognized as the familiar sucked-in-bulb type of Kerridge.[13] Although easier to make, the Kerridge bulb electrodes compared with the cylindrical type have several disadvantages: (1) their asymmetry potentials are less stable; (2) they are less easily washed, rinsed, and flushed free of air bubbles; (3) the Kerridge electrodes are more fragile and are easily broken by a sudden movement of the liquid inside; (4) the junction with a reference electrode must be formed somewhere below or above the active membrane, which, as will be shown later, is sometimes undesirable. With one exception, included for illustrative purposes, all the measurements reported in the following pages were obtained by use of the cylindrical type of electrode.

A rigid mounting of the membrane within a jacket by use of rubber or cement is more desirable and trustworthy than a glass seal because even slight heating produces noticeable deterioration of the glass electrode. The permanent combination on the outside of the membrane, including hydrochloric acid and hydrochloric acid–calomel cell C_1 is used merely to complete the electrical circuit and ensure constancy of e. m. f.—the prime consideration.

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[8] This is the special electrode glass developed by MacInnes and Dole [THIS JOURNAL, **52**, 29 (1930)] and made commercially by Corning Glass Co.

[9] Ellis and Kiehl, *Rev. Sci. Inst.*, **4**, 131 (1933). A description is given of the electrical measuring circuit which was used during the present work.

[10] Hughes, *J. Chem. Soc.*, 491 (1928).

[11] Sokolov and Passinski, *Z. physik. Chem.*, **A160**, 366 (1932).

[12] Lengyel and Blum, *Trans. Faraday Soc.*, **30**, 461 (1934).

[13] Kerridge, *J. Sci. Instruments*, **3**, 404 (1926).

The second calomel cell C_2 of the saturated potassium chloride type requires no other comment than to call attention to its removable (interchangeable) tip (Fig. 1) of which several may be available for special requirements. The tip is used to form the liquid junction inside the glass electrode tube during flow of the liquid being measured.

Of the various devices available for filling the glass electrode the two which have been found most satisfactory are illustrated by the sketch of Fig. 1. A three-way stopcock located at the top of the glass electrode may be employed in either of two ways, V_1 or V_2. By use of V_1 the electrode filled through the top may be kept full of liquid at all times. To eliminate all air bubbles from the electrode tube itself, from which expulsion is sometimes difficult, and rigorously to avoid atmospheric contamination, a preliminary flushing through the waste tube is necessary. By V_2 the glass electrode may be rinsed and filled either from the top by means of a siphon tube or from the bottom by means of suction. Either entrance may be reserved for the standard reference buffer, while the other is used for the solution of which the *p*H value is desired. Thus for a continuous record a solution may be passed through the siphon tube with an interruption of flow only for purposes of comparison with a standard buffer during which the rubber bulb or a second siphon tube may be utilized. As another alternative, the top entrance may be used for rinse water through the siphon tube, while all solutions to be measured are admitted at the bottom. By this scheme the electrode may be washed with distilled water by a turn of the stopcock and may be filled ready for a measurement by squeezing the bulb a few times. The rubber bulb may, however, be displaced by another siphon tube. For rigorous exclusion of atmospheric contamination the electrode must always be filled through a closed tube.

In supporting any glass electrode assembly it is important to insulate very carefully one side of the membrane. The outside of the membrane therefore was insulated by means of a Bakelite support which clamped the electrode at the top only (Fig. 1). The HCl–calomel cell C_1 was connected by a short lead directly to the highly insulated terminal of the vacuum tube potentiometer.

Measuring Technique

In making a measurement the procedure is essentially that of comparing the solution of unknown *p*H with a standard reference buffer by means of their respective potentials in the glass electrode. The simple mathematics described by Clark[14] and Britton[15] needs no discussion. The reference buffer was without exception 0.05 molar potassium acid phthalate, *p*H 3.97.

Solutions having a small buffering capacity (*e. g.*, 0.01 *M* disodium hydrogen phosphate) are very easily measured by almost any technique which might be suggested in connection with the glass electrode assembly described above. However, if the liquid or solution being measured (*e. g.*, potassium chloride solution) has little or no buffering capacity, the contamination occurring at the glass surface may change the e. m. f. and produce erroneous results. Even though the ordinary soft glass used for all electrodes in the present work is very much better than Corning 015 or other similar electrode glass as regards solubility, it is still not ideal.

The most obvious procedure for sensitive unbuffered solutions is to complete the measurement as quickly as the system could be expected to reach equilibrium under ordinary circumstances and disregard subsequent drifting. Since glass electrodes do not always reach their stable equilibrium potentials in the same length of time, the question of how soon to accept such a reading is difficult to answer. Readings should be repeated, however, until successive trials check each other. When this procedure is used with solutions of appreciable conductivity, fair results may be obtained—results which check within possibly a millivolt of those obtained by the improved technique to be described below.

Even if one is satisfied, however, to accept an e. m. f. reading which is in the initial stages of a steady drift, the method has further faults when applied to a liquid of relatively low conductivity like purified water.[16] After the glass electrode is flushed and filled with highly purified water,[16] the electromotive force shows various anomalous effects which indicate the generation and subsequent slow dissipation of electrical charges. The time required for apparent dissipation of the charges is variable, but in general the effects last for a sufficient time (a few minutes to half an hour) to vitiate the measurement. The trouble is very much less pronounced with water of less purity.

To satisfactorily overcome the alkaline effects due to the glass, the contents of the electrode should be continuously renewed by flow while the measurement is being made When very dilute solutions or purified water are measured, such flow may cause trouble with streaming potentials,[17] unless the liquid junction is established at the center of the glass electrode. By moving the liquid junction (tip of calomel cell C_2) to different positions within the glass electrode and the tube below it, the presence or absence of streaming potentials may be readily determined.

When the liquid junction is located at the center of the cylindrical membrane S (Fig. 1), it seems highly unlikely that any streaming potential of appreciable magnitude may be superimposed upon the measured electromotive force. This theoretical conclusion is supported by subsequent experimental evidence that the electromotive force is independent of the rate of flow when other factors are eliminated. As the liquid junction is moved downward below the membrane, streaming potentials increase rapidly (water charged positively with respect to the glass). Near the center of the cylindrical membrane, however, a small displacement of the potassium chloride junction causes little change in the measured electromotive force. Therefore the liquid junction need not be located with extreme accuracy; the central position as judged by the eye is entirely satisfactory.

With the Kerridge sucked-in-bulb type of electrode, unless it is of distorted and impractical proportions, the liquid junction cannot be located at a central position with regard to the active membrane. The best that may be

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(14) Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 1928.

(15) Britton, "Hydrogen Ions," D. Van Nostrand Co., Inc., New York, 1932.

(16) The term "purified water" is used to indicate the best product obtainable by the methods described by Ellis and Kiehl [THIS JOURNAL, **57**, 2145 (1935)].

(17) Michaelis, Chapter 26 of Alexander's "Colloid Chemistry," 1926.

done is to bring the junction to a point immediately under the thinnest portion of the membrane. It is therefore difficult if not impossible to eliminate small streaming potentials when the Kerridge electrode is used for measuring a liquid whose conductivity is unusually low (*e. g.*, highly purified water).

Typical Measurements

When electromotive force (or *p*H) is determined at different rates of flow, the results depend in general upon the type of solution. A number of typical examples of this are illustrated by Figs. 2 and 3. The data for the most part are given in graphical form only because the exact numbers are of little consequence to the present discussion. In Fig. 2, curve A illustrates the general behavior of highly purified water when it is measured in an electrode (C5) of the cylindrical type. The horizontal portion of the curve indicates the *p*H of the water. The fairly sudden break in the curve at a flow of about 25 cc./min. is typical of such systems, and the behavior is suggestive of a transition from streamline to turbulent flow. However, that such a transition did not occur was proved by several experiments in which a fine colored band of methylene blue was used. Turbulence did not commence until a flow of about 150 cc./min. was reached.

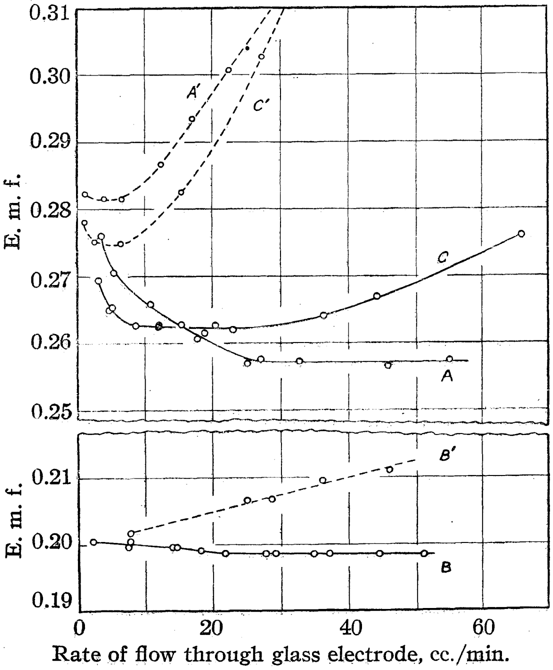

Fig. 2.—A and A', purified water measured in cylindrical electrode, C5; B and B', Columbia distilled water measured in C5; C and C', purified water measured in Kerridge electrode K10. Dashed curves indicate streaming potentials; data obtained by same method as for solid curves except that the potassium chloride junction was located 9 cm. below the bottom of the membrane.

Curve B of Fig. 2 represents the behavior of the stock distilled water^{18} in the same cylindrical electrode, C5. The pronounced difference between curves B and A illustrates a perfectly general behavior which is of considerable interest and importance. The stock distilled water, a high grade commercial distilled water, is practically unaffected at low rates of flow by alkali from the glass, whereas the highly purified water shows a large increase in *p*H value. The stock distilled water in comparison with the purified water is evidently buffered by minute traces of carbon dioxide and ammonia, evidence and confirmation for which appear in another paper.^{16}

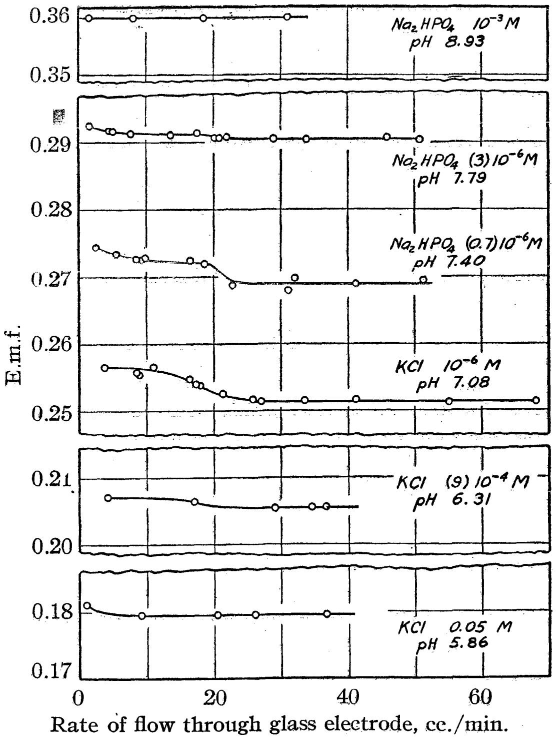

Fig. 3.

When an electrode made of Corning 015 glass was used for measuring the stock distilled water, the curve (not shown) was similar to A of Fig. 2 except for the horizontal portion which it lacked. If the flow was increased to 60 cc./min. the *p*H value was still decreasing but was nevertheless

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(18) "Stock distilled water" refers to the distilled product furnished in the Havemeyer Chemical Laboratories of Columbia University; specific conductivity in the neighborhood of 10^{-6} reciprocal ohms and *p*H from 6.1 to 6.5.

0.16 *p*H unit higher than that obtained by use of the ordinary soft glass electrode. By this experiment the stock distilled water was shown to be very sensitive to changes of *p*H value which were caused by the solubility of Corning 015 glass.

The dashed curves A′ and B′ of Fig. 2 were obtained in exactly the same way as A and B, except that the potassium chloride junction was moved down to a position about 9 cm. below the bottom part of the active membrane. The measured e. m. f. in this case included a streaming potential superimposed upon the same e. m. f. previously shown in A and B. The difference between the ordinates of A and A′ gives the streaming potentials for purified water; the difference between B and B′ gives the streaming potentials for the stock distilled water.

Curves C and C′ of Fig. 2 illustrate the use of a Kerridge type of electrode for the measurement of purified water. Its general characteristics are similar to those of the cylindrical electrode but its shape prevents centering of the potassium chloride junction and, consequently, there is definite evidence of streaming potentials at the higher rates of flow.

In Fig. 3 some typical curves are shown illustrating the measurement of dilute salt solutions. The solutions were very carefully prepared by distilling highly purified water[16] directly into "No-solvit" and Pyrex glass receivers, containing a weighed quantity of purified salt.

A very pure potassium chloride was further purified by three crystallizations from distilled water and dried at 100°. The disodium hydrogen phosphate, of very good quality, was crystallized four times and dried under vacuum at 30°. For the more dilute solutions a 2-liter quantity of water was used and the salts were weighed out by means of a micro-balance. Rigorous protection from acid or basic constituents of the atmosphere was maintained in all cases, just as was done with purified water itself.

The curves in the center of Fig. 3 for the most dilute solutions show the alkaline effect of the glass at the lower rates of flow, but their shape is different from that obtained when purified water was measured. The characteristic inflected form of the curves indicates that the buffering capacity of these extremely dilute solutions is less if they are relatively pure (flowing rapidly) than they are if contaminated by alkali from the glass. This is to be expected since it is a familiar fact that weak acids or bases show less resistance to *p*H change (smaller buffering capacity) if pure than if partially neutralized. The exact nature of the material dissolved from the glass and the detailed mechanism of the buffering reactions, are investigations beyond the scope of the present problem.

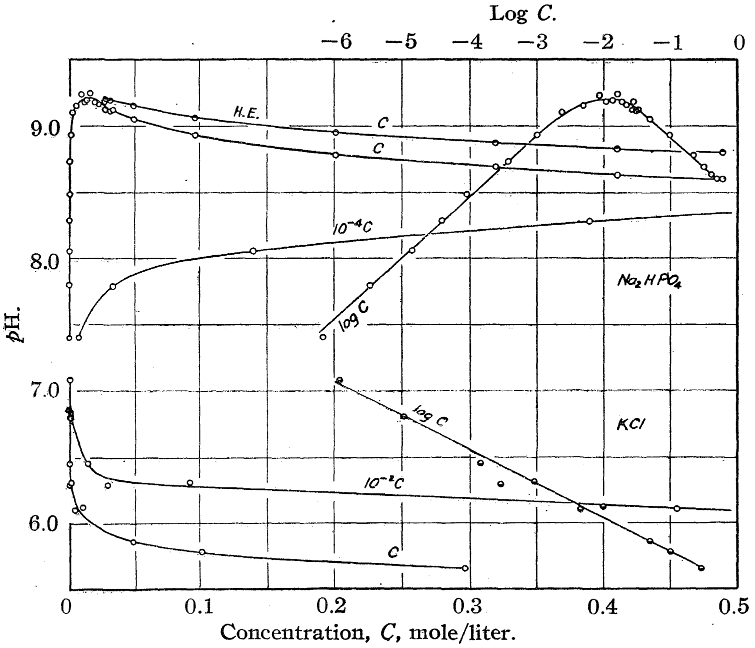

Fig. 4.

As the solutions of Fig. 3 are made more concentrated the alkaline effect from the glass rapidly becomes less pronounced, and the inflection of the curves disappears. It is quite evident from the experiments that even such a solution as potassium chloride has a definite, though very small, buffering capacity which increases with the concentration.

The *p*H values of the salt solutions, potassium chloride and disodium hydrogen phosphate, were measured over a wide range of concentrations, extending from millionth molar to half molar. The results listed by Tables I and II are shown graphically by Fig. 4, where *p*H is plotted against concentration (C) and also against log C. In the curves marked 10^{-4} C and 10^{-2} C the abscissas should be multiplied by 10^{-4} or 10^{-2}, respectively, in order to obtain the correct scale. These two curves afford a magnified view of the extremely dilute region and include only the first few points which on the normal scale of abscissas (C curves) appear as vertical lines.

TABLE I

THE *p*H OF DISODIUM HYDROGEN PHOSPHATE SOLUTIONS[a]

Solution	$C\ 10^3$	Room temp., °C.	ΔE	*p*H	*p*H by hydrogen electrode
1	0.00070	29	0.2056	7.40	
2	.0033	28	.2282	7.79	
3	.014	28	.2440	8.05	
4	.039	30	.2587	8.28	
5	.0895	28.5	.2696	8.48	
6	.366	30	.2863	8.73	
7	1.016	28.5	.2966	8.93	
8	2.40	28	.3062	9.10	
9	4.93	30	.3111	9.15	
10	8.85	27.5	.3138	9.23	
11	11.02	30	.3130	9.18	
12	13.08	29.5	.3135	9.19	
13	15.76	27.5	.3144	9.24	
14	18.80	29.5	.3125	9.18	
15	22.07	29	.3113	9.16	
16	26.96	28.5	.3082	9.12	9.20
17	27.32	27.5	.3104	9.18	
18	31.55	28.5	.3074	9.11	9.19
19	33.53	29	.3088	9.12	
20	49.07	28.5	.3041	9.05	9.15
21	97.33	28.5	.2969	8.93	9.06
22	201	28.5	.2881	8.78	8.95
23	319	28.5	.2826	8.69	8.87
24	410	28.5	.2793	8.63	8.83
25	489	28.5	.2769	8.60	8.80

[a] ΔE represents the potential difference as determined by the glass electrode, between the solution being measured and the standard phthalate buffer, *p*H 3.97. C represents the molar concentration of the salt solutions.

TABLE II

THE *p*H OF POTASSIUM CHLORIDE SOLUTIONS[a]

Solution	$C\ 10^3$	Room temp., °C.	ΔE	*p*H
1	0.00122	25.5	0.1847	7.08
2	.0105	25	.1672	6.80
3	.144	30.5	.1490	6.45
4	.288	25.5	.1376	6.29
5	.932	25.5	.1387	6.31
6	4.55	27.5	.1269	6.10
7	9.98	27.5	.1285	6.12
8	48.6	27.5	.1128	5.86
9	102	27.5	.1078	5.78
10	296	27	.0998	5.65

The upper curve for disodium hydrogen phosphate marked H. E. (Fig. 4) shows some measurements made in the more concentrated region by means of the hydrogen electrode. The discrepancy between the hydrogen and the glass electrode measurements is about what should be expected on the basis of the investigations of MacInnes and Belcher.[19] As the phosphate solutions are made more dilute, however, the discrepancy rapidly decreases. The agreement would probably be very close in the dilute region, which is most difficult for application of the hydrogen electrode. Calibration of the glass electrode against the hydrogen electrode in various buffers indicated that there was no significant difference at *p*H values less than 8 (extreme acid range not included).

The definitely acidic character of the purified potassium chloride merits notice. If this behavior could be substantiated with samples of the salt purified with extreme precaution, it would be of considerable interest. Perhaps of even greater interest is the shape of the disodium hydrogen phosphate curve, reported by Kiehl and Loucks,[20] with a maximum *p*H at a concentration of approximately 0.015 molar. The straight line character of the respective logarithmic curves, with two branches for the disodium hydrogen phosphate is of singular interest.

The curves of Fig. 4 are presented for the purpose of illustrating the practical possibility of making consistent *p*H measurements in extremely dilute weakly buffered systems. The consistency of the measurements over the entire range of concentration is best demonstrated by the logarithmic curves.

The data of Fig. 4 support the other data of this investigation in proving beyond question that the glass electrode offers important opportunities for research in unbuffered systems.

The authors take this opportunity of expressing their appreciation to Professor John R. Dunning of the Physics Department, for his many helpful suggestions and advice during the development of the electrical measuring circuit.

Summary

The practical measurement of *p*H in the most difficult of unbuffered aqueous systems has been accomplished by means of the glass electrode. General technique has been developed, and some examples are given.

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(19) MacInnes and Belcher, THIS JOURNAL, **53**, 3315 (1931); *Ind. Eng. Chem., Anal. Ed.*, **5**, 199 (1933).

(20) Kiehl and Loucks, *Trans. Am. Electrochem. Soc.*, **67**, 81 (1934).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Purification of Water and its pH Value

BY SAMUEL B. ELLIS AND SAMUEL J. KIEHL

A series of experiments relative to purification of water and the determination of its pH value by the glass electrode[1] is described in this article.

The Still.—The still (Fig. 1) was designed to incorporate the principles both of Bourdillon[2] and of Weiland.[3] In the still of Bourdillon purified air is passed upward through a long condenser tube, countercurrent to the condensing water. In Weiland's still purified air is passed through the hot boiler before the actual distillation is started. Thus the combination of Weiland's method with that of Bourdillon allows volatile impurities to be partly or largely driven from the boiler before or during distillation while the remainder is removed as far as possible in the condenser tube.

The condenser, including joints, was made entirely of block tin. The tapered delivery tip and the small side tube near it were cast, machined to the required dimensions, and sealed to the main condenser tube. Two water jackets of brass were joined to the condenser tube by means of solder. The top water jacket was constructed so that cold water could enter at the top and provide more efficient condensation while the one at the bottom served to control the temperature of the dsitillate. The boiler, a round-bottomed Pyrex flask of 12-liter capacity, with long ring neck ground flat on top, was joined to the machined surface of the condenser by clamps. Heat was supplied by a gas hot-plate.

The neck of the flask, inclined and filled with glass beads, served as a very efficient spray arrester. The angle of inclination left most of the cross-section fairly dry and open for the free passage of steam and air. By this method the elimination of all spray, an absolute necessity in work of this type, was accomplished satisfactorily.

The glass tube through the top of the boiler was used for three purposes: (1) for filling the boiler *in situ;* (2) for eliminating volatile impurities with purified air; (3) for the prevention of bumping. As all three purposes are important, combined they make this tube indispensable.

Purification of Air.—The air was passed through the following train: (1) a capillary flow-meter; (2) four gas washing bottles (5 cm. × 18 cm.) half full of glass beads, the first three of which contained, respectively, sulfuric acid about 6–10 normal, sulfuric acid about 1 normal, sodium hydroxide about 6–10 normal, the final bottle being used to catch spray; (3) a series of five towers (3.5 × 29 cm.) each containing soda-lime, 8–14 mesh, 15% moisture; (4) a final tower (3.5 cm. × 29 cm.) containing a filter of tightly packed glass wool and cotton.

From this purification train the air passed directly to the still through glass tubing, connected by short lengths of extra heavy-walled rubber tubing. The rubber tubing and stoppers were steamed for half an hour and impregnated with castor oil *in vacuo* at 60 to 90°.

Receiving Vessels.—Walker and Smither[4] in a study of the characteristics of various glasses, concluded that Pyrex and Libbey varieties are about equally insoluble in water, and that in this respect they both excel "Non-sol," Jena, and all the other resistance glasses studied. Pyrex has been very popular as a container for very pure water.[5]

Other materials (*e. g.*, quartz, platinum, silver, and tin) have been used occasionally as containers, but there has been no definite comparison with glass.

In these experiments three different kinds of receiving vessels were used: (1) Pyrex Erlenmeyer flasks of 500-cc. capacity with Pyrex siphons; (2) "No-solvit" bottles of 2-liter capacity with Pyrex siphons; (3) silver flasks of 1-liter capacity with silver siphons.

In general, if the container is suitable, the pH value of the purified water will not change on standing, or will change very slowly. Also, if the pH values of water collected in containers of different material agree, this confirms the conclusion that none of them contaminate the water appreciably. By both of the above criteria, the three materials used were found reasonably satisfactory. Further refinement of the experiments would justify investigation of other materials. Tin especially, should be used since the condenser itself is made of tin.

Preliminary cleaning of all vessels was accomplished by scrubbing with soap solution, rinsing thoroughly, and steaming for an hour. Siphon tubes were similarly treated. This method of cleansing was found to be more satisfactory than the other well known methods.

Collecting a Sample.—The sample was collected and kept in a purified atmosphere at all times. To accomplish this, the receiver was closed with an impregnated rubber stopper through which the delivery tip of the condenser extended (Fig. 1), so as to avoid contact of water with the rubber. Purified air passed through the siphon tube into the receiver at a rate of 20–25 liters per hour and thence up through the condenser tube by way of the by-pass and stopcock V instead of the delivery tip of small bore, 2.5 mm. On account of the small bore of the tip and the continually renewed water held therein, atmospheric contamination of the lower condenser was prevented during times that the receiver was disconnected. A very slow distillation was sufficient to keep fresh relatively pure water at the bottom of the tip.

Before the receiver was connected to the condenser, it was flushed with purified air for a period of time. For this purpose, the hose was connected at both i and o; the unoccupied hole in the stopper, ultimately occupied by the delivery tip, was closed with a glass plug; and the

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[1] Ellis and Kiehl, THIS JOURNAL, **57**, 2139 (1935).

[2] Bourdillon, *J. Chem. Soc.*, **103**, 791 (1913); Bourdillon's still was later modified by: Clevenger, *J. Ind. Eng. Chem.*, **11**, 964 (1919); Bennett and Dickson, *Science*, **50**, 397 (1919); Bengough, Stuart and Lee, *J. Chem. Soc.*, 2156 (1927).

[3] Weiland, THIS JOURNAL, **40**, 131 (1918).

[4] Walker and Smither, *Technol. Papers Bur. Standards*, No. 107 (1918).

[5] Acree and Fawcett, *Ind. Eng. Chem., Anal. Ed.*, **2**, 78 (1930); Kolthoff and Kameda, THIS JOURNAL, **53**, 825 (1931).

three-way stopcock, V, was turned so as to discharge directly into the atmosphere instead of through the condenser. After thus flushing the receiver, stopcock V was turned so as to pass the purified air stream through the condenser again. After ten minutes longer the glass plug was removed, and the receiver quickly attached.

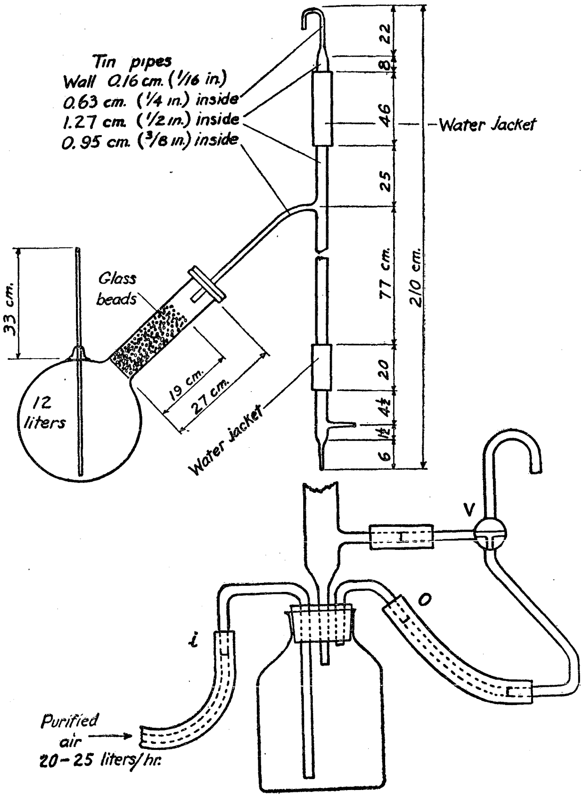

Fig. 1.

During and after disconnecting the receiver the air, uninterrupted, was forced through the hole previously occupied by the delivery tip. A three-way T-bore stopcock was then inserted and closed after the expulsion of the impure air. The hose connection at o was then broken and the glass tube tightly stoppered with a small impregnated rubber stopper or a paraffined cork. Hose connection i on the siphon tube was finally broken. The sample of purified water was then ready for use. A pressure of purified air through the three-way stopcock was used to obtain a portion of the sample through the siphon tube. The impure air was expelled from the stopcock through its side-tube, before the pure air passed into the receiver. The siphon tube in all experiments was attached directly to the top of the glass electrode.

Preliminary Experiments.—The once distilled water furnished to the chemical laboratories of Columbia University was always used for filling the boiler. This water which will be conveniently referred to as the stock distilled water, had a specific conductivity of roughly 10^{-6} reciprocal ohms, and a *p*H value of 6.1 to 6.5. Upon standing in the open, the *p*H soon dropped to approximately 5.8. A carefully conducted Nessler test on this water indicated that ammonia was present to approximately 0.004 part per million. Ammonia-free water prepared by distillation from phosphoric acid was used for comparison and for making all test solutions and standards of reference. "Aeration" of the stock distilled water by purified air caused its *p*H value to change in general from 6.3 to beyond 8.0. Continued aeration then caused this value to drop very slowly. The water contained both carbon dioxide and ammonia. Carbon dioxide is easily eliminated by aeration. Ammonia is removed very slowly. Table I illustrates the type of data which were obtained.

Table I

Aeration of Columbia Distilled Water

Hours aerated	0	6	8	9.5	12	19.5	21
*p*H	6.3	8.05	8.13	8.18	8.22	8.17	8.13

Thirty to forty per cent. of the stock distilled water had to be distilled before a Nessler test of the distillate became negative or uncertain. The first fractions from the Bourdillon–Weiland apparatus always contained ammonia (0.1–0.2 part per million) and had a high *p*H (8.5 or more). Therefore from these experiments it appears that the Bourdillon still is capable of eliminating carbon dioxide but not ammonia.

Aeration of various fractions (32 in all) obtained from the Bourdillon–Weiland still, confirmed in a very conclusive way the general picture already described. The first fractions, those of *p*H higher than about 7.5, gave without exception a drop in *p*H when aerated. The later fractions of lower *p*H value showed very little change during prolonged aeration. Those samples with a *p*H value of 7.2 or less had a tendency slowly to become more alkaline, but seldom greater than 0.1 *p*H unit in twenty-four hours.

The *p*H values of water samples such as the above which are freed of volatile impurities may change during aeration because of contamination from containing vessels or the air stream, or because of an imperfectly closed container. The fact that very little change was actually observed over periods as long as forty-eight hours indicated that these combined effects were very small.

Purification of Water

The best method of procedure for preparing water of high purity is indicated by the data of Table II, shown graphically in Fig. 2.

When the stock distilled water was used in the boiler either alone (curve A) or with sodium hydroxide (curve B), the *p*H value of the first distillate was high (presence of ammonia). As distillation proceeded the *p*H value dropping finally tended to become constant at a value slightly higher than 7. Constancy was approached only after 50% of the charge in the boiler had been distilled. Even then there was probably a tendency to change as distillation proceeded. The *p*H value of the last fraction tended, in general, to be slightly higher than that of water distilled from phosphoric acid, which, as will be seen from curve

TABLE II (*cf.* FIG. 2)

COMPLETE DISTILLATIONS WITH VARIOUS REAGENTS IN BOILER

A. Stock Distilled Water

% distilled	6–10	20–25	44–49	58–64	69–85
*p*H	8.62	8.02	7.26	7.19	7.12

B. Sodium Hydroxide, about 0.025 molar

% distilled	1–5	6–13	13–18	20–39	41–49	51–57
*p*H	8.96	8.76	8.44	7.64	7.19	7.07
% distilled	58–64	64–70	70–76	77–84	85–92	
*p*H	7.19	7.21	7.11	7.26	7.29	

C. Nessler Reagent, 25 cc. per liter of water

% distilled	5–10	19–24	44–58	62–81
*p*H	8.31	7.31	6.80	6.52

D. Stock Distilled Water Following Nessler Reagent

% distilled	0–5	9–14	17–22	27–47	55–60	69–74
*p*H	8.24	7.54	7.05	6.30	6.58	6.59
% distilled	76–81	82–87				
*p*H	6.81	6.69				

E. Phosphoric Acid, about 0.025 molar

% distilled	4–10	10–14	16–21	22–33	34–39	40–44
*p*H	7.09	7.09	6.99	7.06	7.02	7.12
% distilled	45–50	51–64	65–73	73–78	78–86	
*p*H	6.98	7.00	7.02	7.15	6.94	

E, was constant throughout the distillation. It seems perfectly logical on this basis to conclude that the samples distilled from alkali or from water alone were never entirely freed of ammonia.

Confirmation of this conclusion is afforded by a study of the curves shown in Fig. 3 for the different fractions distilled from alkali. E. m. f., or apparent *p*H, is plotted against rate of flow through the glass electrode.[1] The first fraction distilled contained sufficient ammonia (easily verified by a Nessler test) to make the solution definitely alkaline and to render its measurement in a glass electrode very easy—curve A of Fig. 3. The second fraction gave a curve (not shown) very similar to A with the horizontal part not quite so perfect at lower rates of flow. The third fraction, curve B of Fig. 3, began to show a slight somewhat doubtful inflection, and a definite indication that the glass was contaminating the water at lower rates of flow. The fourth fraction gave a typical inflected curve C, with a considerable alkaline effect from the glass at lower rates of flow. Curve C remained more or less representative of all subsequent fractions—the last of which was taken when 92% of the water in the boiler had been distilled. A comparison of the curves of Fig. 3 with the types described in the previous paper[1] demonstrates their similarity to those obtained with contaminated water (*e. g.*, millionth molar KCl or Na_2HPO_4). None of them have the same shape as that for highly purified water distilled from phosphoric acid. Hence, this evidence contributes further to the conclusion that ammonia was not entirely eliminated at any time during the distillation of neutral or alkaline water.

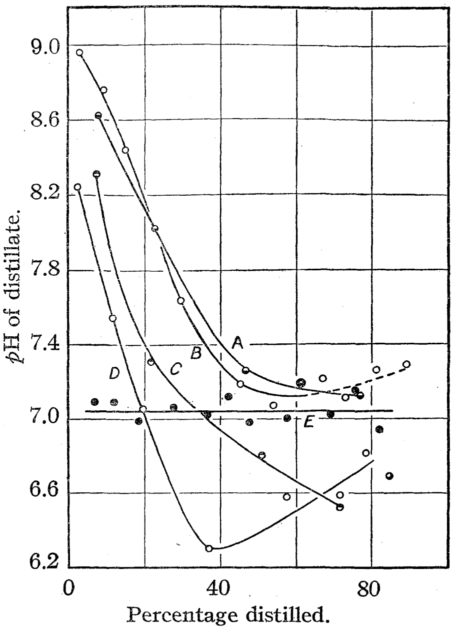

Fig. 2.—Distillations with various reagents in boiler (*cf.* Table III).

Any non-volatile reagent, which added to the boiler could hold or destroy both carbon dioxide and ammonia, would obviously be a valuable aid in purifying water. For this purpose Kendall,[6] and Fales and Nelson[7] have used Nessler reagent. Some data for Nessler reagent are plotted in curve C of Fig. 2. That it failed to hold ammonia was demonstrated not only by the high initial *p*H values, but also by direct Nessler tests for ammonia which were made on the distillate. Furthermore, as distillation proceeded, the *p*H of the supposedly purified water continued to drop. The most reasonable explanation for this anomalous gain of acidity seems to be that a small amount of iodine set free from the Nessler reagent was carried over with the current of air and steam.

After the distillation from the Nessler reagent, the boiler was disconnected from the condenser and cleaned by thorough rinsing with distilled water (a dozen or more separate rinsings). Stock distilled water was then added and a distillation completed as shown by curve D of Fig. 2. Ammonia came over with the first fractions as usual,

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[6] Kendall, THIS JOURNAL, **38**, 2460 (1916).

[7] Fales and Nelson, *ibid.*, **37**, 2782 (1915).

but the *p*H of the distillate continued to drop to a minimum value of 6.3, after which it rose again to about 6.8. From this behavior it would seem reasonable, as a speculation, that sufficient iodine had accumulated in the condenser from the previous distillation to contaminate the water for a considerable time afterward. In any event the experiments (C and D of Fig. 2) leave no doubt concerning the utter futility of attempting to use Nessler solution in the boiler. In consequence of the experiments with Nessler reagent it was necessary to cleanse the system thoroughly. To accomplish this the still was operated for a whole day with the cooling water off part of the time.

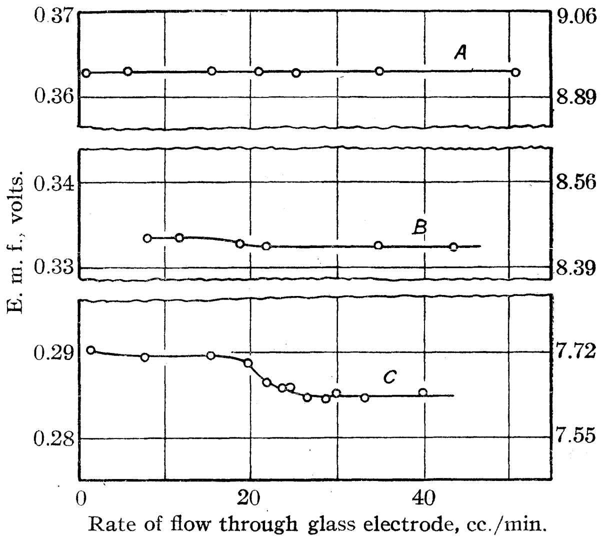

Fig. 3.—Samples of water distilled from NaOH (Table III) and measured with cylindrical glass electrode C5: A, first fraction collected, boiler emptied 1–5%; B, third fraction, boiler emptied 13–18%; C, fourth fraction, boiler emptied 20–39%.

The horizontal line E of Fig. 2, representing a distillation from phosphoric acid, shows that the acid retained all ammonia in the boiler, and that the modified Bourdillon still was capable of eliminating the carbon dioxide. The first fraction distilled had the same *p*H as the later fractions, and upon the rough basis of streaming potentials measured in the glass electrode,[1] they had about the same low conductivity. During the entire course of the distillation, samples of high purity could be collected. The superiority of such a distillation over the others is strikingly emphasized by the curves.

To eliminate volatile matter, the phosphoric acid was carefully heated for twenty minutes with the evolution of white fumes. Phosphorus pentoxide used without preliminary treatment was satisfactory.

Potassium permanganate both in acid and alkaline solution has been very commonly used in boilers for the purification of water. When permanganate was added to the boiler in the presence of alkali, curve B of Fig. 2 remained essentially unchanged; in other words ammonia was not thus eliminated by oxidation. When permanganate was used in the presence of acid, it likewise served no useful purpose; the acid held the ammonia in any case. The situation as regards the use of permanganate may be different if the boiler water contains appreciable quantities of organic or other oxidizable impurity. No such water has, however, been used in this research.

The *p*H of Purified Water

A series of measurements, summarized by Table III, was undertaken for the purpose of estimating as accurately as possible by the technique previously described the *p*H of purified water. During a series of four complete distillations at the rate of 800 cc. per hour from phosphoric acid (20 g. of P_2O_5 in the boiler) samples were collected in Pyrex, "No-solvit" and silver containers. The lower water jacket on the condenser was used to control the temperature of the condensate and keep it as nearly as possible that of the room. Hence the *p*H values could be measured immediately. Although more samples were collected in silver than in glass, the data for silver, nevertheless, cover exactly the same series of distillations as are covered by the two kinds of glass. Therefore, differences between the various containers cannot be due to differences between successive distillations. The four distillations themselves showed no significant difference of any kind.

A single glass electrode of cylindrical shape[1] made of ordinary soft (soda-lime) glass was used for all the measurements of Table III. Potassium acid phthalate (0.05 molar, *p*H 3.97) was employed as the reference buffer, and the difference of potential (ΔE) between it and the water is listed in the second column of the table. The buffer and the glass electrode were both checked by means of the hydrogen and quinhydrone electrodes. All measurements were made with the purified water flowing through the glass electrode[1] and each value listed in the table is the

TABLE III

THE pH OF PURIFIED WATER

Room temp., °C.	ΔE[a]	pH	Room temp., °C.	ΔE[a]	pH
			Pyrex containers		
28.5	0.1854	7.07	28.5	0.1900	7.15
27.5	.1880	7.12	26.0	.1858	7.10
28.5	.1870	7.09	25.0	.1880	7.15
31.0	.1889	7.10			
			"No-solvit" containers		
28.5	.1826	7.04	31.0	0.1864	7.06
27.0	.1861	7.09	29.5	.1822	7.00
26.0	.1880	7.14			
			Silver containers		
28.0	.1818	7.01	28.5	0.1774	6.94
28.5	.1774	6.94	24.5	.1825	7.06
28.0	.1824	7.02	25.5	.1835	7.07
27.0	.1817	7.02	26.5	.1730	6.88
27.0	.1797	6.99	25.5	.1816	7.03
27.5	.1864	7.09	27.5	.1770	6.94
29.0	.1810	6.99	27.5	.1861	7.09
31.5	.1846	7.02	24.5	.1771	6.97
30.5	.1815	6.98	25.5	.1840	7.08
29.0	.1828	7.02			

[a] ΔE represents the potential difference as determined by the glass electrode, between water and the standard phthalate buffer pH 3.97.

MEAN VALUES

Containers	Average temp., °C.	Average, pH	Average deviation from mean pH
Pyrex	27.9	7.11	0.024
"No-solvit"	28.4	7.07	.039
Pyrex and "No-solvit" comb.	28.0	7.09	.034
Silver	27.4	7.01	.045

mean of two or three (sometimes more) readings taken at different rates of flow. Obviously only rates of flow on the straight horizontal part of the e. m. f.–flow curve were used.

The significant difference between measurements made in silver and those made in glass (Table III) indicates that the glass contributes a very small alkalinity to the water. Whether or not the silver likewise contributes alkalinity is left in doubt. However, the results of experiments previously described in which samples of water were kept for comparatively long periods in the various containers would indicate that if any such effect is present it must be very slight.

The most probable pH value of water to be deduced from the data of Table III is undoubtedly the mean of the silver series, namely, 7.01 at approximately 27.5°. The precision of this figure is about 0.01 pH unit, measured in terms of the so-called "average deviation of the mean," commonly abbreviated A. D. The fluctuations of temperature as they ordinarily occur in a room could account for a greater pH change than this, but it is probable that successive series of nineteen measurements would give averages that were consistent within the meaning of this precision.

The value for the pH of water here obtained is in substantial agreement with accepted figures and with the best previous direct measurements.[4,5,8,9] The present measurements, however, are unique in that they represent a direct determination made upon a highly purified water to which no foreign material of any kind had been added, neither "isohydric" indicator nor gaseous hydrogen with platinum black.

Summary

1. Methods for the purification of water have been investigated and important information concerning this general problem has been obtained.

2. The pH value of the purest water, collected in silver vessels, has been measured directly by means of the glass electrode and found to be 7.01 at 27.5°.

NEW YORK CITY RECEIVED MAY 29, 1935

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(8) Beans and Oakes, THIS JOURNAL, **42**, 2116 (1920).

(9) Kling and Lassieur, *Ann. chim.*, **15**, 201 (1931).

[CONTRIBUTION FROM THE LABORATORY OF THE CORNING GLASS WORKS]

Extraction and Analysis of Gases from Glass[1]

BY R. H. DALTON

Introduction

In the course of a study of gases in glass there arose the problem of working out an apparatus for extracting and quantitatively analyzing the gases from molten glass. A fairly successful system has been developed and thoroughly tested in use. Since the procedures differ considerably from any previously described and involve some points of general interest in high temperature technique it was thought worth while to publish a brief description of them. To illustrate the behavior of the apparatus it was also decided to include the results of some test analyses and of some determinations on typical glasses that are of general interest.

Various other investigators have studied the gases in glass, but most of them have confined their observations to temperatures below the softening point. At these lower temperatures the quantity and nature of the gas is different, as is also the procedure necessary for extraction, so it is beyond the scope of this paper to discuss these investigations. The earliest work at high temperatures was that of E. S. Shepard mentioned in an article by Allen and Zies.[2] This was followed by the more extensive work of Washburn, Footitt and Bunting.[3] Both of these investigations failed to provide for the detection and estimation of water vapor, which is almost always an important constituent of gases coming from glass. A more complete investigation has been reported by Salmang and Becker.[4] The results of the present work are in general agreement with theirs, although the analytical and extraction methods differ considerably in the two cases.

Some earlier experiments by the author[5] indicated that water, carbon dioxide, sulfur dioxide and oxygen were the principal gases to be expected. It was also apparent that it would be an advantage from the viewpoint of extraction to keep the size of the glass samples down to a gram or so. This meant dealing with gas samples averaging around 0.5 cc. in volume but falling as low as 0.01 cc. in special cases.

The apparatus divides itself naturally into two parts, the extraction apparatus and the analytical apparatus. The extraction is carried out by melting the glass in vacuum and pumping off the gases. The analysis is carried out at low pressure using physical methods of separation where possible.

Extraction Apparatus

The general problem in the extraction process is that of designing an apparatus which will be gas tight at 1400° in vacuum and which can be baked out so that it will not itself give off appreciable quantities of gas. Sillimanite has been found to be the material most nearly fulfilling these conditions.

Figure 1 shows a cross section of the apparatus. The outgassing takes place in the sillimanite (Champion 6060) tube (F). Fortunately this can be sealed directly to "Pyrex" brand chemical glass of which the whole apparatus is constructed, thus making it possible to eliminate all wax and greased joints. This porcelain to glass seal is easily made in diameters up to 1.3 cm. and is quite useful for vacuum technique at high temperatures. Sillimanite tubes up to 1.3 cm. diameter and 1.6 mm. wall will stand a full atmosphere at 1450° without appreciable collapse. A new tube is used in each determination.

The heating is done by means of a winding of 75 mil tantalum wire embedded in alundum. Tantalum has been found superior to molybdenum as its oxide is not volatile and the wire is more easily bent into form (when new). The heater (H) is surrounded by two concentric cylindrical shields (C_1) and (C_2) of tantalum or molybdenum to act as radiation reflectors. To protect the metals from oxidation the whole furnace system is enclosed in an evacuated glass tube (D). This serves the additional purpose of eliminating any possibility of gases getting into (F) and of cutting down heat loss from the furnace. The tube (D) has its own vacuum pump and there is no connection with the main vacuum system. The ground glass joint (J) is sealed with wax and the whole tube is surrounded by a water jacket (not shown). A sample tube (G) with magnetic plunger furnishes a means of introducing the sample which is in the form of short lengths of rod. This is done after the apparatus has been evacuated and baked out. The bake out is continued until tests show that the gas evolved is negligible compared to that expected from the glass. This normally requires about a thirty-minute

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(1) Presented at the New York Meeting of the American Chemical Society, April 22, 1935.

(2) E. T. Allen and E. G. Zies, *J. Am. Ceram. Soc.*, **1**, 739 (1918).

(3) Washburn, Footitt and Bunting, Univ. of Ill. Eng. Expt. Sta. Bull. 118 (1920).

(4) H. Salmang and A. Becker, *Glastech. Ber.*, **5**, 520 (1928); **6**, 625 (1929); **7**, 241 (1930).

(5) R. H. Dalton, *J. Am. Ceramic Soc.*, **16**, 425 (1933).

treatment at 50° above the temperature at which the glass is to be outgassed. The temperature is measured through the window (W) by means of an optical pyrometer and any temperature up to the melting point of sillimanite can be attained. The glass samples are usually outgassed at 1400°, however. The tube (L) leads to the pumps and the analytical apparatus. The pumping system consists of a two stage mercury vapor pump backed by an oil pump.

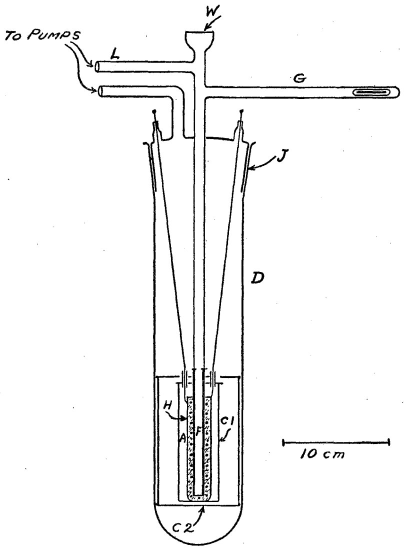

Fig. 1.—Outgassing furnace.

There is one serious source of error in this method of extraction which we have found no way to eliminate entirely. This error is due to the volatilization of oxides such as Na_2O, B_2O_3, etc., which condense in the tubing just above the furnace and reabsorb part of the gases before they reach the analytical apparatus. In view of this, coupled with the fact that the work is in a fairly new field where it is of greater interest to obtain approximate results on a number of glasses than very accurate results on a few, no attempt has been made to push the accuracy of the analytical part of the apparatus to the limit.

Analytical Apparatus

The analytical apparatus must provide means of pumping the gases from the furnace and of analyzing for water, carbon dioxide, sulfur dioxide and oxygen. It was desired also to provide for hydrogen and carbon monoxide in case these should be present. Nitrogen plus other inert, non-condensable gases could be determined together as a residue. The fact that the gas samples come from glass at 1400° simplifies the problem in that oxidizing and reducing gases cannot come off together. The procedure consists in general of freezing out the water, sulfur dioxide and carbon dioxide in the order named, then removing oxygen by hot copper and finally oxidizing carbon monoxide and hydrogen with copper oxide.

A brief mention will be made of an early form of the apparatus as it worked fairly well and had a great advantage in simplicity. This apparatus is shown diagrammatically in Fig. 2. The gas evolved from the molten sample enters the system through the special stopcock (S_1) which is in position to connect 1 and 2 and close off 3. The gases then pass through the trap (T) where water is frozen out by cooling with solid carbon dioxide and thence into the bulb (B). From here the gas can be pumped into the space between (S_1) and (S_2) by raising the mercury from the reservoir (R_2). In this way the bulb (B) acts as a form of Toepler pump, withdrawing the gas from the furnace and transferring it to the small volume above (S_2). The water that has been collected in (T) is determined by confining it between the points (AA) and measuring the pressure that develops when the trap and connecting tubes are completely immersed in boiling water. The volume between (AA) is accurately known and is such that the water vapor is always well below the saturation pressure at the temperature of the surrounding bath. The total volume of gas other than water is measured by letting the gas expand back into B, and measuring the pressure at one of the points of known volume (V_0–V_5). This measurement is in error, of course, by the ratio of the volume (S_1–S_2) to the total volume above (P), but this error can be made smaller than that from other sources.

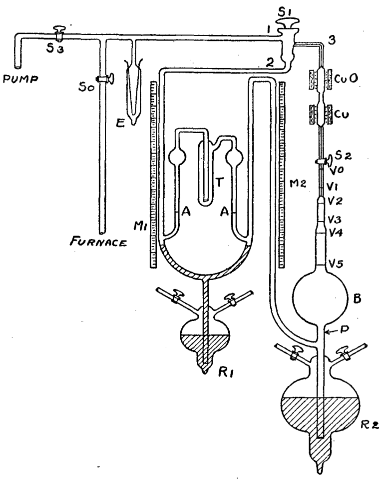

Fig. 2.—Analytical apparatus.

To determine the other gases the sample is recirculated through appropriate refrigerants and reagents as will be described in detail later in connection with final form of the apparatus.

This simple apparatus worked quite satisfactorily in most respects but in order to eliminate occasional trouble with leaking and plugging at the stopcock (S_2) it was decided to go over to a system in which there were no stopcocks. This would have the additional advantage of avoiding any contamination by vapors of stopcock grease. The method of determining water was simplified at the same time and the error due to the volume (S_1–S_2) was eliminated. The final form of the apparatus is shown in Fig. 3. In order to show things clearly the small parts have been drawn to a magnified scale so no indication of relative size is given by the diagram. Also the whole thing has been compressed vertically to save space.

The apparatus is best understood by tracing through the procedure, which is as follows. After the reading of the Pirani gage (E) indicates that a good vacuum has been obtained the mercury is raised in (H_1) and (H_3), thus cutting off the pumps and the reagent tubes. The glass sample is then added to the extraction furnace and the Toepler pump (B_1) is operated thus drawing the gas from the furnace through the trap (T) and compressing it into the gas buret (G) where the volume can be measured. The water vapor is removed from the gas as it passes through (T) which is cooled with solid carbon dioxide. When the major part of the gas has been extracted, which takes usually around half an hour, the furnace is closed off at (H_2) and the water is allowed to vaporize, filling the space between (H_1), (H_2), (H_3) and the trap in the capillary leading to (G). The volume of this space is known, and from the pressure reading on the Pirani gage which has been calibrated for water vapor, the quantity of water can be determined. The electrical circuit is that suggested by Campbell[6] in which the gage is in one arm of a Wheatstone bridge, the three other resistances of which have fixed values such that the bridge balances when the filament is around 100°. The bridge voltage necessary to obtain a balance is a measure of the gas pressure in (E).

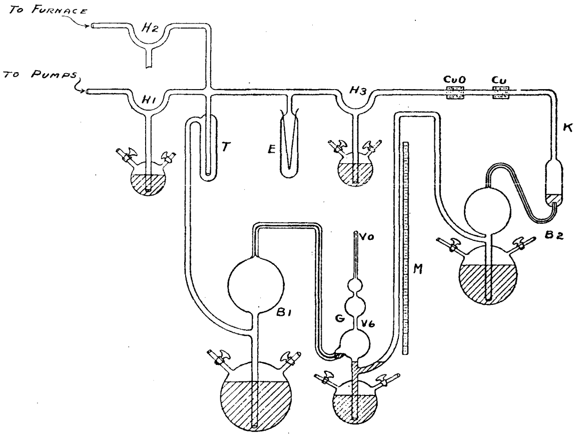

Fig. 3.—Analytical apparatus.

Using a gage with a filament of 28 cm. of 2 mil platinum wire, the voltage reading ran from 1 volt in vacuum to about 9 volts with a pressure of 4.59 mm. of water vapor. The voltmeter reading could be made to 0.01 volt. This method of determining water vapor has proved fairly satisfactory and is much easier and quicker than that described before. It has a disadvantage, however, in that there is sometimes a gradual drift in the gage reading, probably due to changes in the adsorbed gases on the filament surface. In this case it is necessary to wait until a steady value is reached before making the reading. The gage is immersed in a water-bath (not shown) maintained at an approximately constant temperature. After being determined, the water is removed from the apparatus by opening (H_1) to the pumps.

Sulfur dioxide is determined next by cooling (T) to −140° with a special bath and pumping the gas around with the Toepler pumps (B_2) and (B_1). The cut-off (H_1) is, of course, closed and (H_3) open. The cooling bath consists of petroleum ether in a heavy copper tube, the lower end of which terminates in a copper rod dipping in liquid air. The tube is wound around with a resistance heater. By properly balancing the cooling effect of the liquid air and heating effect of the current it is possible to hold the temperature of the bath within two or three degrees, which is close enough for our purpose. Temperature is measured with a small thermocouple immersed in the ether. The decrease of pressure in (G) when all the gas has been returned gives the sulfur dioxide content. If the Pirani gage were calibrated for this gas, it could also be determined in the same way as water.

For carbon dioxide the gases are circulated again as above except that the trap is cooled in liquid air. To be sure of the nature of the gas frozen out, the vapor pressure may be followed as the trap is allowed to warm up gradually. The vapor pressure of a gas is a fairly characteristic property and in a case like the present where only a few gases can conceivably be present it serves as a satisfactory identification.

Oxygen is determined by heating the tube containing metallic copper to around 350 or 400° and recirculating the gases. Before the gases are admitted, the reagent tube is given a good bake-out while open to the pumps. This is necessary to avoid errors due to gases given off by the hot glass or by the copper itself. As an additional precaution (T) may be immersed in liquid air, as most of the evolved gas is removed at that temperature. If only a small quantity of oxygen is expected the gas can be compressed over the reagents by closing (H_3) and filling the trap and tube (K) with mercury from (B_2). This accelerates the reaction.

For the measurement of carbon monoxide and hydrogen the gases are circulated over hot cupric oxide. The oxidation is quite slow in the case of carbon monoxide so the gas must be compressed as much as possible and left in contact with the cupric oxide for some time. In this case the previous outgassing of the reagent tubes must be particularly thorough as water vapor is the principal gas given off by the glass walls of the tube. Any water formed is collected in (T) by cooling with solid carbon dioxide and measured as before. It could also be obtained by the drop in pressure in the gas buret provided, as in our case, oxidizing and reducing gases cannot be present together. The carbon dioxide is measured as was that in the original sample.

Any inert, non-condensable gas which remains in (G) after the analysis would probably be nitrogen or one of the inert gases. In the samples we have run which came from glass there has never been any appreciable residue at this point.

The complete analysis of a gas sample requires about half a day. This does not include the time for outgassing the glass sample.

Analytical Results

The results of some test analyses are given in Tables I and II. Table I gives the results with the first form of the apparatus and Table II with the present one. With the latter, the errors vary from 0.5% or less in samples of 1 cc. or so up to several per cent. in small samples.

Since the apparatus was completed gas analyses have been run on several hundred glass samples. All samples except those that had been

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(6) Campbell, *Proc. Phys. Soc.* (London), **33**, 287 (1921).

previously outgassed gave off appreciable quantities of gas. On the average it may be said that the volume of gas at standard conditions is at least as great as the volume of the glass sample. Table III gives some typical results obtained by three different analysts. A separate glass sample was used in each check analysis. The symbol R stands for residue of inert gas.

As may be seen from the table, it is impossible to check successive samples as closely as would be anticipated from the results of test analyses. This is due to difficulties in the extraction apparatus, previously mentioned, the principal of which is reabsorption of the gases by materials that are volatilized from the glass and condense in the cool upper section of the furnace tube. Sodium oxide probably causes the most trouble. Ways have been found to diminish this effect, but so far no way has been found to eliminate it. The best system is to clean the furnace tube thoroughly after each run, use a new crucible, and pump the gases away from the furnace as rapidly as possible.

TABLE I

TEST ANALYSIS RESULTS

	Composition, %					
Sample, cc.		Synthetic	Detd.		Synthetic	Detd.
1.47	SO_2,	48	48	CO_2,	52	51
1.52	SO_2,	40	41	CO_2,	60	59
2.79	O_2,	21	20	N_2, etc.	79	80
1.82	O_2,	21	21	N_2, etc.	79	79

0.39 cc. CO; found, 0.38 cc. 1.20 cc. H_2O; found, 1.22 cc.

TABLE II

TEST ANALYSIS RESULTS

Sample, cc.	Composition, % Synthetic		Detd.
0.0284	O_2,	21.0	21.8
	N_2, etc.	79.0	78.2
.114	CO_2,	37.7	36.8
	SO_2,	62.3	63.2
.526	H_2,	0.526 cc.	0.523 cc.
.890	CO_2,	20.2	20.3
	O_2,	16.8	16.8
	N_2, etc.,	63.2	63.0
1.006	H_2O,	71.0	71.1
	O_2,	6.1	6.3
	N_2,	22.9	22.6

TABLE III

			Percentage composition of gases									
No.	Glass type	Gas, cc.	H_2O		SO_2		CO_2		O_2		R	
I	Barium (optical)	0.71	24	22	..	..	40	37	36	41	0.1	0.1
II	Soda-lime (milk bottle)	.93	51	51	33	34	3	3	12	11	0.1	0.1
III	Borosilicate (heat resistant)	.40	91	92	..	..	5.5	4.5	3.5	3.5	..	..
IV	Soda-lime (bulb)	.90	44	44	35	36	4.5	7	16	13	..	..
V	Borosilicate (heat resistant)	.36	92	89	0.3	0.3	3	4	5	7	..	..
VI	Borosilicate (bulb)	.74	94	94		2.5	3		3	3.5	..	..
VII	Lead (sign tubing)	.70	33	39		8	7		59	54	..	..
VIII	Soda-lime (expt.)	1.41	28	28		10	8		62	64	..	..
IX	Borosilicate (heat resistant)	0.44	93	93		2	4		5	3	..	..

The table gives, in addition to the composition of the gas, the general type of the glass and the volume of gas at standard conditions obtained from a gram of sample. The latter is many times that obtained at low temperatures where the glass is still solid. All glasses examined contained water and this was usually the most abundant constituent. Carbon dioxide is also nearly always present though often only in small quantities. Sample No. 1 contained a large volume of carbon dioxide due to the basic character of barium oxide. Glasses which contain sodium sulfate give off sulfur dioxide, and those containing higher oxides of arsenic or iron give off oxygen. The gases carbon monoxide and hydrogen were rarely found present, and there was never an appreciable residue of inert gas. Glasses VI to IX may contain some sulfur dioxide but no test was made for this gas so the figure given represents the sum of sulfur dioxide and carbon dioxide. Sample No. VIII was an experimental glass of unusually high arsenic content.

In conclusion the author wishes to express his thanks to Messrs. W. C. Taylor and H. P. Hood for supervising the work and to A. Jacoby for valuable assistance in carrying out the experiments.

Summary

An apparatus is described for collecting and analyzing the gases evolved by glass when heated in vacuum. The apparatus takes samples of from 1 cc. to 0.01 cc. and analyzes for H_2O, CO_2, SO_2, O_2, H_2, CO and N_2, etc. (by difference). Results of test analyses and results with some typical glasses are given.

CORNING, N. Y.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

Heats of Adsorption of Gases and Vapors upon Crystallogenetic Adsorbents

BY ARTHUR B. LAMB AND EDWIN N. OHL

The heats of adsorption of many gases and vapors upon amorphous substances and particularly upon charcoal have been measured and a number of relationships affecting them have been discovered.[1] No such measurements have been made, so far as we are aware, upon *crystallogenetic* adsorbents, *i. e.*, adsorbents whose interior architecture retains to a greater or less degree the original structure of the crystalline material from which they have been prepared.[2]

Information on this score is of particular interest not only because of the high adsorptive capacity which certain of these adsorbents exhibit, for instance chabasite, but also because the greater uniformity in the fineness of the porosity of these adsorbents might well lead to heats of adsorption more divergent among themselves, *i. e.*, more specific, but individually less variable with the amount adsorbed than is the case with ordinary amorphous adsorbents.

We have therefore undertaken the measurement of the heats of adsorption of a number of gases and vapors upon three crystallogenetic adsorbents: chabasite, brucite and thomsonite.

Experimental Procedure

The Adsorbed Substances.—Samples of the best commercially available grades of the substances to be adsorbed were tested to ensure the absence of recognized impurities and were then subjected to further appropriate purifications. If the substance was liquid at ordinary temperatures, the final step in every case was distillation through an efficient fractionating column, only the middle fraction, boiling always within a range of 0.05°, being used in our measurements; if it was a gas, it was condensed either to a liquid or a solid and volatile impurities removed by evacuation, after which the condensed gas was allowed to warm up and to evaporate into the apparatus.

The *methyl alcohol* was twice redistilled over sodium. The absolute *ethyl alcohol* was refluxed for several hours over quicklime. The *carbon disulfide* was shaken exhaustively with mercury and distilled over sodium.

The *methyl chloride* was passed through two washbottles containing a concentrated solution of potassium hydroxide and then over phosphorus pentoxide. It was thereafter liquefied with carbon dioxide snow, evacuated for some time and then allowed to evaporate into the apparatus. The *ethyl chloride* and the *hydrogen sulfide* were dried over phosphorus pentoxide and repeatedly recrystallized by means of liquid nitrogen and then subjected to a high vacuum. In the case of the ethyl chloride freshly purified samples were employed for each run to avoid the presence of impurities which might have resulted from the action of diffuse light.

The *ethylene* and *nitrous oxide* were passed over phosphorus pentoxide and liquefied. They were then boiled for some time under reduced pressure, frozen with liquid nitrogen and the solid subjected to pumping for some time. The ethylene was further purified by repeated melting and recrystallization. The gas gave no condensate when chilled with solid carbon dioxide. Analysis by absorption in fuming sulfuric acid showed a purity of 99.7%.

The *carbon dioxide* was from a selected cylinder and contained by analysis only 0.12% of impurity. It was dried by passage over phosphorus pentoxide and introduced into the apparatus.

The *methane* was a sample specially purified by Dr. Woodhouse, which is described elsewhere.[3] Analysis by combustion indicated a purity of 99.0–99.4%, but it was probably purer than this.

The Adsorbents

Chabasite.—This was in every case material said to have been collected in the vicinity of Aussig, Bohemia. The clear samples were freed from adventitious material, crushed, sorted to pass a 14- and be retained on a 20-mesh screen, and equilibrated over 24% sulfuric acid for at least two weeks according to the procedure described elsewhere.[3] The activation of the chabasite by dehydration at 500–550° has been described elsewhere. In four representative cases the losses of water were as follows:

Sample no.	9	11	14	16	Average
Loss, %	21.62	21.35	21.37	21.38	21.42

These values agree closely with those obtained by Lamb and Woodhouse with comparable material similarly treated. They found that chabasite dehydrated under these conditions and to this extent had the maximum adsorptive capacity for a variety of gases. Exhaustive dehydration at a higher temperature, accompanied by a marked loss of adsorptive capacity, gave a total water content of 22.3%, so that the activated material can be taken as 96.0% dehydrated.

Brucite.—Our material was all from one lot collected near Cleevelah, Washington. It was cleaned, pulverized, and sorted by the same procedure used with chabasite and was dehydrated at 550° at a pressure of 2–5 mm. Two samples showed a loss of water amounting to 27.33 and 27.15%, average 27.24%, which agrees closely with the values obtained by Lamb and Woodhouse under similar

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(1) For an excellent summary, see "The Sorption of Gases," by J. W. McBain, G. Routledge & Sons, Ltd., London, 1932; and a brief discussion of recent work, "The Adsorption of Gases by Solids," by S. J. Gregg, London, 1934.

(2) The heat of adsorption of water vapor on dehydrated chabasite has recently been measured by Tiselius and Brohult, *Z. physik. Chem.*, **A168**, 248 (1934).

(3) Lamb and Woodhouse, THIS JOURNAL (to appear).

conditions. They found that brucite dehydrated to this extent (88.3% of complete dehydration) exhibited maximum adsorptive capacity.

Thomsonite.—This material came from Table Mountain, Golden, Colorado, and was prepared and activated in the same way as the chabasite. Two samples heated at 550° to constant weight lost 13.17 and 13.20%; average 13.19%. Since the original material contained 13.72% of water, these samples were dehydrated to 96.0 and 96.2% of completion.

Apparatus and Manipulation.—Following the lead of Titoff[4] and many subsequent investigators in this field, we have employed the ice-calorimeter in our measurements. This and the accessory apparatus are shown in Fig. 1.

The adsorption cell L had a volume which never differed greatly from 6.5 cc. and was connected to the buret A and the manometer N·P by capillary tubing of 1 mm. bore. L was surrounded by mercury in the inner tube of the ice-calorimeter proper, F, which was completely covered by a mixture of washed ice and distilled water in the Dewar flask H which in turn was surrounded by ice and water in a large, tall beaker, G. A drop of alcohol was added, as usual, to the water-filling of the ice-calorimeter.

The position of the mercury thread in the capillary tube J was read by means of an attached millimeter scale and a suitable telescope with micrometer eyepiece, to within 0.1 mm. The tube was carefully calibrated throughout its whole length and corrections to within 0.1 mm. were applied when required.

The weight of mercury per centimeter length of thread in this capillary was determined in three successive measurements to be 20.48, 20.51 and 20.47 mg.; average 20.49 mg. Taking 0.01546 g. as the weight of mercury corresponding to one calorie,[5] one centimeter length of thread corresponds to 1.325 cal.

The gas buret was provided with a water jacket which could be stirred with a current of air and was calibrated throughout its length to 0.01 cc. The volume of the capillary tube between the buret and the fiduciary mark in N was 0.24 cc.

The thermometers were calibrated to 0.01°, at the ice-point and at the transition temperature of sodium sulfate decahydrate.

The rate of heat-leak was determined before and after each measurement of the heat of adsorption. Usually it amounted to about 1 mm. per hour, but it was frequently even less. Since the heat evolution accompanying adsorption was usually complete within about fifteen minutes, the heat-leak could often be neglected. The room temperature was usually about 23°; no measurements were carried out when it exceeded 29° or was less than 15°.

The pressure in the system was measured by observing the difference in height of the mercury surfaces in the two limbs of N by means of a cathetometer reading to 0.05 mm. For high pressures the right-hand limb was open to the atmosphere; for low pressures it was exhausted to a negligible pressure as determined by the McLeod gage P. In every case the mercury level in the left-hand limb was brought to the fiduciary mark just below the beginning of the capillary tube.

Preparation of the Adsorbent.—A fresh adsorption cell was used for each new sample of adsorbent. These cells, before they were filled, consisted of a tube about 12 mm. in bore and 60 mm. long sealed on one end to a short length of capillary tubing and on the other to a short length of tubing with a bore of about 3 mm. bearing a mark near the seal. The volume of the cell from the capillary tube to the mark in the other tube was first carefully measured. The cell was then dried, filled with the granular adsorbent, the small tube sealed off sharply at the mark without heating the absorbent, and the capillary tube of the cell sealed onto the capillary tube of the apparatus.

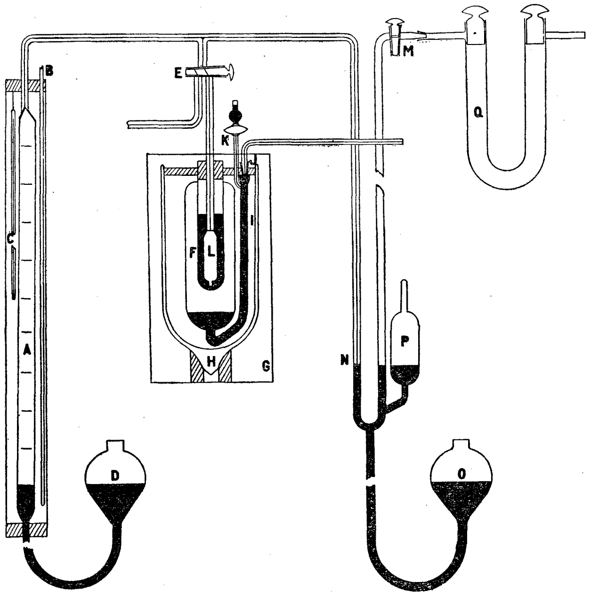

Fig. 1.

The phosphorus pentoxide tube Q was then attached and the whole system evacuated through it with a mercury diffusion pump. A cylindrical furnace was placed around the adsorption cell and its temperature raised gradually to 300° and then more rapidly to 500–550° as indicated by a mercury-in-quartz, nitrogen-filled thermometer with its bulb beside the cell. The pressure was maintained at 0.03 mm. After a suitable interval the stopcocks were closed, the furnace was removed and the tube Q disconnected and weighed.

Calorimetric Measurements.—The ice-calorimeter assembly was now raised by a jack so as to surround the adsorption cell, the position of the mercury thread was adjusted by means of the stopcock K and the measurement of the initial heat-leak was commenced. The tube Q was re-

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(4) Titoff, *Z. physik. Chem.*, **74**, 641 (1910).

(5) Ostwald-Luther, "Physiko-chemische Messungen," 1925, p. 397.

placed, the system exhausted, the mercury in N brought to the fiduciary mark, the buret charged with gas and its temperature and pressure accurately ascertained.

After a constant heat-leak had been maintained for at least twenty minutes, gas was introduced into L and G, the stopcock E was closed and the pressure and volume in the buret were measured. A constant heat-leak was in general reestablished in about fifteen minutes, but observations were usually continued for an additional half hour.

After one such determination of the heat of adsorption, an additional amount of gas was admitted to the adsorbent and the resultant heat evolution again measured. This procedure was repeated until the rate of the adsorption became unduly slow.

Computation of the Results.—The observed pressures of the gases before and after adsorption were corrected to 0° by the usual formula applicable to mercury and a brass scale. They were also corrected for molecular attraction by means of the values of the term *a* in the van der Waals equation as listed in the Landolt–Börnstein tables. From these corrected pressures and the observed temperatures the volumes under standard conditions of the gas in the buret were computed by means of the simple gas law. Their difference, corrected for the dead space, gave the volume of gas actually taken up by the adsorbent.

The total excursion of the mercury thread corrected for the heat-leak and for any inaccuracies in the bore of the capillary multiplied by the above mentioned factor gave the apparent heat of adsorption. From this was subtracted the relatively small amount of heat given off by the gas in cooling from the observed room temperature to zero degrees as computed from the known specific heat of the gas. Finally, dividing by the weight of the adsorbent, the heat of adsorption per gram of adsorbent was obtained.

Reliability of the Measurements.—The volume of gas taken up by the adsorbent could be ascertained to within about 0.02 cc. and since volumes of 10 cc. or more were usually involved, the error on this score would amount to about 0.2%. Usually the uncertainty due to the unknown volumes created by the removal of water from the adsorbent was considerably less than this, but in some instances where the saturation pressure was high and the amount adsorbed small, an additional error of about the same magnitude was introduced. The thermal measurements were subject to an experimental uncertainty of about 0.02–0.03 cal., and since heats of 5–10 cal. were usually evolved, the error here was about 0.3%. The over-all error attached to a typical measurement of the heat of adsorption can therefore be estimated as about 0.5%. An examination of the plotted results (see Fig. 3) indicates that the average deviation from a smooth curve of the measurements within the above ranges is no greater than this estimate.

Results

Heats of Adsorption.—The experimental data and the results computed therefrom for a single measurement of the heat of adsorption of carbon dioxide upon chabasite are given in full in Table I in order to illustrate the procedure followed in all of our measurements and in the computations based upon them.

TABLE I

HEAT OF ADSORPTION OF CARBON DIOXIDE ON DEHYDRATED CHABASITE

Sample $16B_3$; weight 1.4922 g.

Movement Hg, cm.	11.85
Heat, gross cal.	15.70
Heat capacity, cal.	0.22
Heat, net cal.	15.48
Heat, cal. per gram	10.37
Initial temperature, °C.	24.1
Initial pressure	
Observed, mm. Hg	564.2
Correction (a) mm. Hg	+2.6
Corrected, mm. Hg	566.8
Initial volume, cc.	48.20
Initial volume, S. T. P., cc.	33.04
Final temperature, °C.	23.6
Final pressure	
Observed, mm. Hg	27.89
Correction (a) mm. Hg	0.00
Corrected, mm. Hg	27.89
Final volume, cc.	48.20
Final volume, S. T. P., cc.	1.62
Volume adsorbed	
Gross, cc.	31.42
Correction dead space, cc.	−0.11
Corrected, cc.	31.31
Per gram, cc.	20.99

An abridged presentation of all of our experimental results is given by Tables II–IV, and Figs. 2 and 3. In these tables successive determinations without intervening reevacuation of the sample are represented by the sample number followed by a letter with numerical subscripts ($8 A_1$, $8 A_2$, $8 A_3$, etc.). The data under *X* repre-

TABLE II

HEATS OF ADSORPTION ON DEHYDRATED CHABASITE

Sample no.	7	8	9	10	13	14	15	16
Weight (anhydrous)	2.9300	1.4186	1.0324	1.0060	1.6170	1.5687	2.9612	1.4922

Sample and run	X, cc./g.	Pressure range, cm. Hg	$h_{\text{obsd.}}$, cal. per g.
		CH_4	
15 A_1	3.90	37–25	1.80
15 A_2	8.08	49–35	2.69
15 A_3	11.36	38–14	3.20
15 B_1	1.66	29–19	0.90
15 B_2	3.90	29–12	1.84
		C_2H_4	
8 A_1	5.13	77–44	3.17
8 A_2	9.03	77–39	5.60
8 B_1	6.79	76–51	4.37
8 B_2	13.83	76–38	7.79
8 B_3	19.16	76–15	9.54
		N_2O	
8 A_1	7.58	76–58	4.31
8 B_1	5.33	77–63	3.03
8 C_1	7.05	75–45	4.03
8 C_2	15.28	75–50	8.76
8 C_3	22.67	75–45	13.33
8 C_4	29.95	75–42	17.18
		H_2S	
9 A_1	6.29	76–56	4.05
9 A_2	13.60	76–46	9.00
10 A_1	15.08	77–51	8.88
10 A_2	28.61	78–44	17.76
10 A_3	34.46	77–47	20.83
10 A_4	43.51	77–14	25.76

Sample and run	X, cc./g.	Pressure range, cm. Hg	$h_{\text{obsd.}}$, cal. per g.
		CO_2	
8 A_1	7.60	74–55	3.99
8 A_2	12.91	74–56	6.90
8 A_3	17.35	74–54	8.94
8 A_4	21.21	74–51	11.21
16 A_1	15.20	39–0.2	8.55
16 A_2	35.38	53–0.1	19.21
16 A_3	56.37	57–3	29.58
16 B_1	0.93	2–0.1	0.31
16 B_2	4.97	10–0.3	2.74
16 B_3	18.03	36–0.3	10.59
		CH_3Cl	
14 A_1	1.34	4–0.0	0.85
14 A_2	4.89	10–0.8	2.99
14 A_3	10.09	16–0.9	6.34
16 B_1	1.51	4–0.0	1.03
16 B_2	3.11	4–0.1	2.14
16 C_1	1.81	5–0.2	1.36
16 C_2	5.07	9–0.6	3.03
16 C_3	16.31	29–1.5	9.00
		C_2H_5Cl	
8 A_1	4.45	76–64	2.49
8 A_2	10.75	76–56	5.05
7 A_1	1.83	76–68	0.60
7 B_1	3.04	76–59	1.74
7 B_2	6.42	76–53	3.51
7 C_1	10.78	76–23	5.28

Sample and run	X, cc./g.	Pressure range, cm. Hg	$h_{\text{obsd.}}$, cal. per g.
		CH_3OH	
16 A_1	1.09	3–0.3	1.55
16 A_2	1.84	3–0.4	2.29
16 B_1	0.42	1–0.2	0.55
16 B_2	1.67	4–0.6	1.98
16 B_3	2.79	4–0.7	3.16
16 B_4	3.54	3–1.1	3.69
16 B_5	4.14	3–1.5	4.08
16 C_1	2.95	10–1.5	3.27
16 C_2	5.07	8–1.7	5.35
16 C_3	7.70	9–2	8.18
16 C_4	12.10	9–2	13.28
		CS_2	
13 A_1	4.92	15–4	3.94
13 A_2	9.77	14–3	7.72
13 A_3	14.49	14–8	11.12
15 A_1	0.83	11–6	0.38
15 A_2	2.85	17–6	2.00
15 A_3	4.81	16–4	3.72
		C_2H_5OH	
16 A_1	1.89	6–1	1.37
16 A_2	3.80	6–1	2.02
16 A_3	5.68	6–1	2.23
16 B_1	0.33	0.8–0.0	0.32
16 B_2	0.77	1–0.1	0.59
16 B_3	2.15	4–0.2	1.32

TABLE III

HEATS OF ADSORPTION OF CARBON DIOXIDE ON DEHYDRATED BRUCITE

Weight (anhydrous), 4.7568

Sample and run	X, cc./g.	Pressure range, cm. Hg	$h_{\text{obsd.}}$, cal. per g.
2 A_1	0.34	29–28	0.97
2 A_2	1.84	28–27	2.20
2 A_3	5.51	27–25	3.41
2 A_4	7.69	25–23	4.01
2 B_1	1.53	7–5	1.94
2 B_2	3.51	5–4	3.08
2 B_3	4.91	4–3	3.21
2 C_1	2.92	6–4	2.49
2 C_2	4.01	4–3	2.88

TABLE IV

HEATS OF ADSORPTION OF CARBON DIOXIDE ON DEHYDRATED THOMSONITE

Weights (anhydrous): Sample 1, 0.8253 g.; 2, 5.1136 g.

Sample and run	X, cc./g.	Pressure range, cm. Hg	$h_{\text{obsd.}}$, cal. per g.
1 A_1	2.21	36–33	1.27
2 B_1	4.10	43–8	2.27
2 C_1	3.56	58–28	1.54
2 D_1	3.23	56–28	1.85
2 E_1	2.25	56–36	1.03

sent the corrected volumes of gas adsorbed per gram of *completely* dehydrated adsorbent, those under $h_{\text{obsd.}}$ the heat evolutions accompanying these adsorptions.

In Fig. 2 the heats of adsorption are plotted against the amount adsorbed. Most of the curves differ but slightly, and in two cases not at all, from straight lines. This means that the heat of adsorption per cubic centimeter of adsorbed gas is nearly or quite independent of the amount adsorbed. This is the same behavior previously observed with charcoal.[6] Indeed, the empirical equation, $h = ax^n$, which was there found to express the experimental results satisfactorily is equally applicable here, as is shown by Fig. 3 where these deviations are plotted on a large scale against the amount adsorbed. It can be seen that the deviations are usually small and for the most part lie upon smooth curves to within the previously estimated accuracy of our

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[6] Lamb and Coolidge, THIS JOURNAL, **42**, 1146 (1920).

measurements irrespective of the sample taken and of the number of times it had been re-evacuated. The only marked exception to this is with carbon dioxide where the measurements with sample No. 8 give definitely different results than those with sample No. 16. The values of the constants in these formulas are collected in Table V and it can be seen that here, as in the case with charcoal, the value of *n* is usually not far from unity.

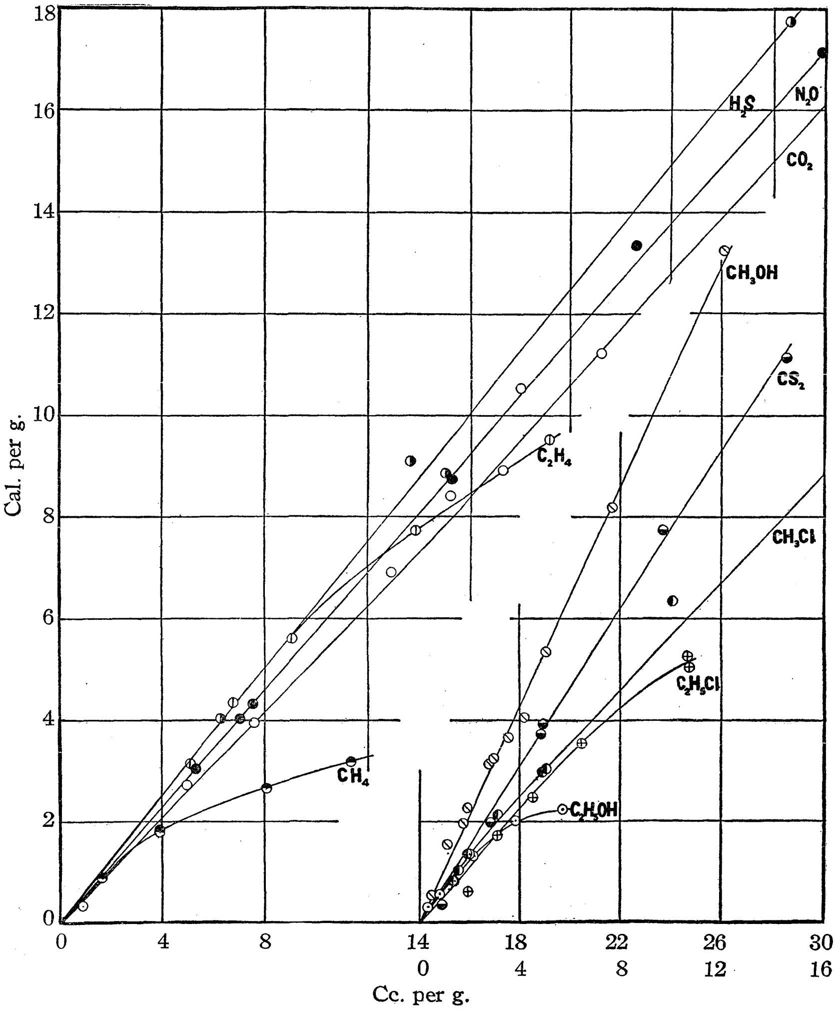

Fig. 2.—○, CO_2; ⦶, C_2H_4; ⊘, CH_3OH; ⊕, C_2H_5Cl; ⊙, $C_2H_5O_4$; ◑, H_2O; ◐, CH_3Cl; ◒, CS_2; ●, N_2O; ⊖, CH_4.

Molar Heat of Adsorption.—The empirical formulas permit a convenient calculation of the molar heats of adsorption of the respective gases at the same molar concentration in the adsorbent. Values thus computed for 11 cc. of gas per gram (0.0005 mole per gram), which is in general within the range of the empirical equations, are given in the fourth column of Table V. It is interesting that these values are not very different from those previously found for adsorption upon charcoal (Col. 5).

The curves in Fig. 4 present our results for the heat of adsorption of carbon dioxide on dehydrated chabasite, thomsonite and brucite along with corresponding results of others with charcoal and silica gel. The constants of the empirical formulas which express these results and the molar heats of adsorption calculated from them are collected in Table VI.

It is clear that the crystallogenetic adsorbents show a considerably greater heat of adsorption for carbon dioxide than do charcoal and silica gel.

It is of interest that while most of the curves in Fig. 4 are straight lines (and the exponent *n* in the empirical equation nearly unity), that of dehydrated brucite has a marked curvature showing that the molar heat of adsorption increases decidedly for small amounts adsorbed. The heat of reaction of magnesia and carbon dioxide to form massive magnesium carbonate is 26.7 kg. cal. and is represented by the dotted line shown in Fig. 4. It can be seen from the position of this line that the molar heat of adsorption for small amounts adsorbed is as great or greater than this heat of reaction. A similar behavior has been reported in other cases.[7]

Effect of Dehydration on Heat of Adsorption.—In order to ascertain the relation between the extent of dehydration of these adsorbents and the heats of adsorption to which they give rise, we have measured the heat evolved when methyl alcohol is adsorbed on chabasite and on brucite after successive portions of water have

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[7] Keyes and Marshall, THIS JOURNAL, **49**, 156 (1927); Ward and Rideal, *J. Chem. Soc.*, 3117 (1927); Marshall and Bramston-Cook, THIS JOURNAL, **51**, 2019 (1929); Buck and Garner, *Nature*, **124**, 409 (1929); Cameron, *Trans. Faraday Soc.*, **26**, 239 (1930).

TABLE V

NET HEATS OF ADSORPTION

Substance	a, cals.	n	$h$molar Chabasite, kg. cal.	$h$molar Charcoal,[e] kg. cal.	ϕ	hm − ϕ chabasite, kg. cal.	hm − ϕ charcoal, kg. cal.	Mol. vol. liq. at 0°, cc.	hm − ϕ per cc. liq. 0°
CH_4	0.875	0.537	6.43	...	0	6.43	...	..	..
C_2H_4	.807	.857	12.89	...	1.50	11.39	...	81.2	0.140
CO_2	.593	.968	12.41	7.7[a]	2.46	9.95	5.2	47.6	.209
N_2O	.573	1.000	12.83	7.76[b]	2.59	10.24	5.1	48.3	.212
H_2S	.689	0.963	14.23	...	4.24	9.99	...	36.8	.271
CH_3Cl	.676	.948	13.47	7.18[c]	4.95	8.52	2.23	52.9	.161
C_2H_5Cl	.671	.870	11.06	13.49[d]	6.00	5.06	7.49	69.8	(.073)
CH_3OH	1.230	.928	23.32	14.3[d]	9.10	14.22	5.2	39.5	.359
CS_2	0.770	1.000	17.25	13.9[d]	6.80	10.45	7.1	58.8	.178
C_2H_5OH	.747	0.753	9.27	16.4[d]	10.12	...	6.3	57.1	(..)

[a] Titoff, Ref. 4. [b] Gregg, *J. Chem. Soc.*, 1494 (1927). [c] Wood charcoal. Chappuis, *Wied. Ann.*, **19**, 21 (1883). [d] Lamb and Coolidge, Ref. 2. [e] Coconut charcoal.

TABLE VI

HEATS OF ADSORPTION OF CARBON DIOXIDE ON VARIOUS ADSORBENTS AT 0°

	a in $h = ax^n$	n in $h = ax^n$	Molar heat of adsorption, kg. cal.
Chabasite dehydrated	0.593	0.968	12.89
Thomsonite dehydrated	.552	.973	12.32
Brucite dehydrated	1.603	.443	9.44
Charcoal[a]	0.184	.957	7.70
Silica gel[b]	.248	.96	7.01

[a] Titoff, Ref. 4. [b] Magnus and Kalberer, *Z. anorg. Chem.*, **164**, 357 (1927).

been removed from them. The procedure was the same as in the preceding measurements except that at the completion of a run the phosphorus pentoxide tube was attached and the alcohol was pumped off at room temperature, *after* which additional quantities of water were removed by gradual and gentle heating and pumping.

It proved to be impossible at low degrees of dehydration to remove all of the alcohol in this way without removing some of the water at the same time. The stated values for the degree of dehydration must therefore in these cases be considered as only approximate. At higher degrees of dehydration no such effect was detected. The experimental results are collected in Fig. 5.

It can be seen from these figures that the heats of adsorption on the slightly dehydrated material are decidedly less than on the more completely dehydrated material; however, the difference is proportionately smaller as the water content becomes less. The relationship is brought out even more clearly by Fig. 6, where the heats of adsorption of 0.000178 mole per gram, expressed as percentages of the maximum heat of adsorption, are plotted against the percentage of complete dehydration. It is evident that the points, with a single exception, for both adsorbents lie on a single curve which is nearly a straight line.

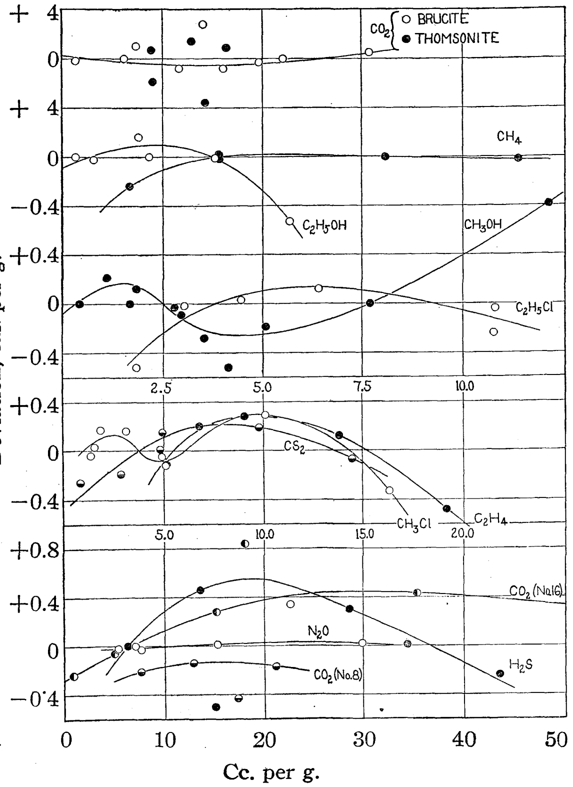

Fig. 3.—Deviations from empirical equation.

These effects would appear to indicate that the heat of adsorption per mole is decidedly greater at high degrees of dehydration than at low. On the other hand, since water is certainly desorbed from the slightly dehydrated adsorbents along with alcohol on pumping at room temperatures, it is probable that some desorption of water occurs under these conditions when the alcohol is adsorbed in the calorimeter and this would diminish the true heat of adsorption of the alcohol by the (negative) heat of desorption of the water. The observed heat of adsorption would therefore be too small by the amount of this disturbing factor. It is unlikely, however, that this can have affected the points for the more completely dehydrated samples or that it would give curves that are so nearly linear.

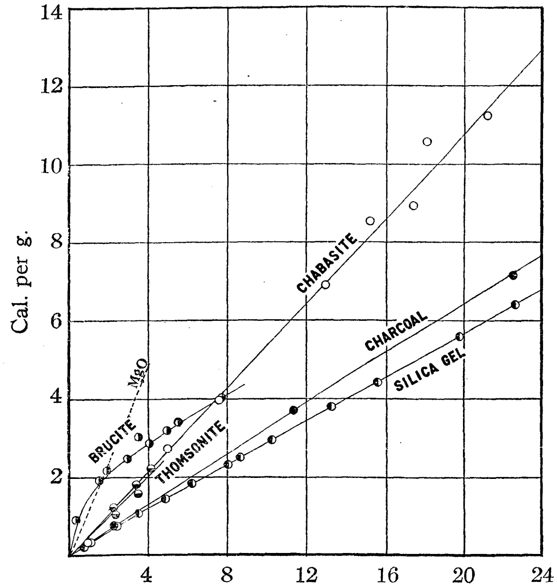

Fig. 4.—Heats of adsorption of carbon dioxide on various adsorbents.

Net Heats of Adsorption.—The *net* heats of adsorption have been obtained by subtracting from the molar heats of adsorption (h_m) the molar latent heats of vaporization of 0° (ϕ). The resulting values listed in the seventh column of Table V are, except for the value for methane which was obtained by using the empirical equation far beyond its range and those for ethyl chloride and ethyl alcohol which are aberrant for other reasons to be explained later, not very divergent among themselves and are in general considerably larger than the corresponding values upon charcoal at the same concentration (Column 8).

It has been shown[6] in the case of eleven volatile organic liquids, first, that while the net *molar* heats of adsorption vary considerably among themselves (from 6.22 to 10.65 kg. cal.) the net heats of adsorption per cubic centimeter of the *liquid* are nearly identical (0.0877 kg. cal. ±7.4%) and second, that the pressures which would be required to produce, by compression, heats equal to these net heats of adsorption are even more nearly identical (28,100 atmospheres ±4%).

To test the first relationship by the present data we have computed the net heats of adsorption per cubic centimeter of the liquids by dividing the net heats of adsorption per mole by the molar volumes of the liquids at zero degrees. The resulting values, given in Column 10, while they are all of about the same magnitude (average deviation from the mean ±25%) are by no means as concordant as in the case of the abovementioned organic liquids adsorbed on charcoal and are indeed less concordant than the net molar heats. This is, however, not surprising, for this relationship would only be expected to hold closely when the molar volumes are measured under the high virtual pressures prevailing in the adsorption layer or when they are proportional to the molar volumes at zero degrees measured at atmospheric pressure. In the case of the organic liquids with similar critical temperatures and compressibilities this proportionality probably exists, but in the case of the substances here studied with quite different critical temperatures and compressibilities it presum-

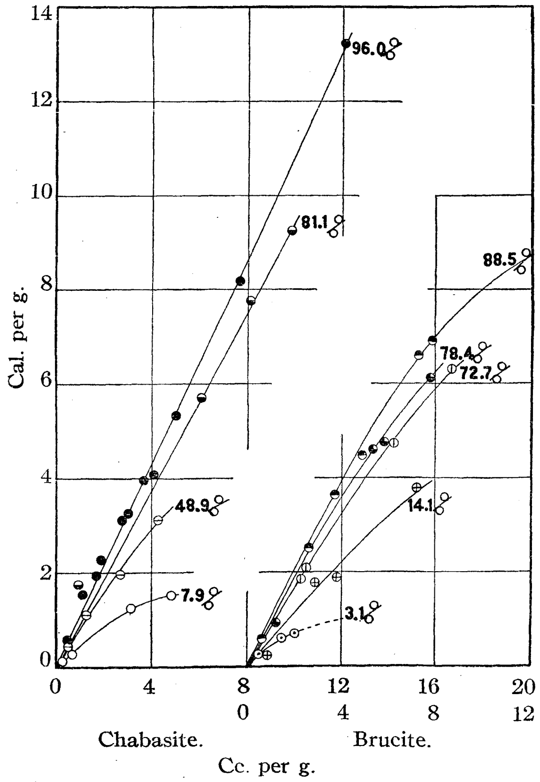

Fig. 5.—Methanol on partially dehydrated adsorbent.

ably does not and hence no such close concordance is to be expected.

We have not been able to test the second relationship since the data necessary to compute the heats of compression are lacking. It is clear, however, that in order to produce by real or virtual compression of the adsorbed layer, the considerably greater net heats of adsorption observed in these crystallogenetic adsorbents, the adsorptive pressure must be correspondingly greater than was found for charcoal.

The marked difference in the behavior of ethyl chloride and ethyl alcohol as compared with the other substances which we have studied should also be remarked. These substances are adsorbed but slightly, their heats of adsorption vary considerably with the amount adsorbed and their net heats of adsorption are small; indeed, that of ethyl alcohol is apparently negative. The explanation of this behavior is doubtless to be found in the decidedly greater dimensions of the molecules of these substances computed from known atomic radii and atomic distances, as compared with those of the other substances that we have studied. As has been pointed out previously,[8] molecules larger than a certain size are apparently unable to enter the fine pores of these crystallogenetic adsorbents, and the slight adsorption observed in these instances is presumably chiefly confined to the outer surfaces and to the inter- rather than intra-crystalline porosity. It is not surprising that this slight and mostly unoriented adsorption should evolve less heat than the more extensive and oriented adsorption within the dehydrated crystals.

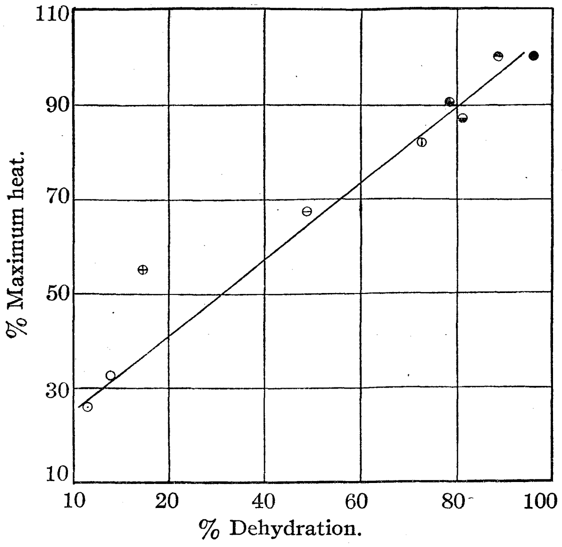

Fig. 6.

Summary

1. The heats of adsorption of a number of gases and vapors on dehydrated chabasite, thomsonite and brucite have been measured at 0°.

2. The molar heats of adsorption of such of these substances as are copiously adsorbed by these materials are in general somewhat larger than those previously observed on charcoal and silica gel but, like them, vary only slightly with the amount adsorbed and can be represented by the same empirical equation.

3. The net heats of adsorption are also considerably greater than those previously observed with charcoal and this indicates that the adsorbate on these adsorbents is subjected on the average to a more intense adsorptive and compressive force than on charcoal.

CAMBRIDGE, MASS.

RECEIVED AUGUST 1, 1935

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[8] Lamb, U. S. Patent 1,813,174 [Applied for Sept. 25 (1925)]; McBain, "Colloid Symposium Monograph," 1926, Vol. IV, p. 1; *Kolloid Z.*, **40**, 1 (1926); Schmidt, *Z. physik. Chem.*, **133**, 280 (1928).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Configuration of the Mercuric Halides

BY W. J. CURRAN AND H. H. WENZKE

The Raman spectra of the mercuric halides have been interpreted[1] to indicate a linear structure for these compounds. Bell[2] calculated the moments of the mercuric halides from solubility data. He obtained 4.0, 5.7 and 6.6 × 10^{18} for the chloride, bromide and iodide, respectively. Braekken and Scholten[3] concluded from x-ray data that the molecular configuration of mercuric chloride was linear but that of mercuric bromide was not. The solubility of the mercuric halides in benzene is so small that it is difficult to use this solvent in the determination of electric moments. These halides are more soluble in dioxane and it is for this reason that the latter solvent was used. In order to determine whether or not the dioxane formed a coördinate compound with the mercury, it was used as a solvent in the determination of the moment of mercury diphenyl. The moment of mercury diphenyl had already been determined in benzene by Hampson.[4] He obtained the value 0.41.

TABLE I

DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS OF MERCURIC HALIDES

(Solvent, Dioxane; *T*, 25°)

c_2	d	ϵ
	Mercury diphenyl	
0.00000	1.0270	2.3373
.04965	1.1288	2.3929
.05998	1.1489	2.4046
.06813	1.1673	2.4139
	Mercuric chloride	
0.00000	1.0260	2.2267
.00502	1.0388	2.2444
.00507	1.0390	2.2444
.00547	1.0400	2.2456
.00564	1.0405	2.2471
	Mercuric bromide	
0.00000	1.0244	2.3334
.00691	1.0478	2.2607
.00906	1.0533	2.2695
.01047	1.0578	2.2748
.01335	1.0677	2.2858
	Mercuric iodide	
0.00000	1.0260	2.2267
.01099	1.0738	2.2881
.01236	1.0802	2.2938
.01260	1.0819	2.2959
.01299	1.0832	2.2986

TABLE II

POLARIZATIONS AND MOMENTS OF MERCURIC COMPOUNDS

Comopund	P_∞	P_E[a]	P_{A+0}	$10^{18}\ \mu$
Mercury diphenyl	69.02	65.30[4]	3.72	0.42
Mercuric chloride	65.03	30.36[5]	34.67	1.29
Mercuric bromide	78.63	55.30[5]	23.33	1.06
Mercuric iodide	101.40	94.28[5]	7.12	0.58

[a] The electronic polarizations were obtained from the literature according to the references given.

Discussion of Results

The value of 0.42 obtained for the moment of mercury diphenyl in dioxane is practically the same as that obtained by Hampson[4] in benzene, namely, 0.41. This shows that the oxygen of the dioxane does not form a coördinate covalent link with the mercury and that the dioxane is a satisfactory solvent for these compounds. It is apparent from the moments of these compounds that the mercuric halides are not linear in structure. The decrease of the moment with increase in atomic weight of the halogen is no doubt due in part to steric effects which cause a widening of the valence angle of the mercury as the atomic weight of the halogen increases. It is no doubt also true that the moment of the mercury-to-halogen linkage decreases with increase in size of the halogen atom. Unfortunately the electric moment data do not permit the calculation of the valence angle of the mercury in these halides. The measured moments are very much smaller than those obtained in the calculations of Bell.[2] The force relationships existing between the solute and solvent are of such a complex nature that at present no quantitative relation between them and dipole moments is known.

Summary

1. Electric moments have been determined for mercury diphenyl, mercuric chloride, mercuric bromide and mercuric iodide.

2. The configuration of the mercuric halides is not linear, as has been sometimes assumed from other lines of investigation.

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(1) Kohlrausch, "Der Smekal-Raman Effekt," 1931.

(2) Bell, *J. Chem. Soc.*, 1371 (1931).

(3) Braekken and Scholten, *Z. Krist.*, **89**, 448 (1934).

(4) Hampson, *Trans. Faraday Soc.*, **30**, 877 (1934).

(5) Bergmann, Engel and Wolf, *Z. physik. Chem.*, **B17**, 81 (1932).

3. The moments obtained by direct measurement are much smaller than has been calculated from solubility data. While dipole forces undoubtedly play a part in determining solubility, apparently not enough is known about them to permit an even semi-quantitative calculation of electric moments by this method.

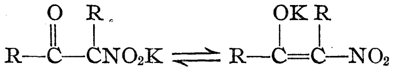
Notre Dame, Indiana Received September 10, 1935

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

Asymmetric Syntheses. IV. The Action of Optically Active Nitrates on 2-Bromofluorene

By J. T. Thurston and R. L. Shriner

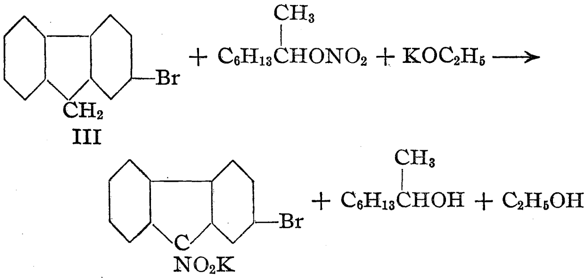
The reaction between optically active nitrates and cyclic ketones[1] led to the formation of salts which could possess either structure[2] I or II. In order to avoid this, a study has been made of the action of optically active nitrates on an active methylene compound which cannot undergo such tautomerization.



$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{R}{|}}{C}NO_2K \rightleftharpoons R{-}\overset{\overset{OK}{|}}{C}{=}\overset{\overset{R}{|}}{C}{-}NO_2}$$

I II

Since Wislicenus and Waldmüller[3] showed that fluorene would react with ethyl nitrate in the presence of potassium ethoxide to give the potassium salt of 9-nitrofluorene, it was decided to study the reaction between the optically active 2-octyl nitrates and 2-bromofluorene (III).

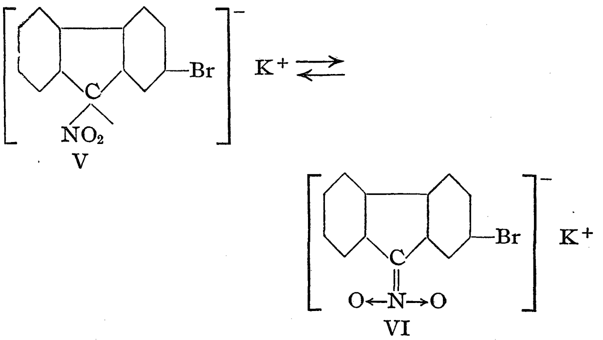


III

IV

The latter compound (III) contains an active methylene group but cannot undergo enolization. The presence of the bromine in one ring renders the molecule unsymmetrical so that carbon atom 9 in the product (IV) may be asymmetric.

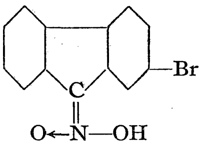
Treatment of 2-bromofluorene with *d*-2-octyl nitrate in the presence of potassium ethoxide yielded the potassium salt of 9-nitro-2-bromofluorene which possessed a very slight optical activity. Two independent preparations gave specific rotations[4] of +4.48 and +4.33°. The observed rotations were very low, +0.06 ± 0.01° and +0.05 ± 0.01°, but the absolute alcohol solutions of the salts were distinctly optically active. The *l*-2-octyl nitrate gave a very low specific rotation of −1.71°. The salts racemized readily. The activity of these salts indicates that at least a partial asymmetric synthesis was achieved by the optically active reagents. At least part of the salt must exist as the asymmetric ion (V) since the other form of the ion (VI) is not asymmetric.



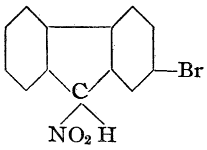
V

VI

Immediate treatment of the *d*-potassium salt with acid gave the *aci*-9-nitro-2-bromofluorene (VII) which was optically inactive. This *aci*-form (VII) was a solid, m. p. 132°. It was readily soluble in sodium carbonate solution, and gave a green color with ferric chloride. This *aci*-form was transformed into the *normal*-nitro compound (VIII) by heating it in alcoholic solution. The *normal*-nitro compound (VIII) gave



VII



VIII

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(1) Shriner and Parker, This Journal, **55**, 766 (1933).

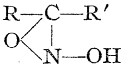
(2) Horne and Shriner, *ibid.*, **55**, 4652 (1933).

(3) Wislicenus and Waldmüller, *Ber.*, **41**, 3334 (1908).

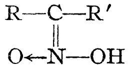
(4) All specific rotations reported in this paper were determined at 25° with sodium D light.

no color with ferric chloride, and was insoluble in sodium carbonate solution. These two compounds, therefore, constitute another case in which both the *aci*- and *normal*-forms have been isolated. It is worth pointing out that there should be two geometric isomers of the *aci*-form (VII); one, in which the hydroxyl is *syn* to the bromine in the ring, and a second in which the hydroxyl is *anti* to the bromine. Only one form of VII was obtained in the present work.

Air oxidizes these potassium salts to 2-bromofluorenone and potassium nitrite, a reaction which has been observed previously by Wislicenus and Waldmüller in the case of the salts of 9-nitrofluorene.[3] Bromine converted the *d*-potassium salt into 9-nitro-2,9-dibromofluorene, which was optically inactive. A quantitative bromine titration of the potassium salt, according to the general procedure of Meyer and Wertheimer,[5] showed that 90% of the theoretical amount of bromine was taken up. Titration of the *aci*-form VII gave a 50% absorption of bromine, whereas the *normal*-nitro form VIII did not absorb bromine at all under the conditions of the titration. The fact that the *aci*-form changes over to the *normal*-form probably accounts for the bromine titration value of 50%. These results are of importance since they constitute some evidence against the cyclic structure, IX, which was originally proposed for the *aci*-form by Holleman,[6] and Hantzsch and Schultze.[7] The ready formation of the bromonitro compound from the salt and the absorption of bromine by the *aci*-form are best explained by the structure X for the *aci*-modification rather than by IX. These *aci*-forms parallel the nitrogen alkylated ketoximes which have been shown[8] to possess the structures XI and XII. As mentioned above, none of the *syn* and *anti* forms of *aci*-nitro compounds have been obtained as yet.

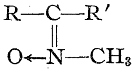


IX



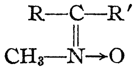
$R-C(=N(\rightarrow O)-OH)-R'$

X



$R-C(=N(\rightarrow O)-CH_3)-R'$

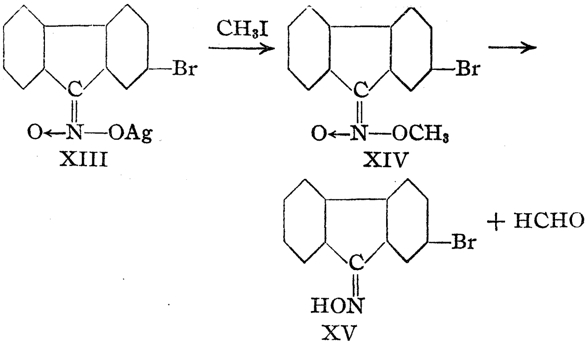
XI



$R-C(=N(\rightarrow O)-CH_3)-R'$

XII

Nenitzescu and Isacescu[9] have found that alkylation of sodium or potassium salts of nitro compounds leads to degradation products which may be best explained by an intermediate nitronic ester. In the present study it was found possible to obtain the methyl nitronic ester (XIV) by treating the silver salt of 9-nitro-2-bromofluorene (XIII) with methyl iodide.



This nitronic ester (XIV) was very unstable, and readily decomposed into 2-bromofluorenone oxime (XV) and formaldehyde. This decomposition is characteristic of nitronic esters[10] and shows that alkylation occurred on the oxygen atom, and not on the carbon atom.

Experimental

2-Bromofluorene.—To 125 g. of fluorene and about 1 g. of iodine, dissolved in 350 cc. of boiling benzene, was added during the course of three hours 120 g. of dry bromine dissolved in 200 cc. of cold benzene. This solution was refluxed for another hour, cooled, washed with water and finally with sodium bisulfite solution. After distilling the benzene and water, the product was fractionated twice. About 20 g. of unchanged fluorene, 75 g. of product boiling at 157–162° (1–2 mm.) and 40–50 g. of undistillable tar were obtained. The crude product was recrystallized from three 500-cc. portions of alcohol, and melted sharply[11] at 113°. The yield was 65 g., or 35% of the theoretical.

Anal. Calcd. for $C_{13}H_9Br$: Br, 32.65. Found: Br, 32.66.

***dl*-, *d*- and *l*-2-Octyl Nitrates.**—These were prepared according to the method previously described.[1] *dl*-2-Octyl nitrate boiled at 92–94° (17 mm.); n^{20}_D 1.4240. *d*-2-Octyl nitrate boiled at 96–97° (16 mm.; $[\alpha]^{25}_D$ +16.00°; n^{20}_D 1.4270. *l*-2-Octyl nitrate boiled at 95–97° (20 mm.); $[\alpha]^{25}_D$ −15.28°; n^{25}_D 1.4292.

Condensation of 2-Bromofluorene with *dl*-2-Octyl Nitrate.—A solution of 5.6 g. of *dl*-2-octyl nitrate and 6 g. of 2-bromofluorene in 80 cc. of absolute ether was added to a solution of potassium ethoxide prepared from 1 g. of potassium, 7 cc. of absolute ethyl alcohol and 25 cc. of absolute ether. The reaction mixture was maintained at 45° by means of a water-bath; after about two hours half of the ether was distilled. The remaining solution was filtered and poured into 200 cc. of low-boiling petroleum ether. The yellow, precipitated potassium nitro salt was purified by dissolving in a very small amount of ethyl

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(5) Meyer and Wertheimer, *Ber.*, **47**, 2374 (1914).

(6) Holleman, *Rec. trav. chim.*, **13**, 405 (1894); **14**, 129 (1895).

(7) Hantzsch and Schultze, *Ber.*, **29**, 699, 2251 (1896).

(8) Brady and Mehta, *J. Chem. Soc.*, **125**, 229 (1924); Sutton and Taylor, *ibid.*, 219 (1931).

(9) Nenitzescu and Isacescu, *Ber.*, **63**, 2484 (1930).

(10) Wislicenus and Waldmüller, *ibid.*, **41**, 3334 (1908); Arndt and Rose, *J. Chem. Soc.*, 1 (1935).

(11) Courtot, *Ann. chim.*, [10] **14**, 56 (1930).

acetate and reprecipitated with equal parts of benzene and petroleum ether. The product, which gave a green color with a drop of ferric chloride, was obtained in yields of 62.5% of the theoretical.

Anal. Calcd. for $C_{13}H_7O_2NBrK$: K, 11.89; Br, 24.36; N, 4.27. Found: K, 12.11; Br, 24.50; N, 4.05.

Condensation of 2-Bromofluorene with *d*-2-Octyl Nitrate.—The same general procedure as above was followed, using *d*-2-octyl nitrate. However, the temperature was maintained at 35°, and the ether was removed at diminished pressure. The yield of the crude salt, giving an immediate specific rotation[4] in absolute alcohol of +4.33°, was 1.5 g. Another sample of the salt, prepared in the same manner, gave an immediate specific rotation in absolute alcohol of +4.48°. Below 30° the reaction did not take place, and between 30 and 35° the yields were very small. The order of addition or molar ratio of the reactants had no effect on the yield or optical activity of the salt.

Anal. Calcd. for $C_{13}H_7O_2NBrK$: K, 11.89. Found: K, 11.51.

Condensation of 2-Bromofluorene with *l*-2-Octyl Nitrate.—Exactly the same procedure as above was followed using *l*-2-octyl nitrate, and the specific rotation[4] of the salt in absolute alcohol was immediately determined and found to be −1.71°.

Reaction between *dl*-2-Octyl Nitrate and Potassium Ethoxide.—A control experiment identical with the above procedure except that the 2-bromofluorene was omitted showed that the potassium 2-octoxide was soluble in the concentrations of alcohol, ether and petroleum ether used in the above reactions, and, therefore, could not contaminate the salts of the nitro compounds.

2-Bromofluorenone from the Potassium Nitro Salt.—The potassium nitro salt in alcohol solution on exposure to air for several days was oxidized to potassium nitrite and 2-bromofluorenone melting at 146°. The latter yielded an oxime which melted at 196°, while the recorded[12] melting point is 194–195°.

Anal. Calcd. for $C_{13}H_7OBr$: Br, 30.88. Found: Br, 31.49.

Aci-9-Nitro-3-bromofluorene.—The bright yellow precipitate, obtained by the action of dilute acetic acid upon an aqueous solution of the *dl*-potassium nitro salt, after recrystallization from hot alcohol, melted at 132°. It was soluble in dilute alkalies and gave a green color with a drop of ferric chloride. The optically active salts gave the same optically inactive *aci*-form.

Anal. Calcd. for $C_{13}H_8O_2NBr$: N, 4.83; Br, 27.55. Found: N, 5.01; Br, 27.78.

9-Nitro-2-bromofluorene.—When an alcoholic solution of the *aci*-nitro form was boiled it was converted into the normal nitro form which crystallized when the solution cooled. The colorless plates, after recrystallization from ethyl acetate, melted at 170°, were insoluble in dilute alkalies and did not give a color with a drop of ferric chloride. On longer standing, the original filtrate deposited crystals of 2-bromofluorenone, melting at 146°.

Anal. Calcd. for $C_{13}H_8O_2NBr$: N, 4.83; Br, 27.55. Found: N, 4.84; Br, 27.59.

2,9-Dibromo-9-nitrofluorene.—An alcoholic solution of the *dl*-potassium nitro salt on treatment with a solution of bromine in absolute alcohol gave the dibromo compound, which was precipitated by the addition of water. After recrystallization from an alcohol–ethyl acetate mixture, the yellow needles melted at 139°.

Anal. Calcd. for $C_{13}H_7O_2NBr_2$: Br, 43.32; N, 3.79. Found: Br, 43.38; N, 4.03.

The *d*-potassium nitro salt, by exactly the same procedure as above, gave the same dibromo compound, which was washed with a small amount of alcohol, dried in a vacuum desiccator and the optical rotation immediately taken. It was optically inactive.

Methylation of the Silver Salt.—The silver salt was prepared in almost quantitative yields by the addition of silver nitrate solution to an aqueous solution of the potassium salt. To 2 g. of the dried silver salt suspended in 5 cc. of ether cooled to −10° was added 3 cc. of methyl iodide dissolved in 6 cc. of ether. After shaking the suspension for six hours, the mixture was filtered and the filtrate evaporated at diminished pressure. After four recrystallizations from a mixture of ether and petroleum ether the product still melted over a wide range, 72–80°. When stored in a desiccator the odor of formaldehyde was noted in a short time. The analysis for nitrogen was high indicating the presence of some of its decomposition product, 2-bromofluorenone oxime.

Anal. Calcd. for $C_{14}H_{10}O_2NBr$: N, 4.60. Found: N, 4.96.

When the above nitronic ester was dissolved in alcohol and warmed for about thirty minutes, the transformation into the oxime was complete. The 2-bromofluorenone oxime melted at 195° and a mixed melting point with an independently prepared specimen showed no depression.

Bromine Titrations.—The general procedure of Meyer and Wertheimer was followed, using a weighed amount of the *dl*-potassium nitro salt, which was dissolved in cold alcohol and quickly titrated with a freshly prepared methyl alcohol solution of bromine. The excess bromine was removed by adding 2–3 cc. of 10% β-naphthol solution. After excess 20% potassium iodide solution was added and warmed for twenty minutes, the liberated iodine was titrated with 0.1 *N* thiosulfate solution using starch as an outside indicator.

Compound	Bromine absorption % of calcd.
dl-Potassium salt	89.2–90.4
Aci-nitro form	50.4
Normal nitro form	0.0
Nitronic ester	48.8–53.5
2-Bromofluorenone oxime	50.76

Since the nitronic ester breaks down into the oxime, the values for these two compounds are similar.

Summary

The condensation of 2-bromofluorene with *d*- or *l*-2-octyl nitrate produced the potassium salts of 9-nitro-2-bromofluorene. These salts were slightly optically active.

Acidification of the salts gave optically inactive

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(12) Courtot, *Ann. chim.*, [10] **14**, 62 (1933).

aci-9-nitro-2-bromofluorene. Treatment with bromine gave 9-nitro-2,9-dibromofluorene which was also optically inactive.

Methylation of the silver salt of 9-nitro-2-bromofluorene gave an unstable nitronic ester which readily decomposed into 2-bromofluorenone oxime and formaldehyde.

The *aci*-nitro form of 9-nitro-2-bromofluorene readily rearranged to the *normal* form. The latter did not absorb bromine whereas the *aci*-form absorbed 50% of the theoretical amount.

URBANA, ILLINOIS RECEIVED AUGUST 2, 1935

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

Some Derivatives of *p*-Fluorophenyl Sulfinic Acid[1]

BY RAYMOND M. HANN

In connection with a study of the action of certain sulfur compounds as possible chemotherapeutic agents in the treatment of pneumonia, a series of derivatives of *p*-fluorophenyl sulfinic acid has been prepared. The sodium salt of *p*-fluorophenyl sulfinic acid was readily obtained from fluorobenzene by the synthesis of Knoevenagel and Kenner[2] and proved to be a suitable material for the introduction of various substituents in the sulfinic acid group. Such compounds as were applicable in regard to solubility and toxicity were tested upon pneumococcus infections in mice by Dr. Sanford Rosenthal, of the Division of Pharmacology, National Institute of Health, but proved to be without therapeutic effect.

Experimental

Sodium *p*-Fluorophenyl Sulfinate Dihydrate.—Dry hydrochloric acid gas was bubbled through an ice-cold suspension of 15 g. of anhydrous aluminum chloride in a solution of 10 g. of fluorobenzene in 25 cc. of carbon disulfide until it was saturated. Dry sulfur dioxide was then introduced in a slow steady stream until the crystalline aluminum chloride was completely changed to a heavy green oily layer (three hours), which became crystalline on standing overnight at room temperature. The reaction mixture was decomposed with 200 cc. of ice water, 20% sodium hydroxide added to strong alkalinity (about 70 cc.), the suspension digested for an hour on the steam-bath, filtered, the soluble aluminum precipitated by passing in carbon dioxide, and, following a second filtration, the mother liquor concentrated to a volume of 50 cc. when a first crop of 12.7 g. of pure salt separated. A second crop, upon further concentration, brought the total yield to 17.0 g. (75% based on dihydrate). Recrystallized from one part of hot water it separated in glistening diamond shaped crystals of the dihydrate.

Anal. Calcd. for $C_6H_4O_2SNaF \cdot 2H_2O$: Na, 10.5; H_2O, 16.5. Found: Na, 10.4; H_2O, 16.7.

Benzyl-ψ-thiourea Salt of *p*-Fluorophenyl Sulfinic Acid.—Cold solutions of 1 g. of benzyl-ψ-thiourea hydrochloride in 10 cc. of 0.25 *N* hydrochloric acid and of 0.9 g. of sodium *p*-fluorophenyl sulfinate in 10 cc. of water were mixed, the resulting thiourea salt filtered and recrystallized from 25 cc. of 0.25 *N* acid, when it separates in elongated prismatic columns showing a melting point of 161° (corr.).

Anal. Calcd. for $C_{14}H_{15}O_2N_2S_2F$: N, 8.6. Found: N, 8.7.

Benzyl-ψ-thiourea Salt of *p*-Fluorophenyl Sulfonic Acid.—A solution of 1 g. of sodium *p*-fluorophenyl sulfinate in 5 cc. of *N* sodium hydroxide was treated dropwise with 5 cc. of 30% hydrogen peroxide, and following the original heating up and gas evolution, it was heated on the steam-bath for one-half hour to complete the oxidation. The oxidized solution was carefully neutralized with *N* hydrochloric acid and added to a solution of 1.1 g. of benzyl-ψ-thiourea hydrochloride in 10 cc. of 0.25 *N* hydrochloric acid. The precipitated salt was filtered and recrystallized from 15 cc. of 0.25 *N* hydrochloric acid, being obtained in brilliant plates, melting at 166° (corr.).

Anal. Calcd. for $C_{14}H_{15}O_3N_2S_2F$: N, 8.2. Found: N, 8.3.

***p*-Fluorophenylphenacyl Sulfone.**—A solution of 1 g. of sodium *p*-fluorophenyl sulfinate in 5 cc. of water and 15 cc. of 95% alcohol was refluxed for fifteen minutes with 1.1 g. of ω-bromoacetophenone and the precipitate which separated on cooling was recrystallized from 30 cc. of 95% alcohol. The sulfone separates in large elongated colorless plates melting at 151° (corr.).

Anal. Calcd. for $C_{14}H_{11}O_3SF$: S, 11.5. Found: S, 11.3.

***p*-Fluorophenyl *p*-Nitrobenzyl Sulfone.**—This sulfone was obtained from the sulfinate and *p*-nitrobenzyl chloride and crystallized from 95% alcohol in slightly yellow brilliant plates melting at 185° (corr.).

Anal. Calcd. for $C_{13}H_{10}O_4NSF$: N, 4.8. Found: N, 5.0.

***p*-Fluorophenyl Sulfone Acetic Acid.**—A solution of 3 g. of sodium *p*-fluorophenyl sulfinate and 1.6 g. of monochloroacetic acid in 15 cc. of water was neutralized with *N* sodium hydroxide, evaporated over a free flame to crystallization and then to dryness on the steam-bath. The dry salt was taken up in 10 cc. of water, acidified to Congo red

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(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

(2) Knoevenagel and Kenner, *Ber.*, **41**, 3315 (1908).

with hydrochloric acid, extracted with ether and the residue remaining after evaporation of the ether recrystallized from benzene when the free acid was obtained in colorless needles melting at 110–111° (corr.).

Anal. Calcd. for $C_8H_7O_4SF$: S, 14.7. Found: S, 14.4.

Benzyl-ψ-thiourea Salt of *p*-Fluorophenyl Sulfone Acetic Acid.—This salt was obtained in microcrystalline glistening prismatic needles melting at 144° (corr.) with decomposition.

Anal. Calcd. for $C_{16}H_{17}O_4N_2S_2F$: N, 7.3; S, 16.7. Found: N, 7.7; S, 16.6.

***p*-Bromophenacyl Ester of *p*-Fluorophenyl Sulfone Acetic Acid.**—This ester crystallizes from 95% alcohol in colorless glistening needles melting at 126° (corr.).

Anal. Calcd. for $C_{16}H_{13}O_5SBrF$: S, 7.7. Found: S, 8.0.

***p*-Fluorophenylsulfonyl Acetone.**—A suspension of 5.5 g. (10% excess) of finely powdered sodium *p*-fluorophenyl sulfinate in 25 cc. of 95% alcohol containing 2.1 g. of monochloroacetone was refluxed for one-half hour, the alcohol driven off by an air current and the oily residue crystallized by trituration with water; yield quantitative.

The sulfonyl acetone was obtained in elongated needle-like plates melting at 66° (corr.) by recrystallization from 10 parts of 95% alcohol.

Anal. Calcd. for $C_9H_9O_3SF$: S, 14.8. Found: S, 14.7.

α-γ-Di-*p*-fluorophenylsulfonyl Acetone.—The difluorophenylsulfonyl ketone was similarly prepared from α-γ-diiodoacetone and crystallized from 95% alcohol in long colorless needles melting at 144° (corr.).

Anal. Calcd. for $C_{15}H_{12}O_5S_2F_2$: S, 17.1. Found: S, 16.8.

Summary

A series of derivatives of *p*-fluorophenyl sulfinic acid has been prepared and characterized.

WASHINGTON, D. C. RECEIVED AUGUST 27, 1935

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

The Chemistry of the Acetylenes. II. Pharmacological Properties of the Acetylenic Linkage

BY G. BRYANT BACHMAN

Although the number of medicinals containing acetylenic linkages which have been prepared is relatively small, the available evidence points to a lesser pharmacological activity for these substances than for the corresponding olefinic and saturated isologs. Shonle[1] has found this to be true of a group of hypnotics of the barbital series, and Gilman and Pickens[2] still earlier report β-diethylaminoethylphenyl propiolate to be intensely irritating rather than anesthetic in its action. In order to investigate this lesser activity of acetylenic compounds more thoroughly and to study further the relative values of aliphatic novocaine analogs,[3] a number of amino esters of α-octynoic, α-octenoic and octanoic acids have been prepared and tested for local anesthetic action on the sciatic nerves of frogs. From the results obtained it may be said that in so far as sensory anesthesia is concerned, the same order of activity holds for these anesthetics as holds for the hypnotics tested by Shonle. On the motor and sensory nerves of frogs the compounds tested exhibited a potency comparable to or slightly better than that of novocaine. The octanoic acid esters, however, were the best and the octynoic esters the poorest of the entire group. All of the esters were somewhat irritating although not intensely so. Of the esters of any single acid, those were best having the greatest molecular weight and those poorest having the least molecular weight. On the basis of these results it appears that the local anesthetic effectiveness of novocaine analogs in the aliphatic series is directly proportional to the molecular weight of the alcohol portion of the molecule (probably within limits) and inversely proportional to the degree of unsaturation in the acid portion of the molecule. None of the compounds tested in this work exhibited anesthetic action on mucus membranes.

Experimental

The esters were prepared by cautiously adding a slight excess of the acid chlorides in an equal volume of benzene to the amino alcohols also in benzene. The mixture was then refluxed for one hour, poured into water and made alkaline with aqueous potassium hydroxide. The benzene solution of the ester was separated, dried and then distilled under diminished pressure.

α-Octenic acid chloride, a new compound, was prepared by reaction of the acid with thionyl chlo-

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[1] Shonle, *J. Ind. Eng. Chem.*, **23**, 1104 (1931); Shonle and Waldo, THIS JOURNAL, **55**, 4649 (1933).

[2] Gilman and Pickens, *ibid.*, **47**, 245 (1925).

[3] *Cf.* Brill and Bulow, *ibid.*, **55**, 2059 (1933).

TABLE I

PROPERTIES OF SOME AMINO ESTERS OF OCTANOIC, α-OCTENOIC AND α-OCTYNOIC ACIDS

Ester	B. p., °C.	Mm.	n^{20}_D	d^{20}_4	Anal. for N		Time, min., for anesthesia	
					Calcd.	Found	Sensory	Motor
$C_5H_{11}CH_2CH_2COOCH_2CH_2N(C_2H_5)_2$	162–164	20	1.4390	0.883	5.76	5.63	4	23.5
$C_5H_{11}CH_2CH_2COOCH_2CH_2CH_2N(C_2H_5)_2$	178–181	20	1.4405	.886	5.45	5.19	4	12.5
$C_5H_{11}CH_2CH_2COOCH_2CH_2CH_2N(C_4H_9)_2$	212–215	20	1.4451	.876	4.47	4.21	3.5	11.5
$C_5H_{11}CH{=}CHCOOCH_2CH_2N(C_2H_5)_2$	171–173	20	1.4560	.901	5.81	5.47	6.5	15
$C_5H_{11}CH{=}CHCOOCH_2CH_2CH_2N(C_2H_5)_2$	183–186	20	1.4565	.901	5.49	5.54	5	27.5
$C_5H_{11}CH{=}CHCOOCH_2CH_2CH_2N(C_4H_9)_2$	217–220	20	1.4574	.888	4.50	4.25	4	10
$C_5H_{11}C{\equiv}CCOOCH_2CH_2N(C_2H_5)_2$	150–152	7	1.4723	.916	5.86	5.81	8	24
$C_5H_{11}C{\equiv}CCOOCH_2CH_2CH_2N(C_2H_5)_2$	164–166	7	1.4739	.921	5.53	5.62	6	22
$C_5H_{11}C{\equiv}CCOOCH_2CH_2CH_2N(C_4H_9)_2$	193–195	7	1.4750	.900	4.53	4.41	4.5	10
Novocaine							8	15

ride and has the constants: b. p. 109–111° (30 mm.); n^{20}_D 1.4649; d^{20}_4 0.9841. *Anal.* Calcd. for $C_8H_{13}OCl$: Cl, 22.13. Found: Cl, 22.10, 22.21.

The table lists the properties and analyses of the compounds prepared and shows their relative anesthetic activity as measured by the time elapsed between contact with the drug and complete anesthesia.[4]

Some difficulty was experienced in obtaining satisfactory aqueous solutions of the compounds tested. Apparently excess acid (hydrochloric) was necessary to attain complete solution and undoubtedly this contributed to the irritating qualities noted for each compound. Novocaine is included in the table for the sake of comparison.

Summary

1. A number of amino esters of octanoic, α-octenoic, and α-octynoic acids have been prepared and their local anesthetic powers reported.

2. Within the limits of the compounds here described it appears that the anesthetic power of these amino esters is directly proportional to the molecular weight of the amino alcohol part of the molecule and inversely proportional to the degree of unsaturation of the acid.

COLUMBUS, OHIO RECEIVED AUGUST 10, 1935

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[4] The writer is indebted to Dr. T. H. Rider of the Wm. S. Merrell Company of Cincinnati for the pharmacological testing.

[CONTRIBUTION FROM THE D. I. MENDELEYEFF CHEMICAL-TECHNOLOGICAL INSTITUTE]

Thermodynamical Calculations of Solubilities of Nitrogen and Hydrogen in Water at High Pressures

BY I. R. KRICHEVSKY AND J. S. KASARNOVSKY

Much attention is given nowadays to the experimental investigation of solubilities of gases at high pressures in liquids, chiefly in water and liquid ammonia. This paper gives a method of calculation of solubilities of gases in one special, but very important, case where the solubility of gas is small and the vapor pressure of solvent is not great. The solubilities in water of such important technical gases as hydrogen, nitrogen, carbon oxide, methane, oxygen and helium fall in this classification.

When the concentration of a solute is small the fugacity of the solvent can be calculated by means of Raoult's law, the fugacities of the components being connected according to the equation of Gibbs–Duhem

$$N_1 \mathrm{d} \ln f_1 + N_2 \mathrm{d} \ln f_2 = 0 \qquad (1)$$

(N_1, N_2 and f_1, f_2 are mole fractions and fugacities of either solvent and solute); it is not difficult to prove that there exists direct proportionality between f_2 and N_2, known as Henry's law

$$f_2 = KN_2 \qquad (2)$$

where K is Henry's coefficient.

Wiebe, Gaddy and Heins[1] nevertheless have shown that their experimental data on the solubility of nitrogen in water are poorly expressed by the equation (2). This is also true for the data on the solubility of hydrogen in water. The solubilities of these gases in water are so small, even at a pressure of 1000 atmospheres, that the fugacity of water in solution can be calculated according to Raoult's law. From this, however, it would seem to follow as a thermodynamical

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[1] Wiebe, Gaddy and Heins, THIS JOURNAL, **55**, 947 (1933).

consequence that Henry's law would be obligatory for the dissolved gas. But the experimental data are evidently in contradiction to this theoretical deduction.

We shall prove that the stated contradiction occurs on account of erroneous application of the Gibbs–Duhem equation. This equation assumes that the pressure remains constant throughout the integration. In case the pressure changes but little it is possible to disregard this change as is usually done, sometimes unconsciously, when examining, for instance, the solubilities of gases at small pressures. On the contrary, when the solubilities of gases are measured at high pressures there can be no question of disregarding its influence.

It is easy to show how the usual equation of Henry has to be corrected in order to predict the solubilities of gases even at very high pressures.

When the concentration of dissolved gas changes from $N_2 = 0$ to a certain N_2, the pressure rises from $p_1°$ to P, where $p_1°$ is the vapor pressure of the pure solvent, and P is the total pressure at a concentration N_2. Agreeing that the vapor pressure of the solvent is not great, the total pressure can without any sensible error be identified with the partial pressure of gas. In order to eliminate the influence of the change of pressure on the solubility, we shall expose the solution to tension (negative pressure) which is every moment equal to $P - p_1°$. The tension must naturally affect only the solution, and not the gas phase. At such a compensation the pressure upon the solution remains constant and equal to the primary pressure $p_1°$. The integration of the Gibbs–Duhem equation becomes lawful, and supposing that the fugacity of the solvent is submitted to Raoult's law, we must obtain for the dissolved gas Henry's law

$$f_2 = KN_2' \qquad (3)$$

N_2' is, certainly, not the experimentally measured concentration of the soluted gas. N_2' is the concentration which could be obtained through compensation of the gas pressure by means of corresponding tension of the solution. K is the usual Henry's coefficient, because it is in principle determined at the zero partial pressure of gas.

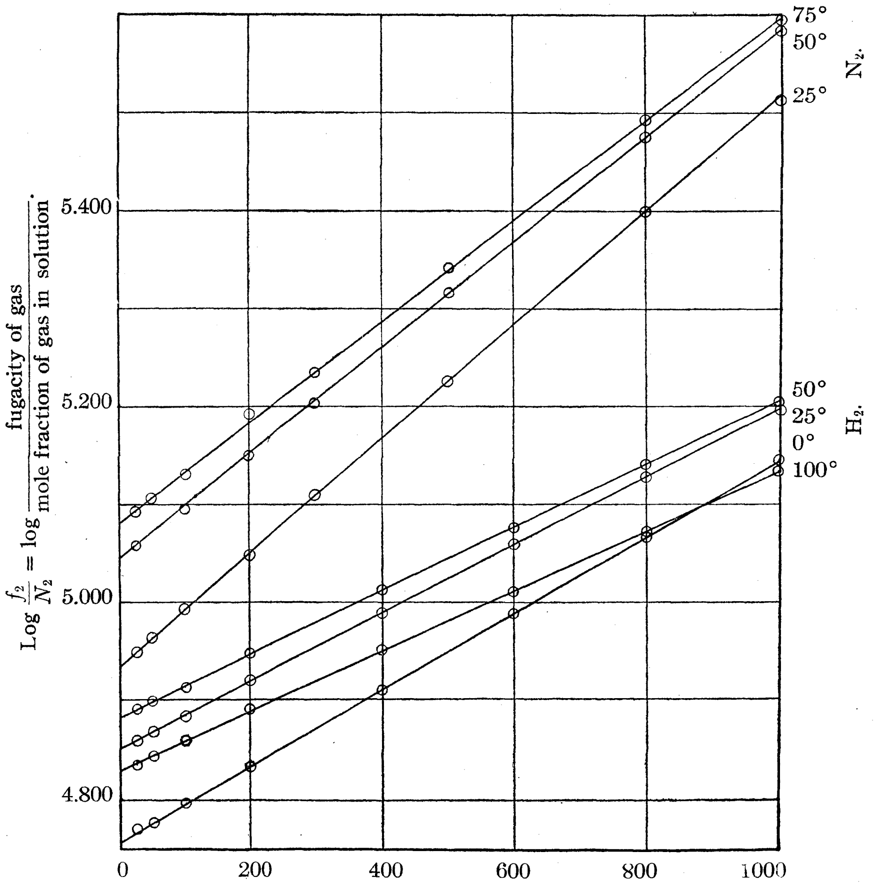

Fig. 1.

The transition from N_2' to N_2 can be made by means of the well known equation

$$\left(\frac{\partial \overline{F}_2}{\partial p}\right)_T = \bar{v}_2 \qquad (4)$$

where $\overline{F}_2$ is the partial molal free energy of the dissolved gas and $\bar{v}_2$ is its partial molal volume.

Since the concentration of gas in solution is small

$$\mathrm{d}\overline{F}_2 = RT\,\mathrm{d}\ln N_2 \qquad (5)$$

Substitution from equation (5) in the equation (4) gives us

$$\left(\frac{\partial \ln N_2}{\partial P}\right)_T = \frac{\bar{v}_2}{RT} \tag{6}$$

Integration of equation (6) by the supposition of independence of $\bar{v}_2$ from pressure gives

$$\ln N_2 = \ln N_2' - \frac{\bar{v}_2 P}{RT} \tag{7}$$

From equations (3) and (7) we receive

$$\lg \frac{f_2}{N_2} = \lg K + \frac{\bar{v}_2 P}{2.303\ RT} \tag{8}$$

TABLE I

SOLUBILITY OF NITROGEN IN WATER

	25° $N_2 \times 10^3$		50° $N_2 \times 10^3$		75° $N_2 \times 10^3$		100° $N_2 \times 10^3$	
P, atm.	Obs.	Calcd.[a]	Obs.	Calcd.[b]	Obs.	Calcd.[c]	Obs.	Calcd.[d]
25	0.280	0.281	0.219	0.221	0.204	0.204	0.214	0.212
50	.542	.542	.436	.420	.397	.397	.415	.415
100	1.015	1.014	.8124	.8121	.760	.752	.792	.789
200	1.812	1.804	1.470	1.473	1.391	1.386	1.463	1.467
300	2.455	2.463	2.034	2.037	1.937	1.932	2.043	2.056
500	3.558	3.560	2.982	2.996	2.873	2.881	3.046	3.064
800	4.909	4.924	4.181	4.188	4.054	4.054	4.296	4.295
1000	5.720	5.710	4.900	4.879	4.750	4.736	5.006	4.981

[a] From $\lg f_2/N_2 = 4.9333 + 0.0005813\ P$. [b] From $\lg f_2/N_2 = 5.0398 + 0.0005455\ P$. [c] From $\lg f_2/N_2 = 5.0787 + 0.0005184\ P$. [d] From $\lg f_2/N_2 = 5.0608 + 0.0005130\ P$.

TABLE II

SOLUBILITY OF HYDROGEN IN WATER

	0° $N_2 \times 10^3$		25° $N_2 \times 10^3$		50° $n_2 \times 10^3$		100° $N_2 \times 10^3$	
P, atm.	Obs.	Calcd.[a]	Obs.	Calcd.[b]	Obs.	Calcd.[c]	Obs.	Calcd.[d]
25	0.4306	0.4344	0.350	0.350	0.3265	0.3263	0.3705	0.3673
50	.8635	.8631	.696	.698	.6493	.6493	.7315	.7309
100	1.709	1.703	1.386	1.380	1.293	1.289	1.448	1.449
200	3.351	3.331	2.720	2.720	2.536	2.538	2.838	2.846
400	6.390	6.395	5.250	5.250	4.929	4.935	5.466	5.507
600	9.252	9.235	7.640	7.650	7.192	7.209	7.961	7.992
800	11.91	11.87	9.910	9.918	9.337	9.359	10.32	10.31
1000	14.25	14.32	12.06	12.03	11.44	11.40	12.51	12.45

[a] From $\lg f_2/N_2 = 4.7569 + 0.0003866\ P$. [b] From $\lg f_2/N_2 = 4.851 + 0.0003465\ P$. [c] From $\lg f_2/N_2 = 4.8822 + 0.0003210\ P$. [d] From $\lg f_2/N_2 = 4.8307 + 0.0003035\ P$.

The experimental data on the solubilities of nitrogen[1] and hydrogen[2] in water agree very well with equation (8) (see Tables I and II and Fig. 1). The values of the fugacities of nitrogen and hydrogen are taken from the papers of Deming and Shupe[3] and Ångström[4] measured the increase of the volume of water due to solubility of nitrogen and hydrogen in water at 1 atmosphere.

We have calculated from his data the partial molal volumes of nitrogen and hydrogen in water solution and they are in good agreement with the values calculated from equation (8) (Table III).

For the integration of equation (6) we assumed the partial molal volume of dissolved gas to be independent of pressure, and the errors caused by this assumption appeared beyond the range of the accuracy of experimental measurements. Generally $\bar{v}_2$ is to be regarded as a function of pressure. For instance, it may be assumed to follow the simple equation

$$\bar{v}_2 = \bar{v}_2{}^\circ - \beta P \tag{9}$$

where $\bar{v}_2{}^\circ$ is the partial molal volume at zero pressure and β is the coefficient of compressibility. Differently from pure substances β can have for the partial molal volume a negative value.[5]

TABLE III

PARTIAL MOLAL VOLUMES OF NITROGEN AND HYDROGEN IN WATER SOLUTION

	0°	25°	50°	75°	100°
			Nitrogen, cc.		
$\bar{v}_2$ obsd.	32.5				
$\bar{v}_2$ calcd.		32.8	33.4	34.1	36.2
			Hydrogen, cc.		
$\bar{v}_2$ obsd.	23.9				
$\bar{v}_2$ calcd.	20.0	19.5	19.6		21.4

In view of the accuracy of determination of the solubility of gases, it may not be very advisable

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(2) Wiebe and Gaddy, THIS JOURNAL, **56,** 76 (1934).

(3) Deming and Shupe, *Phys. Rev.*, **37,** 638 (1931); **40,** 848 (1932).

(4) Ångström, *Wied. Ann.*, **15,** 297 (1882).

(5) Adams, THIS JOURNAL, **53,** 3769 (1931); **54,** 2229 (1932).

to use equation (9) for the purpose of integrating equation (6).

It may be pointed out that our use of Raoult's law necessitates the independence of $\bar{v}_2$ from N_2.[6]

Equation (8) can also be applied to calculate the mixed solubility of slightly soluble gases, such as the solubility in water of a 3:1 mixture of hydrogen and nitrogen. In such a case in equation (8) f_2 is the fugacity of one of the gases, N_2 is its mole fraction in solution and P is total pressure. Having no experimental data about the mixed solubility of gases, we are unable to verify equation (8) by concrete examples.

Equation (8) can be used also to solve the inverse problem of calculating the fugacity of pure and mixed gases.

Summary

1. A thermodynamical equation is given which allows the calculation of the solubility of slightly soluble gases in solvents with small vapor pressure.

2. The deduced equation is verified in examples of solubilities of nitrogen and hydrogen in water at a pressure up to 1000 atmospheres and temperatures from 0 to 100°.

3. Partial molal volumes of nitrogen and hydrogen in their water solutions are calculated.

4. The possibility of calculation of the fugacity of gases on account of their solubility is shown.

MOSCOW, U. S. S. R. RECEIVED MAY 27, 1935

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[6] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 222.

[CONTRIBUTION FROM THE D. I. MENDELEYEFF CHEMICAL-TECHNOLOGICAL INSTITUTE]

Partial Molal Quantities in an Infinitely Dilute Solution

BY I. R. KRICHEVSKY AND J. S. KASARNOVSKY

The partial molal quantities g_1 and g_2 and the composition of a binary solution, expressed in mole fractions, N_1 and N_2, are connected with each other by a well-known equation, which it will be convenient for the purpose of further argumentation to set forth as follows

$$\frac{\partial \bar{g}_1}{\partial N_2}\Big/\frac{\partial \bar{g}_2}{\partial N_2} = -\frac{N_2}{N_1} \qquad (1)$$

This equation has been submitted by Lewis and Randall for the case of an infinitely dilute solution to a special analysis. "In an infinitely dilute solution of X_2 in X_1, where we may write $N_2/N_1 = 0$, it is evident that either $\partial\bar{g}_1/\partial N_2$ is zero, or $\partial\bar{g}_2/\partial N_2$ is infinite. In other words, when N_2 is zero either the curve $\bar{g}_1$ becomes horizontal, or the curve of $\bar{g}_2$ becomes vertical."[1]

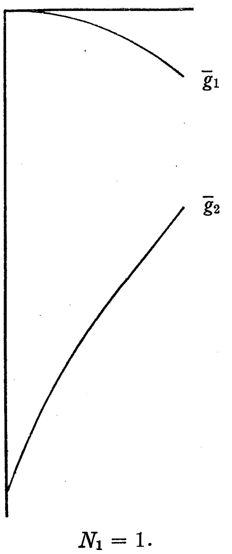

Fig. 1.

The analysis given by Lewis and Randall does not exhaust the question, inasmuch as mathematically (equation (1) is not a thermodynamical one) three other cases are possible: (1) $\partial\bar{g}_1/\partial N_2$ is zero and $\partial\bar{g}_2/\partial N_2$ is zero; (2) $\partial\bar{g}_1/\partial N_2$ is zero and $\partial\bar{g}_2/\partial N_2$ is infinite; (3) $\partial\bar{g}_1/\partial N_2$ is infinite and $\partial\bar{g}_2/\partial N_2$ is infinite.

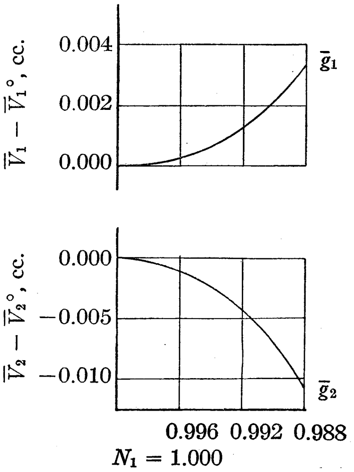

Fig. 2.—Partial molal volumes of water and ethyl alcohol at 40°.

Notwithstanding the fact that, if such allowances are made, the left part of equation (1) turns into indefiniteness, the latter at $N_2 = 0$ may have for its limit zero.

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[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923.

When $\partial \bar{g}_1/\partial N_2$ is tending to attain zero as the first degree of N_2, then at $N_2 = 0$, $\partial \bar{g}_2/\partial N_2$ differs from zero, as it is to be seen from equation (1) (Fig. 1).[2] This is one of the two cases pointed out by Lewis and Randall.

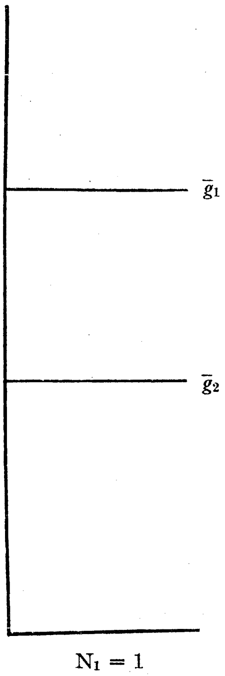

Fig. 3.

When $\partial \bar{g}_1/\partial N_2$ is tending to attain zero as the higher degree of N_2, then $\partial \bar{g}_2/\partial N_2$ is likewise tending to attain zero, but the left part of the equation (1) has for its limit zero (Fig. 2).

Figures 1 and 2 correspond to such partial molal quantities, as for instance the volume (or heat capacity or heat content). According to Fig. 1 in the infinitely dilute solution only the partial molal volume of the solvent is constant. According to Fig. 2 in the infinitely dilute solution the partial molal volumes both of the solvent and solute remain constant. Hence it is natural to turn to such a case, when this constancy extends into the field of finite concentrations (Fig. 3).

As the temperature is rising, *i. e.*, when the abnormality of the solutions is decreasing, it may be expected that the trend will be from Fig. 1 via Fig. 2 to Fig. 3.

The partial molal volumes for the system water–ethyl alcohol[1] (apparently for the temperature 20–25°) calculated by Lewis and Randall correspond to Fig. 1. The calculations made by us of the partial molal volumes for 40° are given in Fig. 2.

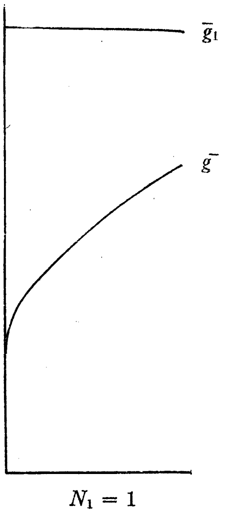

Fig. 4.

With a further rise of temperature it is likely that we shall arrive at Fig. 3.

When $\partial \bar{g}_1/\partial N_2$ is approaching zero as N_2 in a degree below one, then at $N_2 = 0$, $\partial \bar{g}_2/\partial N_2$ is infinite (Fig. 4). The partial molal volumes of the system water–strong electrolyte[3] correspond to this case.

The third case when at $N_2 = 0$, $\partial \bar{g}_1/\partial N_2$ and $\partial \bar{g}_2/\partial N_2$ are infinite, is apparently of no practical value.

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(2) Figure 1 corresponds to Fig. 7 of Lewis and Randall.

(3) Redlich and Rosenfeld, *Z. Elektrochem.*, **37**, 705 (1931).

Moscow, U. S. S. R.

Received May 27, 1935

[Contribution from the Laboratory of Organic Chemistry of the State University of Iowa]

Amides Obtained from Benzenesulfinic Acid

By L. Chas. Raiford and Stewart E. Hazlet

A large number of aryl sulfinic acids have been prepared[1] but few of them have been converted into the corresponding acid chlorides, while the behavior of the latter toward amino compounds has received very little attention.

Hilditch and Smiles[2] obtained benzenesulfinyl chloride in rectangular plates that melted at 38°. Braun and Kaiser[3] may have obtained this product as a solid, but they recorded no melting point. Although they used specially purified starting material, Whalen and Jones[4] could not duplicate Hilditch and Smiles' results, and they did not obtain crystals when they followed Braun and Kaiser's directions. Their product was an oil with a boiling range of 85–90° at 3 to 4 mm.

In the present work, the purpose of which was to test further the action of benzenesulfinyl chloride on amino compounds, the "crude" acid chloride was obtained in nearly quantitative yield by treatment of benzenesulfinic acid[5] with thionyl chloride at room temperature. Distillation, when successful, gave about 83% of a yellow oil at 80–85° and 2 mm. Often rapid and violent decomposition of material took place. Comparison of products obtained by the action of "crude" chlo-

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(1) Gattermann, *Ber.*, **32**, 1136 (1899); Knoevenagel and Kenner, *ibid.*, **41**, 3315 (1908); Claasz, *Ann.*, **380**, 303 (1911).

(2) Hilditch and Smiles, *Ber.*, **41**, 4115 (1908); *J. Chem. Soc.*, **97**, 2585 (1910).

(3) Braun and Kaiser, *Ber.*, **56**, 552 (1923).

(4) Whalen and Jones, This Journal, **47**, 1355 (1925).

(5) Prepared as directed by Gattermann, "Praxis des organischen Chemikers," 18th Auflage, Walter de Gruyter, Berlin, 1923, p. 268.

ride and distilled material showed that little purification was accomplished by distillation.

With the exceptions noted below the sulfinamides listed were obtained by treatment of two molecular proportions of the required amine, dissolved in about three volumes of dry ether, with 1.25 proportions of "crude" benzenesulfinyl chloride in two volumes of ether, with continuous agitation at 0°. The solid that separated was shaken with water to remove amine salt, the residue, if any, was mixed with the ether filtrate and from this the amide was isolated. Analytical

TABLE I

AMIDES FROM BENZENESULFINIC ACID

Starting material	Yield,[a] %	Crystal form[d]	M. p., °C.	Formula	Analyses, % nitrogen	
					Calcd.	Found
o-Chloroaniline[b]	76[c]		107–108	$C_{12}H_{10}ONClS$	5.58	5.40
m-Chloroaniline[b]	Very poor	Tan	106	$C_{12}H_{10}ONClS$	5.58	5.85
p-Chloroaniline	78	Plates[e]	155.5	$C_{12}H_{10}ONClS$	5.58	5.53
o-Bromoaniline[b]	20[c]	Lavendar	108–110	$C_{12}H_{10}ONBrS$	4.73	4.45
m-Bromoaniline	19	Pink[e]	112–114	$C_{12}H_{10}ONBrS$	4.73	4.68
p-Bromoaniline	47	Lavendar[e]	150.5	$C_{12}H_{10}ONBrS$	4.73	4.67
o-Toluidine	29	Pink[e]	124–125	$C_{13}H_{13}ONS$	6.06	5.99
m-Toluidine	44	Needles[e]	102–103	$C_{13}H_{13}ONS$	6.06	5.96
p-Toluidine[b]	56[c]	Yellow plates	100–101	$C_{13}H_{13}ONS$	6.06	5.94
o-Anisidine[b]	Very poor	Purple	113 shrinks 108–113	$C_{13}H_{13}O_2NS$	5.67	5.63
m-Anisidine[b]	Poor	Cubes[e]	133–134	$C_{13}H_{13}O_2NS$	5.67	5.57
p-Anisidine	89	Purple[e]	131	$C_{13}H_{13}O_2NS$	5.67	5.60
p-Aminobenzoic ethyl ester	29		114–115	$C_{15}H_{15}O_3NS$	4.84	4.85
2-Methyl-5-nitroaniline	26	Yellow	133	$C_{13}H_{12}O_3N_2S$	10.14	10.38
β-Naphthylamine	Very poor[g]	Tan rods[e]	143–144	$C_{16}H_{13}ONS$	5.25	5.14
Benzylamine	26	Rods[e]	100–104	$C_{13}H_{13}ONS$	6.06	5.79
4-Aminodiphenyl	High[h]	[f]	165.5	$C_{18}H_{15}ONS$	4.78	4.72
2-Amino-4′-chlorodiphenyl[i]	Very poor[j]	Yellow plates	206	$C_{18}H_{14}ONClS$	4.28	3.89
4-Amino-4′-chlorodiphenyl[i]	Very poor[k]	Pink	165–166	$C_{18}H_{14}ONClS$	4.28	4.05

[a] Unless otherwise noted, yields represent purified material. [b] The amide was ether soluble, and was obtained from the filtrate after removal of the amine hydrochloride by filtration. [c] Represents crude product. [d] When no crystal form is specified, the substance is amorphous; no entry indicates colorless. [e] Crystallized from dilute alcohol. When not designated, a chloroform-ligroin (60–80°) mixture was used. [f] Crystallized from methanol. [g] Largely hydrolyzed during recrystallization. [h] Amide was separated from amine salt by shaking with a mixture of chloroform and water. Treatment of chloroform solution with ligroin precipitated the amide. [i] Prepared in pyridine solution. [j] Reaction mixture stood overnight before being worked up. [k] Reaction seemed complete in half an hour.

TABLE II

ANILIDES OF BENZENESULFONIC ACID

Starting material	Yield, %	Crystal form	M. p., °C.	Formula	Analyses, % nitrogen	
					Calcd.	Found
o-Bromoaniline	72[e]	Needles[a]	130–131	$C_{12}H_{10}O_2NBrS$	4.48	4.47
m-Bromoaniline	69[e]	Plates	117.5–118.5	$C_{11}H_{10}O_2NBrS$	4.48	4.51
o-Toluidine	97[e]	Laven. plates	122–123	$C_{13}H_{13}O_2NS$[g]	..	..
m-Anisidine	Nearly quant.[e]	Needles	82.5–83.5	$C_{13}H_{13}O_3NS$	5.32	5.26
p-Aminobenzoic ethyl ester	Nearly quant.[e]	Plates	183.5–184	$C_{15}H_{15}O_4NS$	4.59	4.46
2-Methyl-5-nitroaniline	88[f]	Cubes	175–176[c]	$C_{13}H_{12}O_4N_2S$	9.61	9.51[d]
4-Aminodiphenyl	67[f]	Needles	147–148	$C_{18}H_{15}O_2NS$	4.53	4.52
2-Amino-4′-chlorodiphenyl	74[f]	Prisms	136–138	$C_{18}H_{14}O_2NClS$	4.07	3.97
4-Amino-4′-chlorodiphenyl	Nearly quant.[f]	Powder[b]	145–145.5	$C_{18}H_{14}O_2NClS$	4.07	4.04

[a] Crystallized from alcohol; in other cases dilute alcohol was used. [b] Chloroform-ligroin (60–80°). [c] Morgan and Micklethwait [*J. Chem. Soc.*, **89**, 1294 (1906)] found 172° and satisfactory analysis for a product obtained by boiling a toluene solution of the amine and acid chloride for three hours, evaporating the mixture to dryness, extracting the residue with sodium carbonate solution and precipitating the amide by acid. No yield was given. In the present work heating ether solution of the reactants, followed by standing, gave no change. Pyridine was then used as a solvent. [d] Determination made by semimicro Dumas method. [e] Reaction carried out in ether solution. [f] The reaction carried out in pyridine. [g] Previously obtained and analyzed by Hinsberg [*Ann.*, **265**, 184 (1891)] who recorded no yield. It was prepared in the present work for comparison with the sulfinamide of the same base, m. p. 124–125°. A mixture of the two melted at 85–95°.

data for these products are given in Table I.

For purposes of comparison of physical properties a number of corresponding sulfonamides were prepared. Data for them are given in Table II.

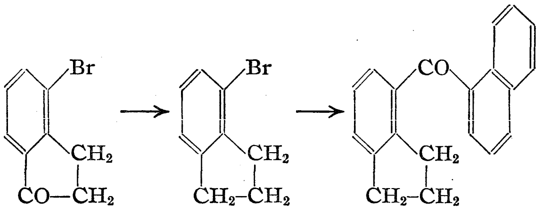
IOWA CITY, IOWA RECEIVED MARCH 23, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

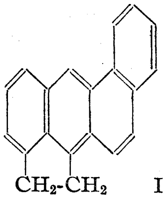
Cholanthrene and Related Hydrocarbons

BY LOUIS F. FIESER AND ARNOLD M. SELIGMAN

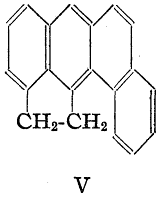
The synthesis of cholanthrene by three different methods has been reported recently by Cook and his associates.[1] We have found that the modified Elbs synthesis[2] provides still another route to this interesting hydrocarbon. The ketone III was prepared from the known 4-bromohydrindone-1 (I)[3] as indicated, and on pyrolysis there was obtained a hydrocarbon corresponding to the description[1] of cholanthrene, IV. From the ketone resulting from the reaction of the Grignard compound of II with β-naphthoyl chloride, the isomeric hydrocarbon V was obtained.



I II III



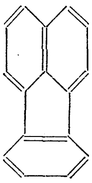
IV



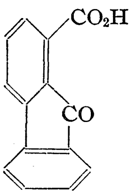
V

Dr. M. J. Shear has observed that crystalline cholanthrene injected subcutaneously in mice produced effects similar to those obtained with methylcholanthrene and in approximately the same time. The hydrocarbon induced ulcerations beginning with the fortieth day and the first tumor, noted on the sixty-second day, took successfully on transplantation. From these preliminary results it appears that a methyl group at C_{20} is of less influence in determining the carcinogenic activity than might have been expected on the basis of the available data.[4]

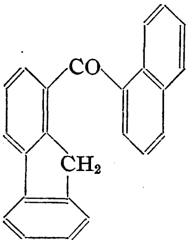
Another hydrocarbon having the cholanthrene ring system was obtained very easily starting with fluoranthene (VI) from coal tar. By the methods of Fittig and Liepmann,[5] modified in some details, fluorene-1-carboxylic acid can be prepared in any desired quantity by the oxidation of fluoranthene, followed by the reduction of the resulting keto acid VII. 1-(α-Naphthoyl)-fluorene (VIII) was obtained from α-naphthylmagnesium bromide and fluorene-1-carboxylic acid chloride, and on pyrolysis it yielded the hydrocarbon IX.



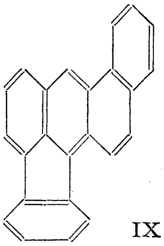
VI



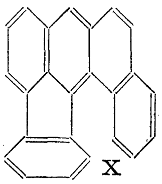
VII



VIII



IX



X

To indicate the relationship to the carcinogenically active parent hydrocarbon, this substance may be called 15,16-benzdehydrocholanthrene.[6]

The Friedel and Crafts reaction of the above acid chloride with naphthalene was investigated, with rather unexpected results. The condensation proceeded poorly in carbon bisulfide, probably because of the sparing solubility of the com-

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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**, 942 (1935).

(3) Miersch, *Ber.*, **25**, 2110 (1892); Mayer, Phipps, Ruppert and Schmitt, *ibid.*, **61**, 1966 (1928).

(4) Cook and co-workers, *Proc. Roy. Soc.* (London), **B111**, 455, 484 (1932); **B117**, 318 (1935).

(5) Fittig and Liepmann, *Ann.*, **200**, 1 (1879).

(6) Fieser and Seligman, THIS JOURNAL, **57**, 1377 (1935).

plex compounds, and there was obtained a mixture which was not separated, but which was found by pyrolysis experiments to contain a considerable proportion of the α-ketone VIII. Using tetrachloroethane the chief reaction product was the higher melting 1-(β-naphthoyl)-fluorene. The results were about the same with nitrobenzene as the solvent. Pyrolysis of the β-ketone afforded the hydrocarbon X.

Experimental Part[7]

4-Bromohydrindone-1 (I) was prepared from *o*-bromohydrocinnamic acid, using the method of ring-closure described by Hoyer,[8] but employing more thionyl chloride. In large-scale experiments the yield of pure ketone, m. p. 97°, was only 70% of the theoretical amount, based on the acid.

Various methods of preparing *o*-bromohydrocinnamic acid were investigated, the one found most satisfactory consisting in the catalytic hydrogenation of *o*-bromocinnamic acid prepared from *o*-bromotoluene by the convenient method of Reich and Chaskelis.[9] The yield reported by these workers (26%) was confirmed. Using material which had been sublimed *in vacuo* the hydrogenation with Adams catalyst proceeded smoothly in absolute alcoholic solution, the acid being largely esterified during the process; yield, 85%. *o*-Bromocinnamic acid was also prepared from *o*-nitrocinnamic acid according to Gabriel,[10] the yields being 89% in the reduction and 67% in the Sandmeyer reaction, but the method requires a much more expensive starting material.

We also investigated the preparation of the desired acid from *o*-bromobenzyl chloride and malonic ester, following the procedure employed previously.[2] The yields were good but the commercial *o*-bromobenzyl chloride, even after repeated careful fractionation, gave rise to unhomogeneous products at every step. The impure *o*-bromohydrocinnamic acid gave a hydrindone preparation which crystallized well but melted persistently low (88°). 4-Bromohydrindene was obtained in a pure condition by repeated fractionation of the mixture obtained on reduction, but with considerable loss of material.

4-Bromohydrindene was prepared in 77% yield by the Clemmensen reduction of pure 4-bromohydrindone-1 by the usual procedure;[2] b. p. 118° at 18 mm.

Anal. Calcd. for C_9H_9Br: C, 54.83; H, 4.60. Found: C, 54.55; H, 4.48.

4-(α-Naphthoyl)-hydrindene (III) was obtained in a form (A) suitable for pyrolysis in 50% yield by the Grignard procedure.[2] On further distillation in vacuum it was obtained as a viscous yellow oil.

Anal. Calcd. for $C_{20}H_{16}O$: C, 88.20; H, 5.93. Found: C, 87.75; H, 5.90.

4-(β-Naphthoyl)-hydrindene was prepared similarly, using β-naphthoyl chloride, in 46% yield: small colorless needles, m. p. 68–69°, from ether–petroleum ether.

Anal. Calcd. for $C_{20}H_{16}O$: C, 88.20; H, 5.93. Found: C, 88.25; H, 6.05.

Cholanthrene (IV).—On pyrolysis of the partially purified ketone III (A) at 400–405° for twenty-five minutes there was obtained, after vacuum distillation and one crystallization from ether–benzene, a pale yellow product melting at 170°; yield, 34%. This material was altered but little on further purification. After passage of a benzene solution through four adsorption towers containing activated alumina, the hydrocarbon was obtained as very faintly yellow plates, m. p. 173–173.5°, corr.

Anal. Calcd. for $C_{20}H_{14}$: C, 94.45; H, 5.55. Found: C, 94.51; H, 5.65.

The *picrate* crystallized from benzene as small, reddish-purple needles, m. p. 169–170°, corr.

Anal. Calcd. for $C_{26}H_{17}O_7N_3$: N, 8.69. Found: N, 8.75.

8,9-Dimethylene-1,2-benzanthracene (V) was prepared similarly, the melting point at various stages of purification being as follows: one crystallization, 172°; chromatographic purification, 173°; treatment with sulfuric acid in benzene solution, very faintly yellow plates from benzene–ether, m. p. 174° (176.5–177°, corr.).

Anal. Calcd. for $C_{20}H_{14}$: C, 94.45; H, 5.55. Found: C, 94.48; H, 5.65.

The *picrate* forms purple-black needles from benzene, m. p. 158–159°, corr.

Anal. Calcd. for $C_{26}H_{17}O_7N_3$: N, 8.69. Found: N, 8.86, 8.98.

Fluorenone-1-carboxylic acid[5] was prepared by adding slowly a solution of 340 g. of chromic anhydride in 300 cc. of water and 200 cc. of glacial acetic acid to a solution of 100 g. of fluoranthene in 2.5 liters of glacial acetic acid, keeping the mixture just below the boiling point. After standing for several hours the solution was heated to the boiling point for one hour and then diluted with about 15 liters of water. The crude acid was collected and extracted with cold alkali, precipitated, and heated with an aqueous suspension of barium carbonate until no further material could be extracted. On acidifying the filtrate, 56 g. (48%) of orange, crystalline material, m. p. 191–193°, was obtained. For reduction to *fluorene-1-carboxylic acid*, 60 g. of the keto acid was added in portions to a mixture of 1920 g. of 4% sodium amalgam and 2 l. of water, heated on the steam-bath. The solution was kept near the neutral point by the frequent addition of hydrochloric acid, a fresh portion of keto acid being introduced only after the precipitate which formed on acidification was nearly colorless. The mixture was heated for two hours after the addition was complete, when it was cooled and filtered. The crude acid which precipitated on acidification was extracted as the barium salt, from which it was recovered in a colorless condition; yield 47.5 g. (84%). After sublimation *in vacuo* the acid (m. p. 245°) was refluxed with a large excess of thionyl chloride for two hours, the excess reagent was removed and the acid chloride was distilled at diminished pressure; yield, 83%.

1-(α-Naphthoyl)-fluorene (VIII).—A solution of the Grignard reagent from 15 g. of α-bromonaphthalene in 70 cc. of ether was added slowly to 26.5 g. of fluorene-1-car-

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[7] Analyses by Mrs. G. M. Wellwood, Dr. R. G. Larsen and Mr. E. L. Martin.

[8] Hoyer, *J. prakt. Chem.*, **139**, 242 (1934).

[9] Reich and Chaskelis, *Bull. soc. chim.*, [4] **19**, 287 (1916).

[10] Gabriel, *Ber.*, **15**, 2294 (1882).

boxylic acid chloride in 250 cc. of dry benzene and 50 cc. of ether at 0°. The mixture was slowly brought to 35–40° and kept at that temperature overnight. The crude ketone was subjected to thorough steam distillation from an alkaline medium and then extracted with ether–benzene, distilled at the oil pump, and crystallized from ether–petroleum ether; colorless needles, m. p. 108–110°; 12.3 g. (56% yield, 10 g. of fluorene-1-carboxylic acid being recovered from the alkaline solution).

The ketone is very readily soluble in benzene, moderately soluble in ether, and sparingly soluble in alcohol. Recrystallized from benzene–ether it formed slender needles, m. p. 113–114°.

Anal. Calcd. for $C_{24}H_{16}O$: C, 89.97; H, 5.04. Found: C, 90.02; H, 5.15.

15,16-Benz-dehydrocholanthrene (IX).—Four grams of the above ketone was heated for twenty-five minutes at 415° under nitrogen and the product was distilled in vacuum and crystallized once from benzene; yield, 2.25 g. (60%) of orange-red material, m. p. 177°. Purification by chromatographic adsorption was more tedious and wasteful than with sulfuric acid and gave no better material. On shaking a dilute benzene solution of the hydrocarbon with small portions of sulfuric acid until the acid acquired only a yellow color, the extraneous red material was removed with little loss of product. The purified hydrocarbon crystallized from benzene, in which it is only moderately soluble, as bright yellow, cottony needles, m. p. 181–181.3° corr.

Anal. Calcd. for $C_{24}H_{14}$: C, 95.33; H, 4.67. Found: C, 95.23; H, 4.98.

The *picrate* crystallizes from benzene as small, brick-red needles, m. p. 174.5–175.5°, corr.

Anal. Calcd. for $C_{30}H_{17}O_7N_3$: N, 7.91. Found: N, 8.22.

1-(β-Naphthoyl)-fluorene was the chief product of the reaction of 14.5 g. of fluorene-1-carboxylic acid chloride with 9 g. of naphthalene, and 9.2 g. of aluminum chloride in 300 cc. of tetrachloroethane, the mixture being initially at 5–10°, then at room temperature. The crude ketone was heated with acetone and alkali in order to hydrolyze unchanged acid chloride, 3.9 g. of acid being recovered after distilling the solvent and extracting the ketone with ether–benzene. After distillation *in vacuo*, one crystallization from benzene–ligroin gave 8 g. of the nearly pure β-ketone, m. p. 145–150°; total yield, 12.5 g. (84%). After several crystallizations of the first crop from benzene–ether the substance formed clusters of pale yellow needles, m. p. 159–162°. The compound is considerably less soluble than the α-isomer.

Anal. Calcd. for $C_{24}H_{16}O$: C, 89.97; H, 5.04. Found: C, 89.97; H, 5.25.

1′,2′-Naphtho-1,2-fluoranthene (X).—The pyrolysis of the above ketone proceeded as in the case of the α-isomer, but the hydrocarbon, which is considerably more soluble than IX, is best purified with the use of an adsorption tower. It crystallized from benzene–ether in the form of flat, golden yellow needles, m. p. 178–179°, corr.

Anal. Calcd. for $C_{24}H_{14}$: C, 95.33; H, 4.67. Found: C, 95.25; H, 5.04.

The *picrate* crystallizes from benzene in the form of crimson needles melting at 181–182° corr.

Anal. Calcd. for $C_{30}H_{17}O_7N_3$: N, 7.91. Found: N, 8.16.

Summary

Cholanthrene and three additional hydrocarbons of the 1,2-benzanthracene series have been prepared by the modified Elbs synthesis.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS.
RECEIVED AUGUST 10, 1935

[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

Halogenation of Phenolsulfonic Acids in Nitrobenzene

BY RALPH C. HUSTON AND ARTHUR H. NEELEY[1]

The replacement of sulfonic acid groups of phenols with nitro groups or halogen takes place with rapidity in the presence of aqueous acid.[2,3] If, however, the reaction is carried on in alkaline solution this group is rendered stable and serves as an effective blocking agent.[4,5]

Fuming sulfuric acid has been used with more or less success in the preparation of 2-nitroresorcinol[6] and to protect the four and six positions of *m*-cresol during nitration.[7,8] Good yields of 2-bromo-*m*-cresol[9] and 2-chloro-*m*-cresol[10] were obtained in this Laboratory by brominating or chlorinating *m*-cresol directly with one mole of halogen in four volumes of fuming sulfuric acid and then removing the sulfonic acid groups by hydrolysis with superheated steam at 180–200°.

Numerous attempts to adapt this method to the preparation of 2,6-dibromophenol and 2-

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[1] Presented in partial fulfilment of the requirements for the Ph.D. degree.

[2] Datta and Bhoumik, THIS JOURNAL, **43**, 303 (1921).

[3] Datta and Mitter, *ibid.*, **41**, 2033 (1919).

[4] Tanaki and Kutani, *J. Pharm. Soc. Japan*, **541**, 196 (1927); *C. A.*, **21**, 2255 (1927).

[5] Huston and Ballard, "Organic Syntheses," John Wiley and Sons, Inc., 440 Fourth Ave., New York City, 1934.

[6] Kauffman and DePay, *Ber.*, **37**, 725 (1904).

[7] Gibson, *J. Chem. Soc.*, **123**, 1269 (1923).

[8] Hodgson and Beard, *ibid.*, **127**, 498 (1925).

[9] Huston and Peterson, THIS JOURNAL, **55**, 3880 (1933).

[10] Huston and Chen, *ibid.*, **55**, 4214 (1933).

bromophenol failed to give satisfactory yields of either compound but indicated that the halogenation might take place as desired if carried out in an inert anhydrous solvent. Accordingly a number of runs were made in various solvents including petroleum ether, gasoline, kerosene and nitrobenzene. It was found that freshly distilled nitrobenzene was very well suited to the purpose and the following procedure was developed which gave excellent yields of 2,6-dibromophenol. Slight modification gave satisfactory yields of 2-bromophenol, 2,6-dichlorophenol or 2-chlorophenol.

2,6-Dibromophenol and 2-Bromophenol.—A mixture of 31.3 g. (one-third mole) of phenol and 50 g. of concentrated sulfuric acid (d. 1.84) was heated with stirring at 100–110° for two hours on an oil-bath. It was cooled and 100 g. of freshly distilled nitrobenzene added. Cooling was continued while 15 g. of fuming sulfuric acid (49%) was added at such a rate that the temperature did not rise above 10°. One hundred seven grams (two-thirds mole) of bromine and 50 g. of nitrobenzene was added dropwise over a period of two hours and stirring was continued for an hour to complete bromination. One liter of water, in which 5–10 g. of sodium bisulfite had been dissolved, was added. The water and reaction mixture was thoroughly stirred for fifteen minutes to facilitate extraction of the brominated phenol sulfonic acids. For the most part, the tribromophenol remained in the nitrobenzene. This was drawn off by means of a separating funnel and the solution of sulfonic acids was evaporated from a 2-liter flask, suitably equipped for steam distillation, on an oil-bath maintained at 200°. The distillate obtained during the evaporation contained a small amount of nitrobenzene and was discarded. When the temperature of the sulfonic acid solution reached 115°, steam, superheated in a copper coil, was passed through it. The temperature of the oil-bath was maintained at 200, while the temperature of the contents of the flask continued to rise to 175–180° during hydrolysis. The brominated phenols were extracted from the distillate with ether and the phenol residue, after evaporation of the ether, was distilled under reduced pressure 4 mm.) from a modified Claisen flask having a 35 cm. column. Under these conditions a 10.4% yield of 2-bromophenol boiling at 55–60° (4 mm.)—190–191° (740 mm.)—and a 72.7% yield of 2,6-dibromophenol (m. p. 55–56°) boiling at 80–90° (4 mm.)—255–256° (740 mm.)—were obtained. Increasing amounts of sulfuric acid used in succeeding runs gave increasing amounts of 2-bromophenol and decreasing amounts of 2,6-dibromophenol. With 95 g. of sulfuric acid a minimum yield of 9.5% of 2,6-dibromophenol and a maximum yield of 46.5% of 2-bromophenol were obtained. Gradual reduction of bromine as the amount of sulfuric acid was increased did not change the yields.

2,6-Dichlorophenol, 2-Chlorophenol.—Reactants were used in the same quantities and under the same conditions as in the preparation of bromo derivatives except that 200 g. of nitrobenzene was used and the nitrobenzene solution of sulfonic acids was maintained at 55° while chlorine was passed in until no further reaction took place. A number of runs made with increasing amounts of sulfuric acid, gave increasing amounts of 2-chlorophenol and decreasing amounts of 2,6-dichlorophenol. The use of 68 g. of sulfuric acid gave a maximum yield of 70.3% of 2,6-dichlorophenol (m. p. 66–67°) boiling at 80–85° (4 mm.)—219–220° (740 mm.)—and a minimum yield of 17% of 2-chlorophenol boiling at 50–55° (4 mm.)—177–178° (740 mm.). Minimum yields of 24% of 2,6-dichlorophenol and maximum yields of 72% of 2-chlorophenol were obtained when 100 g. of sulfuric acid was used.

Anal. Calcd. for $C_6H_4OCl_2$: Cl, 43.5. Found: Cl, 43.4.

6-Bromo-*o*-cresol.—Bromination of 36 g. of *o*-cresol at 5–10°, using 55 g. of concentrated sulfuric acid, 100 g. of nitrobenzene and 60 g. of bromine in 50 g. of nitrobenzene, gave a 60% yield of crude 6-bromo-*o*-cresol boiling at 55–65° (4 mm.) which contained about 8% *o*-cresol. When redistilled through a 90-cm. column (surrounded by an evacuated jacket) a pure product was obtained, b. p. 206–207° (740 mm.).

Anal. Calcd. for C_7H_7OBr: Br, 42.77. Found: Br, 42.3.

A small amount of 4,6-dibromo-*o*-cresol (13%), which boiled at 105° (4 mm.), was obtained.

6-Chloro-*o*-cresol.—Thirty-six grams of *o*-cresol chlorinated at 55°, using 60 g. of concentrated sulfuric acid and 200 g. of nitrobenzene, yielded 30% of 6-chloro-*o*-cresol boiling at 45–50° (4 mm.)—188–189° (740 mm.)—and 12% of 4,6-dichloro-*o*-cresol boiling at 73–78° (4 mm.).

2-Bromo-*m*-cresol, 4-Bromo-*m*-cresol and 2,6-Dibromo-*m*-cresol.—Several runs were carried out using 36 g. of *m*-cresol, 36 g. of concentrated sulfuric acid[11] and other reagents in the amounts given in the procedure for bromophenols. It was found necessary to brominate at 55–60° to prevent precipitation of the sulfonic acids before the reaction was completed. Two fractions were obtained. The first, boiling at 60–70° (4 mm.)—214–215° (743 mm.)—was identified as 2-bromo-*m*-cresol. (6-Bromo-*m*-cresol, which boils at approximately the same temperature, was probably present but was not isolated.) It was obtained in an average yield of 7% and solidified on standing in the receiver. When crystallized rapidly from a small amount of petroleum ether it formed a sheaf of tetragonal crystals. Slower crystallization from a greater amount of solvent gave large solid prisms, m. p. 61–62°.[9]

Anal. Calcd. for C_7H_7OBr: Br, 42.77. Found: Br, 42.4.

The second fraction boiling at 102–105° (4 mm.) also solidified in the receiver. However, toward the end of the distillation a small amount of material came over at about the same temperature which did not solidify. (This mixture was assumed to contain 4-bromo- and 2,4-dibromo-*m*-cresol[12] which have boiling points very near that of 2,6-dibromo-*m*-cresol.) The solid fraction was obtained in about 23% yield and was shown by analysis and the following series of reactions to be 2,6-dibromo-*m*-cresol. It crystallized from petroleum ether in clusters of needles which melted at 36.5–37.5° and formed a *p*-toluenesulfonyl ester[13] melting at 131–132°.

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[11] Claus and Krauss *Ber.*, **20**, 3089 (1887).

[12] Huston and Hutchinson, THIS JOURNAL, **54**, 1505 (1932).

[13] Einhorn and Holland, *Ann.*, **301**, 95 (1898).

Anal. Calcd. for $C_7H_6OBr_2$: Br, 60.15. Found: Br, 59.7.

Proof of Structure of 2,6-Dibromo-*m*-cresol.—Pure 4-nitro-*m*-cresol prepared by the method of Staedel and Kolb[14] was brominated with two moles of bromine in glacial acetic acid and the resulting 2,6-dibromo-4-nitro-*m*-cresol was reduced by means of stannous chloride and hydrochloric acid.[15] The hydrochloride of 2,6-dibromo-4-amino-*m*-cresol was diazotized by the procedure of Bigelow, Johnson and Sanborn[16] and an unsuccessful attempt was made to prepare 2,6-dibromo-*m*-cresol by reducing the diazonium group with alcohol in the presence of finely divided copper. The first fraction obtained by the steam distillation of the reaction mixture remained an oil, while subsequent fractions solidified in the receiver and were shown by analysis to be 2,6-dibromo-4-chloro-*m*-cresol. Recrystallization from petroleum ether gave needle clusters melting at 68.5–69.5°. Analysis of the liquid fraction coming over in the first stages of the steam distillation for halogen indicated a mixture of 2,6-dibromo-*m*-cresol and 2,6-dibromo-4-chloro-*m*-cresol. Direct chlorination of this fraction in chloroform, after repeated attempts to purify it had failed, gave 2,6-dibromo-4-chloro-*m*-cresol melting at 68.5–69.5°. The *p*-toluene sulfonyl ester[13] recrystallized from alcohol melted at 108–109°.

Conclusive proof of the structure of the 2,6-dibromo-*m*-cresol was obtained by chlorinating it directly in chloroform to the 2,6-dibromo-4-chloro-*m*-cresol, which was also prepared by the bromination of 4-chloro-*m*-cresol with two moles of bromine. In all cases the identity of the products was checked by melting point, ester formation and analysis.

An attempt to prepare 2-bromo- and 6-bromo-*m*-cresol was made by brominating 36 g. of *m*-cresol (one-third mole) and 36 g. of concentrated sulfuric acid in nitrobenzene at 5–10°. However, the reaction was found to yield a mixture of 25 g. (40%) of 2-bromo-*m*-cresol boiling at 60–65° (4 mm.) and 5 g. (8%) of 4-bromo-*m*-cresol boiling at 103–104° (4 mm.). The latter compound formed a mass of very fine needles when recrystallized from petroleum ether which melted at 58.5–59.5°. Its *p*-toluene sulfonyl ester[13] melted at 112–113°. Recrystallization of 4-bromo-*m*-cresol, prepared by Huston and Hutchinson[12] from the same solvent, gave the same melting point and its *p*-toluene sulfonyl ester also melted at 112–113°. To further prove the structure of this (higher) fraction, 4-nitro-*m*-cresol was reduced by tin and hydrobromic acid in alcoholic solution and the hydrobromide diazotized in hydrobromic acid solution. Replacement of the diazonium group with bromine by the Sandmeyer reaction[17] yielded 4-bromo-*m*-cresol, which was identified by the melting point and that of its *p*-toluene sulfonic ester.

2-Chloro-*m*-cresol, 2,4-Dichloro-*m*-cresol and 2,6-Dichloro-*m*-cresol.—Adaptation of the method to the chlorination of *m*-cresol gave 2-chloro-*m*-cresol (m. p. 49–50°) boiling at 53–57° (4 mm.)—195–196° (740 mm.)—2,4-dichloro-*m*-cresol (m. p. 58–59°) boiling at 75–80° (4 mm.)—235–236° (745 mm.)—and 2,6-dichlorophenol boiling at 80–85° (4 mm.)—239.5–240.5° (745 mm.). The presence of 2,4-dichloro- and 2,6-dichloro-*m*-cresol in the same reaction is not surprising since Haworth and Lapworth[18] report a mixture of the 4 and 6 sulfonic acids of *m*-cresol when it is sulfonated at 100–120°.

The structure of 2,4-dichloro-*m*-cresol was proved by brominating it in chloroform to the corresponding 2,4-dichloro-6-bromo-*m*-cresol (m. p. 58–59°), which was also prepared by chlorinating 6-bromo-*m*-cresol in chloroform. In order to prepare this in a pure state 6-nitro-*m*-cresol[19] was reduced[20] and the resulting amino group was diazotized and replaced by bromine.[18] It boiled at 70–73° (4 mm.)—210–212° (745 mm.)—and solidified upon standing in the receiver. When crystallized from petroleum ether it melted at 38.5–39.5°.

Similarly, the structure of 2,6-dichloro-*m*-cresol was proved by brominating it to 2,6-dichloro-4-bromo-*m*-cresol[21] (m. p. 64–65°), which was also prepared by chlorinating 4-bromo-*m*-cresol directly.

Summary

1. Bromination of *p*-phenol sulfonic acid in anhydrous nitrobenzene gave excellent yields of 2,6-dibromo- and 2-bromophenol.

2. Chlorination of *p*-phenol sulfonic acids under similar conditions gave 2,6-dichloro and 2-chlorophenol.

3. Bromination or chlorination of the *p*-sulfonic acid of *o*-cresol in anhydrous nitrobenzene gave 6-bromo-*o*-cresol or 6-chloro-*o*-cresol.

4. Bromination or chlorination of the 4- and 6-sulfonic acids of *m*-cresol in anhydrous nitrobenzene gave 2-bromo-*m*-cresol, 2,6-dibromo-*m*-cresol and 4-bromo-*m*-cresol or 2-chloro-*m*-cresol, 2,4-dichloro-*m*-cresol and 2,6-dichloro-*m*-cresol.

5. Sulfonic acid groups on the benzene ring of phenol and phenol derivatives were shown to be stable toward halogenation in the presence of acid if carried out in an inert *anhydrous* solvent.

EAST LANSING, MICHIGAN RECEIVED JUNE 17, 1935

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(14) Staedel and Kolb, *Ann.*, **259**, 210 (1890).

(15) Raiford, *Am. Chem. J.*, **46**, 419 (1911).

(16) "Organic Syntheses," John Wiley and Sons, Inc., 440 Fourth Ave., New York City, 1926, Vol. VI, p. 16.

(17) "Organic Syntheses," Coll. Vol. I, p. 131.

(18) Haworth and Lapworth, *J. Chem. Soc.*, **125**, 1299 (1924).

(19) Staedel and Kolb, *Ann.*, **259**, 210 (1890).

(20) Auwers, Borsche and Weller, *Ber.*, **54**, 1315 (1921).

(21) Raiford and Leavell, THIS JOURNAL, **36**, 1509 (1914).

[CONTRIBUTION FROM THE C. F. KETTERING FOUNDATION FOR THE STUDY OF CHLOROPHYLL AND PHOTOSYNTHESIS]

Occurrence of Decomposition Products of Chlorophyll. III.[1] Isolation of Pyrroporphyrin from Beef Bile[1a]

BY PAUL ROTHEMUND

Since the discovery of the presence of phylloerythrin in beef bile by Löbisch and Fischler,[2] bile has been the source for the preparation of this decomposition product of chlorophyll. The original method of isolation has been improved by different authors[3] and leads to a beautifully crystallized product. Depending upon the method used, one obtains phylloerythrin either in form of $C_{33}H_{34}N_4O_3$, or with one molecule of chloroform of crystallization for every two molecules of phylloerythrin, $(C_{33}H_{34}N_4O_3)_2CHCl_3$. Synthetic phylloerythrin was first prepared by Fischer,[4] but beef bile is still the best source for its preparation, due to the low cost and the ready availability of this starting material.

Using the methods referred to above, large quantities of bile were worked up in our laboratory for the preparation of phylloerythrin. The data of the elementary analyses, as reported in the literature for the product thus prepared, as well as the analyses of our product, showed small but consistent deviations from the theoretical values for phylloerythrin. In some cases, the examination of a solution in pyridine–ether with the Zeiss pocket spectroscope with wave length scale and comparison prism, revealed a faint but distinct absorption band at approximately 625 mμ.

Some time ago, we had demonstrated the occurrence of a number of chlorophyll derivatives in the stomach contents, in the stomach walls, and in the digestive system of herbivorous animals;[5] the presence of other substances of porphyrin character besides phylloerythrin in beef bile could, therefore, be assumed, and the spectroscopic finding proved this assumption to be correct. The method of fractionation of an ether solution of the bile pigments with hydrochloric acid was used for the separation.

Coproporphyrin, which is a physiological constituent of *human* bile[6] and is formed there from the protoporphyrin of the red blood cell,[7] was found in the 0.5% hydrochloric acid fraction only in traces. This finding is interesting in the light of the fact that coproporphyrin can always be detected spectroscopically in cow's milk; the volume of bile necessary to obtain a positive test for this substance is much larger than that of milk.

The chlorophyll porphyrins phyllo- and rhodoporphyrin could not be found in bile; it was, however, possible to demonstrate the presence of pyrroporphyrin. This porphyrin was responsible for the spectroscopic finding mentioned above; the position of its main red absorption band, measured on a large grating spectroscope, is 623.1 mμ in ether. It was isolated from the 3% hydrochloric acid fraction and analyzed. The methyl ester was prepared.

The 10% hydrochloric acid fraction yielded phylloerythrin in approximately the same quantity as obtained by the chloroform/pyridine–alcohol method in which fractionation is omitted.

Two fractions were separated using higher concentrations, 15 and 20% hydrochloric acid, but the quantity of pigment in each of these fractions was too small to permit the isolation. The absorption spectra of these two fractions in ether are given in the experimental part.

Experimental

Twelve liters of beef bile was evaporated to a volume of 1.5 liters, and transferred into a 5-liter separatory funnel by means of 750 cc. of water. After acidification with 10 cc. of concd. hydrochloric acid and thorough shaking, the bile was extracted with a mixture of 1800 cc. of chloroform and 300 cc. of pyridine. The chloroform–pyridine layer was filtered and the chloroform distilled off. To the recovered chloroform about one-tenth of its volume of pyridine was added, and a second extraction of the bile solution was performed with this mixture. The extract was added to the residue from the first extraction, and the chloroform recovered. The combined material from six extractions was concentrated *in vacuo* to a volume of 150 cc., and transferred into 2 liters of ether by means of 200

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(1) Paper II, THIS JOURNAL, **56**, 2400 (1934).

(1a) This investigation was carried out with the experimental cooperation of Miss Eleanor Bates and Mr. Charles Roland.

(2) Löbisch and Fischler, *Monatsh.*, **24**, 335 (1903).

(3) Fischer and Bäumler, *Ann.*, **474**, 65 (1929); **480**, 197 (1930); Marchlewski, *Z. physiol. Chem.*, **185**, 8 (1929); *Bull. Acad. Polon. Sciences*, **Ser. A**, 599 (1929); Noack and Kiessling, *Z. physiol. Chem.*, **182**, 13 (1929); **193**, 97 (1930).

(4) Fischer and Riedmair, *Ann.*, **497**, 181 (1932).

(5) Rothemund and Inman, THIS JOURNAL, **54**, 4702 (1932); Rothemund, McNary and Inman, *ibid.*, **56**, 2400 (1934).

(6) Schumm, *Z. physiol. Chem.*, **153**, 225 (1926).

(7) Hijmans van den Bergh, *Nederland. Tijdschr. Geneeskunde*, **76, I**, 120 (1932); Hijmans van den Bergh, Grotepass and Revers, *Klin. Wochschr.*, **11**, 1534 (1932).

cc. of pyridine; 500 cc. of water was added, and shaken, until the precipitate was dissolved. The water layer was separated, diluted with 500 cc. of water, and extracted with 250 cc. of ether. The combined ether solutions were washed with 150-cc. portions of water, until the water layer showed only slightly yellow color (3 to 6 washings were usually sufficient). The dark red-brown ether solution was subjected to fractionation with hydrochloric acid by Willstätter's method.[8]

0.5% Hydrochloric acid was used in seven portions of 100 cc. each for the first fraction. The pigment from the combined extracts was transferred into 500 cc. of ether by means of concd. sodium acetate solution. This ether was washed acid free and evaporated to a small volume; the coproporphyrin was refractionated with 0.1% hydrochloric acid and identified spectroscopically only. Fifty liters of bile did not yield enough material for esterification and determination of the melting point of the ester.

Ten 100-cc. portions of the 3% hydrochloric acid fraction were combined, the pigment transferred into ether in the usual manner, the ether washed and refractionated with 1.5% hydrochloric acid. The porphyrin was brought back into ether with sodium acetate. Direct spectroscopic comparison with an ether solution of pyrroporphyrin from pheophytin showed identity. The hydrochloric acid number was 1.5. The porphyrin was quantitatively removed from the ether by means of 0.1 *N* potassium hydroxide or a 10% sodium carbonate solution. Esterification with methanolic hydrochloric acid yielded pyrroporphyrin methyl ester of m. p. 241°, spectroscopically identical with the free porphyrin. No depression of the melting point was observed with pyrroporphyrin ester prepared from pheophytin.

Anal. Micro Kjeldahl determinations: pyrroporphyrin (material from 100 l. of bile recrystallized from pyridine–methanol). Calcd. for $C_{31}H_{34}N_4O_2$: N_2, 11.34%. Found: N_2, 11.2%. Pyrroporphyrin methyl ester (recrystallized from pyridine–methanol). Calcd. for $C_{32}H_{36}N_4O_2$: N_2, 11.02. Found: N_2, 10.9.

Phylloerythrin was extracted from the ether solution with 10% hydrochloric acid. In addition to the normal absorption bands of phylloerythrin, a weak band at 656.0 $m\mu$ was observed in the ether solution of phylloerythrin, which had been subjected to hydrochloric acid fractionation. The substance to which this band is due, remained in the mother liquid, when the phylloerythrin was recrystallized from pyridine.

The 15% hydrochloric acid fraction was transferred to ether and exhibited then the following absorption bands: I, 664.4–(656.6)–648.8---635.7; II, 608.0---597.0–(592.3)–587.5---580.0; III, 566.0–(555.7)–545.4; IV, 534.8–(530.8)–526.8; V, 507.2–(499.2)–491.1; E. A. 465. Intensity: I, II, III, IV, V.

The spectrum of the 20% hydrochloric acid fraction in ether was: I, 601.6–(589.3)–577.0; II, 563.4–(558.5)–553.7; III, weak band with its maximum approximately at 521; E. A. 442. Intensity: I, II, III.

Summary

1. Pyrroporphyrin was found in beef bile under physiological conditions; its quantity changed only very slightly with the season of the year. Traces of coproporphyrin were also always present.

2. The separation from phylloerythrin, and from other pigments in bile, was performed by fractionation of an ether extract of the pigments with hydrochloric acid.

3. It is assumed that the occurrence of pyrroporphyrin in beef bile is due to decomposition of chlorophyll, while the presence of coproporphyrin is accounted for by the decomposition of hemoglobin.

4. No evidence for the presence in bile of other chlorophyll porphyrins (phyllo- or rhodoporphyrin) could be obtained; neither was it possible to demonstrate the occurrence of other porphyrins from blood pigment (*e. g.*, proto- or deuteroporphyrin).

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[8] Willstätter and Mieg, *Ann.*, **350**, 1 (1906).

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

Identification of Carboxylic Acids as Carboxylates of Benzylamine and Alpha-Phenylethylamine

BY C. A. BUEHLER, LOUISE CARSON AND RACHEL EDDS

Although simple addition compounds are not regarded generally as being suitable derivatives for the identification of organic compounds, those which benzylamine and α-phenylethylamine form with solid carboxylic acids are exceptions. These amines, with dissociation constants of the order of ammonia,[1] unite with both aliphatic and aromatic carboxylic acids to form stable compounds, but, unfortunately, the derivatives of some of the liquid aliphatic acids are difficult to isolate because of their low melting points, their deliquescent nature, and their tendency to supercool when in the liquid state. It is interesting to note, however, that these carboxylates, melting near room temperature, are of sufficient stability to withstand vacuum distillation. Among the solid derivatives prepared, the stability is such that various solvents such as ethyl acetate or absolute alcohol may be used for purification, although the former is to be preferred because of the lower solubility of the carboxylates in it. The compounds thus obtained are white in color, unless a group such as the nitro or amino is present, and they possesss two easily found constants, the melting point and the neutralization equivalent. The latter was determined by the method[2] recommended for the salts of aliphatic amines. All the compounds listed in Tables I and II are new, and of a 1:1 molecular ratio.

TABLE I

BENZYLAMMONIUM CARBOXYLATES

Acid	Formula	Melting point., °C. Obsd.	Corr.	Neut. equiv. Calcd.	Found	Nitrogen, % Calcd.	Found
Formic[a]	$C_8H_{11}O_2N$	94–96	95–97	153.1	155.9	9.15	9.04
Acetic[a]	$C_9H_{13}O_2N$	95.4–96.2	96.3–97.1	167.1	167.6	8.38	8.47
Propionic	$C_{10}H_{15}O_2N$	46.5–47.3	46.7–47.5	181.1	186.5	7.72	7.59
n-Butyric	$C_{11}H_{17}O_2N$	[b]		195.1	194.0	7.18	6.98
n-Caproic	$C_{12}H_{19}O_2N$	51.6–52.6	51.7–52.7	223.2	224.8	6.28	6.19
Chloroacetic	$C_9H_{12}O_2NCl$	118.4–119.4	119.9–120.9	201.6	200.1	6.95	6.91
Trichloroacetic	$C_9H_{10}O_2NCl_3$	118.8–119.8	120.3–121.3	270.5	275.1	5.18	5.33
Phenylacetic	$C_{15}H_{17}O_2N$	120.4–121.0	122.0–122.6	243.1	241.6	5.76	5.90
o-Toluic	$C_{15}H_{17}O_2N$	143.2–144.2	145.4–146.4	243.1	242.0	5.76	5.84
Cinnamic	$C_{16}H_{17}O_2N$	134.0–134.6	135.9–136.3	255.1	254.4	5.49	5.42
Benzoic	$C_{14}H_{15}O_2N$	125.4–126.6	127.2–128.4	229.1	229.8	6.11	5.96
o-Aminobenzoic	$C_{14}H_{16}O_2N_2$	110.8–112.0	112.0–113.2	244.1	241.0	11.48	11.62
m-Aminobenzoic	$C_{14}H_{16}O_2N_2$	134.0–134.6	135.9–136.5	244.1	247.8	11.48	11.57
p-Aminobenzoic	$C_{14}H_{16}O_2N_2$	194.6–195.6	197.6–198.6	244.1	247.8	11.48	11.33
m-Bromobenzoic	$C_{14}H_{14}O_2NBr$	157.6–158.2	160.6–161.2	308.0	304.9	4.55	4.58
o-Chlorobenzoic	$C_{14}H_{14}O_2NCl$	148.4–149.4	150.5–151.5	263.6	262.9	5.31	5.19
m-Chlorobenzoic	$C_{14}H_{14}O_2NCl$	146.8–147.4	149.2–149.8	263.6	265.4	5.31	5.28
p-Chlorobenzoic	$C_{14}H_{14}O_2NCl$	157.4–158.4	160.3–161.3	263.6	262.3	5.31	5.48
o-Hydroxybenzoic	$C_{14}H_{15}O_3N$	93.4–94.6	94.3–95.5	245.1	245.8	5.71	5.54
m-Hydroxybenzoic	$C_{14}H_{15}O_3N$	184.6–186.0	188.2–189.6	245.1	242.7	5.71	5.87
p-Hydroxybenzoic[c]	$C_{14}H_{15}O_3N$	211.4–212.0	216.6–217.2	245.1	235.4	5.71	5.72
o-Methoxybenzoic	$C_{15}H_{17}O_3N$	119.8–120.6	121.5–122.3	259.1	260.0	5.41	5.62
m-Methoxybenzoic	$C_{15}H_{17}O_3N$	111.8–112.8	113.1–114.1	259.1	255.6	5.41	5.46
p-Methoxybenzoic	$C_{15}H_{17}O_3N$	142.6–143.4	144.8–145.6	259.1	260.4	5.41	5.47
o-Nitrobenzoic	$C_{14}H_{14}O_4N_2$	141.4–143.2	143.9–145.7	274.1	277.1	10.22	10.34
m-Nitrobenzoic	$C_{14}H_{14}O_4N_2$	171.4–172.0	174.9–175.5	274.1	269.6	10.22	10.16
p-Nitrobenzoic	$C_{14}H_{14}O_4N_2$	193.0–194.6	197.3–198.9	274.1	272.1	10.22	10.24

[a] Since this compound was deliquescent, final drying in a desiccator was necessary. [b] B. p. 109–110° (15 mm.).
[c] Compound showed a tendency to decompose below the m. p.

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(1) *K*, for benzylamine, "International Critical Tables," Vol. VI, p. 281, is 2.0 × 10^{-5}; the value for α-phenylethylamine is not available, but, by analogy with the effect of the substitution of a methyl group in the alpha carbon in other cases, it would be expected to be similar to that of benzylamine.

(2) Buehler, Currier and Lawrence, *Ind. Eng. Chem., Anal. Ed.*, **5**, 277 (1933).

TABLE II

ALPHA-PHENYLETHYLAMMONIUM CARBOXYLATES

Acid	Formula	Melting point, °C.		Neut. equiv.		Nitrogen, %	
		Obsd.	Corr.	Calcd.	Found	Calcd.	Found
Formic	$C_9H_{13}O_2N$	97.0–98.0	97.8–98.8	167.1	166.8	8.38	8.52
Acetic	$C_{10}H_{15}O_2N$	91.2–91.6	92.1–92.5	181.1	181.8	7.73	7.75
Propionic	$C_{11}H_{17}O_2N$	[a]		195.1	191.1	7.18	7.23
n-Butyric	$C_{12}H_{19}O_2N$	[b]		209.2	209.1	6.70	6.65
Chloroacetic	$C_{10}H_{14}O_2NCl$	93.6–94.4	94.7–95.5	215.6	209.2	6.50	6.62
Phenylacetic	$C_{16}H_{19}O_2N$	114.0–114.8	115.6–116.4	257.2	259.4	5.45	5.47
o-Toluic	$C_{16}H_{19}O_2N$	111.8–112.2	113.3–113.7	257.2	258.0	5.45	5.37
Cinnamic	$C_{17}H_{19}O_2N$	141.2–141.8	144.5–145.1	269.2	271.4	5.20	5.21
Benzoic	$C_{15}H_{17}O_2N$	138.4–139.0	140.6–141.2	243.1	244.8	5.76	5.72
o-Aminobenzoic	$C_{15}H_{18}O_2N_2$	109.4–110.0	111.0–111.6	258.2	258.4	10.85	10.87
m-Aminobenzoic	$C_{15}H_{18}O_2N_2$	164.6–165.4	168.6–169.4	258.2	258.7	10.85	10.70
p-Aminobenzoic	$C_{15}H_{18}O_2N_2$	180.4–181.2	185.6–186.4	258.2	259.4	10.85	10.82
m-Bromobenzoic	$C_{15}H_{16}O_2NBr$	146.2–147.0	148.9–149.7	322.1	321.7	4.35	4.42
o-Chlorobenzoic	$C_{15}H_{16}O_2NCl$	128.4–129.4	130.9–131.9	277.6	280.4	5.05	4.96
m-Chlorobenzoic	$C_{15}H_{16}O_2NCl$	142.0–142.6	144.7–145.3	277.6	279.7	5.05	5.05
p-Chlorobenzoic	$C_{15}H_{16}O_2NCl$	150.0–151.0	152.2–153.2	277.6	277.5	5.05	5.01
o-Hydroxybenzoic	$C_{15}H_{17}O_3N$	101.0–101.8	102.1–102.9	259.1	260.8	5.41	5.41
m-Hydroxybenzoic	$C_{15}H_{17}O_3N$	135.0–136.2	137.2–138.4	259.1	256.7	5.41	5.51
p-Hydroxybenzoic[c]	$C_{15}H_{17}O_3N$	194.0–194.6	199.3–199.9	259.1	259.4	5.41	5.45
o-Methoxybenzoic	$C_{16}H_{19}O_3N$	155.6–156.0	158.7–159.1	273.2	273.6	5.13	5.16
m-Methoxybenzoic	$C_{16}H_{19}O_3N$	128.6–129.0	131.4–131.8	273.2	273.9	5.13	5.14
p-Methoxybenzoic	$C_{16}H_{19}O_3N$	130.8–131.4	132.8–133.4	273.2	273.5	5.13	5.11
o-Nitrobenzoic	$C_{15}H_{16}O_4N_2$	126.8–127.4	129.5–130.1	288.1	288.5	9.72	9.67
m-Nitrobenzoic	$C_{15}H_{16}O_4N_2$	166.8–167.2	170.7–171.1	288.1	286.8	9.72	9.79
p-Nitrobenzoic	$C_{15}H_{16}O_4N_2$	191.0–192.0	195.8–196.8	288.1	287.0	9.72	9.81

[a] B. p. 120–121° (42 mm.). [b] B. p. 125° (37 mm.). [c] Compound showed a tendency to decompose below the m. p.

Experimental

The benzylamine was the best Eastman grade while the α-phenylethylamine was prepared by the reduction of acetophenone oxime.[3] The fraction of the latter used boiled at 184–187°. Melting points were determined by the method of Mulliken[4] in which a thermometer calibrated by the Bureau of Standards was employed.

To form the carboxylates of the solid acids, 0.01 mole of the acid was dissolved in the smallest possible amount of boiling ethyl acetate, and then a slight excess of the hot solvent was added. Into this hot solution 0.01 mole of the amine was stirred in, after which the resulting solution was poured quickly on a watch glass for crystallization. After the bulk of the crystals had formed, the mother liquor was poured off and the crystals were dried first for a short time in the air and finally between filter paper. For the liquid acids, with the exception of those cited below, equimolecular amounts were mixed, in the absence of any solvent, on a watch glass in which crystallization was induced by gentle tapping at room temperature, or, if necessary, at the lower temperature of an ice–salt mixture. The separation and drying of the crystals were accomplished as before. Final purification in either case was realized by crystallization from ethyl acetate.

Some of the carboxylates in the neighborhood of *n*-butyric acid (see Tables I and II) possess such low melting points that they could not be obtained satisfactorily by crystallization methods. These were prepared by distilling equimolecular amounts of the amine and acid under reduced pressure.

Summary

A series of carboxylates of benzylamine and α-phenylethylamine has been prepared. Those of the solid carboxylic acids are particularly suitable for identification purposes.

KNOXVILLE, TENNESSEE RECEIVED JULY 10, 1935

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[3] Cumming, Hopper and Wheeler, "Systematic Organic Chemistry," D. Van Nostrand Co., New York City, 1924, p. 360.

[4] Mulliken, "Identification of Pure Organic Compounds," Vol. I, John Wiley & Sons, Inc., New York City, 1904, p. 218.

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

Observations on the Rare Earths. XLVI. The Atomic Weight of Gadolinium[1]

BY C. R. NAESER WITH B. S. HOPKINS

The object of the work described in this paper was to determine the atomic weight of gadolinium by the gadolinium chloride-to-silver ratio. Several previous determinations have been made, but none by this method. Marignac,[2] the discoverer of the element, assigned the "equivalent" of 120.5 to it. This was equal to an atomic weight of 156.75. It is probable that this equivalent was referred to sulfur trioxide, which was assumed to have a molecular weight of 80. Bettendorf[3] was the first to publish the determinations with their individual data. He effected the synthesis of the sulfate from the oxide, and obtained 156.75 for the atomic weight. Benedick[4] and Marc,[5] also using the sulfate-to-oxide ratio, obtained 156.52 and 156.39, respectively. Brauner's[6] single determination, made with material contaminated with samarium, may be disregarded. The material used by Urbain[7] in 1905 was probably the purest of all. He calcined the octahydrated sulfate to the oxide and obtained 157.24 as the average of two series of determinations. Feit and Przibylla,[8] using a volumetric method of sulfuric acid against gadolinia, obtained 157.377 and 157.398. The value adopted by the International Union of Chemistry[9] is 157.3. This value, of course, is based on the oxide-to-sulfate ratio. The disadvantages of the oxide-to-sulfate ratio have been discussed critically by Hopkins and Balke[10] and Brauner and Svăgr.[11] Because of these disadvantages and the large difference between the atomic weight of europium and that of gadolinium, it was thought advisable to redetermine the atomic weight of gadolinium, and to use the chloride-to-silver ratio.

Purification of Gadolinium Material

The original source of the gadolinium material was Brazilian monazite and Norwegian gadolinite. The gadolinite ore was broken up and taken into solution at this Laboratory, and the Brazilian monazite was obtained as the crude rare earth oxides from the Welsbach Company. The cerium was removed by the permanganate–phosphate method.[12] The cerium-free material was then converted to the double magnesium nitrates and fractionated as such. The samarium–europium–gadolinium fractions at the more soluble ends of the series were set aside and then put into a new series.[13]

The major part of the fractionation was carried out as described by Meyers and Hopkins[14] in their recent paper on the atomic weight of europium. The resulting fractions which were gadolinium rich and europium poor were run for a time as the double magnesium nitrates with bismuth[15] magnesium nitrate as the separating agent. After 150 fractionations in this fashion the gadolinium material was converted to the simple nitrates and again run with bismuth nitrate present.

At the conclusion of the fractionation, eight fractions were obtained, six of which were used for the atomic weight work. A portion of the bismuth was removed by hydrolysis, and the remainder was precipitated as the sulfide with hydrogen sulfide gas. This procedure was carried out six times to ensure complete removal of the bismuth. The gadolinium material was purified further by five alternate precipitations of the hydroxide and the oxalate. All of these precipitations were carried out in conductivity water. The final oxalate obtained from each fraction was ignited to the oxide in a platinum crucible at 800°.

A spectroscopic analysis of each sample was made, using an E_1 Hilger spectrograph and pure graphite electrodes. The first six fractions, GD-7 to GD-12, showed only gadolinium lines. Fractions GD-13 and GD-14 showed very faintly the most persistent lines of europium. No evidence of either bismuth or magnesium was found in any of the fractions. Similarly, no evidence of platinum was found.

Purification of Reagents

The purification of the reagents was carried out in a manner similar to that described in earlier publications from this Laboratory.[16] The purified gadolinium oxide was dissolved in redistilled hydrochloric acid and twice recrystallized.

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[1] Summary of part of a thesis presented to the Graduate School of the University of Illinois by C. R. Naeser in partial fulfilment of the requirement for the degree of Doctor of Philosophy.

[2] Marignac, "Oeuvres Complètes," Vol. II, p. 704.

[3] Bettendorf, *Ann. Chem. Pharm.*, **270**, 376 (1892).

[4] Benedick, *Z. anorg. Chem.*, **22**, 393 (1899).

[5] Marc, *ibid.*, **38**, 121 (1904).

[6] Brauner in Abegg, "Handbuch der anorg. Chem.," Leipzig, 1906, 3i, p. 304.

[7] Urbain, *Compt. rend.*, **140**, 583 (1905).

[8] Feit and Przibylla, *Z. anorg. Chem.*, **50**, 260 (1906).

[9] Report on Atomic Weights of the International Union of Chemistry, THIS JOURNAL, **57**, 793 (1935).

[10] Hopkins and Balke, *ibid.*, **38**, 2334 (1916).

[11] Brauner and Svăgr, *Coll. Czech. Chem. Commun.*, **4**, 51 (1932).

[12] Neckers and Kremers, THIS JOURNAL, **50**, 955 (1928).

[13] All fractionation of the samarium–europium–gadolinium material was carried out in this Laboratory by Drs. Quill and Selwood and the junior author.

[14] Meyers and Hopkins, THIS JOURNAL, **57**, 241 (1935).

[15] Urbain was probably the first to use a separator element to split in between two elements. For a summary of his work, see *Chem. Rev.*, **1**, 155 (1924).

[16] Kremers, Hopkins and Engle, THIS JOURNAL, **40**, 598 (1918).

Formation of Anhydrous Gadolinium Chloride[17]

The purified gadolinium chloride was transferred to a quartz reaction flask and dissolved in redistilled hydrochloric acid and conductivity water. A mixture of nitrogen and hydrogen chloride was then passed in from a purifying train while the flask was maintained at a temperature of 95°. When the gadolinium chloride began to crystallize, the stream of nitrogen was stopped, and only hydrogen chloride was allowed to pass into the flask. The temperature of the flask was slowly raised to 110° and kept there until the first five molecules of water of crystallization were removed. The temperature was then gradually raised to 180°, at which point the last molecule of water of crystallization began to be evolved. The dehydration was complete when a temperature of 225° was reached. To ensure complete dehydration, however, the temperature was raised to 350° and maintained there for one hour. Then, with hydrogen chloride still passing through the flask, the gadolinium chloride was fused by means of a Bunsen burner. After the flask had cooled, the stream of hydrogen chloride was stopped, and nitrogen was passed through until the exit gas gave no test for a chloride. The nitrogen was then displaced by dry air and the stoppered flask was placed in the balance case, where it was allowed to hang for three hours before being weighed.

The Ratio of Gadolinium Chloride to Silver

After it had been weighed, the gadolinium chloride was dissolved in conductivity water and transferred to a 1.5-liter glass-stoppered bottle. An approximately equivalent amount of silver was weighed out and etched with nitric acid. The silver was then washed, dried and carefully weighed again. After weighing, it was dissolved in redistilled nitric acid, diluted with conductivity water, and added slowly, with constant shaking, to the gadolinium chloride solution. The glass-stoppered flask was placed in a shaking machine for six hours and was then allowed to remain undisturbed for twenty-four hours. After this period of standing, a portion of the clear liquid was removed and tested in the nephelometer for excess of silver or chloride. Weighed portions of 0.01 *N* silver nitrate or sodium chloride solution were added until the nephelometer indicated equivalence. After each addition of the standard solution, the bottle was shaken for an additional six hours and allowed to stand for twenty-four before testing for equivalence again.

In the following table the fraction number in the series, the determination number, and the weight of the anhydrous chloride and silver, ratio of weights, and the atomic weights are given.

Detn.	Fraction number	$GdCl_3$, g.	Ag, g.	Ratio $GdCl_3/3Ag$	Atomic weight of gadolinium
I	GD-7	0.38265	0.47047	0.813333	156.86
II	GD-7	.82483	1.01416	.813311	156.85
III	GD-8	1.56656	1.92608	.813344	156.86
IV	GD-8	0.63482	0.78060	.813247	156.82
V	GD-9	.68899	.84716	.813304	156.85
VI	GD-9	2.27153	2.79249	.813442	156.89
VII	GD-10	1.89197	2.32637	.813289	156.84
VIII	GD-10	1.41902	1.74486	.813262	156.83
IX	GD-11	1.23485	1.51829	.813317	156.85
X	GD-11	1.61684	1.98796	.813315	156.85
XI	GD-12	1.72986	2.12689	.813329	156.86
XII	GD-12	2.48952	3.06091	.813326	156.85
				Average	156.85

All weighings were made by the method of substitution. The tare flask was made of quartz and differed from the reaction flask by only a few milligrams. The balance used was sensitive to 0.01 mg. and the weights were carefully standardized against a set recently checked by the Bureau of Standards. All weighings were corrected to vacuum standard. A sample of thorium oxide was kept in the balance case to eliminate all electrostatic charges.

The density of gadolinium chloride was determined by displacement of xylene and carbon tetrachloride, and checked the value given by Bourion,[18] namely, 4.52. The atomic weight of silver was taken as 107.88, and that of chlorine as 35.457. Other density values used were: silver, 10.49; platinum weights, 21.5; platinum-plated brass weights, 8.4. Since both platinum and platinum-plated brass weights were used, the two densities were used in reducing the weighings to vacuum standard. Both densities were also used in standardizing the weights.

Discussion of Results

The value of 156.85 ± 0.011 is lower than the accepted value for the atomic weight of gadolinium by 0.45 units, but is in good agreement with Aston's[19] latest determination with the mass spectrograph, namely, 156.9 ± 0.2.

Summary

1. The ratio of gadolinium chloride to silver is found to be 156.85, with a mean deviation of 0.011. This is lower by 0.45 than the present accepted value, but is in good agreement with the latest determination made with the mass spectrograph.

2. The density of anhydrous gadolinium chloride is found to check with the value given in the literature, 4.52.

URBANA, ILLINOIS RECEIVED AUGUST 5, 1935

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[17] In the preparation of anhydrous rare earth chlorides in this Laboratory we have been following the methods developed by such careful studies as those of Matignon, *Compt. rend.*, **133**, 289 (1901), and Baxter and Chapin, THIS JOURNAL, **33**, 15–19 (1911).

[18] Bourion, *Ann. chim.*, [8] **21**, 29–131 (1907).

[19] Aston, *Proc. Roy. Soc.* (London), **A146**, 46 (1934).

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

Observations on the Rare Earths. XLV. Preparation of Rare Earth Amalgams by Displacement[1]

BY D. H. WEST WITH B. S. HOPKINS

Rare earth metal amalgams have been prepared by direct combination[2] and by electrolysis[3] in non-aqueous solvents using a mercury cathode. Amalgams prepared electrolytically have been decomposed thermally to obtain metallic lanthanum, cerium and neodymium.[4]

Barium amalgam is conveniently prepared[5] by allowing sodium amalgam to react with aqueous barium chloride solution. Barium is quite closely related to the rare earths, being slightly more active. Since such a method might have advantages over the electrolytic preparation, an investigation of this possibility was entered upon to find out whether displacement can be used and if so to ascertain the most favorable conditions for the reaction.

Experimental

Preparation of Anhydrous Chlorides.—Anhydrous chlorides of the rare earth materials were prepared by the method of Reed[6] with some changes. The dry oxides were first ground in a large mortar with twice the calculated weight of ammonium chloride. Instead of heating this mixture in open casseroles and stirring by hand it was found convenient to carry out the operation in a Pyrex flask. This was slowly rotated at an angle of thirty degrees with the horizontal in an air-bath which was heated to 225–250° until the reaction was complete. The removal of excess ammonium salts was carried out by heating to 300–320° in the evacuated Pyrex apparatus described by Reed.

In this way the anhydrous chlorides of neodymium, a didymium mixture, samarium and yttrium were prepared without difficulty, the product in most cases being free from oxide or basic chloride as shown by complete solubility in water. Cerium dioxide reacted much more slowly with the ammonium chloride but by adding a three or four-fold excess of the latter and continuing the reaction for ten to twelve hours it was possible to prepare a product containing only a small amount of unconverted oxide.

Preparation of Amalgams.—It was found that sodium amalgam would react with the rare earth chlorides in alcohol solution forming the rare earth amalgam according to the equation

$$3NaHg_x + RCl_3 \longrightarrow 3NaCl + RHg_y$$

The sodium chloride is precipitated as is also some rare earth chloride. The displacement reaction begins rapidly forming an amalgam which contains a preponderance of rare earth metal. Although the reaction goes nearly to completion there is always a trace of sodium left in the amalgam. After a time there is a tendency for the amalgam to decompose, both sodium and rare earth metals resulting. Analysis of the amalgams was carried out by allowing them to decompose in air for three to five days and treating the residue with dilute hydrochloric acid. The soluble material was filtered off, evaporated and converted to the nitrate. From this solution the rare earth was precipitated as the oxalate and ignited to the oxide. The filtrate from the latter operation was fumed down with sulfuric acid and the sodium was weighed as the sulfate after ignition in platinum to red heat.

The sodium amalgams used were prepared in pulverized form by direct combination of the metals. Concentrations of 2–2.5% by weight of sodium gave the best results. More concentrated amalgams were so hard that they reacted very slowly with the rare earth chlorides. The sodium amalgam was agitated with the alcohol solutions by means of a stirrer driven by compressed air. The containers used were either large test-tubes or Erlenmeyer flasks.

With cerium, neodymium and "didymium" mixture, one hour was sufficient time to allow for the formation of good amalgams containing 3 to 3.5% rare earth metal and a small amount of sodium. The reaction was slower in the case of yttrium, two to three hours of stirring being required. Yttrium amalgams and amalgams of a mixture containing about 70% yttrium with erbium and other yttrium group earths were prepared in concentrations of 2 to 2.5% rare earth metal. Results of typical runs are given in Table I. In all cases a three to four fold excess of the rare earth salt was used.

TABLE I

Material	Time, min.	% Na in starting amalgam	Wt. Hg recovered, g.	Metals in final amalgam	
				% R. E. metal	% Na
Didymium	21	1.24	105.45	1.74	0.274
Didymium	35	1.63	16.72	2.20	.038
Didymium	60	2.68	6.83	3.38	.141
Didymium	40	2.50	27.07	3.15	.085
Didymium	20	19.60	5.31	3.20	.500
70% Yttrium	60	2.50	23.71	2.58	.342
Yttrium	90	1.76	35.03	1.56	.271
Cerium	45	2.50	22.52	3.40	.120
Neodymium	35	1.88	25.42	3.20	.370

Rare earth amalgams have been prepared electrolytically from water solution. However, no success was encountered by the authors in attempting to carry out the displacement reaction in water solution or in alcohol solutions containing appreciable amounts of water. Methyl

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(1) An abstract of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1935.

(2) Müller, *Monatsh.*, **53–54**, 215 (1929).

(3) Audrieth, Jukkola, Meints and Hopkins, THIS JOURNAL, **53**, 1805 (1931).

(4) Jukkola, Audrieth and Hopkins, *ibid.*, **56**, 303 (1934).

(5) Böttger, *J. prakt. Chem.*, **1**, 305 (1834).

(6) J. B. Reed THIS JOURNAL, **57**, 1159 (1935).

alcohol was satisfactory but best results were obtained with absolute ethyl alcohol saturated with the rare earth salt.

It was found best to cool the reaction tube with tap water since heat is developed by the reaction and at the higher temperature the tendency toward decomposition of the amalgam increases.

Potassium amalgams reacted with the anhydrous rare earth chlorides similarly to the sodium amalgams but were not as satisfactory. Barium amalgam gave partial displacement of the cerium group elements but did not react at all with the yttrium chlorides.

Yttrium amalgam was readily decomposed by heating in an evacuated Pyrex distilling bulb, the product being a pyrophoric powder which contained a small amount of mercury. Attempts to obtain yttrium metal entirely free from mercury have thus far been unsuccessful. The removal of all the mercury from the amalgams of the cerium group metals was successfully accomplished by placing the amalgams in an alundum crucible which had a lining of rare earth oxides and heating in a steel vacuum chamber by means of an electric furnace.

Summary

1. Amalgams of cerium, neodymium, didymium and yttrium have been prepared by displacement from the alcohol solution of their chlorides by sodium amalgam.

2. The most successful runs were made by suspending powdered sodium amalgam, containing 2–2.5% sodium, in a saturated alcoholic solution of the rare earth chlorides. The mixture was thoroughly agitated; the time required varied with the rare earth used.

3. This method takes much less time than the electrolytic method and gives a considerably more concentrated amalgam in the case of yttrium. The amalgams always retain a trace of sodium.

4. Metals of the cerium group were obtained free from the mercury by heating their amalgams in an evacuated chamber. This method did not yield yttrium which was entirely free from mercury.

URBANA, ILLINOIS RECEIVED AUGUST 12, 1935

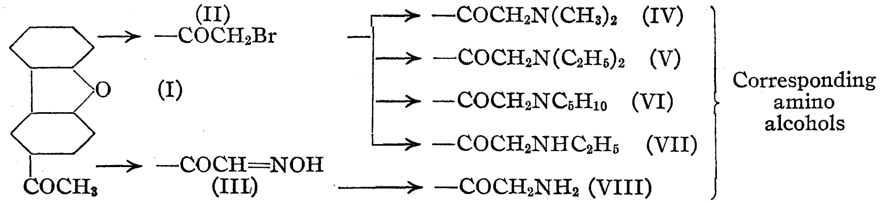
[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Amino Alcohols Derived from Dibenzofuran[1]

BY ERICH MOSETTIG AND RICHARD A. ROBINSON

The structural similarity of dibenzofuran to 4,5-phenanthrylene oxide has led us to the study of dibenzofuran derivatives[2] as a part of our search for morphine substitutes. The present communication deals with dibenzofuran alkamines containing the characteristic side chain —CHOH—CH$_2$—NR$_2$; these compounds were selected for comparison with amino alcohols of the phenanthrene series which have been found to resemble morphine somewhat in physiological action.[3] Such comparison of dibenzofuran and phenanthrene analogs may yield information as to whether the phenanthrene nucleus contributes an essential part to the total physiological action of morphine, or whether it can be replaced by another polynuclear system.

Starting from the known 2-acetyldibenzofuran, the synthesis of the alkamines was accomplished as outlined in the diagram.



The tertiary amino ketones IV, V and VI were prepared by a method similar to that used for the synthesis of their respective phenanthrene analogs.[3] The primary amino ketone VIII was obtained by reduction of the isonitroso compound III according to the method of Hartung and Munch.[4]

The exchange of the bromine atom in II with ethylamine yields only about 30% of the expected ethylamino ketone VII. The yield of the corresponding monomethylamino ketone does not exceed 5%. In the latter case a small amount of

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[1] The work reported in this paper is part of a unification of effort by a number of agencies having responsibility for the solution of the problem of drug addiction. The organizations taking part are: The Rockefeller Foundation, the National Research Council, the U. S. Public Health Service, the U. S. Bureau of Narcotics, the University of Virginia and the University of Michigan.

(2) Mosettig and Robinson, THIS JOURNAL, **57**, 902 (1935).

(3) (a) Mosettig and van de Kamp, *ibid.*, **55**, 3448 (1933); (b) unpublished results by Eddy and co-workers, University of Michigan.

(4) Hartung and Munch, *ibid.*, **51**, 2262 (1929).

DIBENZOFURAN DERIVATIVES

No.	Substituent	Solvent	M. p., °C. (corr.)	Formula	Carbon, %		Hydrogen, %		Nitrogen, %		Halogen, %	
					Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
1	*-2-ω-Bromoacetyl-[a]	Bz.–lig.	105–106	$C_{14}H_9O_2Br$							Br, 27.64	27.66
2	2-[2-(Dimethylamino)-1-oxo]-ethyl[b]	Dil. EtOH	82–83	$C_{16}H_{15}O_2N$	75.82	75.85	5.93	5.97				
	-Hydrochloride[c]	......	212–235	$C_{16}H_{16}O_2NCl$					4.84	4.84	Cl, 12.03	12.25
3	*2-[2-(Diethylamino)-1-oxo]-ethyl-(hydrochloride)[d]	EtOH or dil. HCl	200–212	$C_{18}H_{20}O_2NCl$							Cl, 11.32	11.17
4	2-(2-Piperidino-1-oxo)-ethyl-[e]	Dil. EtOH		$C_{19}H_{19}O_2N$	77.63	77.77	6.58	6.53				
	*-Hydrochloride[f]	Dil. HCl	255–265	$C_{19}H_{20}O_2NCl$					4.34	4.22	Cl, 10.75	10.76
5	2-[2-(Ethylamino)-1-oxo]-ethyl-(hydrochloride)[g]	MeOH	254–256 (dec.)	$C_{16}H_{16}O_2NCl$					5.04	4.84	Cl, 12.45	12.25
6	2-(2-Amino-1-oxo)-ethyl-(hydrochloride)[h]	Dil. HCl	245–255 (dec.)	$C_{14}H_{12}O_2NCl$					5.48	5.36	Cl, 13.52	13.56
7	2-[2-(Dimethylamino)-1-hydroxy]-ethyl-[i]	Dil. EtOH	88–89	$C_{16}H_{17}O_2N$	75.46	75.25	6.76	6.72	5.59	5.49		
	-Hydrochloride[j]	EtOH	173–174	$C_{16}H_{18}O_2NCl$							Cl, 12.29	12.16
	-Benzoic acid ester[k]	EtOH	99–100	$C_{23}H_{21}O_3N$					3.92	3.90		
8	2-[2-(Diethylamino)-1-hydroxy]-ethyl-[l]	MeOH	75–76	$C_{18}H_{21}O_2N$	75.93	76.28	7.33	7.47				
	*-Hydrochloride[m]	EtOH–Et_2O	157–159	$C_{18}H_{22}O_2NCl$					4.36	4.38	Cl, 11.22	11.13
9	*2-(2-Piperidino-1-hydroxy)-ethyl-[n]	EtOH	116.5–117.5	$C_{19}H_{21}O_2N$	77.06	77.24	7.21	7.17	4.68	4.75		
	*-Hydrochloride[o]	H_2O	250–251	$C_{19}H_{22}O_2NCl$							Cl, 10.90	10.70
	-Benzoic acid ester[p]	EtOH	119	$C_{26}H_{25}O_3N$					3.67	3.50		
10	2-[2-(Ethylamino)-1-hydroxy]-ethyl[q]	Bz.–lig.	99.5–101	$C_{16}H_{17}O_2N$	75.07	75.25	6.89	6.72	5.42	5.49		
	-Hydrochloride[r]	MeOH	219–219.5	$C_{16}H_{18}O_2NCl$							Cl, 12.32	12.16
11	2-(2-Amino-1-hydroxy)-ethyl-[s]	Dil. EtOH	132	$C_{14}H_{13}O_2N$					6.08	6.17		
	-Hydrochloride[t]	H_2O	261 (dec.)	$C_{14}H_{14}O_2NCl$	63.57	63.74	5.56	5.35	5.44	5.31	Cl, 13.51	13.45
12	2-(1-Hydroxy)-ethyl-[u]	Dil. EtOH	63–64	$C_{14}H_{12}O_2$	78.84	79.21	5.63	5.70				
13	2-Propionyl-[v]	95% EtOH	101.5–102.5	$C_{15}H_{12}O_2$	79.92	80.32	5.36	5.40				
	-Semicarbazone	Benzene	184–186	$C_{16}H_{15}O_2N_3$					14.62	14.95		
14	2-[2-(Methylamino)-1-oxo]-ethyl- (hydrochloride)?[w]	Dil. HCl	225–250	$C_{15}H_{14}O_2NCl$					4.89	5.08	Cl, 12.19	12.87
15	Methyl-bis-[(2-dibenzofuroyl)methyl]-amine hydrochloride?[x]	EtOH	235–245	$C_{29}H_{22}O_4NCl$					2.91	2.90	Cl, 6.91	7.33

[a] Prepared by bromination of 2-acetyldibenzofuran in absolute ether at 0°. The bromo ketone was purified by recrystallization from benzene–ligroin mixture or from acetic acid. The yield of pure substance was 55%; soluble in benzene. The residue, a lower-melting fraction, could not be greatly purified by further recrystallization and probably consisted of nuclear bromination products. In order to prove that the bromine atom was located in the side chain, the bromo ketone was oxidized with sodium hypochlorite to dibenzofuran-2-carboxylic acid. The 2-acetyldibenzofuran was prepared by the method of Friedel and Crafts.[5] The reaction was carried out at room temperature with nitrobenzene as the solvent (duration of reaction, forty-eight hours). The crude ketone was purified by vacuum distillation (pressure approximately 1 mm.). The unchanged dibenzofuran can be easily separated in this way but the acetyl derivative so isolated is contaminated with about 5% of a compound of m. p. 148–149° that cannot be removed efficiently by distillation. This compound is probably identical with the 2,8-diacetyldibenzofuran reported by Borsche and Schacke.[5] The separation of this impurity from the 2-acetyldibenzofuran is best effected by several crystallizations from ether or isopropyl ether; yield of pure 2-acetyldibenzofuran, 32%, m. p. 82°; in addition, 24% of practically pure substance (m. p. 74–79°).

[b] Five grams of (1), finely pulverized and thoroughly dried, was suspended in 25 cc. of absolute ether and mixed immediately with a solution of 2.2 g. of dimethylamine in 60 cc. of absolute ether (temperature approximately 0°). The powdered bromo ketone, which gradually dissolves, is replaced by a precipitate of dimethylamine hydrobromide. The transformation is complete in one hour. The amino ketone was worked up as the hydrochloride, yield 90%. The free base is moderately stable but becomes colored on long standing or in ethereal solution.

[c] Soluble in water; precipitates almost quantitatively from dilute hydrochloric acid as white needles containing one mole of water of crystallization. *Anal.* Calcd. for $C_{16}H_{16}O_2NCl \cdot H_2O$: H_2O, 5.85. Found: H_2O, 6.57.

[d] Prepared from diethylamine and the bromo ketone by the method given for (2); yield, 97%; soluble in water and ethanol. The transformation is complete in one hour, and coloration of the products can be avoided by working up immediately at this point. With dimethylamine and piperidine there is very little tendency for the reaction products to become colored. The free diethylamino ketone base is a colorless oil. K. and P prepared this substance from chloroacetyldibenzofuran and state as melting point for the hydrochloride 204–206°.

[e] Prepared from piperidine and the bromo ketone by the method given for (2); yield, 96%. The free base is moderately stable but becomes yellow on long standing. It softens at 97–100° and melts over a wide range.

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(5) Galewsky, *Ann.*, **264**, 187 (1891); Borsche and Schacke, *Ber.*, **56**, 2498 (1923).

Moderately soluble in water; K. and P. give m. p., 270–271°.

[g] Prepared from ethylamine and the bromo ketone by the method given for (2). The transformation is complete in one and one-half hours and the reaction mixture always becomes highly colored. The amino ketone was extracted from the filtered ether solution with dilute acetic acid and precipitated as the hydrochloride by the addition of concd. hydrochloric acid to the acetic acid solution; yield, 30%, difficultly soluble in water and alcohol. From 5 g. of bromo ketone, 0.5–1 g. of dibenzofuran-2-carboxylic acid was found as a by-product. The remainder of the material was a highly sensitive substance. The freshly precipitated free base soon turns pink. It melts at 65–75°.

[h] Prepared by reducing 2-isonitrosoacetyldibenzofuran by the method of Hartung.[4] The solvent was prepared by mixing 150 cc. of methanol with 40 cc. of concentrated hydrochloric acid. The amino ketone hydrochloride precipitates after about 90% of the calculated amount of hydrogen has been absorbed and absorption stops completely at this point; yield, 64%. The salt is sparingly soluble in alcohol, moderately soluble in water. It turns pink in warm alcohol or water, but is stable in dilute hydrochloric acid. The free base becomes pink immediately when liberated from the hydrochloride. The isonitroso compound was obtained from 2-acetyldibenzofuran by the method of Claisen and Manasse[6] in a yield of 60%. It is soluble in alcohol and benzene, and was crystallized once from dilute alcohol and reduced without further purification. It decomposes over a wide temperature range starting at 171°.

[i] Prepared by reducing (2) (free base or hydrochloride) in absolute alcohol solution with platinum oxide catalyst; yield, 90%, soluble in alcohol.

[j] Soluble in alcohol and water.

[k] Prepared by the method of Schotten–Baumann.

[l] This compound could not be obtained by reducing the free base of (3). The amino ketone solution became colored during preparation and would not reduce. In two cases the hydrochloride was successfully reduced in absolute ethanol. Exactly one mole of hydrogen was absorbed and the expected compound obtained. In other experiments, when reduced in absolute ethanol, the hydrochloride absorbed 2 to 3 moles of hydrogen, yielding about 25% of unchanged amino ketone hydrochloride and an oily hydrochloride which became colored. By using 70% ethanol we were able to obtain consistently, with the absorption of one mole of hydrogen, the desired amino alcohol in a yield of 80–90%. It is soluble in ethanol and benzene. This amino alcohol and its hydrochloride as well as all other members of this series are, in contrast to the amino ketones, very stable compounds.

[m] Very soluble in ethanol and water. K. and P. give m. p. 137°.

[n] Obtained from (4) (free base) by reducing in absolute ethanol with platinum oxide catalyst; yield 90%; moderately soluble in ethanol. K. and P. state m. p. 103–104°.

[o] Sparingly soluble in water, moderately soluble in alcohol. K. and P. give m. p. 242°.

[p] Prepared by the method of Schotten–Baumann.

[q] Obtained by reducing (5) (hydrochloride) in dry methanol with platinum oxide catalyst; soluble in benzene and alcohol.

[r] Moderately soluble in ethanol, soluble in methanol and water.

[s] Obtained from (6) (hydrochloride) by reduction in dry methanol; yield 90%, soluble in ethanol. If traces of free hydrochloric acid are present (originally added to suppress coloring of the hydrochloride solution) 2 to 6 moles of hydrogen are absorbed. The addition of water in this case does not stop the reduction at one mole of hydrogen.

[t] Soluble with difficulty in water and alcohol.

[u] Obtained from 2-acetyldibenzofuran by reduction in absolute ethanol with platinum oxide catalyst; yield, 90%, soluble in benzene and alcohol. *Anal.* Calcd. for $C_{14}H_{12}O_2$: hydroxyl, 8.02. Found: hydroxyl, 10.3.

[v] A solution of 35 g. of aluminum chloride in 75 cc. of anhydrous nitrobenzene was added slowly at room temperature to a solution of 20 g. of dibenzofuran and 12.5 g. of propionyl chloride in 25 cc. of anhydrous nitrobenzene. The mixture was allowed to react at room temperature for sixty hours and was then worked up in the usual way. For purification the crude ketone was distilled in a vacuum of about 5 mm. and then recrystallized from 95% ethanol; yield of pure substance, 11 g.; moderately soluble in ethanol. For constitutional proof the propionyldibenzofuran was oxidized by means of sodium hypochlorite to dibenzofuran-2-carboxylic acid.

[w] Soluble in water.

[x] Soluble in water and alcohol with difficulty.

Compounds 5, 6, 10, 11, 14 and 15 were extremely difficult to burn even when mixed with copper oxide.

the tertiary amine, methyl-bis-[-(2-dibenzofuroyl)-methyl]-amine, formed by the reaction of one mole of methylamine with two moles of the bromo ketone, could be isolated. In both cases 2-dibenzofurancarboxylic acid could be separated from the reaction products. Its formation in the reaction is as yet unexplained. Attempts to increase the yield of the secondary amino ketones by variation of experimental conditions failed. The amino ketones IV, V and VI were obtained in almost quantitative yield.

While the dimethylamino and piperidino ketones IV and VI can be reduced without any complications, the amino and diethylamino ketones VIII and V absorb two to six moles of hydrogen unless certain conditions are strictly observed.

Dibenzofuran shows as little physiological activity as phenanthrene; with the introduction of simple groups such as —$COCH_3$, COC_2H_5, mild depressant action becomes apparent. The amino alcohols do not give a morphine-like picture in the cat, but are generally more analgesic and more toxic than the corresponding amino alcohols in the phenanthrene series.[3b]

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[6] Claisen and Manasse, *Ber.*, **20**, 2194 (1887).

Experimental Part

The compounds marked with an asterisk have been recently prepared by Kirkpatrick and Parker.[7] We have included descriptions of them here because of some differences in physical properties. The authors will be referred to as K. and P.

Summary

The preparation of a series of amino alcohols derived from dibenzofuran is described. From 2-acetyldibenzofuran derivatives carrying the side chain —CHOH—CH_2NR_2 (NR_2 being the amino, dimethylamino, ethylamino, diethylamino and piperidino group) are obtained.

UNIVERSITY, VIRGINIA RECEIVED JULY 1, 1935

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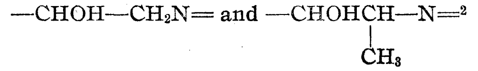
[7] Kirkpatrick and Parker, THIS JOURNAL, **57**, 1123 (1935).

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

Studies in the Phenanthrene Series. IX. Amino Alcohols Derived from 1,2,3,4-Tetrahydrophenanthrene[1]

BY ERICH MOSETTIG AND ALFRED BURGER

Morphine and most of its derivatives may be considered essentially as amino alcohols having the secondary alcoholic hydroxyl and the tertiary nitrogen attached to a partially hydrogenated phenanthrene nucleus. This consideration has led us in the past few years to the synthesis of a series of derivatives of phenanthrene and of partially hydrogenated phenanthrene carrying the side chains



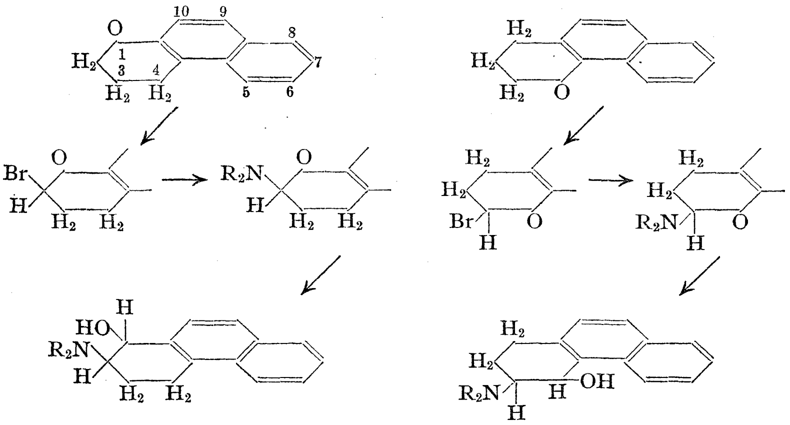
$$\text{—CHOH—CH}_2\text{N= and —CHOH}\underset{\displaystyle\text{CH}_3}{\text{CH}}\text{—N=}^2$$

Some of the amino alcohols of this type show a decided pharmacological resemblance to morphine.[3]

This communication deals with a series of amino alcohols which differ principally from those mentioned above in that the alcoholic hydroxyl and the nitrogen are not located in a side chain, but are attached directly to carbon atoms of the phenanthrene nucleus itself, which must necessarily be hydrogenated in the ring carrying the substituents. It is apparent that the amino alcohols of this type are structurally somewhat more closely related to morphine and hence might be expected to show a morphine-like effect more pronounced than that of the open-chain amino alcohols.

The known 1-keto-1,2,3,4-tetrahydrophenanthrene ("1-tetanthrenone"[4]) and the 4-isomer are convenient starting materials for the synthesis of a series of these new amino alcohols. The synthesis is outlined in the diagram.

The bromination of the tetanthrenones proceeds smoothly. The dimethylamino- and piperidino- ketones are formed in yields of over 80%, the corresponding tetrahydroisoquinolino compounds in yields of 60–70%. It is noteworthy that all attempts to exchange the bromine in the bromotetanthrenones with tetrahydroquinoline were without much success. In the reaction with diethylamine, whether carried out at room temperature or at elevated temperatures, the expected



NR_2 = dimethylamino-, diethylamino-, piperidino- and 1,2,3,4-tetrahydroisoquinolino-.

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[1] The work reported in this paper is part of a unification of effort by a number of agencies having responsibility for the solution of the problem of drug addiction. The organizations taking part are: The Rockefeller Foundation, the National Research Council, the U. S. Public Health Service, the U. S. Bureau of Narcotics, the University of Virginia, and the University of Michigan.

[2] Mosettig and van de Kamp, THIS JOURNAL, **55**, 3448 (1933); van de Kamp and Mosettig, *ibid.*, **57**, 1107 (1935); Burger and Mosettig, *ibid.*, **56**, 1745 (1934).

[3] Unpublished results by Eddy and co-workers, University of Michigan.

[4] Trivial names introduced by G. Schroeter, *Ber.*, **57**, 2025 (1924).

TABLE I

No.	Derivatives of 1,2,3,4-tetrahydrophenanthrene	Solvent	Appearance	Yield, %	M. p., °C. (corr.)	Formula	Carbon, %		Hydrogen, %		Nitrogen, %		Halogen, %	
							Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
1	1-Keto-2-bromo-	MeOH	Colorless	90	84– 85	$C_{14}H_{11}BrO$							Br, 29.06	29.16
2	2-(Dimethylamino)-1-keto-hydrochloride	EtOH–ether	Little needles	75	218–220 (dec.)	$C_{16}H_{18}ONCl$					5.08	5.19		
3	-Picrate	EtOH	Yellow prisms		180 (dec.)	$C_{22}H_{20}O_8N_4$					11.97	12.18		
4	2-(Dimethylamino)-1-hydroxy-[a]	MeOH	Colorless		105–108	$C_{16}H_{19}ON$	79.62	79.43	7.94	7.98	5.81	6.02		
5	-Hydrochloride[b]	EtOH–ether	Colorless	91	223–224 (dec.)	$C_{16}H_{20}ONCl$					5.05	4.99	Cl, 12.77	12.54
6	-Benzoyl derivative hydrochloride[c]	EtOH–ether	Colorless		179–181 (dec.)	$C_{23}H_{24}O_2NCl$					3.67	3.68		
7	2-(Diethylamino)-1-keto-hydrochloride[d]	EtOH–ether	Colorless	33	143–148	$C_{18}H_{22}ONCl$	71.14	70.85	7.30	7.76	4.61	4.73		
8	2-(Diethylamino)-1-hydroxy-[e]		Colorless flakes		70– 72	$C_{18}H_{23}ON$	80.24	80.41	8.61	8.80				
9	-Hydrochloride[b]	EtOH–ether	Colorless flakes	59	221–223 (dec.)	$C_{18}H_{24}ONCl$					4.58	4.55	Cl, 11.60	11.75
10	-3,5-Dinitrobenzoyl deriv.[c]	EtOH	Slightly yellow		209–211 (dec.)	$C_{25}H_{25}O_6N_3$					9.07	9.08		
11	2-Piperidino-1-keto-[f]	MeOH	Yellow leaflets	81	138–140	$C_{19}H_{21}ON$					5.02	5.16		
12	-Hydrochloride	EtOH–ether	Colorless		236–238 (dec.)	$C_{19}H_{22}ONCl$					4.44	4.52		
13	2-Piperidino-1-hydroxy-[g]	EtOH	Colorless		121–126	$C_{19}H_{23}ON$	81.08	81.04	8.24	8.40	4.98	4.92		
14	-Hydrochloride	EtOH–ether	Colorless	95	259 (dec.)	$C_{19}H_{24}ONCl$	71.78	71.59	7.62	7.93	4.41	4.40	Cl, 11.16	11.33
15	2-(1,2,3,4-Tetrahydroisoquinolino)-1-keto-hydrochloride	EtOH–ether	Slightly yellow	56	226–227 (dec.)	$C_{23}H_{22}ONCl$					3.85	3.91		
16	2-(1,2,3,4-Tetrahydroisoquinolino)-1-hydroxy-[h]	Ether	Colorless		155–156	$C_{23}H_{23}ON$	83.85	84.04	7.04	7.38	4.26	4.41		
17	-Hydrochloride[b]	EtOH–ether	Colorless	91	227 (dec.)	$C_{23}H_{24}ONCl$					3.83	3.94	Cl, 9.70	9.66
18	3-Bromo-4-keto-	MeOH	Colorless prisms	87	104–105	$C_{14}H_{11}OBr$							Br, 29.06	28.85
19	3-(Dimethylamino)-4-keto-hydrochloride	EtOH–ether	Glittering leaflets	99	208–210 (dec.)	$C_{16}H_{18}ONCl$					5.08	5.06		
20	3-(Dimethylamino)-4-hydroxy-hydrochloride	EtOH–ether	Colorless	81	230 (dec.)	$C_{16}H_{20}ONCl$	69.16	69.02	7.26	7.36	5.05	5.26		
21	-Benzoyl derivative[c]	Dil. EtOH	Colorless		89– 90	$C_{23}H_{23}O_2N$	79.96	80.21	6.72	7.06	4.06	4.41		
22	-Benzoyl derivative hydrochloride	EtOH–ether	Colorless		177–178	$C_{23}H_{24}O_2NCl$					3.67	3.55		
23	3-(Diethylamino)-4-keto-hydrochloride	EtOH–ether	Colorless	28	184–185 (dec.)	$C_{18}H_{22}ONCl$					4.61	4.77		
24	-Picrate	EtOH	Yellow prisms		173–174 (dec.)	$C_{24}H_{24}O_8N_4$					11.29	11.32		
25	3-(Diethylamino)-4-hydroxy-hydrochloride	EtOH–ether	Colorless	78	239.5–240 (dec.)	$C_{18}H_{24}ONCl$	70.67	70.54	7.91	8.13	4.58	4.45		
26	-Picrate	EtOH	Yellow needles		206–208 (dec.)	$C_{24}H_{26}O_8N_4$					11.25	11.13		
27	-Benzoyl deriv. picrate[c]	EtOH	Large yellow needles		173–174 (dec.)	$C_{31}H_{30}O_9N_4$					9.30	9.36		
28	-3,5-Dinitrobenzoyl deriv.[c]	EtOH	Faintly yellow		216–217.5	$C_{25}H_{25}O_6N_3$					9.07	9.00		
29	3-Piperidino-4-keto-hydrochloride	EtOH–ether	Colorless	81	248–250 (dec.)	$C_{19}H_{22}ONCl$					4.44	4.47		
30	3-Piperidino-4-hydroxy-hydrochloride	EtOH–ether	Colorless	87	246–247 (dec.)	$C_{19}H_{24}ONCl$	71.78	71.74	7.62	7.91	4.41	4.68		
31	-Benzoyl derivative hydrochloride[c]	EtOH	Fine		181–182 (dec.)	$C_{26}H_{28}O_2NCl$					3.32	3.39		
32	3-(1,2,3,4-Tetrahydroisoquinolino)-4-keto-hydrochloride		color-	69	164–166 (dec.)	$C_{23}H_{22}ONCl$					3.85	3.90		
33	-Perchlorate	MeOH	less		210 (dec.)	$C_{23}H_{22}O_5NCl$					3.28	3.35		
34	3-(1,2,3,4-Tetrahydroisoquinolino)-4-hydroxy-hydrochloride[h]	EtOH–ether	needles	80	230–231 (dec.)	$C_{23}H_{24}ONCl$	75.48	75.15	6.62	6.72	3.83	3.97		
	Substance													
35	1-Hydroxyphenanthrene[i,j]	Dil. EtOH	Colorless		153	$C_{14}H_{10}O$	86.56	86.55	5.19	5.33				
36	$C_{14}H_9OH \cdot OC_{14}H_{12}$[i,k]	MeOH	Colorless		119	$C_{14}H_{11}O$	86.11	86.05	5.68	5.53				
37	4-Hydroxyphenanthrene[l]	Bz–lig.	Colorless		113	$C_{14}H_{10}O$	86.56	86.54	5.19	5.41				
38	$C_{14}H_9OH \cdot OC_{14}H_{12}$[l,m]	MeOH	Colorless		107	$C_{14}H_{11}O$	86.11	85.99	5.68	6.01				

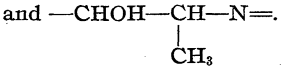
[a] Sinters at 95°, purified by high vacuum sublimation at 90°. [b] The carbon value of this compound was always found about 1% low. [c] Benzoyl and 3,5-dinitrobenzoyl derivatives of amino alcohols were prepared by allowing the hydrochlorides of the bases to stand with the calculated amount of the acyl chloride in pyridine solution at room temperature. [d] The crude hydrochloride was converted to the perchlorate or benzoate through the base and reconverted to the hydrochloride. It sinters at 138° and is completely melted at 156°. [e] Purified by high vacuum distillation at 90°, melts unsharply, begins to soften at 60°. [f] The amino ketone is sparingly soluble in benzene and separates from the reaction mixture. [g] Purified by high vacuum sublimation at 105°. Completely melted at 132°. Gives no benzoyl or dinitrobenzoyl derivative. [h] Gives no benzoyl derivative. [i] Formed as by-product in the preparation of No. 7 and in very small amount in that of No. 2, also in about 50% yield on boiling 2-bromo-1-tetranthrenone with diethylaniline for 4 hours. [j] Identical with 1-hydroxyphenanthrene obtained by heating 1-tetanthrenone with powdered selenium for fourteen hours at 295° (yield, 25%). [k] Molecular weight determination by the Rast method: found, 198, 189; by cryoscopic method in *p*-chlorotoluene, found, 193. Calculated for $C_{14}H_{11}O$, mol. weight 195. Semicarbazide acetate yields under the usual conditions, the semicarbazone of

1-tetanthrenone; 1-hydroxyphenanthrene is found in the mother liquors of the semicarbazone. Dilute potassium hydroxide solution extracts 1-hydroxyphenanthrene from the ethereal solution of the molecular compound decidedly slower than from an equally concentrated control solution of 1-hydroxyphenanthrene. Obtained also by boiling 2-bromo-1-tetanthrenone with diethylaniline as above (yield 30%). [l] Formed as by-product in the preparation of No. 23. [m] Prepared also by allowing molecular quantities of 4-hydroxyphenanthrene and 4-tetanthrenone to crystallize from methanol.

amino ketones are formed in yields of only about 20–30%. In the 1,2-series, 1-hydroxyphenanthrene and another nitrogen-free compound melting at 119° can be isolated from the reaction mixture in a total yield of about 25%. The compound of m. p. 119° sublimes readily at 90° in a high vacuum, and is converted to 1-hydroxyphenanthrene and 1-tetanthrenone by short warming with alcoholic potassium hydroxide. It is apparently a molecular compound and can also be obtained by crystallizing the two components in molecular quantities from methyl alcohol. The molecular compound shows a molecular weight corresponding to the simple formula $C_{14}H_{11}O$. The hydroxyphenanthrene is obviously formed by the loss of hydrogen bromide from the bromo ketone; we have no explanation at present for the formation of the tetanthrenone, the other constituent of the molecular compound. Auwers and Lämmerhirt[5] and later Krollpfeiffer and Schäfer[6] isolated from the reaction of α-halogenated ketones with diethylaniline, the corresponding bromine-free ketones in varying amounts, but offered no explanation for this peculiar reductive action of the amine. When we allowed 1,2-bromotetanthrenone to react with diethylaniline, 1-hydroxyphenanthrene (50%) and the molecular compound of m. p. 119° (30%) were formed. Neither in this reaction nor in that with diethylamine could any free tetanthrenone be found. The reaction of the 3,4-bromotetanthrenone proceeds throughout like that of the 1,2-isomer. In addition to the desired amino ketone, 4-hydroxyphenanthrene and a molecular compound (1 mole of 4-hydroxyphenanthrene with 1 mole of 4-tetanthrenone) can be isolated.

The amino ketones were reduced catalytically (platinum oxide) to the corresponding amino alcohols. In all cases only one of the two possible diastereomeric forms was obtained.

1,2,3,4-Tetrahydrophenanthrene is pharmacologically more effective in all respects, and especially in analgesic action, than either phenanthrene or 1,2,3,4,5,6,7,8-octahydrophenanthrene.[3] Of the two tetanthrenones the 1-keto isomer behaves quite unusually. In sufficient doses it shows a marked and mounting (up to five hours) analgesic action without showing much other effect. The 4-keto isomer is far less effective,[3] a relationship which is also known to hold true in the relative oestrogenic activity of these two isomers.[7]

The cyclic amino alcohols are generally more analgesic than the ones with the open side chain —CHOH—CH_2N= and  $\text{—CHOH—}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{—N=}$. It is remarkable that two of them approach and even excel some of the morphine derivatives. The effective analgesic dose of 2-piperidino-1-hydroxy-1,2,3,4-tetrahydrophenanthrene is 20 mg. per kg.; the corresponding dose of the 3-tetrahydroisoquinolino-4-hydroxy-1,2,3,4-tetrahydrophenanthrene is 15 mg. per kg., comparable with the effective doses of 10 and 20 mg. for codeine and pseudocodeine, respectively.[3]

We are indebted to Mr. Lyon Southworth of this Laboratory for the analyses appearing in this paper.

Experimental Part

Bromotetanthrenones.—Bromine (one mole) was added slowly to a solution or suspension of finely powdered tetanthrenone in absolute ether containing a few drops of ethereal hydrogen chloride. The bromine was taken up rapidly and the bromo ketone either crystallized out or was obtained by distilling the ethereal solution after washing it with water.

Amino Ketones.—A benzene solution of the bromo ketone (one mole) and the respective amine (3 moles) was allowed to stand in a stoppered flask at room temperature for two days. The color of the mixture became gradually yellow and deepened to dark red in some cases. The precipitation of the amine hydrobromide indicates the progress of the exchange. The reaction mixture was diluted with ether, the amine hydrobromide removed with water and the solution evaporated *in vacuo*. The residue was dissolved in acetone and the amino ketone hydrochloride precipitated with ethereal hydrogen chloride. The replacement of the bromine atom by the diethylamine residue proceeds only very slowly at room temperature. Therefore the benzene solution of the components was heated to 100° in a sealed tube for twenty-four hours, poured into dilute hydrochloric acid, and the non-basic reaction products were extracted into ether. The amino ketone hydrochloride crystallized partly from the aqueous solution.

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(5) Auwers and Lämmerhirt, *Ber.*, **53**, 428 (1920).

(6) Krollpfeiffer and Schäfer, *ibid.*, **56**, 620 (1923).

(7) Cook, Dodds, Hewett and Lawson, *Proc. Roy. Soc.* (London), Series B, **114**, No. B, 788, 272 (1934).

Another portion of the amino ketone was obtained from the filtrate in the usual way. The amino ketone hydrochloride was separated from small amounts of high-melting, very insoluble, crystalline by-products by crystallization from alcohol. The ether–benzene solution of the indifferent by-products was evaporated and the residue sublimed in a high vacuum at 90–100°, whereby half of it remained as a tar in the distilling flask. The distillate was separated by crystallization from alcohol. The molecular compounds (m. p. 119 and 107°, respectively) are less soluble than the corresponding phenanthrols. In order to avoid distillation, the residue was repeatedly crystallized from alcohol and ligroin in another experiment; the results were essentially the same. The total yield of crystalline reaction products was about 50%.

Amino Alcohols.—The amino ketone hydrochlorides of the 3,4-series could be hydrogenated in methyl alcoholic solution with a platinum oxide catalyst to the corresponding amino alcohols without any complication. The success of the hydrogenation of the amino ketone hydrochlorides of the 1,2-series with platinum oxide depends apparently upon uncontrollable factors. In some cases the calculated amount of hydrogen was absorbed, and the amino alcohols could be isolated in a pure state; in other cases considerably more hydrogen, up to two moles, was absorbed and the amino alcohol hydrochlorides could be separated from the reaction mixture only in small amounts. However, satisfactory results were obtained consistently by hydrogenating the free amino ketones in methanol solution.

Summary

The synthesis of a series of amino alcohols derived from tetrahydrophenanthrene is described. This new type of amino alcohol is characterized by having the alcoholic hydroxyl and the nitrogen directly attached to the phenanthrene nucleus.

The synthesis is effected by exchanging the bromine atoms in 1-keto-2-bromo-1,2,3,4-tetrahydrophenanthrene and in 3-bromo-4-keto-1,2,3,-4-tetrahydrophenanthrene with the dimethylamino, diethylamino, piperidino and tetrahydroisoquinolino group, and reducing the resulting amino ketones catalytically to the corresponding amino alcohols.

UNIVERSITY, VIRGINIA RECEIVED JULY 12, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Synthesis of Phenanthrene and Hydrophenanthrene Derivatives. II. The Hydrocarbon Synthesis[1]

BY LOUIS F. FIESER AND EMANUEL B. HERSHBERG

The most prominent synthetical routes to members of the phenanthrene series were developed in order to provide methods of identifying degradation products of certain opium alkaloids, resin acids and natural products containing the aetiocholane ring system. The Pschorr synthesis,[2] the phenanthrene syntheses of Bardhan and Sengupta[3] and of Bogert,[4] which employ a common intermediate, and the method of cyclizing suitable arylbutyric acids, which has received particular elaboration in the hands of R. D. Haworth,[5] have been employed further by Cook, in the course of his important work on the cancer problem for the preparation of polynuclear hydrocarbons containing the phenanthrene nucleus.[6] The interest in synthetic compounds of possible sex hormone activity has provided a further impetus for the exploitation of the known methods and for the development of new avenues of approach.

The diene reaction of Diels and Alder has until very recently[6a] found little application to the problem.

Although hydrophenanthrene derivatives would be expected to result from the addition of dienes to β-naphthoquinones, a successful reaction of this type has been reported only in the case of one alkylated quinone,[7] and the reaction is not such as to lend itself to general application. A difficulty in the case of the ortho quinones is that they are perhaps too reactive, and too prone to enter into complicating side reactions. 3,4-Dihydronaphthalene-1,2-dicarboxylic acid anhydride (I), which is but one example of a class of compounds readily available by the Bougault synthesis,[8] is far more stable than the quinones, and, being a cyclic derivative of maleic anhydride, is of a type theoretically amenable to condensation with di-

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[1] Preliminary communication: THIS JOURNAL, **57**, 1508 (1935).

[2] Pschorr, *Ber.*, **29**, 496 (1896).

[3] Bardhan and Sengupta, *J. Chem. Soc.*, 2520, 2798 (1932).

[4] Bogert, *Science*, **77**, 289 (1933).

[5] Haworth and co-workers, *J. Chem. Soc.*, 1125, 1784, 2248, 2717, 2720 (1932); 454 (1934).

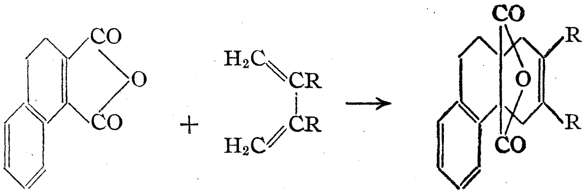
[6] Cook, *ibid.*, 1472 (1932); Cook and Hewett, *ibid.*, 398 (1933); Cook, Haslewood and Robinson, *ibid.*, 667 (1935); Cook and Haslewood, *ibid.*, 767 (1935).

[6a] Barnett and and Lawrence, *J. Chem. Soc.*, 1104 (1935).

[7] Fieser and Seligman, THIS JOURNAL, **56**, 2690 (1934).

[8] Fieser and Hershberg, *ibid.*, **57**, 1851 (1935).

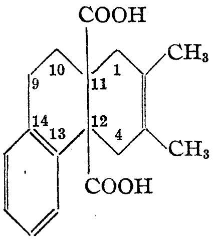
enes. It has been found that such condensations proceed in a highly satisfactory manner. The addition is rather slow, even with a large excess of diene and at a temperature of 100°, but the reaction proceeds smoothly to give in excellent yield nicely crystalline addition products of the type II.



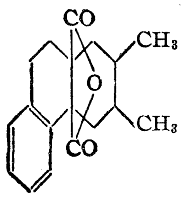
I II

The adducts from I with butadiene and 2,3-dimethylbutadiene have been prepared, together with the 2,3-dimethylbutadiene adducts from the anhydrides of 3,4-dihydrophenanthrene-1,2-dicarboxylic acid[8] and 1,2-dihydrophenanthrene-3,4-dicarboxylic acid.[8] The reaction appears to be one of quite general application.

Thus far we have studied most extensively the hydrophenanthrene derivative obtained from I with 2,3-dimethylbutadiene (II, R = CH_3), and the corresponding acid, 2,3-dimethyl-1,4,9,10,-11,12-hexahydrophenanthrene-11,12-dicarboxylic acid (III).



III



IV

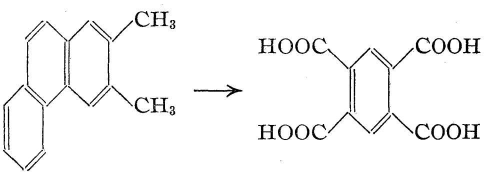
The di-potassium salt of the acid (III) is obtained by warming the anhydride with 6 *N* potassium hydroxide, the anhydride ring being rather resistant to hydrolysis. When the anhydride is heated with methyl alcoholic potassium hydroxide it is converted into a monomethyl ester of the acid III. The dimethyl ester, prepared with the use of diazomethane, is highly resistant to hydrolysis, as would be expected from the tertiary character of both ester groups. Attempts to differentiate between the two groups by partial hydrolysis have not yet been successful. The only method found suitable for effecting a hydrolysis is to fuse the ester with potassium hydroxide, and under these conditions both ester groups are hydrolyzed.

The double bond of the anhydride (II) is easily saturated by catalytic hydrogenation, giving IV. The properties of this substance and of the corresponding acid are similar to those of the unsaturated compounds.

The first attempts to eliminate the anhydride grouping of the adduct and to obtain an aromatic hydrocarbon met with little success. At the high temperature required for dehydrogenation with selenium a reversal of the Diels–Alder reaction apparently occurred, giving the original components or their products of dehydrogenation. The saturation of the double bond did not prevent this reversal, for similar results were obtained with the dihydro compound IV. The two additional hydrogen atoms may in this case be the first eliminated in the selenium treatment. Sulfur apparently is too active a reagent, for both the adduct (II) and its dihydro derivative were converted into a sulfur-containing compound of m. p. 73–74°. The dibasic acids could not be decarboxylated in quinoline solution with copper, for they lost water under these conditions and reverted to the anhydrides. The monomethyl ester of the adduct likewise lost methyl alcohol and suffered cyclization. It seemed necessary to conduct the decarboxylation in a strongly alkaline medium, and the desired result was achieved by fusing the adduct (II) with potassium hydroxide at 320–400° and distilling the product. Hydrocarbon fractions were obtained in this manner in good yield, but the reaction apparently does not follow a single course. Simple decarboxylation of the dipotassium salt would give a hexahydrophenanthrene derivative, but the preparations obtained boiled over a 9° range and the composition corresponded most closely to that of a mixture of the hexahydro and tetrahydro compounds. The material is resistant to hydrogenation in the presence of platinum, and there is but little absorption of hydrogen using palladium. We at first[1] took this as an indication that the principal hydrocarbon present is the 1,2,3,4-tetrahydro derivative, but although such a substance may indeed be present, we were unable to isolate a picrate and we are inclined now to regard the material as a mixture of tetra- and hexa-hydro compounds.

The nature of the gases evolved further points to the occurrence of reactions other than simple decarboxylation. When the dipotassium salt was fused with excess alkali a considerable amount of hydrogen was liberated; when the pure salt was subjected to dry distillation the formation of a large volume of carbon monoxide was noted. In the presence of an excess of potassium hydroxide at the high reaction temperature the cleavage of carbon monoxide, potassium formate or potassium oxalate from the molecule would be obscured by secondary changes, and the course of the reactions is still uncertain. The dihydro compound IV reacted with potassium hydroxide only at a considerably higher temperature, but it gave in good yield a mixture of tetra- and hexa-hydrophenanthrenes. The adduct from I and butadiene (II, R = H) gave a hydrocarbon boiling over a narrow range and having the composition of a hexahydrophenanthrene.

Although the method of fusion with alkali follows a complicated course and gives mixtures of hydrocarbons of varying degree of saturation, these mixtures are entirely suitable for the preparation of the completely aromatic hydrocarbons. The different fractions are dehydrogenated smoothly by selenium, giving pure phenanthrene derivatives in good yield. Phenanthrene itself was prepared by the present synthesis, and in the dimethyl series we obtained a hydrocarbon to which the structure of 2,3-dimethylphenanthrene (V) can be assigned on the basis of the oxidation of the substance to pyromellitic acid (VI).



V VI

Dr. R. D. Haworth has kindly compared our hydrocarbon with the material synthesized by Haworth, Mavin and Sheldrick,[9] and he reports that after further purification of the original sample the melting point is the same as for our material and that there is no depression on admixture.

Further studies of the diene addition products and further applications of the new phenanthrene synthesis are in progress.

Experimental Part[10]

1. The Diels–Alder Reaction

2,3 - Dimethyl - 1,4,9,10,11,12 - hexahydrophenanthrene-11,12-dicarboxylic Acid Anhydride.—For the condensation of 3,4-dihydronaphthalene-1,2-dicarboxylic acid anhydride with 2,3-dimethylbutadiene, 30 g. of the anhydride was heated in a sealed tube with 20–25 g. of the freshly distilled diene in a steam bomb at 100° for twenty to twenty-five hours. The anhydride soon went into solution and after the first five to ten hours it no longer crystallized on cooling the tube. At the end of the reaction the contents of the tube were taken up in ether, treated with Norite and the residue left on distillation of the solvent was distilled, b. p. 175–185° at 1 mm. The colorless oil obtained slowly crystallized, giving a solid, m. p. 92–94°; yield, 94–97%. Recrystallization from benzene–ligroin gave diamond-shaped prisms of the adduct, m. p. 95–96°. The anhydride is very readily soluble in benzene or ether and readily soluble in alcohol or ligroin.

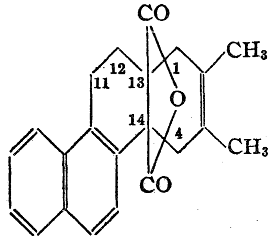
Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.57; H, 6.45. Found: C, 76.56; H, 6.44.

The first experiment, identical with the above but carried out some months earlier, gave a product melting at 75–76°. The sample had been ground for analysis, and when it was reëxamined, subsequent to the later experiments, the melting point was found to have risen to 95–96°.

1, 4, 9, 10, 11, 12 - Hexahydrophenanthrene - 11, 12 - dicarboxylic Acid Anhydride.—The addition of butadiene was definitely slower and it was found advisable to use 5–6 molecular equivalents of the diene and to continue the heating for eighty-five hours. The anhydride distilled at 160–170° at 1 mm.; yield, 63%; colorless prisms, m. p. 83.5–84°, from benzene–ligroin.

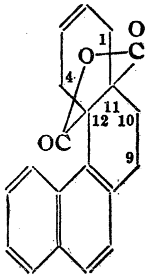
Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.56; H, 5.55. Found: C, 75.61; H, 5.97.

2,3 - Dimethyl - 1,4,11,12, 13,14 - hexahydrochrysene-13,14-dicarboxylic Acid Anhydride.—Because of the sparing solubility of the starting material the addition of 2,3-dimethylbutadiene was carried out in dioxane solution (45 hours). The yield in one small scale experiment was good; colorless prisms from cyclohexane, m. p. 196–196.5°. It is only slightly less soluble than the anhydrides described above.



Anal. Calcd. for $C_{22}H_{20}O_3$: C, 79.47; H, 6.07. Found: C, 79.51; H, 6.21.

5,6 - Benz - 1,4,9,10,11,12 - hexahydrophenanthrene - 11,12 - dicarboxylic Acid Anhydride.—A mixture of 10 g. of 1,2-dihydrophenanthrene - 3,4 - dicarboxylic acid anhydride, 15 cc. of dioxane and 14 g. of butadiene (added in portions on successive days) was heated in a sealed tube at 100° for 160 hours. The bright yellow color of the starting material faded during this time, but the solution retained a dull yellow color due to a by-product. A part of the adduct crystallized on cooling the tube and more was obtained by concentrating the mother liquor and adding petroleum ether; yield, 76%. The anhydride is readily soluble in benzene and crystallizes well from benzene–



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[9] Haworth, Mavin and Sheldrick, *J. Chem. Soc.*, 454 (1934).

[10] See Note 4 of the first paper (Ref. 8).

ligroin, forming large, colorless prisms, m. p. 161.5–162°. On attempted distillation at the pressure of the oil pump the material became highly yellow-colored as the result of the partial reversal of the diene addition.

Anal. Calcd. for $C_{20}H_{16}O_3$: C, 78.92; H, 5.30. Found: C, 78.82; H, 5.39.

The 2,3-dimethyl derivative of the above compound was obtained in a similar manner in dioxane solution; yield, 68%, colorless prisms, m. p. 128–128.5°.

Anal. Calcd. for $C_{22}H_{20}O_3$: C, 79.49; H, 6.07. Found: C, 79.38; H, 6.40.

2. Characterization of the Anhydrides

2,3 - Dimethyl - 1,4,9,10,11,12 - hexahydrophenanthrene-11,12-dicarboxylic Acid (III).—A mixture of 2 g. of the anhydride and 15 cc. of 6 *N* potassium hydroxide was heated at the boiling point until the solid had dissolved (ten minutes), stronger alkali was added and the dipotassium salt was allowed to crystallize. On acidifying a solution of the salt in cold water the acid was precipitated. The acid is very readily soluble in alcohol and crystallizes only slowly on diluting the solution with water; it is very sparingly soluble in benzene. To obtain a pure sample the acid was dissolved in a small quantity of acetone and the solvent was largely displaced by adding successive portions of benzene and evaporating the solution. The acid then crystallized slowly as colorless microcrystals melting sharply at 176–177° with loss of water.

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 71.95; H, 6.73. Found: C, 71.97; H, 6.81.

Monomethyl Ester.—The anhydride was recovered unchanged after being refluxed with methyl alcohol for four hours. To prepare the ester a solution of 3 g. of the anhydride in 150 cc. of methyl alcohol containing 1 equivalent of potassium hydroxide was refluxed for twelve hours. The solution was diluted with water and neutralized, the product separating as an oil which slowly solidified. Recrystallization from benzene–ligroin gave 2 g. of colorless prisms, m. p. 157–159° with loss of alcohol and formation of the anhydride.

Anal. Calcd. for $C_{19}H_{22}O_4$: C, 72.57; H, 7.07. Found: C, 72.52; H, 7.15.

Dimethyl Ester.—This was prepared by the action of diazomethane on either the acid or the monomethyl ester. Crystallized from methyl alcohol, in which it is moderately soluble, the ester formed prisms, m. p. 93.5–94°.

Anal. Calcd. for $C_{20}H_{24}O_4$: C, 73.13; H, 7.37. Found: C, 73.20; H, 7.53.

The ester was not appreciably hydrolyzed by boiling a mixture of the material (0.2 g.) with 10 cc. of 6 *N* potassium hydroxide and 2 cc. of alcohol for four hours. A paste of the ester with 50% potassium hydroxide was heated carefully until the material was partially converted into a hard potassium salt. This was extracted with water from the unchanged ester, and the acid obtained on acidification was identified as the original dibasic acid in a very pure form.

2,3 - Dimethyl - 1,2,3,4,9,10,11,12 - octahydrophenanthrene-11,12-dicarboxylic Acid Anhydride (IV).—The hydrogenation of the addition product II proceeded smoothly in glacial acetic acid solution with Adams catalyst, the dihydro compound forming transparent octahedra from ligroin, m. p. 117–118°.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.00; H, 7.11. Found: C, 76.24; H, 7.17.

The **acid**, prepared and purified as above, crystallized with one-half molecule of benzene which was retained on drying the sample at room temperature. The substance melted at 183–184°; loss in weight on melting, 18.3% (calcd., 16.7%).

Anal. Calcd. for $C_{18}H_{22}O_4 \cdot (C_6H_6)^1/_2$: C, 73.81; H, 7.44. Found: C, 74.05, 74.06; H, 7.53, 7.70.

3. Decarboxylation

In a typical experiment a mixture of 5.7 g. of the (dimethyl) adduct II, 11 g. of potassium hydroxide, and 10 cc. of water in a Pyrex distilling flask with a sealed-on receiver was warmed until the at first molten anhydride had been converted into the solid potassium salt. The mixture was then heated in a nitrate bath to about 200° to distil off the bulk of the water and the temperature was raised to 325–350°, collecting the oily distillate and some water in the receiver. After bringing the bath to a temperature of 400–420° to complete the distillation, the product was dried in ether and fractionated. The total yield of colorless hydrocarbon suitable for dehydrogenation and boiling over a range of about 9° was 70–85% of the theoretical amount; middle fraction, b. p. 201–204° at 24 mm. The composition of the product was between that of the tetrahydro and hexahydro derivatives as shown in the following analyses of typical preparations.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63; for $C_{16}H_{20}$: C, 90.50; H, 9.50. Found: preparation (a), C, 91.25, 91.31; H, 8.99, 9.12; (b) C, 90.86; H, 9.11.

No absorption of hydrogen by the hydrocarbon mixture was noted in alcoholic solution using Adams catalyst. With palladinized calcium carbonate the amount of hydrogen absorbed corresponded to approximately half that calculated for the presence of one reactive double bond, as in a pure hexahydro compound. The tetrahydro derivatives, if present, appear to resist hydrogenation.

The pyrolysis of the dry di-potassium salt (CO evolved) gave a yellow hydrocarbon fraction, b. p. 213–218° at 24 mm., in 64% yield.

When the dimethyloctahydrophenanthrene dicarboxylic acid anhydride (IV) was submitted to a similar fusion with excess alkali, the decomposition occurred only at a higher temperature (about 395°), and the reaction was conducted at a bath temperature of 400–420°. The hydrocarbon fraction, b. p. 200–210° at 24 mm., was obtained in 80% yield. The composition was about the same as above, indicating a mixture. (Found: C, 91.04, 91.02; H, 9.10, 9.24.)

The unmethylated adduct from butadiene (II, R = H) on fusion with alkali as above gave after redistillation a colorless liquid, b. p. 179–180° at 23 mm., in 55% yield. This apparently homogeneous **hexahydrophenanthrene** formed no picrate.

Anal. Calcd. for $C_{14}H_{16}$: C, 91.26; H, 8.74. Found: C, 91.23; H, 8.93.

On dehydrogenation of this material with selenium, there was obtained in 86% yield a hydrocarbon, m. p. 96.5–97.5°, identical with **phenanthrene** from coal tar.

4. Dehydrogenation

2,3-Dimethylphenanthrene.—Various hydrocarbon mixtures obtained as described above were submitted to dehydrogenation with entirely similar results. After heating 2.1 g. of a mixture of the tetra- and hexahydrides with 3 g. of selenium, added in portions, at 310° for twenty hours, the melt solidified completely on cooling. After extracting and distilling the product, one crystallization from methyl alcohol gave 1.6 g. (78%) of plates, m. p. 77–78°. On recrystallization from alcohol or petroleum ether the hydrocarbon formed fluorescent plates, m. p. 78–78.5°.

Anal. Calcd. for $C_{16}H_{14}$: C, 93.16; H, 6.85. Found: C, 92.86; H, 7.08.

The **picrate** formed light yellow needles from alcohol, m. p. 146–147°. The **quinone** crystallized from glacial acetic acid as glistening orange plates, m. p. 237.5–238.5° (**quinoxaline derivative,** m. p. 208–209°).

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.32; H, 5.13. Found: C, 81.23; H, 5.37.

In a letter to one of us Dr. R. D. Haworth states that the original specimen of 2,3-dimethylphenanthrene picrate prepared by his method[9] melts, after two recrystallizations from alcohol, at 144–145°; the regenerated hydrocarbon melts at 79–80°, and the styphnate (Found: C, 58.47; H, 3.95) melts at 137–148° (the m. p. given as 165–167° by a typographical error should have been 145–147°). Dr. Haworth compared his hydrocarbon, picrate, quinone and quinoxaline derivative with ours and observed no depressions; the constants are all in close agreement.

A mixture of 0.5 g. of 2,3-dimethylphenanthrene, 1 cc. of concentrated nitric acid, and 2 cc. of water was heated at 180–200° for twelve hours. As the reaction was not complete, an additional 1 cc. of acid was introduced and the tube was reheated. On concentrating the clear yellow solution and adding fuming nitric acid, the oxidation product was caused to separate. The crude acid was heated at 250° and the anhydride was sublimed in vacuum and crystallized from dioxane, giving prisms containing dioxane of crystallization. After drying at 150° in vacuum to remove the solvent, the substance melted at 277–279° and gave no depression when mixed with a sample of pyromellitic anhydride purified in the same way.

Summary

A new synthesis of phenanthrene has been developed which, in its simplest complete form, involves the following steps: (1) the preparation of γ-phenylbutyric ester, for example, by the condensation of benzene with succinic anhydride, followed by Clemmensen reduction and esterification; (2) condensation with oxalic ester; (3) cyclization to the anhydride of 3,4-dihydronaphthalene-1,2-dicarboxylic acid (the Bougault reaction, as applied by von Auwers and Möller); (4) the addition of butadiene (Diels–Alder reaction); (5) decarboxylation by fusion with alkali (a reaction which may yield a mixture of hydrophenanthrenes, but in which the carbon skeleton is not disturbed); (6) dehydrogenation.

The yields throughout are excellent, and pure products are obtainable at every step except (5). Some variation is possible in step (4), and the compounds required in (1) are already available in wide variety. Successful experiences with reactions (2), (3) and (4), using γ-arylbutyric esters of both the benzene and naphthalene series, indicate that the synthesis probably is capable of wide application.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS.
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Oxidation of Carbon Monoxide Catalyzed by Nitrogen Dioxide[1]

BY R. H. CRIST AND O. C. ROEHLING

The oxidation of carbon monoxide is recognized as being of the chain type. The rate at high temperatures is explosive and exhibits the familiar pressure limits.[1] The explosive reaction as shown by Dixon, and Weston and Garner is changed by the presence of water vapor and hydrogen. A homogeneous reaction outside of the explosive region has not been measured. However, studies of a heterogeneous reaction have been made by Bodenstein and Ohlmer in a quartz vessel at 308°, the rate being proportional to the oxygen and inversely proportional to the carbon monoxide and by Langmuir, who found similar results with platinum at 700°. McKinney[2] studied the oxidation at 80° on platinum oxide. The explosive system has been shown by Semenoff and his co-workers[1] to be very sensitive to traces of nitrogen dioxide.

The present investigation is concerned with this reaction under conditions such that the rate of the oxidation in the presence of nitrogen dioxide is measurable. Preliminary experiments show[3]

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[1] For a discussion of this reaction and the literature see Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford Univ. Press., 1933, and Semenoff, "Chemical Kinetics and Chain Reactions," The Clarendon Press, Oxford, 1935.

[2] McKinney, THIS JOURNAL, **56**, 2577 (1934).

[3] Crist and Roehling, *Science*, **80**, 338 (1934).

that the rate increases very rapidly with the nitrogen dioxide pressure and after passing a maximum decreases rapidly. Hydrogen and water were also found to increase the rate.

Experimental Methods

Preparation of Gases.—The nitrogen dioxide was prepared from lead nitrate, pumped free from other oxides of nitrogen, redistilled, and stored as the solid by means of solid carbon dioxide. It was passed over phosphorus pentoxide before using.

The carbon monoxide was made by adding formic acid to concentrated sulfuric acid. The gas was passed through a solution of potassium hydroxide to remove carbon dioxide and dried by sulfuric acid and phosphorus pentoxide. When used it was passed through a liquid air trap.

Oxygen was taken from a commercial tank. The hydrogen was removed by passing it over hot copper oqide and then drying with magnesium perchlorate. The reaction was very sensitive to small traces of hydrogen so that the removal procedure had to be followed carefully.

Hydrogen was taken from a commercial cylinder and was dried before using.

Procedure.—The investigation was carried out at 527° in a Pyrex vessel of 260-cc. capacity. The vessel was put into the well of a sulfur boiler. The boiling point of the sulfur was controlled by maintaining a constant pressure of nitrogen over the sulfur vapor by means of a barostat arrangement.[4] The barostat consisted of a gas reservoir containing a heating element controlled by contact points on a manometer. The temperature variation on the boiler wall was less than 0.3°. The actual value of the temperature was read from a millivoltmeter giving a temperature accuracy of $\pm 2.5°$.

The measurement of the pressure of nitrogen dioxide was made by a Pirani type gage.[5] The filament consisted of a thin-walled U-shaped Pyrex capillary filled with mercury[6] with a total length of 20 cm. and a resistance of 31.2 ohms. The gage was calibrated against a McLeod gage using carbon dioxide. The pressure of a sample of nitrogen dioxide in contact with the solid at $-63.5°$ (melting chloroform) was read from the calibrated Pirani gage as 0.450 mm. while the value from the "International Critical Tables" is 0.467 mm. The error is thus 3.7%. The precision of measurement as determined from the instrument set-up was $10 \rightarrow 2.5\%$ for the pressure limits of $0.061 \rightarrow 1.53$ mm.

The nitrogen dioxide was measured in an auxiliary system and frozen into a capillary U-tube next to the reaction vessel and it was then carried into the reaction vessel by the carbon monoxide or oxygen.

The filling of the reaction vessel was first tried in the ordinary manner but certain mixtures were found to react so rapidly that it became difficult to determine the initial pressures. It was necessary, therefore, to use a special filling method for the last gas, usually the carbon monoxide. A vessel was filled to the required pressure and the gas was then forced into the reaction vessel by mercury through capillary connecting tubes. The known ratios of the volumes involved then enabled a satisfactory calculation of the initial pressures in the reaction vessel.

Experience showed that consistent results could be obtained only if a definite procedure for introducing the gases was carefully followed. The experiments with hydrogen in the reacting mixture were the most troublesome. The best results were obtained when the vessel was twice filled with hydrogen-free oxygen and evacuated. It was also found necessary to fill the system with dry oxygen before such operations as regreasing of stopcocks, for if filled with air several runs were required before consistent results could be obtained.

Results

Oxidation of Carbon Monoxide Catalyzed by Nitrogen Dioxide.—This study consisted in determining the rates of the reaction with different concentrations of nitrogen dioxide, the partial pressures of carbon monoxide and oxygen being kept approximately constant at 500 and 250 mm., respectively. The temperature was 527°. The highest pressure of nitrogen dioxide was 4.85 mm., this giving a rate that was as fast as could be measured reliably. The results are given in Table I and Figs. 1 and 2.

TABLE I

THE EFFECT OF NITROGEN DIOXIDE

No.	p_{O_2}	p_{CO}	p_{NO_2}	Δp (5 to 35 min.)
1	249.2	501.0	0.061	15.0
2	253.2	512.0	.133	36.0
3	250.1	502.6	.171	46.8
4	253.0	501.4	.171	48.0
5	246.9	490.2	.171	50.0
6	249.4	504.6	.204	55.6
7	250.9	499.4	.221	47.0
8	242.6	502.8	.265	56.2
9	249.5	506.8	.265	49.4
10	246.8	504.8	.315	62.6
11	248.1	498.4	.315	39.2
12	250.9	503.6	.320	43.4
13	252.6	493.8	.375	42.0
14	253.7	492.8	.398	44.4
15	243.5	498.6	.585	22.8
16	249.1	509.8	1.22	17.4
17	254.3	507.4	1.72	21.4
18	253.2	511.6	2.35	40.6
19	247.8	504.6	2.42	33.4
20	248.1	500.6	4.85	114.6
21	260.8	530.0	4.85	123.2

The pressures are expressed in mm. and the rates have been determined by taking the pressure change from five to thirty-five minutes. Examination of some typical curves given in Fig. 1 for experiments at 527° with carbon monoxide and oxygen pressures approximately 500 and 250 mm., respectively, and with nitrogen dioxide at 0.061

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[4] C. C. Coffin, THIS JOURNAL, **55**, 3646 (1933).

[5] Dunoyer and Smith, "Vacuum Practice," Van Nostrand and Co., Inc., New York City, 1926.

[6] G. K. Rollefson, THIS JOURNAL, **51**, 804 (1929).

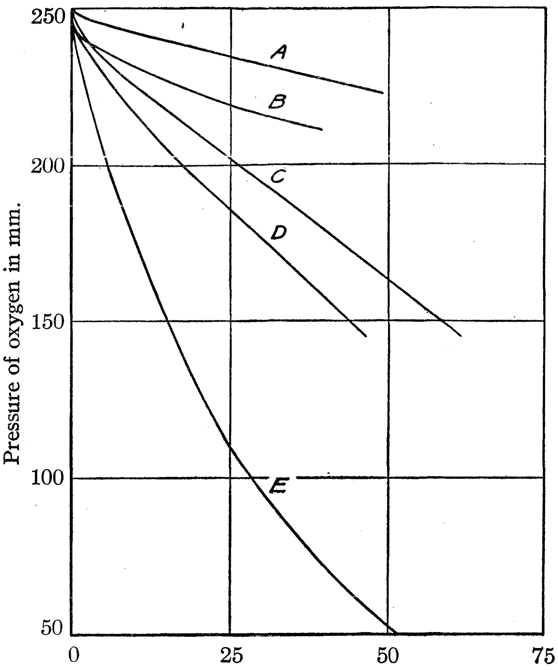

Fig. 1.—Typical runs with $CO/O_2 \sim 2$ and nitrogen dioxide as indicated: A, 0.061 mm. nitrogen dioxide; B, 0.580; C, 0.171; D, 0.315; E, 4.85.

TABLE II

THE EFFECT OF CARBON MONOXIDE

No.	p_{O_2}	p_{CO}	Δp (5 to 35 min.)
1	198.2	102.4	2.4
2	200.7	215.6	6.8
3	195.2	307.4	8.4
4	197.7	504.6	26.6
5	196.4	404.6	16.4

TABLE III

THE EFFECT OF OXYGEN

No.	p_{O_2}	p_{CO}	Δp (5 to 35 min.)
1	101.6	207.6	4.0
2	200.7	215.6	5.8
3	303.1	200.8	7.4
4	414.8	192.2	10.6
5	500.0	192.6	14.0

TABLE IV

THE EFFECT OF TOTAL PRESSURE; RATIO $CO/O_2 \sim 2$

No.	p_{O_2}	p_{CO}	$p_{O_2} + p_{CO}$	Δp (5 to 35 min.)
1	54.0	103.4	157.4	2.8
2	101.6	207.6	309.2	4.0
3	196.4	404.6	601.0	16.4
4	158.8	398.2	557.0	14.2
5	249.8	504.6	754.4	32.0
6	251.5	509.6	761.1	31.6
7	247.2	506.0	753.2	26.2

mm. shows that this should provide a satisfactory measure of the rate. Curve B of Fig. 2, where the conditions were the same as for Fig. 1, shows the very striking effect of nitrogen dioxide in the acceleration and the equally effective inhibition by the catalyst. This is similar to the catalysis by nitrogen dioxide of the hydrogen oxidation as found by Norrish.[7] In the case of carbon monoxide, however, an increasing rate is again observed with still higher concentrations of the catalyst.

The dependence of the reaction on the other components of the system was found by maintaining a constant pressure of nitrogen dioxide and varying in turn the carbon monoxide and oxygen. From these data and also from some additional runs, the effect of total pressure was obtained. The results are given in Tables II, III and IV, and in Fig. 3. The rate was estimated as before, no marked change in rate being observed in the course of the reaction during the five to thirty-five minute interval. In all cases the temperature was 527° and the pressure of nitrogen dioxide was constant at 0.585 mm.

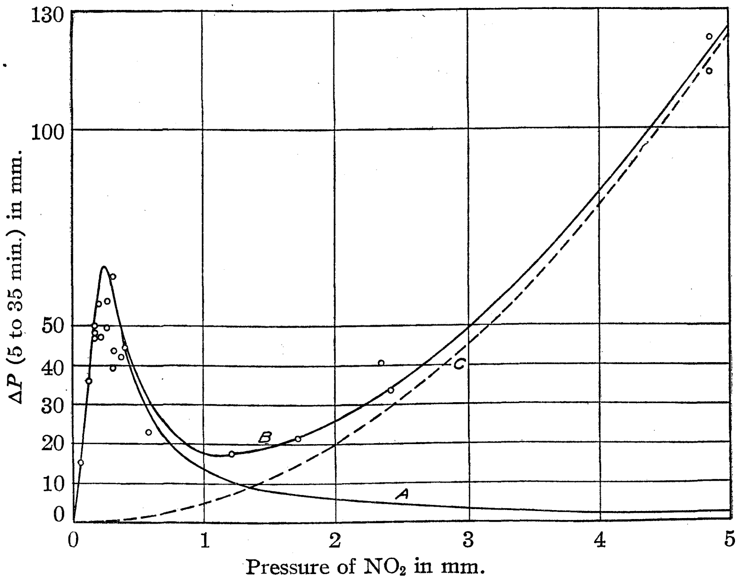

Fig. 2.—The rate of the oxidation of carbon monoxide as a function of the pressure of nitrogen dioxide; Curve B is the sum of A and C. A represents a chain process and C the trimolecular oxidation of nitric oxide.

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[7] Norrish and Griffiths, *Proc. Roy. Soc.* (London), **A139**, 147 (1933).

The Effect of Hydrogen and Water on the Catalyzed Oxidation of Carbon Monoxide.—It was found difficult to obtain a consistent set of data in this study. Some of the uncertainties may have been due to the time factors involved in introducing the gases. It was not possible to mix the gases prior to their introduction into the flask, because of the danger of explosion for which the apparatus was not designed. However, by a rigorous adherence to the definite procedure outlined in the first part it was possible to obtain fairly satisfactory data. The mixtures with more than 0.53 mm. of hydrogen had reacted completely by the time the gases were introduced, as was shown by the carbon dioxide obtained. In some cases, however, the initial rate was measurable but within a minute the manometer would drop suddenly and the reaction would be complete as evidenced by the total pressure change and by the yield of carbon dioxide. The pressures of water vapor were obtained by passing the carbon monoxide over ice at the required temperature. The results are shown in Figs. 4, 5 and 6. The carbon monoxide and oxygen pressures were approximately 500 and 250 mm. for all but Fig. 5, where the pressures were 270 and 230 mm., respectively. Figure 4 shows the relative effects of water vapor and hydrogen.

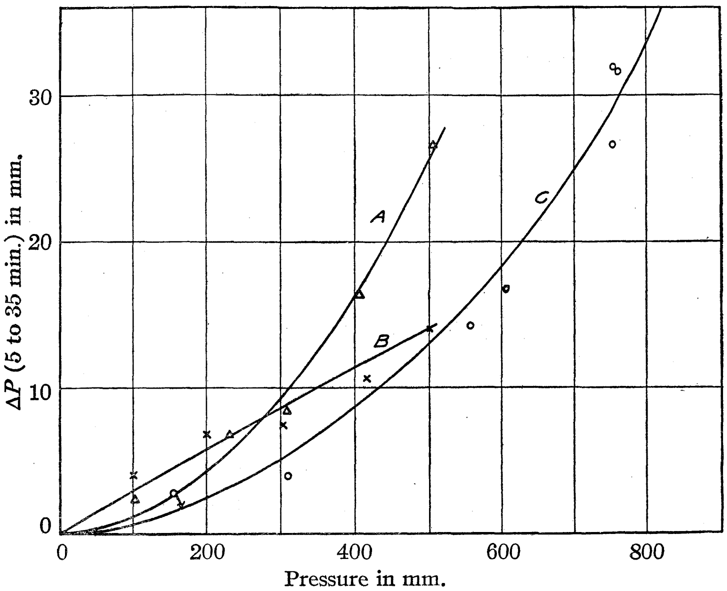

Fig. 3.—Curves A and B show the effect of carbon monoxide and oxygen, respectively. Curve C shows the rate as a function of the total pressure of carbon monoxide and oxygen. It is a composite of A and B. The pressure of nitrogen dioxide was 0.585 mm.

Discussion of Results

The Catalysis by Nitrogen Dioxide.—The character of the curve, Fig. 2 for the effect of nitrogen dioxide suggests that it is a composite of two separate processes. A formal mathematical analysis on any other basis is difficult. If the analogous nitrogen dioxide catalyzed hydrogen oxidation[7] is considered one process would be that represented by Curve A in Fig. 2, which is expressed by the equation

$$y = ax/(b - cx + x^2)$$

where x is the nitrogen dioxide pressure and y the rate. The other process is the remainder of the experimental curve and is shown as Curve C. This has the form, $y = k_3x^2$, where k_3 has the value of 5.0.

The nature of the second process can be understood by an examination of Experiment 21, Table I, where the pressure of nitrogen dioxide was 4.85 mm. The rate of this reaction was sufficiently rapid so that the course of the reaction was followed conveniently to three-fourths completion. This rate was found to be first order with respect to the oxygen. The constants given in Table V are calculated for the equation

$$k_2 = \frac{2.3}{t} \log \frac{(O_2)t_0}{(O_2)t}$$

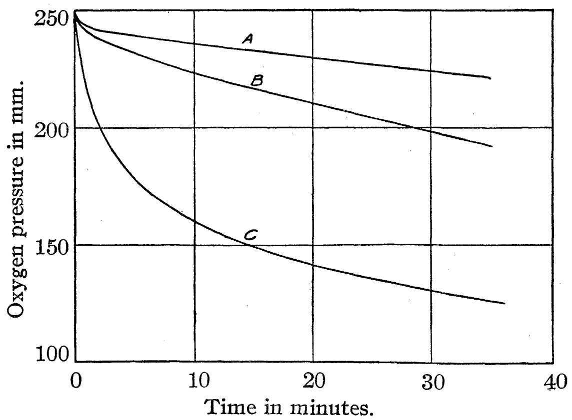

Fig. 4.—Individual runs to show the relative effect of water and hydrogen on the rate: A, no hydrogen or water; B, 0.100 mm. H_2O; C, 0.100 mm. H_2; pressure of nitrogen dioxide, 1.22 mm.; temperature, 527°.

The value for p_{O_2} at $t = 0$ was obtained from the plot of log p_{O_2} against time and is given in parentheses.

Table V

Rate of Reaction for $-d(O_2)/dt = k_2(O_2)$

t, min.	p_{O_2}	k_2
0	(248.3)	...
1	244.8	0.0143
2	237.0	.0234
5	217.0	.0269
10	186.6	.0285
15	161.2	.0288
18	147.6	.0289
22	132.2	.0286
35	93.8	.0278
40	82.8	.0274
45	73.8	.0270
53	61.2	.0264
63	51.2	.0251

Let it be assumed that the nitrogen dioxide is removed rapidly by the reaction

$$NO_2 + CO \longrightarrow CO_2 + NO$$

which is followed by

$$2NO + O_2 \longrightarrow 2NO_2$$

Then, if the second reaction determines the rate, the observed velocity would be

$$-d(O_2)/dt = k_1\,(NO)^2(O_2) \qquad (1)$$

Since the concentration of nitric oxide is kept constant by the first of the above reactions, the rate is then

$$-d(O_2)/dt = k_2\,(O_2) \qquad (2)$$

where $k_2 = k_1\,(NO)^2$. This is confirmed by the data of Table V. If the nitric oxide pressure (or nitrogen dioxide pressure) is varied and the oxygen pressure is kept constant, the rate is given by

$$-d(O_2)/dt = k_3(NO_2)^2$$

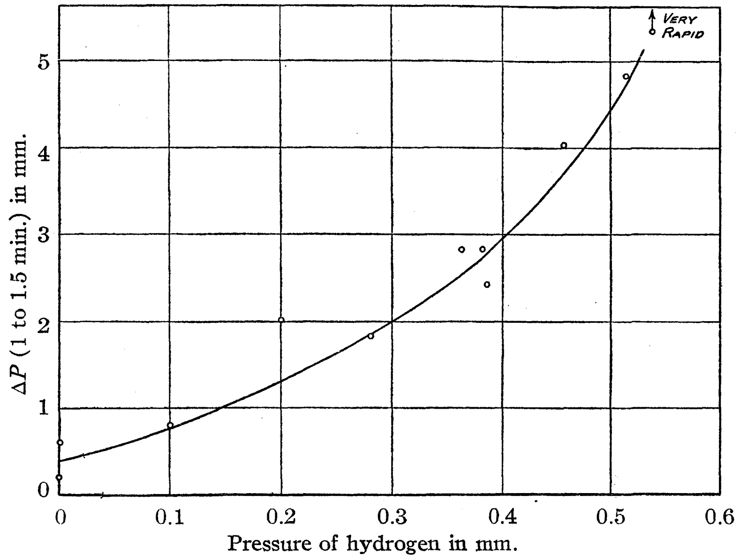

Fig. 5.—The effect of hydrogen: pressure of nitrogen dioxide, 1.22 mm.; temperature, 490°.

These are the conditions under which the data represented by Curve B of Fig. 2 were obtained and Curve C represents the equation, Rate = $5.0[NO_2]^2$.

The average value for k_2 from Table V is 0.0272 min.$^{-1}$ = 4.53×10^{-4} sec.$^{-1}$. By equations (1) and (2)

$$k_2 = k_1(NO)^2 \text{ or } k_1 = k_2/(NO)^2$$

Using (NO) = 4.85 mm. = 9.72×10^{-8} mole cc.$^{-1}$, $k_1 = 4.79 \times 10^{10}$ cc.^{2} mole^{-2} sec.$^{-1}$. A comparison of this value with previous experimental data on the oxidation of nitric oxide cannot be made since the highest temperature used for the direct measurement of the rate was 390°. From liquid air temperatures to this temperature the rate decreases about 16 fold, and present theories concerning the rate of this reaction[8] predict an increasing rate with temperature at high temperatures. For the temperature used in this investigation a rate of $1.3 \longrightarrow 9.8 \times 10^9$ cc.^{2} mole^{-2} sec.$^{-1}$ is predicted.[9] The experimental result put forward here is in line with this prediction.

It was found in this investigation that light of 3650 Å. in the first predissociation region of nitrogen dioxide had no effect on the rate. This result is rather surprising since Norrish[7] noticed a great increase in the rate of the oxidation of hydrogen catalyzed by nitrogen dioxide upon irradiation with such light. However, this negative result is in accord with the assumption that the nitrogen dioxide is removed rapidly by the carbon monoxide.

The next part of the discussion is concerned with Curve A of Fig. 2. The empirical equation for Curve A is

$$R = \frac{9.46\,(NO_2)}{0.0625 - 0.354\,(NO_2) + (NO_2)^2}$$

This equation can be derived on a formal chain theory. Thus, if (S) represents the number of chains in operation, then on the usual assumption of the steady state[10]

$$d(S)/dt = k_1(NO_2) + k_2(NO_2)(S) - k_3(S) - k_4(NO_2)^2(S) = 0$$

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[8] Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York City, 1932, p. 168; Gershinowitz and Eyring, This Journal, 57, 985 (1935).

[9] Private communication from Dr. Gershinowitz.

[10] Nitrogen dioxide is used here to conform with the empirical equation. In the interpretation of this equation to follow we have used equations involving nitric oxide. We may assume that the nitric oxide concentration is proportional to the nitrogen dioxide concentration so that the equation here would be altered by the necessary proportionality factors.

From the equation we get $(S) = k_1(\mathrm{NO_2})/[k_3 - k_2(\mathrm{NO_2}) + k_4(\mathrm{NO_2})^2]$. If the rate is proportional to the number of chains (S), we have the equation of the rate as given above.

It is difficult to find an acceptable mechanism for this development. There is not sufficient information at hand to determine the nature of the initial process. The absence of a photochemical effect, which was explained previously, eliminates that as a clue to the initial step. In the case of the hydrogen–oxygen reaction catalyzed by nitrogen dioxide, the results obtained by Norrish were similar to those obtained here, showing the same kind of maximum. Also the rates were greatly enhanced by light of 3650 Å. From the known primary process on the absorption of light of wave length λ = 3650 Å. by nitrogen dioxide, namely

$$\mathrm{NO_2} + h\nu \longrightarrow \mathrm{NO} + \mathrm{O}$$

Norrish proposed a chain mechanism involving atomic oxygen in order to account for the kinetics of the light reaction. He suggested that since the thermal reaction is similar to the photo-reaction, the oxygen atoms for the thermal reaction could be provided by such reactions as

$$\mathrm{NO_2} \longrightarrow \mathrm{NO} + \mathrm{O} - 72.6\ \text{kcal.}$$
$$\mathrm{NO} + \mathrm{O_2} \longrightarrow \mathrm{NO_2} + \mathrm{O} - 44.4\ \text{kcal.}$$

With these considerations in mind the following mechanism can be suggested for the oxidation of carbon monoxide.

$$\mathrm{O} + \mathrm{O_2} \longrightarrow \mathrm{O_3} \qquad (1)$$
$$\mathrm{O_3} + \mathrm{CO} \longrightarrow \mathrm{CO_2'} + \mathrm{O_2'} \qquad (2)$$
$$\mathrm{O'} + \mathrm{CO} \longrightarrow \mathrm{CO_2} + \mathrm{O} \qquad (3)$$
$$\mathrm{NO} + \mathrm{O_2'} \longrightarrow \mathrm{NO_2} + \mathrm{O} \qquad (4)$$
$$\mathrm{NO} + \mathrm{NO} + \mathrm{O} \longrightarrow \mathrm{NO_2} + \mathrm{NO} \qquad (5)$$

The oxygen atoms could be supplied originally by nitrogen dioxide as above. Reactions (4) and (5) are set up in order to yield the equation for the Curve A of Fig. 2. Reaction (4) would require a very unusual stability to collision of the excited oxygen molecules with other molecules than the nitric oxide. Also, it would seem that any third body would serve as well as nitric oxide in (5). With regard to reactions (1) and (2), the recent work of Jackson[11] must be considered. He found that the illumination of oxygen–carbon monoxide mixtures with light of wave length λ = 1700 Å., which is capable of dissociating the oxygen molecules into atoms, produced ozone and little or no carbon dioxide at room temperature. At 500° only carbon dioxide was formed. The author does not discuss the mechanism of this formation of carbon dioxide, *i. e.*, whether it occurs directly with oxygen atoms or through the intermediate formation of ozone. The important facts of his paper in the present connection are: (1) his observation that the rate is independent of the total pressure, the ratio of the gases remaining constant; and, (2) the rate decreases if the carbon monoxide is increased, the total pressure remaining constant.

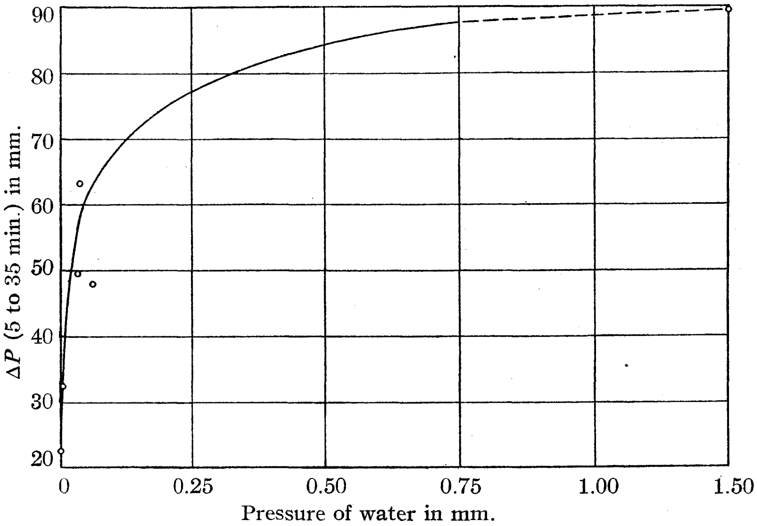

Fig. 6.—The effect of water: pressure of nitrogen dioxide, 0.585 mm.; temperature, 527°.

The study given in Tables II, III, IV and Fig. 3 shows the effect on the rate of the ratio of the gases and of the total pressure with constant pressure of nitrogen dioxide of 0.585 mm. The rate is directly proportional to the first power of the oxygen pressure and to the square of the carbon monoxide pressure, as is shown by Curves B and A of Fig. 3. Curve A is represented by the equation

$$R = 1.03 \times 10^{-4}(\mathrm{CO})^2$$

The effect of carbon monoxide is rather unusual, as all previous work has involved the first and negative powers of the carbon monoxide pressure. Curve C, which gives the effect of changing the total pressure with the ratio constant at 2:1, can be shown to be a composite of the separate oxygen and carbon monoxide curves.

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(11) Jackson, THIS JOURNAL, **56**, 2631 (1934).

Some further information concerning the effect of total pressure of carbon monoxide and oxygen with the ratio constant at 2:1, can be obtained from a study of individual curves. In the case of No. 15, Table I, with nitrogen dioxide = 0.585 mm., the rate dropped to 59% when the reaction had progressed 20%, while curve C of Fig. 3 would predict a drop of 64%. This agreement is to be expected as all the data of Curve C are for conditions the same as No. 15. For No. 21, the nitrogen dioxide = 4.85 mm. and at 40% completion the rate has been reduced to 71%, while if this change in rate were due to change in carbon monoxide pressure only the prediction from Curve C would be 53%. This disagreement would be expected, if our earlier interpretation of the run is correct, namely, that the rate-determining step at these pressures of nitrogen dioxide is the trimolecular oxidation of nitric oxide. If we examine the results for a very low pressure of nitrogen dioxide as given by those runs on the rising part of Curve A, the one carried farthest (40% completion) was No. 8 and it was found to be linear throughout. This result would indicate that under these conditions the rate is independent of the total pressure of the reacting gases. The work of Jackson showed that the rate was independent of the total pressure and inversely proportional to the carbon monoxide pressure. It is found here that only at very low pressures of nitrogen dioxide is the rate independent of the total pressure and further that the rate increases with carbon monoxide pressure except for very low pressures of nitrogen dioxide, where it appears to be independent. This disagreement with the work of Jackson would indicate that an atomic chain is of some doubt though it is not definitely excluded.

The Effect of Hydrogen and Water Vapor.—The study of the effect of hydrogen on the nitrogen dioxide catalyzed oxidation of carbon monoxide is somewhat complicated by the formation of water which undoubtedly occurs during the progress of the reaction. This effect of the loss of "catalyst" has been largely eliminated in the results given in Fig. 5 by taking the rate as the pressure change from one to one and one-half minutes. The experimental points are considerably scattered and do not justify a thorough mathematical analysis, but the rate is approximately proportional to the square of the hydrogen pressure. The curve would rise much faster if tangents to zero time could be drawn. Whether the rates above 0.53 mm. of hydrogen were very rapid or explosive could not be determined.

In order to explain the effect of hydrogen, an atomic chain mechanism can be assumed. In the work of Norrish on the oxygen–hydrogen–nitrogen dioxide system, the atomic chains are assumed to be initiated by atomic oxygen. Recently Geib and Harteck[12] have shown that when hydrogen atoms are introduced into a mixture of hydrogen, oxygen and carbon monoxide, the ratio of the water to the carbon dioxide formed increases only slightly on going from room temperature to 100°. From a consideration of their results, and assuming that there is only a slight change in the ratio of water to carbon dioxide formed on further increase of temperature, the following mechanism is reasonable

$$
\begin{aligned}
O + H_2 &\longrightarrow OH + H + 0.8\text{ kcal.} && (1)\\
OH + CO &\longrightarrow CO_2 + H + 23.8\text{ kcal.} && (2)\\
H + O_2 + O_2 &\longrightarrow HO_2 + O_2 && (3)\\
H + O_2 + CO &\longrightarrow CO_2 + OH && (4)\\
HO_2 + CO &\longrightarrow CO_2 + OH && (5)\\
OH + OH &\longrightarrow H_2O + O && (6)\\
OH + H_2 &\longrightarrow H_2O + H + 31.1\text{ kcal.} && (7)
\end{aligned}
$$

(2), (6) and (7) are probably fast. (3) has a collision efficiency of about 1 and (4) has an efficiency of about 0.1 while (5) is somewhat less. In view of previous considerations, there is uncertainty about the initiation of the hydrogen chains as given in reaction (1).

The comparative effect of hydrogen and of water is given in Fig. 4; the former is seen to be very much greater. Now, if the hydrogen concentration were the most important factor in determining the rate, its complete disappearance in the formation of water would be indicated by a rate equal to that for water of the same concentration. This is indicated by the fact that the slopes of Curves B and C of Fig. 4, thirty minutes, are about the same. Final decision must be reserved until the effect of change in carbon monoxide and oxygen with water present is known. It is not possible to predict this from the earlier results, as we are now dealing with a very different mechanism. As a mechanism for the effect of water vapor, we may suggest

$$H_2O + CO \longrightarrow CO_2 + H_2$$

together with the hydrogen–oxygen–carbon monoxide mechanism previously discussed.

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(12) Geib and Harteck, *Z. physik. Chem.*, **170A**, 1 (1934).

Summary

1. The oxidation of carbon monoxide catalyzed by nitrogen dioxide has been measured at 527°. The rate-determining reaction at low concentrations of the catalyst appears to be a chain mechanism, and at higher concentrations to be the trimolecular oxidation of nitric oxide.

2. The rate is first order with respect to oxygen at high concentrations of the catalyst and at low concentrations it is proportional to the oxygen and also to the second power of the carbon monoxide.

3. The initial rate is approximately proportional to the square of the hydrogen pressure and is infinite with the hydrogen greater than 0.53 mm.

4. The effect of water has been found.

5. The oxidation of nitric oxide at 527° has been discussed.

NEW YORK, N. Y. RECEIVED JUNE 24, 1935

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

The Solubility of Ammonium Oxalate in Water

BY ARTHUR E. HILL AND EDGAR F. DISTLER[1]

The figures on the solubility of ammonium oxalate in water as given in "International Critical Tables,"[2] cover the range from 0 to 50°; they are based upon a small number of individual determinations[3] and lead to a curve with an estimated variation of ±3%. The present investigation was undertaken to extend the temperature range and to improve the probable accuracy.

For the experimental work, analyzed ammonium oxalate was recrystallized, giving a product which agreed upon analysis with the formula for the monohydrate. Samples were enclosed with water in glass-stoppered Pyrex vessels and rotated in thermostats; equilibrium was reached in a few hours with good stirring. The 0° temperature was obtained in an ice-bath, temperatures up to 45° in a water-filled thermostat, and higher temperatures in a glycerol-filled thermostat; the temperature variation was not greater than ±0.05° at the lower temperatures, about ±0.1° at 60 and 75° and about ±0.2° at 87 and 100°; the thermometer was compared with a standard and corrected for emergent stem. Samples for analysis were withdrawn through cotton and paper filters into pipets at the lower temperatures, and aspirated through heated tubes at the higher temperatures; the oxalate was determined by titration with 0.1 *N* potassium permanganate solution, using the method of McBride;[4] the permanganate was standardized with a sample of sodium oxalate from the Bureau of Standards.

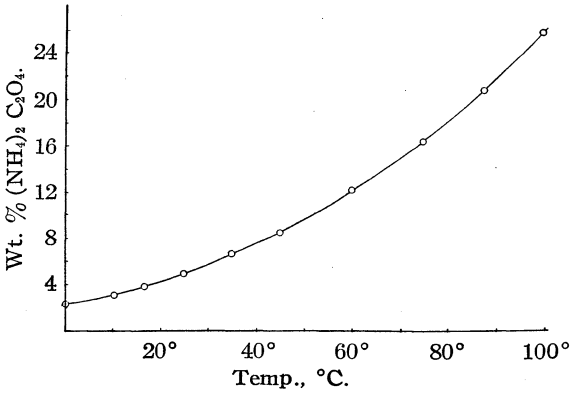

Fig. 1.

The results are shown in Fig. 1 and Table I. The curve shows no break to indicate the existence

TABLE I

SOLUBILITY OF AMMONIUM OXALATE IN WATER

T, °C.	Wt. per cent. found Undersatn.	Supersatn.	Average
0.0	2.264	2.275	2.269
10.3	3.107	3.107	3.107
16.78	3.897	3.887	3.892
25.0	4.995	4.976	4.985
34.97	6.627	6.634	6.630
44.75	8.617	8.621	8.619
60.3	12.28	12.31	12.30
74.8	16.43	16.44	16.44
87.7	20.82	20.91	20.86
99.8	25.80	25.79	25.79

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[1] The material of this paper is from the thesis of Edgar F. Distler, offered in partial fulfilment of the requirements for the degree of B.S. in Chemical Engineering at New York University, 1935.

[2] "International Critical Tables," New York City, 1928, Vol. IV, p. 219.

[3] Engel, *Ann. chim. phys.*, [6] **13**, 348 (1888); Foote and Andrew, *Am. Chem. J.*, **34**, 153 (1905); Woodstra, *8th Int. Cong. Chem.*, **22**, 25 (1912); Colani, *Bull. soc. chim.*, [4] **10**, 405 (1916); see also Rivett and O'Conner, *J. Chem. Soc.*, **115**, 1346 (1919).

[4] McBride, THIS JOURNAL, **34**, 393 (1912).

of any solid phase other than the monohydrate; cooling curves also gave no indication of a change of phase down to the eutectic temperature, −0.75°.

By the method of least squares, the parabolic curve for the solubility was calculated with the following constants: wt. per cent. solubility = $2.314 + 0.06272t + 0.001714t^2$. The solubilities at round temperatures calculated by this equation are given in Table II. When compared with the figures of Table I, the solubilities calculated from the equation show an average deviation of ±0.073% with respect to the total solution, or ±0.84% with respect to the ammonium oxalate concentration; when comparison is made with the average curve given in "International Critical Tables,"[2] it is indicated that that curve is approximately 5% too low at 0° and 3.9% too low at 50°.

TABLE II

SOLUBILITY OF AMMONIUM OXALATE IN WATER

Calculated by equation:
Soly. = $2.314 + 0.06272t + 0.001714t^2$

T, °C.	Wt. per cent. $(NH_4)_2C_2O_4$	T, °C.	Wt. per cent. $(NH_4)_2C_2O_4$
0	2.314	50	9.735
10	3.112	60	12.25
20	4.254	70	15.10
25	4.953	80	18.30
30	5.738	90	21.84
40	7.565	100	25.73

Summary

The solubility of ammonium oxalate in water has been determined from 0 to 100°; the solid phase is the monohydrate throughout the entire range; the average figures in "International Critical Tables" are distinctly too low at 0 and at 50°.

NEW YORK CITY RECEIVED JULY 19, 1935

[CONTRIBUTION FROM THE KENT AND GEORGE HERBERT JONES CHEMICAL LABORATORIES, UNIVERSITY OF CHICAGO]

The Catalytic Hydrogenation of Aldonic Acid Delta and Gamma Lactones and of the Aldoses

BY J. W. E. GLATTFELD AND G. WEBER SCHIMPFF[1]

These laboratories have been occupied for some time in the development of a practical method for the reduction of the C_4-saccharinic (dihydroxybutyric and dihydroxyisobutyric) acids to the corresponding aldehydes and also in the reduction of *dl*-erythronic lactone to *dl*-erythrose. The work reported in this paper was carried out chiefly in connection with the second of these problems. Since difficulties were encountered when the reduction of *dl*-erythronic lactone was attempted, a study was made of the reduction of similar but less expensive lactones. As a result of this work the conditions for the reduction of *dl*-erythronic butyl ester to crystalline erythritol in good yield have been established,[2] but, as yet, *dl*-erythrose has not been obtained. Efforts in this direction are being continued.

A preliminary study of the method of catalytic hydrogenation in the presence of platinic oxide as applied to the aldonic acids was made by Glattfeld and Shaver.[3] They found it possible to reduce *d*-gluconic acid, freshly liberated from its calcium salt by means of sulfuric acid, to *d*-glucose in 14–28% yield (measured as osazone).

In the present study the procedure used by Glattfeld and Shaver was modified and applied to the reduction of the delta and gamma lactones of certain of the aldonic acids, and it was further extended to the reduction of several of the aldoses. Efforts were made to determine the conditions for the production, in the first case, of a maximum yield of the corresponding sugar with a minimum of the corresponding alcohol (hereinafter called alcohol), and in the second, of a high yield of alcohol.

The work was begun with a study of the hydrogenation of the pure delta lactone of *d*-gluconic acid. This substance should upon reduction give the sugar with the 1,5-ring, which should be less easily reduced to the alcohol than the sugar with the 1,4-ring that would be expected to result from the reduction of the gamma lactone of the acid. Glacial acetic acid was the solvent first used, because it was thought that in this solvent the conversion of the delta lactone to gamma lac-

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(1) This article is from the dissertation presented by G. Weber Schimpff in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

(2) Results to be communicated in a forthcoming article.

(3) Glattfeld and Shaver, THIS JOURNAL, 49, 2305 (1927).

TABLE I

REDUCTION OF ALDONIC ACID LACTONES IN AQUEOUS SOLUTION

Expt. no.	Lactone	Agitation cycles/min.	Vol. of soln., ml.	Molarity	Catalyst, g.	Time of hydrogenation, min.	$[\alpha]_D$		Sugar, %	Acid, %	Alcohol, %
							Unreduced soln.[a]	Reduced soln.			
1	*d*-Gluconic delta	120	100	0.281	0.9[b]	1200		+31.1	50.6	36.7	13
2	*d*-Gluconic delta	120	50	.200	.2	780		+21.0	27.0	73.0	0
					.2	1200		+31.6	48.0	38.0	14
					.2	1500		+40.4			
					.2	1980		+35.4	48.8	20.0	31
3	*d*-Gluconic delta	120	100	.200	.2	1980		+31.6	55.1	17.8	27
4	*d*-Gluconic delta	120	100	.281	1.2	840		+30.2	42.1		
5	*d*-Gluconic delta	120	100	.281	0.4	180		+19.5	24.5		
6	*d*-Gluconic delta	120	100	1.123	2.1[c]	3000		+30.2	40.3		
7	*d*-Gluconic delta	120	175	1.123	0.6	4440		+24.0	25.8		
8	*d*-Gluconic delta	120	200	1.123	1.0	1200		+30.0	44.6		
9	*d*-Gluconic delta	120	200	0.168[d]	0.5	1080		+33.3	51.6		
10	*d*-Gluconic delta	350	100	.200	1.0	30			47	49.8	3
11	*d*-Gluconic delta	350	100	.200	1.0	60			51	43.1	6
12	*d*-Gluconic delta	350	100	.200	2.0	20			72	27.2	0
13	*d*-Gluconic delta	350	100	.200	2.0	30			78	23.0	0
14	*d*-Gluconic delta	350	100	.200	2.0	35			80	19.0	0
15	*d*-Gluconic delta	350	100	.200	2.0	35			80	19.0	0
16	*d*-Gluconic delta	350	100	.200	2.0	40			78	23.2	0
17	*d*-Gluconic delta	350	100	.200	3.0	10			68	19.6	12
18	*d*-Gluconic delta	350	100	.200	3.0	20			61	12.0	27
19[e]	*d*-Gluconic delta	120	200	.042	0.6	30			28	58.0	14
					.3	80			38.9	38.4	23
					.2	110			44.8	33.5	22
					.2	140			43.0	23.0	34
					.2	170			39.1	15.1	46
20	*d*-Gluconic gamma	350	100	.200	2.0	20			23.4	53	24
21	*d*-Gluconic gamma	350	100	.200	2.0	60			46.8	12.4	41
22	*d*-Mannonic delta	350	100	.200	1.0	30		+31.5	51	44	5
23	*d*-Mannonic delta	350	100	.200	1.0	60		+10.9	76	20	4
24	*d*-Mannonic delta	350	100	.200	1.0	90		+ 5.1	37	15	48
25	*d*-Mannonic delta	350	100	.200	2.0	20		+11.2	70	28	2
26	*d*-Mannonic delta	350	100	.200	2.0	40			77	20	3
27	*d*-Mannonic gamma	350	25	.100	0.5	5		+38.2	69.4		
28	*d*-Mannonic gamma	350	25	.100	0.5	20		+35.9	76.4		
29	*l*-Rhamnonic delta	350	24	.100	0.5	5	−73.6	−48.2	13.9	76.3	10
30	*l*-Rhamnonic delta	350	24	.100	0.5	20	−73.6	−33.9	19	61.1	20
31	*l*-Rhamnonic gamma	350	24	.100	0.5	5	−36.8	−29.6	3.5	80.5	16
32	*l*-Rhamnonic gamma	350	24	.100	0.5	20	−36.8	−21.0	6.2	74.2	20
33	Lactobionic delta	350	24	.100	2.0	5	+38.2	+34.1	38	25.3	36.7
34	Lactobionic delta	350	24	.100	2.0	20	+38.2	+33.0	32	17	51
35	Lactobionic delta	350	24	.100	0.5	5	+42.3	+38.5	72	26.8	1.2
36	Lactobionic delta	350	24	.100	0.5	20	+42.3	+38.5	79	24	0

[a] A portion of the original solution was set aside; the rotations of this sample and of the reduced solution were observed in rapid succession at the close of the period of hydrogenation. [b] Catalyst was added in 0.3-g. portions, *t* = 0, 9, 15 hrs. [c] Addition of catalyst: 0.6 g. at 0 hrs.; 0.3 g. portions at 4, 9, 29, 31, 38 hrs. [d] This solution consisted of 30 ml. of the final solution from Experiment 7, diluted to a volume of 200 ml. [e] Glacial acetic acid was used as the solvent. The acid was removed by reduced pressure distillation before analyses were made.

tone and free acid[4] would be less rapid than in water. Although a reduction of 44.8% was obtained, this solvent was abandoned, because it was found that the use of aqueous solutions resulted in a greater reduction and permitted a simpler experimental procedure.

The effects of other variables—(1) concentration of solution, (2) amount of catalyst, (3) time of hydrogenation and (4) rate of agitation—on the reduction of *d*-gluconic delta lactone were also studied. It was found that an increase in the concentration of the lactone was attended by a marked decrease in the rate of reduction. A con-

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[4] (a) Nef, *Ann.*, **403**, 306 (1914); (b) Hedenburg, THIS JOURNAL, **37**, 345 (1915).

centration of 0.2 molar was finally chosen as satisfactory, for it favored rapid reduction and at the same time permitted the treatment of rather large quantities of lactone. In regard to the amount of catalyst, it was observed that large quantities favored the production of alcohol, and small quantities necessitated an increase in the time of hydrogenation, a factor which in itself tended to increase the amount of alcohol formed. The rate of shaking of the solution was found to be a factor of the utmost importance. In solutions of approximately the same concentration, with equal quantities of catalyst, it was found that the time necessary to secure a 50% reduction was decreased from twenty hours to thirty minutes when the rate of shaking was increased from 120 to 350 cycles per minute (see experiments 1 and 10, Table I).

Various other lactones were then used in place of the delta lactone of *d*-gluconic acid. When the gamma lactone of *d*-gluconic acid was used, it was found that it was reduced more slowly than was the delta lactone and that it gave a higher yield of alcohol. Under conditions that resulted in an 80% yield of *d*-glucose with no alcohol from the delta lactone, there was obtained from the gamma lactone 23.4% sugar and 24% alcohol. In marked contrast was the behavior of the two lactones of *d*-mannonic acid. Both were reduced very readily. On the other hand, both lactones of *l*-rhamnonic acid were reduced slowly and both gave relatively high yields of alcohol; the gamma lactone gave three to four times as much alcohol as sugar, whereas the delta lactone gave approximately equal amounts of the two products. These results led to the same conclusion as did the work with the lactones of *d*-gluconic acid, *viz.*, the gamma lactone yields a sugar which is more readily reduced to the alcohol than the sugar from the delta lactone. In the case of lactobionic acid only the delta lactone is known. This substance was reduced to the extent of 79% in twenty minutes, with the production of practically no alcohol. The variations in experimental conditions with the results obtained are recorded in detail in Table I.

The method of catalytic hydrogenation developed for the aldonic acids was then applied to the reduction of aldoses in aqueous solution. It was found possible to reduce almost completely *d*-glucose, *d*-mannose, *l*-arabinose, *d*-xylose, *l*-rhamnose hydrate and lactose monohydrate. In several of the experiments the alcohols were isolated in yields varying from 63 to 80%. The results of these experiments are recorded in Table II.

Further work is in progress in these Laboratories both on the method herein described and on modifications which may render it applicable to reactions at high pressure and high temperature.

Experimental Part

Apparatus.—The apparatus possessed the essential features of the equipment used by Glattfeld and Shaver,[3] but the details of design were similar to those of the hydrogenation apparatus now manufactured by the Burgess–Parr Company of Moline, Illinois.

TABLE II

REDUCTION OF ALDOSES IN AQUEOUS SOLUTION

Expt. no.	Sugar	Agitation, cycles/min.	Vol. of soln., m	Molarity	Catalyst, g.	Time of hydrogenation, hrs.	$[\alpha]_D$ Initial soln., $t = 0$	$[\alpha]_D$ Reduced soln.	Sugar, %	Alcohol, %	Amount isolated, g.	Yield,[a] %	M. p., °C.
37	*d*-Mannose	120	195	1.00	15	122	+14.3	+ 0.1	9.3[b]	90.7	25.2	75	164–165
38	*d*-Galactose	120	190	1.11	4.5	287	+74.1	+ 0.1			29.5	77.6	186–187
39	*d*-Glucose	120	100	0.20	5.1	99	+51.6	+ 0.9	nil	99.9			Sirup[c]
40	*l*-Arabinose	120	190	1.00	6	64	+92.2	− 0.8	0.4[d]	99.6	21.6	80	97– 99
41	*d*-Xylose	120	190	1.00	6	594	+19.7	+ 1					Sirup
42	*l*-Rhamnose monohydrate	120	100	1.00	5	69			8[e]	92	8.2	54[f]	120–122
43	Lactose monohydrate	350	95	0.20	12	12	+52.8	+17.8	1[g]	99	8[h]	63	79– 80
44	Lactose monohydrate	350	95	0.20	12	12	+52.8	+16.4	1	99			

[a] The yield was calculated on the basis of the amount of alcohol theoretically present in the solution which remained at the end of the experiment, after various samples had been removed for analysis. [b] The reducing value of *d*-mannose was considered equivalent to that of *d*-glucose. [c] The dibenzaldehyde derivatives of the sirup and of *d*-sorbitol (Pfanstiehl) were prepared. Both derivatives, which were amorphous, melted at 195–200°. A mixture of the two products melted at the same temperature. [d] The conversion factor 0.92 was used [Vogel and Georg, "Tabellen der Zucker und ihrer Derivate," Verlag Julius Springer, Berlin, 1931, p. 9]. [e] The conversion factor of *l*-rhamnose was found to be 0.97. [f] A second crop could have been obtained, but time did not permit. [g] The conversion factor 0.655 was used [Vogel and Georg, *ibid.*, p. 49]. [h] The solutions of experiments 43 and 44 were combined for the isolation of the lactitol.

Materials.—(1) Commercial electrolytic hydrogen was used without purification. (2) Platinic oxide monohydrate was prepared according to the method described by Adams, Voorhees and Shriner.[5] However, it was found possible to prepare at a single fusion ten times the quantity specified. (3) *d*-Mannose was prepared according to the method of Clark;[6] $[\alpha]_D$ +14.1°. (4) *d*-Mannonic delta lactone was prepared from calcium *d*-mannonate dihydrate.[7] This salt was converted into the sodium salt by means of sodium oxalate. After the removal of the calcium oxalate, the filtrate was taken to dryness under diminished pressure at 50–60°. The solid residue was dried in a vacuum desiccator over concentrated sulfuric acid; yield, 96%. The sodium salt was then converted into the delta lactone according to the method of Brackenbury and Upson;[8] yield, 77.8%; m. p. 156–157°; $[\alpha]_D$ +113.4° (four min.). (5) *d*-Mannonic gamma lactone was prepared by an adaptation of the methods reported by Nef,[4a] by Hedenburg,[4b] and by Isbell and Frush.[9] A dry mixture of 23.32 g. (0.05 mole) of calcium *d*-mannonate dihydrate and 6.30 g. (0.05 mole) of powdered oxalic acid dihydrate was added to 24 ml. of boiling water. The hot thick paste was kept on a steam-bath with constant stirring for twenty minutes. The calcium oxalate was separated and washed with a total of 50 ml. of hot water. The washings and 4 drops of concentrated hydrochloric acid were added to the filtrate, and the entire solution was concentrated to a thick sirup at 50° under reduced pressure. This sirup was diluted with 20 ml. of water, transferred to a crystallizing dish, and placed in a vacuum desiccator over concentrated sulfuric acid. Crystals soon appeared; when the mass became solid, it was transferred to a Büchner funnel and the solid washed with about 200 ml. of absolute ethanol. The crystals were dried in a vacuum desiccator; m. p. 151–152°; $[\alpha]_D$ +51.7° (50 min.); yield, 12.1 g. (68%). (6) The delta and gamma lactones of *d*-gluconic acid were purchased from the Pfanstiehl Chemical Company, Waukegan, Illinois. (7) *l*-Rhamnonic delta lactone was kindly supplied by Professor Fred W. Upson, Department of Chemistry, University of Nebraska; m. p. 172–177°, $[\alpha]_D$ −97.9° (5 min.). (8) *l*-Rhamnonic gamma lactone was prepared by Mr. B. D. Kribben of this Laboratory from *l*-rhamnose monohydrate isolated from quercitrin; m. p. 147–149°; $[\alpha]_D$ −37.6° (20 min.). (9) Lactobionic delta lactone was kindly supplied by Dr. Horace S. Isbell of the Bureau of Standards, Washington, D. C.; m. p. (dec.) 195–196°; $[\alpha]_D$ +53.4° (2 min.). (10) *d*-Galactose, *l*-arabinose, *d*-xylose and lactose monohydrate were purchased from the Kahlbaum Chemical Company. (11) *l*-Rhamnose monohydrate was kindly supplied by Dr. M. E. Hanke, Department of Physiological Chemistry, University of Chicago; m. p. 101–103°; $[\alpha]_D$ +8.64° (final).

Reduction of Lactones.—An experiment with *d*-gluconic delta lactone (see experiment 3, Table I) will be described, since the operations are typical of those used in all the experiments conducted in aqueous solution. A 3.562-g. sample (0.02 mole) was dissolved in water and the volume made up to 100 ml. The solution was transferred to the reaction bottle and 0.2 g. of catalyst added; the bottle was thoroughly evacuated, filled with hydrogen until the gage registered a pressure of 35 pounds,[10] and shaken at the rate of 120 cycles per minute for thirty-three hours. At the end of that time the platinum black was allowed to settle; the rotation of the solution was observed; a sample was analyzed for reducing material by means of a micromodification of the Benedict method;[11,12] and a sample was titrated for total acidity. The percentage alcohol was calculated by subtracting from 100 the sum of the percentages of sugar and acid. In some experiments (see experiment 2, Table I) the shaking was interrupted, samples were removed for analysis, more catalyst was added and then the hydrogenation continued.

Isolation of *d*-Glucose.—In experiment 6 (Table I), the platinum black was removed by filtration after the final analysis, and the volume of the solution measured (84 ml. which contained 6.72 g. of *d*-glucose by analysis). The solution was diluted to 200 ml., warmed in a water-bath at 50°, and neutralized with calcium carbonate. The filtrate from the excess carbonate was concentrated to a thick sirup at reduced pressure (water-bath 50°). This sirup was diluted to 30 ml. with hot water and triturated with about 1200 ml. of absolute ethanol. The solid calcium *d*-gluconate which separated was powdered and washed with 200 ml. of absolute ethanol (weight 11.6 g., air dry). The ethanol solutions were combined and concentrated at reduced pressure to a volume of about 250 ml. (bath 40°). The volume was further reduced to about 30 ml. in a vacuum desiccator. The crystalline *d*-glucose was separated by filtration, washed with absolute ethanol and absolute ether, and dried in a vacuum desiccator; weight 5.2 g.; recovery 77.4%. After two recrystallizations from absolute ethanol, the m. p. was 145.5–146.6°; $[\alpha]_D$ +51.9° (17 min.).

Reduction of Aldoses.—The procedure used for the reduction of the sugars was practically identical with that outlined above, except that the process was usually interrupted at convenient intervals for the analysis of the solution and the introduction of catalyst. The process was discontinued when analysis showed 10% or less of sugar. The alcohol was usually isolated from the solution left after the removal of the platinum black, by the addition of an appropriate mixture of 95% ethanol and ordinary ether followed by storage of the solution in the refrigerator until crystallization had taken place. After the removal of the crystals, the mother liquor was concentrated under diminished pressure at 50° to a small volume, and the above treatment repeated for the obtaining of a second crop. It was not possible to obtain the *d*-sorbitol or the xylitol in crystalline form.

Isolation of Lactitol.—After the removal of the platinum black, the solution was evaporated to dryness at reduced

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[5] Adams, Voorhees and Shriner, "Organic Syntheses," 1928, John Wiley and Sons, Inc., New York City, Vol. VIII, p. 98.

[6] Clark, *Sci. Papers Bur. Standards*, **17**, 567 (1922).

[7] The method used for the preparation of the calcium salt was similar to that used by Hudson and Isbell [THIS JOURNAL, **51**, 2225 (1929)] for calcium *d*-gluconate.

[8] Brackenbury and Upson, *ibid.*, **55**, 2512 (1933).

[9] Isbell and Frush, *Bur. Standards J. Research*, **11**, 649 (1933).

[10] A pressure of two to three atmospheres was used throughout the work.

[11] Mathews, "Physiological Chemistry," William Wood and Company, Baltimore, Md., 5th ed., p. 1188.

[12] In the calculation of the percentage of reducing material, the molecular weights of the sugar and acid lactone were considered identical, even though their formulas differ by two hydrogen atoms.

pressure (bath 50°). The residue was triturated for several hours with absolute acetone. The resulting white solid, which was very hygroscopic, was carefully dried in a vacuum desiccator over phosphorus pentoxide (weight 8.0 g., 63%). A 0.900-g. sample was weighed rapidly, dissolved in water, and the solution diluted to 10 ml. The rotation of the solution in a 1-dcm. tube was found to be +1.48°; $[\alpha]_D$ +16.4°. The only value given in the literature is the one reported by Senderens,[13] who found $[\alpha]_D$ +12.2° for the monohydrate of lactitol. He reported the m. p. to be 78°. Our product melted to a milky liquid at 79–80° and increased in volume about five-fold; at 130–140° the mass turned to a yellow glass-like solid which decomposed at 190–200°. Neuberg and Marx[14] reported that anhydrous lactitol decomposed at 200°.

Summary

1. A method of catalytic hydrogenation has been developed whereby the delta lactones of aldonic acids are reduced in good yield to the corresponding sugars. The gamma lactones are also reduced, but they usually give lower yields of the sugars owing to the further reduction of the sugars to the corresponding sugar alcohols.

2. The method has been adapted to the reduction of the sugars to the corresponding sugar alcohols. It is possible to obtain practically complete reduction and to isolate the sugar alcohols in 63–80% yields.

CHICAGO, ILLINOIS RECEIVED AUGUST 29, 1935

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[13] Senderens, *Compt. rend.*, **170**, 47 (1920).

[14] Neuberg and Marx, *Biochem. Z.*, **3**, 539 (1907).

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

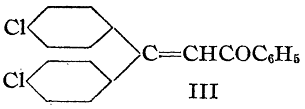
The Reversibility of the Friedel–Crafts Condensation. Hydrogenation Phenomena

BY L. L. ALEXANDER, A. L. JACOBY AND REYNOLD C. FUSON

It was to be predicted that the reversible addition of aromatic hydrocarbons to α,β-unsaturated carbonyl compounds[1] would be prevented by the presence of suitable substituents on the *beta* carbon atom. Several examples of conjugated systems have now been found which do not yield addition products but instead undergo hydrogenation. Thus, 1,1-diaryl-2-acylethylenes do not condense with benzene in the presence of aluminum chloride, but, instead, *are hydrogenated to the corresponding saturated diaryl ketones.*

$$\underset{\text{I}}{(Ar)_2C{=}CHCOR} \xrightarrow[AlCl_3]{C_6H_6} \underset{\text{II}}{(Ar)_2CHCH_2COR}$$

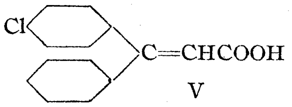
For example, 1,1-di-(p-chlorophenyl)-2-benzoylethylene (III) is converted to α-benzohydrylacetophenone (IV).



III

$(C_6H_5)_2CHCH_2COC_6H_5$

IV



V

$(C_6H_5)_2CHCH_2COOH$

VI

$(C_6H_5)_2C{=}CHCOC_6H_5$

VII

$(C_6H_5)_2C{=}CHCOC(CH_3)_3$

VIII

Similarly, β-(p-chlorophenyl)-cinnamic acid (V) gives β,β-diphenylpropionic acid (VI). In both of these examples replacement as well as hydrogenation is involved. However, the chlorine-free analog of III—1,1-diphenyl-2-benzoylethylene (VII)—appears to undergo only the latter change; it gives IV. In a similar fashion, 1,1-diphenyl-2-trimethylacetylethylene (VIII) is transformed into its hydrogenation product, α-benzohydrylpinacolone.

However, it seemed possible that this type of transformation might not be dependent on the presence of a hetero conjugated system, but might be simply a property of stilbenes. In order to clear up this point stilbene, p-bromostilbene and p,p'-dichlorostilbene were each subjected to treatment with benzene in the presence of anhydrous aluminum chloride. *In each case the product was dibenzyl.* The generalized form of the equation is $XC_6H_4CH{=}CHC_6H_4X + 2C_6H_6 + 2H = C_6H_5CH_2CH_2C_6H_5 + 2C_6H_5X$. It is seen that this process involves replacement of aryl groups as well as hydrogenation at the double bond.

The various mechanisms which suggest themselves for these processes raise the question as to whether the addition of benzene, the elimination of the substituted phenyl group and the hydrogenation are related processes and, if so, in what sequence they occur. The work is being continued from this point of view.

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[1] For references to earlier papers of this series, see Woodward, Borcherdt and Fuson, THIS JOURNAL, **56**, 2103 (1934).

Experimental Part

α-Benzohydrylacetophenone (IV)

A. From 1,1-Di-(*p*-chlorophenyl)-2-benzoylethylene (III).—A mixture of 0.75 g. of the dichloro ketone, 1.5 g. of aluminum chloride and 20 cc. of dry benzene was saturated with dry hydrogen chloride and allowed to stand at room temperature for twelve hours. The product melted at 91.5–92°, and was shown by the method of mixed melting points to be α-benzohydrylacetophenone.

B. From 1,1-Diphenyl-2-benzoylethylene (VII).—α-Benzohydrylacetophenone was also obtained by applying the foregoing procedure to 1,1-diphenyl-2-benzoylethylene.

α-Benzohydrylpinacolone.—In a like manner, the interaction of 5 g. of 1,1-diphenyl-2-trimethylacetylethylene (VIII), 10 g. of aluminum chloride, 100 cc. of dry benzene, and dry hydrogen chloride gave 3.6 g. of α-benzohydrylpinacolone. The product melted at 83–84.5°, and the melting point was not depressed when this sample was mixed with an authentic specimen of the ketone.

Ethyl β-Phenyl-β-(*p*-chlorophenyl)-β-hydroxypropionate.—A mixture of 54.1 g. of *p*-chlorobenzophenone, 50 g. of ethyl bromoacetate and 225 cc. of dry benzene was treated with 19.6 g. of granulated zinc. The mixture was warmed and stirred for an hour and then decomposed with dilute acid in the usual manner. The product (from alcohol) melted at 79–80.5°; yield, 79%.

Anal. Calcd. for $C_{17}H_{17}O_2Cl$: C, 67.0; H, 5.6. Found: C, 67.3; H, 5.7.

β-Phenyl-β-(*p*-chlorophenyl)-β-hydroxypropionic acid was obtained by saponification of the ester. It crystallized from dilute alcohol in light yellow needles melting at 188.5–189°, with decomposition.

Anal. Calcd. for $C_{15}H_{13}O_3Cl$: C, 65.1; H, 4.7. Found: C, 64.9, 65.2; H, 4.9, 4.7.

β-(*p*-Chlorophenyl)-cinnamic Acid (V).—A mixture of 44.2 g. of β-phenyl-β-(*p*-chlorophenyl)-β-hydroxypropionic acid, 24.6 g. of acetic anhydride and 10.9 g. of freshly fused sodium acetate was heated for four hours under reflux. The solution was then poured into water and the mixture allowed to stand at room temperature for two weeks. The cinnamic acid was recrystallized from alcohol; m. p. 168°.

Anal. Calcd. for $C_{15}H_{11}O_2Cl$: C, 69.6; H, 4.3; neut. equiv., 258.5. Found: C, 69.6; H, 4.4; neut. equiv., 260.8.

β,β-Diphenylpropionic Acid (VI).—The chloro acid was shaken with a mixture of benzene, aluminum chloride, and hydrogen chloride over a period of twenty hours. The product (from an ether–petroleum ether mixture) melted at 151–152°, and was shown by the mixed melting point method to be β,β-diphenylpropionic acid.

Dibenzyl

A. From *p,p'*-Dichlorostilbene.—One and a half grams of powdered aluminum chloride was added to a mixture of 1 g. of *p,p'*-dichlorostilbene and 20 cc. of dry benzene. The mixture became dark red in color. Dry hydrogen chloride was bubbled through the mixture for thirty minutes. The reaction mixture was then stirred at room temperature for sixteen hours and poured on a mixture of ice and hydrochloric acid. The product melted at 51.5° and when mixed with *dibenzyl* did not depress the melting point; yield, 70%.

B. From Stilbene.—By a similar procedure involving stilbene and in which the reaction time was fifty-four hours, a 20% yield of dibenzyl was obtained.

C. From *p*-Bromostilbene.—In this experiment, in which the reaction time was seventeen hours, 2.9 g. of dibenzyl was obtained from 5 g. of the bromostilbene. The color change from brown to red was again noticed.

Summary

1. 1,1-Di-(*p*-chlorophenyl)-2-benzoylethylene and β-(*p*-chlorophenyl)-cinnamic acid react with benzene in the presence of aluminum chloride to give, respectively, α-benzohydrylacetophenone and β,β-diphenylpropionic acid.

2. Under the same conditions, 1,1-diphenyl-2-benzoylethylene and 1,1-diphenyl-2-trimethylacetylethylene undergo hydrogenation to α-benzohydrylacetophenone and α-benzohydrylpinacolone.

3. Similar treatment converts stilbene, *p*-bromostilbene and *p,p'*-dichlorostilbene into dibenzyl.

URBANA, ILLINOIS RECEIVED AUGUST 8, 1935

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Pyrolysis of Allyl-*p*-phenetidine

BY F. L. CARNAHAN

The predominating type of pyrolytic decomposition followed by the allylanilines has been shown[1] to differ from that encountered in the simpler allyl phenyl ethers. The allylanilines formed propylene, the corresponding primary amine and tarry material rather than products of allyl group migration from nitrogen to the aromatic nucleus. This behavior in some respects resembles that of 2,4-dimethyl-6-propylphenyl allyl ether,[2] which gave allene, diallyl, propylxylenol and resinous material. Previous work[1] on allylaniline, diallylaniline and diallyl-*p*-phenetidine has been extended to include allyl-*p*-phenetidine.

In connection with the proposed mechanism for the thermal decomposition of allylanilines, it is important to know if hydrogen is evolved at reflux temperatures. None was present in the gases from the diallylanilines, but some was found when allylaniline was heated at 600–700°. While allylaniline did not decompose at its reflux temperature (218°) it has been found that allyl-*p*-phenetidine is slowly decomposed on refluxing at 270°. Per mole of allyl-*p*-phenetidine, 0.465 mole of *p*-phenetidine was found, the loss in weight corresponded to 0.40 mole of propylene, resin equivalent to 0.447 mole was formed, and material equivalent to 0.10 mole was unidentified. No hydrogen was present. A search for 6-ethoxyquinoline and 6-ethoxytetrahydroquinoline failed to disclose either. At higher temperatures allylaniline gave some quinoline; this effect is extensive in the presence of lead dioxide.[3]

The most probable mechanism for these data is the one previously set forth wherein the initial step was formation of radicals

$$ArNHC_3H_5 \longrightarrow ArNH— + C_3H_5—$$

but instead of assuming that these radicals undergo disproportionation it is proposed that they become hydrogenated to *p*-phenetidine and propylene, respectively, by collision with neighboring undecomposed molecules. The latter molecules would thus be converted into an acrolein-anil, $ArN{=}CHCH{=}CH_2$, which is regarded as the forerunner of the resinous material. The absence of hydrogen as a reaction product makes it appear certain that molecular hydrogen plays no part in the reaction mechanism. It might be argued, for example, that molecules of $ArNHC_3H_5$ changed first into $H_2 + ArN{=}CHCH{=}CH_2$ with the hydrogen thus formed splitting another molecule of allyl-*p*-phenetidine into phenetidine and propylene. Three facts eliminate this possibility. Molecular hydrogen is sufficiently inert to escape partly as such but none is found. The mechanism would fail with the tertiary amines, diallylaniline and diallyl-*p*-phenetidine, which have been found actually to pyrolyze more readily than does allyl-*p*-phenetidine itself. Again, when hydrogen is removed from an allylaniline, especially by the aid of lead dioxide,[3] the product is related to quinoline and not a resin.

Experimental

Allyl-*p*-phenetidine.—Allyl-*p*-phenetidine was prepared by the general method of Hepp.[4] Allyl bromide was added to the reaction product of sodium on phenacetin; the thick oil resulting was hydrolyzed by sodium hydroxide in alcohol. Steam distillation of the product, followed by vacuum fractionation with a nitrogen leak gave allyl-*p*-phenetidine free from *p*-phenetidine. The yield was 31%; 37% if recovered *p*-phenetidine was taken into account.

The compound boils at 134.5° at 10 mm., 140° at 15 mm., and with decomposition at 265° at 745 mm. pressure. It shows $d^{20}{}_4$ 1.0096; $n^{20}{}_D$ 1.5493.

Anal. Calcd. for $C_{11}H_{15}ON$: C, 74.52; H, 8.53. Found: C, 74.55; H, 8.48.

Allyl-*p*-toluenesulfon-*p*-phenetidine.—Allyl-*p*-phenetidine was treated with 1.5 equivalents of *p*-toluenesulfonyl chloride and 5 equivalents of 2 *N* potassium hydroxide. The usual treatment gave crude alkali-insoluble material in a yield of 86% of the calculated amount. Crystallization from methyl alcohol and water accompanied by treatment with bone black gave the derivative in white needles melting at 81°.

An identical product was obtained by treating *p*-toluenesulfone-*p*-phenetidide[1] with an excess of allyl bromide in *N* potassium hydroxide solution at room temperature. Considering a small proportion of the starting material recovered unchanged, the yield was 99.5%.

Anal. Calcd. for $C_{18}H_{21}O_3NS$: C, 65.21; H, 6.39. Found: C, 65.49; H, 6.37.

Pyrolysis of Allyl-*p*-phenetidine by Refluxing.—Several runs were made with the same general results. The following experiment may be taken as representative.

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[1] Carnahan and Hurd, THIS JOURNAL, **52**, 4586 (1930).

[2] Claisen and Tietze, *Ann.*, **449**, 94 (1926).

[3] Koenigs, *Ber.*, **12**, 453 (1879).

[4] Hepp, *ibid.*, **10**, 327 (1877).

A 70.8-g. (0.4 mole) sample was placed in a 125-cc. flask to which was sealed 75 cm. of 1 cm. inside diameter tubing to serve as an air condenser. A thermometer rested on the bottom of the flask and extended into the condenser. Through a 15-cm. tube sealed to the flask nitrogen could be passed into the apparatus. Provision was made for the collection of gaseous products over water. The flask was heated in a fused salt bath to maintain a reflux about 15 cm. above the liquid level. The refluxing was continued for one hundred twenty hours with the temperature of the liquid in the flask averaging 270°.

During the pyrolysis gas was slowly evolved. Analysis showed 93.0% soluble in 85% sulfuric acid, 1.4% oxygen, 5.6% nitrogen. Passed through a solution of dry bromine in dry carbon tetrachloride, the gas formed propylene bromide, $n^{20}\text{D}$ 1.5181. The amount of gas over water was 965 cc. at 21° and 740 mm. equivalent to 0.035 mole propylene. The small amount collected is partly owing to the fairly high solubility of propylene in water (44.6 cc. per 100 cc. of water) and the long time of contact. The loss of weight in this experiment was 7.3 g. If this loss is considered to be represented by propylene evolved, it would correspond to 0.174 mole or 0.44 mole of propylene per mole of allyl-*p*-phenetidine. Another experiment in which the loss of weight of the refluxed material was ascertained quantitatively indicated 0.404 mole of propylene per mole of the amine.

Liquid products of the pyrolysis were poured while hot into a 200-cc. balloon flask with a side-neck carrying a nitrogen leak. Distillation through a 1.5 × 38 cm. packed column was carried out at 9 mm. pressure. The first fraction was colorless, boiled at 114–116°, and weighed 20.5 g. The second fraction was also colorless, boiled at 116–130°, and weighed 5.05 g. Both these fractions gave *p*-toluenesulfone-*p*-phenetidide,[1] m. p. 108°, in yields as high as obtained from pure *p*-phenetidine. Melting points in mixture with an authentic specimen of the derivative were unchanged.

When distillation through the column became impossible, the procedure was continued in a Claisen flask. The deep yellow liquid collected through the range 160–235° at 19 mm. weighed 6.75 g. Of this liquid, 40% was soluble in 3 *N* hydrochloric acid. In the soluble portion attempts were made to identify 6-ethoxyquinoline[5] (b. p. 290–292°) and 6-ethoxytetrahydroquinoline[6] (b. p. 164–166° at 17 mm.). On account of their high boiling points, these compounds should be present in this fraction rather than one composed predominantly of *p*-phenetidine. The procedures of Sonn and Benirschke[6] were followed in the preparation of 6-ethoxyquinoline and 6-ethoxytetrahydroquinoline. The methiodide of the former melted at 193–194°, that of the latter at 208–209°. A search for the two compounds in the acid-soluble material above as well as in the intermediate (116–130° at 9 mm.) fraction did not disclose either of them.

The non-basic material was not further investigated. Possibly it may represent a lower stage of polymerization than the resin itself.

The residue from the distillation procedures was a dark brown brittle resin weighing 31.25 g., m. p. 68–88°.

The resin was soluble in ether, acetone, benzene, xylene and concentrated sulfuric acid, giving in each case a solution with a green-blue fluorescence. This phenomenon may indicate the presence of nitrogen rings in the resin since certain salts of 6-ethoxyquinoline and quinine exhibit fluorescence. On long boiling with 3 *N* hydrochloric acid about 6% of the resin dissolved. No simple water-insoluble material such as *p*-phenetidine was produced by boiling 5.0 g. of the resin with 25 cc. of 25% hydrochloric acid for twenty-seven hours. Likewise, boiling for twelve hours with 60% sulfuric acid effected no decomposition.

Summary

1. Allyl-*p*-phenetidine and allyl-*p*-toluenesulfon-*p*-phenetidide have been prepared and characterized.

2. Allyl-*p*-phenetidine has been found to decompose on refluxing at atmospheric pressure into *p*-phenetidine, propylene and resinous material. The initial step of this process appears to be a splitting into radicals at the carbon-to-nitrogen bond.

STATE COLLEGE, PA. RECEIVED AUGUST 26, 1935

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[5] Grimaux, *Bull. soc. chim.*, [3] **15**, 23 (1896).

[6] Sonn and Benirschke, *Ber.*, **54**, 1732 (1921).

[Contribution from the Chemical Laboratory of Harvard University]

The Induction Period in Gaseous Thermal Explosions[1]

By O. K. Rice,[1a] Augustine O. Allen and Hallock C. Campbell

We have recently studied the explosions of azomethane[2a] and ethyl azide,[2b] and have shown that they are probably thermal explosions, due to self-heating of the gas on account of the exothermicity of their slow decompositions. In these papers we have compared our results with the theory of Semenoff,[3] which gives the critical explosion pressure as a function of the temperature. Now it is observed when the gases are admitted to the reaction vessel that an appreciable time elapses before the explosion occurs. These lag times or induction periods have been measured in many cases, and in this paper we shall present these data, and discuss the theory. We shall see that this enables us to make an estimate of the heat of decomposition.

The basis of the theory which we shall present consists in following the change of temperature of the gas as reaction proceeds. An equation giving the amount, T, by which the temperature of the reacting gas exceeds that of its container as a function of the time and from which the induction period can be obtained has been given by Allen and Rice.[2a] The rate of production of heat is given by the expression $QknV$, where Q is the heat of reaction per mole of gas decomposed, V the volume of the reaction vessel, n the number of moles of reacting gas per unit volume, and k the rate constant. $k = Ae^{-E/R(T + T_0)}$, A being a constant, R the gas constant, E the activation energy for the unimolecular decomposition, and $T + T_0$ the temperature of the gas; T_0 is the temperature of the reaction vessel. We may write $n = n_0e^{-kT}$, where n_0 is the initial value of n and t is the time, provided we assume as an approximation that k is constant during the induction period. Heat is removed from the gas by conduction and convection at the rate axT, a being the wall area and x a constant. Subtracting the rate of loss of heat from the rate of production and dividing by C, the total heat capacity of the gas in the vessel, we get the rate of change of the temperature of the gas; making a slight reduction we obtain the equation

$$\mathrm{d}T/\mathrm{d}\tau = e^{-E/R(T + T_0)}\, e^{-k(C/B)\tau} - (ax/B)T \quad (1)$$

where $B = QAn_0V$ and $\tau = tB/C$; here t is measured from the moment the gas is admitted to the vessel, assuming that it warms up instantly to the temperature T_0, an assumption that will be discussed later. Since C as well as B is proportional to n_0, we may, for any given series of runs involving a definite substance and reaction vessel at a definite external temperature, T_0, but with varying pressure, consider τ to be a measure of the time from the start of the experiment expressed in a special set of units. Likewise the quantity B/ax, assuming that x is independent of the pressure, is a measure of the pressure used in a given experiment, and its value determines whether or not an explosion occurs in an experiment performed at a given temperature, T_0. In a case in which an explosion occurs integration of (1) will show that the temperature rises very suddenly after a lapse of time, and the time at which this sudden rise occurs may be set equal to the induction period,[4] while if explosion does not occur the temperature merely rises to a maximum and falls off again.

The differential equation (1) cannot be integrated analytically, but it may be solved numerically by the use of the Runge–Kutta formula.[5] In order to compare with the experimental data it is necessary to go through this process for different values of T_0 and ax/B. When this is done the value of τ at which the explosion occurs is known for any given conditions; this may be compared with the observed induction period t and B/C found. Now $B/C = QAn_0V/n_0VC_\mathrm{M} = QA/C_\mathrm{M}$ where C_M is the heat capacity per mole of azomethane; as A is known, we can calculate Q/C_M which should be practically constant for all experiments with a given composition of gas. If there are r moles of inert gas per mole of azo-

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[1] Presented at the New York Meeting of the American Chemical Society, April, 1935.

[1a] Present address, University of California, Berkeley, Calif.

[2] (a) Allen and O. K. Rice, This Journal, **57**, 310 (1935); (b) Campbell and O. K. Rice, *ibid.*, **57**, 1044 (1935).

[3] Semenoff, *Z. Physik*, **48**, 571 (1928).

[4] The same principles have been used by Tizard and Pye [*Phil. Mag.*, **44**, 79 (1922)] in discussing the oxidation of certain hydrocarbons, but their experiments were of a different type than ours, and their equations cannot be used in treating the experiments of the type considered here.

[5] Scarborough, "Numerical Mathematical Analysis," The Johns Hopkins University Press, p. 273.

methane, then $C_M = C_A + rC_G$, where C_A is the molal heat capacity of azomethane and C_G that of the inert gas.

In order to take into account the correction factor $e^{-k(C/B)\tau}$, which allows for the amount of gas decomposed before explosion takes place, and which affects the induction period near the explosion limit and also changes the value of the critical explosion pressure somewhat, it is necessary to assume a preliminary value of C/B, which is precisely the quantity we are trying to obtain. One is thus required to make a series of successive approximations, a very long process on account of the tedious calculation involved in the use of the Runge–Kutta formula. This fact, together with the desirability of having an easy way to perform the integration for a considerable range of values of the constants involved, has led us to seek an approximate method of calculation. This will be presented in §2. It is first necessary, however, to carry out the more exact integration of Equation (1) for some special values of the constants involved, in order to gain some information about the general character of the solutions of (1) and to be able to verify the accuracy of the approximate method.

For this purpose we have taken among others the case where T_0 = 630°K. and $kC/B = 1.27 \times 10^{-21}$ and E = 51,200 calories per mole. These values were estimated to correspond roughly to the situation with azomethane at 630°K. Figure 1 shows the calculated T *vs.* τ curves for various values of ax/B. It is seen that, as expected, the curves are definitely of two classes, the curves for small values of ax/B (large values of the pressure) being such as one would expect to correspond to an explosion, while the curves for large values of ax/B correspond to a quiet decomposition in which the temperature reaches a relatively low maximum, and then drops off. In the case of the explosive curves, the theory does not predict an exact instant for the explosion to occur, but certainly fixes it within an interval of time much smaller than the experimental error in determining the induction period. The critical value of ax/B appears to lie between 2.86×10^{-19} and 2.87×10^{-19}. It is, however, not certain that this value can be determined as closely as indicated by these figures, for very close to the explosion limit the curves are very sensitive to slight inaccuracies in the calculation, and it is quite possible that one which appears to be explosive actually should not be, or *vice versa.* But if the curve is only so far from the explosion limit as the one for $ax/B = 2.84 \times 10^{-19}$ in Fig. 1, the critical τ for explosion is no longer sensitive to slight errors. For values of the pressure very near the explosion limit very large values of τ are theoretically possible, but experimentally these have not been realized. It is, in general, impossible to adjust the pressure closely enough to get within the critical range of pressures, and it is also probable that the theory fails in this region, as k is not actually constant as we have assumed.

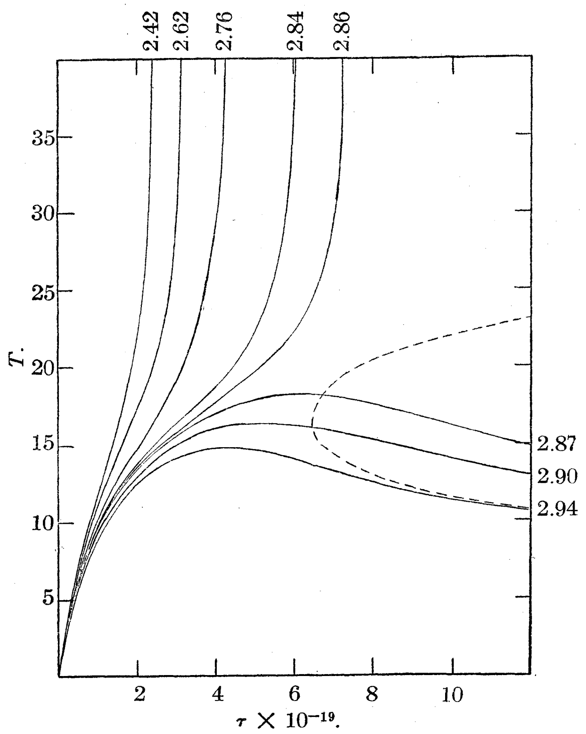

Fig. 1.—Theoretical temperature time curves at 630°K. for various values of $(Ax)/B(\times 10^{19})$.

In spite of the probable failure of the theory for pressures very close to the explosion limit it will not be without interest to examine a little more closely the nature of the solutions of the differential equation (1). Every one of the T *vs.* τ curves will ultimately reach a maximum, even though it be of the explosive type. This maximum will necessarily lie on the locus

$$(kC/B)\tau = -E/R(T + T_0) - \ln(ax/B) - \ln T \quad (2)$$

which makes $dT/d\tau$, as given by Equation (1), zero. The locus defined by Equation (2) for $ax/B = 2.86 \times 10^{-19}$ is shown (broken curve) in Fig. 1; the loci for other values of ax/B near this will be of just the same shape, but displaced along the τ axis a short distance. These loci are s-shaped, starting at $\tau = \infty$ for $T = 0$ and eventually reaching $\tau = -\infty$ for $T = \infty$. There are two points where the locus (2) has a vertical slope; one is shown, the other one is at a value of T approximately equal to

E/R, which is of the order of 25,000°, and a value of τ approximately $(B/kC)\ (E/RT_0 - 1 + 2\ \ln(RT_0/E))$, or about 32×10^{19}, greater than the value of τ for the first point of vertical slope. This value of τ gives the longest theoretically possible induction period. The explosive curves theoretically reach the upper branch of (2), that is, the part of the locus defined by (2) which is going out to $\tau = -\infty$; the values of T thus theoretically attained are greater than 25,000°. Such values will obviously not actually be reached, for one reason because k will not actually be independent of T and therefore the azomethane is used up before such temperatures are reached. The curves which have their maxima on the lower and middle branches of (2), up to the second point of vertical slope, where the locus defined by (2) turns around and heads toward $\tau = -\infty$, are the non-explosive curves. Theoretically there is a perfectly continuous transition between explosive type and non-explosive type curves, the transition occurring in an astonishingly small range of values of ax/B.

§2. Approximate Integration of Equation (1)

In order to get an approximate integration of Equation (1) we first see what can be done if the term $e^{-k(C/B)\tau}$ is set equal to 1. Under these circumstances we may, from Equation (1), write for τ_c, the critical value of τ at which explosion takes place

$$\tau_c = \int_0^{2RT_0^2/E} [e^{-E/R(T + T_0)} - (ax/B)T]^{-1}\,\mathrm{d}T \qquad (3)$$

The upper limit in this integral is obtained in the following way. In the theory of Semenoff the rise in temperature at the explosion limit is equal approximately to[2a] RT_0^2/E, this being also very approximately the temperature at which the locus defined by Equation (2) has infinite slope, as shown in Fig. 1. From Fig. 1 it is obvious that, though τ_c cannot, as we have said, be exactly defined, it will be very reasonable to determine a value by integrating to the temperature where T is equal to twice the value RT_0^2/E.

If we make the allowable approximation[6] $(1 + T/T_0)^{-1} = 1 - T/T_0$ then we may write Equation (3) in the form

$$\tau_c = \int_0^{2RT_0^2/E} [e^{-E/RT_0}\, e^{ET/RT_0^2} - (ax/B)T]^{-1}\,\mathrm{d}T \qquad (4)$$

If we set $y = ET/RT_0^2$ and $f = (ax/B)\ (RT_0^2/E)\ e^{E/RT_0 - 1}$ this takes the form

$$\tau_c = (RT_0^2/E)e^{E/RT_0 - 1}\, I_0 \qquad (5)$$

where

$$I_0 = \int_0^2 (e^{y - 1} - fy)^{-1}\,\mathrm{d}y \qquad (6)$$

I_0 may be evaluated as a function of f from Equation (6) by numerical integration. By its definition, f is inversely proportional to P, the pressure, x being assumed independent of pressure.

Now the equation for the critical explosion pressure[7] is also based on the same approximations made so far in the considerations of this section. Using this equation we see that at the critical explosion pressure f is equal to 1 and we may set

$$f = P^*/P \qquad (7)$$

where P^* is the critical explosion pressure of the approximate theory. For explosive runs, of course, $f < 1$.

Allowance for the term $e^{-k(C/B)\tau}$ of Equation (1) may be made in an approximate manner as follows. In the actual calculation of the curves in Fig. 1 one finds that the value of τ at which the curve begins to rise rapidly is largely determined by its behavior in the neighborhood of the inflection point, which occurs at a value of τ very near to $\tau_c/2$ and a value of T very near RT_0^2/E. This suggests that we replace the exponential term in question by a sort of average value, namely, $e^{-k^*(C/B)\tau_c/2}$, where k^* is the value of the rate constant at the temperature $T_0 + RT_0^2/E$. We then get in place of Equation (4), the equation

$$\tau_c = \int_0^{2RT_0^2/E} [e^{-E/RT_0}\, e^{ET/RT_0^2}\, e^{-k^*(C/B)\tau_c/2} - (ax/B)T]^{-1}\,\mathrm{d}T \qquad (8)$$

in which τ_c is involved inside the integral sign as well as on the left-hand side of the equation. This equation is to be solved for τ_c. It is convenient to define a quantity I, similar to the quantity I_0 of Equation (5) by the relation

$$\tau_c = (RT_0^2/E)e^{E/RT_0 - 1}\, I \qquad (9)$$

the difference between the value of τ_c obtained from Equation (8) and that given by Equation (4) being expressed by the difference between I and I_0. If we make the substitutions following Equation (4) and, further, set

$$\Theta = k^*(C/2B)(RT_0^2/E)e^{E/RT_0 - 1} \qquad (10)$$

then it is readily seen from Equations (8) and (9) that

$$I = e^{\Theta I} \int_0^2 (e^{y - 1} - e^{\Theta I} fy)^{-1}\,\mathrm{d}y \qquad (11)$$

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(6) We may note that under this approximation Equation (1) may be written in the form

$$\mathrm{d}y/\mathrm{d}J = e^{y - 1}\, e^{-\phi J} - fy$$

where

$$J = \tau(E/RT_0^2)e^{1 - E/RT_0}$$
$$\phi = k(C/B)(RT_0^2/E)e^{E/RT_0 - 1}$$

and y and f are defined just following Equation (4). This would make the Runge–Kutta calculations much easier, for the effects of T_0 and $k(C/B)$ are both taken care of essentially by the one parameter ϕ. This would greatly lessen the number of calculations needed, but they are still sufficiently laborious to make it seem worth while to develop the approximation method of this section.

(7) Ref. 2a, Equation (5).

Now the integral appearing in Equation (11) is simply the integral I_0 with the argument $fe^{\Theta I}$ appearing in place of f. We can thus write a functional equation connecting I and I_0

$$I(f) = e^{\Theta I(f)} I_0(fe^{\Theta I(f)}) \qquad (12)$$

in which the quantity in parentheses following an I or I_0 is the argument of which that I or I_0 is a function. This functional equation for I may be solved and I found as a function of f by the method presented in the Appendix. The results of these calculations for a number of different values of Θ are shown in Fig. 2. (The values given on the curves are 1760 Θ.)

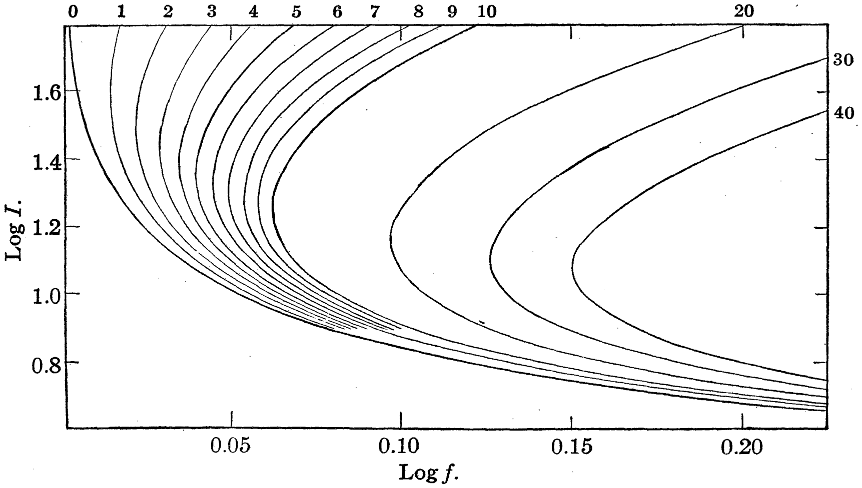

Fig. 2.

Now the fact that the curves bend back indicates that for any given value of Θ there is a certain largest value of f above which there are no real solutions of the functional Equation (12). This suggests that this largest value of f corresponds to the corrected explosion limit. Equation (7) gives f in terms of P and P^*, the latter being the uncorrected critical pressure. If we wish to get I for any Θ as a function of P/P_1^* where P_1^* is the corrected critical pressure we can do this by noting that[8]

$$P/P_1^* = f_\Theta/f \qquad (13)$$

where f_Θ is the largest value of f for the given Θ. Thus, to get I as a function of P/P_1^* or f_Θ/f we simply move the curves of Fig. 2 to the left till the point of infinite slope touches the axis, $\log f = 0$. The result is shown in Fig. 3. The real justification of this procedure is that in special cases the curve obtained agrees with the result obtained by integrating Equation (1) directly, using the Runge–Kutta formula. This is shown in Fig. 3. The circles and triangles represent the values $\tau_c/(RT_0^2/E)e^{E/RT_0 - 1}$, where τ_c has been calculated by means of the Runge–Kutta formula from (1), and P/P_1^* has been set equal to the critical value of Ax/B divided by the value of Ax/B corresponding to the particular value of τ_c. It is seen that the agreement is very good, especially when one bears in mind that the Runge–Kutta method does not give the explosion limit very accurately, and that all points of a given set of calculations should be shifted horizontally by an amount corresponding to the error in the explosion limit. We may therefore use the the approximation developed in this section with some confidence, except very close to the explosion limit where all calculations break down. Since all our calculations do break down near the explosion limit it is not surprising that an attempt to go beyond the explosion limit results in the upper branches of the curves of Fig. 2, which can have no physical meaning.

In an experiment we have a measurement of the time lag, which we may call t_c and which we may assume gives us $(C/B)\tau_c$. Furthermore, we know the ratio of the pressure to the critical pressure, which gives P_1^*/P. We also know T_0 and k^*. We therefore choose from among the curves of Fig. 3 that one which gives us the correct value of $(C/B)\tau_c = 2\Theta I/k^*$ (see Equations (9) and (10)) at the given value of P_1^*/P. We thus find the value of Θ corresponding to the particular experiment, and from this we can get Q/C_M, where C_M is the heat capacity of the reacting gas per mole of azomethane. This quantity is obtained from Θ by noting that $k^* = Ae^{-E/R(T_0 + RT_0^2/E)}$, which is approximately equal to $Ae^{1 - E/RT_0}$. Substituting this into Equation (10), and remembering the definitions of C and B we get

$$\Theta = (C_M/Q)(RT_0^2/2E) \qquad (14)$$

Since Q/C_M will not be expected to vary very much over the range of temperatures which can

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[8] Equation (13) can be used to correct the critical pressure given by the Semenoff theory. However, Equation (14) shows that Θ should be practically constant for any given explosive reaction over the range of temperatures in which it can be studied. The correction to $\log P^*$ is therefore essentially a constant independent of the temperature, and hence is of no practical importance. However, for purposes of notation, it is assumed hereafter in this paper that the experimental critical pressure gives a measure of P_1^*.

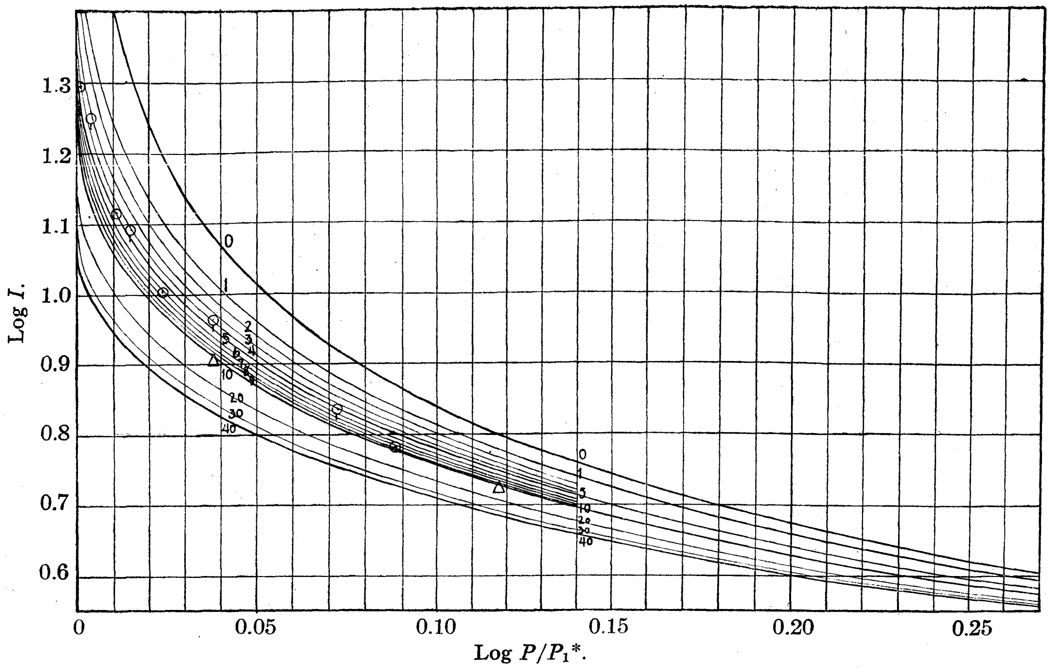

Fig. 3.—Data for Runge–Kutta points: ♀, E = 51,200, T_0 = 630°K., 1760 θ = 3.66; ○, E = 51,200, T_0 = 614°K., 1760 θ = 6.66. △, E = 41,500, T_0 = 553°K., 1760 θ = 7.82.

be studied, we should get the same value for all experiments with a given substance or mixture, and this will be a test of the theory

§3. The Heating of the Gas

In the above discussion we have neglected the time it takes to heat up the gas when it enters the reaction vessel. It is rather difficult to make an exact calculation of this quantity because the gas enters the reaction vessel through a hot tube where it receives a preheating, in what is probably a negligible length of time. If this heats the gas to a temperature equal to $T_0 - T'$, then the time (multiplied by B/C) for the gas to heat up to the wall temperature, T_0, is, from Equation (1) (which should hold for this process as it does for the heating up of the gas after the temperature T_0 has been reached)

$$\tau' = \int_{-T'}^{0} [e^{-E/R(T+T_0)} - (ax/B)T]^{-1}\,dT \qquad (15)$$

In this we have set the term $e^{-k(C/B)\tau}$ equal to 1, which is surely reasonable in this case. τ' determines the time which elapses before "zero time," that is before the time at which the gas is at the temperature T_0, and it is to be added to τ_c before comparing with the experiments. Making the same substitutions as were made to get τ_c in the form (5) we find

$$\tau' = (RT_0^2/E)e^{E/RT_0} - 1\,I' \qquad (16)$$

where

$$I' = \int_{-T'/T^*}^{0} (e^y - 1 - fy)^{-1}\,dy \qquad (17)$$

where $T^* = RT_0^2/E$. We have evaluated I' for a number of values of f for $T'/T^* = 5$ and for $T'/T^* = 10$. These values are given in Table I together with values of I_0. It will be seen from this table that I' is not very sensitive to T'/T^* when the latter is as great as 5, and all our subsequent calculations have been carried out using this value.

Table I

Values of I_0 and I'

f	I_0	$I'(T'/T^* = 5)$	$I'(T'/T^* = 10)$
0.99	40.81	3.091	3.791
.98	27.22	...	...
.96	18.80	...	...
.95	....	3.184	3.914
.94	14.82	...	...
.90	10.89	3.317	4.087
.85	....	3.464	4.280
.80	7.04	...	...
.70	5.392	4.010	...
.50	3.819	5.152	...

§4. Comparison with Experiment

Tables II and III show all measurements of the induction period with azomethane and all of those made with ethyl azides No. 5 and No. 8,[9]

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[9] See the discussion by Campbell and Rice, Ref. 2b, of the various samples of azide used.

with the exception of some in which the temperature was uncertain. These runs are arranged in groups, all in any group having been done at the same time and at very approximately the same temperature, and the data for the highest pressure non-explosive run in each group are also given at the beginning of each group. These non-explosive runs are designated by the symbol ∞ in the "t_c, obs." column. In Table IV we give some examples illustrating the method by which Q/C_M is calculated from the observed time. The first row gives the absolute temperature; the second the logarithm of the ratio of the pressure P of the particular experiment to the critical explosion pressure P_1^*; the third row gives the observed induction period in seconds; the fourth row gives log A, which differs in different cases because of the falling off of the rate constant

TABLE II

INDUCTION PERIODS FOR AZOMETHANE EXPLOSIONS

Expt.	Temp., °C.	Press. (total), mm.	Ind. period, sec.
	100% $(CH_3)_2N_2$ 200-cc. bulb		
255	341.0	189	∞
253	341.0	193	7.5
248	370.0	30	∞
247	370.4	31.5	2.0
244	358.3	54.5	∞
245	358.3	56.5	3.8
242	357.7	55.5	4.0
158	371.9	27	∞
157	371.9	29	2.2
156	371.5	32	1.4
153	346.8	101.5	∞
155	347.0	103	5.2
154	347.2	104.5	4.8
151	353.3	66	∞
150	353.3	68	5.5
147	386.5	17.5	∞
148	385.7	19	1.0
144	378.2	22	∞
146	378.5	23	1.4
145	378.5	24.5	1.2
141	363.5	37.5	∞
142	363.4	38.5	4.0
140	363.6	41	3.1
	100% $(CH_3)_2N_2$ 50-cc. bulb		
265	353.0	149	∞
263	353.5	152	3.2
261	355.3	132	∞
260	355.0	137.5	3.4
	50.7% $(CH_3)_2N_2$, 49.3% N_2 200-cc. bulb		
287	374.8	44.5	∞
286	375.1	45.5	4.1
285	375.2	49	2.0
284	374.8	53	2.0
279	361.3	90	∞
283	361.0	91	4.1
282	361.4	93	3.6
281	361.3	95	3.6
	32.5% He, 67.5% $(CH_3)_2N_2$ 200-cc. bulb		
180	376.8	38	∞
179	376.8	38.5	2.0
177	377.0	41.5	<1.0
176	377.3	44	<1.0
186	352.0	139	∞
185	352.0	141	4.5
172	352.0	144	3.0
171	352.0	147.5	3.0
170	352.0	150	2.6
169	352.0	153	2.6
174	363.7	69	∞
175	363.7	71.5	4.2
173	363.9	77	2.0
	59.2% He, 40.8% $(CH_3)_2N_2$ 200-cc. bulb		
221	377.2	75.5	∞
223	377.2	77	2.0
222	377.0	79	1.8
218	372.0	99	∞
217	372.0	101.5	3.0
213	367.9	121	∞
215	367.9	122	3.0
214	368.3	123.5	2.0
212	367.9	126.5	2.4
210	359.2	166.5	∞
209	359.4	168	4.0
207	359.5	172	3.0
206	359.4	181	2.8
205	356.9	209	∞
203	356.9	210	4.4
202	356.7	219.5	3.2
201	356.8	231	3.0
200	349.9	296.5	∞
199	351.3	307	4.0
190	372.0	90	∞
192	372.3	95.0	1.4
191	371.7	99.5	1.4
187	359.5	214	2.0
	76.3% He, 23.7% $(CH_3)_2N_2$ 200-cc. bulb		
241	338.7	143	∞
240	339.0	144	2.0
234	369.4	220.5	∞
231	369.5	221.5	3.2
235	369.3	223	3.0
230	361.8	322	∞
229	362.0	323	5.0
228	362.0	328.5	3.8
226	361.8	336	3.2
225	361.8	357	2.4
224	362.0	377.5	2.2

The apparently anomalous value of t_c for Expt. 217 as compared with Expts. 191 and 192 is due to the former having been performed with a different preparation (probably slightly impure) which gave a higher explosion limit than the preparation used in the latter two experiments.

TABLE III

INDUCTION PERIODS FOR ETHYL AZIDE EXPLOSIONS

Expt.	Temp., °C.	Press. (total), mm.	Ind. period, sec.
8th Azide 50-cc. bulb			
428	265.5	108.7	∞
429	265.0	111.0	4
401	269.8	73.2	∞
402	270.0	74.2	4
400	269.8	74.5	4
399	270.0	75.1	2
423	274.2	50.9	∞
425	274.3	51.8	4
408	279.7	34.1	∞
406	280.0	35.5	1.5
411	290.1	17.9	∞
412	290.0	18.9	2
416	300.3	9.6	∞
414	300.4	11.7	0.5
413	300.1	15.1	.5
8th Azide 200-cc. bulb			
336	258.5	104.7	∞
337	258.6	105.7	6
335	258.6	107.0	5
330	259.8	90.4	∞
332	260.0	92.9	5
331	259.9	94.0	4.5
444	260	85.0	∞
443	260	86.1	5
442	260	86.9	5
324	262.8	64.4	∞
325	262.1	72.0	6
323	263.1	63.5	∞
322	263.0	65.7	4.5
320	265.0	51.8	∞
319	265.0	53.3	5
318	264.7	54.0	5
317	264.9	54.5	4
316	265.0	55.2	4
315	265.2	55.2	3.5
314	265.0	55.5	3.5
201	265.1	58.5	∞
202	265.3	59.6	3
206	265.1	55.5	∞
204	265.4	56.3	4
203	265.0	58.0	3.5
195	265.0	54.5	∞
194	265.0	55.5	5
191	270.0	36.0	∞
192	270.1	36.8	4.5
189	270.2	34.6	∞
188	270.4	35.2	3.5
187	270.0	36.9	3
380	270.0	32.3	∞
379	270.0	34.2	4
378	270.0	37.0	3
208	274.5	24.7	∞
207	274.5	25.5	3.5
383	280.0	15.3	∞
382	280.0	16.5	2
365	300.0	5.0	∞
364	299.8	6.2	1
5th Azide 200-cc. bulb			
102	269.5	36.8	∞
103	270.0	38.8	4
130	269.7	36.7	∞
129	270.1	36.4	4.5
118	279.6	17.3	∞
117	280.0	17.4	3
101	280.0	15.0	∞
100	280.0	16.8	3
122	289.8	9.5	∞
120	289.8	10.4	2
123	290.0	10.4	1.5
50.1% 5th Azide, 49.9% CO_2 200-cc. bulb			
107	269.9	73.0	∞
106	269.8	73.8	3
115	280.0	34.9	∞
116	280.0	36.0	3
126	289.9	19.0	∞
125	289.7	19.8	2.5
124	289.8	19.8	1.5
49.9% 8th Azide, 50.1% He 200-cc. bulb			
241	270.4	103.0	∞
240	270.7	103.5	3
247	279.9	49.8	∞
248	280.0	52.7	1.5
251	284.9	37.0	∞
250	285.3	38.6	1.5
253	289.9	28.5	∞
252	289.9	29.0	1
258	300.0	21.4	∞
256	299.8	22.7	0.5
255	299.3	23.0	.5
254	300.0	24.6	.5
66.3% 8th Azide, 33.7% He 200-cc. bulb			
265	270.0	67.7	∞
264	270.0	68.8	3
266	274.2	48.7	∞
267	274.9	47.0	3.5
268	280.1	31.0	∞
270	280.2	32.0	3
271	285.0	23.7	∞
272	285.0	25.0	2
276a	295.2	12.8	∞
276	295.3	13.8	1.5
283	305.6	8.3	∞
280	305.7	11.0	1

with pressure; the fifth row gives the value[9a] of k^*; the sixth row gives trial values of 17.6 Θ; from these are calculated I and I', which are given in rows seven and nine; to get I' requires also the value of f, given in row eight, which is obtained from the values of P/P_1^* and Θ by use of Equation (13) and Fig. 2; in the tenth row are given the calculated values for

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[9a] This quantity was calculated using 40,000 as the activation energy for ethyl azide; this was not the final best value, but a corresponding value of A was used, and the error thus made was small. For azomethane the activation energy is 51,200.

TABLE IV

CALCULATIONS OF Q/C_M FOR EXPTS. 156 AND 187 OF TABLE II AND 316 OF TABLE III

T_0	644.5	632.5	538.0
Log (P/P_1^*)	0.048	0.106	0.020
t_c (obs.)	1.4	2.0	4.0
Log A	15.85	15.95	13.915
k^*	0.083	0.049	0.0313
17.6 Θ	.09–0.10	.09–0.10	.08–0.09
I	7.60–7.50	5.61–5.56	10.22–10.02
$-\log f$	0.107–0.111	0.165–0.169	0.074–0.079
I'	3.69–3.71	4.08–4.11	3.49–3.52
t_c (calcd.)	1.39–1.54	2.02–2.24	3.98–4.43
17.6 Θ expt.	0.091	0.089	0.080
Q/C_M	1560	1530	1580

the induction period, obtained from the formula $t_c = 2\Theta(I + I')/k^*$; from these we obtain by comparison with the observed value of t_c and by interpolation the experimental value of 17.6 Θ, and this enables us to calculate Q/C_M from Equation (14). Table IV shows the order of magnitude of the various quantities involved. The first run presented is an extreme case as regards the relative importance of I' and I. In all others, I is considerably larger than I', the other examples given being typical.

In Table V we give in condensed form the results of all calculations of Q/C_M. This table covers all experiments given in Tables II and III in which the pressure was more than 1.04 times the critical pressure. In most cases the critical pressure used was simply the average of the pressures of the highest non-explosive and the lowest explosive runs of the particular group of experiments to which the run belonged, all runs having been made primarily to determine the explosion limits; but in the case of pure azomethane it was considered more accurate (on account of temperature fluctuations in a given series) to draw a smooth curve through the values of P_1^* plotted as a function of T and then to read P_1^* from the curve.

TABLE V

CALCULATION OF Q/C_M AND Q

Expt.	T_0, °K.	Log P/P_1^*	Log A	t_c, obsd., sec.	Q/C_M	C_M cal./mole deg.	Q cal./mole
100% $(CH_3)_2N_2$							
156	644.5	0.048	15.85	1.4	1560	25.7	40000
145	651.5	.041	15.82	1.2	1410		36200
140	636.6	.028	15.88	3.1	1170		30000
67.5% $(CH_3)_2N_2$, 32.5% He							
173	636.9	0.040	15.91	2.0	1570	27.1	42500
171	625.0	.023	15.96	3.0	2230		60500
170	625.0	.030	15.96	2.6	2450		66400
169	625.0	.038	15.96	2.6	2310		62600
177	650.0	.035	15.83	1.0	1780		48200
40.8% $(CH_3)_2N_2$, 59.2% He							
191	644.7	0.032	15.88	1.4	1560	30.0	46800
201	629.8	.042	15.95	3.0	1450		43500
202	629.7	.020	15.95	3.2	1590		47700
206	632.4	.034	15.93	2.8	1430		42900
187	632.5	.106	15.95	2.0	1530		45900
212	640.9	.017	15.91	2.4	1180		35400
222	650.0	.015	15.86	1.8	1020		30600
23.7% $(CH_3)_2N_2$, 76.3% He							
224	635.0	0.068	15.95	2.2	1280	35.3	45200
225	634.8	.044	15.94	2.4	1350		47700
226	634.8	.018	15.94	3.2	1190		42000
50.7% $(CH_3)_2N_2$, 49.3% N_2							
281	634.3	0.021	15.91	3.6	1130	30.5	34500
284	647.8	.071	15.84	2.0	830		25300
285	648.2	.037	15.83	2.0	940		28700
100% $C_2H_5N_3$ No. 8							
314	538.0	0.023	13.915	3.5	1790	25.3	45300
316	538.0	.020	13.915	4.0	1580		40000
378	543.0	.044	13.900	3.0	1340		33900
315	538.3	.021	13.915	3.5	1800		45500
413	573.2	.150	13.857	0.5	1200		30400
49.9% $C_2H_5N_3$ No. 8, 50.1% He							
255	572.4	0.018	13.842	0.5	1970	28.3	55700
254	573.1	.047	13.846	.5	1500		42500

In order to get Q we have made an attempt to estimate roughly the specific heats of azomethane and ethyl azide. Though the Raman spectra of these substances have apparently not been obtained, we may nevertheless assign approximate frequencies to each of the bonds or modes of vibration in these molecules, on the basis of the Raman spectra of similar compounds.[10] These can then be translated into contributions to the specific heat. Table VI gives the results. The degeneracy values in the second column were obtained from simple geometrical considerations. The azide radical was assumed to be linear. The frequencies in the third column are estimated, following Kohlrausch. The N=N frequencies in both azomethane and ethyl azide are assumed equal to the C=O frequency in ketones. The "skeleton bending" frequencies are merely a very rough guess; but their values are undoubtedly lower than the other frequencies, and since at the temperatures used such low frequencies are nearly fully excited, their exact value does not matter much. Contributions to C_v (fourth column) are calculated for each vibrational de-

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(10) Kohlrausch, "Der Smekal–Raman Effekt," Verlag Julius Springer, Berlin, 1931, especially pp. 154, 157, 206, 314; *Z. Elektrochem.*, **40**, 429 (1934).

gree of freedom by the formula $C_v = R(h\nu)^2 e^{h\nu/kT}/(kT)^2\,(1-e^{h\nu/kT})^2$, with T taken as 620°K. for azomethane and 550°K. for ethyl azide. The result can lay no great claim to accuracy; we should expect, however, that its probable percentage error is no greater than that of our determination of Q/C_M. In view of the other uncertainties involved we have not thought it worth while to consider the change of specific heat with temperature for the small temperature range available.

TABLE VI

CALCULATION OF SPECIFIC HEATS

Degree of freedom	Degeneracy	ν, cm.$^{-1}$	C_v, cal. per mole
	Azomethane		
Translation	3		2.98
Rotation	5		4.96
C—H stretching	6	2940	0.62
C—N stretching	2	1035	2.52
N=N stretching	1	1714	0.62
C—H bending	10	1430	8.94
Skeleton bending	3	600	5.10
Total C_v for azomethane =			25.7
	Ethyl azide		
Translation	3		2.98
Rotation	5		4.96
C—N stretching	1	900	1.28
C—C stretching	1	1050	1.08
N=N stretching	2	1800	0.81
C—H stretching	5	2940	.27
C—H bending	7	1430	4.87
C—H bending	2	1200	1.83
Skeleton bending	4	400	7.23
Total C_v for ethyl azide =			25.3

Using these values of C_v, we have calculated Q for azomethane and ethyl azide. For the mixtures the formula of §1 for C_M is used, C_G being taken as 3.0 cal. per mole for helium, and 4.9 for nitrogen.[11] The results are given in the last column of Table V.

Over the temperature range for which it is possible to make measurements Q should be approximately constant. It will be seen that the values actually obtained vary considerably, but in view of the considerable errors necessarily involved the variation does not seem excessive. Errors may occur in the actual measurement of the induction period, which is very short, and may also be due to slight changes in temperature during a series of runs, which causes the explosion limit to be determined for a slightly different temperature than that at which the given run was made. Any error in the explosion limit due to this or any other cause produces a relatively large error in Q. But perhaps the greatest source of error is the finite time which is required for the gas to enter the reaction vessel. This was especially great in the case of ethyl azide, as noted in the preceding paper,[2b] and the pressure in the reaction bulb had not, in general, become quite equalized with the storage bulb before the stopcock was closed. However, since the largest portion of the gas undoubtedly rushes in almost immediately, and since in almost all cases the stopcock can be closed before the explosion occurs, we believe that the results are of significance even though considerable error can no doubt be caused, and the effect should be partly neutralized by the fact that the same error enters into the determination of the explosion limit. In general, the variations in Q seem to be quite random, the only apparent exception being the values of Q for azomethane in the presence of nitrogen. It is impossible to say whether this variation, for which no obvious explanation is available, is real or not.

The final average values of Q are 43,000 calories per mole for azomethane and 42,000 for ethyl azide. It is possible that these values not only are subject to the errors inherent in the experiments, but also contain systematic errors due to the assumptions made in the theory, particularly the assumption that the rate at which heat is removed from the vessel is simply proportional to the difference in temperature between the gas and the wall of the vessel. However, since the proportionality constant in this expression does not enter into the final results at all, it seems likely that the result will not be very sensitive to the form of the expression, either. We believe that the values of Q given are probably correct to within about 10,000 calories per mole.

§5. The Attainment of Temperature Equilibrium in a Reaction which Is Not Exothermic

When the rate of an ordinary non-explosive reaction is measured, the gas is admitted to a heated reaction vessel at a certain time, and it is assumed that the time required to heat it to the temperature of the vessel is negligible. The considerations of the present paper give us the possibility of discussing this assumption; we can learn something about heat transfer in non-explosive gases, whose decompositions are slightly exothermic or endothermic (or which do not react at all) by in

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(11) "International Critical Tables."

ference from the properties of the explosive gases as deduced in the preceding sections of this paper.

The results of the last section show that the length of time required to heat the gas up to the temperature of the vessel is generally only a fairly small fraction of the entire induction period. This is due in part to the fact that, as the temperature of the vessel is approached, the gas begins to decompose, giving out heat and warming itself up. If the reactions were not so exothermic it would take considerably longer for the final temperature adjustment to occur, and if it were endothermic the situation would be even less favorable. In the case in which the reaction neither gives out nor absorbs heat, the rate of increase of temperature is given by Equation (1) with the first term on the right-hand left out, and, using t instead of τ, we see that the time required to heat up the gas from a temperature $T_0 - T'$ to a temperature, $T_0 - T''$, say, is given by

$$t = -\int_{-T'}^{-T''} \frac{C}{ax}\frac{\mathrm{d}T}{T} = \frac{C}{ax} \ln T'/T'' \qquad (18)$$

If we could determine x it would thus be possible to find how long it takes for a gas to heat up to within, say, 1° of the temperature T_0 from a temperature, say, 100° below. Now x can be determined for the explosive gases from the value of f, and we may reasonably assume that it is the same order of magnitude for all gases. From the definitions of f (following Equation (4)) and B, we have

$$\frac{ax}{Qn_0} = VA \frac{E}{RT_0^2} e^{1 - E/RT_0} f = \frac{VEk^*}{RT_0^2} f \qquad (19)$$

Remembering that $C = C_{\mathrm{M}} n_0 V$ we have

$$\frac{ax}{C} = \frac{Q}{C_{\mathrm{M}}} \frac{Ek^*}{RT_0^2} f \qquad (20)$$

Taking, for example, the data from the first run in Table IV we get $ax/C = 6.3$ sec.$^{-1}$, while if $T'/T'' = 100$ then t from Equation (18) is equal to about 0.7 second. In this case the total pressure is about 32 mm. and the experiment was done with a 200-cc. flask. Since C is proportional to n_0 and V it is seen that this time would be increased at higher pressures and with larger vessels. The matter is somewhat complicated by the fact that the results of our previous work[2] indicate that x is not a true constant, but it is fairly obvious that with pressures up to an atmosphere and with conditions under which reaction rates are usually run, the gas will come to nearly the temperature of the flask within at most half a minute. It may be well to note that this is far faster than equilibrium could be established by heat conduction alone, and convection must play an important role in the mechanism of heat transfer.

In the case of a non-explosive run of a gas which does react exothermally, the time necessary to reach what is essentially a steady state temperature should require a length of time of the order of magnitude of the induction period in an explosive run. According to the simple Semenoff theory the temperature rise T should never reach a value greater than $T^* \cong RT_0^2/E$ in a non-explosive run. An examination of Fig. 1 shows that actually in a run near the explosion limit the temperature surges up above that value and then drops back again. Excepting for a run exceedingly close to the explosion limit we may judge from Fig. 1 that all this will take place in a time not more than two or three times that occupied by the actually observable induction periods. Since this time is, in general, small compared to the half life of the decomposing substance, the calculation made in §5 of the paper of Allen and Rice[2a] should be valid in almost all cases.

Appendix

The solution of the functional equation (12) may be obtained by a series of successive approximations in the following manner. We define a quantity f' by the equation

$$f = f' e^{-\Theta I_0(f')} \qquad (\mathrm{A})$$

and take as a first approximation to $I(f)$ the quantity $I_1(f)$ defined by

$$I_1(f) = e^{\Theta I_0(f')} I_0(f') \qquad (\mathrm{B})$$

We then insert this quantity $I_1(f)$ into the right-hand side of Equation (12) in place of $I(f)$ to get a second approximation

$$I_2(f) = e^{\Theta I_1(f)} I_0(f e^{\Theta I_1(f)}) \qquad (\mathrm{C})$$

We now insert $I_2(f)$ into the right-hand side of Equation (12) and continue the process, getting finally for the nth approximation

$$I_n(f) = e^{\Theta I_{n-1}(f)} I_0(f e^{\Theta I_{n-1}(f)}) \qquad (\mathrm{D})$$

If the process converges, that is, if $I_n(f)$ approaches a limit as n becomes large, then it is easily seen that the limiting value of $I_n(f)$ satisfies Equation (12) and may thus be identified with $I(f)$. That the process does converge readily appears when one attempts to carry it out; in fact, I_1 is a sufficiently good approximation for our purposes and has been used in Fig. 2. The easiest way to get I_1 as a function of f is to start with given values of f' and Θ. Equation (A) then determines a value of f and Equation (B) gives the corresponding value of I_1; together they give a point on the curve for the given value of Θ.

Summary

When the differential equation connecting temperature with time in an exothermic gas reaction is integrated, a sudden temperature rise, corresponding to an explosion, is found to be indicated above a certain sharply defined pressure. From curves of this type, an approximate method for calculating the induction period in thermal explosions has been obtained, and has been applied to the explosions of azomethane and ethyl azide. Rough values of the heats of decomposition of these compounds are thereby obtained. A discussion is given of the rate at which a gas not reacting exothermically comes into thermal equilibrium when admitted to a heated vessel.

CAMBRIDGE, MASS. RECEIVED JUNE 1, 1935

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

The Hydrogenation of Carbon Dioxide and a Correction of the Reported Synthesis of Urethans

BY MARK W. FARLOW AND HOMER ADKINS

In an attempt to prepare N-pentamethylene salicylamide through the reaction of methyl salicylate and piperidine at 250° under hydrogen, Wojcik and Adkins[1] obtained a product which they reported as phenyl N-pentamethylene urethan, *i. e.*, $C_6H_5OC(O)NC_5H_{10}$. They suggested that the supposed urethan might be formed through the decarboxylation of salicylic acid followed by the reaction of phenol, carbon dioxide and piperidine. They apparently confirmed this hypothesis by obtaining the same product from phenol, carbon dioxide and piperidine as from methyl salicylate and piperidine. A further study of the postulated reaction has shown that the alleged urethan was a mixture of phenol and formylpiperidine, $C_5H_{10}NC(O)H$. An equimolecular mixture of these two compounds has a constant and narrow boiling range about 10° higher than either component and shows an analysis for nitrogen very nearly the same as for the urethan. Similarly, the products reported as phenyl N-*n*-amyl and *n*-butyl-N-pentamethylene urethans have been found to be mixtures of formyl amines with phenol or butanol-1.

The identification and isolation of formylamines from the reaction products of hydrogen, carbon dioxide, amines and alcohols led to a study of the hydrogenation of carbon dioxide. The significant numerical results are given in the table and may be summarized as follows.

The hydrogenation of carbon dioxide to formic acid in the presence of an amine takes place at 80° or less over Raney nickel.

$$CO_2 + H_2 \longrightarrow HCO_2H$$
$$HCO_2H + RNH_2 \longrightarrow HCO_2NH_3R$$

For example, after one hour at 80° 1-Ph-2-aminopropanol-1 was converted to the formate in a yield of 55% based upon the amine, the carbon dioxide and hydrogen being in excess. The rate and temperature necessary for hydrogenation apparently varies with the structure of the amine as well as with the catalyst. At a sufficiently high temperature (250°) sheet brass, such as has been used in this Laboratory for fabricating liners for steel reaction vessels, is an active catalyst for the hydrogenation. If the hydrogenation is carried out at a temperature much above 100° in the presence of a primary or secondary amine, the formate is dehydrated and the amide (formylamine) is obtained.

$$HCO_2NH_3R \longrightarrow HC(O)NHR + H_2O$$

Since a variety of substances may be present under the conditions used for the hydrogenation, it is not possible to formulate with certainty the course of the reaction. Carbon dioxide might react with a primary or secondary amine with the formation of a carbamate

$$2R_2NH + CO_2 \longrightarrow R_2NC(O)ONH_2R_2$$

or since traces of water are present a carbonate might be formed

$$R_2NH + CO_2 + H_2O \longrightarrow (R_2NH_2)_2O_2CO$$

Dehydration of the carbonate would give the

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[1] Wojcik and Adkins, THIS JOURNAL, **56**, 2461 (1934).

TABLE I

HYDROGENATION OF CARBON DIOXIDE IN PRESENCE OF AMINES[a]

	T, °C.	Time, hours	G. catalyst	Moles	Yield of products
2,2,6,6-Tetra-Me-4-OH piperidine (in EtOH)	100	6	5 Ni(R)	0.10	57% formate of amine
2,2,6,6-Tetra-Me-4-OH piperidine (in EtOH)	100	3	5 Ni(R)	.10	47% formate of amine
Piperidine (in EtOH)	150	9	5 Ni(R)	.25	76% N-formyl-piperidine[b]
n-Amylamine (in EtOH)	150	5	5 Ni(R)	.25	45% N-formyl-*n*-amylamine
1-Ph-2-aminopropanol-1 (in EtOH)	80	1	5 Ni(R)	.04	55% formate of amine
α-Oximinopropiophenone (in EtOH)	80	1	5 Ni(R)	.10	[c]Formate of 1-Ph-2-NH_2-propanol-1
N-*n*-Bu-2-Me-piperidine (in EtOH)	100	6	5 Ni(R)	.10	[c]Formate of amine
Piperidine (in phenol)	250	5	Brass	.50	50% N-formylpiperidine
β-Ph-Et-amine (in phenol)	250	4	Brass	.50	35% N-formyl-β-Ph-Et-amine
n-Amylamine (in phenol)	250	5	Brass	.50	33% N-formyl-*n*-amylamine

[a] Carbon dioxide was admitted to the amine dissolved in EtOH or PhOH until the pressure was constant at about 60 atm. Hydrogen was admitted until the total pressure was 100 to 200 atm. The bomb was then heated to the indicated temperature, the pressure being then 200 to 400 atm. [b] The percentage yield as given is based upon analysis for nitrogen of the product which was made up of the formylpiperidine and phenol. [c] Formic acid was identified but the formate was not isolated in sufficient purity to justify the calculation of a % yield.

TABLE II

PROPERTIES AND ANALYSES OF PRODUCTS

Name	B. p. or m. p., °C.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
N-Formyl-*n*-amylamine	124–125 (10 mm.)	$C_6H_{13}NO$	62.6	62.4	11.39	11.31
N-Formyl-β-phenylethylamine	180–181 (14 mm.)	$C_9H_{11}NO$	72.4	72.4	7.45	7.54
N-N′-Di-*n*-amyl urea	88 (m. p.)	$C_{11}H_{24}N_2O$			N, 14.00	14.01
β-Phenylethylamine formate	128–129 (m. p.) (dec.)	$C_9H_{13}NO_2$	64.7	64.65	7.84	7.89
2,2,6,6-Tetramethyl-4-hydroxypiperidine formate	207 (m. p.) (dec.)	$C_{10}H_{23}NO_2$	59.1	59.2	10.43	10.35
1-Phenyl-2-aminopropanol-1 formate	160 (m. p.) (dec.)	$C_{10}H_{15}NO_3$	60.9	60.8	7.69	7.67

carbamate and further dehydration a disubstituted urea. The latter type of product was actually isolated in two instances. The action of hydrogen upon these various types of compounds might well result in the formation of a formyl amine. However, since formates were obtained even with primary amines and since a tertiary amine was as effective as primary and secondary amines in facilitating the hydrogenation of carbon dioxide there seems no reason to assume that the amine plays any other role than to neutralize the formic acid produced by direct hydrogenation.

The formyl derivatives reported in Table I were isolated by fractionation of the reaction mixture through a Widmer column. These various formyl derivatives showed the physical properties and analyses given in Table II. Formylpiperidine[2] was also identified through the preparation of a double salt with mercuric chloride, m. p. 147–148°. The derivative was prepared by heating 5 g. of mercuric chloride and 1 ml. of formylpiperidine in 100 ml. of water until solution was complete. The derivative crystallized out upon cooling the solution and was recrystallized from a mixture of ethyl acetate and petroleum ether. Since formylpiperidine and phenol cannot be separated by fractional distillation the mixture was dissolved in alkali and the amide extracted with ether. The mercuric chloride derivative was then prepared from the material extracted by ether.

The formates were isolated by crystallization from mixtures of alcohol and ether or alcohol and ethyl acetate. Because of the solubility of these salts the yields reported in Table I are in all cases considerably less than the amount of amine formate produced. This is especially true of the formate of 1-Ph-2-amino-propanol-1. The formates were identified by analysis and by comparison with authentic specimens prepared from equimolecular quantities of amine and formic acid in ether.

Diamyl urea $(C_5H_{11}NH)_2CO$ (4.5 g.) and *sym*-diphenylethyl urea[3] $(C_6H_5CH_2CH_2NH)_2CO$ (5.0 g.) were isolated from the reaction products of the last two experiments recorded in Table I.

Summary

Carbon dioxide may be hydrogenated to formic acid in the presence of a variety of amines. If the hydrogenation is carried out at a temperature much above 100°, the formate of the amine may be dehydrated to the substituted formamide.

MADISON, WISCONSIN

RECEIVED AUGUST 8, 1935

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(2) Bischler and Napieralski, *Ber.*, **26**, 1908 (1893).

(3) Thiele and Pickard, *Ann.*, **309**, 200 (1899).

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

Surface Potentials and Force–Area Relations of Monomolecular Films. II. *d*-Pimaric Acid and Tetrahydro-*d*-pimaric Acid

BY WILLIAM D. HARKINS, HERMAN E. RIES, JR., AND EVERETT F. CARMAN

I. Introduction

Through the kindness of Professor Ruzicka the writers have been able to investigate the surface potentials and force–area relations of *d*-pimaric acid, an unsaturated compound, and tetrahydro-*d*-pimaric acid, the corresponding saturated compound. These compounds contain a phenanthrene residue, and are related to certain hormones and vitamins. The carboxyl group is displaced one position from the hydroxyl group of cholesterol, and the area for the pimaric acid is slightly larger.

II. Apparatus and Procedure

The apparatus and general procedure are essentially the same as described by Harkins and Fischer.[1] The modifications that have been introduced will appear in a paper which is now being prepared for publication. A more recent improvement will be discussed here in connection with the method adopted to obtain "zero" or clean surface potentials. It has increased the accuracy of the surface potential values.

The procedure is as follows. The trough is filled with the aqueous solution (0.01 molal hydrochloric acid in these experiments) and the surface swept several times to remove initial contamination. The electrode is then lowered into a position 2 to 3 mm. above the surface and the cage closed. The system is allowed to remain in this condition for about one hour. It seems that during this time most of the additional contamination settles out from above the surface and rises from below. At the same time the surface of the silver–polonium electrode reaches equilibrium with the water vapor.

One of the features of the procedure involves the use of mechanical arms to perform the final sweepings without opening the cage or otherwise disturbing the immediate surroundings of either the surface or the electrode. It is unnecessary to raise the electrode in order to accomplish the final sweepings as thin barriers have been constructed which easily pass under the lowered silver–polonium disk. After the hour has elapsed, the surface is swept until the potential is constant to within 1 mv. for periods of ten to twenty minutes. Readings are taken immediately after the individual sweepings to ensure a clean surface during the measurement. The additional barriers for the final sweepings are taken from racks conveniently suspended above the two ends of the tray.

The importance of an accurate clean surface potential cannot be overemphasized, as it is obvious that an error here vitiates all of the film potential values. It might be added in connection with these precautions that capillary active contamination falling on the spread films has a negligible effect on the potential compared to the change introduced by the same contamination on a cleaned surface.

The films were spread from redistilled benzene solutions on 0.01 molal aqueous hydrochloric acid. Surface potential and pressure measurements were made simultaneously at minute intervals. The experiments were carried out at room temperature (28 to 30°).

III. Pressure–Area Relations and Thickness of the Films

The saturated and unsaturated compounds form monomolecular films, which give almost identical pressure–area curves until collapse begins (Figs. 1, 2 and 3). The film which is composed of the unsaturated compound withstands higher pressures than that of the saturated, and its maximum pressure is about 17 dynes on 0.01 molal hydrogen chloride. The film pressure of the unsaturated compound approaches a state of equilibrium. The maximum thickness of the mono-layer is about 12 Å. for both compounds, or slightly less than half that for a similar film of stearic acid. These compounds exhibit orientation of the perpendicular type. The films are much thicker than those in which a single chain lies flat in the surface.

The films are highly compressible, and the coefficient $[a_0 - a_1)/a_0]/(f_1 - f_0)$ has a value of 0.0068 for the saturated acid and 0.010 for the unsaturated compound.

The extrapolated molecular area at zero pressure for both the saturated and unsaturated compounds is about 53 sq. Å. but it seems possible to compress the films to an area of about 43 sq. Å. before collapse occurs. This is practically the area of two hydrocarbon chains. Our unpublished data on large rings up to thirty-four carbon atoms in the ring, and the values of Büchner, Katz and Samwel[2] on rings up to thirty carbon atoms, also give minimum areas equal to that exhibited by two single oriented hydrocarbon chains.

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[1] Harkins and Fischer, *J. Chem. Phys.*, **1**, 852 (1933).

[2] Büchner, Katz and Samwel, *Z. physik. Chem.*, **B5**, 327 (1929).

The work of Harkins and Morgan[3] showed that phenanthrene spreads on water only when much salt is present. The compounds used in our work are much more saturated, which probably reduces resonance in the molecule, but has only a minor effect on the polarity. However, the presence of the dipole due to the carboxyl group, as is usual, orients the molecule with this group toward the water.

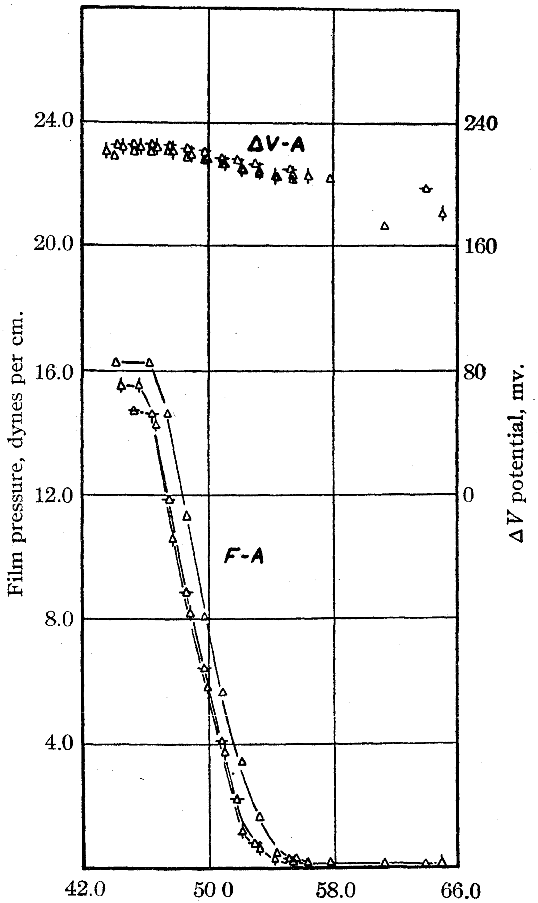

Fig. 1.—Tetrahydro-*d*-pimaric acid on 0.01 molal hydrochloric acid.

	Expt.	Temp. °C.
Δ	199	28.0
Δ̩̍	200	28.0
-Δ-	206	29.5

IV. Structure and Orientation of the Pimaric Acids

It is of interest to compare the structures and orientations in films of the pimaric acids with those of cholesterol. If the side chains, which, due to interpenetration of the molecules probably contribute very slightly to the cross-sectional area, are neglected the similarity between the pimaric acid nucleus (phenanthrene residue) and the A, B, C ring structure of cholesterol (Fig. 4) is obvious. The significant point of difference is the location of the polar, water-attracting group.

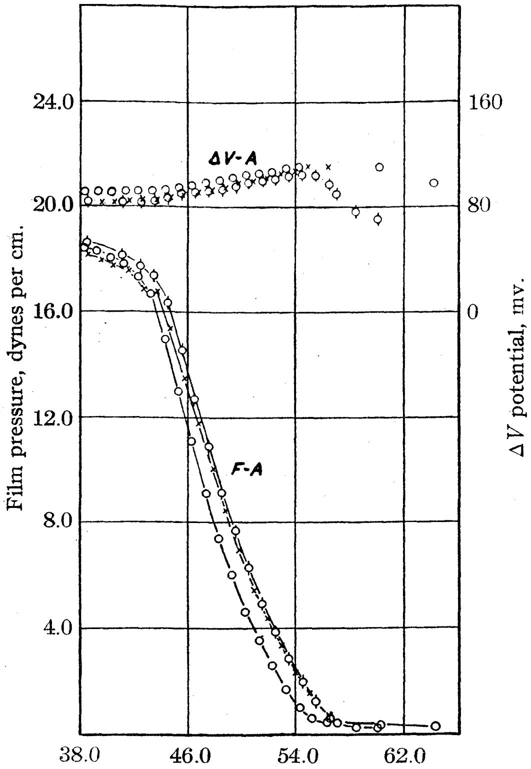

Fig. 2.—*d*-Pimaric acid on 0.01 molal hydrochloric acid.

	Expt.	Temp. °C.
×	197	30.0
ϕ	198	28.0
○	205	28.0

In pimaric acid the carboxyl group is on carbon atom number 4, whereas in the cholesterol compound the hydroxyl group occupies position number 3. It is evident that if the molecule is oriented so that the polar group is located at the lowest point, one would expect the pimaric acids should be tilted in such a way as to occupy more area in the surface than the vertically oriented cholesterol. The cross-sectional area of a molecule obtained from film balance measurements is of course dependent on the orientation.

Measurements of molecular models indicate that for oriented sterol ring systems with the polar group in position 3, the cross-sectional area should be about 37 sq. Å. and for the same system with the polar group in position 4 about 42

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(3) Harkins and Morgan, *Proc. Nat. Acad. Sci.*, **11**, 637 (1925).

sq. Å. Measurements on models and the effects of the positions of polar groups in similar compounds have been discussed in a paper by Danielli and Adam.[4] The calculations agree quite well with the film areas per molecule at the collapse pressure. The area obtained for the unsaturated acid at the collapse pressure is about 43 sq. Å. The extrapolated area, 53 sq. Å., is considerably greater because of the expanded nature of the film.

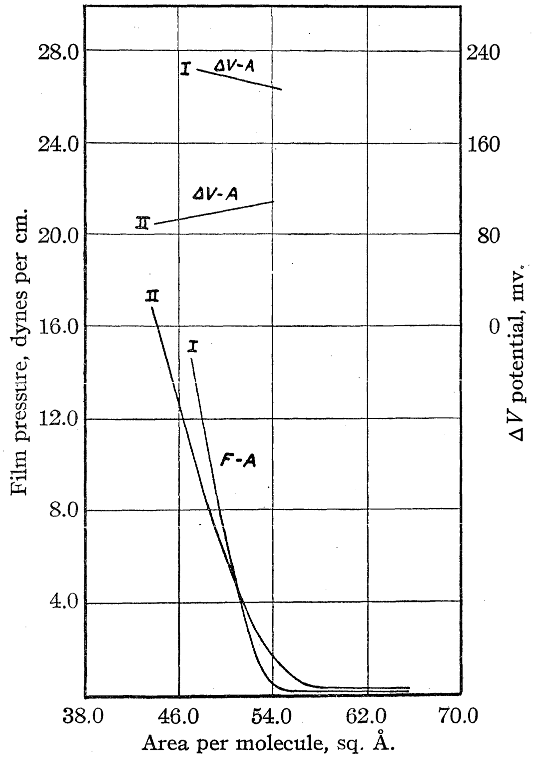
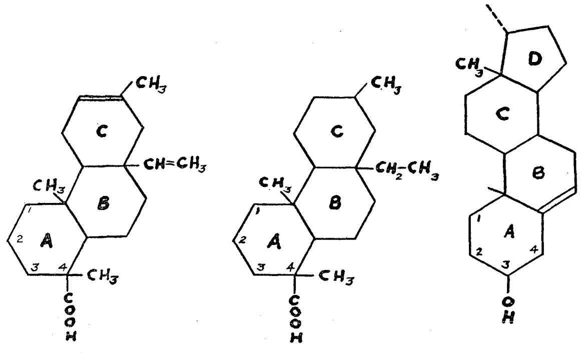


Fig. 3.—Average curves: I, tetrahydro-*d*-pimaric acid; II, *d*-pimaric acid.

It may be noted here that the curve of the more condensed film of tetrahydro-*d*-pimaric acid crosses the curve for the unsaturated acid. Consequently, the reduced compound has a larger area at the collapse point and a smaller extrapolated area at zero pressure than does the unsaturated acid. The increased polarity of the unsaturated compound is probably the cause of the expanded nature of the film. This will also account for the greater adhesion to the water surface and the resultant higher pressure.

V. Surface Potentials

The surface potential (ΔV), defined as the difference in the contact potential when the film is present and when it is absent, exhibits some anomalies not previously found. The surface potentials of the condensed films are low, with a value of about 100 mv. for the unsaturated and about 200 mv. for the saturated compound. The film of *d*-pimaric acid exhibits a behavior heretofore unobserved in that the surface potential of the condensed film *decreases* as the film is compressed.



(a) (b) (c)

Fig. 4.—Vertical orientation of molecules at air–water interface: (a) *d*-pimaric acid; (b) tetrahydro-*d*-pimaric acid; (c) cholesterol (chain omitted).

In connection with the surface potential of tetrahydro-*d*-pimaric acid, it should be noted that the measurements for this compound gave about 200 mv., which is approximately half of the value obtained for a straight chain acid of the type of stearic acid. This is largely because the area per molecule or area per polar group for this reduced pimaric acid is roughly twice that of the stearic acid type, so its polar group surface density is approximately half that of condensed stearic acid films. However, there are a number of complicating factors which include effects due to orientation of adjacent dipoles, water dipoles, and shifts of electrolyte ions.

As indicated above the surface potential of the unsaturated *d*-pimaric acid is about 100 mv., or one-half that of the saturated compound, although the two substances have practically the same molecular surface density. One would therefore be led to believe that the dipoles associated with the double bond in the ring or in the side chain or possibly in both are oriented in such a way as to oppose the dipole of the carboxyl group, even at the initial stages of the compression. Then, on compression, further internal opposition or compensation of the dipoles may be said to result in the decreasing surface potential observed. As shown by Harkins, Ries and Carman[5] the surface

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[4] Danielli and Adam, *Biochem. J.*, **28**, 1583 (1934).

[5] Harkins, Ries and Carman, This Journal, **57**, 776 (1935).

potential (ΔV) may rise considerably less rapidly than the surface density of the film (13% less rapidly in the case of certain polymers of ω-hydroxydecanoic acid). This is usually attributed to the mutual effect of the surrounding dipoles. However, it is quite probable that in the case of the *d*-pimaric acid, the conspicuous *decrease* in the surface potential with increased surface density is due to a changing orientation of the individual molecules in such manner as to further the opposition or compensation of the intramolecular dipoles.

Additional studies relating potential variations to temperature changes are now in progress.

VI. Summary

1. Surface potential and force–area relations for monomolecular films of a saturated and unsaturated pimaric acid were studied. The corresponding curves are shown.
2. An improved procedure for obtaining more accurate clean-surface potentials is described.
3. The maximum thickness of the mono-layer is about 12 Å. for both compounds. The coefficients of compressibility are calculated.
4. The structures of the pimaric acids are compared with that of cholesterol, and their orientations in surface films are related to the different positions in which the polar groups are located. The experimental data compare favorably with the results to be expected from model measurements.
5. The surface potential of the tetrahydro-*d*-pimaric acid is about 200 mv., whereas that of the unsaturated compound is about 100 mv. An unprecedented decrease in the surface potential on compression was observed in the case of the unsaturated acid films. It is considered probable that these facts may be related to an increasing intramolecular dipole compensation on compression.

CHICAGO, ILLINOIS

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

Heterogeneous Reaction Kinetics. The Effect of Light Exposure on the Kinetics of Thermal Decomposition of Silver Oxalate

BY ARTHUR F. BENTON AND GEORGE L. CUNNINGHAM

In reactions of the type A(s) = B(s) + C(g), which are normally autocatalytic in nature, existing evidence shows that the rate depends on two separate factors, formation of nuclei of product and subsequent growth of these reaction centers. However, a satisfactory quantitative treatment of the kinetics has not yet been attained. With this objective in view we have studied, both experimentally and theoretically, the rate of decomposition of a light-sensitive solid on which nuclei have previously been produced by controlled irradiation.

Silver oxalate was chosen as a suitable material, since it decomposes at convenient temperatures and apparently yields only silver and carbon dioxide, uncomplicated by side reactions. MacDonald and Hinshelwood[1] found the reaction to be autocatalytic, and the rate sensitive to adsorbed ions and to oxygen. Sheppard and Vanselow[2] showed that sulfur compounds greatly accelerate the reaction. Arens and Eggert[3] found that silver oxalate–gelatine plates were made developable by exposure, and resembled silver chloride emulsions both in sensitivity and spectral range.

Experimental Methods

Approximately 1-g. samples of silver oxalate were decomposed in the dark in Pyrex bulbs heated by suitable vapor baths provided with electric heating and regulated pressure. The evolved gas was continuously removed by means of a Sprengel pump and fed into the lower end of a water-jacketed, mercury-filled buret, where its volume was measured at regular intervals. Absence of leaks in the all-glass apparatus was assured by overnight test before each experiment.

In the later experiments (Oxalate II), samples were illuminated when desired with light from a 1000-watt tungsten-filament lamp provided with a reflector. The light, after traversing in order a lens system, 6 cm. of running water, a suitable color filter and a shutter, was reflected downward to the bulb by a metallic mirror. The filter was Corning G586AW, which transmits from about 320 to 400 mμ, with a maximum at 370 mμ. All exposures were made with the oxalate at room temperature. The

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[1] MacDonald and Hinshelwood, *J. Chem. Soc.*, **127**, 2764 (1925); see also Hoitsema, *Z. physik. Chem.*, **21**, 137 (1896).

[2] Sheppard and Vanselow, THIS JOURNAL, **52**, 3468 (1930).

[3] Arens and Eggert, *Phot. Korr.*, **67**, Congress No., 17 (1931).

sample was contained in a cylindrical bulb 4 cm. in diameter, closed at the top by fusing to a plane disk of Pyrex glass. At its lower end the bulb was drawn down to a funnel shape, terminating in a 2-mm. capillary, through which air or other gas was drawn in, to stir the sample during exposure. This procedure occasioned only a negligible loss of sample, *e. g.*, 1.7% in eight hours.

The light absorbed by the oxalate was measured by surrounding the reaction bulb with a 2-mm. layer of a 1% solution of *o*-nitrobenzaldehyde in purified acetone. Based on the measurements of Hyman, quoted by Weigert and Brodman,[4] this arrangement absorbed 99.6% of λ 366, and thus substantially all the light in our experiments, centering at 370 mμ. The light absorbed by the solution, at least between λ 366 and λ 436, produces 0.5 molecule of *o*-nitrosobenzoic acid per quantum.[5] The acid was determined by conductance measurements, with known mixtures of aldehyde and acid containing a constant total amount (1%) of the two isomers as standards. For stirred samples 40 to 50% of the incident light was absorbed.

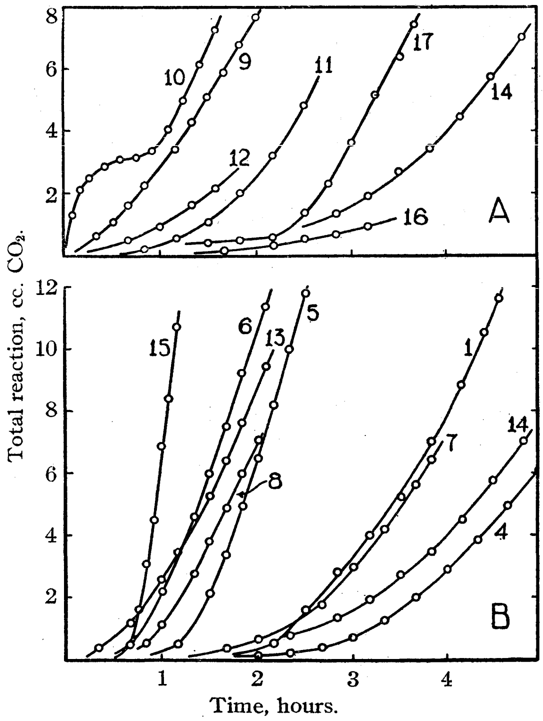

Fig. 1.—Decomposition of oxalate I: effect of various factors (Table I).

Materials.—The first batch of silver oxalate (Runs 1–17) was prepared by continuously adding, during seventy-five minutes, a solution of 25 g. of C. P. silver nitrate in one liter of distilled water to a solution containing 20 g. of C. P. sodium oxalate dissolved in 3 liters of water, with vigorous mechanical stirring. After ten thorough washings the precipitate was dried in a vacuum desiccator over sulfuric acid. Exactly the same procedure was followed for the second batch. The oxalate was prepared and stored in a dark room, only a minimum of red light being used when necessary.

Experimental Results

In the data given below, the course of reaction is expressed as total cc. of carbon dioxide evolved by the whole weight of sample as a function of time. The gas volumes represent an average temperature of 26° and an average pressure of 750 mm. (at 0°). Since we were primarily interested in the earlier stages, the reaction was usually followed only to 5–10% of completion, except at higher temperatures.

Silver Oxalate I.—The experiments with this preparation were designed to show the influence of various factors on the course of decomposition. All except Run 15 were made at 100 ± 0.2°. The results are shown in Fig. 1 (A and B), and the necessary data in Table I. All exposures were made with a 100-watt tungsten filament lamp at a distance of 20 cm. The numbers listed in Column 4 of Table I give the disposition of the samples during exposure: (1) spread out in thin layer in air, (2) stirred magnetically in vacuum, (3) stirred in water, then dried in air. Color filters were used only in Run 11 (Wratten 16, passing λλ > 520 mμ) and Run 12 Wratten 47A, passing λλ 360–520).

TABLE I

DATA FOR FIGURE 1

Run	Sample, g.	Hr.	Exposure Method
4	0.88	0	..
7	.86	0	..
14[a]	1.52	0	..
15[b]	0.89	0	..
1[c]	1.28	0	..
5	0.86	1	(1)
8	.80	3	(1)
6	.93	18	(1)
13	1.42	3	(2)
16[d]	1.4	0	..
17[e]	1.48	0	..
9	0.80	3	(3)
10	.97	54	(3)
11	.78	3	(3)
12	1.34	3	(3)

[a] Sample dried ten months in vacuum. [b] Decomposed at 118.5°. [c] Decomposed in carbon dioxide at 1 atm. [d] Sample mixed with residue from Run 15 in stream of carbon dioxide. [e] Sample ground in agate mortar.

These experiments show that the decomposition was not markedly affected by long drying of the

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(4) Weigert and Brodman, *Trans. Faraday Soc.*, **21**, 453 (1925–6). Slightly higher values were obtained by Weigert and Prückner, *Z. physik. Chem.*, Bodenstein Festband, 775 (1931).

(5) Weigert and Brodman, *ibid.*, **120**, 24 (1926); Leighton and Lucy, *J. Chem. Phys.*, **2**, 756 (1934).

oxalate, by the presence of carbon dioxide, or by contact of the sample with *foreign* particles of silver. The rate was somewhat increased by fine grinding. Previous exposure to light greatly increased the rate, the effect being relatively greater for shorter exposures. Wave lengths longer than 520 mμ were surprisingly effective, but the effect per quantum was undoubtedly much greater for shorter wave lengths.

After the last point shown for Run 7, a twelve-hour exposure at room temperature produced 0.06 cc. of gas. That light alone could effect decomposition was also indicated by the discoloration from exposure in Run 10. On carrying Run 8 to completion the evolved gas was 99.6% of theoretical; not more than 0.04% was unabsorbed by potassium hydroxide.

Silver Oxalate II.—With this material all exposures were conducted as described under "Methods." The results of a series of runs at 100°, with different stirring gases during exposure, are shown in Fig. 2A, and the pertinent data in Table II. It may be observed that the unexposed sample (19) decomposed much more slowly than Oxalate I, in spite of the identical method of preparation. Another run (18) under the same conditions gave results practically identical with 19. Contact with air (Run 22) retarded the initial decomposition, doubtless due to the strong chemosorption of oxygen by silver,[6] but this effect was later overcome. During the exposure in Run 26 the sample evolved 0.05 cc. of gas, or 0.12 molecule per quantum absorbed.

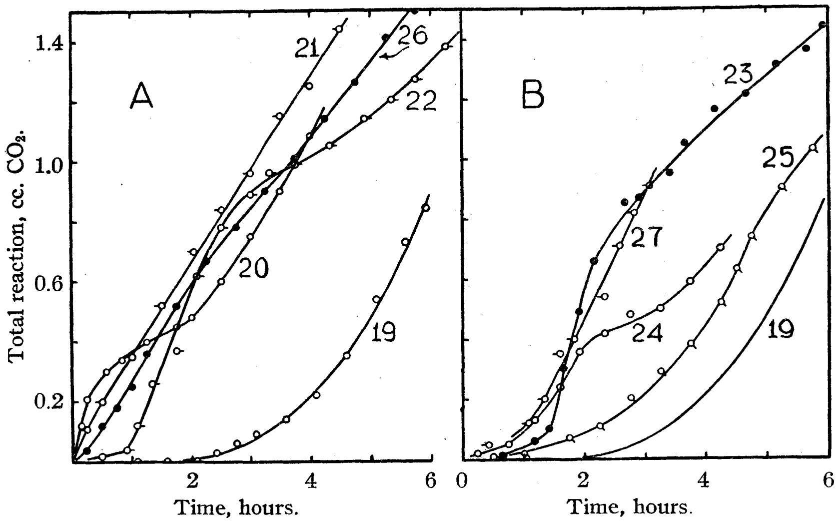

Fig. 2.—Decomposition of oxalate II at 100°: A, effect of gas used for stirring during exposure (Table II): B, effect of exposure time (Table III).

TABLE II

RUNS AT 100° FOLLOWING EXPOSURE IN DIFFERENT GASES

Run	Wt., g.	Gas	Exposure, hr.	Quanta absorbed × 10⁻¹⁸
19	1.42	None	0	0
20	0.91	CO_2	8	7.1
21	1.02	N_2	8	8.7
22	1.09	Air	8	5.5
26	1.42	None	20	11.9

Figure 2B shows the results obtained at 100° with samples previously exposed for varying times, all being stirred with air. Table III gives the necessary data. It is evident that while these early stages of the reaction are more rapid with increasing exposure, the effect is relatively much less for the longer exposures.

A series of runs at 118°, following varying exposure with air stirring, is detailed in Table IV and in Fig. 3, where *rate* is plotted against time. At this temperature exposure evidently has relatively little effect, but the actual increase in total reaction at any time, as compared with unexposed samples, is much greater than at 100°.

TABLE III

RUNS AT 100° WITH VARYING EXPOSURE

Run	Wt., g.	Exposure, hr.	Quanta absorbed × 10⁻¹⁸
19	1.42	0	0
25	0.96	1/3	0.37[a]
24	1.56	1	1.2
27	1.02	4	4.4[a]
22	1.09	8	5.5
23	1.19	20	22.2

[a] Calculated on basis of Run 23.

TABLE IV

RUNS AT 118° WITH VARYING EXPOSURE

Run	Wt., g.	Exposure, hr.	Quanta absorbed × 10⁻¹⁸
34	0.90	0	0
36	1.11	1	0.5[a]
35	1.06	8	3.7
44[b]	1.18	0	0

[a] Calculated on basis of Run 35. [b] 117°.

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(6) Benton and Drake, THIS JOURNAL, **56**, 255 (1934); Drake and Benton, *ibid.*, **56**, 506 (1934).

In Run 44 the unexposed sample was subjected to occasional rapid changes in temperature between 117 and 100°. Comparison of the average of the rates at 117° before and after each temperature change with the intervening rate at 100° gives ratios of 5.1, 3.9 and 4.5, or an average of 4.5. The general effect of a wider range of temperature on unexposed samples is shown in Fig. 4, to which the following data apply.

Run	19	42	34	37	30
Wt., g.	1.42	1.38	0.90	0.92	1.30
Temp., °C.	99.9	109.8	118	131	138

At the upper limit of the curves shown for Runs 30 and 37 the samples exploded.

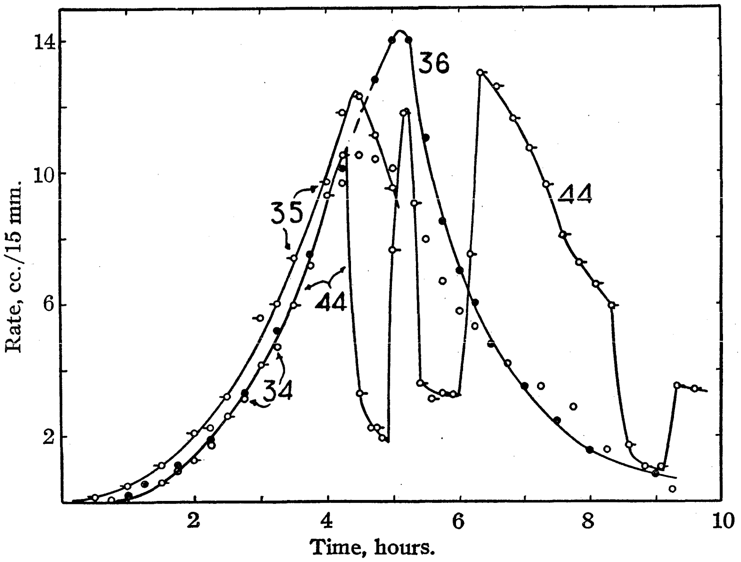

Fig. 3.—Rate of decomposition of oxalate II at 118° (Table IV).

At 80° a 1.53-g. sample gave no measurable evolution of gas in thirteen and one-half hours. Another sample (1.20 g.) gave no gas in seven hours at 80°; on changing the bath temperature to 100°, the course of reaction was practically identical with that in Run 19 where the sample had not been preheated. Hence the rate of formation of nuclei at 80° must be inappreciable. A third sample (1.15 g.) was exposed to room light for thirty minutes and then heated for two and three-tenths hours at 80°, during which time not more than 0.01 cc. of gas was evolved. When the temperature was raised to 100° decomposition began at once in the normal manner for exposed samples. After 0.6 cc. had been given off, the temperature was brought back to 80°, where in two and one-half hours only 0.02 cc. was evolved. Thus the rate of growth of nuclei at 80° is extremely small, but appreciable.

A single granule of Oxalate II, weighing perhaps 1 mg., was decomposed at 118° in a tiny bulb protected from light (Run 45). The evolved gas was measured by the depression of the mercury level in an adjoining 1-mm. capillary, the pressure being maintained at 1 mm. When readings (cm.) on the capillary are plotted against time, the curve is almost identical with that shown in Fig. 4 for Run 42.

Silver Oxalate III.—This material was prepared in exactly the same manner as I and II except that, instead of a slight excess of sodium oxalate, a 100% excess of silver nitrate was used. In a run at 100° an unexposed sample (1.27 g.) gave yields only about half as great as Oxalate II (Run 19). Another sample (1.11 g.), exposed for one hour exactly as in Run 24, gave rates at 100° practically identical with the latter. Although it is possible that adsorbed silver nitrate retards the reaction, the much greater difference in activity between Oxalate I and II, which were prepared alike, renders this conclusion doubtful.

Theoretical Results

The following considerations are based on the assumption that the formation of nuclei and their subsequent growth are essentially independent processes. Without sharply defining the size of a "nucleus," we may let the number of them which have formed up to time t equal n. Let the volume of the solid which has reacted around a particular nucleus be $x = f(t - \tau)$, where τ is the time at which the nucleus came into existence, and f is some function. Then at any time the number $\mathrm{d}n$ of nuclei which appeared in the interval $\mathrm{d}\tau$ will have spread through a volume $x\mathrm{d}n$, and the total volume decomposed at time t will be

$$V = \int_{\tau=0}^{\tau=t} x\mathrm{d}n \qquad (1)$$

To integrate this expression it is necessary to make assumptions regarding the variation of x and n with time.

Solutions of the problem for certain special cases have already been given. Thus Topley and Hume[7] assumed that reaction in each particle spread from a single nucleus, and that all particles were nucleated simultaneously at zero time. Bradley, Colvin and Hume,[8] assuming nucleation according to a probability law, treated the case in which the reaction, once started on a particular granule, spreads instantaneously over its whole surface. In each case the relations obtained were successful in reproducing the later stages in the decomposition of certain salt hydrates, but failed to account adequately for the earlier stages. It is our belief that the early stages of interfacial reactions are particularly amenable to a general treatment, such as that which follows.

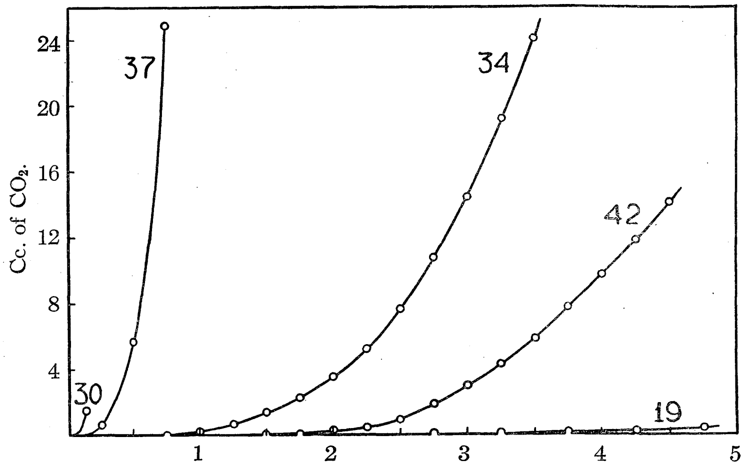

Fig. 4.—Decomposition of oxalate II (unexposed) at different temperatures.

In single crystals decomposition, once started, has been found to progress in directions parallel to prominent lattice planes,[9] and with a *constant* velocity characteristic of each direction.[10] The porous, disperse product remaining usually retains the gross size and shape of the original material, and exerts no retarding effect on the rate. Let u be the *mean* linear velocity of advance of the interface. Then the volume decomposed at any time becomes $u^3(t - \tau)^3$ if the nucleus appeared at a corner, twice this if the start occurred on an edge, and four times if it began on a face. If reaction is assumed to spread out with a spherical front, these values must be multiplied by $\pi/6$. In general we may write for the volume decomposed

$$x = Bu^3(t - \tau)^3 \qquad (2)$$

Since most workers have observed that nucleation occurs preferentially at corners, B will doubtless be near unity. Even for a typical microcrystalline material, complicated by intergrowths and other irregularities, Eq. 2 might be expected to hold for a given granule until the reaction zones spreading from two or more neighboring nuclei begin to overlap.

The problem of the rate of formation of nuclei is less clear. An obvious assumption is that $\mathrm{d}n = k(N - n)\mathrm{d}\tau$, where n is the number formed up to time τ, and N is the total number of potential nuclei in the whole sample (possibly "active spots"), all assumed equally active. This expression leads to $\mathrm{d}n = k(N - n_0)e^{-k\tau}\mathrm{d}\tau$, where n_0 is the number of nuclei, if any, present at the start.

With these values inserted in Eq. 1 the total volume decomposed at time t becomes

$$V = \int_{\tau=0}^{\tau=t} Bu^3(t - \tau)^3 k(N - n_0)e^{-k\tau}\mathrm{d}\tau$$
$$= k(N - n_0)Bu^3\,[6e^{-kt}/k^4 + (t^3/k)(1 - 3/kt + 6/k^2t^2 - 6/k^3t^3)]$$

If the exponential term is now expanded as a power series in t, all terms below t^4 cancel, and

$$V = (k/4)(N - n_0)Bu^3t^4(1 - kt/5 + k^2t^2/5\cdot 6 - \cdots)$$

But this does not include the reaction due to growth of the n_i nuclei, such as those produced by irradiation, which were present at zero time. Including these, and multiplying by the ratio r of measured product (in our case cc. of carbon dioxide) to the volume of solid reactant, we have for the total yield

$$Y = r[(k/4)(N - n_0)Bu^3t^4(1 - kt/5 + \cdots) + n_iBu^3t^3 - v_0n_i] \qquad (3)$$

n_i and n_0 will be equal provided photochemical and thermal nucleation involve the same "active spots." The last term, representing the purely photochemical yield in the production of the n_i nuclei, each of volume v_0, may be neglected. Unless the rate of nucleation k is very great, the higher terms in the parentheses are also small; thus when $n = N/3$, $kt/5$ is only 0.08. Hence, as a fair approximation for the earlier stages, the yield for unexposed samples (n_i and $n_0 = 0$) should vary nearly as t^4, with a smaller average

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(7) Topley and Hume, *Proc. Roy. Soc.* (London), **A120**, 211 (1928).

(8) Bradley, Colvin and Hume, *ibid.*, **A137**, 531 (1932); *Phil. Mag.*, [7] **14**, 1102 (1932).

(9) Kohlschütter, *Kolloid Z.*, **42**, 254 (1927).

(10) Hume and Colvin, *Proc. Roy. Soc.* (London), **A125**, 635 (1929).

power of t for exposed samples. These relations will of course fail to hold after the time when the first granules nucleated have been completely decomposed.

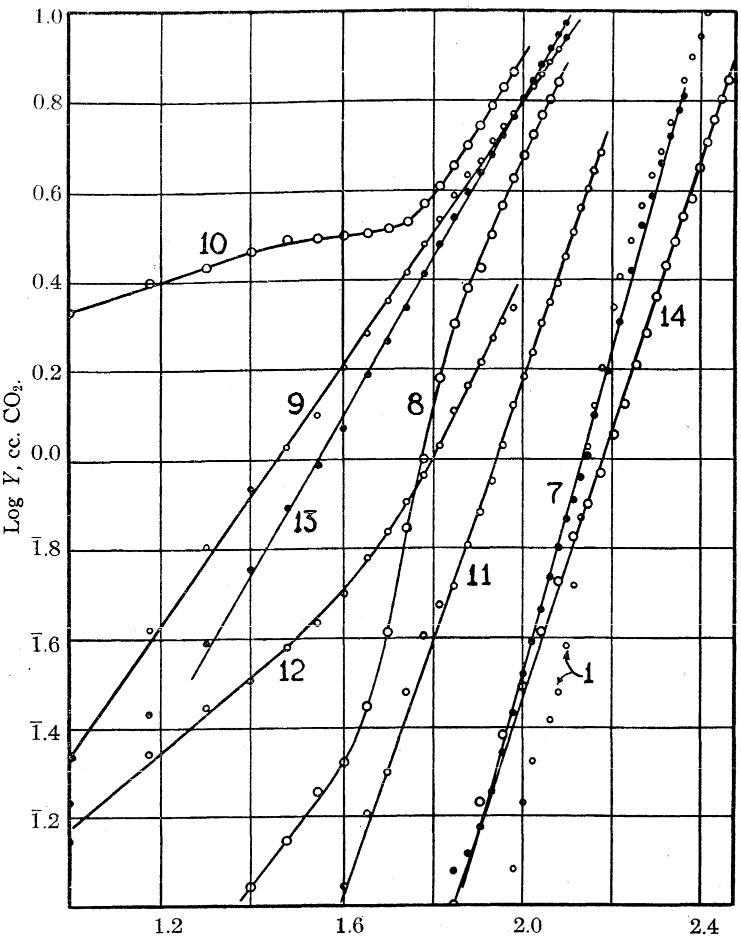


Fig. 5.—Log–log plot for decomposition of oxalate I at 100°.

TABLE V

OBSERVED AND CALCULATED YIELDS IN RUN 44

$Y = 1.176 \times 10^{-7}t^{3.60}$

Time, min.	Y, obsd., cc.	Y, calcd., cc.
60	0.21	0.30
75	.69	.66
90	1.29	1.28
105	2.24	2.22
120	3.52	3.59
135	5.47	5.49
150	8.07	8.03
165	11.4	11.3
180	15.6	15.5
195	20.5	20.6
210	26.4	26.9
225	34.3	34.6
240	43.6	43.6
255	54.1	54.2

It has been assumed that the reaction, even though its early rate may be very small, actually begins at zero time, in other words there is no "incubation" period. This is the case for silver oxalate decomposition and nearly all other interfacial decompositions. The mechanism of nucleation here assumed cannot be applied to cases, such as many reduction reactions, where a real incubation period occurs.

Discussion

The above development suggests that plots of log Y *versus* log t should give nearly straight lines for the earlier stages of decomposition. (Complete decomposition of a 1-g. sample is equivalent to Y = 160 cc.) Such plots for representative runs are shown in Figs. 5 and 6. In the majority of cases the curves closely approximate straight lines. Prolonged exposure tends to make the early yield relatively too large. In a few cases the curves are S-shaped, particularly in Run 8 (also 5 and 6) where the sample was exposed in air without stirring. The gaps in Curves 14 and 19 represent overnight interruptions with the sample at room temperature. Table V indicates the extraordinary fidelity with which the results for an unexposed sample (44) may be repro-

TABLE VI

CONSTANTS IN THE EQUATION $Y = at^m$

Run	m	$-\log a$
	Oxalate I, 100°	
7	3.6	7.6
14	3.1	6.7
11	2.9	5.7
12	1.9	3.5
13	1.7	2.7
9	1.4	2.1
10	1.6	2.3
	Oxalate II, 100°	
19	3.5	9.1
	Oxalate II, 118°	
34	3.4	6.5
44	3.6	6.9
36	3.2	6.0
35	2.9	5.2
45	3.9	(13.3)

duced by the simple expression $Y = at^m$. The last observed value represents 28% of the total reaction.

In Table VI are recorded the values of m and a (cc. at 26°, 750 mm.) in the equation $Y = at^m$, for all runs in which this relation was followed over a major part of the observed data.

Runs are listed downward in order of increasing exposure to the active wave lengths. In general, the requirements of Eq. 3 are qualitatively fulfilled, that is, m decreases and a increases with increasing exposure. It is noteworthy that for unexposed samples, m is close to 3.5, for both batches and for different temperatures, whereas the corresponding values of a differ widely. The difference from the theoretical value of $m = 4$ might be ascribed to a fraction of the crystals having one very small dimension, or to a variation among the N "active spots" in ability to form nuclei. The most probable explanation, however, is to be found in a continuing exhaustion of those granules which happened to be nucleated early, any sharp change in rate being obscured because of variation in particle size.

Likewise, for exposed samples, Eq. 3 calls for $m = 3$ near the start of reaction, whereas slopes only half of this value were occasionally found. It is proper to note here, however, that slopes much below 3 were found only when the exposed sample had been in contact with air before decomposition (Runs 12, 9, 10) or when, as in Run 13, the illumination was nonuniform due to inadequate stirring.

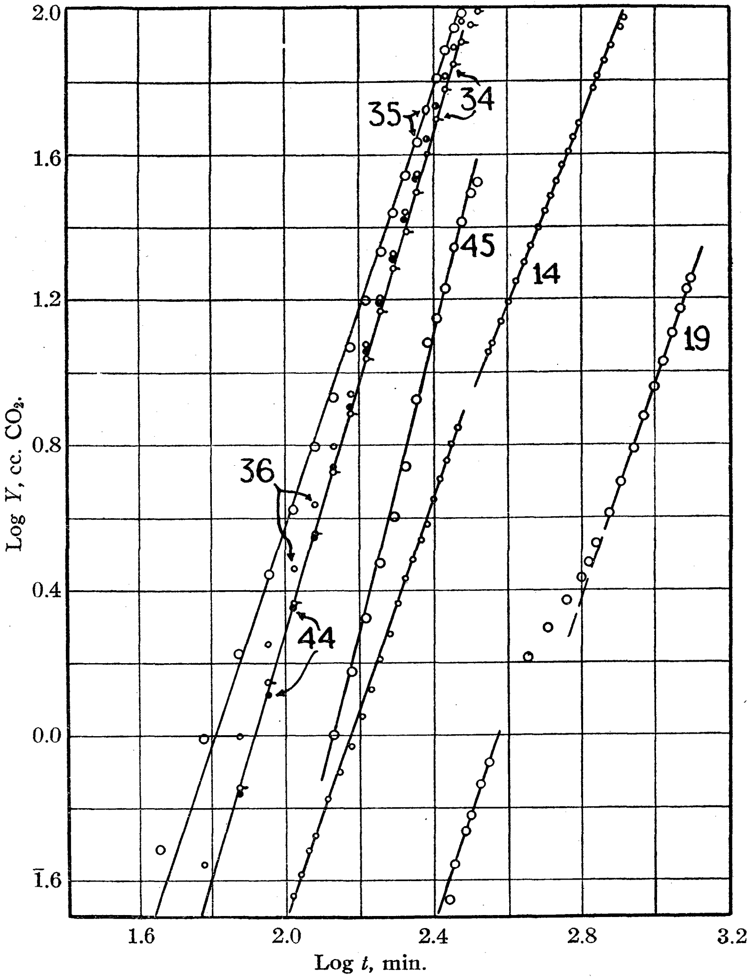


Fig. 6.—Log-log plot for decomposition of oxalate II.

In cases of short exposure (n_i and $n_0 \ll N$) the yield from thermally produced nuclei will be the same with or without exposure, so that ΔY, the increase due to exposure, should be proportional to the n_i photonuclei. This relation is roughly valid for exposures up to one hour (Fig. 2B). The increasing importance of n_0 may explain the relatively smaller effect of longer exposures, or it may be that the number of photonuclei increases less rapidly than the number of quanta absorbed.

For a given (short) exposure and time the values of ΔY at two temperatures should be proportional to the corresponding values of u^3. For Oxalate II a quantum absorption of 0.5×10^{18} produced at t = two hours a ΔY of about 0.15 cc. at 100° (based on Runs 24 and 25), and 0.77 cc. at 118° (Run 36). Hence u^3 increased by a factor of 5.1 and u by a factor of 1.7, corresponding to an activation energy E_u of 8600 cal. An independent value of E_u may be obtained from the relative rates at 117 and 100° in Run 44 (Fig. 3)—a procedure which is justified because at 100°, as Run 19 shows, new nuclei make no appreciable contribution to Y for at least two hours. Over the 17° interval in Run 44 u increased by a factor of $\sqrt[3]{4.5} = 1.65$, equivalent to $E_u = 8500$ cal., in agreement with the former value.

For the early stages of reaction with unexposed samples the relative yields at a given time should vary as kNu^3, and the yields per gram of sample as ku^3. For Runs 34 and 19 the relative yields per gram at twenty-five-minute intervals from $t = 195$ to $t = 300$ min. were 300, 280, 290, 290, 260. Hence, in this 18.5° interval ku^3 increased by a factor of 290, so that k increased by a factor of $290/5 = 58$, equivalent to an activation energy E_k of 64,000 cal. for the nucleation process. The conclusion that the temperature coefficient of nucleation is much greater than that of growth of nuclei is confirmed by the qualitative experiments at 80°.

An E_k of 64,000 cal. is equivalent to an einstein of λ 445 mμ. With Oxalate I wave lengths $>$ 520 mμ caused nucleation, but the much greater rates of decomposition of this material suggest that its E_k may have been less than 64,000.

Summary

In the decomposition of solid silver oxalate variations in rate due to long drying, preparation with excess of one or the other reagent, or fine grinding, were scarcely greater than the differences between two samples prepared and treated alike. Exposure to light, particularly to λλ $<$ 520 mμ, greatly increased the rate of the subsequent thermal reaction. Contact with oxygen during exposure resulted in a marked initial poisoning as compared with exposure in nitrogen, carbon dioxide or vacuum. The increase in yield at any time over that for unexposed samples was roughly proportional, for the shorter exposures, to the number of quanta absorbed, but relatively much less for longer exposures. The effect of exposure was relatively less at higher decomposition temperatures. In the exposure itself λ 370 mμ produced about 0.1 molecule of carbon dioxide per quantum absorbed.

The earlier stages of decomposition have been found to be in fair agreement with a quantitative formulation of the kinetics (Eq. 3), based on simple assumptions regarding the formation of nuclei of product and their subsequent growth. In agreement with the theory, the extent of reaction at any time t, in the earlier stages, is approximately proportional to t^m, where m is found to be 3.5 for unexposed samples, but progressively less for increasing exposure.

For a particular sample of oxalate the activation energy of nucleation is about 64 kcal., while that for growth of nuclei is 8.5 kcal.

UNIVERSITY, VA. RECEIVED JUNE 3, 1935

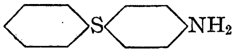
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Molecular Rearrangement of Sulfanilides. II

BY MAURICE L. MOORE[1] AND TREAT B. JOHNSON

In a previous paper[2] on this subject we have discussed the rearrangement of certain aromatic sulfanilide compounds of type I. We have shown

I



II

that on heating these alone or in the presence of an excess of the corresponding amine they undergo rearrangement to the corresponding aromatic para-amino sulfides II. In this paper we shall describe a second type of rearrangement characteristic of sulfanilides which is brought about by the action of alcoholic sodium hydroxide solution.

Smiles and his co-workers,[3] who have recently investigated the chemical behavior of *o*-amino sulfones and sulfides, have made the interesting observations that certain representatives of both series undergo molecular rearrangement in alkaline media to form the corresponding sulfinic acid and mercaptan derivatives of diphenylamine, respectively. The same type of rearrangement was also found to take place with the *o*-hydroxy sulfones.[4] The amino sulfide compound shows an irregularity in chemical behavior as is illustrated by the following observation. It was found that the acetyl and the 2-nitrobenzoyl derivatives of 2-nitro-2′-aminodiphenyl sulfide, for example, would undergo rearrangement to the corresponding diphenylamine structures, whereas under the same conditions the parent amine itself, the picryl and the benzenesulfonyl deriva-

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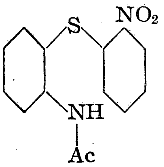
(1) A. Homer Smith Research Fellow in Organic Chemistry, 1934–1935.

(2) THIS JOURNAL, **57**, 1517 (1935); see also *Science*, **81**, 643 (1935).

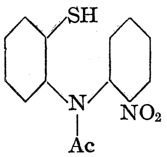
(3) (a) Warren and Smiles, *J. Chem. Soc.*, 914 (1931); 2774 (1932); (b) Evans and Smiles, *ibid.*, 181 (1935); (c) Wight and Smiles, *ibid.*, 340 (1935).

(4) (a) Warren and Smiles, *ibid.*, 1040 (1932), (b) Levi and Smiles, *ibid.*, 1488 (1932); (c) Kent and Smiles, *ibid.*, 422 (1934).

tives were not altered. A theory coördinating the factors influencing this rearrangement was proposed by Smiles[3b] in which he postulated that the rearrangement of III to IV was favored in cases of substituted derivatives when the acyl groups were derived from relatively weak acids. It was later found that the formyl[3c] derivative of VI rearranged with deacylation to form the mercaptan derivative VII.



III



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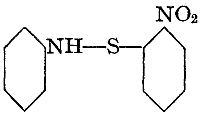

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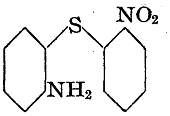
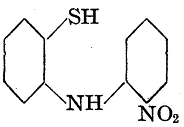


VI



VII

As our rearrangement of the sulfanilides of type I by application of heat appeared to be predominately of the para type, it was of especial interest to determine their behavior when warmed in alcoholic sodium hydroxide solution. We found that 2-nitrophenylsulfanilide, V, gave an excellent yield of the sodium salt of the aromatic mercaptan, VII, by heating it in sodium hydroxide solution for three hours. This rearranged product, VII, was isolated as a red crystalline compound, and was converted easily into the corresponding thiomethyl ether previously described by Smiles. This investigator prepared this thioether by methylation of the compound resulting by the rearrangement and deacylation of 2-nitrophenyl-2′-formamido-diphenyl sulfide.[3c] 2-Nitrophenylsulf-*o*-toluidide and the *p*-toluidide give the corresponding mercaptodiphenylamines by rearrangement when treated under similar conditions with sodium hydroxide. These results show conclusively that the 2-nitro-sulfanilides are capable of undergoing both ortho and para types of rearrangements. The first change is favored by the alkali treatment according to the technique of Smiles, leading to the formation of a mercaptodiphenylamine derivative, VII, while direct heating causes rearrangement to a stable para-substituted amino sulfide II. In the case of 2-nitrophenyl-5′-methyl-2′-aminophenyl sulfide, however, we obtained no rearrangement of the diphenylamine type after refluxing in alkaline solution for six hours. 2-Nitrophenyl-4′-aminophenyl sulfide and 2-nitrophenyl-3′-methyl-4′-aminophenyl sulfide obtained by rearrangement of the corresponding sulfanilides by heat underwent no further change by action of sodium hydroxide, as was to be expected. These observations are in accord with the results obtained by Smiles. In regard to the mechanism of the transformation of nitrosulfanilides V to diphenylamines VII it would appear that intermediates of the structure of ortho-amino sulfides VI are first formed which then undergo the second type of rearrangement in presence of alkali, giving the final product of reaction, VII. We have at present, however, insufficient evidence to substantiate such a conclusion and further research on the subject will be conducted in this Laboratory.

Experimental Part

Procedure for Rearrangement.—The necessary sulfanilide (5 g.) as previously prepared[2] was placed in alcohol (25 ml.) containing 20% sodium hydroxide (5 ml.) and refluxed until a given sample shows that all of the material has rearranged, usually after about three hours of heating. After allowing to cool, the solution was then diluted to twice its volume with water and upon chilling in an ice-bath the sodium salt of the mercaptan derivative was obtained as a red, glistening, crystalline mass. The mother liquor on concentration yielded a further quantity of the same material. The sodium salt was soluble in alcohol and

TABLE OF RESULTS

2-Nitrophenylsulfur-			Anilide		*o*-Toluidide		*p*-Toluidide	
Sodium salt of mercaptan	Yield, %		87		80		90	
	S, %	Calcd.	11.94		11.35		11.35	
		Found	12.08		11.56	11.41	11.40	11.20
Thiomethyl ether	Yield, %		60		65		60	
	M. p., °C.		97–98[a]		94		84–85	
	S, %	Calcd.	12.31		11.68		11.68	
		Found	12.39		11.76	11.84	11.61	
	N, %	Calcd.	10.77		10.22		10.22	
		Found	10.62	10.70	9.96	10.03	9.98	10.12

[a] Smiles reports m. p. 98° for the same compound prepared from the formamido derivatives of the residue.

water but insoluble in ether and benzene. Upon dissolving in water and neutralizing with dilute hydrochloric acid, the free mercaptan was obtained as an oily precipitate which was very difficult to purify.

Methylation of the Mercaptan.—The sodium salt from above operation (2 g.) was dissolved in alcohol (10 ml.) and refluxed for one hour with an excess of methyl iodide (2 ml.). The solution was then diluted with water, when the required thioether crystallized out upon cooling. The wall of the container was rubbed vigorously with a glass rod to facilitate crystallization. The methyl sulfides prepared were soluble in ether, alcohol and benzene but insoluble in water.

In the table are recorded the results of the different products obtained by rearrangement of different sulfanilides under the influence of alkali.

Summary

Certain sulfanilides have been rearranged by digestion in alcoholic sodium hydroxide solution to give the corresponding *o*-mercaptodiphenylamines, whereas, upon heating alone, the same compound gives *p*-amino sulfides. The free *o*-amino sulfides, so far as examined, do not suffer a rearrangement under the same conditions, hence, the question arises, do the sulfanilides pass through this intermediate stage before forming the *o*-mercaptan derivative. As yet this point has not been clarified.

NEW HAVEN, CONN. RECEIVED JULY 5, 1935

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Chloroform-d (Deuteriochloroform)[1]

BY F. W. BREUER

As part of the program on organic compounds of deuterium in progress in this Laboratory,[2] the reaction of chloral with sodium deutroxide has been studied. Chloroform-d, $CDCl_3$, is formed exclusively as shown by the Raman spectrum.[3] The boiling point and freezing point were about 0.5° higher and lower, respectively, than those of ordinary chloroform. No difference was found in the refractive index, $n^{20}\text{D}$ 1.4450. The most significant difference other than the Raman spectrum is in the density, d^{20}_4 1.5004 as compared with 1.4888 for ordinary chloroform determined in an identical manner. Assuming identical molecular volumes for $CHCl_3$ and $CDCl_3$, the calculated value is 1.5013.

Experimental

The various manipulations for making chloroform were first carefully worked out with ordinary water.

Chloral Deuterate, $Cl_3CCH(OD)_2$.—Chloral (E. K. Co.) was distilled through a still head (30 × 0.9 cm.) packed with glass helices[4] to give a middle fraction which was redistilled, the vapors being passed over anhydrous calcium sulfate (Drierite)[5] kept at 100°. After a third distillation, the middle cut ($n^{20}\text{D}$ 1.4568) was used. To 14.72 g. (0.1 mole) of the purified chloral was gradually added with cooling 5.47 g. (0.22 mole) of deuterium oxide (d^{20}_{20} 1.1079).

Reaction of Chloral Deuterate and Sodium Deutroxide.—In a container permitting the interaction of water vapors with metallic sodium a solution of sodium deutroxide in deuterium oxide was prepared from 2.2 g. (0.096 g. atom) of C. P. sodium metal and 5 g. (0.25 mole) of the deuterium oxide. The oxide was added slowly from a dropping funnel and the deuterium gas evolved collected under a pressure slightly below atmospheric. At first the reaction seemed to proceed at about the same rate as with ordinary water, as evidenced by the amount of gas formed. Soon, however, a coating of sodium deutroxide formed on the metal and the reaction rate decreased considerably. After five days the volume of gas remained constant during a period of twenty hours. A white crystalline precipitate had formed, whereas with ordinary water a clear solution was obtained. Apparently, sodium deutroxide or a deuterate of it is less soluble in deuterium oxide than the proto compounds in ordinary water. This is in accord with the decreased solubility of the chlorides of sodium and barium in heavy water.[6] In the present study chloral deuterate was found to be considerably less soluble in deuterium oxide than chloral hydrate in natural water.

In order to condense vaporized heavy water the reaction flask was cooled to −78° and the gas container heated for five hours with a stream of warm air.

After connection between the two vessels had been severed the reaction flask was equipped with a reflux condenser and the chloral deuterate solution was admitted from a dropping funnel over a period of five hours, the flask being kept below 5°. The first few drops caused a rather vigorous reaction; afterward the formation of chloroform-d continued smoothly. After standing overnight the reaction was completed by gentle warming of the flask for ten minutes. Complete separation into two layers, which occurs with the proto compounds, did not

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[1] Presented before the Division of Organic Chemistry at the New York Meeting, April, 1935.

[2] *Cf.* Whitmore and co-workers, THIS JOURNAL, **56**, 749 (1934).

[3] Wood and Rank, *Phys. Rev.*, [2], **48**, 63 (1935).

[4] Wilson and others, THIS JOURNAL, **55**, 2795 (1933).

[5] Hammond and Withrow, *Ind. Eng. Chem.*, **25**, 653, 1112 (1933).

[6] Taylor and others, THIS JOURNAL, **56**, 5334 (1934); Bingham and Stephens, *J. Chem. Phys.*, **2**, 107 (1934).

occur even after two days. The separation was finally effected by centrifuging. The reaction product was dried over freshly ignited calcium oxide, distilled, and redistilled. The yield of $CDCl_3$ was 7.85 g.

Boiling Point, Freezing Point, Density, Refractive Index and Raman Spectrum of Chloroform-d.—The difference in boiling points of the product and of ordinary chloroform prepared by the same reaction was determined with a set of two micro Cottrell apparatus,[7] each of a capacity of 5 cc., one junction of the thermopile being inserted in each of the instruments. At 732 mm. the deuteriochloroform boiled 0.5° higher than its light analog. Good checks were obtained with Emich's micro boiling point determination.[8]

In order to ascertain the degree of purity of the compound freezing and melting point determinations on a 1.5-cc. sample were run, and compared with the constants of highly purified chloroform and also of ordinary chloroform prepared from chloral hydrate and sodium hydroxide. The determinations were carried out in a double-jacketed container with air insulation. A copper–constantan thermopile of 2 couples enclosed in a flattened platinum tube was used with a glass container of similar shape which by the reduced volume allowed the entire thermopile to be covered with the liquid. The determinations were carried out under a pressure of 3 mm. to ensure removal of all gases which might have been formed by partial decomposition of chloroform during the Raman exposure.

	M.p. or range, °C.	F. p., °C.	
$CHCl_3$, esp. pure	−63.62	....	
$CHCl_3$, from chloral hydrate	−63.77 to −63.33	−63.49	−63.62
$CDCl_3$	−64.69 to −64.15	−64.12	−64.12

The melting range of the samples of light and heavy chloroform prepared on a small scale indicates that these compounds are not quite pure. Refractionation was not possible because of the small quantities obtained.

However, the observed values indicate that the deuteric compound melts definitely lower, which is in accordance with the lower melting points of other organodeuterium compounds.

A density determination of a middle fraction, using a 0.5-cc. pycnometer, gave d^{20}_4 1.5004.

The index of refraction was determined by means of a new carefully calibrated Bausch and Lomb refractometer of the Abbe type with temperature control at 20 ±0.05°: n^{20}_D for $CDCl_3$ 1.4450, for $CHCl_3$ 1.4450.

Because of the close similarity in properties of $CHCl_3$ and $CDCl_3$ it would have been most difficult to determine the nature of the product except for the Raman spectrum obtained and analyzed by Professor R. W. Wood of Johns Hopkins University and Dr. D. H. Rank of this Laboratory.[3] All lines appearing on the plates correspond to those for $CDCl_3$. No evidence of any $CHCl_3$ lines was detected.

Grateful acknowledgment is made to Professor Wood and Dr. Rank and to Mr. G. H. Fleming of this Laboratory for his help in portions of the work.

Summary

1. Chloroform-d, $CDCl_3$, free from ordinary chloroform, has been prepared.
2. The properties of the new substance closely resemble those of ordinary chloroform.

STATE COLLEGE, PENNA. RECEIVED AUGUST 5, 1935

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[7] To be published elsewhere by Mary L. Willard and Delcena E. Crabtree of this Laboratory.

[8] Emich–Schneider, "Microchemical Laboratory Manuel," John Wiley and Sons, Inc., 440 Fourth Ave., New York City, 1932.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

The Preparation of Dialkylmagnesium Compounds from Grignard Reagents

BY ARTHUR C. COPE

Schlenk's dioxane precipitation method[1] for the removal of the RMgX and MgX_2 components of the Grignard reagent $2RMgX \rightleftharpoons R_2Mg + MgX_2$ is now in common use for the preparation of ether solutions of dialkylmagnesium compounds. There is need for proof that the system is in mobile equilibrium, however, and for evidence concerning the accuracy of the dioxane method of analysis, since the equilibrium may shift during precipitation. Research in this Laboratory on these problems has revealed several factors which affect the yield of R_2Mg obtainable from Grignard reagents. They are reported in this communication.

The amount of R_2Mg obtained from all of the Grignard reagents investigated increased with increasing temperature. Thus the data summarized in Table I show that the amount of diphenylmagnesium present in solutions of phenylmagnesium bromide increased by about 10% for a 50° temperature rise. The point of equilibrium was also determined in *n*-butyl ether, in order to determine the effect of still higher temperatures. Both phenylmagnesium bromide and methylmagnesium iodide proved to be much less disproportionated in butyl ether than in ethyl ether at the same temperature. The data are recorded in Table II. Preliminary experiments at low temperatures showed a continued decrease in the amount of R_2Mg present and an apparently rapid rate of equilibration, for in solutions of ethylmagnesium iodide, ethylmagnesium bromide and phenylmagnesium bromide the amount of R_2Mg present decreased by approximately 30, 20 and 10%, respectively, on cooling from room temperature to −20 to −30° in forty to fifty seconds.

TABLE I

EFFECT OF TEMPERATURE ON THE DISPROPORTIONATION OF C_6H_5MgBr

Concn. of C_6H_5MgBr[a]		Basic Mg present as $(C_6H_5)_2Mg$, % at *T*, °C.			
Basic Mg, *N*	Br^-, *N*	−15	0	20	35
0.1325	0.1381	59.5	62	67	69
.2178	.2257	62	64	68	70
.2772	.2897	61.5	65	69	70

[a] The slight apparent increase in $(C_6H_5)_2Mg$ with increasing concentration may be due to a rise in temperature during precipitation, which in the case of the most dilute of the above solutions amounted to 5°.

TABLE II

DISPROPORTIONATION OF C_6H_5MgBr AND CH_3MgI IN BUTYL ETHER

RMgX	Concentration		Basic Mg present as R_2Mg, % at *T*, °C.			
	Basic Mg, *N*	X^-, *N*	20	60	100	140
C_6H_5MgBr	0.1108	0.1752	24	39	56	65
CH_3MgI	.2803	.2739	0.2			20

Another factor influencing the yield of R_2Mg obtainable from phenylmagnesium bromide is the reversibility of the precipitation; the yields of diphenylmagnesium increased if the precipitate with dioxane was allowed to stand in contact with the solution. Thus a 0.1818 *N* solution of phenylmagnesium bromide was found to contain 67% of diphenylmagnesium by the usual method of analysis. On allowing the precipitated samples to stand for one, two, three, twenty-four and seventy-two hours before separation of the precipitate by centrifuging, however, the amounts of diphenylmagnesium increased to 72, 73, 74, 75 and 75%, respectively. This reversibility of the precipitation is not general, for the yields of dimethylmagnesium from methylmagnesium iodide and methylmagnesium chloride did not increase on allowing the precipitated solutions to stand.

From these results, in the preparation of dialkylmagnesium compounds from Grignard reagents for synthetic purposes, the precipitation should be made by the addition of dioxane to refluxing solutions of the alkylmagnesium halides in order to obtain maximum yields. Due to the high disproportionation of the common Grignard reagents[1b,2,3] (especially the chlorides), all of the ordinary dialkylmagnesium compounds with the exception of dimethylmagnesium are thus available for practical synthetic use. Methylmagnesium iodide and methylmagnesium bromide are not highly disproportionated, however, so that Bartlett[4] was able to obtain dimethylmagnesium from methylmagnesium bromide in only 4% yield. Investigation of the disproportionation of methylmagnesium iodide at higher tempera-

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(1) (a) Schlenk and Schlenk, *Ber.*, **62**, 920 (1929); (b) Schlenk, *ibid.*, **64**, 735 (1931).

(2) Johnson and Adkins, THIS JOURNAL, **54**, 1943 (1932).

(3) Cope, *ibid.*, **56**, 1580 (1934).

(4) Bartlett and Berry, *ibid.*, **56**, 2683 (1934).

tures and of methylmagnesium chloride showed that dimethylmagnesium can also be prepared in the fair yield of 50% from the chloride (Table III).

TABLE III

EFFECT OF TEMPERATURE ON THE DISPROPORTIONATION OF CH_3MgX

	Concentration		Basic Mg present as $(CH_3)_2Mg$, % at T, °C.			
CH_3MgX	Basic Mg, N	X^-, N	20	35	80 (in benzene)[a]	100[b]
CH_3MgI	0.2232	0.2331	2	10	17.5	44
CH_3MgCl	.2418	.1894	47	50		54

[a] The benzene solution was obtained by dissolving the liquid residue of methylmagnesium iodide etherate remaining after distilling off the ether in benzene. Note that the disproportionation is higher in benzene at 80° than in ether at 35°. The use of benzene as a solvent at 80° was recently assumed to decrease the disproportionation of cyclohexylmagnesium bromide by Miller and G. B. Bachman [*ibid.*, **57**, 767 (1935)]. Further work on the effect of solvents on the equilibrium was discontinued following the notice by these authors that they intended to study the problem.

[b] The samples at 100° were obtained by distilling off the ether and heating the residue at 100°. The methylmagnesium iodide etherate was a liquid, the chloride a white crystalline solid and mechanical difficulties probably account for the relatively low yield in the latter case.

All of the solutions of methylmagnesium chloride prepared contained more basic magnesium than chloride ion. Consequently the precipitate always formed in the preparation of this reagent is magnesium chloride etherate, not only from the Wurtz reaction, but also from the Grignard equilibrium. Thus, in the solution of methylmagnesium chloride described in Table III, 21.5% of the total basic magnesium was present as dimethylmagnesium regardless of any disproportionation of the methylmagnesium chloride remaining in solution. This amount was fairly constant for several preparations which had the following concentrations: (a) basic Mg, 0.2481 N, Cl^-, 0.1963 N (therefore 21% $(CH_3)_2Mg$; (b) basic Mg, 0.5404 N, Cl^-, 0.4168 N (therefore 23% $(CH_3)_2Mg$). A similar precipitation of magnesium chloride etherate was observed by Schlenk[1a] from benzylmagnesium chloride but precipitation was slow in that case, beginning only after several days, while with methylmagnesium chloride, concentrations similar to the above are observed immediately after preparation of the reagent.

Experimental Part

The Grignard reagents used in this investigation were prepared and stored under nitrogen. They were filtered through a plug of asbestos inserted in a stopcock sealed to the side of the flask in which they were prepared. If they were allowed to stand for a short time before filtering (or twelve hours in the case of methylmagnesium chloride), most of the filtration amounted to a decantation and could be made quite rapidly. The analyses for percentage R_2Mg were made as previously described.[3] The amount of dioxane used in each case to precipitate the halides was four moles to each mole of halide ion in the sample, made up to 10 cc. with the ether used in preparing the Grignard reagent. This amount was an excess, and apparently the excess employed does not affect the results given by the method. In all cases, the dioxane solution was at the same temperature as the solution being precipitated. In making the rapid cooling measurements, the samples were immersed in a carbon dioxide–ether mixture. In the other cases, since the equilibria appear to be established rapidly, the solutions were held at the recorded temperature for only fifteen minutes. The removal of halide ion from the solutions was practically complete in all cases, no more than 0.4% of the original quantity remaining in any case. For the measurements in which the ether was removed, the centrifuge tubes were fitted with a small dry exit tube and heated to the indicated temperature (80 or 100°) while the ether distilled off. In the measurements in benzene 20 cc. of dry benzene was then added and the tubes stoppered, while in the 100° determinations the tubes were stoppered and the residues heated at that temperature for fifteen minutes. The precipitation was made by adding 2 cc. of pure dioxane in each of these cases. In the samples precipitated in the absence of a solvent, dry ether was added to the tubes as soon as the rather vigorous reaction with dioxane was over and the rest of the determination made as before. Since heat is evolved during the precipitations, no attempt was made to control the temperature with an accuracy greater than 1°. The order of accuracy of the measurements is indicated by the average deviation of the duplicate analyses which were made in each case, which was 0.5% for basic magnesium; 0.2% for halide ion; 1% for per cent. R_2Mg.

Summary

The extent of the disproportionation $2RMgX \rightleftharpoons R_2Mg + MgX_2$ depends upon the solvent

employed and increases with increasing temperature, as determined by the dioxane precipitation method.

The precipitate formed during the preparation of the Grignard reagent from methyl chloride contains magnesium chloride etherate from the disproportionation of methylmagnesium chloride, so that the reagent contains 20% of dimethylmagnesium in addition to that formed by the disproportionation of the methylmagnesium chloride remaining in solution.

BRYN MAWR, PA. RECEIVED JUNE 4, 1935

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

The Photobromination of Tetrachloroethylene and of Chloroform with Special Reference to the Effects of Oxygen

BY JOHN WILLARD AND FARRINGTON DANIELS

Oxygen, present as an incidental impurity, is known to have a marked effect on the rate of certain chemical reactions,[1] and very likely it is a factor in others where its influence has not yet been suspected. The matter is of interest both from a theoretical and from a practical standpoint.

The photobromination of cinnamic acid has been under investigation in this Laboratory for several years[2] and it seemed desirable to investigate also the photobromination of the very simple molecules, tetrachloroethylene for addition, and chloroform for substitution. These two substances are valuable for investigational purposes not only on account of their simple structure but also on account of the fact that they have high vapor pressures and can be studied in the gas phase as well as in the liquid phase.

All of the photochemical work described here was carried out with a large quartz monochromator and capillary lamps of high intensity,[3] and a large area thermopile.[4]

Photobromination of Tetrachloroethylene

Experimental Procedure

Tetrachloroethylene.—Chlorine was passed into Eastmen tetrachloroethylene and exposed to light.[5] After washing several times with sodium hydroxide and with water the liquid was dried with calcium chloride and twice distilled through a Widmer column in an all-glass still, the middle fraction being retained. It was further purified by freezing in an all-glass reservoir equipped with a dozen taps which could be opened with magnetically operated hammers.

Bromine.—Merck reagent quality bromine was distilled from potassium bromide onto phosphorus pentoxide which had been resublimed in a stream of oxygen. It was then fractionally distilled four times and fractionally crystallized three times, all steps in the purification process being carried out in an all-glass system. After degassing in the manner to be described shortly, it was distilled into a dozen small bulbs.

Oxygen.—Commercial tank oxygen was liquefied in a liquid air trap and the middle-boiling fraction was used to fill a series of bulbs of 1 cc. or less in volume. The pressure of oxygen was determined with a glass manometer.

Degassing Liquids.—Dissolved oxygen was removed from the reservoirs of liquid tetrachloroethylene and bromine by a repeated cycle of freezing with liquid air, evacuation with a mercury vapor pump, melting and brief boiling. When gas from the frozen liquid was no longer able to support a discharge from a Tesla coil, the material was deemed to be sufficiently free from oxygen. It was usually necessary to go through a series of six or seven freezings and evacuations before the oxygen and other permanent gases were sufficiently removed to meet this criterion.

Apparatus.—The experiments were carried out in a fused quartz cell 1 × 2 cm. in cross section and 8 cm. deep. The cell was equipped with a head as illustrated in Fig. 1. Side arm A contains bulbs of reactants which may be shaken into depression C to be broken by the glass-enclosed hammer B. D-E-G is a sealed-in, magnetically-operated stirrer designed to give efficient stirring in the illuminated portion of the cell, without interrupting the beam of light. It consists of the quartz-enclosed iron core D, the quartz landing button E and the quartz rod which terminates in the stirring button G. When an experiment is in progress the circuit through the solenoid M is opened and closed about twice a second by means of a contact operated by a metronome or by a cam on a pulley wheel. This jerks the stirrer up several centimeters and then allows it to fall under its own weight to the point where E is stopped by the quartz platform, F. In falling rapidly the button G sets into motion a body of liquid which travels on into the illuminated region of the cell. The button G has to be 5 mm. or less in diameter, in order to pass through the neck

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[1] See, among others, Deanesly, THIS JOURNAL, **56**, 2501 (1934); Bauer and Daniels, *ibid.*, **56**, 2014 (1934); Dunnicliff and Joshi, *J. Ind. Chem. Soc.*, **6**, 121 (1929); Kistiakowsky, "Photochemical Processes," Chemical Catalog Company, New York City, 1929, pp. 118, 119, 166, 183.

[2] Bauer and Daniels, THIS JOURNAL, **54**, 2564 (1932).

[3] Heidt and Daniels, *ibid.*, **54**, 2381, 2384 (1932).

[4] Damon, Ph.D. Thesis, University of Wisconsin, 1932.

[5] Dickinson and Leermakers, THIS JOURNAL, **54**, 3853 (1932).

of the cell and its shape makes little difference in the effectiveness of stirring.

Part H of the cell-head is a quartz-to-Pyrex graded seal which allows the cell to be sealed to Pyrex systems.

To fill the cell it was first sealed through the outlet K to the glass tap M of a reservoir of purified and degassed tetrachloroethylene. It was then evacuated by a mercury vapor pump through J and protected by a liquid air trap. While evacuation was taking place all portions of the cell except that containing the bulbs of reactants were flamed. The pump was then sealed off at J, the tap M was broken by the hammer L and tetrachloroethylene was distilled into the cell and sealed off at P and at K. The glass tap I allowed the cell to be opened without contamination of air, for addition of materials or removal of the reaction mixture for analysis. When the cell had been filled with tetrachloroethylene and sealed, its light transmission was compared with that of a similar blank cell. A bromine bulb was then broken in C. The bromine vaporized and was quickly absorbed by the tetrachloroethylene. The solution was then illuminated and readings of the light transmitted by the reaction cell and by the blank were taken at frequent intervals in order that the reaction might be followed by Beer's law. When a sufficient number of readings had been taken to show the course of the reaction in the absence of oxygen a bulb of oxygen was broken in C and the readings were continued. At the end of each experiment three graphs were made in which light absorption, concentration and quantum yield were plotted against time.

Measurements were confined to 4360 Å. because liquid tetrachloroethylene itself showed absorption for the ultraviolet lines of the mercury spectrum. The absorption at 3650 Å. was very slight. It was determined qualitatively, that light of 3650 and 5780 Å. causes the addition of bromine when oxygen is absent. It was shown experimentally that absorption of light at 4360 Å. by the product is negligible.

Calculations

A straight line was obtained when the logarithm of the transmission of light of 4360 Å. was plotted against the concentration of bromine used in the solutions. The averaged value of E, defined by the relation $E = 1/lc \log I_0/I$, was 197 ± 3 where l is the length of the light path in cm. and c is the concentration of bromine in moles per liter. This value is the same as that obtained by Bauer and Daniels[6] for the extinction coefficient of bromine dissolved in carbon tetrachloride, namely, 195 ± 3.

From the transmission of light by the reaction mixture the concentration of bromine at any time was determined by reference to the logarithmic plot. Transmissions were determined by readings of the galvanometer deflections when the light passed through the reaction cell, when it passed through a blank cell and when it was cut off by a shutter. All readings were corrected for reflection losses at the several windows. The same galvanometer readings, calibrated in terms of a U. S. Bureau of Standards standard radiation lamp, permitted a calculation of the number of ergs and the number of quanta absorbed.

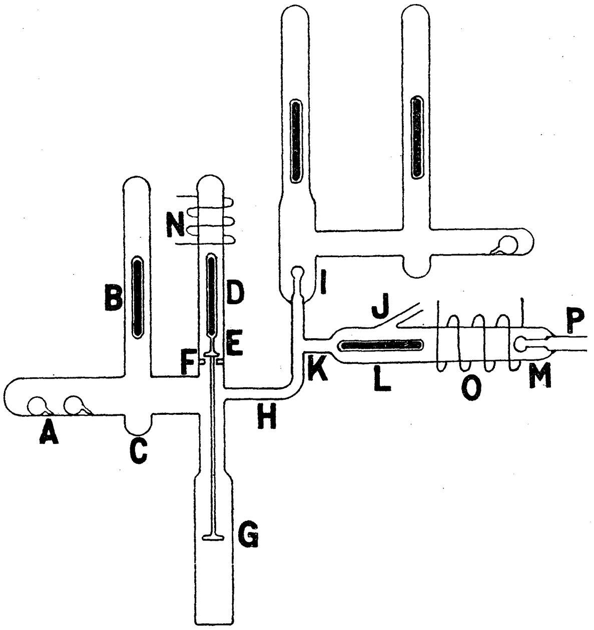

Fig. 1.—Reaction cell.

The concentration of bromine was plotted against time of illumination and the slope of the smooth curve, determined with a Richards–Roope tangent meter, gave the rate of the reaction at any time. The quantum yield at any time was determined by expressing this rate of reaction in terms of the number of molecules reacting per second and dividing by the number of quanta absorbed per second.

Results

Effect of Oxygen.—When reaction mixtures of bromine and tetrachloroethylene, which had been treated to free them from oxygen, were illuminated bromine was consumed at a readily measurable rate. When a bulb of oxygen was broken in the reaction chamber, giving a partial pressure of 20 to 50 mm. of the gas, the rate showed a sharp increase, indicating that small amounts of oxygen accelerate this reaction. Curves E and H of Fig. 2 illustrate this fact. Curves for other experiments indicate that the accelerating oxygen is gradually used up during the exposure to light. When oxygen at one atmosphere pressure was admitted to the cell the reaction was almost com-

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[6] Bauer and Daniels, THIS JOURNAL, **56**, 380 (1934).

pletely inhibited as shown in Fig. 3, where the readings which give the curve A were made with a reaction mixture from which oxygen had been removed and those for part B were made with the same mixture after oxygen at one atmosphere pressure had been admitted to the cell. Many experimental measurements were made which cannot be recorded here in detail,[7] but it should be emphasized that the results are all in substantial agreement even though the purification and procedures were considerably altered.

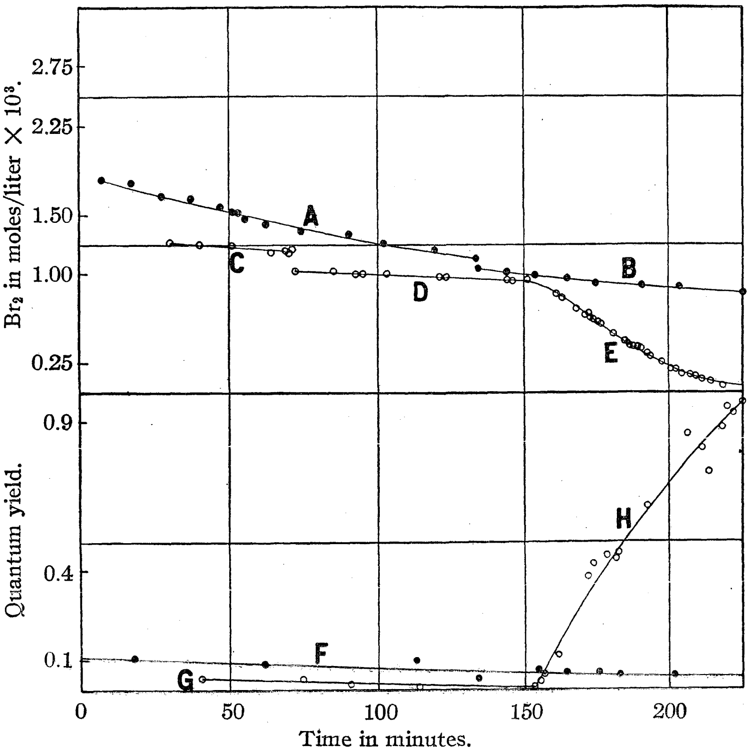

Fig. 2.—A, plot of concentration of bromine against time for reaction mixture in which considerable concentration of product has previously been built up. B, continuation of A after nine hour dark interval. C, continuation of B after breaking a fresh bulb of bromine in the reaction chamber; 225 minutes should be added to the time scale for curves C, D, E, G and H. D, continuation of C after a thirty-seven hour dark interval. E, continuation of D after breaking bulb containing about 1.5×10^{-5} mole of oxygen in the cell of 35-cc. capacity. F, plot of quantum yield against concentration corresponding to curves A and B. G, plot of quantum yield against concentration corresponding to curves C and D. H, curve showing increase in quantum yield after breaking oxygen bulb.

Inhibition by Products.—The two curves in each section of Fig. 2 represent the reactions which occurred after the breaking of two different bromine bulbs in the same solution of tetrachloroethylene. Since the concentration of tetrachloroethylene may be considered to remain essentially constant during these experiments, the fact that the slope of curves C and D in Fig. 2 is less than that of curves A and B at points of equal bromine concentration, indicates that the apparent rate of reaction has been decreased by the accumulation of products in the reaction mixture. This inhibition is also shown by the fact that curve G shows lower quantum yield values than does curve F.

Stirring.—If, during the course of an experiment, the stirrer was operated only during alternate intervals of illumination, the plot of concentration against time was of a sawtooth nature, indicating that bromine was consumed in the path of the light much more rapidly than it diffused in from the surrounding solution. If, however, a complete experiment was carried out without stirring, a smooth curve resulted, but such experiments differed from those in which stirring was used, in that the plot of percentage of incident light absorbed against time which they gave was convex to the axes of the plot while that for the stirred solutions was concave. This difference can probably be ascribed to the accumulation of the reaction product in the illuminated region of the unstirred reaction mixtures.

Temperature Effect.—One experiment was made with a deoxygenized system, in which readings were taken first at 0 and then at 25°. The quantum-yield values for the 0° illumination were extrapolated over a seven-minute interval of illumination which occurred between the last 0° reading and the first 25° reading. The value thus obtained divided into the quantum yield corresponding to the first reading of the 25° illumination gave a 25° temperature factor of 1.33. This gives a 10° temperature factor of $\sqrt[2.5]{1.33}$ or 1.12.

Concentration of Tetrachloroethylene.—Two experiments were carried out with carbon tetrachloride solutions of bromine and tetrachloroethylene. The amount of bromine consumed was determined by volumetric analysis after several

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(7) Complete details may be found in part of a Ph.D. thesis filed in the Library of the University of Wisconsin by John Willard in August, 1935.

hours of illumination and quantum yields were calculated. The bromine concentrations, the light intensities and the amounts of bromine consumed were of the same order of magnitude in the two cases. One reaction was carried out at 0° and the other at 25°, and the concentration of tetrachloroethylene was about 0.17 mole/liter in one case and about 5 moles/liter in the other. When the quantum yield for the reaction at 0° was corrected to 25° by means of the temperature factor given above, it was found that the yield for the solution of higher tetrachloroethylene concentration was only about 2.5 times greater than for the solution in which the concentration was one twenty-fifth as great. Both yields were of the same order of magnitude as those obtained with solutions of bromine in tetrachloroethylene which were not diluted with carbon tetrachloride. These facts indicate that the concentration of tetrachloroethylene is not important in determining the rate of the bromination reaction.

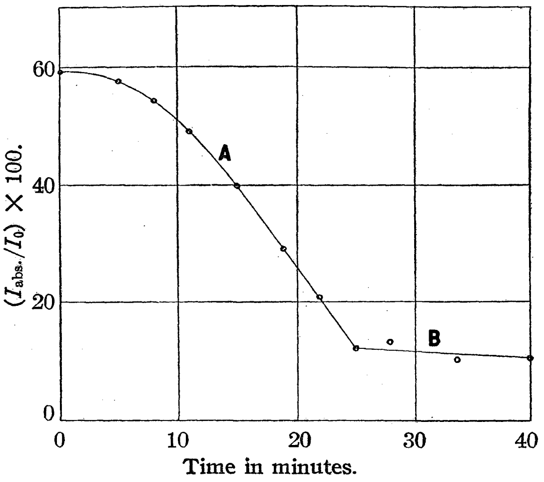

Fig. 3.—Inhibition of the photobromination of tetrachloroethylene by an excess of oxygen.

Dark Reaction.—The vertical drops between curves A and B and between curves C and D in Fig. 2 show that a slight dark reaction occurred over dark intervals of nine and thirty-seven hours. The rate of the dark reaction thus observed and also that observed when mixtures of bromine and tetrachloroethylene were allowed to stand in the dark while exposed to air was very much less than the rate reported by Herz and Rathmann.[8]

Gas Phase.—A few experiments were made on the gas phase reaction of bromine and tetrachloroethylene at temperatures between 50 and 60°. In one case a curve showing decreasing concentration of bromine with time of illumination was observed. In another, crystals of product formed on the windows of the reaction cell. In two others there was no indication of a bromination occurring even after long-continued illumination. These two experiments, however, showed a decrease in light absorption after the contents of the cell had been frozen out and then allowed to return to room temperature. When the cell was illuminated after such a treatment the light absorption increased from its reduced value to a rather definite maximum. This phenomenon is illustrated in Fig. 4 where A, B, C and D represent periods of illumination at 50° separated by dark periods in which the temperature was lowered. A three-hour period intervened between B and C. A bulb of oxygen was broken between C and D at the lower temperature. These facts may be explained by the assumption that during the liquefaction and freezing a small amount of dibromotetrachloroethane is formed and that on illumination of the revaporized mixture it is decomposed through a bromine sensitized photodecomposition of the type shown to exist by the recent work of Carrico and Dickinson,[9] which was published after the present research was completed.

Quantum Yields.—The quantum yields observed in the liquid phase experiments dropped rapidly during the first periods of illumination of a given reaction mixture. The quantum yield represented by the lowest point of curve G, Fig. 2, is 0.009. This is the lowest observed in any experiment. In the experiments shown in Fig. 2

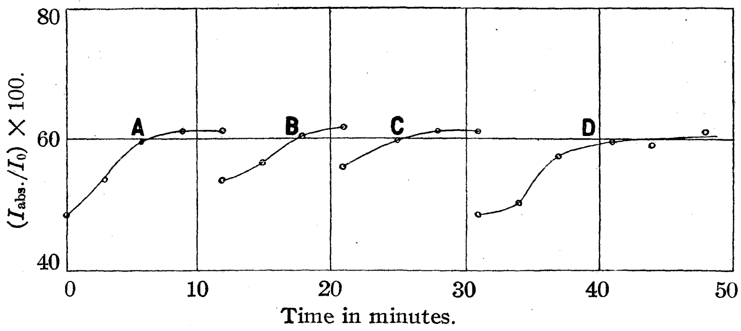

Fig. 4.—Influence of alternate periods of low temperature (dark), and high temperature and light on the concentration of bromine in gaseous mixtures, with tetrachloroethylene.

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(8) Herz and Rathmann, *Ber.*, **46**, 2588 (1913).

(9) Carrico and Dickinson, THIS JOURNAL, **57**, 1343 (1935).

the solution originally contained an excess of bromine which was removed by illumination before the transmission measurements were begun, with the result that a concentration of the reaction product had been built up. This fact accounts for the low values of the quantum yields and for the fact that the yield is decreasing only slowly with time as contrasted to its rapid rate of change when the concentration of product is smaller.

The quantum yields varied with the individual fillings of the cell and with the concentration of products. The highest quantum yield observed was 24 molecules of bromine disappearing for each quantum absorbed; the lowest was 0.009. Under the conditions of most of the experiments with the removal of oxygen but with the accumulation of some dibromotetrachloroethane, quantum yields from one to five were commonly obtained.

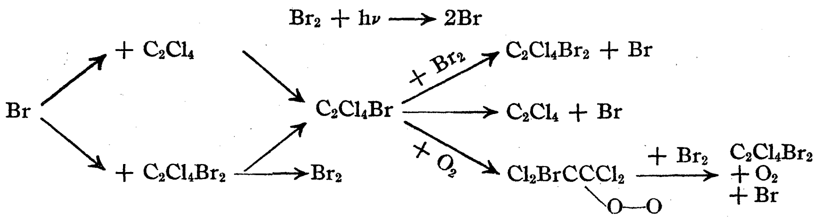
It is clear that both the straight addition of bromine to the double bond in tetrachloroethylene, and also the oxygen-accelerated reaction, involve chains. Large quantities of oxygen cause a different reaction to take place, in which the bromine is not consumed.

Mechanism

Carrico and Dickinson have established the fact that in the gas phase at temperatures between 100 and 135° the photobromination of tetrachloroethylene occurs only slightly if at all but that the bromine-sensitized photodecomposition of dibromotetrachloroethane occurs through reaction chains which may be as much as 45 molecules long. This fact may be correlated with the characteristics of the addition reaction in the liquid phase at room temperatures by a mechanism which postulates that a bromine atom may react with either tetrachloroethylene or dibromotetrachloroethane to form a mono-bromo free radical, C_2Cl_4Br. This radical may either undergo a unimolecular decomposition to form tetrachloroethylene and a bromine atom as suggested by Carrico and Dickinson, or it may react with a bromine molecule to form dibromotetrachloroethane and a bromine atom. The first possibility is a step in a dibromotetrachloroethane decomposition chain, the second is a step in a chain causing the addition of bromine to tetrachloroethylene. Decomposition predominates when the life of the radical is short; addition predominates when the life is long enough to give opportunity for radicals to undergo collision and reaction with a bromine molecule. The rate of decomposition of this free radical is assumed to have a high temperature coefficient, an assumption which is in agreement with the value of about 2 for the 10° temperature factor of the decomposition reaction which may be calculated from the data of Carrico and Dickinson. As a result only the decomposition reaction is observed at high temperatures while the addition reaction is the one experimentally apparent at low temperatures. This hypothesis is in accord with a test made since the publication of the results of Carrico and Dickinson, which shows that if a liquid reaction mixture that has been illuminated until it becomes nearly colorless at 25° is then illuminated at 65° a distinct bromine coloration reappears.

The accelerating effect of oxygen on the addition reaction may possibly be accounted for by the formation of a monobromoperoxy free radical which is capable of reacting with a bromine molecule but which is capable of existing longer without decomposition than is the mono-bromo free radical. The formation of peroxy free radicals by the reaction of oxygen with free radicals has been suggested by Haber and Willstätter,[10] and by Ziegler.[11] The latter author conceives these peroxy free radicals to be capable of giving off their oxygen and being regenerated as the original free radical which is then capable of taking on more oxygen.

The inhibition of the photobromination of tetrachloroethylene by large quantities of oxygen and the fact that small accelerating quantities of oxygen are gradually used up in the photochemical reaction may be well explained by the assumption that a bromine-sensitized photo-oxidation takes precedence over the addition of bromine, just as the chlorine-sensitized photo-oxidation takes pre-



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(10) Rice and Rice, "The Aliphatic Free Radicals," Johns Hopkins Press, Baltimore, Md., 1935, p. 173.

(11) Ziegler and Ewald, *Ann.*, **504**, 162 (1933).

cedence over the chlorination of tetrachloroethylene as shown by Dickinson and Leermakers.[5]

In a system containing bromine, tetrachloroethylene, dibromotetrachloroethane and oxygen the reactions indicated may occur according to the mechanisms already discussed.

All the reactions at the right are capable of continuing chains which can be stopped by the reaction

$$\mathrm{Br} + \mathrm{Br} + \text{third body} \longrightarrow \mathrm{Br_2}$$

The bromine-sensitized oxidation reaction may be represented by

$$\mathrm{Br^*} + \mathrm{O_2} \longrightarrow \mathrm{Br} + \mathrm{O_2^*}$$
$$\mathrm{O_2^*} + \mathrm{C_2Cl_4} \longrightarrow \text{oxidation products}$$

The asterisk which passes from the bromine atom (or molecule) to the oxygen is used to indicate the fact that the bromine has been made incapable of reacting with tetrachloroethylene while making the oxygen capable of doing so.

Other mechanisms may be developed for this reaction some of which involve the concept of transitory bromine oxide, or of a peroxide formed on the double bond. The one which has been presented seems, however, to be the most serviceable in accounting for the characteristics of both photobromination and bromine sensitized photochemical decomposition.

This hypothesis, that the life period of the free radical $\mathrm{C_2Cl_4Br}$ is the factor which determines the relative amount of decomposition and addition, suggests possibilities for explaining the facts of certain iodination and chlorination reactions.

The Photobromination of Chloroform

The photobromination of liquid chloroform was studied at room temperatures with light of wave length 2650 Å. from the large monochromator using reaction mixtures with concentrations of bromine sufficient to absorb 100% of the light. Bromine was introduced from weighed capillaries which could be sealed in the side-arm of a quartz reaction cell and broken by heating. The bromine consumed was determined by volumetric analysis after several hours of illumination; and quantum yields were calculated.

When it was desired to carry out experiments in the absence of oxygen the reaction cell was filled with chloroform; this was partially boiled away, and the cell was sealed while the boiling continued. In cases where this technique was used practically no bromination occurred during long periods of illumination. In other cases approximately known amounts of oxygen were obtained in the cell by first boiling the chloroform and then allowing a chloroform vapor and air or oxygen equilibrium to be attained in the cell at a temperature at which the vapor pressure of chloroform was known. The outlet from the cell to the air or to an oxygen tank led through a tube of phosphorus pentoxide.

When pressure of oxygen of about 30 mm. was present above the liquid reaction mixture in the cell, quantum yields of about 2 were obtained. When a pressure of 660 mm. of oxygen was present the yields dropped to negative values, indicating that halogen had been liberated by an oxidation of chloroform.

Tests to determine at what wave lengths the bromination would take place in the presence of air showed negative results at 3650 and 3130 Å. but bromine was used up at 2850 and 2650 Å.

Summary

1. It has been found that photobromination of tetrachloroethylene is inhibited by the product of the reaction, that the concentration of the tetrachloroethylene is not an important factor in the rate, and that the temperature effect is small.

2. Small amounts of oxygen accelerate the photobromination of tetrachloroethylene. When large amounts of oxygen are present, the rate of bromination approaches zero, probably on account of a competing bromine-sensitized photooxidation.

3. Mixtures of liquid chloroform and bromine do not react appreciably in the absence of oxygen when illuminated at 25° with light of 2650 Å. Reaction occurs in the presence of oxygen.

4. A mechanism postulating a bromo free radical is suggested to account for the characteristics of the photobromination of tetrachloroethylene and for the fact that the reaction is reversed at higher temperatures. It is assumed that the life period of this radical is dependent on temperature and that the radical is partially stabilized by oxygen.

5. An effective method for degassing liquid systems is described.

6. A magnetically-operated, sealed-in stirrer for use in photochemical work is described.

MADISON, WISCONSIN RECEIVED AUGUST 20, 1935

[CONTRIBUTION FROM THE GOESSMANN CHEMISTRY LABORATORY, MASSACHUSETTS STATE COLLEGE]

A Study of the Kinetics of the Permanganate–Oxalate Reaction. I. The Effect of Various Salts upon the Rate of Reaction[1]

BY R. W. FESSENDEN AND BRYAN C. REDMON

Since the classical work of Harcourt and Esson[2] the kinetics of the reaction between permanganate and oxalate ions in acid solution have been studied by several investigators.[3,4,5] The development of a sound theory of kinetic salt effect by Brönsted[6] offers another method of investigating the mechanism of this reaction. Launer[5a] has shown that a positive salt effect is found when the reaction occurs in the presence of relatively large concentrations of oxalate and of added manganous ion.

A mechanism for the reaction is presented here as a basis for discussion.

$$x\mathrm{MnO_4^-} + y\mathrm{Mn^{++}} + 8x\mathrm{H^+} \longrightarrow z\mathrm{Mn^{++++}} + [(x+y) - z]\mathrm{Mn^{+++}} + 4x\mathrm{H_2O} \quad (1)$$

(Sum of series of rapid reactions)

$$\mathrm{Mn^{++++}} + \mathrm{Mn^{++}} \rightleftarrows 2\mathrm{Mn^{+++}} \text{ (rapid, reversible)} \quad (2)$$

$$\mathrm{Mn^{+++}} + 3\mathrm{C_2O_4^{=}} \rightleftarrows \mathrm{Mn(C_2O_4)_3^{\equiv}} \text{ (rapid, reversible)} \quad (3)$$

$$\mathrm{Mn^{++}} + 2\mathrm{C_2O_4^{=}} \rightleftarrows \mathrm{Mn(C_2O_4)_2^{=}} \text{ (rapid, reversible)} \quad (4)$$

$$\mathrm{Mn^{++++}} + \mathrm{C_2O_4^{=}} \longrightarrow \mathrm{Mn^{+++}} + \mathrm{CO_2} + \mathrm{CO_2^-} \text{ (measurable)} \quad (5)$$

$$\mathrm{Mn^{++++}} + \mathrm{CO_2^-} \longrightarrow \mathrm{Mn^{+++}} + \mathrm{CO_2} \text{ (rapid)} \quad (6)$$

$$\mathrm{Mn^{+++}} + \mathrm{C_2O_4^{=}} \longrightarrow \mathrm{Mn^{++}} + \mathrm{CO_2} + \mathrm{CO_2^-} \text{ (measurable)} \quad (7)$$

$$\mathrm{Mn^{+++}} + \mathrm{CO_2^-} \longrightarrow \mathrm{Mn^{++}} + \mathrm{CO_2} \text{ (rapid, slower than (6))} \quad (8)$$

If the reduction of the permanganate ion to the intermediate valences occurs in a series of rapid bi-molecular reactions, as seems probable to the authors, both $\mathrm{Mn^{++++}}$ and $\mathrm{Mn^{+++}}$ ions are produced. Due to the existence of the equilibrium represented by equation (2), this point is not easily demonstrated and is not essential to the rest of the mechanism.

The formula of the manganic oxalate complex ion in equation (3) differs from that proposed by Launer.[5a] Evidence for the formula $\mathrm{Mn(C_2O_4)_3^{\equiv}}$ will be presented in another paper. The existence of the equilibrium represented in equation (4) is shown by the work of Scholder and Linström.[7]

Equations (5), (6), (7) and (8) are those proposed by Launer and Yost.[5b] The existence of reaction (7) is difficult to prove because of the existence of the equilibrium represented by equation (2) and reaction (5).

From an inspection of the mechanism it is evident that, if the rate-determining equation is either (5) or (7), the salt effect should be negative according to the Brönsted theory. Launer[5a] in his investigation of the salt effect used a relatively high concentration of the oxalate ion and added manganous ion. Under these conditions, the reactions from left to right in the equilibria represented by equations (2) and (3) are favored, and the rate of reaction becomes inversely proportional to the concentration of the manganic oxalate complex ion. The effect of added salts on this equilibrium would be to increase the dissociation of the manganic oxalate complex ion and so increase the rate of reaction. From these considerations the positive salt effect found by Launer is apparently not a kinetic salt effect, but a salt effect on the equilibrium represented by equation (3) or a secondary salt effect according to the Brönsted theory.

If the reaction is carried out in the presence of relatively low concentrations of oxalate and no added manganous ion, the reactions from left to right in equations (2) and (3) will be greatly decreased, and it might be expected that the true kinetic salt effect on equations (5) or (7) would not be hidden by the secondary salt effect on the equilibrium (3). The purpose of this investigation was to study the salt effect under these conditions.

Experimental Procedure.—The velocity of the reaction was measured iodimetrically by adding aliquots drawn from the reaction mixture to a solution containing excess potassium iodide and titrating the liberated iodine immediately with standard thiosulfate solution. According to Launer[5a] this method is not accurate unless care is taken to exclude oxygen from the reaction

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[1] The material in this paper is taken from a thesis submitted by Bryan C. Redmon to the Graduate School of the Massachusetts State College in partial fulfilment of the requirements for the degree of Doctor of Philosophy in April, 1934.

[2] Harcourt and Esson, *Phil. Trans.*, **156**, 193 (1866).

[3] Schilow, *Ber.*, **36**, 2735 (1903).

[4] Skrabal, *Z. anorg. Chem.*, **42**, 1 (1904).

[5] (a) Launer, THIS JOURNAL, **54**, 2597 (1932); (b) Launer and Yost, *ibid.*, **56**, 2571 (1934).

[6] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); **115**, 337 (1925).

[7] Scholder and Linström, *Ber.*, **63B**, 2831 (1930).

mixture. In determining the relative rates of reaction in solutions which are identical except for added electrolytes, such an error is not believed to be important.

The procedure used in making the rate measurements was as follows. The permanganate solution was placed in one flask and the remaining constituents of the reaction mixture in a second flask. The two flasks were placed in a thermostat and allowed to reach thermal equilibrium. The contents of the two flasks were poured together and then poured from one flask to the other to complete mixing as rapidly as possible. A stop watch was started simultaneously with the first mixing of the solutions. The reaction mixture, now contained in one flask, was replaced in the thermostat and aliquots withdrawn at suitable time intervals. The pipet used to remove the aliquots was a 5-ml. Mohr, with the tip cut off to ensure rapid delivery. The total time necessary for complete delivery of the sample was not more than three seconds. Calibration of the pipet showed an average deviation from the mean delivery of 1.2% in eight trials.

A good grade of C. P. chemicals was used without further purification, except for a sample of sodium oxalate from the Bureau of Standards which was used as the primary standard for the permanganate and oxalate solutions. All solutions were prepared and standardized by accepted quantitative methods.

All experiments were conducted at a temperature of 25.00 ± 0.05°.

Experimental Results.—The results of the investigation of the kinetic salt effect are given in Table I. The reaction mixture used in all experiments recorded in Table I was made up to be 0.01 molar with respect to sodium oxalate, 0.00241 molar with respect to potassium permanganate and 0.0965 molar with respect to sulfuric acid. The values of x, the loss in oxidizing value in time t, are given in milliliters of 0.005 M sodium thiosulfate solution. Values listed in columns 2, 3, 4, 5 and 6 are averaged from two or more determinations. Duplicate experiments agreed very closely.

The data contained in Table I are plotted in Fig. 1. A comparison of the curves for the rate in the absence of added salts, and for the rate in the presence of added sodium or potassium sulfate demonstrates the existence of a negative kinetic salt effect. The curve for the rate in the presence

TABLE I

THE EFFECT OF VARIOUS SALTS ON THE RATE OF THE PERMANGANATE–OXALATE REACTION

Time, min.	Value of x in milliliters of 0.005 M sodium thiosulfate									
	No added salt	0.125 M Na_2SO_4	0.111 M K_2SO_4	0.222 M K_2SO_4	0.258 M $MgSO_4$	0.155 M $CdSO_4$	0.259 M $CdSO_4$	0.050 M $ZnSO_4$	0.125 M $ZnSO_4$	0.125 M $Al_2(SO_4)_3$
1									0.10	0.31
2						0.06	0.06	0.20	.25	1.86
3	0.09				0.09			.45	.45	4.16
4		0.12	0.09	0.03		.34	.26	.65	.93	5.61[a]
6	.54			.08	.53	.91	1.11	1.28	2.69	
7						1.33	1.71	1.80	5.72	
8		.58	.52	.39		1.91	2.51	2.50	10.85	
9	1.80				1.33	2.31	3.26	3.65		
10	2.50				1.78	3.36	4.86	5.73		
11	3.35				2.24	4.68		10.05		
11.5						5.34	10.01			
12	4.49	1.75	1.54	.91	2.80					
13	6.01				3.54					
14	9.64	2.68	2.34		4.46					
14.5	10.59									
15		3.27		1.83	5.96					
16		3.95	3.46	2.28	8.36					
18		5.98	4.91	2.88						
19		8.33	6.19							
20		10.39	8.47	3.86						
20.5			9.87							
22				5.03						
23				6.23						
24				8.03						
25				10.03						

[a] Precipitate of MnO_2 appeared.

of magnesium sulfate also shows a negative effect, but the effect is less than might be expected from the concentration and valence type of this salt.

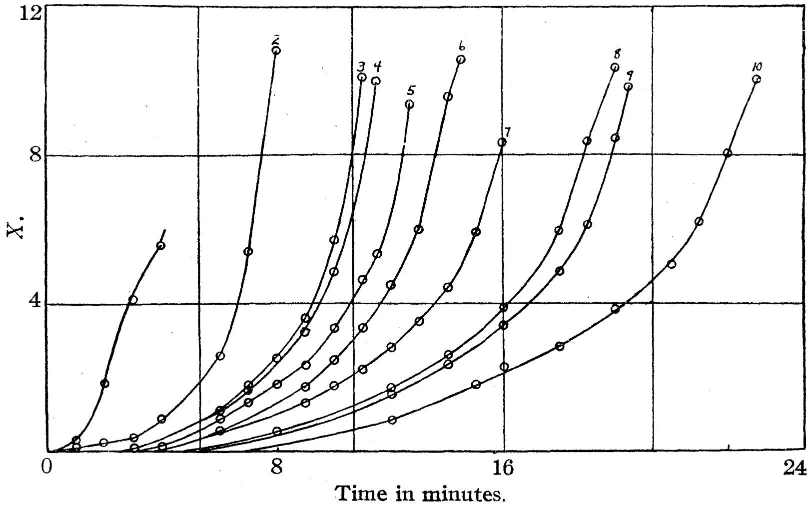

Fig. 1.—The effect of various salts on the rate of the permanganate–oxalate reaction: (1) 0.125 *M* $Al_2(SO_4)_3$; (2) 0.125 *M* $ZnSO_4$; (3) 0.05 *M* $ZnSO_4$; (4) 0.259 *M* $CdSO_4$; (5) 0.155 *M* $CdSO_4$; (6) no added salt; (7) 0.258 *M* $MgSO_4$; (8) 0.125 *M* Na_2SO_4; (9) 0.111 *M* K_2SO_4; (10) 0.222 *M* K_2SO_4

All of the remaining salts studied show a positive salt effect. The case of the aluminum ion is peculiar in that the initial rate is very rapid, but after about one-half the oxidizing value has disappeared, a precipitate of manganese dioxide forms and the reaction becomes heterogeneous.

These apparently contradictory results may be explained by the kinetics of the reaction and the chemistry of the cations of the added salts. The velocity of the reaction is inversely proportional to the concentration of the oxalate under the conditions of these experiments as is shown by the data in Table II. The data in this table are the results of experiments in which the concentration of the sodium oxalate was varied as indicated, while the concentrations of the other reactants were the same as in the experiments given in Table I. Considering the portions of the curves shown in Fig. 2, for the induction period,[4] where the rate is rapid and the greater part of the reaction takes place, it is evident that the velocity of the reaction is inversely proportional to the concentration of sodium oxalate from 0.00753 molar to 0.0301 molar. From 0.0301 molar to 0.301 molar, the rate increases with the concentration of the oxalate. The concentration of oxalate used in the experi-

Table II

The Effect of the Variation of the Concentration of Sodium Oxalate upon the Rate of Reaction

Time, min.	Value of *x* in milliliters of 0.002 *M* sodium thiosulfate					
	0.00753 *M*	0.01506 *M*	0.0301 *M*	0.0753 *M*	0.1506 *M*	0.301 *M*
1				0.13	0.25	
2	0.05	0.15	0.23	.53	.41	
3				.75	.48	0.25
4	.63			1.43	.75	
5		.58	0.73	2.73	1.71	
6	1.31					.87
7				8.83	19.75	
8	3.08	2.08	2.31			
9				17.73	22.28	3.35
10	6.33					7.77
10.5				21.98		14.10
11	8.75	4.93				21.50
12	12.61		5.85		22.28	22.05
12.5				22.98		
13	26.53	8.03				22.05
14	27.71		9.01			
15					22.58	
15.5		13.73				
16			12.63			
17		18.23				
18		22.35	16.65			
20		26.58	20.59			
23			24.47			

ments on salt effect, 0.010 molar, falls in the range where the rate varies inversely with the oxalate concentration.

The cations of the salts showing a positive salt effect are known to form oxalate complexes. In the case of the zinc ion, two complex ions, $Zn(C_2O_4)_3^{\equiv}$ and $Zn(C_2O_4)_2^{=}$ depending on the concentration of the oxalate ion, are reported.[8] Kohlschütter[9] postulates the existence of cadmium oxalate complexes, notably the $Cd(C_2O_4)_2^{=}$ ion. Peters,[10] working on the quantitative separation of cadmium from copper, found that copper oxalate was much less soluble than cadmium oxalate in acid solution, which may indicate the formation of a cadmium acid oxalate complexion. Salts containing stable alumino-oxalate anions of the types $Al(C_2O_4)_3^{\equiv}$ and $(Al(C_2O_4)_2(H_2O)_2)^-$ have been prepared by Burrows and Lauder.[11]

The apparent positive kinetic salt effect may thus be explained as due to the decrease in the concentration of the oxalate ion resulting from the formation of oxalate complexes. The fact that the effect of the magnesium ion is less than expected may be explained in a similar manner as magnesium oxalate is known to be weakly dissociated.[12]

The reversal of the effect of oxalate ions on the rate, as demonstrated by the data in Table II and Fig. 2, seems to be due to reaction (4). The removal of the manganous ion to form the manganous oxalate complex ion should decrease the rate in the incubation period. In accord with this reasoning the rate during this part of the reaction for concentrations of oxalate greater than 0.0301 *M* decreases with increasing oxalate ion concentration as is shown in Fig. 2.

Furthermore, the decrease in the concentration of manganous ion by reaction (4) decreases the reaction from left to right in equation (2) and consequently decreases the effect of the reaction from left to right in equation (3). Therefore, the rate during the induction period varies directly with the oxalate ion concentration in accordance with the mass effect.

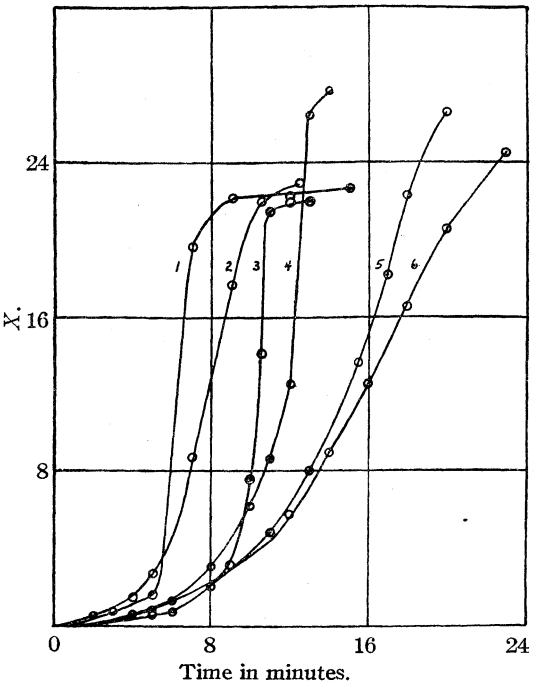

Fig. 2.—The effect of the variation of the concentration of sodium oxalate upon the rate of reaction: (1) 0.1506 *M* $Na_2C_2O_4$; (2) 0.0753 *M;* (3) 0.301 *M;* (4) 0.00753 *M;* (5) 0.01506 *M;* (6) 0.0301 *M.*

The reason that the equilibrium (4) does not seem to be important in the lower concentrations of oxalate is believed to be due to the instability of the $Mn(C_2O_4)_2^{=}$ ion in these low concentrations.

Summary

A negative kinetic salt effect has been found in the case of the permanganate–oxalate reaction.

The effect of oxalate upon the rate of reaction varies with its concentration.

An explanation is offered for the apparent positive salt effect found with certain cations which form oxalate complexes.

AMHERST, MASS. RECEIVED JULY 11, 1935

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[8] Gmelin-Kraut, "Handbuch der anorganischen Chemie," Band IV, Abteilung 1, Winters, Heidelberg, 1911, p. 684, sec. C.

[9] Kohlschütter, *Ber.*, **35**, 483 (1902).

[10] Peters, *Am. J. Sci.*, **10**, 359 (1900).

[11] Burrows and Lauder, THIS JOURNAL, **53**, 3600 (1931).

[12] Noyes and Falk, *ibid.*, **34**, 454 (1912).

[Contribution from the School of Chemistry of the University of Minnesota]

Equilibrium Studies on the Exchange Reaction between Acetylene and Heavy Water[1]

By L. H. Reyerson and Bruce Gillespie

As a result of the discovery in this Laboratory that an isotopic exchange occurs between acetylene and alkaline solutions of heavy water, it was decided to study the equilibria involved. The reaction takes place due to the ionization of the acetylene, but the determination of the change in the density of the heavy water makes it possible to calculate K_X. The results here reported give the values obtained at 0, 25 and 100° using water containing 9.77 and 18.97% deuterium oxide.

Experimental Procedure

A calibrated liter bulb was attached to the high vacuum line shown in Fig. 1, and then thoroughly evacuated and flamed. Dry carbon dioxide-free air was admitted to the bulb before and after flaming. Opening A was stoppered during evacuation but a slow stream of this same air was passed in through A during the cooling of the bulb. About 1 g. of N alkaline solution of known percentage of D_2O was then introduced from a pycnometer through A and A immediately sealed off in such a way that no water from the flame could condense inside the bulb. Part C of the bulb was then immersed in liquid air for from twenty to thirty minutes, after which the bulb was carefully evacuated. Tests made at this point showed no dissolved air. The bulb was now placed in an ice-bath and carefully purified acetylene run in through B from storage bulb Q to the desired pressure. This acetylene was prepared by the action of carefully purified water vapor on the purest of calcium carbide. The gas was further purified by the method recommended for acetylene. After pressure equilibrium had been established the pressure was read, B closed and the contents frozen out at C with liquid air. The bulb was sealed off at D, placed in a thermostat at the desired temperature and occasionally removed and rotated to redistribute the solution over the walls. At the close of the reaction E was sealed to the vacuum line and the system exhausted. The contents of the bulb were frozen out with liquid air and the capillary F broken. The liquid air bath was then transferred to H and about half of the acetylene was distilled over to H. At this point a salt–ice bath of −20° was placed about C and the remaining acetylene distilled. At this point the manometer reading was found to be approximately zero. About a liter of dry carbon dioxide was then condensed in J by a bath of liquid air and all of the non-condensable gases pumped from the system. The carbon dioxide was allowed to warm up and expand into the reaction bulb to a pressure of about 1 atmosphere, when B was closed. The carbon dioxide remained in the bulb for several hours during which time C was warmed to 70–80° occasionally. This treatment converted the sodium hydroxide to sodium carbonate, restoring the combined water.

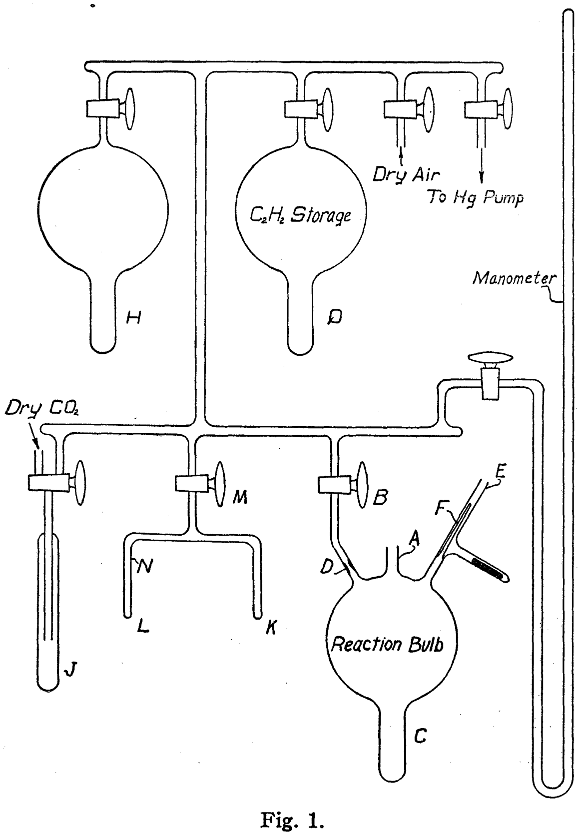

Fig. 1.

The carbon dioxide was removed in the same manner as the acetylene. With K immersed in liquid air the water was then carefully distilled into K from C. K was warmed until the water had melted. With K held at 0° M was cautiously opened to a pressure of about 1 cm. to remove any dissolved carbon dioxide. The pressure external to M was lowered slowly until the water at 0° just started to boil when M was closed, and the water distilled from K to L. Dry carbon dioxide free air was admitted at atmospheric pressure to K and L and L then removed from the system at N and thermostated to constant temperature. The density of the water was determined in a pycnometer of 0.55 cc. capacity. With care the loss of water in the whole operation was of the order of magnitude of 0.1 to 0.15 cc. Finally the reaction bulb was removed, opened at A and D, and the contents washed out with from 8 to 10 small portions of hot freshly distilled water. The washings were combined and titrated with 0.1 N hydrochloric acid using methyl orange as indicator. This gave the amount of alkali used in the original solution.

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(1) This investigation was made possible by grants from the National Research Council and the Graduate School of the University of Minnesota.

EXPERIMENTAL RESULTS

Temp., °C.	Time in hours	Initial concn. of D_2O, %	Corr. press. of acetylene, mm.	Moles at equilibrium				K_X
				C_2H_2	HDO	C_2HD	H_2O	
0	264	9.77	614.05	0.036	0.00667	0.00202	0.0424	0.35
0	288	9.77	361.31	.0212	.00725	.00143	.0417	.38
25	143	9.77	483.6	.0276	.00671	.00184	.0415	.41
25	216	9.77	221.1	.0122	.00753	.00115	.0414	.51
25	113	18.97	733.52	.0398	.01147	.00547	.0378	.45
25	118	18.97	417.38	.0224	.0131	.00369	.0354	.44
100	113	9.77	267.7	.0153	.00736	.00128	.0414	.47
100	168	9.77	562.63	.0323	.0061	.00253	.0433	.55

Results

From the change in density of the water during a given run the amount of deuterium that had reacted with the acetylene could be determined. Table I gives the results of several experiments at the temperatures indicated. The moles of initial and final products of the principal reaction are given and K_X values are calculated for the reaction $C_2H_2 + HDO \rightleftharpoons C_2HD + H_2O$. While there are four possible reactions between solutions of deuterium oxide and acetylene, the concentrations of deuterium oxide justified the calculation for the above reaction alone. Practically all of the deuterium was in the form of HDO at these concentrations. Furthermore, mass spectral analysis of the acetylene at equilibrium showed only a trace of C_2D_2 while the amount of C_2HD present agreed well with the value calculated from the density change. The authors do not attach much significance to the second figure of the K_X values. The averages of the K_X values at the three temperatures are as follows: at 0° K_X is 0.365, at 25° K_X is 0.45 and at 100° K_X is 0.51.

In connection with this investigation, it should be noted that R. P. Bell,[2] as a result of experiments performed at Oxford, questioned the exchange reaction which we had previously reported.[3] In addition to the evidence for this exchange reported in the above equilibrium studies, we have obtained positive proof of the existence of the molecule C_2HD in the equilibrium gas. This was obtained by mass spectroscopic investigation and the amount found compared favorably with the amount determined from the equilibrium study. Furthermore, Glockler and Morrell[4] obtained lines in the Raman spectra for the molecule C_2HD in a sample of gas taken from one of our equilibrium reactions. We feel therefore that the above equilibrium studies represent real equilibrium values within the limit of error of our experimental technique.

The authors wish to acknowledge the valuable suggestions of R. S. Livingston and the assistance of S. T. Yuster which aided greatly in the investigation. Further studies are being carried on at higher deuterium concentrations.

Summary

1. Equilibrium studies have been carried out at 0, 25 and 100° between acetylene and solutions of heavy water.

2. Average values of K_X for the reaction $C_2H_2 + HDO = C_2HD + H_2O$ were found to be 0.365 at 0°, 0.45 at 25° and 0.51 at 100°.

MINNEAPOLIS, MINN. RECEIVED AUGUST 5, 1935

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[2] Bell, THIS JOURNAL, **57**, 778 (1935).

[3] Reyerson, *ibid.*, **56**, 1426 (1934).

[4] Glockler and Morrell, to be published in the *Journal of Chemical Physics.*

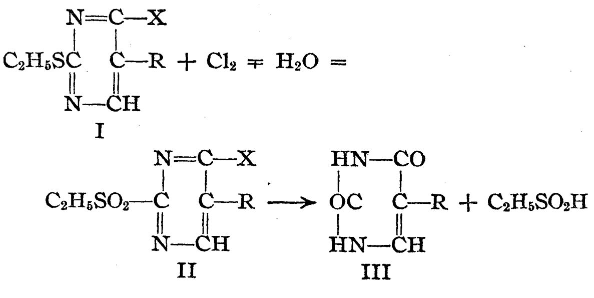
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Researches on Pyrimidines. CXLVIII. Action of Chlorine on Mercaptopyrimidines

BY JAMES M. SPRAGUE[1] AND TREAT B. JOHNSON

Although considerable work has been done on the application of mercaptopyrimidines to synthesis in the pyrimidine series,[2] no extensive investigation has been made of reactions in this heterocyclic series involving changes in the mercapto group. The chief reactions, in which the mercapto grouping functions, have been its replacement by a hydroxyl group by hydrolysis, and by its substitution with an amino radical by interaction with various amines.[2] Recent developments in the field of "vitamin chemistry" have induced the authors to undertake an exhaustive study of characteristic reactions of the mercapto grouping in different heterocyclic combinations. Because of the postulated existence of a pyrimidine nucleus in the sulfur containing vitamin B_1,[3] a better knowledge of the chemistry of different types of mercapto- and thiopyrimidines becomes very important. A study has been made, therefore, of the behavior of several mercaptopyrimidines toward such reagents as alkalies, sodium alkoxides, nitric acid and chlorine. In this paper the authors will discuss fundamental changes resulting from the action of chlorine upon some ethylmercaptopyrimidines.

When a 2-ethylmercaptopyrimidine (I) is suspended in water and treated with chlorine gas at a low temperature, a pyrimidine sulfone compound is formed (II).

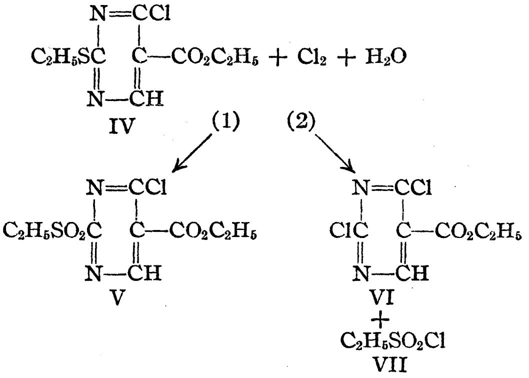


I

II

III

This reaction was applied with success to a series of 2-ethylmercapto-4-ethoxy- (I, X = OC_2H_5), and 2-ethylmercapto-4-chloropyrimidines (I, X = Cl) where R was hydrogen, methyl and bromine. With a slight modification of experimental conditions we also succeeded in synthesizing the 2-ethyl sulfone derivative of 2-ethylmercapto-4-amino-5-carbethoxypyrimidine (I, X = NH_2, R = $CO_2C_2H_5$). The results of our experiments are recorded in Table II. When 2-ethylmercapto-4-chloro-5-carbethoxypyrimidine (IV) is treated with chlorine according to the above technique the pyrimidine VI and ethylsulfonyl chloride (VII) together with the corresponding pyrimidine sulfone (V), were obtained.



IV

V

VI

VII

The relative amounts of the products of these two reactions depended largely upon the temperature. When the treatment with chlorine gas was carried out below 5°, a 60% yield of the sulfone (V) was obtained. Nevertheless, at this temperature, a 15–20% yield of the product of the second reaction was also obtained. When the chlorination was conducted at a higher temperature, 30–40°, reaction 2 predominated and 2,4-dichloro-5-carbethoxypyrimidine (V) (69–75%), and ethylsulfonyl chloride (VII) (47–75%) were obtained. Under these conditions the yield of the sulfone (V) was reduced to 7%.

That the sulfone (V) is not an intermediate in the formation of compounds (VI) and (VII) through a cleavage by chlorine is shown by its inertness toward chlorine in either water or benzene. This behavior is analogous to that observed in the case of diethyl-sulfone, which remained unaffected while the corresponding diethyl sulfoxide was readily cleaved by chlorine to ethylsulfonyl chloride and ethyl chloride.[4] This suggests that the pyrimidine sulfoxide derivative of the original mercaptopyrimidine is an inter-

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[1] Sterling Professorship of Chemistry Research Assistant in Organic Chemistry, 1934–35.

[2] Johnson and Hahn, *Chem. Rev.*, **13**, 193 (1933).

[3] Windaus, *Z. physiol. Chem.*, **228**, 27 (1934); Williams, Buchman and Ruehle, THIS JOURNAL, **57**, 1093 (1935).

[4] Spring and Winssinger, *Ber.*, **15**, 447 (1882).

mediate in both reactions 1 and 2.[5] Conditions have not yet been found which will yield pyrimidine sulfones from 2-ethylmercapto-4-oxypyrimidine (I, X = OH) by the action of chlorine.

That an ethylmercapto group occupying the 4-position of the pyrimidine nucleus may also be converted into a sulfone was shown with 2,4-diethylmercaptopyrimidine (I, $X = SC_2H_5$, R = H). This compound, on treatment with chlorine, gave smoothly the disulfone, 2,4-diethylsulfonylpyrimidine (II, $X = SO_2C_2H_5$, R = H). Although 2,4-diethylmercapto-5-methylpyrimidine (I, $X = SC_2H_5$, $R = CH_3$) gave a product insoluble in petroleum ether, it could not be crystallized or distilled. Similar results were obtained with 2-ethylmercapto-4-ethoxy-5-carbethoxypyrimidine.

To establish definitely the point of attack of the chlorine, as well as to establish the structure, our sulfones were subjected to hydrolysis. On refluxing with 20% hydrochloric acid, there were obtained, beside the corresponding dioxypyrimidine, sulfur dioxide and a small amount of ethylsulfonic acid.

Ethylsulfonic acid was found to be stable under the conditions of hydrolysis; this fact, coupled with the production of a 2,4-dioxypyrimidine (III) rather than a monoxypyrimidine, suggests that the immediate product of the hydrolysis was probably ethylsulfinic acid. Although most of this acid decomposed to sulfur dioxide a small amount underwent oxidation to ethylsulfonic acid during the working-up process.

Experimental Part

2 - Ethylmercapto - 4 - chloropyrimidines.—These compounds, 2-ethylmercapto-4-chloropyrimidine,[6] 2-ethylmercapto-4-chloro-5-methyl pyrimidine,[6] 2-ethylmercapto-4-chloro-5-bromopyrimidine,[6] and 2-ethylmercapto-4-chloro-5-carbethoxypyrimidine[7] have all been previously prepared in this Laboratory, but largely by the use of phosphorus pentachloride. For this investigation they were all prepared in the usual manner[8] from the corresponding 4-oxypyrimidine by action of phosphorus oxychloride.

2-Ethylmercapto-4-ethoxypyrimidines.—An alcohol solution of the 2-ethylmercapto-4-chloropyrimidine was added slowly to a well-cooled solution of sodium (10–20% excess) in dry ethanol. The reaction mixture was allowed to stand at room temperature for three or four hours and the reaction completed by heating on a steam-bath for ten minutes. The alcohol was then removed under diminished pressure. Water was added to the residue and the reaction product of 2-ethylmercapto-4-ethoxypyrimidine extracted with ether. After drying over calcium chloride, the ether extract was distilled. The results of the experiment are collected in Table I. 2-Ethylmercaptopyrimidine had been prepared previously by a different procedure.[9]

In the preparation of 2-ethylmercapto-4-ethoxy-5-carbethoxypyrimidine (I, $X = OC_2H_5$, $R = CO_2C_2H_5$) it was necessary to modify the above procedure since in alcohol solution there was a loss of ethylmercaptan. The corresponding 4-chloropyrimidine in boiling benzene was treated with an equivalent amount of sodium ethoxide prepared in benzene from powdered sodium and the calculated amount of dry ethanol. The rate of addition of the sodium ethoxide was adjusted so that the reaction mixture was never alkaline to moist litmus. After heating for an additional fifteen minutes, the reaction was worked up as described below for the diethylmercaptopyrimidines.

2,4-Diethylmercaptopyrimidine.—A solution of 2,4-dichloropyrimidine[10] in toluene was added to a suspension of sodium ethylmercaptide (10% excess) which had been prepared in toluene from powdered sodium and ethyl mercaptan. After heating on a steam-bath for four hours, water was added and the toluene layer was dried and distilled. 2,4-Diethylmercapto-5-methylpyrimidine was prepared by the same procedure from 2-ethylmercapto-4-chloro-5-methylpyrimidine and sodium ethylmercaptide (Table I).

Ethylsulfonylpyrimidines. General Procedure.—The liquid 2-ethylmercaptopyrimidine (1–5 cc.) was suspended in water (20–75 cc.) and chlorine gas vigorously passed into the mixture which was well cooled in ice. Heat was evolved but the temperature did not rise above 20°. Most of the mercaptopyrimidine went into solution which immediately became turbid and a heavy oil precipitated. This gradually solidified and the treatment with chlorine was continued until the reaction mixture had a distinct green color of excess chlorine. The solid sulfone was filtered off, and, after drying over phosphorus pentoxide, recrystallized from a mixture of benzene and petroleum ether. These sulfones were readily soluble in the common organic solvents except petroleum ether in which they were practically insoluble. The purified sulfones may be kept over phosphorus pentoxide for several months without decomposition. However, in moist air they decompose rapidly.

Occasionally difficulty was experienced in obtaining the sulfones as solids on the first preparation. Usually this was due to incomplete chlorination or insufficient cooling during the reaction. However, the solid sulfone was obtained when an ether extract, which had been washed with sodium thiosulfate and dried over calcium chloride, was evaporated. If the residue from the ether extract did not solidify, it was triturated with petroleum ether. Subsequent preparations of the sulfone were obtained as solids directly from the reaction by seeding with a solid sulfone.

2-Ethylsulfonyl-4-ethoxypyrimidine (II, $X = OC_2H_5$, R = H) was a liquid which, when pure, distilled without decomposition.

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[5] The mechanism of these transformations is being investigated and the results will be discussed in a future paper.

[6] Wheeler and Johnson, *Am. Chem. J.*, **31**, 596 (1904).

[7] Johnson and Chi, THIS JOURNAL, **52**, 1580 (1930).

[8] Wheeler and Johns, *Am. Chem. J.*, **38**, 597 (1907).

[9] Wheeler and Johnson, *ibid.*, **31**, 597 (1904).

[10] Hilbert and Johnson, THIS JOURNAL, **52**, 1152 (1930).

TABLE I

MERCAPTO-PYRIMIDINES

2-Mercapto-pyrimidines	B. p., °C.	Mm.	n_D/°C.	Yield, %	Formula	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
4-Ethoxy-5-carbethoxy-	175	8	1.5420 (24.5°)	90	$C_{11}H_{16}O_3N_2S$	10.93	10.86	12.51	12.49
4-Ethoxy-	123–124	11	1.5405 (24.5°)	88	$C_8H_{12}ON_2S$	15.20	15.14	17.41	17.52
4-Ethoxy-5-methyl-	135–136	12	1.5365 (24°)	90	$C_9H_{14}ON_2S$	14.13	14.00	16.17	16.23
4-Ethoxy-5-bromo-[a]	140	6	1.5787 (22.5°)	82	$C_8H_{11}ON_2SBr$	10.64	10.62	12.19	12.02
4-Ethylmercapto-	135–137	6	1.5974 (24°)	92	$C_8H_{12}N_2S_2$	13.98	14.05	32.02	32.14
4-Ethylmercapto-5-methyl-	158–161	11	1.5900 (23°)	80	$C_9H_{14}N_2S$	13.07	13.12	29.93	29.98

[a] Analysis for bromine (Br), calcd., 30.38; found, Br, 30.71.

TABLE II

PYRIMIDINE SULFONES

2-Ethylsulfonyl-pyrimidines	M. p., °C.	Yield, %	Formula	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found	Halogen, % Calcd.	Halogen, % Found
4-Ethoxy-5-methyl-[a]	67–68	80	$C_9H_{14}O_3N_2S$	12.16	12.12	13.94	14.13	...	...
4-Chloro-5-methyl-	67.5–68	80	$C_7H_9O_2N_2SCl$	12.70	12.74	14.54	14.71	16.08	16.24
4-Ethoxy-5-bromo-	89.5–90.5	77	$C_8H_{11}O_3N_2SBr$	9.48	9.43	10.86	11.10	27.08	26.68
4-Chloro-5-bromo-	81–82	97	$C_6H_6O_2N_2SClBr$	9.81	9.78	11.25	11.57	[b]	
4-Ethoxy-	Liquid[c]	50	$C_8H_{12}O_3N_2S$	12.95	12.96	14.83	15.15	...	...
4-Chloro-	57–58	84	$C_6H_7O_2N_2SCl$	13.56	13.58	15.53	15.76	17.18	17.48
4-Chloro-5-carbethoxy-	72.5–73.5	60	$C_9H_{11}O_4N_2SCl$	10.05	9.98	11.58	11.70	12.71	12.36
4-Ethylsulfonyl-	87–88	63	$C_8H_{12}O_4N_2S_2$	10.60	10.62	24.27	24.35	...	...
4-Amino-5-carbethoxy-	143.5–144.5	93	$C_9H_{13}O_4N_3S$	16.20	16.23	12.37	12.59	...	...

[a] Calcd.: C, 46.92; H, 6.27. Found: C, 47.08; H, 6.18. [b] 0.2424 and 0.2106 g. gave 0.2850 and 0.2455 g. of silver halide, respectively; calcd., 0.2818 and 0.2443 g. [c] B. p. 183–185° (4 mm.), n^{25}_D 1.5225.

2-Ethylsulfonyl-4-chloro-5-carbethoxypyrimidine.—To obtain this sulfone (II, X = Cl, R = $CO_2C_2H_5$) in practical yields it was necessary to carry out the chlorination in an ice–salt bath (−10°). The temperature of the reaction was not allowed to rise above 5°. Even at this temperature 15–20% of the cleavage product (reaction 2) was obtained by extracting the reaction mixture with petroleum ether (see below). This sulfone is very unstable and decomposes rapidly even over phosphorus pentoxide, giving a product insoluble in benzene.

The cleavage reaction of 2-ethylmercapto-4-chloro-5-carbethoxypyrimidine was carried out as follows. Five cubic centimeters (6.3 g.) of 2-ethylmercapto-4-chloro-5-carbethoxypyrimidine was suspended in 60 cc. of warm water (30–40°) and chlorine rapidly passed into the mixture. The temperature was kept within the above limits by cooling in water. When the oil had separated completely, the mixture was shaken with petroleum ether and the sulfone derivative which separated as a solid at the water–petroleum ether interface was removed by filtration (0.5 g., 7%). After washing with dilute sodium thiosulfate and drying over calcium chloride the petroleum ether extract was fractionated with the following results: fraction 1, b. p. 68–74° (18 mm.) 1.5–2.5 g. (47–75%); fraction 2, b. p. 118–120° (4 mm.) 3.9–4.2 g. (69–75%).

Fraction 1.—This was redistilled, b. p. 67–68° (17 mm.), $n^{21.50}_D$ 1.4520 and identified as ethylsulfonyl chloride (VII) by formation of ethylsulfonamide[11] (m. p. 59–60°), ammonium ethylsulfonate[12] (m. p. 208–209°), and aniline hydrochloride.

Fraction 2.—This solidified on cooling and was recrystallized from ether, m. p. 36–37°, and was identified as 2,4-dichloro-5-carbethoxypyrimidine (VI) by analysis and hydrolysis with hydrochloric acid to uracil-5-carboxylic acid.[13]

Anal. Calcd. for $C_7H_6O_2N_2Cl$: N, 12.67; Cl, 32.09. Found: N, 12.63; Cl, 31.88.

2-Ethylsulfonyl-4-amino-5-carbethoxypyrimidine (II, X = NH_2; R = $CO_2C_2H_5$).—Five grams of 2-ethylmercapto-4-amino-5-carbethoxypyrimidine (m. p. 102°) was suspended in 60 cc. of water and concentrated hydrochloric acid (8 cc.) added. A small amount of solid remained undissolved but went into solution when treated with chlorine. The chlorination was carried out in an ice-bath. The yield was 5.3 g.

Hydrolysis of Pyrimidine Sulfones.—The sulfones (1–2 g.) were refluxed with 20% hydrochloric acid and the evolved gases swept into solutions of potassium permanganate, bromine water, or iodine–potassium iodide solution. The test solutions were decolorized and gave tests for sulfate. The acid solution was then evaporated to dryness on a steam-bath. The residue was triturated with alcohol and the filtered solid identified as a dioxypyrimidine by analysis and by comparison with authentic

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[11] James, *J. prakt. Chem.*, [2] **26**, 384 (1882).

[12] This was compared with the ammonium ethylsulfonate prepared from ethylsulfonic acid, m. p. 208–209° from alcohol–ethyl acetate mixture. N, calcd., 11.04; found, 11.10.

[13] Wheeler, Johnson and Johns, *Am. Chem. J.*, **37**, 392 (1907).

preparations. The alcohol filtrate was evaporated and the residue was freed of solid by triturating with alcohol or water, filtering and evaporating to dryness. This was repeated several times and the residual sirup treated with concentrated ammonium hydroxide. The solid obtained on evaporation was then recrystallized from an alcohol-ethyl acetate mixture and identified as the ammonium salt[12] of ethylsulfonic acid.

The sulfone (2 g.), 2-ethylsulfonyl-4-ethoxy-5-methylpyrimidine (II, X = OC_2H_5, R = CH_3), on refluxing for several hours with 2.5% sodium hydroxide in 90% alcohol gave 2,4-diethoxy-5-methylpyrimidine.[14] The diethoxypyrimidine (0.9 g.) was extracted with petroleum ether after removal of the alcohol under diminished pressure.

Summary

The action of chlorine gas on ethylmercaptopyrimidines has led to the preparation of nine ethylsulfones in the pyrimidine series.

It has been shown that this method is applicable to ethoxy-, chloro-, amino- and carbethoxy-ethylmercaptopyrimidines.

On acid hydrolysis the pyrimidine sulfones yield the corresponding oxypyrimidines.

New Haven, Conn. Received September 5, 1935

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[14] Johnson and Schmidt-Nickels, This Journal, **52**, 4514 (1930).

[Contribution No. 161 from the Experimental Station of E. I. du Pont de Nemours & Company, Inc.]

Acetylene Polymers and their Derivatives. XXIII. The Preparation and Polymerization of Oxyprenes

By Harry B. Dykstra

Recent studies[1] have revealed that of the various derivatives of butadiene-1,3 which are known, those having a single substituent in the 2-position have outstanding properties from the standpoint of rubber synthesis. The term orthoprene has been suggested for compounds of this type.[2] Only a few orthoprenes are known. Prior to the discovery of the haloprenes, chloro-2-butadiene-1,3[3] and bromo-2-butadiene-1,3,[4] isoprene and ethylbutadiene were the only members of this class which had been described. To this list have recently been added the butyl, *t*-butyl, hexyl, phenyl and benzyl butadienes,[5] and the formoxy, acetoxy, chloroacetoxy and butyroxy butadienes.[6]

The interesting properties of the orthoprenes, particularly those containing a negative substituent, have prompted the preparation and examination of other members of this class. The present paper is concerned with orthoprenes in which the substituent is an ether group. The designation "oxyprene" is suggested for these compounds. They are obtained by the series of reactions illustrated below for ethoxyprene (V).

$$\underset{\text{I}}{CH_2{=}CHC{\equiv}CH} + H_2O \longrightarrow \underset{\text{II}}{CH_2{=}CHCOCH_3}$$

$$\text{II} + C_2H_5OH \longrightarrow \underset{\text{III}}{C_2H_5OCH_2CH_2COCH_3}$$

$$\text{III} + HC(OC_2H_5)_3 \longrightarrow \underset{\text{IV}}{C_2H_5OCH_2CH_2C(OC_2H_5)_2CH_3} + HCOOC_2H_5$$

$$\text{IV} \longrightarrow \underset{\text{V}}{CH_2{=}CHC(OC_2H_5){=}CH_2} + 2C_2H_5OH$$

The hydration of vinylacetylene to methyl vinyl ketone[7] and the addition of alcohols to methyl vinyl ketone[8] are recorded elsewhere and will not be described in detail. The conversion of the ether ketones (III) into the ether ketals (IV) by means of orthoformic esters takes place almost quantitatively at room temperature in the presence of alcohol and hydrogen chloride. Physical and analytical data for the ether ketals are given in Table IA.

At sufficiently high temperatures, generally above 130°, the decomposition of the ketal (IV) to the oxyprene (V) is fairly complete, but at lower temperatures intermediate compounds involving the elimination of only one molecule of alcohol are formed. These are the unsaturated ketals (VI) formed when acidic catalysts are used, and the unsaturated ethers (VII) formed with basic catalysts. By further heating, these compounds, particularly VI, are in turn converted to the oxyprenes. Physical and analytical data for the intermediates VI and VII are given in

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[1] Whitby and Gallay, *Can. J. Research*, **6**, 280 (1932); Carothers, *Ind. Eng. Chem.*, **26**, 30 (1934).

[2] Carothers and Berchet, This Journal, **55**, 2813 (1933).

[3] Carothers, Williams, Collins and Kirby, *ibid.*, **53**, 4203 (1931).

[4] Carothers, Collins and Kirby, *ibid.*, **55**, 786 (1933).

[5] Carothers and Berchet, *ibid.*, **55**, 2813 (1933); Backer and Strating, *Rec. trav. chim.*, **53**, 524 (1934).

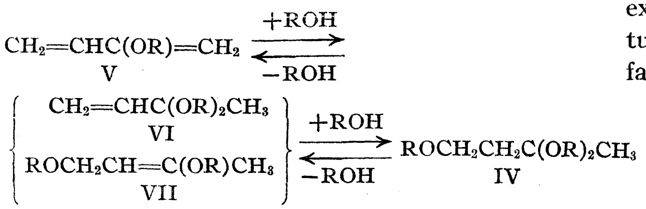
[6] Werntz, This Journal, **57**, 204 (1935).

[7] Nieuwland, Calcott, Downing and Carter, *ibid.*, **53**, 4197 (1931); Carter, U. S. Patent 1,896,161 (1933); Conaway, U. S. Patent 1,967,225 (1934).

[8] Rothrock, U. S. Patent 2,010,828 (1935).

Table IB and IC. Similar data for the oxyprenes are recorded in Table ID.

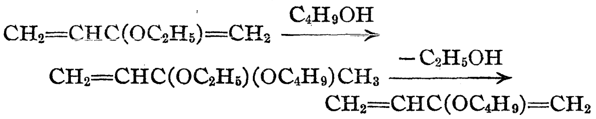
Below the dissociation temperatures any of the compounds V, VI and VII will reunite with alcohols yielding the ketals (IV). The reaction therefore is reversible as illustrated in the equations



$$\underset{\text{V}}{CH_2{=}CHC(OR){=}CH_2}\ \underset{-ROH}{\overset{+ROH}{\rightleftarrows}}$$
$$\left\{\begin{array}{c} CH_2{=}CHC(OR)_2CH_3 \\ \text{VI} \\ ROCH_2CH{=}C(OR)CH_3 \\ \text{VII}\end{array}\right\} \underset{-ROH}{\overset{+ROH}{\rightleftarrows}} \underset{\text{IV}}{ROCH_2CH_2C(OR)_2CH_3}$$

The unsaturated compounds also unite with phenols and mercaptans.

The ease with which compounds, such as V, VI and VII, add alcohols or phenols makes it possible to prepare mixed ethers and ketals of types IV, VI and VII. This also provides a method for converting one oxyprene into another as illustrated in the following scheme.



$$CH_2{=}CHC(OC_2H_5){=}CH_2 \xrightarrow{C_4H_9OH} CH_2{=}CHC(OC_2H_5)(OC_4H_9)CH_3 \xrightarrow{-C_2H_5OH} CH_2{=}CHC(OC_4H_9){=}CH_2$$

The oxyprenes which have been prepared are clear, mobile liquids having ethereal odors. The structures assigned to these products are based on the following reactions observed for the ethoxy derivative. On treatment with dilute mineral acids the ethoxy derivative is converted into methyl vinyl ketone which has been identified by its odor and its reaction product with phenylhydrazine, namely, methyl-3-phenyl-1-pyrazoline.[9] The structure of the ethoxy derivative has been further confirmed by its reaction with naphthoquinone (Diels–Alder diene reaction) to yield, after oxidation, ethoxy-2-anthraquinone.[10] In carbon tetrachloride solution the ethoxy derivative absorbs four atoms of bromine, the end-point being fairly sharp. On hydrogenation at room temperature with a platinum black catalyst it absorbs but two atoms of hydrogen, forming what appears to be ethoxy-2-butene-2. Its behavior toward alcohols and phenols has already been indicated.

Under ordinary conditions the oxyprenes show much less tendency to polymerize than chloroprene. Samples can be stored in the laboratory for several months without the formation of more than a few per cent. of polymer. Polymerization is greatly accelerated by light, heat and various catalysts, such as peroxides, sodium, metallic halides, iodine and certain acids, including acetic and hydrocyanic. The polymers may be liquids, resins or rubber-like products, depending upon experimental conditions. Use of low temperatures and the absence of diluents and catalysts favor the formation of rubber-like polymers. Thus, a 20% yield of rubber-like polymer comparatively free from liquid and resinous polymers is obtained by exposing ethoxyprene to ultraviolet light at room temperature for one week. Elevated temperatures promote the formation of liquid polymers. At 100° a 15% yield of polymer is obtained in six days, the product consisting of about 25% of liquid polymer (largely dimer) and 75% of rubber-like resin. At 130° substantially complete polymerization occurs in two weeks, the amounts of liquid and rubber-like polymer being approximately equal. A comparison of these data with those reported for isoprene[11] and for chloroprene[1] would indicate that ethoxyprene polymerizes about one-third as fast as isoprene and $^1/_{2000}$ as fast as chloroprene. Certain catalysts, notably iodine and hydrogen cyanide, bring about rapid polymerization of ethoxyprene to liquid polymers of low molecular weight. On the other hand, metal halides and acetic acid cause polymerization to resinous polymers. The polymerization of oxyprenes, like that of vinyl ethers,[12] takes place almost explosively in the presence of metal halides, such as stannic chloride.

The rubber-like polymer derived from ethoxyprene (and other oxyprenes) is plastic and readily soluble in ethyl acetate and in benzene. It is elastic and resilient but lacks the snap and high tensile strength of natural rubber or polymerized chloroprene. On heating with dilute hydrochloric acid the polymer is hydrolyzed to a polymeric ketone, identical in composition with methyl vinyl ketone.

As already indicated two types of intermediates, VI and VII, are formed in the preparation of the oxyprenes. Compounds VI are assigned the unsaturated ketal formula, $CH_2{=}CHC(OR)_2CH_3$, on the basis of the following reactions of the diethoxy derivative. On treatment with dilute acids, the diethoxy derivative is readily hydrolyzed to methyl vinyl ketone.

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(9) Maire, *Bull. soc. chim.*, (4) **3**, 272 (1908).

(10) Liebermann and Hagen, *Ber.*, **15**, 1798 (1882).

(11) Whitby and Crozier, *Can. J. Research*, **6**, 203 (1932).

(12) Chalmers, *ibid.*, **7**, 472 (1932).

TABLE I

R	B. p., °C./mm.	d^{20}_{4}	n^{20}_{D}	MR Calcd.	MR Found	Analyses, % Calcd. C	Calcd. H	Found C	Found H
A. PHYSICAL AND ANALYTICAL DATA FOR ETHER-KETALS, $ROCH_2CH_2C(OR)_2CH_3$									
CH_3	61–63/20	0.9398	1.4112	39.45	39.15	56.71	10.84	56.82	10.72
C_2H_5	75/9	.8940	1.4148	53.31	53.25	63.10	11.66	64.14	11.83
C_4H_9	120/3	.8745	1.4310	81.02	81.19	70.36	12.50	69.42	12.04
B. PHYSICAL AND ANALYTICAL DATA FOR UNSATURATED KETALS, $CH_2{=}CHC(OR)_2CH_3$									
CH_3	98–100/760	0.8756	1.4038	32.73	32.41	62.01	10.42	62.51	10.47
C_2H_5	69/100	.8470	1.4062	41.96	41.82	66.61	11.19	66.82	11.04
C_4H_9	79–80/8	.8497	1.4238	60.44	60.09	71.93	12.09	70.69	12.10
C_2H_5	81/2	1.0345	1.5128	56.83	55.79	74.96	8.38	75.31	8.37
C. PHYSICAL AND ANALYTICAL DATA FOR UNSATURATED ETHERS, $ROCH_2CH{=}C(OR)CH_3$									
C_2H_5	101/100	0.8711	1.4242	41.96	42.24	66.61	11.19	66.01	10.98
C_4H_9	91–93/4	.8633	1.4342	60.44	60.42	71.93	12.09	71.09	11.92
D. PHYSICAL AND ANALYTICAL DATA FOR OXYPRENES, $CH_2{=}CHC(OR){=}CH_2$									
CH_3	75/760	0.8281	1.4442	26.00	26.98	71.37	9.58	70.73	9.31
C_2H_5	96.5/760	.8153	1.4401	30.62	31.71	73.41	10.28	73.81	10.55
C_4H_9	65/54	.8223	1.4445	39.85	40.78	76.12	11.19	76.13	11.02

Unlike vinyl ethers, it is not polymerized appreciably by iodine. It reacts with hydrogen in the presence of platinum black to form the diethyl ketal of ethyl methyl ketone.

The structure of compounds VII has not been established with absolute certainty. Structure $ROCH_2CH{=}C(OR)CH_3$ appears most probable on the basis of the following data. The diethoxy derivative yields beta-ethoxyethyl methyl ketone (III) on hydrolysis with dilute acid. It is readily polymerized by iodine. On oxidation with potassium permanganate it yields ethyl acetate and acetic acid.

Experimental Part

Triethoxy-1,3,3-butane.—A mixture of 232 g. of beta-ethoxyethyl methyl ketone, 315 g. of ethyl orthoformate, 282 g. of absolute alcohol and 0.136 g. of hydrogen chloride was placed in a stoppered flask. After four days the mixture was made alkaline with ammonium hydroxide, dried over magnesium sulfate and distilled. The yield of the triethoxy compound, boiling at 72–75° at 9 mm., was 351 g. or 92% of the theoretical. This compound can also be prepared directly from methyl vinyl ketone and ethyl orthoformate.

The corresponding trimethoxy and tributoxy compounds were prepared in a similar manner.

Ethoxy-2-butadiene-1,3.—During the course of about four hours triethoxy-1,3,3-butane was dropped slowly into a heated distilling flask containing 0.01 g. of potassium bisulfate. The triethoxy compound was added at such a rate that approximately 20 g. was present in the flask at all times. The temperature of the flask was maintained at 120–140° to cause steady distillation of the decomposition products, *i. e.*, ethyl alcohol and ethoxy-2-butadiene-1,3. Some of the intermediate, diethoxy-3,3-butene-1, also distilled off. The decomposition products were collected in dilute potassium carbonate solution and were worked up by further washing with potassium carbonate solution, followed by drying and distilling. From 126 g. of the triethoxy compound there was obtained in this manner 39 g. of ethoxybutadiene (59% conversion) and 12 g. of diethoxybutene (13% conversion). The latter can be returned to the process to yield more ethoxybutadiene.

Methoxybutadiene and butoxybutadiene were similarly prepared. Other catalysts which have been used in the preparation of the oxyprenes are magnesium sulfate, *p*-toluenesulfonic acid and *d*-camphorsulfonic acid. When aluminum oxide is used as catalyst, the chief product is dialkoxy-1,3-butene-2.

Butoxy-2-butadiene-1,3.—A mixture of 15 g. of ethoxy-2-butadiene-1,3 and 11 g. of butyl alcohol was heated in a distilling flask until the temperature of the distilling vapors reached 95° and then distillation was continued under reduced pressure. The distillate consisted of 2 g. of ethyl alcohol, 6 g. of butyl alcohol and 6 g. of dibutoxy-3,3-butene-1. The residue in the flask was a viscous brown oil. On heating the dibutoxybutene with potassium bisulfate it decomposed into butyl alcohol and butoxy-2-butadiene-1,3.

Ethoxybutadiene plus Alcohols.—Seven grams of ethyl alcohol and 3.5 g. of ethoxy-2-butadiene-1,3 were heated together in a sealed glass tube at 100° for twenty-four hours and then distilled under 10 mm. pressure. The products consisted chiefly of ethyl alcohol (4.5 g.), triethoxy-1,3,3-butane (4 g.) and polymerized ethoxybutadiene (1 g.). When the reaction was carried out at 130°, only a small amount of the triethoxy compound was obtained, the chief product being diethoxy-3,3-butene-1. The latter compound adds alcohol at 100° to form the triethoxy compound.

A mixture of 14.7 g. of ethoxy-2-butadiene-1,3 and 12.4 g. of ethylene glycol was heated in a sealed tube for twenty-four hours at 110°. Distillation of the homogeneous reaction mixture thus obtained gave 9 g. of ethyl alcohol, 12 g. of a compound boiling at 56° at 100 mm. and 5 g. of resinous product. The compound boiling at 56° at 100 mm. gave methyl vinyl ketone on hydrolysis with dilute acid, indicating that it was either $CH_2{=}CHC(OCH_2CH_2OH){=}CH_2$ (VIII) or $CH_2{=}CH{-}\overline{C(CH_3)OCH_2CH_2{-}O}$, (IX). The product showed no tendency to polymerize. These data, together with the following, favor structure IX: d^{20}_4 0.9547; n^{20}_D 1.4213; MR calcd. for VIII, 33.24; MR calcd. for IX, 31.63; MR found, 30.32.

Anal. Calcd. for $C_6H_{10}O_2$: C, 63.11; H, 8.83. Found: C, 63.39; H, 8.58.

Phenol and thiophenol add readily to ethoxy-2-butadiene-1,3 at ordinary temperatures.

Reaction of Ethoxybutadiene with Naphthoquinone.—A mixture of 12 g. of ethoxy-2-butadiene-1,3, 10 g. of 1,4-naphthoquinone and 15 g. of benzene was refluxed for six hours and then allowed to stand overnight. The yellow crystalline mass which separated was dried in air. This caused the mass to become gray. The product was next suspended in a water–alcohol mixture containing sodium hydroxide, and air was passed through the dark colored mixture until it took on a yellowish-orange appearance. The solid was separated and recrystallized twice from acetic acid. The product, ethoxy-2-anthraquinone, melted at 136° as compared with 135° reported by Liebermann and Hagen.[10]

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.16; H, 4.80. Found: C, 76.01; H, 4.68.

The identity of the ethoxy-2-anthraquinone was further established by heating it with concentrated sulfuric acid as described by Liebermann and Hagen. The product, hydroxy-2-anthraquinone, melted at 302° as reported by these authors and gave a red coloration with alkali.

Hydrolysis of Ethoxybutadiene.—A small amount of ethoxy-2-butadiene-1,3 was added to dilute hydrochloric acid. Solution took place readily and the sharp odor of methyl vinyl ketone developed. On reaction of this mixture with phenylhydrazine, methyl-3-phenyl-1-pyrazoline was obtained, melting at 75–76° as compared with a value of 76–77° reported by Maire.[9]

Hydrogenation of Ethoxybutadiene.—A solution of 14.4 g. (0.147 mole) of ethoxy-2-butadiene-1,3 in 30 cc. of absolute alcohol was hydrogenated in a Burgess–Parr apparatus using 0.2 g. of platinum oxide as the catalyst. Reaction ceased within one and one-half hours after 0.17 mole of hydrogen had been absorbed. Addition of fresh catalyst failed to bring about further absorption. The hydrogenated product boiled almost completely from 88 to 93° and had a refractive index of n^{20}_D 1.4006. These properties suggest that the product is ethoxy-2-butene-2, ethoxy-2-butene-1 or a mixture of these compounds.[13] In a similar experiment using acetone as solvent, 0.117 mole of ethoxybutadiene absorbed 0.129 mole of hydrogen.

Polymerization of Ethoxybutadiene.—Forty grams of ethoxy-2-butadiene-1,3 was heated in a sealed glass tube at 130° for thirteen days. The product consisted of 20 g. of liquid polymer (mainly dimer, b. p. 105–125° at 5 mm.) and 17 g. of solid polymer. The latter was a light-colored, soft, rubber-like resin soluble in acetone, ethyl acetate and benzene, but insoluble in water and in alcohol.

A few drops of a 25% solution of stannic chloride in benzene was added to 5 g. of ethoxybutadiene. A vigorous reaction occurred which converted the ethoxybutadiene into a dark viscous mass within a few minutes. Acetic acid also converted ethoxybutadiene into resinous products, but the reaction was less violent and gave a lighter-colored product. When iodine was used as catalyst, 65% of the polymer consisted of liquid dimer and trimer and the remainder of soft resin.

Polymerization of Butoxybutadiene.—Exposure of butoxy-2-butadiene-1,3 in a quartz tube to ultraviolet light from a mercury arc for one week resulted in a 13% yield of polymer. The polymer was a white, opaque, fibrous solid which was somewhat sticky and elastic. It was insoluble in alcohol, acetone and ethyl acetate; in chloroform and benzene it lost its opacity but did not dissolve.

Diethoxy-3,3-butene-1.—This product, obtained in yields of 10–30% when triethoxy-1,3,3-butane was heated in the presence of acidic catalysts, was readily hydrolyzed by shaking with dilute hydrochloric acid. The product of the hydrolysis, methyl vinyl ketone, was characterized by its odor and reaction product with phenylhydrazine.

An ethanol solution of the diethoxy compound was treated with hydrogen in the presence of platinum oxide in a Burgess–Parr apparatus. Approximately 0.7 equivalent of hydrogen was absorbed. Distillation of the hydrogenated products showed that side reactions had occurred; only a 40% yield of the expected $CH_3CH_2C(OC_2H_5)_2CH_3$ was obtained. Properties observed for this product are: b. p. 68–69° at 100 mm.; d^{20}_4 0.8423; n^{20}_D 1.4012; MR calcd., 42.43; MR found, 42.18. A boiling point of 68° at 100 mm. is reported for this compound.[14]

Diethoxy-1,3-butene-2.—A mixture of 57 g. of $C_2H_5OCH_2CH_2C(OC_2H_5)_2CH_3$ and 0.1 g. of aluminum oxide was heated in a distilling flask. Decomposition started at about 110° and proceeded smoothly at 110–165° with the removal of alcohol. On distilling the residue in the flask under diminished pressure, 41 g. (95% yield) of product believed to be diethoxy-1,3-butene-2 was obtained.

Ten grams of this diethoxy compound was treated with 20 cc. of 1% hydrochloric acid and shaken for a few minutes. The product (6 g.) of the hydrolysis, separated by extraction with ether, proved to be beta-ethoxyethyl methyl ketone, identical with that obtained by addition of ethyl alcohol to methyl vinyl ketone. Some of its properties are: b. p. 57° at 24 mm.; d^{20}_4 0.9024; n^{20}_D 1.4089.

A mixture of 58 g. of the diethoxy compound and 600 g. of water was treated with potassium permanganate (350 g.) until no further reaction occurred. From the oxidation products, there was separated in the usual way 40 g. of an acetic acid–ethyl acetate mixture. The acetic acid was identified by its *p*-toluidide (m. p. 145–147°) and the ethyl acetate by its physical properties (odor, b. p. 78°; n^{20}_D 1.3780).

The author wishes to express his thanks to Dr. Wallace H. Carothers for his interest in this work and for his helpful suggestions.

Summary

The methyl, ethyl and butyl ethers of hydroxy-2-butadiene-1,3 have been prepared and characterized. The designation oxyprene is suggested for products of this structure. The oxyprenes

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[13] Lauer and Spielman, This Journal, **53**, 1533 (1933).

[14] Reitter and Hess, *Ber.*, **40**, 3020 (1907).

polymerize slowly to rubber-like products, but as substitutes for rubber these products are inferior to polychloroprene.

A method for the synthesis of oxyprenes from vinylacetylene has been described which involves as its final step the thermal decomposition of compounds of the formula $ROCH_2CH_2C(OR)_2CH_3$. A number of intermediates of types $ROCH_2CH_2COCH_3$, $ROCH_2CH_2C(OR)_2CH_3$, $ROCH_2CH{=}C(OR)CH_3$ and $CH_2{=}CHC(OR)_2CH_3$ have been prepared and characterized.

WILMINGTON, DELAWARE RECEIVED AUGUST 27, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF OHIO WESLEYAN UNIVERSITY]

Alkyl Ethers of 2,2-Bis-(4-hydroxyphenyl)-propane. I. Some Dialkyl Ethers[1]

BY G. R. YOHE AND J. F. VITCHA

The condensation of two molecules of phenol with one of acetone in the presence of hydrogen chloride or sulfuric acid yields 2,2-bis-(4-hydroxyphenyl)-propane, $HOC_6H_4C(CH_3)_2C_6H_4OH$. This compound, with some of its simple derivatives, has been described in the literature.[2] Of the ethers of this compound only the dimethyl ether has been described.[2a,2b,3]

Some time ago the writers began the preparation of a series of the monoalkyl ethers of this dihydric phenol. The preparation of these monoalkyl ethers resulted in the incidental formation of the corresponding dialkyl ethers as well; several of these are described herewith. The monoalkyl derivatives will be described in a subsequent communication.

The general method followed was to allow an excess of the phenol in aqueous sodium or potassium hydroxide solution to react with the suitable dialkyl sulfate. Commercial dimethyl and diethyl sulfates were used, *n*-propyl and *n*-butyl sulfates were prepared by the method of Barkenbus and Owen,[4] while *n*-amyl sulfate was prepared by the action of sulfuryl chloride on *n*-amyl alcohol[5] and used without being isolated for the alkylation reaction. The ethers described herein were isolated from the alkali-insoluble portions of the reaction mixtures and purified by distillation or by recrystallization from methanol or ethanol solution cooled with a solid carbon dioxide–ether mixture; in some cases both distillation and crystallization procedures were used. In general the yields were low and the compounds rather difficult to purify.

The di-*n*-propyl ether gave the most difficulty in purification. It was contaminated with a rather large amount of a substance of similar boiling point, but of higher refractive index. Isolation was finally accomplished by dissolving the crude compound in petroleum ether (b. p. 40–60°) and cooling the solution with solid carbon dioxide–ether mixture, whereupon the impurity separated out as a gum, leaving the desired dipropyl derivative in solution. The identity of the impurity has not been established.

The solid dialkyl ethers of 2,2-bis-(4-hydroxyphenyl)-propane are white needle crystals; in the molten state they may be easily supercooled to liquids of moderate viscosity. These compounds are soluble in the usual organic solvents; the higher members of the series are only sparingly soluble in methanol.

The properties of these *n*-alkyl ethers through amyl are listed in Table I.

The reactions described below are typical of the relative amounts and conditions used in all reactions. No doubt higher yields of the dialkyl derivatives could have been obtained by using the alkyl sulfates in excess. This, however, would have minimized the formation of the monoalkyl ethers.

Experimental Part

Dibutyl Ether of 2,2-Bis-(4-hydroxyphenyl)-propane. Use of the Dialkyl Sulfate.—A mixture of 114 g. (0.5 mole) of 2,2-bis-(4-hydroxyphenyl)-propane, 60 g. (1.5 moles) of sodium hydroxide and 300 cc. of water was heated to boiling, 42 g. (0.2 mole) of di-*n*-butyl sulfate added,

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(1) A part of this work was reported at the 44th annual meeting of the Ohio Academy of Science at Columbus, Ohio, March 30, 1934.

(2) (a) Beilstein's "Handbuch," 4th ed., Vol. VI, pp. 1011, 1012, Supplement Vol. VI, p. 493; (b) A. Dianin, *J. Russ. Phys.-Chem. Soc.*, **23**, 492 (1891); (c) T. Zincke and M. Grueters, *Ann.*, **343**, 85 (1905); (d) T. Szeky, reprint from *Ber. d. med.-naturw.*, Section d. Siebenbürg. Museumvereines, 1–13 19/11 (1904); *Chem. Zentr.*, **75**, II, 1737 (1904); (e) J. Schmidlin and R. Lang, *Ber.*, **43**, 2814 (1910); (f) L. H. Baekeland and H. L. Bender, *Ind. Eng. Chem.*, **17**, 225–37 (1925); (g) J. v. Braun, *Ann.*, **472**, 65 (1929).

(3) Wulff, *J. Russ. Phys.-Chem. Soc.*, **23**, 498 (1891).

(4) C. Barkenbus and J. Owen, THIS JOURNAL, **56**, 1204 (1934).

(5) Unpublished work from the writer's laboratory.

TABLE I

DIALKYL ETHERS OF 2,2-BIS-(4-HYDROXYPHENYL)-PROPANE, $ROC_6H_4C(CH_3)_2C_6H_4OR$

R	CH_3	C_2H_5	C_3H_7	C_4H_9	C_5H_{11}
M. p., °C.	59–61.5	49–50	....	20	34.5–35.5
B. p., °C. (mm.)	190 (5)	....	200–202 (3)	212–213 (3)	225–230 (3)
$n^{20}{}_D$	1.5696[a]	1.5556[a]	1.5448	1.5368	1.5306[a]
$d^{20}{}_4$	....	....	1.0156	0.9961	....
Calcd. % C	79.63	80.23	80.72	81.11	81.46
Found % C	....	79.81	80.65	80.79	81.34
Calcd. % H	7.88	8.52	9.03	9.49	9.86
Found % H	....	8.57	9.14	9.37	9.89

[a] Value determined using the supercooled liquid.

and the heating continued for three hours. The alkali-insoluble portion of the reaction product was isolated by ether extraction, and the dibutyl derivative obtained by distillation of this solution. The yield was 35 g., or 51% of the theoretical, assuming the utilization of only one of the alkyl groups of the sulfate. It was necessary to further purify this material.

Diamyl Ether of 2,2-Bis-(4-hydroxyphenyl)-propane. The Alcohol–Sulfuryl Chloride Method.—One mole (88 g.) of pentanol-1 was cooled with an ice-bath, and 0.5 mole of sulfuryl chloride added slowly so that the reaction mixture remained cold. This was allowed to stand protected from moisture for one week. It was then neutralized with sodium hydroxide solution (approximately 0.75 mole in the form of a 10 *N* solution was needed), and a solution of 0.5 mole of 2,2-bis-(4-hydroxyphenyl)-propane in 150 cc. of potassium hydroxide (500 g. per liter) added. This was then treated and worked up as described above. The yield was 24 g., or 26% of the theoretical, assuming the formation of 0.5 mole of diamyl sulfate and the utilization of one of the alkyl groups of this sulfate in the alkylation. The product was further purified by recrystallization from methanol.

The writers wish to thank E. I. du Pont de Nemours and Co. and The Goodyear Tire and Rubber Co. for supplying certain of the materials used, and Mr. C. A. Sluhan for help with the experimental work.

Summary

This paper describes the preparation and properties of the di-*n*-alkyl ethers of 2,2-bis-(4-hydroxyphenyl)-propane from methyl to amyl.

DELAWARE, OHIO RECEIVED SEPTEMBER 3, 1935

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

The Chemistry of the Tetrose Sugars. I. A Crystalline Triacetate of *d*-Threose from the Degradation of Strontium Xylonate with Hydrogen Peroxide. Nomenclature in the Tetrose Group[1]

BY ROBERT C. HOCKETT

Within recent years so many sugars previously prepared by synthetic methods in the laboratory have been found playing an important role in natural processes that new attention is focused upon the necessity of filling those gaps which still remain in the sugar family. Particularly does this necessity apply to the sugars of low carbon atom content which are those most likely to be encountered as intermediates in the physiological degradation of glucose. The tetroses are still among the least known members of the sugar group despite the fact that the first efforts toward their preparation were made nearly fifty years ago.[2] The general methods of degrading sugars devised by Wohl and Ruff seemed at first to furnish a very promising means of attacking the problem, and centered an interest upon the tetroses particularly from 1899 to 1901,[3] but the results proved disappointing in that all the classic methods of preparing sugars are beset by special difficulties when applied to this group, so that very few crystalline compounds were prepared and few data recorded. Except for the later application of Weerman's[4] method of degradation

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[1] Publication authorized by the Surgeon General, U. S. Public Health Service. An abstract of this paper was presented before the Organic Division of the American Chemical Society in Chicago, September, 1933.

[2] Fischer and Tafel, *Ber.*, **20**, 1090 (1887).

[3] Wohl, *Ber.*, **26**, 743 (1893); *ibid.*, **32**, 3666 (1899); Ruff and Meusser, *ibid.*, **32**, 3672 (1899); Ruff, Meusser and Kohn, *ibid.*, **34**, 1362 (1901); Maquenne, *Compt. rend.*, **130**, 1402 (1900); Bertrand, *ibid.*, **130**, 1330 (1900); Fenton and Jackson, *J. Chem. Soc.*, **75**, 1 (1899); Morrell, *ibid.*, **81**, 674 (1902); Jackson, *ibid.*, **77**, 130 (1900).

[4] Weerman, *Rec. trav. chim.*, **37**, 16 (1918).

which resulted in little actual new success, the field was abandoned until recent years.

In January, 1931, we decided to undertake a complete resurvey of the known methods of degradation to determine whether advancing knowledge would now permit some of the difficulties to be surmounted. *d*-Threose was chosen as the object of search because it has received much less attention than the erythroses, and the Ruff degradation was selected as a method. In the undertaking, we had certain advantages over predecessors. (1) Xylose, our starting material, once very rare, is now available in quantity. (2) Our independent preparation of crystalline strontium xylonate[5] made possible the use of a pure anhydrous salt in the oxidation experiments. The results were far superior to those obtained by using amorphous calcium xylonate. (3) The announcement by Isbell and Frush[6] of their electrolytic oxidation of aldoses provided us with a method which proved very efficient when applied to the preparation of strontium xylonate. (4) A new method of making the ferric acetate catalyst proved to be very rapid and reliable.[7]

With these advantages, colorless strontium-free *d*-threose sirups were prepared in relatively good yield. One of these which was acetylated, after a year or more yielded crystals of the acetate which is fully described in the experimental part, and which thereafter was obtained readily. It represents a substance which can be highly purified, weighed and deacetylated almost quantitatively to give an aqueous solution of the tetrose whose concentration is pretty accurately known, thus making the sugar available in a form suitable for a variety of chemical investigations and for biological experiments, some of which are in progress.

This acetate was rigidly identified by the determination of carbon, hydrogen, acetyl and molecular weight, while the free sugar was converted into four known crystalline derivatives: erythrosazone, dibenzylidene-*d*-threitol, brucine *d*-threonate and potassium levo-bitartrate.

A standard aqueous solution of the free sugar prepared as described was used for determining its equilibrium specific rotation, which was found to be approximately[8] $-12.3°$. This result was surprising because W. Freudenberg[9] had meanwhile announced the preparation of a crystalline *d*-threose showing a positive specific rotation in water of $+19.59°$. Deulofeu[10] had also announced the preparation of *l*-threose diacetamide rotating $-7.68°$ in cold $N/3$ sulfuric acid, which changed to $-24.6°$ after heating for forty-five minutes to remove the acetamide groups. His conclusion was that the latter value represents the rotation of *l*-threose. These two reports, harmonious with one another and opposite to our result, suggested the possibility that an acetyl group had failed to be dislodged by our method of saponification with sodium methylate. Experiments involving two successive deacetylations or the use of other agents such as barium hydroxide, however, all gave us levorotatory solutions of the sugar. The discrepancy was therefore left to be explained when a totally different method of preparing *d*-threose could be carried out and the products compared. The second paper of this series will discuss this work.

It was observed that the deposition of the crystalline threose acetate always leaves a levorotatory mother liquor which suggests the presence of isomeric acetates as in the case of higher-carbon sugars. Stronger evidence is provided by the fact that a threose sirup prepared by saponification of pure acetate, when reacetylated, yields only one-third of the original acetate and two-thirds of a levorotatory sirup rotating roughly $-19.4°$ in chloroform. When the deacetylation and reacetylation is repeated upon this sirup, again one-third is recovered as the crystalline acetate and two-thirds as levorotatory sirup, strongly suggesting the existence of two (or more) closely related isomers of which at least one presumably is a ring form.

A dried *d*-threose sirup when treated with 2% dry hydrogen chloride in methanol, loses all reducing power and reaches a constant rotation in about twenty minutes at room temperature. Such behavior is to be expected of a sugar whose chain is too short for the formation of methyl pyranosides and which must form either methyl furanosides or a dimethyl acetal (Fig. 1).

Nomenclature in the Tetrose Group

Several errors and inconsistencies have arisen in the nomenclature of substances in the four-

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[5] Hockett, THIS JOURNAL, **56**, 994 (1934). *Cf.* Isbell, *Bur. Standards J. Research*, **14**, 359 (1935).

[6] Isbell and Frush, *ibid.*, **6**, 1145 (1931).

[7] Hockett and Hudson, THIS JOURNAL, **56**, 1632 (1934). *Cf.* National Formulary, 3rd edition, Baltimore, 1906, p. 219.

[8] Throughout this paper, rotations refer to specific rotations of the sodium line at 20° unless otherwise specified.

[9] W. Freudenberg, *Ber.*, **65**, 168 (1932).

[10] Deulofeu, *J. Chem. Soc.*, **225**, 2458 (1929). See also *ibid.*, 2602 (1930) and 2973 (1932).

carbon group owing in part to the small attention they have received during developments elsewhere.

In 1906, Rosanoff[11] proposed certain reforms in Fischer's nomenclature involving a change in the name of dextrorotatory xylose from *l*- to *d*-xylose. This change, promptly accepted by American[12] and British chemists in the interest of logical harmony within the system, came into general acceptance about 1923.[13] It has repercussions among names formerly assigned to certain derivatives of xylose which should be brought into conformity, as will be shown.

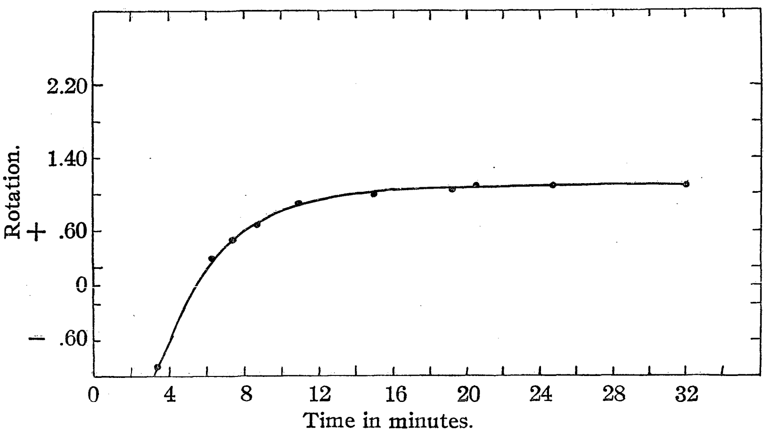

Fig. 1.—The action of 2% hydrogen chloride in methanol upon threose.

Maquenne,[3] by degrading what we now call *d*-xylose, prepared a sirup of *d*-threose (Fig. 2, I) which he erroneously called *l*-erythrose. By reducing this sugar, he obtained the alcohol which should be known as *d*-threitol (II), but which he called *l*-erythritol. Bertrand[3] meanwhile made a four-carbon ketose by the action of sorbose bacteria on the natural inactive erythritol (III). His product might *a priori* have been either *d*- or *l*-erythrulose depending upon which carbon was attacked (IV or V). That he actually obtained *l*-erythrulose (V) is indicated by the behavior of the ketose on reduction. We should expect two products, the original inactive erythritol (III) and an active alcohol either identical or enantiomorphous with Maquenne's *d*-threitol (II or VI). The products actually obtained were inactive erythritol and *l*-threitol (VI)[14] (which they called *d*-erythritol). In no text or reference work that we have examined has Bertrand's name "*d*-erythrulose" been corrected to "*l*-erythrulose" as required by consistency.

Consistency also strongly urges limiting the term "erythritol" to the natural inactive alcohol (m. p. 120–121.3°) which may also be obtained by reduction of either *d*- or *l*-erythrose, and using the terms "*d*-threitol" (rotating +4.33° in water) and "*l*-threitol" (rotating −4.4° in water) for the active tetritols derived, respectively, from the two threoses, since elsewhere in the sugar group, only enantiomorphous alcohols bear the same name, being distinguished by prefix, and forms of different configuration bear different names.

On oxidation with nitric acid, *d*-threose is converted into a dibasic acid which might consistently be called *d*-threodihydroxysuccinic acid were it not already well known as *l*-tartaric acid (VII). The latter, long ago named from its actual rotation, is not in harmony with the arbitrary standard set up by Fischer for assignment of prefixes in the sugar group, and appears destined to constitute a permanent anomaly in our nomenclature.

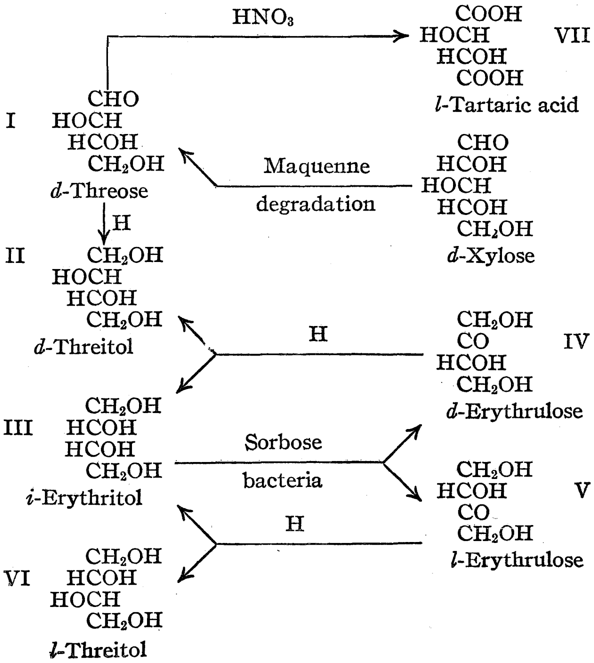

Fig. 2.

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[11] Rosanoff, This Journal, 28, 114 (1906); *cf.* Fischer, *Ber.*, 40, 102 (1907).

[12] Hudson and Brauns, This Journal, 38, 1217 (1916); *cf.* Armstrong, "The Simple Carbohydrates and the Glucosides," Longmans, Green & Co., London, 1919, pp. 78 and 80.

[13] Wohl and Momber, *Ber.*, 50, 455 (1917); Wohl and Freudenberg, *ibid.*, 56, 309 (1923).

[14] Maquenne and Bertrand, *Compt. rend.*, 132, 1419 (1901).

Experimental

Strontium *d*-xylonate.[5]—One hundred grams of xylose, 20 g. of sodium bromide, 130 g. of strontium carbonate and two liters of water are warmed to 60°, placed in a glass cell equipped with carbon electrodes providing about 200 sq. cm. of anode surface, and electrolyzed with the current from a tungar battery charger at about 10 volts and 2.6 amperes for twenty-four hours with good mechanical stirring. Another 100 g. of xylose is added each twenty-four hours until 400 g. has been used and electrolysis is continued until the reducing power toward Fehling's solution is virtually gone. After filtering, evaporating to one-half its volume, cooling and seeding, the solution crystallizes rapidly and must be stirred to prevent formation of a too solid cake. Filtered, washed with 50% alcohol and dried at 60°, the combined first and second crops represent 95% of the theoretical yield. The salt is readily recrystallized from water as the pentahydrate; drying as described yields the powdery anhydrous salt rotating +13.2° (0.4266 g. in 25 cc. of soln. in water; 2-dm. tube; 0.45° to the right).

Anal. Calcd. for $(C_5H_9O_6)_2Sr\cdot 5H_2O$: H_2O, 17.74. Found: H_2O, 17.72. Calcd. for $(C_5H_9O_6)_2Sr$: Sr, 20.98; C, 28.72; H, 4.34. Found: Sr, 20.79, 20.77; C, 28.77; H, 4.49.

***d*-Threose Triacetate.**—Seventy-five cubic centimeters of molar barium acetate and 50.2 cc. of half-molar ferric sulfate are added to two liters of water. Then 200 g. of anhydrous strontium xylonate is added, the solution is heated to boiling, allowed to settle, filtered through filtercel, diluted with a liter of water and cooled to 35°. One hundred twenty cubic centimeters of 30% hydrogen peroxide is added and a vigorous evolution of gas ensues. When the reaction has ended (ten minutes) the solution is cooled to 35°, and another 120 cc. of hydrogen peroxide added.

After settling the solution is filtered on filtercel, concentrated *in vacuo* to 250 cc., taken up in 1500 cc. of dry methanol, warmed and shaken, and ultimately filtered. The salts are washed with 300 cc. of warm methanol. Nine hundred cubic centimeters of ether or acetone is added to the filtrate, which is stirred and allowed time to separate a flocculent precipitate. The colorless filtrate is concentrated *in vacuo* to blubbering, taken up in dry methanol and reconcentrated. Finally it is distilled down in the presence of a little ethyl acetate to remove alcohol. Ten grams of fused sodium acetate and 100 cc. of acetic anhydride are added and the mixture is warmed on a steam-bath for an hour with frequent shaking. After acetylation is complete, the mixture is poured into ice water and neutralized with sodium bicarbonate. The solution is extracted several times with chloroform, which is separated, dried with anhydrous sodium sulfate, filtered through carbon and concentrated *in vacuo*. The thick sirup is taken up in absolute alcohol, transferred to a beaker and seeded with threose acetate, which separates on cooling; yield, to 12 g. Since the crystalline isomer represents one-third of the total, the yield represents about 15% of the theoretical.

Recrystallized from absolute alcohol as very sharp, well-formed prisms, the substance after pulverizing and drying at 60° shows m. p. 117–118° (corr.) and rotates +35.55° (0.8910 g. in 26.18 cc. of chloroform soln.; 4.83° to the right; 4-dm. tube). The acetate is somewhat soluble in hot water, sparingly so in absolute alcohol, methanol and ether, and easily in chloroform, acetone and ethyl acetate.

Anal. Calcd. for $C_{10}H_{14}O_7$: C, 48.76; H, 5.73; CH_3CO, 52.44. Found: C, 48.51; H, 5.77; CH_3CO, 52.64.

Molecular Weight of Threose Acetate.—Cottrell's ebullioscopic apparatus was used with acetone as the solvent. The sample was weighed in a calibrated 25-cc. flask, made up to the mark with acetone and reweighed. An aliquot was introduced into the apparatus by pipet. A weight of 2.6272 g. of the acetate caused a dT of 0.203° in 117.6 cc. of acetone. Molecular weight found, 240; calculated for $C_{10}H_{14}O_7$, 246. The substance is clearly a monomer.

***d*-Threose.**—Five grams of crystalline *d*-threose triacetate was dissolved in 10 cc. of dried chloroform, cooled below zero and treated with 10 cc. of approximately 2% sodium methylate in dry methanol. After twenty minutes, below 0°, 10 cc. of water was added with shaking and then an exactly equivalent volume of approximately 0.5 *N* sulfuric acid (as determined by previous titration against the sodium methylate). The whole mixture was concentrated nearly to dryness *in vacuo* at a low temperature and the sugar was taken up in 90% alcohol, leaving behind most of the sodium sulfate. Successive extractions eliminated all but a trace of salt and yielded a colorless solution of the sugar.

An accurately weighed sample, so deacetylated, concentrated to dryness and then made up to volume with water in a 50-cc. calibrated flask showed an equilibrium rotation for the free sugar of −12.3° (1.1268 g. of sugar (calcd.) in 50 cc. soln. in water; 0.277° to the left; 1-dm. tube). After elimination of practically all the sodium sulfate, the rotation was virtually unchanged.

Another sample was deacetylated with a clear aqueous solution of barium hydroxide at 30°. After complete solution of the acetate and quantitative removal of barium, the solution was levorotatory.

Barium methylate did not remove the acetyls completely.

After two successive deacetylations with sodium methylate, the same specific rotation was obtained.

***d*-Threosazone (*d*-Erythrosazone).**—An aqueous solution of *d*-threose, acidified with acetic acid and warmed for three-quarters of an hour with 5 cc. of phenylhydrazine, deposited yellow needles on cooling. Recrystallized from benzene and dried at 55°, these showed m. p. 164–165° when heated at one degree per minute. Erythrosazone has been reported about a dozen times[3] with melting point from 163 to 174°. The most frequent value is 164°.

Dibenzylidene-*d*-threitol.—The sugar from five grams of the triacetate was diluted to 100 cc. with water and well stirred at room temperature while 2% sodium amalgam was added in 50-g. portions and 20% sulfuric acid added dropwise to maintain a slight acidity to Congo red. After addition of 450 g. of amalgam, the reducing power had disappeared. The mercury was separated, the solution neutralized to phenolphthalein, concentrated to a sirup and the threitol extracted from sodium sulfate with 50 cc. of hot absolute alcohol. The extract was concentrated to a thick sirup, taken up in absolute alcohol, filtered from traces of sodium sulfate, and then reconcentrated. Finally, the sodium-free substance in 30 cc. of alcohol solution was saturated with dry hydrogen chloride and 5 cc. of benzaldehyde added whereupon fine needles promptly separated. Refrigerated, filtered, washed free of acid with absolute alcohol and dried, they weighed 7 g. After recrystallization from fifteen parts of hot benzene as clusters of fine needles, filtration, washing with cold benzene and drying *in vacuo* at 75°, they rotated $-78.2°$ (0.1860 g. in 25 cc. of chloroform soln.; 1.163° to the left; 2-dm. tube) and melted 214–216° (corr.).

After further recrystallization from a mixture of 50 cc. of chloroform with 15 cc. of absolute alcohol and drying at 90° in a high vacuum, the substance showed m. p. 218–222° (corr.) with heating at a half-degree per minute, and rotated $-78.3°$ (0.2102 g. in 25 cc. of chloroform soln.; 1.315° to the left; 2-dm. tube).

The substance dissolves in cold chloroform to about one part in one hundred; much more on warming. About seven parts per hundred dissolve in boiling benzene and less in alcohol.

Ruff[3] gives a melting point of 204–205° for dibenzylidenethreitol. Ours is the first report of its rotation.

Brucine *d*-Threonate.—The sugar from 5 g. of the triacetate was dissolved in 150 cc. of water and treated with 1.2 cc. of bromine in the presence of 12 g. of barium benzoate for forty-eight hours. The reducing power having then disappeared, the solution was worked up in the usual way[15] and the concentrated aqueous solution of threonic acid was treated with a slight excess of purified brucine. On concentrating further, the salt crystallized in the flask; free brucine was extracted with absolute alcohol and the salt purified by two recrystallizations from 85% alcohol as fine clear needles. Dried for two hours in a vacuum at 60°, they melted 197–198° (corr.) with heating at 3° per minute. The rate of heating had a strong effect upon the melting point which was only 187–190° at 1° per minute. The crystals rotated $-36.8°$ (0.4420 g. in 25 cc. of water soln.; 1.025° to the left; 2-dm. tube). Anderson[16] gives m. p. 213–214° and rotation $-32.40°$. On account of our limited amount of material, we did not attempt to set a new standard of value for these constants, but consider the agreement good evidence of identity. Wohl and Momber[13] give m. p. 204° and rotation $-29.9°$ (at 17°).

Oxidation of *d*-Threose to *l*-Tartaric Acid.—A solution of 1.5 g. of threose in 6 cc. of nitric acid (sp. gr. 1.2) was allowed to stand at room temperature until a violent reaction had occurred. The next morning the acid was distilled off *in vacuo* to a thin sirup which was several times taken up in water and reconcentrated. The sirup nearly free of nitric acid was dissolved in water and neutralized with caustic potash. Then several cubic centimeters of 10% acetic acid were added, and alcohol to a concentration of 50%, which precipitated a gum. After several days, the mother liquor was decanted and fresh 50% alcohol added to the gum whereupon it became crystalline through the separation of needles of potassium *l*-bitartrate. They were recrystallized by dissolving in a little water, filtering through carbon, and adding alcohol, were washed with dilute, then pure alcohol, and dried at 50°.

Anal. Subs. 0.1845 g. Calcd. for titration of $KH(C_4H_4O_6)$, 4.91 cc. of 0.2000 *N* NaOH. Found: 4.89 cc.

The neutralized solution of sodium potassium *l*-tartrate rotated $-29.40°$ (at 24°) (0.2061 g. in 50 cc. of water soln.; 0.242° to the left; 2-dm. tube). Landolt[17] gives $+29.7°$ for sodium potassium *d*-tartrate.

We wish to express to Dr. C. S. Hudson, Chief of the Division of Chemistry, our gratitude for the patient and sympathetic interest which made this work possible. Our thanks are also due Dr. F. H. Goldman, Dr. E. L. Jackson and Mr. C. G. Remsburg for analyses reported in this paper.

Summary

1. Ruff's method of degrading sugars has been applied in an improved form to the preparation of *d*-threose from crystalline strontium *d*-xylonate.

2. The electrolytic oxidation of xylose and preparation of the strontium salt is described.

3. The oxidation of strontium *d*-xylonate with 30% hydrogen peroxide yielded 15% of *d*-threose in an impure sirup.

4. The sugar was separated as a crystalline triacetate which is described, and from which after purification, aqueous threose sirups of known concentration can be prepared for chemical and biological study.

5. The sugar was identified by conversion into four known crystalline derivatives.

6. Its equilibrium rotation in water was found to be approximately $-12.3°$, a result in conflict with two reports by other investigators of a dextrorotation.

7. Some errors in nomenclature in the tetrose group are corrected.

WASHINGTON, D. C. RECEIVED AUGUST 2, 1935

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[15] Hudson and Isbell, THIS JOURNAL, **51**, 2225 (1929).

[16] Anderson, *Am. Chem. J.*, **42**, 423 (1909).

[17] Landolt, *Ber.*, **6**, 1076 (1873).

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

The Chemistry of the Tetrose Sugars. II. The Degradation of *d*-Xylose by the Method of Wohl. The Rotation of *d*-Threose[1]

BY ROBERT C. HOCKETT

The first communication of this series[2] described the preparation of a crystalline threose triacetate by the Ruff degradation and recorded for *d*-threose prepared from the purified acetate, an equilibrium levorotation in water of −12.3°.[3] This rotation is of a sign opposite to that determined by W. Freudenberg[4] and by Deulofeu.[5] No source of error was discovered in the experiments leading to our measurement, and it was promised that further evidence would be sought in the preparation of *d*-threose by a totally different method of degradation, as one step in the complete resurvey of degradation methods which we announced in the first paper.[2] The method devised by Wohl[6] was selected as the second one to be studied, particularly because Deulofeu used this method in attempting to determine the specific rotation of *l*-threose which he reported as *to the left.*

d-Xylose, when treated with hydroxylamine, yielded a sirupy mixture of oximes of which no constituent has ever been obtained crystalline. Acetylation of this sirup gave a 48% yield of crystalline tetraacetyl-xylonic nitrile. This reaction is very exothermic so that there is great danger of the mixture becoming charred unless an inert diluent such as dioxane is used, and the acetic anhydride is added in small successive quantities.

By warming the tetraacetyl-*d*-xylonic nitrile on a steam-bath with strong aqua ammonia (28%), it is simultaneously degraded and deacetylated. The threose is obtained as a crystalline combination with two molecules of acetamide in a yield of about 78%, which is much greater than the yield obtained by using ammoniacal silver nitrate (17%).[5] Deulofeu reports the isolation of about half a gram of *l*-threose diacetamide to which he attributes a specific rotation in dilute sulfuric acid of −7.68°. The *d*-isomer, however, prepared in 50-g. batches, many times recrystallized as colorless, well-built prisms, and analyzed, has a specific rotation in water of −10.9°. Obviously the *l*-isomer should have a dextrorotation of equal numerical value and we are forced to the conclusion that Deulofeu did not have pure *l*-threose diacetamide. Moreover, acetylation of the diacetamide compound yields a crystalline triacetate, well-built prisms, m. p. 179-180°, rotation in chloroform, +74.2°, which after thorough purification and deacetylation regenerates beautifully crystalline *d*-threose diacetamide rotating −10.8°. We consider this good evidence of the purity of the latter.

To determine the equilibrium rotation of the sugar itself, Deulofeu hydrolyzed his acetamide compound to constant rotation with $N/3$ sulfuric acid. He reports a change from specific rotation −7.68° for the diacetamide compound to −24.6°, calculated for the sugar, the direct readings being unreported. In a preliminary experiment using about the same quantities, we detected a downward drift barely greater than the experimental error. We were doubtful whether an hydrolysis had occurred until tests showed that the acid-treated solution had a powerful reducing action whereas threose diacetamide fails to reduce Fehling's solution even on boiling. The necessary conclusion that the change of rotation during hydrolysis is very minute was wholly in accord with our previously determined rotations for the diacetamide compound and the sugar, respectively (−10.9 and −12.3°).

By refinements of technique, it was possible to follow the course of hydrolysis quantitatively. Control tests indicated that threose may be titrated with consistent results by Cajori's iodine oxidation method,[7] that the diacetamide compound is unaffected by the reagents employed, and that the presence of free acetamide does not interfere with the titration. It was possible, therefore, to follow the course of the hydrolysis by removing samples periodically, dropping them

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[1] Publication authorized by the Surgeon General, U. S. Public Health Service. A part of this material was presented as a paper before the Organic Division of the American Chemical Society in Cleveland, Sept., 1934.

[2] Hockett, THIS JOURNAL, **57**, 2260 (1935).

[3] In this paper rotations refer to specific rotations of sodium light at 20° unless otherwise specified.

[4] W. Freudenberg, *Ber.*, **65**, 168 (1932).

[5] Deulofeu, *J. Chem. Soc.*, 2458 (1929).

[6] Wohl, *Ber.*, **32**, 3666 (1899); Maquenne, *Compt. rend.*, **130**, 1402 (1900).

[7] Cajori, *J. Biol. Chem.*, **54**, 622 (1922).

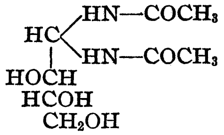
at once into dilute sodium carbonate solutions to stop action and completing the titrations within a reasonable period of time. Figure 1 shows the curve obtained. After removing the last sample for analysis, the remaining solution was immediately cooled and its rotation read. Knowing the concentration of free sugar, the concentration of diacetamide compound (by difference), the rotation of the mixture and the specific rotation of the starting substance, we calculated the equilibrium specific rotation of the sugar in dilute acid as −12.5°, a value in excellent agreement with that previously determined for *d*-threose from the acetate. (By accident, the agreement is actually closer than the experimental errors permit us to expect.)

The change in rotation during hydrolysis, though small, is measurable when a 2% soln. is read in a 4-dm. tube. Figure 2 shows the curve obtained in such an experiment. This, in contrast with Deulofeu's report, shows a downward trend, for although the specific rotation of the starting substance is less levorotatory than that of the sugar released, the molecular rotation of the former is much greater. At the end, the solution was titrated and another calculation of the specific rotation of *d*-threose was made, which gave −10.8°. This we consider to be in satisfactory agreement. The rates of reaction as determined from the two methods also agree satisfactorily.

In order to prove rigidly that the reducing substances obtained from threose acetate and from threose diacetamide are actually identical, the sugar from hydrolysis of a sample of the latter was reduced to *d*-threitol with sodium amalgam and the latter converted into dibenzylidene-*d*-threitol.[2] By rigid purification of this derivative, it was shown by rotation, melting point and mixed melting point observations to be identical with dibenzylidene-*d*-threitol from threose acetate.

Thus the equilibrium specific rotation of *d*-threose, both in water and in dilute sulfuric acid, appears well established as approximately 12° *to the left*, and sources of error are to be sought in the work of those who have found other values.

The formation by *d*-threose diacetamide of a triacetate indicates the absence of a ring in the former and establishes it as a derivative of aldehydo-*d*-threose:



The subject of ring structure among tetrose derivatives will be elucidated further in another communication.

In the search for cheaper and more efficient methods of making the tetroses, the Wohl method suffers from the disadvantage that every aldose forms several oximes so that it does not appear easy to increase the yield of the isomer necessary for this degradation.[8]

Experimental

Tetraacetyl-*d*-xylonic Nitrile.—Hydroxylamine hydrochloride (25g.) is dissolved in 15 cc. of water and a solution of sodium methylate (8.2 g. sodium in 200 cc. of dry methanol) added to the point of neutrality (phenolphthalein). After chilling the solution and filtering the precipitated sodium chloride, 45 g. of powdered *d*-xylose is added and the mixture allowed to stand overnight, then warmed on the steam-bath as long as is necessary to dissolve all the sugar. After filtering, the solution is concentrated *in vacuo* to a thick sirup, the outer bath not being allowed to rise above 75°. The sirup is dehydrated twice by adding a little dioxane and reconcentrating. Then 12 g. of fused sodium acetate and 25 cc. of dioxane are added, the mixture is warmed to 40° and 10 cc. of acetic anhydride added. The mixture is shaken vigorously until the spontaneous heating has ceased and the flask has begun to cool, then 10 cc. more of acetic anhydride is added, etc., until 120 cc. has reacted. The solution becomes homogeneous when about 20 cc. of acetic anhydride has reacted. At the end, the colorless mixture is warmed gently for an hour and poured over cracked ice. The solution is partially neutralized by stirring in solid sodium bicarbonate and the precipitated sirup soon becomes crystalline; yield, 45 g. or 48% of the theoretical. Tetraacetyl-xylonic nitrile is recrystallized from absolute alcohol as triangular plates of m. p. 81–82° (corr.) and rotation +50.3° (0.7615 g. in 25 cc. of chloroform soln., 3.06° to the right, 2-dm. tube).[9]

***d*-Threose Diacetamide.**—Thirty grams of tetraacetyl-*d*-xylonic nitrile is mixed with 300 cc. of concentrated aqua ammonia (28–29%), warmed on a water-bath until the solid is all dissolved and allowed to stand for three hours. The solution is then concentrated *in vacuo* to a thick sirup, taken up in aqua ammonia and reconcentrated. The final thick sirup is dissolved out of the flask with absolute alcohol, ether is added to turbidity and the mixture is refrigerated for forty-eight hours; yield, 16.5 g. or 78% of the theoretical. The substance is recrystallized by dissolving in two volumes of warm 75% alcohol, filtering through carbon and adding an equal volume of absolute alcohol. It crystallizes slowly, forming clear, sharp needles or prisms in rosets. When purified these show m. p.

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(8) Deulofeu, Wolfrom, Cattaneo, Christman and Georges, THIS JOURNAL, **55**, 3488 (1933).

(9) *Cf.* Deulofeu, *Nature*, **131**, 548 (1933).

165–167° (corr.) and rotate −10.86° (0.5979 g. in 25 cc. of aqueous soln.; 0.519° to the left; 2-dm. tube). The substance sometimes requires frequent recrystallization to get rid entirely of a gummy substance which contaminates the crude compound. A sample of the compound made by deacetylating purified triacetyl-*d*-threose diacetamide rotated −10.8° (0.9495 g. in 25 cc. of aqueous soln., 0.817° to the left; 2-dm. tube). The substance is exceedingly soluble in water, nearly insoluble in absolute alcohol, methanol, ether and chloroform.

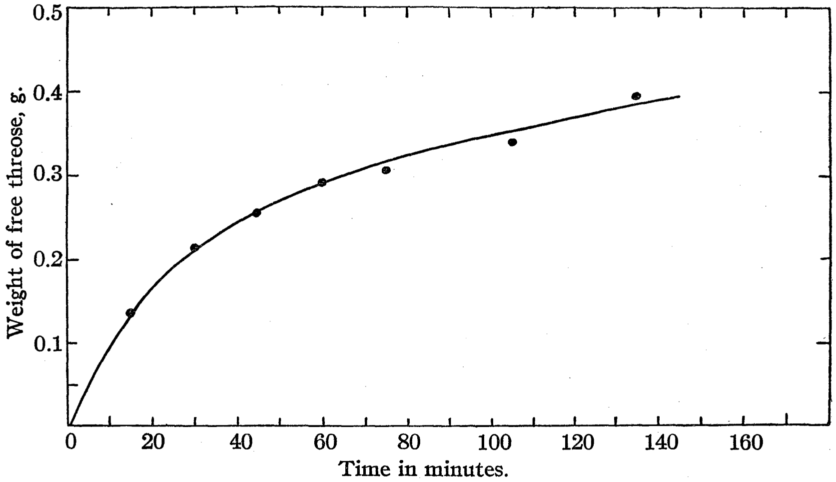

Fig. 1.—Hydrolysis of threose diacetamide by 0.100 *N* sulfuric acid (iodine titration).

Anal. Calcd. for $C_8H_{16}O_5N_2$: N, 12.72. Found: N, 12.65, 12.72.

Triacetyl-*d*-threose Diacetamide.—Two grams of purified threose diacetamide is treated with 10 cc. of acetic anhydride and 10 cc. of pyridine, warmed until the crystals dissolve and let stand overnight. The mixture is filtered through carbon, then concentrated to dryness *in vacuo*. The remaining material which crystallizes solid in the flask is dissolved in absolute alcohol and reconcentrated to dryness to remove additional pyridine; then the crystals are dissolved out of the flask with absolute alcohol, from which clear needles separate on the addition of ether. Recrystallized from the same solvents until free from pyridine, the substance shows m. p. 179–180° (corr.) and rotates +74.2° (0.3434 g. in 25 cc. of chloroform; 2.04° to the right; 2-dm. tube). The crystals are fairly soluble in water and alcohol, soluble in chloroform and practically insoluble in ether.

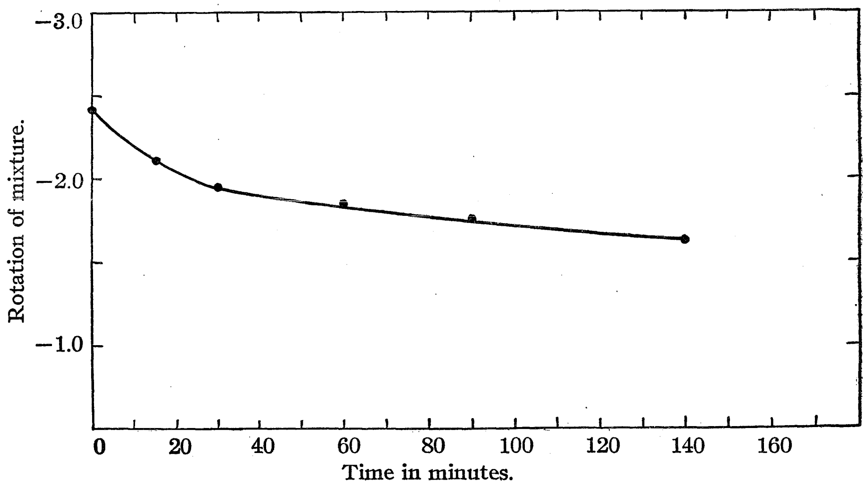

Fig. 2.—Hydrolysis of threose diacetamide by 0.100 *N* sulfuric acid (change of rotation).

Anal. Calcd. for $C_{14}H_{22}O_8N_2$: N, 8.10; acetyl, 37.29. Found: N, 8.17, 8.17; acetyl, 37.18, 37.14.

Hydrolysis of *d*-Threose Diacetamide.—After showing by control experiments that threose may be titrated quantitatively with hypoiodite, and that threose diacetamide and free acetamide are unaffected by the reagents used, the following experiment was performed. A sample of 0.9437 g. of pure threose diacetamide was made up to 50 cc. with 0.100 *N* sulfuric acid. This solution was poured by funnel into a 200-cc. flask submerged to the middle of the neck in a bath of boiling water and the time noted. At intervals 5-cc. samples were removed by pipet and run into Erlenmeyer flasks containing 5 cc. of water and 2 cc. of 15% sodium carbonate each, the time being noted and a glass stopper inserted as promptly as possible. As soon as convenient, the free sugar in these solutions was determined by adding 25 cc. of iodine–potassium iodide solution, letting stand twenty minutes in the dark, acidifying with 3 cc. of 10% sulfuric acid and titrating back with standard sodium thiosulfate using starch paste indicator. The results are shown in the curve of Fig. 1. The curve corresponds approximately to the unimolecular law; on the assumption that the reaction is unimolecular, *k* (minutes and decimal logarithms) = 0.0063 ± 0.0013.

The Equilibrium Rotation of *d*-Threose.—At withdrawal of the last sample, the whole solution was cooled and its rotation at 20° was found by two independent observers to be −0.29°. Titration showed 0.0395 g. of tetrose in 5 cc., equivalent to 0.395 g. of tetrose in a volume of 50 cc., after one hundred and thirty-five minutes of hydrolysis at 100°. At complete hydrolysis 0.515 g. of tetrose would be present. At one hundred and thirty-five minutes, therefore, 76.7% of the threose diacetamide was hydrolyzed and 23.3% or 0.220 g. unchanged. The specific rotation of threose diacetamide is −10.9°. Therefore

$$-10.9° = X \times 50/2 \times 0.220$$

and $X = -0.096°$, the rotation due to unchanged threose diacetamide. Subtracting this from −0.29°, we find −0.198° contributed by the 0.395 g. of tetrose present in 50 cc.

$$[\alpha]^{20}\text{D} = -0.198° \times 50/2 \times 0.395 = -12.5°$$

This value for the specific rotation of *d*-threose agrees well with the value −12.3° announced in the previous paper. No difference between the rotations in pure water and in dilute acid was observed.

Change in Rotation during Hydrolysis of *d*-Threose Diacetamide.—A sample of 0.9843 g. of threose diacetamide was made up to 50 cc. in a calibrated flask with 0.100 *N* sulfuric acid and poured at a noted time into a flask submerged in boiling water. At noted intervals, the whole solution was cooled and its rotation read in a 4-dm. tube. The curve of Fig. 2 shows the readings obtained. At the time of the last reading, a titration was made showing the presence of 0.4056 g. of free tetrose in 50 cc. (75.5% hydrolysis) and 0.2411 g. of diacetamide remaining. The rotation due to the latter was −0.21° and that due to the sugar −0.35°, which corresponds to a specific rotation of −10.8°. The velocity constant could not be determined with great accuracy because the range of the change is so small but the value of *k* (minutes and decimal logs) calculates to 0.0093 ± 0.0023, which is of the same order of magnitude as the constant more accurately determined by the other method.

Dibenzylidene-*d*-threitol.—The solutions remaining from the hydrolysis experiments were combined, freed from sulfuric acid with barium hydroxide and repeatedly extracted with ether to remove acetamide. Then the solution was shaken with 2% sodium amalgam under mildly acid conditions until 100 g. of amalgam had been used and all reducing action had disappeared. The dibenzylidenethreitol was prepared just as described in the previous paper.[2] After several slow recrystallizations from warm chloroform by the addition of benzene, the new sample melted from 220–222° (corr.). The old sample from threose acetate, after several recrystallizations, melted from 218–222° (corr.) and an intimate mixture of the two gave m. p. 220–223° (corr.). The new sample, after the first recrystallization, rotated −77.9° (0.1167 g. in 25 cc. of chloroform soln.; 0.727° to the left; 2-dm. tube). The value previously found was −78.2°.

***d*-Erythrosazone.**—A small volume of hydrolysate, when treated with phenylhydrazine in the usual way,[2] yielded *d*-erythrosazone of m. p. 164° (corr.).

We wish to express to Dr. C. S. Hudson, Chief of the Division of Chemistry, deep gratitude for the sympathetic and patient interest which permitted these investigations to be carried out. Our thanks are due also to Mr. C. G. Remsburg of this Laboratory for nitrogen analyses.

Summary

1. Wohl's method of degrading sugars has been applied to *d*-xylose, and *d*-threose diacetamide has been prepared in relatively large quantity.

2. This *d*-threose derivative is found to have a specific levorotation in water of −11°, which is opposite in sign to that indicated by Deulofeu, who found −7.68° for *l*-threose diacetamide.

3. Quantitative hydrolysis of *d*-threose diacetamide with 0.100 *N* sulfuric acid at 100° shows a rate corresponding to *k* (minutes and decimal logs) = 0.0063 ±0.0013 and permits determination of the equilibrium specific rotation of *d*-threose in dilute acid as −12.5°, which is in agreement with our previously determined value and contrary to the findings of W. Freudenberg and Deulofeu.

4. During hydrolysis of *d*-threose diacetamide, the rotation is found to drift toward a smaller levorotation, in opposition to the reported observation of Deulofeu, and in agreement with the rotations determined by us for *d*-threose diacetamide and for *d*-threose.

5. The formation of a *tri*acetate by threose diacetamide indicates an aldehydo structure for this compound.

6. The preparation of *d*-erythrosazone and dibenzylidene-*d*-threitol from threose diacetamide hydrolysates, shows the identity of the sugar formed with that obtained by deacetylation of *d*-threose triacetate.

WASHINGTON, D. C.

RECEIVED AUGUST 2, 1935

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

The Action of Hydrogen Peroxide upon Simple Carbon Compounds. III. Glycolic Acid[1]

BY H. SHIPLEY FRY AND KENNETH L. MILSTEAD[2]

The action of hydrogen peroxide upon glycolic acid has been studied extensively and a notable variety of apparently contradictory results has been recorded. This is due to the widely different experimental conditions under which the action has been investigated and to the omission of a standardized quantitative experimental method of procedure whereby the yields of each and every product of the reaction have been checked with the quantities of hydrogen peroxide participating in the severally occurring reactions.

A brief review of the several reactions recorded by previous investigators is pertinent to the present study, the purpose of which is to *correlate quantitatively the extent of the occurrence of the most likely reactions with the amounts of the hydrogen peroxide therein participating.*

Fenton and Jones[3] reported a quantitative yield of glyoxylic acid when hydrogen peroxide reacted with glycolic acid in the presence of ferrous salts.

Heimrod and Levene,[4] with 30% hydrogen peroxide in alkaline solution, obtained formic, carbonic and glyoxylic acids.

Dakin[5] reported that glycolic acid in the presence of ferrous sulfate gave a small amount of glyoxylic acid, the main product being formaldehyde which was almost entirely oxidized to formic acid. It should here be noted that Dakin did not mention the formation of hydrogen, which would be an expected product of the reaction if formaldehyde is an intermediate product, in conformity with the established equation[1] $2HCHO + H_2O_2 \longrightarrow 2HCOOH + H_2$.

Spoehr[6] found that glycolic acid in alkaline solution was partly converted into equimolecular quantities of formic and carbonic acids, but, in the presence of ferrous sulfate, carbonic acid was much in excess. This indicated further oxidation of the intermediately formed formic acid. Spoehr made no mention of the formation of hydrogen but maintained, as did others, that glyoxylic acid was the first intermediate product of oxidation.

Wieland[7] detected glyoxylic, formic and carbonic acids and formaldehyde in the reaction mixtures. He also observed the evolution of hydrogen and naturally assumed that its formation was due to a secondary reaction between the intermediately formed formaldehyde and hydrogen peroxide.

Hatcher and Holden,[8] in attempting to clear up the conflicting opinions of previous investigators, found neither formaldehyde nor hydrogen but maintained that glycolic acid is first converted into a peracid, which, in turn, gives glyoxylic, formic and ultimately carbonic, acids.

Theoretical

From a review of the previous investigations, it follows that the present quantitative study of the action of hydrogen peroxide upon glycolic acid should not only explain the formation of the variously reported intermediate products, but also correlate quantitatively the yields of each of the recovered products of the reaction, notably hydrogen, formic and carbonic acids, with the amounts of hydrogen peroxide initially used which function in the formation of these products, both respectively and totally.

To this end, an explanatory scheme of reactions, based upon and serving further to illustrate the previously published *perhydrolysis* reaction mechanism of Fry and Payne,[1] is proposed. The equations for the involved reactions are recorded in formulas sufficiently graphic to illustrate the perhydrolysis type of reaction.

The first product of the reaction of hydrogen peroxide upon glycolic acid is generally conceded to be glyoxylic acid, which, according to Hatcher and Holden,[8] is preceded by (a) the formation and (b) the decomposition of perglycolic acid, thus

$$CH_2OHCOOH + HOOH \longrightarrow CH_2OOHCOOH + H_2O \quad (a)$$

$$CH_2OOHCOOH \longrightarrow CHOCOOH + H_2O \quad (b)$$

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[1] Fry and Payne, THIS JOURNAL, **53**, 1973, 1980 (1931); Part I. Methyl Alcohol, Formaldehyde and Formic Acid; Part II. The Mechanism of the Reactions.

[2] Synopsis of Doctorate Thesis of Kenneth L. Milstead.

[3] Fenton and Jones, *J. Chem. Soc.*, **77**, 69 (1900).

[4] Heimrod and Levene, *Biochem. Z.*, **29**, 46 (1900).

[5] Dakin, *J. Biol. Chem.*, **1**, 271 (1906); *ibid.*, **4**, 91 (1908).

[6] Spoehr, *Am. Chem. J.*, **43**, 248, 253 (1910).

[7] Wieland, *Ann.*, **436**, 253 (1924).

[8] Hatcher and Holden, *Trans. Roy. Soc. Can.*, **20**, 395, 407 (1926).

$$\Sigma(a, b)\ CH_2OHCOOH + HOOH \longrightarrow CHOCOOH + 2H_2O \quad (c)$$

The glyoxylic acid thus formed undergoes perhydrolysis

$$CHOCOOH + HOOH \longrightarrow HCOOH + [HOCOOH \longrightarrow H_2O + CO_2] \quad (d)$$

$$\Sigma(c, d)\ CH_2OHCOOH + 2H_2O_2 \longrightarrow HCOOH + CO_2 + 3H_2O \quad (A)$$

Thus, glycolic acid, through the intermediate formation of glyoxylic acid, may yield not only formic and carbonic acids, but it may also undergo another concomitant reaction, namely, a direct perhydrolysis to yield formaldehyde and carbonic acid

$$CH_2OHCOOH + HOOH \longrightarrow HCHO + H_2O + [HOCOOH \longrightarrow CO_2 + H_2O] \quad (e)$$

Formaldehyde, in turn, reacts with hydrogen peroxide to give formic acid and hydrogen

$$2CH_2O + H_2O_2 \longrightarrow 2HCOOH + H_2 \quad (f)$$

The summation of equation (e), doubled, and equation (f) represents the conversion of glycolic acid to formic and carbonic acids and hydrogen.

$$\Sigma(e, f)\ 2CH_2OHCOOH + 3H_2O_2 \longrightarrow H_2 + 2HCOOH + 2CO_2 + 4H_2O \quad (B)$$

This derivation of each of the summation equations, (A) and (B), for the two principal concomitant reactions, indicates the conversion of glycolic acid to the final products, formic and carbonic acids. Equation (B) indicates the formation of hydrogen also.

The marked susceptibility of oxidation of formic acid to carbonic acid by hydrogen peroxide explains our quantitative observations, subsequently recorded, that in all experimental runs, with varied concentrations of hydrogen peroxide, the yields of carbonic acid (carbon dioxide) were greater than the yields of formic acid. This secondary reaction of intermediately formed formic acid necessitates the postulation of a third equation

$$HCOOH + HOOH \longrightarrow H_2O + [HOCOOH \longrightarrow H_2O + CO_2] \quad (C)$$

The generally reported final products of the action of hydrogen peroxide upon glycolic acid—formic and carbonic acids and hydrogen—have been identified, and their quantitative yields have been determined in the present investigation. Their formation is explained in terms of three reactions represented by the above derived equations (A), (B), and (C). The first two will be shown to be concomitant, while the third is a secondary reaction.

In order to correlate quantitatively the yields of each of the three products of the reaction with the quantities of hydrogen peroxide *active in their formation*, both respectively and collectively, it was necessary to determine how much of the hydrogen peroxide initially used did not participate in reactions (A), (B) and (C). This is the hydrogen peroxide which suffered direct decomposition into water and oxygen. The quantity of oxygen liberated in each experimental run would be equivalent to this inactive quantity of hydrogen peroxide. The difference between this and the initially used quantity is the active hydrogen peroxide. Hence, it was necessary in all experimental runs and related calculations to include a fourth equation (D) for the concomitant reaction

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \quad (D)$$

It is highly probable that the extents of the occurrence, or the rates of reactions A, B, C and D, are different in alkaline solution, in acid solution and in the presence of ferrous salts, as the observations of previous investigators apparently indicate. It should here be noted, however, that the present study is limited to the determination of the extent of the occurrence of the reactions A, B, C, and D *in acid solution*, with increasing concentrations of hydrogen peroxide, as described in the experimental part.

Experimental

The train of apparatus and the experimental method of procedure employed in this study have been previously described in detail by Fry and Payne.[1]

In five successive experimental runs (I–V), each conducted in duplicate, one-quarter mole of pure glycolic acid was added to successively increased quantities of 30% hydrogen peroxide, free from organic preservatives, specially prepared by the Roessler and Hasslacher Chemical Company, namely, (I) one-eighth, (II) one-fourth, (III) one-half, (IV) three-fourths, and (V) one mole, respectively. Each of these mixtures of hydrogen peroxide and glycolic acid was further acidified by the addition of 2.16 g. of sulfuric acid, diluted with water to a total volume of 125 cc., and heated continuously for nine hours in a 250-cc. round-bottomed Pyrex flask submerged in a water-bath at 100°.

The hydrogen formed (equation B) and the oxygen evolved (equation D) were collected in

TABLE I

MOLAR QUANTITIES OF HYDROGEN PEROXIDE AND GLYCOLIC ACID USED AND OF PRODUCTS FORMED

Run	1 Initial H_2O_2 mole	2 Initial $CH_2OHCOOH$, mole	3 HCOOH found, mole	4 H_2CO_3 found, mole	5 H_2 found, mole	6 O_2 found, mole	7 $CH_2OHCOOH$ found, mole
Ia	0.1250	0.2500	0.0142	0.0267	0.0024	0.0410	0.229
Ib	.1250	.2500	.0141	.0268	.0023	.0408	.225
IIa	.2500	.2500	.0271	.0566	.0055	.0801	.2044
IIb	.2500	.2500	.0246	.0563	.0047	.0799	.2106
IIIa	.5000	.2500	.0353	.1000	.0083	.1786	.1787
IIIb	.5000	.2500	.0339	.0979	.0087	.1726	.1781
IVa	.7500	.2500	.0374	.1530	.0134	.2605	.158
IVb	.7500	.2500	.0363	.1540	.0132	.2622	.156
Va	1.0000	.2500	.0399	.194	.0138	.3489	.1270
Vb	1.0000	.2500	.0416	.208	.0161	.3447	.1219

the gasometer at the end of the apparatus train. The total yields of each gas, determined by standard methods of gas analysis, serve to measure the extent of the occurrence of reactions represented by equations (B) and (D).

The total carbonic acid formed (equations A, B, and C) was calculated from the amounts of carbon dioxide absorbed in weighed ascarite towers.

The resultant reaction mixtures, containing practically only formic acid (equations A and B) and some unaffected glycolic acid, gave the fuchsin test for traces of aldehydes, the quantities of which, however, were too small to be determined quantitatively. Tests for the presence of glyoxylic and oxalic acids were negative.

Aliquot portions of the reaction mixture were titrated for total acidity with standard alkali. Subtracting the acidity due to the initially added sulfuric acid, gave the acidity due to the formic acid and unreacted glycolic acid. The yields of formic acid, determined gravimetrically by the standard mercuric chloride method, permitted calculations, by difference, of the quantities of glycolic acid remaining unchanged in the reaction mixtures.

In calculating the extents of the occurrence of the two principal concomitant reactions, equations (A) and (B), and the secondary reaction, equation (C), the quantity of glycolic acid which reacts to give hydrogen, as well as some of the formic and carbonic acids, is based upon the yield of hydrogen in conformity with equation (B). The remainder of the glycolic acid reacting serves as the basis for calculating the yields of formic and carbonic acids in conformity with equation (A). The difference between the sum of the yields of carbonic acid, obtained in conformity with equations (A) and (B), and the total yield of carbonic acid, measures the extent of the occurrence of the secondary reaction, equation (C).

All of the analytical data thus secured are embodied in the tables. For convenience in reference thereto, the equations for the four postulated reactions are herewith retabulated.

$$CH_2OHCOOH + 2H_2O_2 \longrightarrow HCOOH + CO_2 + 3H_2O \quad (A)$$

$$2CH_2OHCOOH + 3H_2O_2 \longrightarrow H_2 + 2HCOOH + 2CO_2 + 4H_2O \quad (B)$$

$$HCOOH + H_2O_2 \longrightarrow CO_2 + 2H_2O \quad (C)$$

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \quad (D)$$

Table I records the molar quantities of the hydrogen peroxide and glycolic acid initially present in the reaction mixtures of the five successive duplicate sets of runs, and the molar yields of the respective resultant products.

Table II records in columns 1, 2, 3 and 4, the percentages of hydrogen peroxide equivalent to the products of the reaction as calculated from the respective equations for the proposed reactions. Column 5 notes the sum total percentage of hydrogen peroxide used.

TABLE II

PERCENTAGE QUANTITIES OF HYDROGEN PEROXIDE USED EQUIVALENT TO YIELDS OF PRODUCTS FORMED

Run	1 % $H_2O_2 \Leftrightarrow HCOOH$ Eq. (A)	2 % $H_2O_2 \Leftrightarrow H_2$ Eq. (B)	3 % $H_2O_2 \Leftrightarrow H_2CO_3$ Eq. (C)	4 % $H_2O_2 \Leftrightarrow O_2$ Eq. (D)	5 Total % $H_2O_2 \Leftrightarrow$ Eqs. (A, B, C, D)
Ia	25.44	5.759	5.200	65.60	102.00
Ib	25.28	5.520	5.040	65.28	101.12
IIa	24.72	6.601	5.921	64.07	101.31
IIb	24.80	5.640	6.322	63.93	100.69
IIIa	20.40	4.979	6.460	71.44	103.28
IIIb	19.40	5.223	6.398	69.04	100.06
IVa	18.13	5.359	7.68	69.45	100.62
IVb	18.40	5.279	7.40	69.90	100.98
Va	17.88	4.14	7.71	69.78	99.51
Vb	18.56	4.83	8.34	68.94	100.67

Table III records in columns 1 and 2 the percentage quantities of glycolic acid reacting according to equations (A) and (B), respectively. Column 3 gives the percentages of the initially used glycolic acid which did not react. The sums of the percentages recorded in columns 1, 2 and 3, given in column 4, account for all of the initially used glycolic acid, active and non-reactive.

Table III

Percentage Quantities of Glycolic Acid, Reactive, Non-reactive, and Total

Run	1 % CH_2OH-COOH $\Leftrightarrow$ HCOOH Eq. (A)	2 % CH_2OH-COOH $\Leftrightarrow H_2$ Eq. (B)	3 % CH_2OH-COOH unchanged	4 Total % CH_2OH-COOH $\Sigma(1, 2, 3)$
Ia	6.630	1.920	91.60	99.88
Ib	6.322	1.841	90.01	98.17
IIa	12.36	4.400	81.75	98.51
IIb	12.40	3.760	84.24	100.40
IIIa	20.40	6.640	71.48	98.52
IIIb	19.40	6.960	71.24	97.60
IVa	27.20	10.72	63.22	101.14
IVb	27.60	10.56	62.44	100.60
Va	35.76	11.04	50.81	97.61
Vb	37.12	12.88	48.75	98.75

Table IV records the percentage yields of carbon dioxide as calculated in relation to the reactions represented by equations (A), (B), and (C). The relative yields facilitate comparisons of the extent of the occurrence of each of these reactions as affected by the increasing concentrations of hydrogen peroxide used in the successive runs, I–V.

Table IV

Percentage Yields of Carbon Dioxide in Relation to Occurring Reactions

Run	1 % CO_2 Eq. (A)	2 % CO_2 Eq. (B)	3 % CO_2 Eq. (C)
Ia	58.80	17.98	23.22
Ib	58.96	17.17	23.89
IIa	54.61	19.44	25.97
IIb	55.07	16.69	28.24
IIIa	51.00	16.60	32.40
IIIb	49.53	17.77	32.68
IVa	44.58	17.52	37.90
IVb	44.54	17.14	38.32
Va	46.08	14.22	39.69
Vb	44.61	15.48	39.90

A survey of the analytical data of the above tables in relation to the derived equations for the reactions assumed to occur leads to the summary and conclusions given below.

Grateful acknowledgments are extended to Mrs. Ernst Twitchell, whose renewal of the Ernst Twitchell Fellowship in Chemistry made this study possible, and to the Roessler and Hasslacher Chemical Company for kindly donating the specially prepared hydrogen peroxide used in this investigation.

Summary and Conclusions

1. Since the ratio of the yields of formic acid to those of hydrogen (Table I, columns 3 and 5) were invariably greater than 2:1, which ratio, according to the single equation (B), is 2:1, it follows that the reactions represented by equations (A) and (B) were concurrent.

2. The extents of the occurrence of the reactions represented by equations (A), (B), and (C) *with increasing concentrations of hydrogen peroxide* are shown by the data in columns 1, 2, and 3, respectively, of Table II, and likewise columns 1, 2, and 3, respectively, of Table IV, to be as follows: (A) shows a tendency to decrease; (B), small variations; and (C), a tendency to increase.

3. The sums of the percentage quantities (Table II) of the hydrogen peroxide *active* in the several reactions, equations (A), (B), and (C), and the *inactive* or directly decomposed hydrogen peroxide, equation (D), are, within the limits of experimental error, practically 100% of the initial quantities of the hydrogen peroxide employed in each experimental run.

4. In parallel with (3), the sums of the percentage quantities (Table III) of glycolic acid oxidized, equations (A) and (B), and recovered unchanged, are, within the limits of experimental error, practically 100% of the initial quantities of the glycolic acid employed in each experimental run.

5. The above results, particularly (3) and (4), serve to check quantitatively the accuracy not only of the experimental method employed, but also of the equations derived for the three reactions assumed to occur, and the extents of their occurrence, respectively, when hydrogen peroxide reacts with glycolic acid.

Cincinnati, Ohio Received July 22, 1935

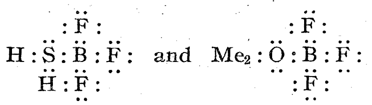
[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Thermal Analysis of the System Argon–Boron Trifluoride. Compounds with the Inert Gases of the Atmosphere[1,2]

BY HAROLD SIMMONS BOOTH AND KARL STUART WILLSON

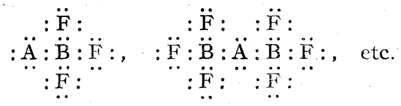
Although numerous attempts have been made to prepare compounds of the rare gases, practically all investigations have served only to show the inertness of these elements. Villard,[3] however, in 1896, reported a very unstable hydrate of argon, and since then hydrates of krypton and xenon[4] have been reported.

For some time this Laboratory has been studying compounds formed by boron trifluoride in which boron acts as acceptor for electrons from an element in another compound, usually an element with a completed octet such as oxygen in methyl ether and sulfur in hydrogen sulfide,[5] *i. e.*



$$\begin{array}{l} \phantom{\mathrm{H}:\ddot{\mathrm{S}}:}:\ddot{\mathrm{F}}: \\ \mathrm{H}:\ddot{\mathrm{S}}:\ddot{\mathrm{B}}:\ddot{\mathrm{F}}: \\ \phantom{\mathrm{H}:}\mathrm{H}:\ddot{\mathrm{F}}: \end{array} \quad \text{and} \quad \begin{array}{l} \phantom{\mathrm{Me_2}:\ddot{\mathrm{O}}:}:\ddot{\mathrm{F}}: \\ \mathrm{Me_2}:\ddot{\mathrm{O}}:\ddot{\mathrm{B}}:\ddot{\mathrm{F}}: \\ \phantom{\mathrm{Me_2}:\ddot{\mathrm{O}}:}:\ddot{\mathrm{F}}: \end{array}$$

It seemed reasonable to expect therefore that under the right conditions boron trifluoride could likewise accept electrons from elements such as argon which have self-contained octets, *i. e.*



$$\begin{array}{l} \phantom{:\ddot{\mathrm{A}}}:\ddot{\mathrm{F}}: \\ :\ddot{\mathrm{A}}:\ddot{\mathrm{B}}:\ddot{\mathrm{F}}:, \\ \phantom{:\ddot{\mathrm{A}}}:\ddot{\mathrm{F}}: \end{array} \quad \begin{array}{l} \phantom{:\ddot{\mathrm{F}}}:\ddot{\mathrm{F}}: \quad :\ddot{\mathrm{F}}: \\ :\ddot{\mathrm{F}}:\ddot{\mathrm{B}}:\ddot{\mathrm{A}}:\ddot{\mathrm{B}}:\ddot{\mathrm{F}}:, \\ \phantom{:\ddot{\mathrm{F}}}:\ddot{\mathrm{F}}: \quad :\ddot{\mathrm{F}}: \end{array} \quad \text{etc.}$$

Preliminary Study.[6]—Preliminary experiments were made with an apparatus similar to that used for thermal analysis of the systems mentioned above, save that the freezing points were measured by a two-junction copper–constantan thermocouple recorded by a special Leeds and Northrup Micromax potentiometer.

The first appearance of crystals on cooling was established in three ways: by the appearance of points of light in the field when the cell was placed between crossed Nicols, by the inflection in the cooling curves recorded on the potentiometer, and visually. It was found that the three methods of observation checked. Freezing point curves, one of which is shown in Fig. 1, revealed maxima and minima indicating compound formation corresponding to $A\cdot8BF_3$ and $A\cdot16BF_3$. However, the relatively large volume in the gas space above the liquid mixture permitted some segregation of the mixture, thus displacing the curve.

This was finally overcome by adopting the basic design of the Cailletet apparatus, using a fine capillary connecting tube and a relatively large cell similar to that used earlier in this Laboratory for determining the critical phenomena of pure gases[7] and gas mixtures.[8]

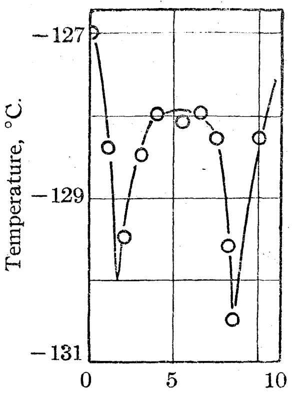


Fig. 1.—Preliminary freezing points.

Apparatus.—The all glass apparatus for preparing the samples is shown in Fig. 2. Cailletet sample tubes of Pyrex glass were joined to the system by the ground glass conical joints (J). The sample tube (L) had a volume of about 100 cc. and the cell itself where the phenomena were to be observed had a volume from 0.1 to 0.5 cc. depending on the composition of the mixture being studied. If the cells were too large, the mercury would freeze in the capillary above the cell before many points had been determined, and if the cells were too small, liquid would rise into the capillary, adequate stirring could not be obtained and erroneous results would be secured.

The mixture in the cell was stirred by the glass enclosed iron wire actuated by the electromagnets shown in Fig. 3. The lower magnet was found helpful in securing positive stirring action at the freezing point and at other points where the liquid became viscous.

Pressure was measured by a differential dead-weight gage used by Booth and Swinehart[7] which under the conditions of this investigation was observed to ±0.1 atm.

Temperature was recorded by a special high speed, high precision Leeds and Northrup Micromax potentiometer using copper–constantan thermocouples described later.

Ordinary stopcock grease is attacked by boron trifluoride but a mixture of four parts of white vaseline and one

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[1] From a part of a thesis submitted by K. S. Willson to the Graduate Faculty of Western Reserve University, May, 1935, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] On the advice of the Editor we withheld publication of a preliminary note submitted July 17, 1932.

[3] Villard, *Compt. rend.*, **123**, 377 (1896).

[4] DeForcrand, *ibid.*, **176**, 355 (1923); **181**, 15 (1925).

[5] Germann and Cleaveland, *Science*, [2] **53**, 582 (1922); Germann and Booth, *J. Phys. Chem.*, **30**, 369 (1926).

[6] During the preliminary part of this investigation, we enjoyed the collaboration of Mr. M. J. Bahnsen of this Laboratory.

[7] Booth and Carter, *J. Phys. Chem.*, **36**, 1359 (1932); Booth and Swinehart, THIS JOURNAL, **57**, 1337 (1935).

[8] Booth and Carter, *J. Phys. Chem.*, **34**, 2801 (1930).

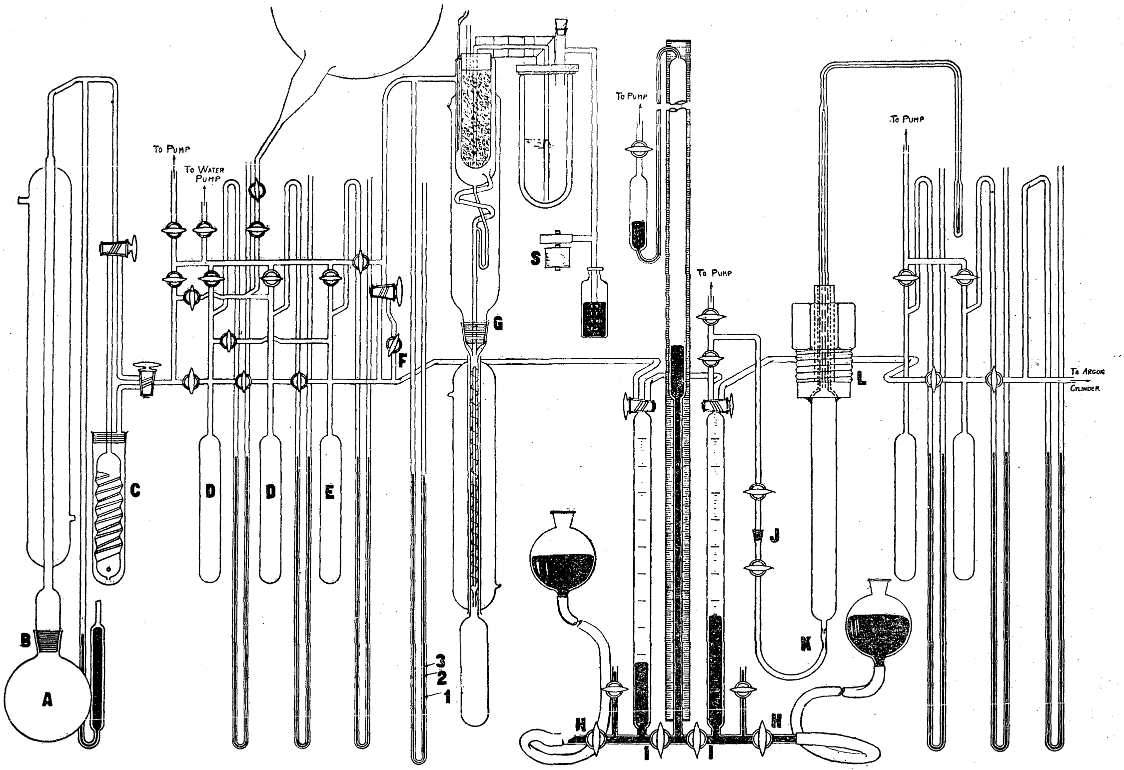

Fig. 2.

part of paraffin, saturated with boron trifluoride at 140°, then evacuated and 5% beeswax added, was found to be satisfactory.

Preparation of the Samples.—The boron trifluoride was prepared from sodium fluoborate (300 g.), boric oxide (50 g.) and sulfuric acid (300 cc.). The solid chemicals were mixed, placed in the flask (A) (Fig. 2), the acid added and the liquid mass thoroughly mixed. The flask was joined to the system by the greased conical joint (B). A rubber sleeve was placed over the joint and water circulated around it in an inverted bottle with bottom removed. The water prevented melting of the grease with subsequent sticking or leaking at the joint.

Since any silicon tetrafluoride, formed from impurities in the sodium fluoborate, was evolved at room temperature and boron trifluoride was not, the tetrafluoride was largely removed along with air, by pumping the flask with the stopcocks turned to by-pass the wash-bottle (C). After rinsing the entire system, except the generating unit and wash-bottle (C), twenty times with dry, carbon dioxide-free air, the stopcocks were reversed to include the wash-bottle, and the charged flask heated, gently at first, to avoid frothing. The boron trifluoride generated passed through the water-cooled condenser, the wash-bottle filled with sulfuric acid saturated with boric oxide to remove water and hydrogen fluoride and, after discarding the first part of the generation product through the water pump, was condensed in the ampoules (D) by means of liquid nitrogen. This method gave little silicon tetrafluoride, and by distilling to (E) and then to the still pot at a low pressure and discarding the tailings, little of the tetrafluoride was carried into the still.

The boron trifluoride was purified in the distilling column (G) described by Booth and Stillwell.[9] By distilling at about 10 cm. pressure, the temperature was such that the vapor pressure of silicon tetrafluoride, the most probable impurity, was very small and the absence of this substance in the purified gas was doubly assured. The gas, after a single distillation in the column using great care to rinse the lines with the pure gas before collecting in the ampoule, was shown to be spectroscopically pure by Mr. H. M. Strong of the Physics Department at Ohio State University.

At the beginning of series D the still head cracked and a new head of simpler design[10] was used with satisfactory results.

In operation, the boron trifluoride was permitted to reflux about fifteen minutes after any air blocks had been removed. The gas was then bled off very slowly by "cracking" the stopcock at (F), being sure that a high reflux ratio was maintained. After discarding the first few cc. of the solid distillate, about one-fifth of the gas was condensed in the nearest ampoule (D), then the middle three-fifths in the ampoule (E) where it was held until used to rinse the mixing apparatus and sample tubes, and to prepare the samples.

The argon, 99.9 + pure, was condensed from the cylinder into ampoules and then further purified by ampoule to ampoule distillation with generous discarding of first and last portions. After this treatment it was found to be spectroscopically free from nitrogen by Mr. Strong.

The purified gases were introduced into their respective

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[9] Booth and Stillwell, THIS JOURNAL, **56**, 1529 (1934).

[10] To be described shortly by Booth and Bozarth.

burets of the baro-buret which had been previously dried and rinsed with the pure gases, and the pressures and volumes recorded as described by Booth and Carter.[8]

After measuring each gas, thorough mixing was assured by forcing the gases alternately from one buret to the other.

Meanwhile, the sample tubes were rinsed twenty times with dry, carbon dioxide-free, air, being flamed while pumping, and were then rinsed twenty more times with pure boron trifluoride and argon, allowing the gases to remain in the tubes some time before pumping.

The gas mixture was introduced into a sample tube to a pressure a centimeter or two less than one atmosphere. Stopcocks above and below the conical joint (J) were closed, the sample tube removed from the apparatus, and the tube broken off under dry mercury at the constriction (K). The inner seal prevented bits of glass from rising into the body of the tube. The sample tube was then placed in the steel well as shown in Fig. 3, keeping the lower end under mercury, and screwed down onto the fiber gasket. After connecting the pump line, pressure was increased to test for leaks and weakness in the glass. After releasing the pressure, the bath was raised to surround the cell.

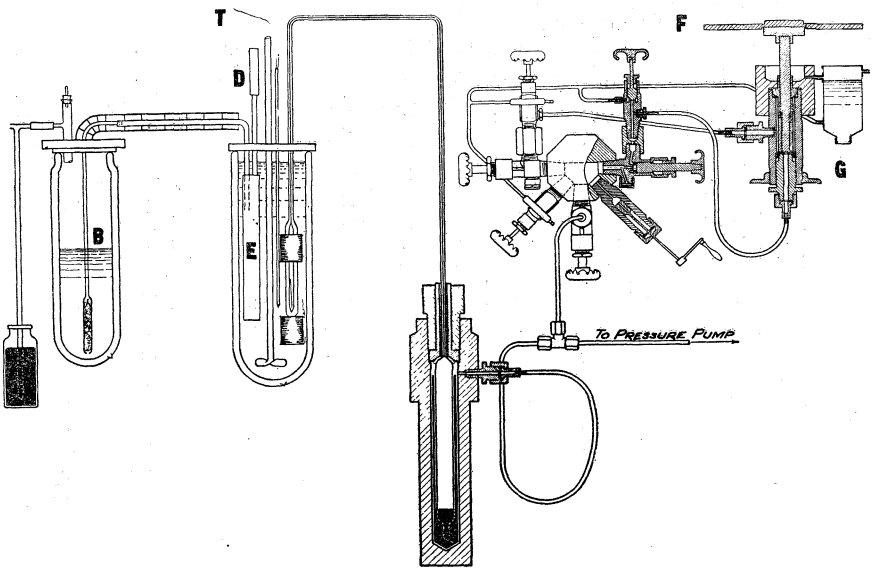


Fig. 3.

Experimental Procedure

For the freezing point determinations weights were placed on the piston of the dead weight gage and the pressure equilibrium established while the liquid butane bath was cooling. Liquid nitrogen was forced into the evaporator (E) (Fig. 3), rapidly at first, then slowly as the freezing point was approached. By adjusting a screw clamp at (D), cooling could be secured at less than 0.3° per minute, this having been found a sufficiently slow rate to prevent error due to lag in the cell, thermocouples or recorder. In the first determinations, a current was passed through a heater coil in the bath to adjust the rate of cooling, but this was later found unnecessary.

When the first crystals appeared, the temperature was noted. Since warming the sample after obtaining a freezing point would cause argon to boil off, giving rise to segregation, care was taken to raise the temperature as little above the freezing point as possible, usually not more than 3°. While the temperature was rising, more weights were placed on the piston, thus decreasing the volume of the gas and preventing segregation due to expansion. Pressure was increased and freezing points determined until the liquid rose into the capillary, preventing mixing, or until the mercury froze in the capillary.

The freezing point determinations were made in five different series.

Series A covered the preliminary work shown in Fig. 1, while series B, C, D and E were made with the Cailletet apparatus.

Series B includes all points measured by a two-junction thermocouple which had a total maximum error of ±0.4°. Ice served as the reference point. In series C, D and E greater precision was obtained by using a five-junction thermocouple with carbon dioxide snow as the reference point. The snow point was found to remain constant for long periods and was checked against an ice-bath by an identical five-junction thermocouple several times during a set of freezing point determinations. By this method a maximum error of ±0.2° in the differential temperature was secured although considerably greater accuracy was obtained since the final freezing point was the average of many values. The two and five-junction couples were also checked against each other.

The absolute temperature in the region of the freezing points was secured by comparing the couples with a platinum resistance thermometer, and by extrapolating from −123.3°, the freezing point of ether. The absolute temperature of the freezing points therefore probably shows the same order of error as the differential temperature.

After completing series C the entire purification apparatus was rebuilt to eliminate stopcock grease which had contaminated the lines. A new stopcock grease was made and new drying tubes installed. The five-junction thermocouple was recalibrated, found to check its previous value and series D and E undertaken. In series B and C, liquid nitrogen was forced into the evaporator (E) at a rapid cooling rate, adjusted by controlling the heat input of the heater. In series D and E the liquid nitrogen input was considerably slower and was adjusted to give the desired cooling rate without using the heater. The agreement between the values for the different series indicates the constancy of temperature maintained in the bath by means of the propeller, which was driven at 3600 r. p. m.

Before beginning series E every possible source of error was considered and all precautions for purity of the samples were redoubled. The cells were rinsed and flamed even more thoroughly, and the mercury used for the Cailletet well was run through a nitric acid tower and dried instead of merely washed and dried before each run.

To eliminate silicon tetrafluoride as much as possible even from the crude generation product which might contaminate the lines, fresh boron trifluoride was made using ammonium instead of sodium fluoborate. The ammonium fluoborate was recrystallized by cooling with agitation from a hot solution to give only a 50% yield, thus leaving the more soluble fluosilicates in the mother liquor.

In series D and E, before making up the samples the boron trifluoride was distilled in the column to a constant melting point measured in a cell similar to that used in the preliminary runs and stored under a mercury seal out of contact with stopcocks (not shown in Fig. 2).

TABLE I

FREEZING POINTS

Series B—Two-Junction Thermocouple

Mole % argon	Pressure, atm.	T., °C.
1.0	2.8	−130.6
2.0	3.8	131.2
3.0	2.3	130.6
	2.8	130.6
	4.0	130.4
	4.8	130.4
5.0	7.9	129.4
	9.8	129.4
	12.0	129.2
	14.1	129.2
18.5	27.9	129.2
	29.0	129.4
	33.0	129.2
	33.0	129.0
	36.7	128.8
	40.5	129.0
20.2	13.8	131.9
	30.6	130.0
	38.2	129.9
30.0 A	10.2	133.5 A
30.0 B	15.3	133.5 B
	25.5	132.3 A
	27.9	132.5 B
	39.3	131.7 A
	55.6	131.6 A
40.1 A	10.7	133.3 A
39.9 B	11.8	133.1 B
	11.9	133.1 A
	18.8	131.7 B
	20.3	131.9 A
	29.2	131.7 A
	31.1	131.7 A
	39.3	131.7 A
59.9	22.2	131.4
	24.5	131.4
	36.3	131.2

TABLE II

FREEZING POINTS

Series C—Five-Junction Thermocouple

Pressure, atm.	Temp., °C.
17.0 Mole % argon	
8.7	−131.2
14.0	130.1
19.4	129.5
21.3	129.4
26.7	129.0
29.5	128.6
33.0	128.6
52.5	128.3
18.5 Mole %	
9.6	131.8
12.3	131.1
19.0	129.9
32.3	129.3
19.9 Mole %	
12.9	131.3
15.6	130.9
19.4	130.5
22.8	130.3
24.5	130.3
28.2	130.1
32.3	129.8
34.0	129.6
21.3 Mole %	
8.9	131.5
11.6	131.2
15.4	130.3
15.4	130.1
18.9	129.3
19.7	129.3
20.6	129.1
22.7	129.0
22.9	129.3
24.6	129.0
25.5	129.0
27.0	129.2
28.7	129.0
29.2	129.0
32.3	129.1
32.3	128.6
34.7	129.0
34.7	128.5
22.9 Mole % argon	
9.0	−131.0
10.8	130.7
17.8	130.2
18.0	130.1
21.5	129.2
21.5	129.1
23.7	129.3
30.0	129.0
32.8	128.7
36.5	128.6
38.2	128.4
40.6	128.6
25.0 Mole %	
12.3	129.6
15.4	129.3
19.0	129.1
21.1	129.0
24.8	128.7
28.3	128.2
30.3	128.3
36.9	128.4
33.3 Mole %	
11.6	129.0
15.4	128.6
19.0	128.3
24.5	128.0
28.5	127.4
31.8	127.6
34.1	127.4
37.7	127.1
41.7	127.2
43.1	127.3
50.0 Mole %	
13.0	130.3
16.7	129.6
19.0	129.2
22.6	129.1
24.9	128.6
28.5	128.4
30.4	128.4
34.1	128.7
37.7	128.6

Results.—The freezing points are found to increase with increase in pressure at first and then become independent of further increase in pressure within the experimental limits. This is exactly what would be expected with unstable compounds. Thus, at low pressures, the compound formed will be appreciably dissociated, shifting the equilibrium

$$A + xBF_3 \rightleftharpoons A \cdot xBF_3$$

to the left. The A and BF_3 units acting as impurities in the compound $A \cdot xBF_3$, will lower its freezing point as shown in region A, Figs. 4–6. As the pressure is increased, the equilibrium will shift to the right and less A and BF_3 units will be present, hence the freezing point will be lowered to a lesser extent.

As more and more pressure is applied, the equilibrium will shift farther and farther to the right and the freezing point will be raised until the separate A and BF_3 particles are present in too small quantities to lower the freezing point appreciably. The freezing point will then, of course, become independent of further increase in pressure as shown in region B, Figs. 4–6. The normal effect of increase in pressure tending to change the melting point in the direction of decreasing vol-

TABLE III

FREEZING POINTS

Series D—Five-Junction Thermocouple

Press., atm.	Temp., °C.
1.3 Mole % argon	
3.2	−131.0
4.9	130.9
5.9	131.0
2.5 Mole %	
3.2	130.9
6.5 Mole %	
9.2	130.0
10.5	130.9
11.2	130.2
7.5 Mole %	
3.2	130.2
5.1	130.3
8.5 Mole %	
10.8	131.7
12.6	131.8
12.6	131.5
10.9 Mole %	
5.1	129.6
8.9	129.5
10.6	129.6
12.6	129.3
15.1	128.8
16.7	128.5
18.1	128.4
19.4	128.4
26.0 Mole %	
8.9	129.6
11.6	129.2
17.0	128.4
19.0	128.2
21.8	128.1
26.1	128.2
28.3	128.1
32.4	128.2[a]
36.0	128.2
42.9 Mole %	
17.4	130.6
19.5	130.2
21.2	130.1
26.6	130.1
28.9	130.0
30.5	130.0
34.5	129.5[a]
38.0	129.1
39.8	129.1
46.1 Mole %	
9.3	−131.3
15.4	130.3
17.1	130.2
19.5	129.7
21.2	129.7
24.3	129.6
27.7	129.3
29.6	129.4
30.5	129.0
34.1	129.0
34.8	129.0
35.5	128.8
38.1	128.8[a]
39.7	128.8
50.0 Mole %	
11.6	130.9
15.4	130.1
19.5	130.0
21.2	129.7
25.3	129.4
28.9	128.9
30.4	128.8
34.1	128.8
38.0	128.6[a]
57.2 Mole %	
8.9	131.4
11.6	130.8
17.1	130.5
19.5	129.8
22.9	129.5
27.0	129.4
34.6	129.0
38.0	128.4[a]

TABLE IV

FREEZING POINTS

Series E—Five-Junction Thermocouple

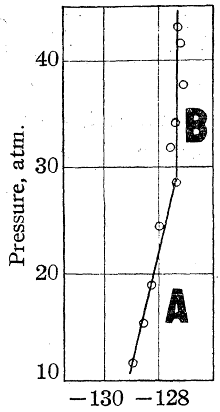
Press., atm.	Temp., °C.
12.5[b] Mole % argon	
7.3	−130.5
8.7	130.4
11.0	130.2
15.6	129.5
19.2	129.1
20.8	128.8
22.7	128.8
13.5[b] Mole %	
8.7	130.7
9.9	130.9
13.0	130.3
15.5	129.7
25	128.8
15.0[b] Mole %	
5.6	129.8
7.3	129.7
9.3	129.7
11.0	129.7
13.3	129.5
15.7	129.1
21.0	128.7
25.0	128.3
28.2	128.3
28.0 Mole %	
11.6	130.5
13.3	130.1
15.4	129.8
19.0	129.3
21.2	129.0
24.8	128.7
28.3	128.2
30.0	128.2
31.0	128.2
34.0	128.0
35.6	127.9[a]
37.0	127.8
37.7	127.8
38.2	127.9
31.4 Mole % argon	
11.6	−131.6
13.3	130.9
15.3	130.5
19.0	129.8
21.1	129.3
22.8	129.2
24.4	129.0
26.1	128.6
28.3	128.3
30.0	128.3
31.6	128.2
33.9	128.3
36.0	128.2[a]
38.3	128.2
39.0	128.3
35.8 Mole %	
11.6	131.2
13.3	130.7
15.7	130.5
17.4	129.7
19.4	129.7
25.5	129.6
27.9	129.4
32.5	129.7
34.4	129.4[a]
37.9	129.3
36.9 Mole %	
11.6	132.4
13.3	132.2
22.9	131.1
25.2	130.6
28.7	130.2
30.4	130.2
34.0	129.9
36.0	129.7
36.6	129.9
37.3	129.9[a]
37.7	129.9

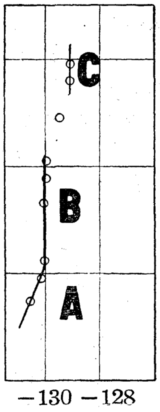
[a] At this and higher pressures a second liquid layer immiscible with the first was noted.

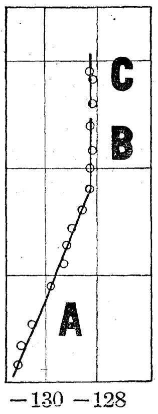
[b] This sample under-cooled considerably but the results are believed accurate to better than ±0.3° since melting points as well as freezing points could be obtained.

ume, is too slight to be measurable with the present method.

One would expect the freezing points to approach some final value asymptotically as the pressure increases. The exact curve, however, is difficult to predict and would not differ to any great extent from the straight lines shown in the figures. No significance is attached to the inflection point as drawn.







Temperature, 0°C.

Fig. 4.—33.3 Mole % argon. Fig. 5.—42.9 Mole % argon. Fig. 6.—31.4 Mole % argon.

For the samples of less than 5% argon, the liquid fills the cells after only one or two readings are taken, and hence an extended pressure range cannot be studied. However, these compositions seem to be stabilized at low pressures, and the points secured are probably for pressures above the decomposition pressure.

The freezing of the samples occurred differently depending on the composition and consequently the place on the curve. For compositions not at maxima or minima a few crystals appeared at first followed by more and more if the temperature was allowed to decrease further. However, stirring could be continued for some time before the stirrer became frozen, indicating freezing over a temperature range. At points near the maxima or minima of the curves, however, the mass tended to freeze solid immediately after the appearance of the first crystals. This phenomenon is characteristic of systems in which compounds are formed.

The possibility of under-cooling was recognized at the beginning of the work and was found to be absent or very slight for samples except those near maxima and particularly those containing 12.5, 13.5 and 15.0% argon. The 12.5, 13.5 and 15% samples showed under-cooling by as much as 2°. Fortunately, the mass did not freeze solid and by careful manipulation, *melting points* were secured although such determinations are less accurate than are the freezing points.

Since under-cooling causes the volume to decrease and subsequent warming causes expansion, fewer points could be determined if segregation was to be avoided. Furthermore, since the decomposition pressure is relatively high and mercury freezes in the capillary at a relatively low pressure, the exact decomposition pressure is less certain than in other parts of the system. However, the isobaric graphs show maxima at about 11 and 15% argon and the points plotted in Fig. 7 in this region are probably correct in relation to each other although it is possible they should be located at a slightly higher temperature.

When the isobaric freezing points are plotted *versus* composition, maxima and minima appear, indicating compound formation. Isobars cannot be plotted over the whole range since only low pressures can be measured for the low argon samples, while low pressure measurements for higher argon percentages are somewhat erratic and of little importance.

Figure 7 shows what might be termed a temperature *versus* composition plot of the "stabilized system." The pressure at which the temperatures are taken is such that it is above the decomposition pressure shown on the freezing point curves. Since the temperature was found to remain constant with increase in pressure within the experimental limits, Fig. 7 may be considered as drawn from the data by extrapolating the temperature upward to a pressure sufficiently high to be above the decomposition pressure for all of the compounds. This seems a reasonable method of drawing the diagram and should introduce only a small error due to the actual slope of the line drawn as vertical. This diagram is probably more truly representative of the system than are isobaric graphs since in the former graph, the only constituents present in appreciable quantities are $A \cdot xBF_3$ and $A \cdot x'BF_3$. In the isobaric graphs, below the inflection points, complexities are certain to be introduced due to unpredictable pressure effects on the complex equilibrium

$$A \cdot xBF_3 \rightleftharpoons A + nBF_3 \rightleftharpoons A \cdot x'BF_3$$

The stabilized diagram, together with the isobaric diagrams, shows that maxima are found corresponding to the ratios $A \cdot BF_3$, $A \cdot 2BF_3$, $A \cdot 3BF_3$, $A \cdot 6BF_3$, $A \cdot 8\ BF_3$ and $A \cdot 16BF_3$, indicating compound formation. While the range in melting points exhibited is small similar short excursions between maxima and minima are known in other systems yielding compound formation.

In the case of certain samples, as the pressure increased, a phenomenon occurred which seems best described as retrograde immiscibility. A second liquid layer, immiscible with the first, appeared as in region C, Figs. 5–6, near 35 atmospheres. Although complete miscibility would probably again be secured if the pressure were increased sufficiently, this could not be determined due to experimental difficulties. That it is not inhomogeneity of the sample, prior to the appearance of the second layer, is evidenced by the fact that while the second layer increases in volume, the first layer also increases in volume, to a comparable extent. Second liquid layers probably formed in all samples where the pressure was sufficiently high (about 35 atmospheres) although their presence was not realized since they were hidden by the electromagnet.

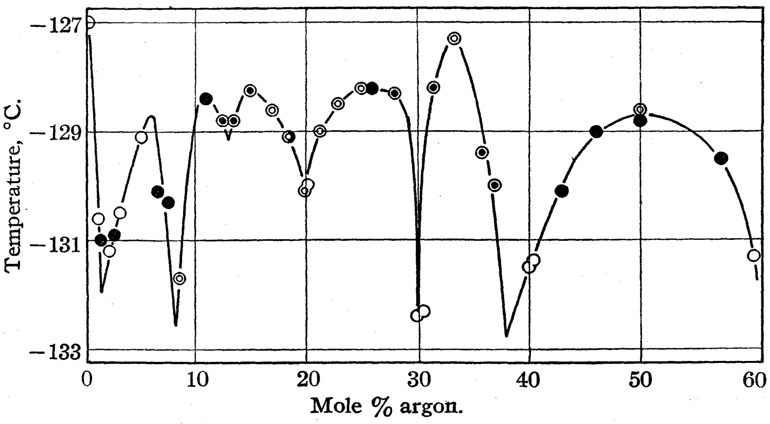


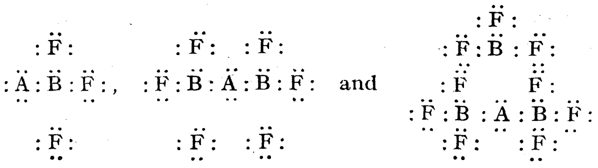
Fig. 7.—Freezing points of the stabilized system: B, ○; C, ◎; D, ●; E, ◉.

This explains the break in several of the freezing point curves. The first vertical line is the normal freezing point. The second line occurs after the second liquid layer has appeared. That the freezing point should change seems entirely reasonable since formation of a second immiscible layer might change the composition of the first liquid. Since a very slight pressure change caused all the vapor to liquefy, a close study of this region could not be made.

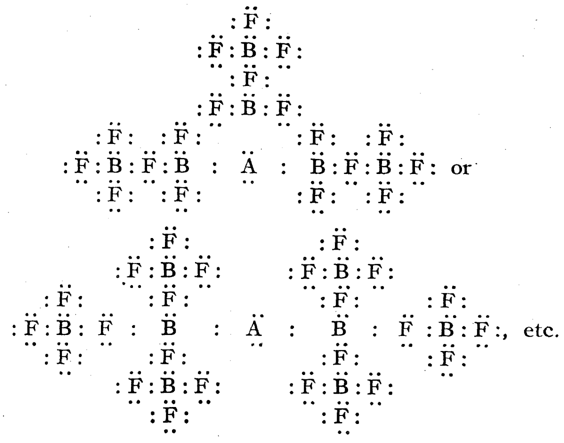
Furthermore, from about 30 to 37 atmospheres, erratic points were found in some cases indicating a metastable state in which the system was undergoing some decided change. For some samples in this pressure region, a light foam appeared on the surface of the liquid on stirring. When the second meniscus appeared the foam disappeared.

The absence of a maximum at 20% argon (Fig. 7) is surprising at first thought but may possibly be due to steric hindrance or may exist but require closer detailed study in this region to reveal it.

The compounds A·BF$_3$, A·2BF$_3$ and A·3BF$_3$ doubtless are formed by coördinate links in which the argon donates electrons to complete the boron octet



In this and other investigations in this Laboratory it has been noticed that liquid boron trifluoride at vapor pressures between five and ten atmospheres becomes viscous, indicating association. The compounds A·6BF$_3$, A·8BF$_3$ and A·16BF$_3$ doubtless contain boron trifluoride molecules linked directly to the argon atom as above and the rest of the boron trifluoride linked to these inner boron trifluoride molecules *via* their fluorine atoms,[11] *i. e.*



Another explanation of the compounds A·6BF$_3$, A·8BF$_3$, A·16BF$_3$ is that the "excess" BF$_3$ groups are merely located in the crystal lattice in more or less symmetrical arrangements.[12] The writers

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[11] Lewis, "Valence and the Structure of Atoms and Molecules," The Chemical Catalog Co., New York City, 1923, page 99.

[12] Sidgwick "The Electronic Theory of Valency," Oxford University Press, London, 1929, pp. 186–187 and 199.

feel, however, that the evidence points to the first explanation analogous to that of Sidgwick (*loc. cit.*, p. 199) for excessive hydration by polymerized water molecules.

Undoubtedly the system krypton–boron trifluoride will show stabler compounds and the system xenon–boron trifluoride still stabler. Investigations of these systems are already under way and will be reported as soon as possible.

Summary

Study of the system boron trifluoride–argon has shown that:

1. The freezing point of any mixture increases with increase in pressure up to a certain value and is in general little affected by any further pressure increase, indicating an equilibrium $A + xBF_3 \rightleftharpoons A{\cdot}xBF_3$ or $A{\cdot}xBF_3 + yBF_3 \rightleftharpoons A{\cdot}(x + y)BF_3$.

2. A graph of the freezing points *versus* composition exhibits maxima and minima, the maxima corresponding to the ratios $A{\cdot}BF_3$, $A{\cdot}2BF_3$, $A{\cdot}3BF_3$, $A{\cdot}6BF_3$, $A{\cdot}8BF_3$ and $A{\cdot}16BF_3$, indicating compound formation. These compounds are unstable and dissociate above their melting points. From the shape of the curve the ratio $A{\cdot}2BF_3$ appears to be the stablest.

3. The freezing points of the argon–boron trifluoride mixtures of compositions approximating that of the maxima and minima were sharp and immediately complete while intermediate compositions melted over a range of temperatures. This is typical of systems in which compounds are formed.

4. At pressures in the neighborhood of 35 atmospheres, a second liquid layer appears which is probably best explained as retrograde immiscibility.

CLEVELAND, OHIO RECEIVED JUNE 19, 1935

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Critical Phenomena of the System Argon–Boron Trifluoride[1]

BY HAROLD SIMMONS BOOTH AND KARL STUART WILLSON

In view of the fact that thermal analysis of the system argon–boron trifluoride[2] showed maxima indicating compound formation, it was thought interesting to see whether or not this tendency would result in abnormalities in the critical phenomena.

The gases were purified and samples prepared as previously described.[2] Temperatures were measured by the Leeds and Northrup Micromax potentiometer using a two-junction copper–constantan thermocouple with ice as reference point. The couple was calibrated at the ice and carbon dioxide snow point and the calibration curve drawn through these points guided by the theoretical curve. Temperatures are subject to a maximum error of ±0.4°.

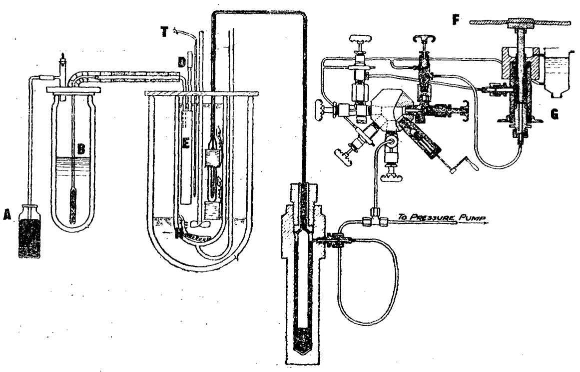

Fig. 1.—Critical apparatus.

The thermostat (Fig. 1) consisted of a pint Dewar flask set in a gallon Dewar. The temperature of the thermostat was controlled in either of two ways. For temperatures down to −85°, alcohol was used as the bath liquid and cooling was effected by placing liquid nitrogen in the outer Dewar. The rate of cooling of the bath was controlled by the depth of the liquid nitrogen in the outer bath and also by adjustment of the vacuum of the inner Dewar. The control contacts on the recording potentiometer were adjusted to close the relay heating circuit and warm the bath by means of the coil (H) when the bath cooled below the desired temperature. By adjusting the rate of cooling and the heating circuit, the bath temperature could be held within the limits of sensitivity of the recorder (±0.2°) for determination of the critical constants of the mixtures. For critical constants of pure boron trifluoride, manual control and observation of a calibrated mercury thermometer permitted an accuracy of ±0.05°.

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(1) From a part of a thesis submitted by K. S. Willson to the Graduate Faculty of Western Reserve University, May, 1935, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Booth and Willson, THIS JOURNAL, **57**, 2273 (1935).

To secure rapid cooling and for controlling the bath at the lower temperatures, liquid nitrogen was forced into the evaporator (E) by closing the outlet from the reservoir (B) at (A). By adjusting a screw clamp at (D) a very slow cooling rate could be secured and then the temperature maintained constant by the heater (H) operated by the relay control circuit. For these lower temperatures commercial butane served as the bath liquid.

The experimental procedure used in determining the critical constants was similar to that employed and described in detail by Booth and Carter.[3] Pressures were measured by the dead weight gage described by Booth and Swinehart.[4]

Experimental Results.—The tables and figures present the critical data. The points listed are those at which the first liquid appeared, when approached from the gaseous region.

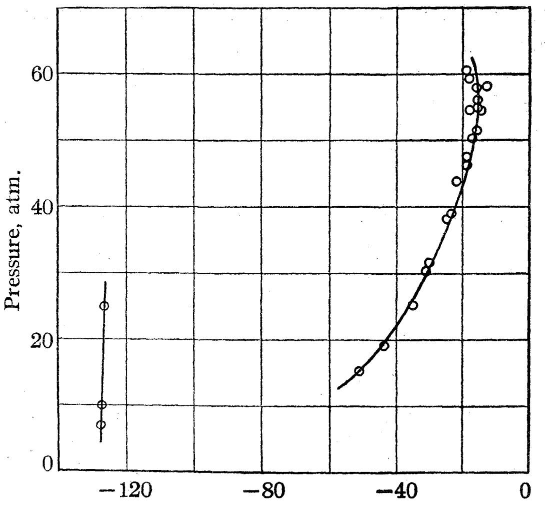

Fig. 2.—10 mole % argon.

The freezing points[2] are also plotted although the scale used does not represent adequately the experimental details found.

TABLE I

CRITICAL CONSTANTS OF THE PURE GASES

	P_c, atm.	T_c, °C.
BF_3	49.3 ± 0.1	−11.8 ± 0.05
	(49.2 ± 0.1	−12.25 ± 0.03°)[5]
Argon	47.7 ± 0.1	−120.6 ± 0.5
	(48.0	−122.4)[6]

TABLE II

CRITICAL PHENOMENA OF MIXTURES

The points listed are those at which the first liquid appeared when approached from the gaseous region.

Press., atm.	Temp., °C.
Mol % argon	
10.0	Sample A
10.0	B
9.9	C
15.3	−51.6 A
19.2	44.4 A
25.4	35.6 A
30.4	31.7 A
30.5	30.4 C
38.0	25.6 A
39.0	24.0 C
40.4	22.5 B
43.8	22.5 A
46.4	19.5 C
50.4	17.9 B
50.5	16.9 C
54.5	15.1 B
54.7	18.9 A
55.0	16.2 C
58.0	16.6 A
58.2	13.9 B
59.3	18.9 A
60.6	20.0 A
20.7	Sample A
20.2	B
12.8	−55.2 A
19.0	45.8 A
22.7	42.4 A
30.0	36.6 A
32.4	35.4 A
34.1	34.6 A
36.5	33.1 A
39.8	30.8 A
40.3	28.3 B
44.4	25.7 B
47.1	−24.4 B
51.7	23.0 B
54.0	21.9 B
57.7	20.6 B
59.7	20.5 B
63.4	20.0 B
67.1	20.0 B
68.8	20.5 B
70.2	21.8 B
70.3	21.8 B
75.3	25.2 B
76.9	25.8 B
80.8	28.7 B
82.4	30.8 B
87.2	34.3 B
87.6	34.4 B
91.6	37.3 B
95.0	46.0 B
30.0	Sample A
30.0	B
14.1	−54.9 A
22.7	41.7 A
24.3	45.8 A
32.0	38.6 B
32.9	34.6 A
34.3	39.5 A
37.4	31.9 A
40.4	33.1 B
45.7	29.5 A
49.0	28.5 A
50.4	28.3 B
54.1	26.7 B
57.8	25.1 B
59.8	24.4 B
63.8	24.0 B
67.4	23.5 B
71.1	23.4 B
73.6	23.8 B
77.2	25.0 B
80.3	28.7 B
85.4	31.4 B
89.5	35.7 B
91.6	38.0 B
93.0	38.8 B
101.8	46.0 B
102.5	50.8 B
107.6	56.6 B
108.3	61.2 B
109.0	66.0 B
39.9	Sample A
40.0	B
12.1	−59.6 A
14.4	56.6 A
18.6	52.8 A
22.5	48.7 A
33.5	44.4 A
34.1	44.4 A
38.8	44.3 A
41.8	41.5 A
51.3	38.0 A
62.3	32.3 B
70.8	31.3 B
80.9	32.0 B
91.0	37.7 B
94.3	41.6 B
98.5	46.0 B
101.6	50.5 B
103.8	55.2 B
105.8	59.8 B
107.2	64.3 B
107.9	72.3 B
49.7	
20.8	−64.6[a]
27.1	58.7
34.9	53.4
39.8	50.6
45.6	48.6
51.2	46.6
53.2	45.9
59.9	44.2
70.1	43.0
77.8	42.9
59.9 Mol % argon	
16.3	−70.3
17.4	67.7
19.1	64.4
23.2	61.2
28.7	59.4
30.8	57.9
42.1	53.1
42.8	51.4
43.0	50.5
46.7	49.5
49.4	50.0
50.9	49.0
55.2	48.4
60.0	47.7
63.0	46.3
70.7	45.5
79.5	44.6
90.9	46.9
97.4	48.7
90.0 Mol % argon	
20.4	−115 (approx.)
40.5	94.3
48.9	94.2
50.5	95.0
50.5	94.0
50.5	92.8
54.2	92.8
54.5	94.2
58.4	95.5
58.4	93.7
59.8	92.8
59.8	92.8
62.8	96.7
63.3	95.7
67.5	93.5
68.5	95.4
70.0	93.5
79.3	105.0

[a] Since this sample was not carried to the point where increase in pressure causes lowering of the maximum temperature of liquefaction, the values of T_m and P_m could not be plotted.

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(3) Booth and Carter, *J. Phys. Chem.*, **34**, 2801 (1930).

(4) Booth and Swinehart, THIS JOURNAL, **57**, 1337 (1935).

(5) Booth and Carter, *J. Phys. Chem.*, **36**, 1359 (1932).

(6) Crommelin, *Comm. Phys. Lab. Univ. Leyden*, **115**, 118a 1910)

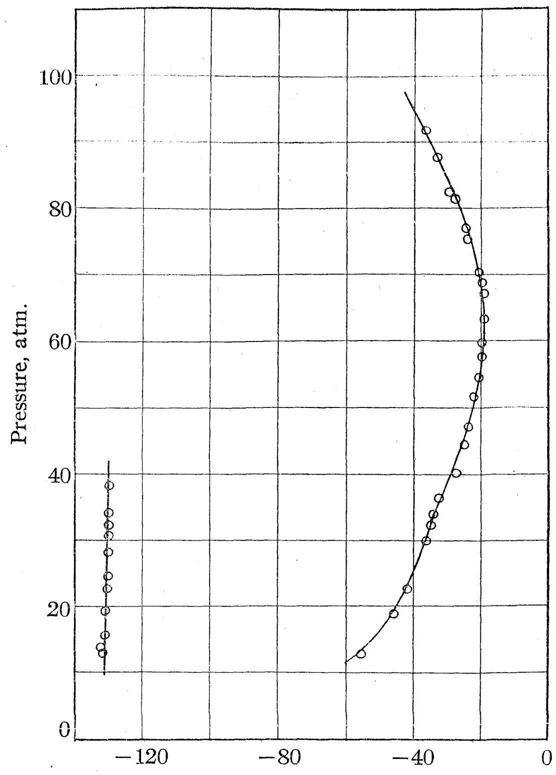

Fig. 3.—20 Mole % argon.

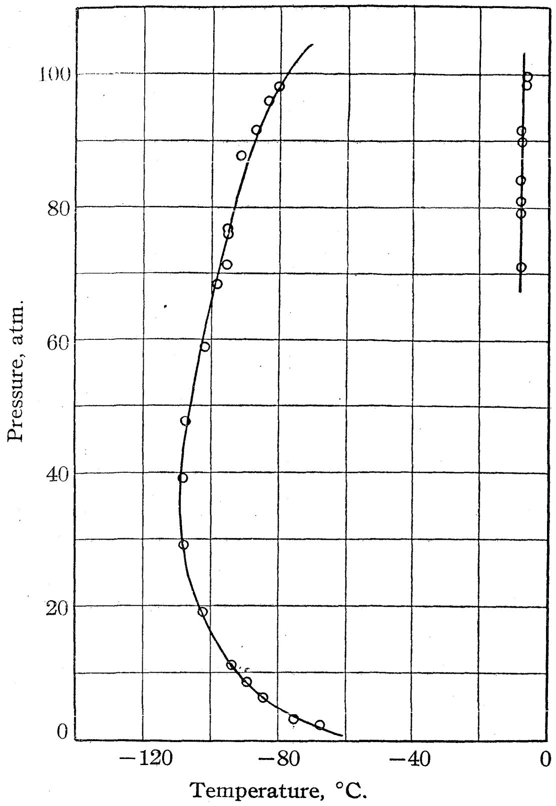

Fig. 5.—40 Mole % argon.

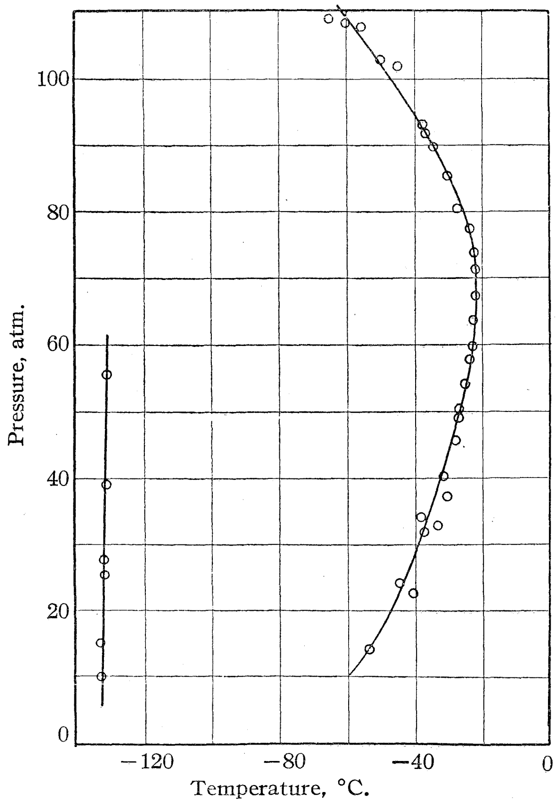

Fig. 4.—30 Mole % argon.

TABLE III

MAXIMUM TEMPERATURE OF LIQUEFACTION AND CORRESPONDING PRESSURE

Bracketed figures are interpolated from Fig. 10.

Mole % argon	T_m, °C.	P_m, atm.
0	−11.8	49.3
10	15	57
20	20	63
30	24	70
40	30	75
50	(36)	(78)
60	45	75
70	(58)	(71)
80	(75)	(65)
90	96	(57)
100	120.6	47.7

Discussion of Results

As commonly reported in the studies of critical phenomena of two component mixtures retrograde condensation was observed and also what may be described as a new phenomenon, retrograde immiscibility. This latter phenomenon is described in the previous paper.

In the range from 0 to 60% argon, the curve T (Fig. 9) giving the maximum temperature of liquefaction is only slightly distorted from the normal curve. On reflection this is not surprising in view of the fact that the critical region lies about 110° above the temperature at which the compounds $A \cdot xBF_3$ dissociate.

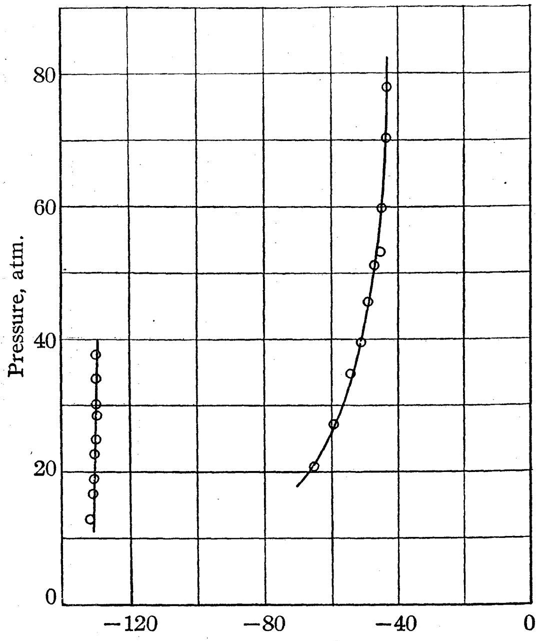

Fig. 6.—50 Mole % argon.

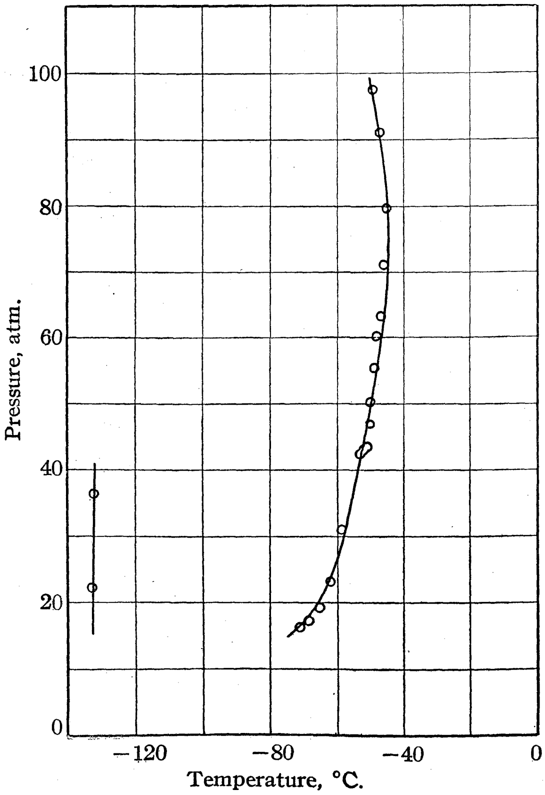

Fig. 7.—60 Mole % argon.

The maximum temperature of liquefaction T_m decreases along a smooth curve as the argon percentage is increased. The pressure P_m corresponding to T_m increases as the argon percentage increases to 50% and then decreases. The erratic points in the highest pressure regions on some of the curves are due to the liquid rising into the capillary tube and preventing adequate stirring.

The regions surrounding the critical point of a mixture have been little studied and merit an accurate investigation, but could not be studied in this work due to the low temperatures involved which caused the mercury to freeze in the capillary tubes. In the high argon samples, great difficulty in getting accurate critical data was encountered due to the small amount of liquid formed even over a wide temperature and pressure variation. Thus, the conditions under which the first trace of liquid appeared were difficult to determine, and an additional complication arose due to the liquid adhering to the walls of the cell and the stirrer, instead of falling to the bottom of the cell. The plot of the 90% argon sample shows the lack of reproducibility of the points and gives only a general idea of the critical data in that region.

Appearance of a second liquid layer in the freezing point curves for high pressures suggests pos-

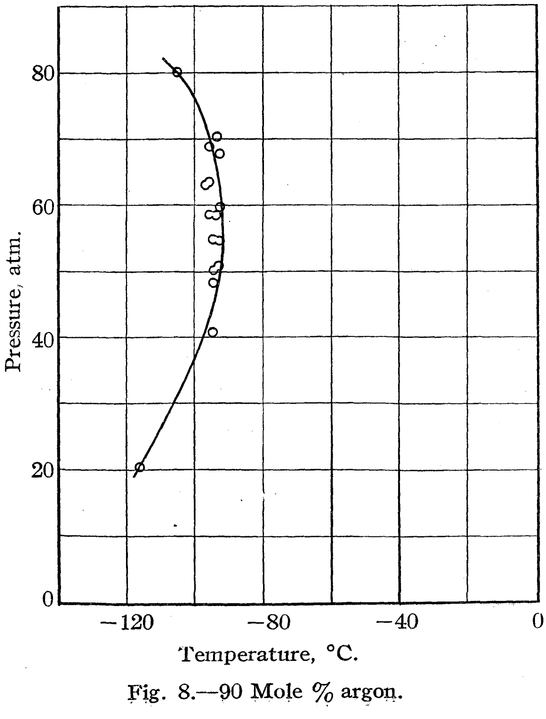

Fig. 8.—90 Mole % argon.

sible abnormalities in the high pressure, low temperature part of the critical curves but experimental difficulties precluded an investigation of this region.

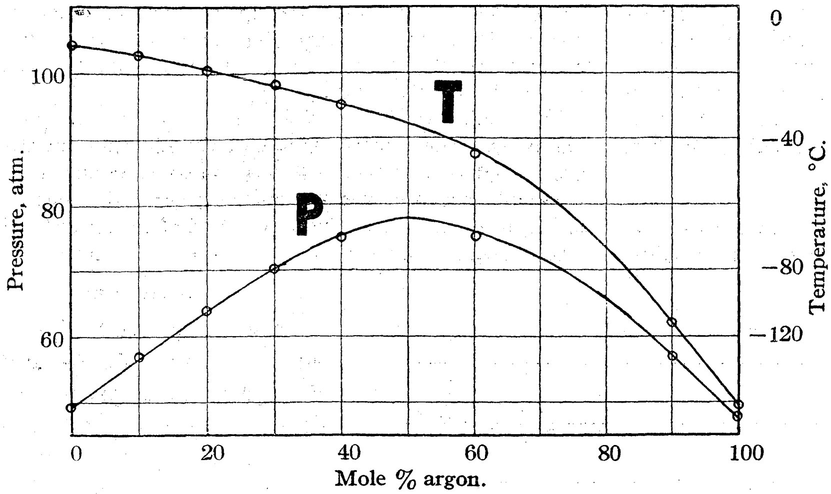

Fig. 9.—Maximum temperature of liquefaction and corresponding pressure.

Summary

The critical phenomena of the system boron trifluoride–argon exhibited the usual retrograde condensation and a new phenomenon best described as retrograde immiscibility at the low temperature, high pressure range.

The compounds formed by the gases at their melting point are practically completely dissociated at the "critical temperature region" which is about 100° higher, and so affect the curve of the maximum temperature of liquefaction only very slightly.

CLEVELAND, OHIO

RECEIVED JUNE 19, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Temperature Coefficients in the Acid Hydration of Sodium Pyrophosphate

BY SAMUEL J. KIEHL AND EDWARD CLAUSSEN, JR.

Introduction

Normal sodium pyrophosphate in aqueous or alkaline solution on long standing at room temperature or even at the boiling point does not change to orthophosphate.[1,2] In acid solution, however, this change takes place, and its rate is dependent upon the concentration both of pyrophosphate and of the acid, used as the so-called catalyst, and the temperature.[3] The rate of change to the orthophosphate in the presence of hydrochloric acid has been measured at 45°,[3] and under very special conditions at 20 and 40° by Muus,[4] who also mentioned work at 100° although no data were presented. In general data at higher temperatures are meager.[5]

In the literature many procedures for measuring the rate of this and similar reactions are published, among which have been methods based upon gravimetric analysis, change of concentration of hydrogen ions, conductivity, colorimetry, nephelometry and volumetric analysis. For purposes of this investigation, however, a modification of the method devised earlier[2] was found to be most convenient. The unchanged pyrophosphate was determined gravimetrically in the presence of orthophosphate which was formed and the velocities at 30, 45, 60, 75 and 90° were secured. From data thus obtained temperature coefficients at fifteen-degree intervals were determined.

Preparation of Materials and Apparatus

The normal sodium pyrophosphate, the disodium orthophosphate and the hydrochloric acid were prepared as described previously.[3]

In the preparation of the zinc acetate reagent used in the analysis both the zinc acetate and the acetic acid were carefully purified to eliminate possible traces of heavy metals—especially iron and lead whose pyrophosphates would interfere in subsequent operations. The final solution of the zinc acetate reagent contained a 0.2 molar zinc acetate with sufficient acetic acid to give a *p*H value of 3.3.

A magnesia mixture without ammonia was prepared by dissolving 50 g. of $MgCl_2 \cdot 6H_2O$, 100 g. of NH_4Cl, and 5 cc. of 13 *M* HCl in one liter of water.

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(1) Rose, *Ann.*, **76**, 2 (1850).

(2) Kiehl and Coats, THIS JOURNAL, **49**, 2180 (1927).

(3) Kiehl and Hansen, *ibid.*, **48**, 2802 (1926).

(4) Muus, *Z. physik. Chem.*, **A159**, (4) 268 (1932).

(5) Abbott, THIS JOURNAL, **31**, 763 (1909), studied the conversion of pyrophosphoric acid itself at 75 and 100°.

Water-baths at 30, 45, 60 and 75° and an oil-bath at 90° all of which were controlled by Beaver[6] regulators were used to maintain the required temperatures. The maximum deviation was $\pm 0.02°$.

Bottles of 750-cc. capacity made of acid and alkali resisting glass (trade name "No Solvit") were used to contain solutions in the baths at all temperatures except 90°. For 90° it was necessary, for the prevention of losses due to evaporation, to use a specially designed Pyrex (a borosilicate glass) glass bottle from which samples could be withdrawn through a capillary tube provided with a stopcock.

Method of Analysis

Determination of Pyrophosphates in the Presence of Orthophosphate.—The method of separation of pyrophosphate from orthophosphate and the subsequent determination of pyrophosphate was developed and conditions were established by the analysis of solutions of known mixtures whose respective phosphate content and conditions would correspond to those found in course of the actual hydration in the various solutions. The separations were made in a solution whose volume was 75 cc. and whose *p*H value of 3.3 to 3.5 was obtained by the addition of three molar acetic acid and the required amount of distilled water. The standard for *p*H value was brom phenol blue with the "Wulff" series of color standards. During the precipitation in the development of the method it was found that a slow formation of the zinc pyrophosphate was essential for the formation of a crystalline precipitate and for results of separation and analysis which would meet the required precision. This was accomplished by a dropwise addition of 10 to 30% excess of the reagent with constant and uniform stirring. The precipitate was separated from the supernatant liquid and was washed till free from the excess precipitant by repeated centrifuging and decanting through the filter and was transferred to the filter. The precipitate on the filter was ignited in platinum with the usual precautions, from gentle heating at first over a bunsen flame to constant weight finally over a meker burner. In the preliminary experimentation it was found that reprecipitations were unnecessary if manipulations were carefully and accurately done.

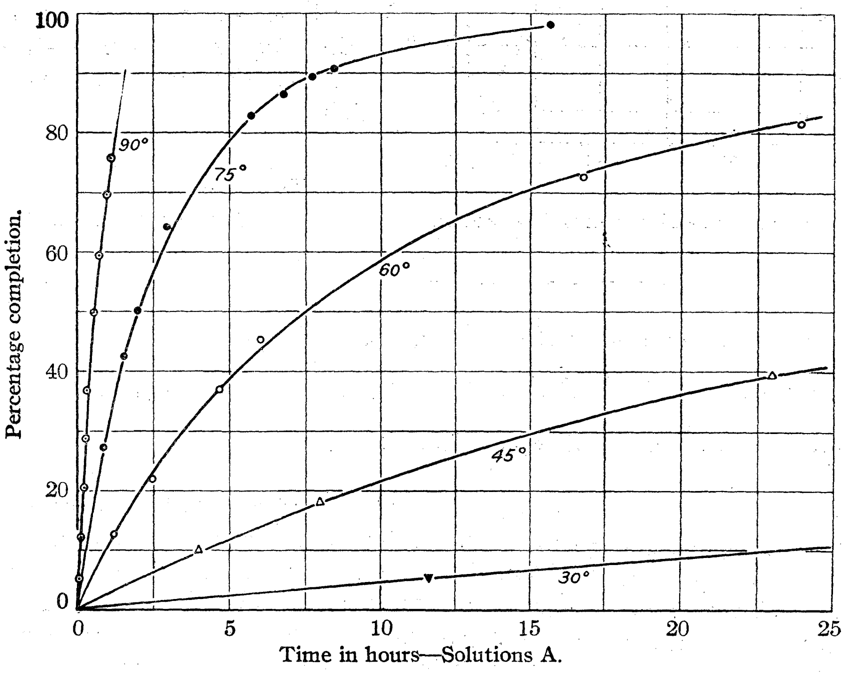

Fig. 1.—Effect of temperature on velocity.

As a further confirmation of the method of separation and analysis the orthophosphate in the filtrate from the zinc pyrophosphate was also determined in known mixtures and some examples of the subsequent hydrations by the modified magnesia mixture method of Epperson[7] the data and results for which are to be found elsewhere.[8]

Experimental

At each of five temperatures, 30, 45, 60, 75 and 90°, the velocity of conversion was measured for 0.125 *M* sodium pyrophosphate in the presence of 0.500 *M* (A), 0.425 *M* (B) and 0.350 *M* (C) hydrochloric acid, respectively.

Convenient samples were withdrawn by pipet, cooled quickly to room temperature, and weighed out in Bailey burets. The volume and hence the total weight of phosphorus was calculated from the known densities. The solution was then made just alkaline with concentrated ammonium hydroxide, and analyzed for the amount of phosphorus as pyrophosphate.

More detailed data for this work at all temperatures are available elsewhere.[8]

In Fig. 1 the effect of the five different temperatures upon the velocity of the reaction is shown for the solution designated A. The solutions styled B and C give the same type of curves.

Figure 2 shows the effect of the three different initial acid concentrations for the solutions at 45°.

In Table I a complete summary of these two effects upon the velocity is given for convenient equally spaced percentages of completion. The data were obtained from the curves for the hydrations in the respective solutions.

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(6) Beaver and Beaver, *Ind. Eng. Chem.*, **15**, 359 (1923).

(7) Epperson, THIS JOURNAL, **50**, 321 (1928).

(8) E. Claussen, Jr., Dissertation, Columbia University, 1934.

TABLE I

EFFECT OF TEMPERATURE ON VELOCITY

Concentration of $Na_4P_2O_7$ = 0.125 *M*

Percentage hydrated	Time in hours for given temperatures, °C.				
	30	45	60	75	90
Solution A; HCl, 0.500 *M*					
10	24.0	4.0	0.8	0.4	0.10
20	48.0	10.0	2.2	.6	.13
30	76.8	17.0	3.6	1.0	.30
40	120.0	25.0	5.2	1.5	.50
50	178.0	35.0	7.3	2.0	.60
60	261.6	47.0	10.5	2.5	.80
70	384.0	67.0	15.0	3.6	1.00
80	528.0	100.0	22.4	5.2	1.40
90	948.0	155.0	36.7	8.4	
Solution B; HCl, 0.425 *M*					
10	45.6	6.0	1.8	0.55	0.16
20	96.0	15.0	3.7	1.05	.29
30	168.0	29.0	6.1	1.60	.45
40	271.2	47.0	9.0	2.30	.62
50	400.8	70.0	13.8	3.30	.83
60	578.4	96.0	20.1	4.50	1.10
70	873.6	146.0	28.4	6.20	1.41
80	1344.0	217.0	40.8	8.70	2.00
90	2184.0	355.0	66.0	12.80	
Solution C; HCl, 0.350 *M*					
10	120.0	19.0	3.8	0.9	0.17
20	268.8	44.0	7.5	1.7	.37
30	468.0	74.0	11.9	2.7	.63
40	756.0	114.0	17.8	3.9	.90
50	1159.2	168.0	25.7	5.4	1.23
60	1728.0	241.0	36.7	7.2	1.60
70	2496.0	342.0	52.0	9.7	2.08
80	3504.0	489.0	80.0	13.7	2.96
90			122.0	21.4	

Discussion and Determination of Temperature Coefficients.—In order that temperature coefficients may be obtained for the reaction under the chosen experimental conditions, an equation will be necessary which will embody a factor that may be employed in establishing a unit of measure for the effect of temperature only upon the rate. This factor should remain constant under the prescribed conditions upon a definite temperature level but its value should change in going from one temperature level to another if it is to be of service for the determination of temperature coefficients. If the reaction under the conditions conformed to one of the classical orders of reaction in which the velocity constants incorporate this factor in the mathematical expression of the reaction which changes with temperature the problem would be simple. But the rate is affected greatly by a variation of the concentration of hydrogen ions[3] which on account of the difference in activity of the pyrophosphoric and orthophosphoric acids undergoes a marked decrease as the reaction proceeds. This decrease is dependent jointly upon the initial concentration of the hydrochloric acid and of the pyrophosphate.[3]

Moreover, for the proportions in which the original acid and pyrophosphate are used, the decrease of concentration of hydrogen ions during the reaction is sufficient to effect a considerable variation in the velocity. The difference in the speeds for A and B is greater at 90% completion than earlier, as reference to the slopes of the curves in Fig. 2 will show.

Therefore, due to the difference in activities of the respective phosphoric acids which causes changes in the concentration of hydrogen ions, it has been found that the reaction under discussion cannot be expressed by any of the orders of reaction unless the concentration of hydrogen ion be made to remain constant or a mathematical relation be obtained whereby it may be expressed in terms of the concentration of the phosphate.

This conclusion is supported by the work of Abbott[5] and by the work of Kiehl and Hansen.[3]

In more recent work by Muus,[4] who used radically different experimental conditions and approximately constant ionic environment at 20 and 40°, it was shown that with an extreme excess of acid (from 38 to 150 times the concentration of pyrophosphate), and in the presence of constant kinetic conditions (about 1000 times as much potassium chloride as the initial concentration of pyrophosphate), a definitely constant first order reaction velocity constant was obtained with a given concentration of hydrogen ion. These constants were directly proportional to the various concentrations of hydrogen ion under which the reaction was studied.

Consequently in this work, where the order of magnitude of the initial concentration of hydrogen ion was the same as that of the pyrophosphate, and where the inevitable consequence was that the concentration of hydrogen ion varied throughout the reaction recourse to an empirical equation to express the reaction rate seemed to be the only resort. The form of the equation was tentatively established by data from solutions at 45°[3] where concentrations of both hydrogen ion and pyrophosphate were known. Since the pyrophosphate concentration was the same in all solutions at the beginning and the initial concentration of hydrochloric acid was fixed for solution C, it was possible to express the concentration of hydrogen

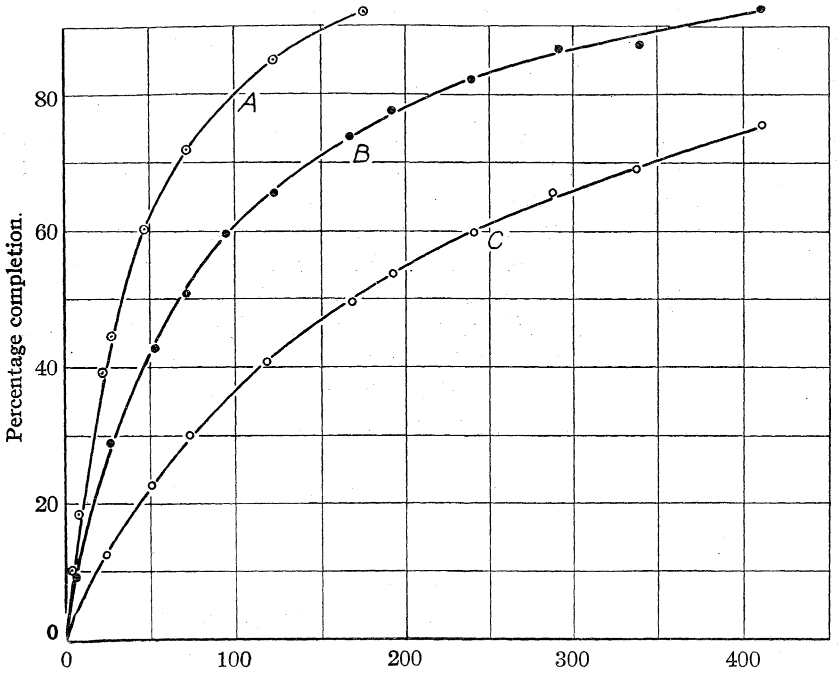

Fig. 2.—45° data—effect of initial acid concentration on velocity.

ion in terms of the pyrophosphate remaining, (x). By using such respective values from actual measurement made in synthetic solution at convenient percentage intervals, an equation of the form $(H^+) = A' + B'x + C'x^2 + D'x^3 + \ldots$, may be developed to express the relationship. The constants A', B', C', D', etc., may then be evaluated by solution of simultaneous equations. The velocity of the reaction accordingly may be expressed in the general equation $dx/dt = kf[x(H^+)]$, which by substitution of the above equation for $[H^+]$, assumes the form, $dx/dt = kx(A' + B'x + C'x^2 + D'x^3 +)$. The integration of this expression gives the final equation

$$kt = A \log x + B + Cx + Dx^2 \ldots$$

with t as time, x the fraction of the concentration of the pyrophosphate remaining, and k, A, B, C, D constants. The constants were evaluated by solving simultaneous equations representing times at 25, 35, 45, 55, 65 and 75% completion which were determined from a large smoothed-out plot of percentage against time for solution A at 60°.

Thus solved, the completed equation is

$$kt = -102.860 \log x - 68.143 + 109.690x - 42.598x^2 \ldots$$

It is noteworthy that although the equation was developed from data for solution A at 60° (0.125 M pyrophosphate and 0.500 M hydrochloric acid), it, with reasonable dependability, expresses the behavior not only of solutions A at all temperatures but also of solutions B and C throughout the entire temperature range.

By the use of this equation with all data within the limits of 25 to 75% completion, Table II was compiled. The values in Column 5 (% a. d.) were calculated from the ratio of the average deviation from the mean values of K.

The comparative constancy indicated by the average deviation of the calculated reaction velocity constants for the various solutions with the same concentration of acid at the same temperature and the consistency of change of constants for the various solutions from temperature to temperature suggest that they represent a reliable conception of the different reaction rates for the changes in initial acid concentrations and the changes in temperature. The equation holds best for the three intermediate temperatures.

TABLE II

REACTION VELOCITY CONSTANTS CALCULATED FROM THE EMPIRICAL EQUATION

Solution	$T.$, °C.	No. calculations	Mean k	Average deviation, %
A	90	4	11.60	7.4
B	90	5	8.74	5.7
C	90	3	5.75	1.0
A	75	4	3.64	2.7
B	75	4	2.17	2.3
C	75	3	1.30	2.7
A	60	3	0.966	0.3
B	60	4	.502	1.9
C	60	4	.276	2.0
A	45	4	.215	1.9
B	45	5	.102	2.3
C	45	6	.0425	3.0
A	30	4	.0393	2.6
B	30	8	.0180	6.3
C	30	7	.00626	7.5

By plotting these reaction velocity constants against temperature (Fig. 3) the customary exponential type of curve is obtained for each of the three solutions.

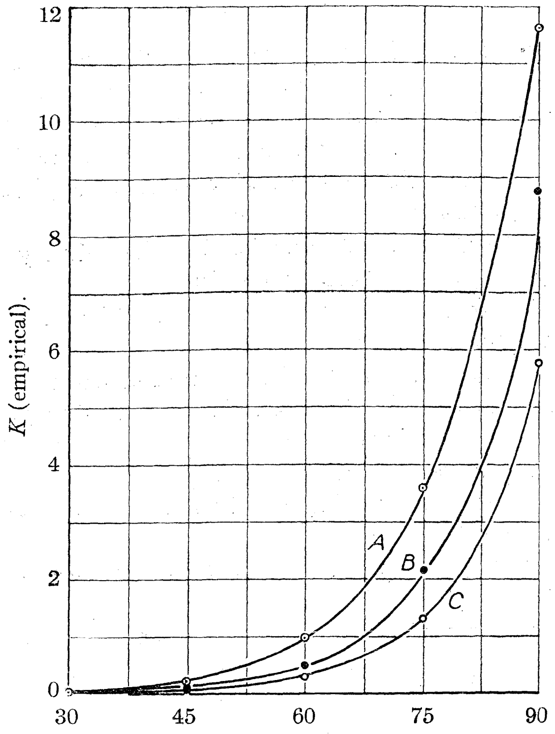

Fig. 3.—Effect of temperature on reaction velocity constant.

Temperature Coefficients

In Table III temperature coefficients calculated from the mean reaction velocity constants obtained by use of the empirical equation are compared with similar coefficients obtained by dividing the time obtained from smoothed-out curves for convenient percentages, such as 40, 50, 60, 70, at one temperature with a similar reading fifteen degrees higher.

The coefficients obtained by each of the methods described are quite comparable. Both decrease

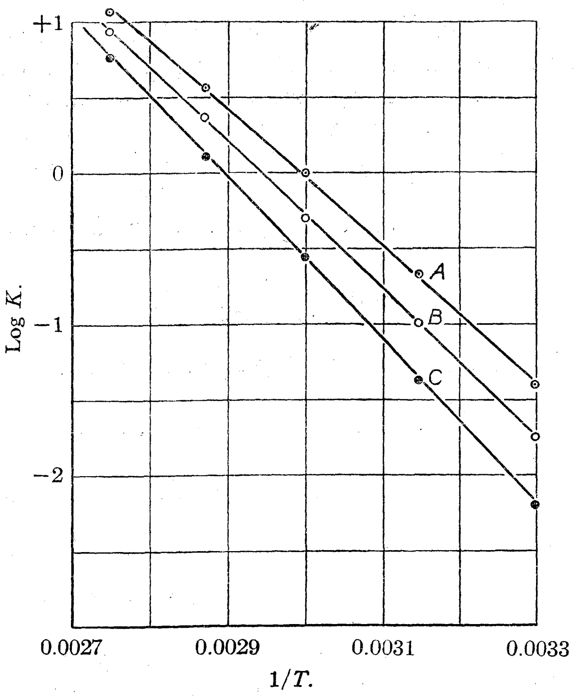

Fig. 4.—Plot of log *K* (empirical) *versus* the reciprocal of the absolute temperature.

TABLE III

TEMPERATURE COEFFICIENTS

Solution			45/30°	60/45°	75/60°	90/75°
A	From mean value of *K*		5.47	4.63	3.65	3.19
	From time data	40% completion	4.8	4.8	3.5	3.1
		50% completion	5.0	4.8	3.7	3.4
		60% completion	5.6	4.5	4.2	3.3
		70% completion	5.7	4.5	4.2	3.6
	Mean		5.3	4.7	3.9	3.4
B	From mean value of *K*		5.67	4.92	4.32	4.03
	From time data	40% completion	5.8	5.2	3.9	3.7
		50% completion	5.7	5.1	4.2	4.0
		60% completion	6.0	4.8	4.5	4.1
		70% completion	6.0	5.1	4.6	4.3
	Mean		5.9	5.1	4.3	4.0
C	From mean value of *K*		6.79	6.49	4.71	4.42
	From time data	40% completion	6.6	6.4	4.7	4.2
		50% completion	6.9	6.5	4.9	4.3
		60% completion	7.2	6.6	5.1	4.5
		70% completion	7.3	6.6	5.4	4.7
	Mean		7.0	6.5	5.0	4.4

rather regularly with increase of initial concentration of hydrochloric acid at all temperatures, as we pass from solution C to B to A. Since the activity of the acid is greater at the beginning than at the end of the reaction the individual coefficients from the time method in any given solution tend to be greater as the reaction proceeds. Consequently the mean coefficients decrease as the temperature is raised.

If the reaction velocity constants which have been determined by use of the empirical equation be plotted, log K against $1/T$ (Fig. 4), in conformance with the differential form of the Arrhenius equation, $\mathrm{d}\ln k/\mathrm{d}T = Q/RT^2$, a straight line is obtained for each of the solutions.

Moreover, from the integral form of this same equation

$$\ln\frac{k_1}{k_2} = \frac{Q}{R}\,\frac{T_1 - T_2}{T_1T_2}$$

values for Q at fifteen degree intervals may be calculated. The values thus obtained are within the usual limits of constancy.

Summary

1. New data are presented for the velocity of conversion of pyrophosphate to orthophosphate in aqueous solution in the presence of three different concentrations of hydrochloric acid at five temperatures, 30, 45, 60, 75 and 90°. $Na_4P_2O_7\cdot 10H_2O$ was used.

2. An empirical equation for the velocity of the reaction has been developed.

3. Temperature coefficients for 15° intervals have been calculated.

4. The values for Q in the equation of Arrhenius are within the usual limits of constancy.

5. A modification of the method for the quantitative determination of pyrophosphate in presence of orthophosphate by use of zinc acetate has been made.

NEW YORK, N. Y. RECEIVED AUGUST 3, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Relative Strengths of Acids in *n*-Butyl Alcohol[1]

BY LELAND A. WOOTEN AND LOUIS P. HAMMETT

We have measured the relative strengths of a series of substituted carboxylic and phenolic acids in *n*-butyl alcohol, a hydroxylic solvent of relatively low dielectric constant, and have found certain relationships between the structure of the acid and the effect upon the relative strength of the transfer of the acid from water to this solvent. The solubility of lithium chloride in this solvent made it possible to work in a medium of high and constant strength, a necessary condition for the measurement of relative acid strength by the potentiometric method if specific salt effects are to be minimized or eliminated and the uncertainty due to liquid junction potentials avoided. Butylate ion was employed as the base.

Experimental

Method.—Concentration cells of the following type were set up and measured

$$\begin{array}{c|c||c||c|c}
 & \dfrac{HA_1}{NaA_1}=1 & & \dfrac{HA_2}{NaA_2}=1 & \\
\text{Au} & & \text{Satd. soln.} & & \text{Au} \\
 & \text{LiCl, 0.05 }M & \text{of LiCl} & \text{LiCl, 0.05 }M & \\
 & \text{Quinhydrone} & & \text{Quinhydrone} & \\
\multicolumn{5}{c}{\qquad\qquad\qquad a \qquad\qquad\qquad b}
\end{array}$$

The electromotive force of this cell at 25° is related to the relative strength of the two acids, HA_1 and HA_2, by the expression

$$\text{E. m. f.}/0.0591 = pK_2 - pK_1 = \Delta pK$$

where $pK = -\log K$, the negative logarithm of the ionization constant of the acid. This expression is a sufficiently precise approximation provided the acids exhibit normal weak-acid titration curves in the solvent under study. Since a fairly high neutral salt concentration (LiCl) was maintained throughout the whole system the junction potentials at a and b should be small and practically constant.

The cell used was essentially that employed by Hammett and Dietz.[2] Mixing of the solutions was minimized by ground glass plugs, which separated the buffer solutions from the salt bridge. The buffer solutions were approximately 0.0025 M and in all cases were made 0.05 M with respect

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(1) Dissertation submitted by Leland A. Wooten to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, April, 1935. The material was presented at the New York meeting of the American Chemical Society, April, 1935.

(2) Hammett and Dietz, THIS JOURNAL, **52**, 4795 (1930).

to lithium chloride. The measurements were made in an atmosphere of dry nitrogen. Rubber stoppers carried the electrodes as well as inlets and outlets for the nitrogen. A trap on the nitrogen outlet, containing *n*-butyl alcohol, sealed the system from the atmosphere. All measurements were made at room temperature, which was 25 ± 3°.

Apparatus

Potentiometer System.—The voltages were measured with a Leeds and Northrup Type K potentiometer in conjunction with a No. 2500-b Type R wall galvanometer of the same make. A newly calibrated Weston Standard cell was used in standardizing the working circuit. This system applied to butyl alcohol solutions permitted voltages to be measured to ±0.1 millivolt.

Electrodes.—In agreement with other workers, notably Hammett and Dietz[2] and Halford,[3] it was found that bright platinum is not a satisfactory electrode material for the quinhydrone reaction in non-aqueous solution. Electrodes made from new C. P. platinum wire, when first used, gave reliable results in *n*-butyl alcohol solution; after some use, however, they became erratic in behavior, disagreeing among themselves and with former measurements on the same buffer. No method of cleaning could be depended upon to restore their original good characteristics. Old platinum wire electrodes which had been used previously in inorganic oxidation–reduction systems in aqueous solution were always very erratic. These observations support the hypothesis of Hammett and Dietz[2] that platinum readily picks up surface impurities which are electromotively active, thus causing variations in the electrode potentials.

Gold-on-glass electrodes similar to those used by Hammett and Dietz[2] were prepared by the method of Newberry[4] except that the gold was deposited from a solution of gold trichloride in *n*-butyl alcohol instead of in ethyl alcohol. They were found to give satisfactory results in *n*-butyl alcohol solution provided they were subjected to a preheating treatment immediately before use. This treatment consisted in washing with ethyl alcohol, heating to dull redness in the tip of a Bunsen flame, and finally cooling in air. When treated by this method immediately before immersion in the solution to be measured, individual electrodes seldom failed to agree with each other within 1 millivolt and usually agreed within a few tenths of a millivolt.

After some use, however, gold-on-glass electrodes sometimes failed to give reproducible values when first immersed in the solution to be measured, even though they had been subjected to the usual heat treatment. In these cases the electrodes would finally attain a reproducible value, but the rate of attainment of equilibrium was very slow. This indicates that the catalytic properties of the electrode change with use. It is possible that as the electrode is used surface impurities are picked up (as in the case of platinum), which either lower the activity of the catalyst, or as a result of a lowered activity of the catalyst, become predominant in their effect on the electrode potential.

Three pairs of electrodes were used in all cells. Criteria of reliability of electrodes were: (1) agreement between several electrodes in the same buffer; (2) rapid attainment of equilibrium; and (3) in later work the reproducibility of the voltage of a given cell. The salicylate–benzoate cell was used many times for this purpose.

In addition to the electrode trouble described above there was observed at times a very slow drift in the potential of the cell being measured. That this drift was the result of a real change in the quinhydrone equilibrium was indicated by the fact that it occurred when all the electrodes were in close agreement. The rate of drift was greater as the buffer solution was made more alkaline and was generally in the direction of reduction of quinone rather than of oxidation of hydroquinone. It was found that in one or two cases the rate of drift was greatly reduced by passing the nitrogen over rather than through the solution, but this behavior could not be reproduced. As a result of these observations, however, the nitrogen was passed through the solutions only for fifteen to twenty minutes initially when the cell was set up, after which it was passed over the solution for the remainder of the period of test. This procedure seemed to give somewhat steadier potentials.

Colorimeter.—A Klett–Beaver comparator was used in the colorimetric work.

Materials

***n*-Butyl Alcohol.**—The Eastman product listed as practical (Cat. No. P-50) was used throughout this work. It was purified by extended treatment with anhydrous barium oxide, followed by distillation from barium oxide at reduced pressure (30 to 40 mm. of mercury) in an all-Pyrex glass distillation apparatus. This apparatus was fitted with a Widmer fractionating column 30 cm. in length. The presence of an excess of porous lumps of the anhydrous barium oxide permitted the distillations to be carried out at low pressure without the introduction of air or gas usually admitted to prevent bumping. The product was acid and aldehyde free. The boiling point was 117 ± 1°. The dielectric constant[5] of the purified solvent was 17.4 ± 0.1 at 24.5° when measured at frequencies of 10 and 100 k.c.

After use, the solvent was re-purified by subjecting it to two or more vacuum distillations as described above, after which it could again be used.

The Alkali Reagent.—A solution of 0.1 *N* sodium butylate was prepared by the interaction of metallic sodium and pure *n*-butyl alcohol. Before adding the sodium, the alcohol was saturated with hydrogen or nitrogen to displace carbon dioxide. After preparation, the solution was immediately stored under hydrogen in a Pyrex bottle made light-proof by painting with black lacquer. The bottle was fitted with a stopper which carried two tubes; one of these was connected through a drying tower to a tank of compressed hydrogen, and the other, which extended nearly to the bottom of the bottle, was connected to a three-way stopcock buret of 10-ml. capacity. The open end of the buret was fitted with a soda-lime tube. Before filling, the air in the buret was swept out by passing through it a stream of hydrogen. It was filled by means of a slight pressure from the compressed hydrogen tank.

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[3] Halford, THIS JOURNAL **53**, 2944 (1931); *ibid.*, **55**, 2272 (1933).

[4] Newberry, *Trans. Electrochem. Soc.*, **64**, 209 (1933).

[5] The dielectric constant was measured by Dr. S. O. Morgan.

An alkali solution thus prepared and stored usually remained constant in titer against standard benzoic acid for at least one month.[6] Its purity was frequently tested by titrating potentiometrically portions of a standard picric acid in butyl alcohol solution, according to the method described by Wooten and Ruehle,[6] which provides a sensitive test for the presence of weak acid salts.

Since lithium chloride was to be added to the solutions under study, an attempt was made to employ lithium butylate as the alkali reagent, thus simplifying the system by limiting it to lithium salts. It was found, however, that lithium butylate is almost completely insoluble in butyl alcohol.

Lithium Chloride.—This salt was obtained from two sources. The fused product from Kahlbaum was found to contain 0.3% free alkali. This proved so troublesome to purify that its use was abandoned for a special anhydrous product obtained from Merck and Company which was practically free from alkali and could be used without further purification. Saturated solutions were prepared by heating in a Pyrex glass reflux apparatus a portion of the pure solvent in contact with an excess of the anhydrous salt. The solutions of lithium chloride in butyl alcohol obtained by this method were approximately 2.1 *M* when allowed to come to equilibrium at room temperature.

Quinhydrone.—The quinhydrone used in most of the work was obtained from the Eastman Kodak Co., melting point 170°. Recrystallization from butyl alcohol did not perceptibly improve its quality.

Owing to its high solubility in *n*-butyl alcohol it was not feasible to employ a saturated solution of quinhydrone. Consequently it was added in equivalent quantities to each half cell in concentration of 50 mg. per 100 ml. of solution. Variation of the concentration of quinhydrone did not influence the voltage of the cell.

Compressed Nitrogen.—Tank nitrogen was purified by passing it through towers containing soda-lime and phosphorus pentoxide and through a fritted glass wash bottle containing *n*-butyl alcohol, which served to saturate the gas with alcohol vapor. No attempt was made to remove the small amount of oxygen known to be present.

Acids.—With the exception of benzoic and trimethylbenzoic, the acids used were obtained from the Eastman Kodak Company. The benzoic acid was the Bureau of Standards Alkalimetric Standard No. 39d, and was employed both as a primary alkalimetric standard and as a standard in the measurement of relative strength. Trimethylbenzoic acid was prepared from bromomesitylene by the method of Bamford and Simonsen.[7,8]

Solid acids were dried in an oven at suitable temperature and stored over phosphorus pentoxide. In some cases they were further purified as indicated in the following table. In general they were considered of sufficient purity if they gave correct melting points within ±1°. Liquid acids were dried by treatment with anhydrous sodium sulfate followed by distillation at reduced pressure, and characterized by their boiling points. An additional check on the purity of the acids was the determination of the equivalent weight by titration in butyl alcohol with standard sodium butylate solution. The analytical results obtained on the acids are listed in Table I.

TABLE I

Acid	Physical constants, m. p., °C.	Analyses, %	Remarks
Benzoic	121.5		
o-Chlorobenzoic	141	99.7	Recryst. from alc.
m-Chlorobenzoic	154	99.7	Recryst. from water
p-Chlorobenzoic	240–241	99.9	Sublimed
o-Nitrobenzoic	147	99.8	Recryst. from hot water
m-Nitrobenzoic	142	99.6	
p-Nitrobenzoic	241–242	99.7	
o-Toluic	102	99.8	
m-Toluic	111–112	99.8	Recryst. from alc.
p-Toluic	177–178	99.7	
o-Methoxybenzoic	102–103	99.6	Recryst. from hot water
Anisic	184–185	99.8	Recryst. from alc.
Salicylic	158	100.0	Recryst. from alc.
Trimethylbenzoic	152–153	99.9	Recryst. from hot CCl_4
Formic	B. p. 100	99.8	
Acetic	B. p. 118	99.9	
Chloroacetic	61–62	99.6	
Dichloroacetic	B. p. 194	99.5	
Trichloroacetic	57	98.0	
Propionic[a]	B. p. 141.3		
α-Chloropropionic	B. p. 186	100.5	
β-Chloropropionic	42	99.8	
Butyric[a]	B. p. 163.3		
n-Valeric[a]	B. p. 186.6		
n-Caproic[a]	B. p. 202		
n-Caprylic	B. p. 237		
Maleic	138	99.7	
d-Camphoric	181	99.7	
p-Nitrophenol	114	99.7	
2,4-Dinitrophenol	112	99.6	
Picric	121	99.6	

[a] Purified by Mr. H. Wadlow. These acids were treated with anhydrous sodium sulfate and triple distilled at low pressure in a special distillation apparatus.

Precision and Reliability

Logarithmic titration curves were employed to demonstrate that the acids studied behave as normal weak acids in *n*-butyl alcohol solutions of high and constant ionic strength. Some of these curves are shown in Figs. 1 and 2. Excluding picric and trichloroacetic acids, which are moderately strong acids even in *n*-butyl alcohol, the average slope of the curves obtained is 58 ± 2 millivolts per logarithmic unit, which is in close agreement with the theoretical slope given by

$$\Delta E/\Delta \log \frac{X}{1 - X} = 59 \text{ mv. at } 25°$$

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[6] Wooten and Ruehle, *Ind. Eng. Chem., Anal. Ed.*, **6**, 449 (1934).

[7] Bamford and Simonsen, *J. Chem. Soc.*, **97**, 1906 (1910).

[8] This acid was prepared and purified by Mr. H. P. Treffers.

where X is the fraction neutralized at voltage E.

Table II shows typical data obtained on two representative cells. Three pairs of electrodes were used in each buffer.

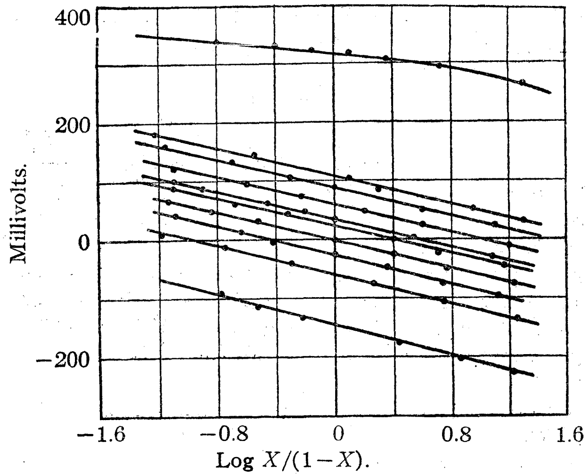

Fig. 1.—Logarithmic titration curves with quinhydrone electrode in *n*-butyl alcohol, 0.002 *M* acids titrated with 0.1 *M* sodium butoxide: in order, from the top, picric, 2,4-dinitrophenol, salicylic, *o*-chlorobenzoic, *m*-chlorobenzoic, *p*-chlorobenzoic, benzoic, *p*-methoxybenzoic, trimethylacetic, *p*-nitrophenol.

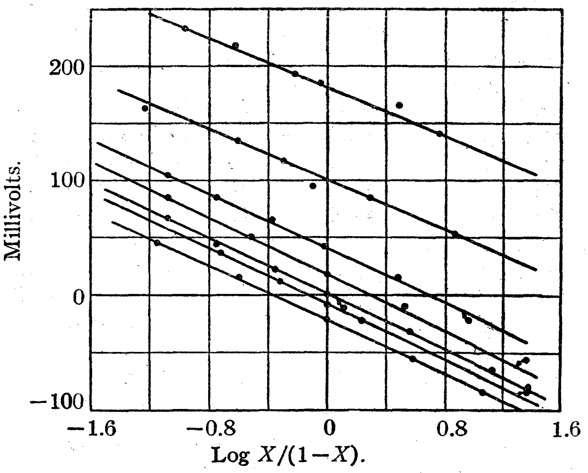

Fig. 2.—Logarithmic titration curves with quinhydrone electrode in *n*-butyl alcohol, 0.002 *M* acids titrated with 0.1 *M* sodium butoxide: in order from the top, dichloroacetic, chloroacetic, trimethylbenzoic, *o*-methoxybenzoic, *o*-toluic, *p*-toluic, *n*-caprylic.

TABLE II

(a) Salicylate–Benzoate Cell

Time	E_1, mv.	E_2, mv.	E_3, mv.
10 min.	88.9	91.3	90.8
15 min.	88.9	90.5	90.0
2 hrs.	89.0	90.6	90.5
20 hrs.	91.6	91.5	91.1

(b) Butyrate–Benzoate Cell

Time	E_1, mv.	E_2, mv.	E_3, mv.
10 min.	19.4	20.0	20.0
30 min.	21.1	20.7	20.7
45 min.	20.9	20.8	20.8
3 hrs.	21.0	20.9	21.0

Table III shows the reproducibility of the method. The values shown were obtained on salicylate–benzoate cells prepared at different times from different reagents. The measurements were made under the same conditions except for small variations in room temperature. Each value is the average of a number of measurements using three electrode pairs over a period of at least two hours.

From the results presented in Tables II and III it is seen that the precision limits of the method are easily within ±0.05 logarithmic units.

TABLE III

SALICYLATE–BENZOATE CELL

Date	E, mv.	Dev. from mean
5/19/34	88.5	−0.4
5/27/34	86.0	−2.9
6/4/34	86.3	−2.6
9/20/34	91.0	+2.1
10/6/34	90.2	+1.3
10/7/34	90.0	+1.1
11/7/34	88.5	−0.4
12/31/34	91.3	+2.4
Average	88.9	±1.6

Effect of Water.—Although precautions were taken to dry the solvent, acids and other reagents before use, the method employed did not permit the measurements to be made without some exposure of the solutions to the atmosphere. It was therefore necessary to determine the influence of water upon the electromotive force of a typical cell. In the following table the effect of water upon the salicylate–benzoate cell is shown. The same effect was observed on a number of different cells.

TABLE IV

Per cent. water added		E. m. f.	
Benzoate arm	Salicylate arm	E_1	E_2
0.0	0.0	90.1	90.1
.1	.0	91.2	91.3
.5	.0	94.5	94.6
1.0	.0	98.8	98.2
2.0	.0	101.5	101.0
3.0	.0	104.7	104.5
5.0	.0	109.5	109.0
5.0	5.0	91.3	91.0

These results show that water has definite basic properties in *n*-butyl alcohol solution and thus causes a decrease in the potential of the half-cell to which it is added. But if it is present in equivalent quantities in both half cells the effect on the voltage of the cell is apparently negligible. Traces of moisture in the solvent therefore should not alter the relative strength of the acids. The linearity of the logarithmic titration curves, however, indicates that the solvent was comparatively free of moisture.

Effect of Varying Neutral Salt.—To determine whether an 0.05 *M* concentration of lithium chloride was sufficient to produce a sensibly constant ionic environment when working with 0.0025 *M* buffer solutions the following experiment was carried out.

TABLE V

EFFECT OF VARYING NEUTRAL SALT CONCENTRATION ON THE SALICYLATE–BENZOATE CELL

Molar salt concentration		E. m. f.	
Salicylate arm	Benzoate arm	E_1	E_2
0.00	0.00	121.2	120.8
.00	.05	77.0	77.5
.05	.05	90.1	90.3
.05	.10	84.4	84.1
.10	.10	90.2	89.5
.10	.15	86.4	86.5
.15	.15	90.6	90.9

The results shown in Table V indicate that as the salt concentration is increased the voltage of the cell becomes less sensitive to changes in salt concentration. Beyond 0.05 *M*, large variations in salt concentration may occur without greatly influencing the electromotive force of the cell. The agreement of the logarithmic titration curves with the theoretical slope (Figs. 1 and 2) also indicates that an 0.05 *M* salt concentration is sufficient to produce a sensibly constant ionic environment when the concentration of the acid is 0.002 to 0.003 *M*.

Effect of Temperature.—Tests on the salicylate–benzoate and acetate–benzoate cells showed that a change in temperature of 10° caused a change in voltage of approximately 2 millivolts. It was concluded from these tests that the error caused by variations in temperature of ±3° was negligible compared to other sources of error in the method.

Results

The results on the relative strengths of acids obtained by the potentiometric method are summarized in Table VI. Variations in relative strength are expressed in logarithmic units. A negative sign indicates that an increase in acid strength relative to benzoic acid occurs when the acid is transferred from water to butyl alcohol, a positive sign that a decrease occurs.

The values for pK_{H_2O} in Table VI are at 25° and are from Landolt–Börnstein "Tabellen" unless otherwise indicated.

TABLE VI

Acid	pK_{H_2O}	ΔpK_{H_2O}	ΔpK_{BtOH}	Change in relative strength
Benzoic	4.20[9]	0	0	0
o-Chlorobenzoic	2.92[9]	−1.28	−1.00	+0.28
m-Chlorobenzoic	3.82[9]	−0.38	−0.60	− .22
p-Chlorobenzoic	3.96[9]	− .22	− .42	− .20
o-Nitrobenzoic	2.19	−2.01	−1.74	+ .27
m-Nitrobenzoic	3.46	−0.74	−1.09	− .35
p-Nitrobenzoic	3.40	− .80	−1.12	− .32
o-Toluic	3.90	− .30	−0.02	+ .28
m-Toluic	4.25	+ .05	+ .09	+ .04
p-Toluic	4.37	+ .17	+ .21	+ .04
o-Methoxybenzoic	4.08[10]	− .12	− .31	− .19
Anisic	4.48[10]	+ .28	+ .40	+ .12
Salicylic	2.97	−1.25	−1.50	− .27
Trimethylbenzoic	3.43	−0.77	−0.68	+ .09
Formic	3.75[11]	− .45	−1.09	− .64
Acetic	4.76[12]	+ .56	+0.05	− .51
Monochloroacetic	2.86[13]	−1.34	−1.71	− .37
Dichloroacetic	1.3	−2.9	−3.1	− .2
Trichloroacetic	0.7	−3.5	−4.1	− .6
Trimethylacetic	5.01	+0.81	+1.01	+ .20
Propionic	4.85	+ .65	+0.41	− .24
α-Chloropropionic	2.83	−1.37	−1.43	− .06
β-Chloropropionic	4.07	−0.13	−0.49	− .36
Butyric	4.83	+ .63	+ .36	− .27
n-Valeric	4.80	+ .60	+ .40	− .20
n-Caproic	4.85	+ .65	+ .39	− .26
n-Caprylic	4.85	+ .65	+ .42	− .23
Maleic (1st)	1.82	−2.38	−3.61	−1.23
Maleic (2d)	6.58	+2.38	+1.96	−0.42
d-Camphoric (1st)	4.37	+0.17	+0.22	+ .05
p-Nitrophenol	7.17	+2.97	+2.41	− .56
2,4-Dinitrophenol	4.10	−0.10	−1.88	−1.78
Picric	0.8	−3.4	−5.4	−2.0

Colorimetric Work.—The relative strengths of 2,4-dinitrophenol and of salicylic, chloroacetic, and *o*-nitrobenzoic acids were determined colorimetrically using 2,4-dinitrophenol as indicator. The strength of the acid (pK_a) is related to the strength of the acid indicator (pK_I) and the degree of dissociation of the indicator (α) in a half-neutralized buffer of the acid in the following way.

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(9) Saxton and Meier, THIS JOURNAL, **56**, 1918 (1934).

(10) "International Critical Tables," Vol. VI.

(11) Harned and Embree, THIS JOURNAL, **56**, 1042 (1934).

(12) Harned and Ehlers, *ibid.*, **55**, 652 (1933).

(13) Wright, *ibid.*, **56**, 314 (1934).

$$pK_a = pK_I + \log \alpha/(1 - \alpha)$$

The buffer solutions were 0.002 molar in acid and salt, the indicator concentration was 0.00004, except for one measurement on the salicylic system, where it was one-half as great. Each item in the tables represents the mean of many colorimetric settings on an individually prepared buffer system. The reference solution for completely ionized dinitrophenol was prepared with sodium butylate in butyl alcohol. The potentiometric values were obtained by the direct comparison of the carboxylic acid with dinitrophenol. They are reasonably consistent with those obtained by comparing both carboxylic acids and dinitrophenol with benzoic acid.

Table VII contains the results obtained in solutions containing 0.05 *M* lithium chloride as in the potentiometric measurements.

TABLE VII

Acid	$pK_a - pK_I$ Colorimetric	Potentiometric
o-Nitrobenzoic	+0.12, 0.08, Av. +0.10	+0.14
Chloroacetic	+0.24	+ .24
Salicylic	+0.55, 0.33, 0.29, 0.22, Av. +0.35	+ .35

The agreement between the potentiometric and the colorimetric work is strong support for the validity of both methods of determining acid strength in this solvent.

Table VIII contains the results of some colorimetric measurements in which no lithium chloride was added.

TABLE VIII

Acid	$pK_a - pK_I$
o-Nitrobenzoic	+0.09, 0.07, 0.27, Av. 0.14
Chloroacetic	+0.21
Salicylic	+0.31, 0.34, 0.32, Av. +0.33

With these acids there does not seem to be any very important change in relative strength with salt concentration in this range.

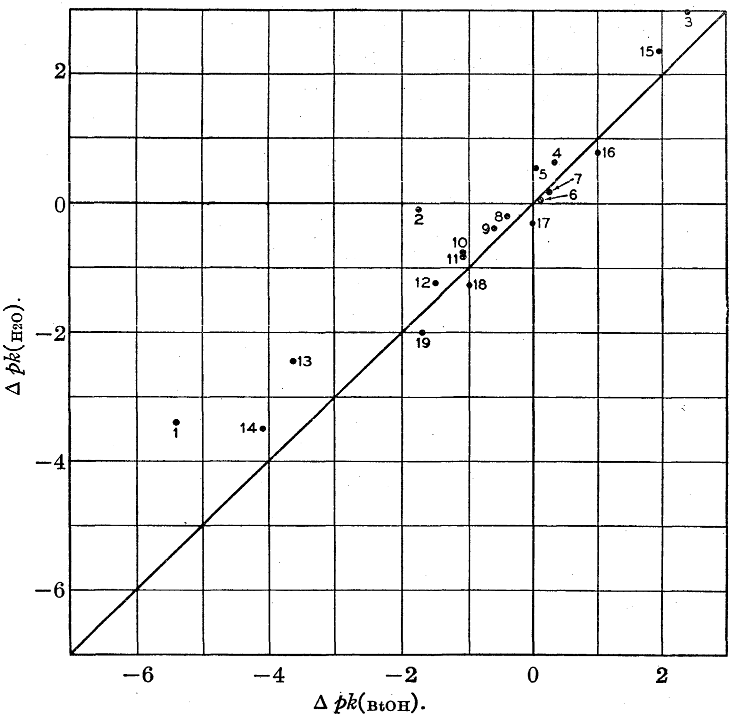

Fig. 3.—Relative strengths of acids in water and in *n*-butyl alcohol referred to benzoic acid: 1, picric; 2, 2,4-dinitrophenol; 3, *p*-nitrophenol; 4, butyric; 5, acetic; 6, *m*-toluic; 7, *p*-toluic; 8, *p*-chlorobenzoic; 9, *m*-chlorobenzoic; 10, *m*-nitrobenzoic; 11, *p*-nitrobenzoic; 12, salicylic; 13, maleic (1); 14, trichloroacetic; 15, maleic (2); 16, trimethylacetic; 17, *o*-toluic; 18, *o*-chlorobenzoic; 19, *o*-nitrobenzoic.

Discussion

Specific variations in relative strengths of acids and bases with changing solvent have been rather generally interpreted in terms of a theory[14] according to which the change in relative strength should be a function of the charge and radius of the ion and of the dielectric constant of the medium. The dependence upon ionic charge has been verified qualitatively by Brönsted,[14c] and the predicted linear dependence upon the reciprocal of the dielectric constant has been shown by Wynne-Jones[14d] to be satisfactorily fulfilled by the existing conductivity data for the solvents water, and methyl and ethyl alcohols.[15] That the variations in relative strength of closely related carboxylic acids should depend upon changes in ionic size seems, however, not very probable and the present results support a different interpretation which re-

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(14) (a) Born, *Z. Physik*, **1**, 45 (1920); (b) Bjerrum and Larsson, *Z. physik. Chem.*, **127**, 358 (1927); (c) Brönsted, *Chem. Rev.*, **5**, 231 (1928); (d) Wynne-Jones, *Proc. Roy. Soc.* (London), **A140**, 440 (1933).

(15) The data obtained in this investigation do not agree with the relationship proposed by Wynne-Jones, but do not provide a fair test of it, since they were obtained in solutions of fairly high ionic strength. Both the theory and its previous tests apply to solutions of zero ionic strength. Our few colorimetric measurements at low ionic strengths do not indeed indicate large variations of relative strength with change in salt concentrations but are not sufficiently comprehensive to be conclusive.

cently has been discussed by Schwarzenbach and Egli.[16]

It should be noted first that there is a marked difference in behavior between acids in which the substituent is adjacent to the carboxyl group and those in which the substituent is more distantly located. Considering only the distantly substituted acids, it appears that any substitution which causes an increase in absolute strength causes an increase in relative strength, while one which causes a decrease in absolute strength causes a decrease in relative strength when the substituted and unsubstituted acids are transferred from water to *n*-butyl alcohol. This generalization is in accord with the expression which gives the additional electrical work ΔW required to ionize an acid containing a substituted polar group as compared with the unsubstituted acid in a solvent of dielectric constant D[16,17]

$$\Delta W = e\,\mu \cos \Theta / Dr^2$$

where r is the distance from the dipole to the carboxyl group, $\mu \cos \Theta$ is the component of the electric moment of the substituent along r, and e is the charge on the ion. A change in solvent resulting in a decrease in dielectric constant of the medium should therefore result in a change in relative strength, the direction of which should depend upon the influence of the substituent upon the ionization of the acid. For example, if the substitution results in an increase in ionization, ΔW is negative in sign and a change to a solvent of lower dielectric constant should result in an increase in relative strength; when substitution results in a decrease in ionization, ΔW is positive and a similar change in solvent should result in a decrease in relative strength. Thus meta and para nitro and chloro benzoic acids show an increase in strength relative to benzoic when transferred to *n*-butyl alcohol solution while meta- and para-methylbenzoic and para-methoxybenzoic acids show a decrease in strength. Similarly, beta-chloropropionic acid shows an increase in strength relative to propionic in agreement with the result expected from the fact that this acid is stronger than propionic acid in aqueous solution.

The changes in relative strength observed for ortho substituted benzoic acids and alpha substituted aliphatic acids show, however, that some quite different effect is involved when the substitution is near the carboxyl group. With the exception of *o*-hydroxy and *o*-methoxybenzoic acids, all of the ortho compounds studied decrease in strength relative to benzoic despite the fact that all substituents in this position cause an increase in the absolute strength of the acid. Likewise, chloroacetic and dichloroacetic acids decrease in strength relative to acetic. These results are similar to those obtained by Schwarzenbach[16] on the effects of substitution on the relative strengths of phenols and thiophenols in water and ethyl alcohol solutions. He concluded that while the results obtained on meta and para compounds could be explained fairly satisfactorily in terms of the electric moments of the substituents, other factors became predominant in the case of ortho substituted compounds.

It seems indeed to be a rather generally valid principle that the effects of an adjacent and of a distant substituent upon the reactions of a particular group in an organic molecule depend upon entirely different properties of the substituent. This is a familiar fact in the kinetics of reactions where an ortho substituent gives rise to a "steric hindrance."[18] With respect to equilibrium quantities it was noted by Flürscheim[19] that the introduction of any substituent into the ortho position in benzoic acid, regardless of its so-called electrochemical nature, has the effect of increasing the strength of the acid. Smallwood[17d] noted that all ortho substituted benzoic acids have especially large temperature coefficients of ionization.

Summary

1. A method for the measurement of the relatives strengths of acids in *n*-butyl alcohol has been developed.

2. The relative strengths of thirty-three representative carboxylic and phenolic acids have been measured.

3. The effect of a substituent upon the variation in relative strength with changing medium is that to be expected from the electric moment of the substituent and the dielectric constant of the medium when the substituent is introduced into the molecule at a point considerably removed from

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[16] Schwarzenbach and Egli, *Helv. Chim. Acta*, **17**, 1176, 1183 (1934).

[17] (a) Waters, *Phil. Mag.*, **8**, 436 (1929); (b) Wolf, *Z. physik. Chem.*, **B3**, 128 (1929); (c) Briegleb, *ibid.*, **B10**, 205 (1930); (d) Smallwood, THIS JOURNAL, **54**, 3048 (1932); (e) Eucken, *Z. angew. Chem.*, **45**, 203 (1932).

[18] See Hammett, *Chem. Rev.*, **17**, 125 (1935).

[19] Flürscheim, *J. Chem. Soc.*, **95**, 718 (1909). See also Lapworth and Manske, *ibid.*, 2533 (1928).

the carboxyl group. Some other influence is however preponderant when the substitution is adjacent to the carboxyl group, that is to say when it is on the alpha carbon in an aliphatic acid, or in the ortho position in benzoic acid.

NEW YORK, N. Y. RECEIVED JULY 30, 1935

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Mechanism of the Slow Oxidation of Propane

BY ROBERT N. PEASE

In his original work[1] on the non-explosive oxidation of propane and the butanes, the writer was especially impressed with the fact that the oxidation reactions induced the dissociation of the hydrocarbons into the normal products, *e. g.*

$$\begin{aligned} C_3H_8 &\longrightarrow C_3H_6 + H_2 \\ &\longrightarrow C_2H_4 + CH_4 \end{aligned}$$

This was discussed briefly in terms of what would now be called an "energy-chain." Since this work was done, F. O. Rice has brought out his "radical-chain" theory of hydrocarbon dissociation.[2] In view of the success of this theory in accounting for such experiments as those of Frey[3] on the dissociation of *n*-butane induced by decomposing dimethyl-mercury, it appeared important to attempt to account for the reactions occurring in hydrocarbon–oxygen mixtures in terms of radical-chains. For this purpose additional information about the products of the reactions was required.

In approaching this problem—the determination of liquid as well as gaseous reaction products—we were at first "side-tracked" by the discovery that substantial quantities of organic peroxides (other than per-acids) were formed.[4] However, it was eventually found that these peroxides could be largely eliminated (by coating the reaction tube with potassium chloride) without greatly affecting the reaction rate, an observation which convinced us that peroxides took no main part in the development of reaction. Had peroxides proven of greater importance, we would have been inclined toward Egerton's energy-chain theory.[5] An exhaustive search for other liquid oxidation products was then undertaken, the result of which was to show that, in the case of propane, only methanol and formaldehyde were of any importance. However, conditions were not favorable to the production of anything like stoichiometric yields of these, and the tentative conclusion was reached that the true primary products had still to be discovered.

Further investigation of this problem now indicates that methanol and formaldehyde, in addition to carbon monoxide and water, are in fact the primary products of propane oxidation, the indicated stoichiometric equation being

$$C_3H_8 + 2O_2 \longrightarrow CH_3OH + HCHO + CO + H_2O$$

How the general result is to be expressed in terms of the radical-chain theory will be discussed following presentation of the experimental data.

Experimental

The general methods of the previous investigations were employed. The gases passed at a known rate through a heated reaction tube of Pyrex glass coated with potassium chloride. Liquid products were separated at −40°, while gaseous products were separately collected over water with the trap at 0°. Methanol was determined by reaction with acetic anhydride (forty-eight hours at room temperature); formaldehyde by the potassium cyanide method; total aldehydes by the bisulfite method; esters by saponification following the alcohol determination. Carbon dioxide was absorbed in caustic; higher olefins (designated C_nH_{2n}) in concentrated sulfuric acid; ethylene in bromine water; oxygen in "Oxsorbent." Hydrogen and carbon monoxide were oxidized over copper oxide at 350°; paraffins were oxidized at 600°.

It was desirable to eliminate the olefin-producing reactions as far as possible. For this purpose, the experiments were conducted at low temperatures (300°, with one set at 260°). This necessitated the use of rather large reaction tubes. In order to minimize secondary oxidations, only mix-

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[1] Pease, THIS JOURNAL, **51**, 1839 (1929).

[2] F. O. and K. K. Rice, "The Aliphatic Free Radicals," Johns Hopkins Press, Baltimore, Md., 1935.

[3] Frey, *Ind. Eng. Chem.*, **26**, 198 (1934).

[4] Pease and Munro, THIS JOURNAL, **56**, 2034 (1934).

[5] Egerton, *Nature*, **121**, 10 (1928); "Activation et Structure des Molecules," Société de Chimie Physique, 1928, p. 489.

TABLE I

Reaction tube					Of 400 cc. reaction mixture in								
					Used cc.		Formed, cc.						
Diam., cm.	Length, cm.	Vol., cc.	Temp., °C.	% O_2	O_2	C_3H_8[a]	CO	CH_3OH	HCHO	Higher CHO	CO_2	CH_4	C_nH_{2n}
2	30	105	300	20	77	40	28	21	14	7	15	1	5
3	22	146			79	41	38	23	12	8	10	4	6
4	12	141			78	50	37	24	11	8	12	8	5
6.5	6.5	162			76	46	38	20	13	5	11	11	7
3	22	146	300	10	39	19	14	16	9	4	4	2	4
				20	79	41	38	23	12	8	10	4	6
				30	119	47	48	27	12	11	17	5	9
6	28	762	260	10	39	17	16	12	7	4	7	5	3
				20	77	44	33	22	12	5	11	7	3
				30	116	65	47	28	14	5	19	9	2
			300	20	76	48	45	20	9	5	10	15	6

[a] "C_3H_8 used" represents the difference of two rather large numbers, and is consequently subject to a considerable error—perhaps 3 to 5 cc.

tures relatively low in oxygen (10 to 30%) were investigated.

Results are presented in Table I. The data refer to runs in which 400 cc. of reaction mixture was passed through the apparatus in ten minutes. Liquid products are calculated as cc. of vapor under standard conditions (760 ± 10 mm.; 25 ± 3°). In addition to the products listed, there were found 0 to 2 cc. of ethylene, hydrogen, acid and ester, with usually traces (<1 cc.) of peroxide. These are omitted in order to simplify the table somewhat.

Tubes of various dimensions were first investigated to determine optimum conditions. Over the range of diameters from 2 to 6.5 cm. there was little choice at 300°.[6] Sets of runs were finally made with 10, 20 and 30% oxygen at 300° with the 3-cm. tube, and at 260° with a large tube 6 cm. in diameter.

It will be noted that roughly two moles of oxygen react for every mole of propane, and one mole of carbon monoxide is formed. Next to carbon monoxide, methanol is the important product; and as the oxygen input is decreased, the amount of methanol tends to approximate the amount of propane reacting (see 10% runs). Formaldehyde behaves similarly, though the agreement is poorer. Nevertheless the *total* aldehyde ("HCHO" plus "Higher CHO") follows the methanol rather closely. Losses are clearly made up by secondary formation of carbon dioxide and methane.

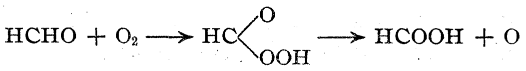
Discussion

Any consideration of the mechanism of propane oxidation must give prominence to two fundamental facts, namely, (1) the persistence of one-carbon oxidation products, particularly methanol, at low temperatures and low oxygen concentrations; (2) the induced dissociation of the hydrocarbon at higher temperatures. Bone's hydroxylation theory[7] makes no provision for lower alcohols,[8] nor for induced dissociation. Norrish's development of the latter to include radical-chains propagated via oxygen atoms and alkylidene radicals[9] comes somewhat closer to what the writer is inclined to believe is the truth, but again it is not obvious how a lower alcohol could arise as a principal product. Norrish writes for the methane-oxidation chain

$$O + CH_4 \longrightarrow CH_2 + H_2O$$
$$CH_2 + O_2 \longrightarrow HCHO + O$$

The chain is started by surface reactions

$$CH_4 + O_2 \longrightarrow HCHO + H_2O$$



$$HCHO + O_2 \longrightarrow HC\langle^{O}_{OOH} \longrightarrow HCOOH + O$$

It is ended by the reactions

$$O + CH_4 + X \longrightarrow CH_3OH + X'$$
$$O + \text{surface} \longrightarrow {}^1/_2\, O_2$$

Provision is thus made for the alcohol of the same number of carbon atoms in the process of ending a chain. This type of mechanism obviously could not account for a stoichiometric yield of alcohol, especially one of fewer carbon atoms than the original hydrocarbon contained. The

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(6) With the 2-cm. tube, reaction had to be started at 325–350° after which it would maintain itself on cooling to 300°. With a 1-cm. tube, a temperature of 400° was required for starting; and reaction would maintain itself only above 375°.

(7) Bone and Townend, "Flame and Combustion in Gases," The Macmillan Co., 60 Fifth Ave., New York City, 1927.

(8) Methanol was identified in every experiment by preparing the 3,5-dinitrobenzoate and taking its melting point. The latter was always sharp and close to the correct value for the methyl ester (108°). The alcohol from isobutane also proved to be methanol. From *n*-butane, the derivative melted from 95–102°, indicating a mixture of methyl and ethyl (m. p. 93°) esters.

(9) Norrish, *Proc. Roy. Soc.* (London), **150A**, 36 (1935).

same objection can be brought against the similar but independently developed theories of Semenoff[10] for hydrocarbon oxidation.

The writer is inclined to go back to Rice's theory of hydrocarbon dissociation[2] as a starting point for the oxidation mechanism of propane. According to this, the dissociation of propane proceeds essentially through the reactions

Chain-starting $C_3H_8 \longrightarrow CH_3 + C_2H_5$

Chain-development $(R = CH_3, (C_2H_5), H)$

$$(1)\quad C_3H_8 + R \longrightarrow RH + C_3H_7$$

$$(2)\quad C_3H_7 \begin{matrix} \nearrow C_3H_6 + H \\ \searrow C_2H_4 + CH_3 \end{matrix}$$

Chain-ending $R + R' \longrightarrow RR'$

Quite apart from the applicability of this scheme to the normal dissociation, one may grant its usefulness in interpreting induced dissociations and allied reactions. In essence, the mechanism requires a radical, R, which is capable of removing a hydrogen atom or methyl group from the propane molecule, and which is reproduced in the subsequent reactions of the residue. Our problem is to determine what reasonable sequence of reactions of this type will yield the observed products of the oxidation reactions.

The mechanism which the writer has in mind postulates the methoxyl radical (CH_3O) and the propyl radical (C_3H_7) as chain carriers

$$CH_3O + C_3H_8 \longrightarrow CH_3OH + C_3H_7$$
$$C_3H_7 + O_2 \longrightarrow C_2H_4O + CH_3O$$

These would yield methanol and the compound C_2H_4O, which is taken to be acetaldehyde. A portion of the acetaldehyde survives (higher CHO). The remainder reacts with oxygen to give formaldehyde and carbon monoxide

$$CH_3CHO + O_2 \longrightarrow HCHO + CO + H_2O$$

The addition of oxygen to acetaldehyde is measurable at 100°. It must be extremely rapid at 300°. That the low-temperature product (peracetic acid) breaks down to yield carbon monoxide at higher temperatures appears plausible from the work of Pope, Dykstra and Edgar[11] on the oxidation of *n*-butyraldehyde and *n*-heptaldehyde. The main oxidation products (CH_3OH, HCHO, CO) are thus accounted for. Further reaction of the propyl radicals will also yield the normal products of dissociation at higher temperatures by Rice's mechanism given above. The suggested scheme thus affords a straightforward explanation of the analytical data.

The starting and stopping of chains is less clear.[12] It is to be remembered that reaction is very strongly inhibited by a packing, and is at least delayed at intermediate temperatures (375–425°) by excess of foreign gases, as well as oxygen, the reaction having a negative temperature coefficient in this range. The effect of packing rather argues against a wall reaction for starting the chains. Homogeneous dissociation of propane into radicals seems to be ruled out. Likewise a homogeneous bimolecular reaction between propane and oxygen seems doubtful since the over-all reaction depends more on the propane than on the oxygen concentration. It is accordingly suggested that the starting reactions are

$$2C_3H_8 \longrightarrow C_3H_8^* + C_3H_8$$
$$C_3H_8^* + O_2 \longrightarrow C_2H_5O + CH_3O$$

the oxidation of $C_3H_8^*$ being much faster than the deactivation of $C_3H_8^*$ by collision.

The chain-stopping reactions are taken to be association of radicals by a 3-body process occurring chiefly at the walls

$$2CH_3O + M \longrightarrow X$$
$$2C_3H_7 + M \longrightarrow Y$$
$$CH_3O + C_3H_7 + M \longrightarrow Z$$

The complete mechanism would therefore be

$$(1)\quad 2C_3H_8 \underset{\longleftarrow}{\xrightarrow{k_1,\ k_1'}} C_3H_8^* + C_3H_8$$

$$(2)\quad O_2 + C_3H_8^* \xrightarrow{k_2} C_2H_5O + CH_3O$$

$$(3)\quad CH_3O + C_3H_8 \xrightarrow{k_3} CH_3OH + C_3H_7$$

$$(4)\quad C_3H_7 + O_2 \xrightarrow{k_4} C_2H_4O + CH_3O$$

$$(5)\quad C_2H_4O + O_2 \xrightarrow{k_5} HCHO + CO + H_2O$$

$$(6)\quad 2CH_3O + M \xrightarrow{k_6} X$$

$$(7)\quad 2C_3H_7 + M \xrightarrow{k_7} Y$$

$$(8)\quad CH_3O + C_3H_7 + M \xrightarrow{k_8} Z$$

Reactions (1) and (2) together are supposed to yield CH_3O at a rate proportional to $[C_3H_8]^2$. At the steady state (point of inflection of the rate curves) we have

$$d[CH_3O]/dt = k_1[C_3H_8]^2 + k_4[C_3H_7][O_2] - k_3[CH_3O][C_3H_8] - k_6[CH_3O]^2M - k_8[CH_3O][C_3H_7]M = 0$$

$$d[C_3H_7]/dt = k_3[CH_3O][C_3H_8] - k_4[C_3H_7][O_2] - k_7[C_3H_7]^2M - k_8[CH_3O][C_3H_7]M = 0$$

Solution for the steady-state concentration of $[CH_3O]$ leads to an unwieldy expression. If we

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[10] Semenoff, "Chemical Kinetics and Chain Reactions," Oxford Press, London, England, 1935.

[11] Pope, Dykstra and Edgar, THIS JOURNAL, **51**, 1875 (1929).

[12] This analysis of the starting and stopping of chains is recognized to be incomplete. In particular, the occurrence of long induction periods, the negative temperature coefficient, and the rôle played by aldehyde oxidation require further consideration.

assume chains are ended only by reaction (6), we find

$$[CH_3O] = \sqrt{k_1/k_6M}\,[C_3H_8]$$

If only reaction (7) is effective

$$[CH_3O] = \frac{1}{k_3}\left(k_1[C_3H_8] + k_4\sqrt{\frac{k_1}{k_7M}}\,[O_2]\right)$$

If only reaction (8) is effective

$$[CH_3O] \cong (k_1/2k_3)\,[C_3H_8]$$

or

$$[CH_3O] \cong \frac{k_1}{4k_3}\,[C_3H_8] \pm \sqrt{\frac{k_1k_4[C_3H_8][O_2]}{2k_3k_8M}}$$

depending upon the approximation which is made. The rate of disappearance of propane will be determined principally by the rate of reaction (3) if chains are long.

$$-d[C_3H_8]/dt \cong k_3[C_3H_8][CH_3O]$$

Substituting the above values of [CH_3O] shows that the rate will depend on a power of [C_3H_8] between 1 and 2, and will be relatively independent of oxygen concentration no matter which reaction is effective in terminating chains.

Mechanisms similar to the above may be written for methane and ethane in terms of hydroxy- instead of methoxyl radicals, yielding water in place of methanol. Such mechanisms are to be considered as an alternative to the Semenoff–Norrish mechanism.

Summary

1. Investigation of the slowoxidation of propane at lower temperatures and oxygen concentrations than heretofore employed indicates that methanol, formaldehyde, carbon monoxide and water are the primary products.

2. Results are interpreted in terms of Rice's radical-chain theory, on the assumption that methoxyl (CH_3O) and propyl (C_3H_7) are the chain carriers.

3. It is pointed out that similar mechanisms involving hydroxyl in place of methoxyl, and producing water in place of methanol, may apply to the oxidation of methane and ethane.

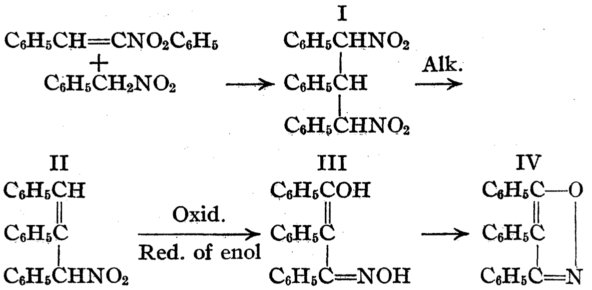
PRINCETON, N. J. RECEIVED JULY 31, 1935

[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

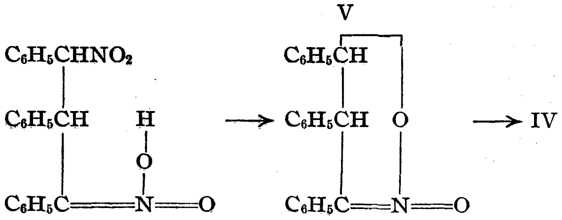
Alcoholic Ammonia as a Reagent in the Nitrostilbene Series

BY DAVID E. WORRALL

Heim[1] assumed the following transformations to account for the presence of triphenylisoxazole as a by-product in the Knoevenagel reaction



He succeeded in isolating the dinitro compound I, likewise an unsaturated nitro compound isomeric with II, but not the monoxime III. Later Kohler and Barrett[2] proved that triphenylisoxazoline oxide (V) is an intermediate between I and IV, using sodium methylate. Consequently they postulate this sequence of events.



It has now been found possible, using a milder reagent, to isolate III and while this does not necessarily mean that the oxime is the sole or even principal precursor of IV, it does fit in with the scheme of Heim.

Ammonia in the absence of water does not react by addition or otherwise with nitrostilbene. A trace of water is sufficient to induce hydrolysis, the starting point of a chain that continues until sufficient phenylnitromethane is liberated to react with unchanged nitrostilbene thereby forming I. It is not improbable that this substance loses nitrous acid so as to form II, which for the most part rearranges into the isoxazoline oxide (V).

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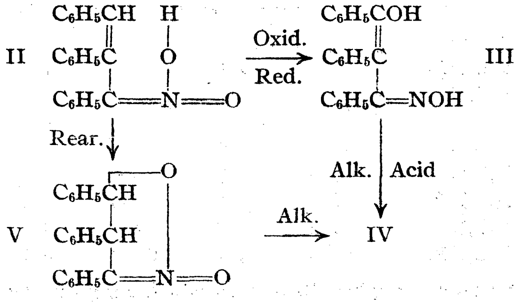
[1] Heim, *Ber.*, **44**, 2021 (1911).

[2] Kohler and Barrett, THIS JOURNAL, **46**, 2106 (1924).

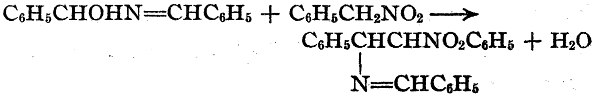
A portion, however, by an internal oxidation reaction changes into III which can be isolated.



Both compounds are rapidly changed into triphenylisoxazole by alkali. The oxime undergoes a similar transformation with acids.

The dinitro compound (I) is also formed from nitrostilbene and phenylnitromethane or even from the latter substance and benzaldehyde in the presence of alcoholic ammonia. Since derivatives of both may be used, a flexible method is available for the synthesis of substituted isoxazoline oxides and isoxazoles that are relatively uncommon. Contrary to the experience of others[3] (using sodium methylate) no difficulty was found in obtaining pure substances with satisfactory yields.

Still another reaction takes place if absolute alcohol is used in which the ammonia is directly concerned. The product probably results from the reaction of phenylnitromethane with a condensation product of ammonia and benzaldehyde. Similar to hydrobenzamide, it is easily changed back into its components by acid or alkali.



$$C_6H_5CHOHN{=}CHC_6H_5 + C_6H_5CH_2NO_2 \longrightarrow C_6H_5CH\underset{\displaystyle N{=}CHC_6H_5}{\underset{|}{C}}HNO_2C_6H_5 + H_2O$$

Experimental

Triphenylisoxazoline Oxide.—A suspension of 10 g. of nitrostilbene in 50 cc. of alcohol saturated with ammonia gas was shaken occasionally. The precipitate disappeared in a relatively short time with slight heat evolution followed by the gradual deposition of the new substance. The product, approximately 6 g. in amount, separated from alcohol in needles melting at 161–162°. An analysis revealed the isoxazoline oxide of Kohler and Barrett.[2]

Dibenzoylphenylmethane Monoxime.—The filtrate after steam distillation to remove benzaldehyde and other volatile impurities hardened to a solid; yield, 0.9 g. It was repeatedly crystallized from alcohol, separating finally as small needles melting at 152–153°.

Anal. Calcd. for $C_{21}H_{17}O_2N$: C, 80.0; H, 5.4. Found: C, 80.4; H, 5.4.

It is much more soluble in alcohol than V and is partially dissolved by sodium hydroxide solution from which it is precipitated unchanged by dilute acid. The most conspicuous property of the substance is the almost instant change into triphenylisoxazole when mixed with hot hydrochloric acid, in marked contrast to the isomeric isoxazoline oxide. A similar change takes place with hot alkali and more slowly when it is heated above the melting point. This substance has been obtained by Marshall from the corresponding diketone by the action of hydroxylamine.[4]

In another experiment 5 g. of nitrostilbene plus the equivalent amount of phenylnitromethane was mixed with alcoholic ammonia. The mixture became decidedly hot and dark red in color, while bubbles of gas doubtless from decomposition of ammonium nitrite escaped. The color faded on standing. Crystal formation took place in a few minutes; yield, 4.6 g. of isoxazoline oxide, and the equivalent of 2.5 g. of oxime estimated as isoxazole. On mixing 5 g. of phenylnitromethane with one equivalent of benzaldehyde and alcoholic ammonia crystal formation started in a few hours; yield, 3.3 g. and 0.8 g., respectively, of oxide and oxime.

Preparation and Properties of Isoxazoline Oxides.—To the nitrostilbene either alone or mixed with phenyl or *p*-bromophenylnitromethane was added a small volume of alcohol saturated with ammonia. The reaction was allowed to proceed spontaneously and the mixture kept overnight, although apparently complete in one to three hours. The product was crystallized from a moderately large volume of alcohol, separating as needles with one exception. The compound obtained from bromophenylnitromethane and anisalphenylnitromethane formed plates. All were indifferent toward hot acid or ammonia but formed yellow solutions with alcoholic potassium hydroxide that changed after heating for a few minutes into the corresponding isoxazoles. No reaction was observed between carefully dried ammonia and nitrostilbene dissolved in dry ether after forty-eight hours. Nitrotriphenylethylene was without action on alcoholic ammonia. Only the normal isoxazoline oxide was obtained on using malonic ester or nitromethane with nitrostilbene in the presence of the reagent.

Preparation of Isoxazoles.—These substances were prepared by the action of alcoholic potassium hydroxide on the isoxazoline oxide or from the crude oxime by steam distillation in the presence of hydrochloric acid. They were purified from alcohol, in which they are difficultly soluble or from acetone.

α-Nitro-α-phenyl-β-phenyl-β-benzalaminoethane.—It was observed that preparations of V melted low (about 120°) if absolute alcohol was used although the total amount of product remained about the same. This was true either with nitrostilbene or with benzaldehyde, phenylnitromethane and alcoholic ammonia. Boiling with hydrochloric acid restored the correct melting point but destroyed approximately 60% of the mixture. It was separated by hand and recrystallized. The new substance was eventually obtained in clusters of narrow pointed plates or scales melting at 137–138°.

Anal. Calcd. for $C_{21}H_{18}O_2N_2$: C, 76.4; H, 5.5; N, 8.5. Found: C, 76.1; H, 5.4; N, 8.8.

It is rapidly hydrolyzed by hot dilute hydrochloric acid

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[3] Kohler and Richtmyer, THIS JOURNAL, **50** 3092 (1928); Meisenheimer and Weibezahn, *Ber.*, **54**, 3203 (1921).

[4] Marshall, *J. Chem. Soc.*, **57**, 521 (1915).

TABLE I

ISOXAZOLINE OXIDES

Isoxazoline Oxide	M. p., °C.	Formula	Analyses, % Calcd. C	Analyses, % Calcd. H	Analyses, % Found C	Analyses, % Found H
4-*p*-Bromophenyl-3,5-diphenyl	172–173	$C_{21}H_{16}O_2NBr$	64.0	4.1	63.8	4.1
3,4-Diphenyl-5-*p*-bromophenyl[a]	213–215 (dec.)	$C_{21}H_{16}O_2NBr$	64.0	4.1	63.8	4.1
3-Phenyl-4,5-di-*p*-bromophenyl	160–161	$C_{21}H_{15}O_2NBr_2$	53.1	3.2	53.3	3.1
3,5-Diphenyl-4-anisyl	145–146	$C_{22}H_{19}O_3N$	76.5	5.5	76.6	5.3
3-Phenyl-4-anisyl-5-*p*-bromophenyl	143–144	$C_{22}H_{18}O_3NBr$	62.3	4.3	62.4	4.1
3,5-Diphenyl-4-piperonyl	165–166	$C_{22}H_{17}O_4N$	73.8	4.7	74.0	4.7
3-Phenyl-4-piperonyl-5-*p*-bromophenyl	192–193	$C_{22}H_{16}O_4NBr$	60.3	3.7	60.0	3.7

[a] Kohler and Richtmyer[3] proved the structure of 3,4-diphenyl-5-*p*-bromophenylisoxazole, which agrees in melting point and properties with the isoxazole obtained from the above isoxazoline oxide. Therefore it has been assumed with other unsymmetrical combinations that in the elimination of nitrous acid, hydrogen adjacent to the unsubstituted benzene ring was more active and paired off with the nitro group.

TABLE II

ISOXAZOLES

Isoxazole	M. p., °C.	Formula	Analyses, % Calcd. C	Analyses, % Calcd. H	Analyses, % Found C	Analyses, % Found H
3,5-Diphenyl-4-*p*-bromophenyl	182–183	$C_{21}H_{14}ONBr$	67.0	3.7	66.6	3.7
3-Phenyl-4,5-di-*p*-bromophenyl	179–180	$C_{21}H_{13}ONBr_2$	55.4	2.9	55.0	3.0
3-Phenyl-4-anisyl-5-bromophenyl	188–189	$C_{22}H_{16}O_2NBr$	65.0	3.9	64.9	3.8
3,5-Diphenyl-4-piperonyl	227–228	$C_{22}H_{15}O_3N$	77.4	4.4	77.1	4.4
3-Phenyl-4-piperonyl-5-bromophenyl	204–205	$C_{22}H_{14}O_3NBr$	62.9	3.3	63.1	3.3
3,5-Diphenyl-4-*o*-chlorophenyl[a]	127–128	$C_{21}H_{14}ONCl$	76.0	4.2	76.3	4.3

[a] Since the corresponding isoxazoline oxide was not isolated, this substance was obtained from the oxime portion; yield about 0.2 g. from 10 g. of nitrostilbene derivative.

into ammonia, benzaldehyde and phenylnitromethane. A similar change takes place with alkali except that part of the phenylnitromethane undergoes further change into triphenylisoxazole.

α-Nitro-α-phenyl-β-*o*-chlorophenyl-β-*o*-chlorobenzalaminoethane is obtained by the action of alcoholic ammonia on 5 g. of *o*-chlorobenzal phenylnitromethane even using ordinary alcohol; yield 2.1 g. Considerable hydrolysis of the nitrostilbene took place but no isoxazoline oxide was observed. It separated from alcohol in prisms melting at 144–145°.

Anal. Calcd. for $C_{21}H_{16}O_2N_2Cl_2$: C, 63.2; H, 4.0; Cl, 17.8. Found: C, 63.1; H, 3.9; Cl, 18.1.

Summary

Nitrostilbenes or their components either alone or in the presence of phenylnitromethane are converted by alcoholic ammonia into isoxazoline oxides, derivatives of the monoxime of dibenzoyl phenylmethane, and, under certain conditions, into benzalammonia condensation products. The rôle of the reagent in these transformations has been discussed.

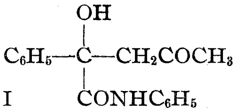
TUFTS COLLEGE, MASS. RECEIVED SEPTEMBER 18, 1935

[CONTRIBUTION FROM THE NICHOLS LABORATORY OF NEW YORK UNIVERSITY]

Condensations of Benzoylformanilide with Acetone, Ethyl Phenylacetate and Diethyl Malonate

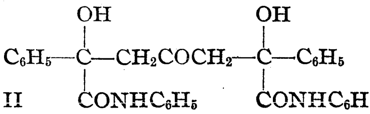
BY JOHN V. SCUDI AND H. G. LINDWALL

Acetone condenses with benzoylformanilide in the presence of diethylamine to yield 2-phenyl-2-hydroxy-4-pentanoneanilide (I), which is analogous to the product obtained with acetophenone.[1] The aldol nature of I is shown by its dissociation into the original reactants when heated with aqueous alkali; it forms a phenylhydrazone and, further, it condenses with benzoylformanilide to yield II.



$$C_6H_5\text{—}\overset{\displaystyle OH}{\underset{\displaystyle CONHC_6H_5}{C}}\text{—}CH_2COCH_3$$

I

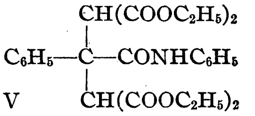


$$C_6H_5\text{—}\overset{\displaystyle OH}{\underset{\displaystyle CONHC_6H_5}{C}}\text{—}CH_2COCH_2\text{—}\overset{\displaystyle OH}{\underset{\displaystyle CONHC_6H_5}{C}}\text{—}C_6H_5$$

II

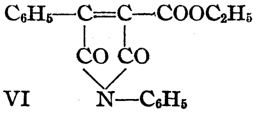
The condensation of benzoylformanilide with ethyl phenylacetate, catalyzed by diethylamine, produces α,β-diphenylmaleinanil (III); this method, while giving a good yield, is too slow to appear practical. Reduction of III gives IV, which was found to be identical with the anil of α,β-diphenylsuccinic acid, prepared by the method of Lapworth and McRae.[2]

Diethyl malonate and benzoylformanilide condense in the ratio of two moles to one, yielding V. Compound V upon being heated *in vacuo* is decomposed into α-carbethoxy-β-phenylmaleinanil (VI) which remains as a residue after diethyl malonate and a low-boiling liquid (probably ethyl alcohol) have distilled over. The corresponding α-carbethoxy-β-phenylsuccinanil (VII) results from the reduction of VI. Hydrolysis of this ester (VII) by hydrochloric acid effects also decarboxylation to yield the known phenylsuccinanil.

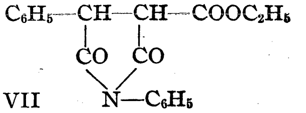


$$C_6H_5\text{—}\overset{\displaystyle CH(COOC_2H_5)_2}{\underset{\displaystyle CH(COOC_2H_5)_2}{C}}\text{—}CONHC_6H_5$$

V



VI



VII

The condensation reactions of benzoylformanilide find a parallel in the case of isatin which also condenses with acetone[3] and diethyl malonate.[4]

Experimental Part

2-Phenyl-2-hydroxy-4-pentanoneanilide (I).—A mixture of 5 g. of benzoylformanilide in 10 cc. of acetone and 5 drops of diethylamine was allowed to stand at room temperature for six hours. The white product was crystallized from toluene as hairy needles, m. p. 137–138°; slightly soluble in ether, more in benzene; yield, 80%.

Anal. Calcd. for $C_{17}H_{17}O_3N$: C, 72.08; H, 6.01. Found: C, 72.17; H, 5.90.

Phenylhydrazone of I.—A mixture of 12.5 g. of phenylhydrazine, 12.5 cc. of glacial acetic acid, 25 cc. of water and 5 g. of I, was allowed to stand for one hour at room temperature. The solid product was recrystallized from an alcohol–ethyl acetate solution (4:1 by volume); white needles, m. p. 174–175°, with decomp.; soluble in alcohol and toluene; yield, 60%.

Anal. Calcd. for $C_{23}H_{23}O_2N_3$: N, 11.26. Found: N, 11.43, 11.45.

2,6-Dihydroxy-2,6-diphenyl-4-heptanonedianilide-1,7 (II).—Compound I (2 g.) and 2.5 g. of benzoylformanilide, dissolved in a minimum amount of alcohol with 5 drops of diethylamine, were allowed to stand at room temperature for two weeks. The yield of product was 25%, but is improved by longer time; white needles after crystallization from alcohol, m. p. 171–172°.

Anal. Calcd. for $C_{31}H_{28}O_5N_2$: C, 73.23; H, 5.51. Found: C, 73.29; H, 5.57.

α-β-Diphenylmaleinanil (III).—A mixture of 1 g. of benzoylformanilide, 1 g. of ethyl phenylacetate and 3 drops of diethylamine produced a 90% yield of III after three months of standing at room temperature; yellow needles after recrystallization from alcohol, m. p. 178–179°.

Anal. Calcd. for $C_{22}H_{15}O_2N$: C, 81.23; H, 4.61. Found: C, 81.23; H, 4.73.

α-β-Diphenylsuccinanil (IV).—To a hot solution of 1 g. of III in 50 cc. of alcohol was added 1 g. of sodium hyposulfite in 30 cc. of boiling water. The yellow color disappeared at once; addition of cold water caused a white precipitation; white needles from ethyl alcohol or from glacial acetic acid; m. p. 234–235°; yield, 80%.

Anal. Calcd. for $C_{22}H_{17}O_2N$: C, 80.73; H, 5.20; N, 4.28. Found: C, 80.96; H, 5.46; N, 4.29, 4.45.

2-Phenyl-2-formanilido-1,1,3,3-tetracarbethoxypropane (V).—Five grams of benzoylformanilide, 5 g. of diethyl malonate and 5 drops of diethylamine in 10 cc. of ethyl alcohol produced a solid mass of V in three hours at

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(1) Bashour and Lindwall, THIS JOURNAL, **57**, 178 (1935).

(2) Lapworth and McRae, *J. Chem. Soc.*, **121**, 1699 (1922).

(3) Braude and Lindwall, THIS JOURNAL, **55**, 325 (1933).

(4) Lindwall and Hill, *ibid.*, **57**, 735 (1935).

room temperature; crude yield, 95%. After washing with ether, the product was crystallized from 60% acetone; colorless crystals, m. p. 107–108°, soluble in alcohol.

Anal. Calcd. for $C_{28}H_{33}O_9N$: C, 63.74; H, 6.31. Found: C, 64.08; H, 6.50.

α-Carbethoxy-β-phenylmaleinanil (VI).—A sample of V (3 g.) was subjected to vacuum distillation; a water-white distillate was obtained, distilling at 101–102° at 25 mm. Fractional distillation of this liquid showed it to consist largely of diethyl malonate, verified by conversion to malonamide. A low-boiling fraction was evidently ethyl alcohol. The residue from the vacuum distillation was dissolved in 20 cc. of diethyl ether, and diluted with 100 cc. of petroleum ether. Hard yellow crystals separated after two hours of cooling; it recrystallized from 80% alcohol as yellow rhombic crystals, m. p. 111°, soluble in alcohol, ether, benzene; yield, 75%.

Anal. Calcd. for $C_{19}H_{15}O_4N$: C, 71.03; H, 4.67; N, 4.36. Found: C, 71.09; H, 4.79; N, 4.31, 4.56.

α-Carbethoxy-β-phenylsuccinanil (VII).—One gram of VI was dissolved in 15 cc. of boiling alcohol and to this was added 1 g. of sodium hyposulfite in 5 cc. of hot water. The mixture was heated for five minutes until it became colorless. Upon addition of 75 cc. of water and cooling, a white oil separated, which gradually solidified to white needles from 10% alcohol, m. p. 104–105°, soluble in alcohol, ether, acetone, ethyl acetate, chloroform, benzene; yield, 85%.

Anal. Calcd. for $C_{19}H_{17}O_4N$: C, 70.59; H, 5.26; N, 4.33. Found: C, 70.60; H, 5.28; N, 4.26.

Phenylsuccinanil from VII.—A solution of 1 g. of VII in 15 cc. of alcohol and 15 cc. of concd. hydrochloric acid was refluxed for one hour and then evaporated to dryness on a steam-bath. The residue was extracted with three 10-cc. portions of boiling water. Concentration of the extract to one-third its volume and cooling gave white needles, m. p. 137–138°; yield, 40%. There was no lowering of melting point when mixed with a known sample.

Summary

Benzoylformanilide condenses in the presence of diethylamine with one mole of acetone and two moles of diethyl malonate to give products analogous to those of isatin. The diethyl malonate product is decomposed by heat, losing a molecule of diethyl malonate and forming a maleinanil derivative through ring closure.

Ethyl phenylacetate reacts slowly with benzoylformanilide under similar conditions to yield symmetrical diphenylmaleinanil.

New York, N. Y. Received August 31, 1935

[Contribution from the Chemical Research Laboratories of the R. & H. Chemicals Department of E. I. du Pont de Nemours & Co., Inc.]

The Preparation of High Molecular Weight Acyloins

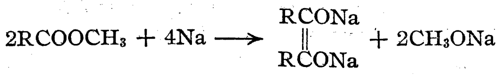
By V. L. Hansley

The simultaneous reaction and condensation of aliphatic esters by means of sodium to give α,β-keto alcohols, the so-called acyloins, has been limited in previous investigations to esters of acids of six or less carbon atoms. Previous work along this line has been summarized by Corson and his co-workers.[1]

By the use of different solvents and by making radical changes in reaction conditions, we have been able to extend this series of acyloins from 12 to 36 carbon atoms and to shorten the reaction time considerably.

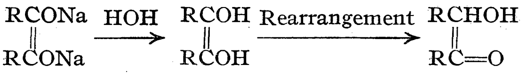
The reaction between sodium and the esters takes place essentially quantitatively according to the following equation, and neither reactant need be employed in excess.

(a)



$$2RCOOCH_3 + 4Na \longrightarrow \begin{array}{c} RCONa \\ \| \\ RCONa \end{array} + 2CH_3ONa$$

(b)



$$\begin{array}{c} RCONa \\ \| \\ RCONa \end{array} \xrightarrow{HOH} \begin{array}{c} RCOH \\ \| \\ RCOH \end{array} \xrightarrow{\text{Rearrangement}} \begin{array}{c} RCHOH \\ | \\ RC{=}O \end{array}$$

While previously recommended methods for the preparation of butyroin and other low molecular weight acyloins[2] do not suggest any difficulty in the preparation of the higher molecular weight acyloins, the work of Corson and his co-workers[1] indicates that the described methods of preparation fail when applied to these higher esters.

The failure of these investigators to obtain acyloins from acids of greater than six carbon atoms was apparently due to the insolubility of the reaction products at the temperatures employed in the particular reaction media used. Previous investigators carried out their reactions in ether or benzene at room temperature or lower, allowing even days for the reaction to take place. A few previous attempts were also made to carry

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[1] Corson, Benson and Goodwin, This Journal, **52**, 3988 (1930); *cf.* Snell and McElvain, *ibid.*, **53**, 750 (1931).

[2] Snell and McElvain, "Organic Syntheses," J. Wiley & Sons, Inc., 440 Fourth Ave., New York City, 1933, Vol. XIII, pp. 24–26.

out the preparation of acyloins in boiling toluene[1] but the reaction products could not be worked up.

By going to reaction conditions where the sodium was kept in a molten and finely dispersed state and the reaction products kept "in solution," we have been able to obtain 80–95% yields of acyloins from aliphatic esters of 8 to 18 carbon atoms. Practically quantitative reaction was obtained between ester and sodium without employing either reactant in excess. Besides carrying out the reaction above the melting point of sodium, the rate and mode of addition of ester, molecular weight of ester and concentration and solubility of reaction products all influenced the fluidity of the reaction mixture and hence the yield. Xylene and toluene were equally good solvent media, provided impurities were absent which would react with sodium. Likewise, the esters had to be free of organic acid or hydroxyl compounds. Both of these tended to cause the reaction mixture to gel, after which the useful reaction between sodium and ester practically ceased. In such cases a large part of the sodium remained unreacted.

The amount of acyloin that could be prepared in a given amount of solvent was greater with methyl laurate than any other ester tried. Esters of higher molecular weights formed more insoluble sodium derivatives while lower molecular weight esters inherently gave a greater amount of sodium methylate which could only be held in "pseudo solution" by use of more solvent. This is probably one of the reasons why previous investigators failed to obtain satisfactory reaction in toluene. They were using acid esters of too low a molecular weight in too high concentration when employing toluene as the solvent. For similar reasons they encountered difficulty when attempting the reaction of high molecular weight esters with sodium in ether at room temperature. In the preparation of lower molecular weight acyloins, *e. g.*, from caproic or caprylic acids, the use of the *n*-butyl or secondary butyl ester permitted the preparation of a considerably larger quantity of acyloin per unit volume of solvent than was possible when the methyl esters were employed.

The reaction products obtained from the straight chain aliphatic acid esters were characterized as the corresponding α,β-keto alcohols by the analysis of their acetates and osazones. The melting points of all the acyloins prepared fall on a smooth curve which flattens out considerably at about 80° when the length of the carbon chain reaches 32–36 carbon atoms. The acyloins are all waxy, white, easily crystallizable compounds, the solubilities of which vary widely from capryloin to stearoin. The stability of the acyloins was found to increase with the molecular weight. A tendency to polymerize was noted in the case of butyroin and to some extent with capronoin. Little, if any, polymerization resulted during the isolation of acyloins from acids of eight or more carbon atoms.

Experimental Part

Preparation of the Methyl Esters.—The mixture of methyl esters obtained by the esterification of commercial coconut oil fatty acids in the usual manner was subjected to careful vacuum fractionation at 15 mm. in 5-liter batches. Pure cuts of 0.2–0.3° range were made taking the boiling points of Haller and Youssoufian[3] for the esters of even carbon atom acids from caproic to myristic esters. Methyl butyrate was obtained from the Eastman Kodak Co., their better grade being usable without further purification. Stearate and palmitate esters were obtained from a catalytically hydrogenated palm oil which was converted to the methyl esters. Methyl palmitate and stearate were fractionated from this ester mixture at 15 mm. The boiling points noted, 190.5° for the palmitate and 212.3° for the stearate, are somewhat lower than those recorded in the literature, 195–196 and 215°, respectively.[3] The nonylic acid was obtained by the ozonolysis of oleic acid and esterified in the usual manner.

Preparation of the Acyloins.—One hundred and fifteen grams of sodium (5 atoms) together with 3 liters of c. p. xylene were charged into a 5-liter 3-necked flask immersed in an oil-bath at 105°. The flask was fitted with a rather high-speed stirrer (2000–2500 r. p. m.). The air over the xylene was replaced by nitrogen or other inert gas. When the temperature of the xylene reached 105° and the sodium melted, the stirrer was started and the sodium dispersed in a finely divided state in the xylene. Methyl laurate, 535 g. or the equivalent quantity of another ester (2.5 moles) was then started into the reaction flask from a separatory funnel. The addition was at such a rate that the temperature due to heat of reaction did not rise above 110°. This required about one hour. Stirring was continued for one-half hour after the ester had been added.

Small particles of unchanged sodium were then decomposed by the addition of an excess of methanol (one to two moles). Then, after cooling to about 80° water, 0.5 to 1.0 liter, was cautiously added until the alkali was taken into an aqueous layer which was then removed by decantation. After one or two more washings with water, the remaining alkali was neutralized with a slight excess of mineral acid and the excess acid finally neutralized with sodium bicarbonate.

The xylene was removed by steam distillation from the acyloin and the resulting oily layer poured into a suitable vessel to solidify. The impure product contained 80–90% acyloin. The acyloins from methyl caproate, laurate and

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(3) Haller and Youssoufian, *Compt. rend.*, **143**, 805 (1905).

myristate were purified by crystallization from 95% alcohol but acyloins corresponding to methyl palmitate and stearate were found to crystallize better from trichloroethylene or acetone.

Other acyloins prepared by this procedure are given in Table I.

TABLE I

SATURATED ALIPHATIC ACYLOINS PREPARED

Acyloin name	Observed m. p., °C.	M. p. of osazone, °C.
Acetoin	Not prepared	242[4]
Butyroin	−10	140–141[1]
Capronoin[1]	+ 9	119–120
Capryloin	39	Not prepared
Nonyloin	45	Not prepared
Caprinoin	51–52	79–80
Lauroin	61–62	61–63
Myristoin	71–72	44–46
Palmitoin	77–78	Not prepared
Stearoin	82–83	Not prepared

ANALYSES OF COMPOUNDS

Compound	Formula		Calcd.	Found
Capronoin osazone	$C_{24}H_{34}N_4$	N	14.8	13.8
Caprinoin osazone	$C_{32}H_{50}N_4$	N	11.4	10.9
Lauroin osazone	$C_{36}H_{58}N_4$	N	10.2	9.6
Myristoin osazone	$C_{40}H_{66}N_4$	N	9.3	8.7
Caprinoin acetate	$C_{22}H_{42}O_3$	CH_3CO	12.1	11.9
Lauroin acetate	$C_{26}H_{50}O_3$	CH_3CO	10.5	10.9
Myristoin acetate	$C_{30}H_{58}O_3$	CH_3CO	9.24	9.28
Palmitoin acetate	$C_{34}H_{66}O_3$	CH_3CO	8.23	7.98

Hydrogenation of the Acyloins to Substituted Ethylene Glycols.—All of the acyloins upon catalytic hydrogenation with a platinum catalyst at room temperature or nickel at 125–150° were converted into the corresponding symmetrically substituted dialkyl ethylene glycols. Due to the double asymmetry in the glycol molecule two forms should occur, meso and racemic. While α- and β- (low and high melting) forms of the glycols from butyroin and capronoin have been described[5] and a liquid isomeric mixture of glycols described as a by-product in the sodium reduction of methyl caprylate,[6] there is still some doubt as to whether the low melting glycols were actually obtained. We were able to obtain only the high melting form pure in each case. The four glycols prepared are shown in Table II together with the previously described glycols from butyrate and caproate esters.

TABLE II

SYMMETRICALLY SUBSTITUTED ETHYLENE GLYCOLS

Ethylene glycol RCHOHCHOHR, R =	Parent ester	M. p., °C.
$C_{17}H_{35}$	Stearate	123–124
$C_{13}H_{27}$	Myristate	124
$C_{11}H_{23}$	Laurate	125–126
C_7H_{15}	Caprylate	129–130
C_5H_{11}[5]	Caproate	135–136
C_3H_7[5]	Butyrate	123–124

ANALYSES

Ethylene glycol diacetate	Formula	Acetyl values Calcd.	Acetyl values Found
sym-Diheptyl-	$C_{20}H_{38}O_4$	327	320
sym-Diundecyl-	$C_{28}H_{54}O_4$	248	245
sym-Tridecyl-	$C_{32}H_{62}O_4$	220	215
sym-Diheptadecyl-	$C_{40}H_{78}O_4$	180	175

Oxidation of Acyloins to the Diketones.—A 1.0202-g. quantity of lauroin was treated in dry chloroform solution with a 100% excess of Wijs solution[7] and allowed to stand overnight: 0.716 g. of iodine was consumed; calcd. for the oxidation of this amount of lauroin to the diketone, 0.695 g. of iodine. The diketone crystallized well from methanol, giving the characteristic yellow diketone which melted sharply at 71–71.5°.

The properties and further reactions of these condensation products will be taken up in a subsequent paper.

Summary

The preparation of the α,β-keto alcohols or acyloins has been carried up to and including stearoin. All acyloins from esters of acids above caproic are new. By the catalytic hydrogenation of these keto alcohols the symmetrically substituted dialkyl ethylene glycol series has been extended from 12 to 36 carbon atoms in the molecule.

The acetates and osazones of the acyloins and the diacetates of the corresponding glycols were also prepared.

One of the acyloins, lauroin, was oxidized to the corresponding *sym*-α,β-diketone.

NIAGARA FALLS, NEW YORK RECEIVED JULY 26, 1935

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[4] L. A. Higley, *Am. Chem. J.*, **37**, 316 (1907).

[5] Bouveault and Blanc, *Compt. rend.*, **136**, 1677 (1903); *Bull. soc. chim.*, [3] **31**, 670 (1904).

[6] Bouveault and Locquin, *ibid.*, [3] **35**, 629–43 (1906).

[7] Lewkowitsch, "Oils, Fats and Waxes," The Macmillan Co. New York City, 1921, Vol. I, p. 416.

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

Detosylation of 4- and 5-Tosyl[1] Monoacetone *l*-Methylrhamnosides

BY P. A. LEVENE AND JACK COMPTON

Since Ferns and Lapworth[2] have pointed out the fact that the group R–SO$_3$–O– functions as a halide atom, it is evident that the replacement of a tosyl group on an asymmetric carbon atom may be accompanied by a Walden inversion. Indeed in the sugar series such occurrences were reported first by Mathers and Robertson[3] and later by Oldham and Rutherford[4] and by Ohle and Just.[5] In all the described cases, however, opportunity existed for an ethylene oxidic ring formation as an intermediate step in the rearrangement. The question naturally arose as to whether a Walden inversion occurs in cases not permitting the oxidic ring formation. Work in this direction was initiated in this Laboratory several years ago and some of the negative results have been reported in a preliminary note.[6]

On the other hand, Muskat[7] thought he had obtained evidence in favor of the occurrence of Walden inversion on alkaline hydrolysis of 5-tosyl monoacetone *l*-methylrhamnoside. Depending upon conditions of hydrolysis, Muskat obtained either an unsaturated derivative distilling at 80° (3 mm.) or a saturated substance distilling at 100° (1 mm.). The latter product on hydrolysis was supposed to form the simple sugar, *d*-gulomethylose. The properties of the substance, its strong reducing power in the cold, mutarotation of the amorphous product and the sign of the equilibrium rotation did not agree with the found properties of *d*-gulomethylose.[8]

However, the possibility was not excluded that the higher boiling material obtained by Muskat was a mixture of several substances containing gulomethylose among the other products. The problem, therefore, required a rigorous reinvestigation.

The Nature of the Higher Boiling Material.—As a result of such an investigation, the conclusion was reached that the higher boiling material obtained by Muskat was slightly impure monoacetone *l*-methylrhamnopyranoside.

1. The tosyl derivative of this material obtained by Muskat with a melting point of 60°, $[\alpha]_D$ +22° (methanol), and the same material obtained by us, on recrystallization gave a product melting at 61–62°, $[\alpha]^{24}_D$ +22° (methanol), and the mixed melting point with 4-tosyl monoacetone *l*-methylrhamnopyranoside showed no depression.

2. The same tosyl derivative on reductive detosylation by the method of Freudenberg and Brauns[9] gave a substance with the properties of monoacetone *l*-methylrhamnopyranoside.

3. On hydrolysis with dilute acid the higher boiling fraction gave a sugar whose *p*-bromophenylhydrazone had the properties of the corresponding hydrazone of rhamnose.

The Origin of the Higher Boiling Material.—The higher boiling material was not a product of a ring shift in course of the reaction but had its origin in the contamination of the monoacetone *l*-methylrhamnofuranoside with the corresponding derivative of the pyranoside. The evidence in favor of this conclusion is as follows.

1. The tosyl derivative obtained from the monoacetone *l*-methylrhamnoside prepared in the conventional way and having a melting point of 79–80° could be separated into several fractions as shown in Table I.

2. It was shown by analysis of the various hydrolytic fractions that only the substance melting at 82–83° was the pure furanoside, and that the remaining fractions were mixtures of the furanoside with pyranoside. More precisely, the results were as follows.

(*a*) The fraction melting at 82–83° on alkaline hydrolysis yielded practically exclusively the unsaturated product (most probably of a mannal nature) together with a minimal residue of the unchanged monoacetone *l*-methylrhamnofuranoside.

The same product on reductive hydrolysis yielded exclusively monoacetone *l*-methylrhamnofuranoside.

(*b*) The other fractions gave smaller yields of low boiling material and increasing quantities of

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[1] Term introduced by Hess and Pfleger to designate *p*-toluene sulfonyl radical [K. Hess and R. Pfleger, *Ann.*, **507**, 48 (1933)].

[2] J. Ferns and A. Lapworth, *J. Chem. Soc.*, **101**, 273 (1912).

[3] D. S. Mathers and G. J. Robertson, *ibid.*, 696, 1076 (1933).

[4] J. W. H. Oldham and J. K. Rutherford, THIS JOURNAL, **54**, 366 (1932).

[5] H. Ohle and F. Just, *Ber.*, **68**, 601 (1935).

[6] P. A. Levene and J. Compton, THIS JOURNAL, **57**, 777 (1935).

[7] I. E. Muskat, *ibid.*, **56**, 2653 (1934).

[8] P. A. Levene and J. Compton, *J. Biol. Chem.*, **111**, 335 (1935).

[9] K. Freudenberg and F. Brauns, *Ber.*, **55**, 3238 (1922).

the higher boiling fractions. From the latter fraction a tosyl derivative could be obtained melting at 61°, showing no depression of melting point when mixed with 4-tosyl monoacetone *l*-methylrhamnopyranoside. On reductive hydrolysis this tosyl derivative yielded a product identical with monoacetone *l*-methylrhamnopyranoside.

(*c*) Pure 4-tosyl monoacetone *l*-methylrhamnopyranoside, m. p. 61–62°, on alkaline hydrolysis, did not yield the unsaturated derivative, but gave exclusively the higher-boiling material which, on retosylation, yielded a tosyl derivative with the properties of the original material.

Thus, it is evident that monotosyl derivatives of rhamnose, in which the opportunity for oxide formation is excluded, behave similarly to the tosyl derivatives of other sugars, namely, they undergo alkaline detosylation without Walden inversion.[10]

It may be added that the two tosyl derivatives with melting point of 82–83° and of 61–62° were shown definitely to have the furanoside and the pyranoside ring structures, respectively.

From the experience gained during this work it is found that absolutely pure monoacetone *l*-methylrhamnofuranoside is obtained most advantageously by reductive detosylation of the tosyl derivative melting at 82–83°.

Experimental

A. Preparations

Monoacetone Methylrhamnofuranoside.—Two methods were employed in the preparation of this material, each resulting in the simultaneous formation of monoacetone methylrhamnopyranoside as an impurity.

(a) Fifty grams of anhydrous rhamnose[11] was suspended in 1000 cc. of acetone containing 5% of absolute methyl alcohol. Anhydrous copper sulfate (100 g.) was then added and sufficient concentrated sulfuric acid to make the solution 0.2%. The mixture was shaken at room temperature for twenty hours, after which it was worked up as previously described; total yield of monoacetone methylrhamnosides, 45.1 g., having the same specific rotations and refractive indices as previously recorded.[11]

(b) Fifty grams of monoacetone rhamnose[12] was dissolved in 1000 cc. of absolute methyl alcohol containing 1% of anhydrous hydrogen chloride. The mixture was allowed to stand at room temperature overnight, after which it was allowed to reflux on the steam-bath for thirty minutes. The solution was made neutral with excess silver carbonate, filtered and concentrated under diminished pressure to a thin sirup which distilled completely under diminished pressure; yield, 40 g.; b. p. 99–100° (0.8 mm.); $n^{25}\mathrm{D}$ 1.4485; $[\alpha]^{25}\mathrm{D}$ −63.0° (*c*, 3.379, methyl alcohol); $[\alpha]^{25}\mathrm{D}$ −45.5° (*c*, 2.504, water).

Anal. Calcd. for $C_{10}H_{18}O_5$: OCH_3, 14.22. Found: OCH_3, 14.22.

There remained after distillation of the monoacetone methylrhamnosides 8 g. of unchanged monoacetone rhamnose, b. p. 130–136° (0.8 mm.), and a small amount (0.5 g.) of methylrhamnopyranoside, b. p. 148–154° (0.5 mm.).

5-Tosyl[1] Monoacetone Methylrhamnofuranoside.—This compound was prepared according to the procedure of Levene and Muskat,[11] with slight modifications.

Monoacetone methylrhamnoside (20 g.) prepared as described in method (a) or (b) above, was dissolved in 30 cc. of dry pyridine and 32 g. of tosyl chloride added. Shaking was maintained until solution was complete, after which the mixture was allowed to stand overnight at room temperature. The mixture was then thoroughly cooled and 2 cc. of water added. After standing for thirty minutes the partially crystallized mass was poured with vigorous stirring into 250 cc. of ice-cold saturated sodium bicarbonate solution. The sirupy product first separating soon solidified and was removed by filtration, washed thoroughly with water and dried; yield 22 g. The product recrystallized from methyl alcohol had a melting point of 80–81°. After a second and third recrystallization, a constant melting point of 82–83° was obtained; $[\alpha]^{26}\mathrm{D}$ −13.6° (*c*, 3.168, methyl alcohol). Continued recrystallization of the mixed crystals obtained from the mother liquors gave fractions having the properties shown in Table I.

TABLE I

FRACTIONATION OF TOSYL DERIVATIVES OF MONOACETONE METHYLRHAMNOSIDE

Fraction	M. p., °C.	$[\alpha]^{26}\mathrm{D}$ in methanol
I	82–83 (max.)	−13.6° (*c*, 3.168)
II	74–75	− 5.6° (*c*, 3.046)
III	68–69	− 1.7° (*c*, 2.964)
IV	64–65	+ 5.6° (*c*, 3.030)
V	57–58	+12.1° (*c*, 2.708)

Monoacetone Methylrhamnopyranoside.—Acetonation of methylrhamnopyranoside according to the procedure of Levene and Muskat[13] led to the formation of pure monoacetone methylrhamnopyranoside, b. p. 104–105° (0.8 mm.); $n^{24}\mathrm{D}$ 1.4545; $[\alpha]^{24}\mathrm{D}$ −11.9° (*c*, 3.366, methanol).

4-Tosyl Monoacetone Methylrhamnopyranoside.—Twenty grams of monoacetone methylrhamnopyranoside was tosylated and the product isolated in the manner described for 5-tosyl monoacetone methylrhamnofuranoside; yield 25.5 g.; melting point after one recrystallization from methyl alcohol, 61–62°. Further recrystallizations from this solvent changed neither the melting point nor specific rotation; $[\alpha]^{24}\mathrm{D}$ +21.94° (*c*, 3.030 methanol).

Anal. Calcd. for $C_{17}H_{24}O_7S$: C, 54.80; H, 6.45; S, 8.60. Found: C, 54.98; H, 6.46; S, 8.69.

B. Alkaline Hydrolysis

1. Pure 5-Tosyl Monoacetone Methylrhamnofuranoside.—(Fraction I, Table I.) Forty grams of pure 5-tosyl

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[10] J. W. H. Oldham and G. J. Robertson, *J. Chem. Soc.*, 685 (1935).

[11] P. A. Levene and I. E. Muskat, *J. Biol. Chem.*, **105**, 761 (1934).

[12] K. Freudenberg, *Ber.*, **59**, 836 (1926).

[13] P. A. Levene and I. E. Muskat, *J. Biol. Chem.*, **105**, 431 (1934).

monoacetone methylrhamnofuranoside (m. p. 82–83°; $[\alpha]^{25}$D −13.5°) was dissolved in 1500 cc. of methyl alcohol and 120 g. (20 moles) of potassium hydroxide dissolved in 1300 cc. of water was added to the boiling solution. The reaction was 95% complete after refluxing on the steam-bath for sixty hours at 78° after which the solution was cooled and the excess of alkali exactly neutralized by means of 25% hydrochloric acid. Sufficient calcium chloride was then added to saturate the solution, after which it was exhaustively extracted with chloroform. The chloroform extract was allowed to stand over calcium chloride for twenty-four hours, filtered, and concentrated under diminished pressure. The resulting sirup distilled in two fractions: *first*, b. p. 56–60° (0.3 mm.), yield 16.0 g. n^{24}D 1.4491; *second*, b. p. 82–85° (0.3 mm.), yield 0.8 g., n^{4}D 1.4501.

Anal. First fraction. Calcd. for $C_{10}H_{16}O_4$: C, 59.97; H, 8.0; OCH_3, 15.49. Found: C, 59.64; H, 8.21; OCH_3, 15.21. *Second fraction.* Calcd. for $C_{10}H_{18}O_5$: C, 55.02; H, 8.30; OCH_3, 14.22. Found: C, 54.85; H, 8.38; OCH_3, 14.42.

A portion of the second fraction (0.6 g.) (b. p. 82–85° at 0.3 mm.), was dissolved in 1 cc. of dry pyridine and 0.8 g. of tosyl chloride added. After standing overnight at room temperature the solution was worked up as described for the tosylation of monoacetone methylrhamnofuranoside (yield 0.65 g.; m. p. 77–78°). After one recrystallization from methyl alcohol a constant melting point of 82–83° was obtained which was unchanged on admixture with an authentic specimen of 5-tosyl monoacetone methylrhamnofuranoside; specific rotation of this material $[\alpha]^{25}$D −13.05° (*c* 3.064, methanol).

The various conditions employed in attempts to obtain from pure 5-tosyl monoacetone methylrhamnofuranoside the product described by Muskat[7] are summarized in Table II.

2. Mixed 4- and 5-Tosyl Monoacetone Methylrhamnosides, m. p. 68°.—(Fraction III, Table I.) Four grams of mixed crystals of 4- and 5-tosyl monoacetone methylrhamnosides (m. p. 68°) was dissolved in 200 cc. of methyl alcohol and 12 g. of potassium hydroxide dissolved in 140 cc. of water added on the steam-bath. Refluxing was maintained for seventy-five hours, when the reaction was complete. After cooling, the hydrolysis products were isolated in the manner described above (1). Two fractions were obtained: first, b. p. 58–60° (0.3 mm.), yield 0.6 g.; second, b. p. 82–85° (0.3 mm.), yield 1.1 g.

Retosylation of the high boiling sirup (0.7 g.) with tosyl chloride (1.2 g.) in the presence of pyridine (1.0 cc.) gave a tosyl compound (0.8 g.) melting at 59–60°. After one recrystallization from methyl alcohol a constant melting point of 60–61° was obtained.; $[\alpha]^{25}$D +20.2° (*c*, 2.868, methanol). A mixed melting point of this material with pure 4-tosyl monoacetone methylrhamnofuranoside (m. p. 61–62°) showed no depression.

3. Impure 5-Tosyl Monoacetone Methylrhamnofuranoside, m. p. 79–80°.—Inasmuch as the 5-tosyl monoacetone methylrhamnofuranoside (m. p. 80°) previously reported[10] had a lower melting point than that employed in experiment 1, a sample of this compound (unfractionated) with m. p. 79–80° was used: 40 g. of 5-tosyl monoacetone methylrhamnoside (m. p. 79–80°) was dissolved in 1500 cc. of methyl alcohol and 120 g. of potassium hydroxide dissolved in 1300 cc. of water added on the steam-bath. The temperature (80°) was maintained for fifty hours when the reaction was about 95% complete. After cooling, the solution was worked up as described above; yield in three fractions: first, 17.1 g., second, 1.5 g., and third, 3.0 g. with b. p. 58–60° (0.3 mm.), 80–82° (0.3 mm.), and 83–85° (0.3 mm.), respectively.

The first fraction consisted of the unsaturated compound, whereas the second consisted of a mixture of monoacetone methylfuranoside and monoacetone methylpyranoside and the third was pure pyranoside, as shown on retosylation.

The second fraction (b. p. 80–82° at 0.3 mm.) was dissolved in 2.5 cc. of dry pyridine and 2.2 g. of tosyl chloride added. The mixture was allowed to stand overnight, after which it was worked up as described above; yield 1.4 g. Recrystallization from methyl alcohol gave a product (m. p. 58°) which after the fourth crystallization had risen to 67–68° $[\alpha]^{27}$D 0.00° (*c*, 2.976 methanol). From the mother liquors there was obtained a small amount of mixed 4- and 5-tosyl compounds, m. p. 55–58°.

The third fraction (b. p. 83–85° at 0.3 mm.) was divided into two parts. (a) A portion of this material (0.5 g.) was retosylated with tosyl chloride (0.8 g.) in the presence of dry pyridine (1.2 cc.) by allowing to stand overnight at room temperature; yield 0.6 g. After one recrystallization a substance of constant melting point of 60–61° was obtained which when mixed with pure 4-tosyl monoacetone methylrhamnofuranoside showed no depression; specific rotation of this material, $[\alpha]^{24}$D +22.1° (*c*, 3.032 methanol).

Anal. Calcd. for $C_{17}H_{24}O_7S$: C, 54.80; H, 6.45; S, 8.60. Found: C, 54.60; H, 6.30; S, 8.72.

TABLE II

EFFECT OF ALKALINE HYDROLYSIS MIXTURES ON PURE 5-TOSYL MONOACETONE METHYLRHAMNOFURANOSIDE (M. P. 82–83°)

Expt.	Wt., g.	KOH, moles	Methanol, cc.	Water, cc.	Temp., °C.	Time, hours	% Yield of unsatd. compd. of b. p. 60° (0.3 mm.)
I	4	20	200	40	74	50	95
II	2	20	100	0	100	30	90
III	4	20	160	180	80	48	95
IV	2	2	200	20	125	18	90
V	2	2	80	60	100	18	90
VI	2	20	100	40	37	2 mo.	No reaction
VII	2	20 ($NaOCH_3$)	100	30	70	50	98

(b) A second portion of this material (third fraction) (1.0 g.) was dissolved in 40 cc. of 1% sulfuric acid solution and allowed to reflux slowly for ninety minutes. The solution was rendered exactly neutral with barium hydroxide, treated with charcoal, and filtered. Upon concentrating under diminished pressure at 40° there was obtained 0.8 g. of sirupy material which on heating reduced Fehling's solution.

Four-tenths gram of this sirup was converted to the *p*-bromophenylhydrazone using one mole of *p*-bromophenylhydrazine in 5 cc. of absolute ethyl alcohol. There was thus obtained 0.35 g. of material, m. p. 168°, unchanged by further recrystallization from ethyl alcohol. A mixed melting point of this material with an authentic specimen of rhamnose *p*-bromophenylhydrazone (m. p. 167–168°) showed no depression. The mutarotation of the above *p*-bromophenylhydrazone in ethyl alcohol was in the same direction as that of rhamnose *p*-bromophenylhydrazone.

$$[\alpha]^{25}\mathrm{D}\ -11.29^\circ \xrightarrow{\text{24 hrs.}} +5.8^\circ \xrightarrow{\text{2 weeks}} -21.29^\circ \text{ the latter,}$$

$$[\alpha]^{23}\mathrm{D}\ -12.5^\circ \xrightarrow{\text{30 hrs.}} +10.2^\circ \xrightarrow{\text{2 weeks}} -23.1^\circ$$

No other *p*-bromophenylhydrazone was found in the reaction product, thus showing that rhamnose was the only sugar present in the third fraction.

Anal. Calcd. for $C_{12}H_{17}O_4N_2Br$: C, 43.24; H, 5.14; N, 8.40. Found: C, 43.35; H, 5.02; N, 8.61.

4. Pure 4-Tosyl Monoacetone Methylrhamnopyranoside.—Four grams of 4-tosyl monoacetone methylrhamnopyranoside (m. p. 61–62°) was dissolved in 150 cc. of methyl alcohol and 130 cc. of water containing 12 g. (20 moles) of potassium hydroxide added to the solution on the steam-bath. After refluxing for sixty hours, hydrolysis was complete and the excess alkali was neutralized with carbon dioxide. The solution was evaporated to dryness at 40° under diminished pressure and the resulting solid thoroughly extracted with ether. The ether extract was dried over calcium chloride, filtered, and concentrated under diminished pressure to a thick sirup which distilled completely, b. p. 84–85° (0.3 mm.); yield 2.0 g.; $[\alpha]^{25}\mathrm{D}$ −20.5° (*c*, 3.230, methanol); $n^{24}\mathrm{D}$ 1.4544.

Anal. Calcd. for $C_{10}H_{18}O_5$: C, 55.02; H, 8.30; OCH_3, 14.22. Found: C, 55.12; H, 8.40; OCH_3, 14.35.

Retosylation of monoacetone methylrhamnopyranoside thus obtained (0.86 g.) with tosyl chloride (1.5 g.) in the presence of dry pyridine (1.2 cc.) followed by isolation and crystallization as previously described yielded 0.90 g. of material, m. p. 61–62°. A mixed melting point of this material with 5-tosyl monoacetone methylrhamnopyranoside showed no depression. Specific rotation $[\alpha]^{25}\mathrm{D}$ +21.8° (*c*, 3.028, methanol).

C. Reductive Alkaline Hydrolysis

1. Pure 5-Tosyl Monoacetone Methylrhamnofuranoside.—(Fraction I, Table I.) Two grams of 5-tosyl monoacetone methylrhamnofuranoside (m. p. 82–83°) was dissolved in 100 cc. of 80% methyl alcohol and 25 g. of 4% sodium amalgam added under good stirring. After fourteen hours at room temperature the reaction was complete. The excess alkali was neutralized with a stream of carbon dioxide and the solution evaporated to dryness at 40° under diminished pressure. The resulting solid was thoroughly extracted with hot ether and the extract dried over calcium chloride, filtered and concentrated under diminished pressure; yield, 1.1 g. with b. p. 78–80° (0.2 mm.); $[\alpha]^{21}\mathrm{D}$ −75.45° (*c*, 2.770, methanol); $n^{24}\mathrm{D}$ 1.4466.

Anal. Calcd. for $C_{10}H_{18}O_5$: C, 55.02; H, 8.30; OCH_3, 14.22. Found: C, 54.99; H, 8.35; OCH_3, 14.21.

Retosylation of 0.5 g. of this pure material with 0.8 g. of tosyl chloride dissolved in 1 cc. of dry pyridine in the usual manner, gave a yield of 0.6 g. of 5-tosyl monoacetone methylrhamnofuranoside (m. p. 82–83°). The melting point was unchanged when mixed with an authentic specimen of 5-tosyl monoacetone methylrhamnofuranoside.

2. Mixed 4- and 5-Tosyl Monoacetone Methylrhamnosides, m. p. 57–58°.—Fraction V, Table I. The mixed crystals of 4- and 5-tosyl monoacetone methylrhamnosides (2.5 g.) dissolved in 250 cc. of 80% methyl alcohol were detosylated by use of 36 g. of 4% Na–Hg amalgam during fourteen hours. The product isolated as described above had a boiling point of 82–85° (0.3 mm.); yield 1.1 g.; $[\alpha]^{25}\mathrm{D}$ −38.18° (*c*, 3.156, methanol); $n^{24}\mathrm{D}$ 1.4520.

3. Pure 4-Tosyl Monoacetone Methylrhamnopyranoside.—(a) Ten grams of 4-tosyl monoacetone methylrhamnopyranoside was dissolved in 500 cc. of 80% methyl alcohol and 125 g. of 4% Na–Hg amalgam added. Good stirring was maintained for fourteen hours, after which the reaction was complete. The solution was worked up and the product isolated as previously described; yield 5.4 g.; b. p. 84–85 (0.3 mm.); $[\alpha]^{25}\mathrm{D}$ −17.76° (*c*, 3.294, methanol); $n^{24}\mathrm{D}$ 1.4541.

Anal. Calcd. for $C_{10}H_{18}O_5$: C, 55.02; H, 8.30; OCH_3, 14.22. Found: C, 54.94; H, 8.41; OCH_3, 14.00.

Retosylation of 0.5 g. of this material with tosyl chloride (0.8 g.) in presence of dry pyridine (1 cc.) yielded in the usual manner, 0.6 g. of material of m. p. 61–62°; $[\alpha]^{26}\mathrm{D}$ +21.88° (*c*, 3.014, methanol). A mixed melting point with original 4-tosyl monoacetone methylrhamnopyranoside showed no depression.

(b) The alkaline hydrolysis of mixed crystals of 4- and 5-tosyl methylrhamnosides (m. p. 68 or 80°) leads to the production of an unsaturated low boiling material and monoacetone methylrhamnopyranoside which in turn, upon tosylation, yields 4-tosyl monoacetone methylrhamnopyranoside (m. p. 60–61°). To prove further that this material was identical with 4-tosyl monoacetone methylrhamnopyranoside, a sample thus obtained was detosylated and the properties of the monoacetone methylrhamnopyranoside obtained were compared with those of the known derivative of this structure.

4-Tosyl monoacetone methylrhamnopyranoside (0.8 g.) with m. p. 60–61° was dissolved in 80 cc. of 80% methyl alcohol and 12 g. of 4% Na–Hg amalgam added. The time of reaction and method of isolation was carried out exactly as described previously; yield 0.4 g.; b. p. 82–85° (0.3 mm.); $[\alpha]^{25}\mathrm{D}$ −21.30° (*c*, 3.380, methanol); $n^{24}\mathrm{D}$ 1.4539.

Anal. Calcd. for $C_{10}H_{18}O_5$: C, 55.02; H, 8.30; OCH_3, 14.22. Found: C, 55.03; H, 8.19; OCH_3, 14.26.

D. Proof of Structure of 4- and 5-Tosyl Monoacetone Methylrhamnosides

Inasmuch as the methylglycofuranosides are hydrolyzed

TABLE III

HYDROLYSIS OF MONOACETONE METHYLRHAMNOSIDES WITH 0.1 *N* HCl AT 100°

	Monoacetone methylrhamnoside obtained by	% Solution	$[\alpha]^{26}_D$ Initial	After 30 min.
(1)	Reductive hydrolysis of tosyl derivative of m. p. 82–83°[a]	3.346	−58.0°	+ 5.0°
(2)	Reductive hydrolysis of tosyl derivative of m. p. 61–62°[b]	4.280	− 6.0°	−35.8°
(3)	Simultaneous methylation and acetonation of rhamnose, or "methylation" of monoacetone rhamnose[b]	2.830	−45.5°	− 8.4°
(4)	Acetonation of methylrhamnopyranoside[b]	3.236	− 4.8°	−35.1°

[a] Final value of specific rotation calculated as free rhamnose.

[b] Final values of specific rotations calculated as methylrhamnosides.

at a much greater rate than the glycopyranosides,[14] the ring structure of such compounds may be determined easily. Accordingly the hydrolysis rates of the monoacetone methylrhamnosides (purified and crude) were determined in the following manner. Known weights of the monoacetone methylrhamnosides were dissolved in hydrochloric acid (0.1 or 0.03 *N*) and diluted to exactly 5 cc. with hydrochloric acid (0.1 or 0.03 *N*). The specific rotation was observed immediately and the solution then heated in a sealed tube at 100° for the time specified. The tubes were now cooled and the rotation of the solution again noted. The results obtained in this manner are given in Table III and in Fig. 1.

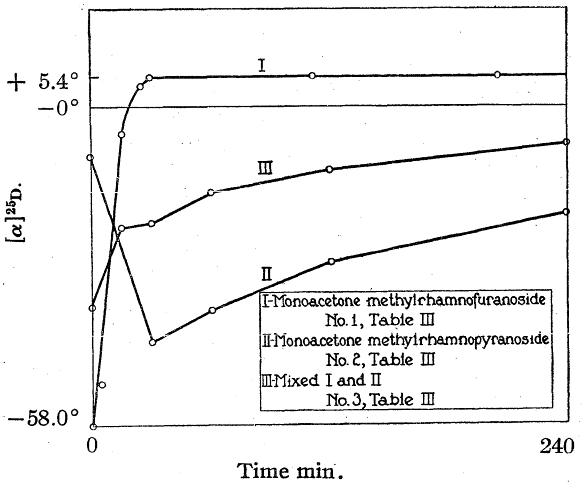

Fig. 1.—Rate of hydrolysis of monoacetone methylrhamnosides with 0.03 *N* HCl at 100°.

We wish to express our thanks and gratitude to Messrs. Geigy and Company for their generous gift of the *l*-rhamnose used in these experiments.

Summary

1. The usual methods of preparing monoacetone *l*-methylrhamnofuranoside are attended by the simultaneous formation of monoacetone *l*-methylrhamnopyranoside, at times to the extent of 30–40%.

2. Alkaline hydrolysis of pure 5-tosyl monoacetone *l*-methylrhamnofuranoside leads to the production of an unsaturated compound in 90–95% yield together with monoacetone *l*-methylrhamnofuranoside.

3. Alkaline hydrolysis of 4-tosyl monoacetone *l*-methylrhamnopyranoside yields quantitatively monoacetone methylrhamnopyranoside.

4. Tosyl monoacetone *l*-methylrhamnoside with m. p. 80° is a mixture containing, in addition to the furanoside, a small proportion of the pyranoside. Alkaline hydrolysis of this product leads to formation of the unsaturated derivative together with a small proportion of monoacetone *l*-methylrhamnopyranoside.

5. Alkaline hydrolysis of the 4- and 5-tosyl monoacetone *l*-methylrhamnosides is accomplished without Walden inversion.

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[14] P. A. Levene and G. M. Meyer, *J. Biol. Chem.*, **78**, 363 (1928); H. G. Bott, E. L. Hirst and J. A. B. Smith, *J. Chem. Soc.*, 658 (1930).

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

The Reaction between Sulfur Dioxide and Olefins. III.[1] Higher Olefins and Some Limitations of the Reaction

BY L. L. RYDEN AND C. S. MARVEL

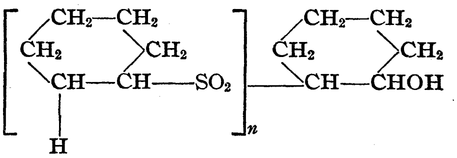
Previous investigations have shown that sulfur dioxide will combine with the simple olefins ethylene,[2] propylene,[1,2] cyclohexene[3] and methylpropene;[4] with a large number of conjugated dienes;[5] and with allyl alcohol and some of its simple ethers.[6] In order to learn more about the limitations of this addition reaction we have made this study of the formation of polysulfones from sulfur dioxide and a variety of unsaturated compounds.

Polysulfones have been obtained by the combination of sulfur dioxide and methylpropene, 1-pentene, 2-pentene, 1-nonene, 3-cyclohexylpropene and 3-methylcyclohexene. Under the same experimental conditions which were used for the production of the above polysulfones, no reaction could be obtained between sulfur dioxide and trimethylethylene, tetramethylethylene, pinene or 1,4-dihydronaphthalene. The failure of these olefins to react with sulfur dioxide indicates that increasing the number of hydrocarbon substituents on the carbon atoms which are attached by a double union will tend to block this addition reaction.

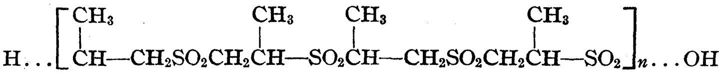
We have also treated sulfur dioxide with the following compounds which contain not only the olefin group but some other functional group as well: 1-chloropropene, trichloroethylene, allyl cyanide, 2-allyl-*p*-cresol, undecylenic acid, sodium undecylenate, ethyl undecylenate, ethyl erucate, crotonaldehyde, oleyl alcohol and undecylenyl alcohol. Of these compounds, only undecylenyl alcohol gave a polysulfone. This confirms Solonina's observation[6] that an alcoholic hydroxyl group in the olefin molecule does not interfere with the formation of a polysulfone. The failure of oleyl alcohol to combine with sulfur dioxide must be due to the fact that the double bond is in the middle of a long chain. While the negative results obtained in our other experiments must be accepted with the usual caution, they do clearly show that many simple functional groups do interfere with the addition of sulfur dioxide to an olefin group. In this connection, it may be mentioned that *d*-limonene, an unconjugated diene, also failed to combine with sulfur dioxide under the conditions of our experiments.

1-Heptyne does combine with sulfur dioxide to produce a polymeric product of the composition $(C_7H_{12}SO_2)_n$. The extension of the reaction to other acetylenes is now under investigation in this Laboratory.

In the earlier work on cyclohexene,[3] it was found that the polysulfone (I) contained an alcohol group which could be chloroacetylated.



I



$$H\cdots\left[\overset{CH_3}{\overset{|}{CH}}-CH_2SO_2CH_2\overset{CH_3}{\overset{|}{CH}}-SO_2\overset{CH_3}{\overset{|}{CH}}-CH_2SO_2CH_2\overset{CH_3}{\overset{|}{CH}}-SO_2\right]_n\cdots OH$$

II

On the other hand, it was found that propylenepolysulfone (II)[1] has a sulfonic acid group at one end of the chain. The polysulfones described in this paper are apparently of the alcohol type, as none of them are alkali soluble, and those which have been treated with an acid chloride have given acyl derivatives.

In previous work[3] an attempt was made to estimate the molecular weight of cyclohexenepolysulfone from the chlorine content of the chloroacetyl derivative. Further work on this phase of the problem has cast some doubt on the molecular weight values which are determined in this manner. It is extremely difficult to purify these compounds, and their chlorine content is

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(1) For the second paper in this series, see Hunt and Marvel, THIS JOURNAL, **57**, 1691 (1935).

(2) Staudinger and Ritzenthaler, *Ber.*, **68**, 458 (1935).

(3) Frederick, Cogan and Marvel, THIS JOURNAL, **56**, 1815 (1934).

(4) Mathews and Elder, British Patent 11,635 (1914); *C. A.*, **9**, 2971 (1915).

(5) De Bruin, *Verslag. Akad. Wetenschappen*, **23**, 445 (1914); *C. A.*, **9**, 623 (1915); Hofmann and Damm, *Chem. Zentr.*, **97**, I, 2342 (1926); Staudinger, German Patent 506,839 (1929); French Patent 698,857 (1930); *C. A.*, **25**, 522, 3360 (1931); Eigenberger, *J. prakt. Chem.*, **127**, 307 (1930); **129**, 312 (1931); Backer and Bottema, *Rec. trav. chim.*, **51**, 294 (1932); Backer and Strating, *ibid.*, **53**, 525 (1934); **54**, 170 (1935); Seyer and King, THIS JOURNAL, **55**, 3140 (1933); Sorokin and Puztizkii, *Sintet. Kauchuk*, **6**, 12–16 (1933); *C. A.*, **28**, 3339 (1934); Staudinger and Ritzenthaler, *Ber.*, **68**, 455 (1935).

(6) Solonina, *J. Russ. Phys.-Chem. Soc.*, **30**, 826 (1898).

low. We have used trichloroacetyl chloride as an acylating agent in our later experiments, but even with the threefold increase in chlorine content, the experimental error is so large that the calculated molecular weight cannot be checked closer than about 50,000. Therefore, the only conclusion we have reached concerning the molecular weights of the various polysulfones is that all are in the region of 100,000 to 200,000. We have repeated some earlier work on the estimation of the molecular weight of propylenepolysulfone by determining the nitrogen content of the anilide, and have found that this polysulfone has a molecular weight of about 50,000 instead of 6000. This new value is in better agreement with the molecular weight of propylenepolysulfone which Staudinger and Ritzenthaler[2] calculated from viscosity measurements.

The alkaline degradation of these new polysulfones has not been extensively studied. 2-Pentenepolysulfone, on heating with sodium hydroxide solution, yields 2-pentene, dipentenylsulfone and sodium sulfite. Methylpropenepolysulfone gives large amounts of methylpropene and sodium sulfite under the same conditions. No other hydrolysis products were obtained. 1-Pentenepolysulfone does not regenerate the olefin when heated with alkali. Therefore, it is probable that the polysulfones derived from all olefins of the type $RCH{=}CH_2$ will be found to be closely related to propylenepolysulfone in structure.

Experimental Part

Polysulfones from Simple Olefins.—The general method developed for the preparation of cyclohexenepolysulfone[3] was followed in this work. Ten volumes of liquid olefin and ten volumes of liquid sulfur dioxide were mixed together in a pressure flask, and one volume of 3% hydrogen peroxide and one volume of paraldehyde was added. The pressure flask was sealed and the mixture allowed to stand for about twelve hours. In most cases, the reaction was then as complete as it could be made to go under these general conditions. In the case of methylpropene, 1-pentene and 1-nonene, it was observed that better results were obtained by mixing the olefin, sulfur dioxide and hydrogen peroxide, and allowing this mixture to stand for twelve hours, then introducing the paraldehyde. Within an hour, the reaction was then finished.

In all cases, the products were isolated by pouring the reaction mixture into water, and were purified by thorough washing with alcohol and ether. The yields, melting points and analyses of the new polysulfones are recorded in Table I.

Methylpropenepolysulfone is a white, amorphous powder, quite brittle and insoluble in common organic solvents. The derivatives of 1-pentene, 2-pentene and 1-nonene were soluble in acetone, and were purified by solution in this solvent and reprecipitation with water. 1-Nonenepolysulfone is a softer and more plastic material than are the polysulfones with shorter carbon chains.

Perbenzoic acid could not be satisfactorily substituted for 3% hydrogen peroxide as a catalyst for the addition reaction.

Trichloroacetyl Derivatives and Calculated Molecular Weights.—The trichloroacetyl derivatives of the polysulfones from cyclohexene, methylpropene, 1-pentene, 2-pentene, 3-cyclohexylpropene and 1-nonene were prepared by allowing a mixture of 1 g. of polysulfone and 3 cc. of trichloroacetyl chloride to stand for about twenty-four hours. Methylpropenepolysulfone was the only one which was completely insoluble in the acid chloride. At the end of twenty-four hours the reaction mixture was poured into water and filtered. Most of the trichloroacetic acid was removed by grinding the product with alcohol, filtering and repeating the process, using ether as a solvent. The trichloroacetyl derivative was then dissolved in a solvent and reprecipitated. This product was then ground up with alcohol and washed on a filter with ether at least three times. Control experiments, using the polysulfone and trichloroacetic acid, showed that all of the chlorine could be removed by this method of purification. Methylpropenepolysulfone was most difficult to purify, since it did not dissolve in any solvent which was tried. The cyclohexene derivative was purified by dissolving in benzene and precipitation with alcohol, and the other products were dissolved in acetone and precipitated with water. The products were carefully dried and analyzed for chlorine by the Parr bomb procedure. A 0.3 to 0.4-g. sample was

Table I

Properties of Some Polysulfones

Olefin used	Yield, %	M. p. (dec.), °C. Bloc Maquenne	Formula	Analyses, %					
				Calcd.		Found			
				C	H	C		H	
Methylpropene[d]	75–90	340	$(C_4H_8SO_2)_n$	40.0	6.66	39.5	39.7	6.84	7.16
2-Pentene	75	290–300[a]	$(C_5H_{10}SO_2)_n$	44.8	7.46	44.34	44.40	7.12	7.28[b]
1-Pentene	80–90	340	$(C_5H_{10}SO_2)_n$	44.8	7.46	42.9	43.9	7.54	7.82
1-Nonene	75–80	>300[c]	$(C_9H_{18}SO_2)_n$	57.0	9.47	56.9	56.7	8.58	9.15
3-Cyclohexylpropene[e]	75	330	$(C_9H_{16}SO_2)_n$	57.5	8.50	57.2	56.7	8.34	8.78
3-Methylcyclohexene	5–10	270	$(C_7H_{12}SO_2)_n$	52.5	7.50	51.8	51.7	7.39	7.25

[a] Decomposes at 215–220° in an ordinary melting-point tube. [b] Calcd. for $(C_5H_{10}SO_2)_n$: S, 23.88. Found: S, 24.04, 23.73. [c] This polymer was quite plastic at 200°, and slowly decomposed at 300°. [d] Calcd.: S, 26.6. Found: S, 26.00, 25.85. [e] Calcd.: S, 17.00. Found: S, 17.12.

used, and 0.05 *N* silver nitrate and ammonium thiocyanate solutions were used. Blanks were run on the reagents in each experiment. The results are summarized in Table II.

Table II

Polysulfone Trichloroacetates

Polysulfone from	Expt. no.	Chlorine, %	Calcd. mol. wt.
Cyclohexene	1	0.107	99,200
Cyclohexene	2	.075	142,000
		.075	142,000
Cyclohexene	3[a]	.109	98,000
		.065	164,000
1-Pentene	4	.077	139,000
		.045	237,000
2-Pentene	5	.045	237,000
	6	.086	124,000
Methylpropene[b]	7	.041	260,000

[a] This sample was prepared by allowing the solution of cyclohexenepolysulfone in trichloroacetyl chloride to stand for ten days.

[b] This derivative was purified by repeated washing with alcohol and ether.

The polysulfones prepared from 1-nonene and 3-cyclohexylpropene reacted with trichloroacetyl chloride to liberate hydrogen chloride. The resulting products were sticky, insoluble materials of such a nature that purification was very unsatisfactory, and hence no attempt has been made to estimate molecular weights from the chlorine content of these esters.

Propylenepolysulfonanilide. — Propylenepolysulfonanilide was prepared as described previously.[1] The product was ground up with 5% hydrochloric acid and filtered, and this process repeated four times. Sample AI was then collected. The hydrochloric acid treatment was repeated five more times, and sample AII was collected. After five more washings, sample AIII was collected. Then the remaining product was suspended in water, exactly neutralized and boiled for thirty minutes (in order to steam distill any remaining aniline). The propylenepolysulfonanilide was then washed with alcohol and ether to give sample AIV. For comparison, a mixture of propylenepolysulfone and aniline were similarly treated, and B samples I′ to IV′ were collected. Nitrogen in these samples was determined by the Kjeldahl method. The results of these experiments are given in Table III.

Table III

Nitrogen Content and Molecular Weight of Propylenepolysulfonanilide

Sample A	N, %	Sample B	N, %	N, % A − B	Calcd. mol. wt.
I	0.065	I′	0.029	0.036	38,880
II	.043	II′	.013	.030	46,600
III	.040	III′	.0076	.032	43,750
IV	.0175	IV′	.0022	.015	93,300

The fact that the nitrogen content of the polymer after correction remains fairly constant through the first three samples seems significant. The low value for nitrogen in sample IV indicates that steam distillation has caused some complex decomposition of the molecule.

Alkaline Degradation of Polysulfones

2-Pentenepolysulfone.—A mixture of 50 g. of 2-pentenepolysulfone and 160 cc. of 20% sodium hydroxide was heated under a reflux condenser for about an hour and a half. During this heating period a considerable amount of 2-pentene was formed. This was collected in a cooled trap at the upper end of the reflux condenser. The olefin was identified by its boiling point (36–37°) and by the boiling point of its dibromo derivative (176°). During the period of refluxing, an oil appeared on the alkaline solution. This product was separated and distilled under reduced pressure. It boiled at 132° at 4–5 mm., decolorized an aqueous solution of potassium permanganate, but did not take up bromine from carbon tetrachloride. It is apparently a diamylenesulfone.

Anal. Calcd. for $C_{10}H_{18}SO_2$: C, 59.04; H, 8.91; S, 15.83; mol. wt., 202. Found: C, 58.5, 58.7; H, 9.52, 9.47; S, 16.9, 16.7; mol. wt. (Rast), 206, 218.

From the alkaline solution considerable sodium sulfite was isolated. No organic sulfonic or sulfinic acid salts could be extracted from these residues.

Methylpropenepolysulfone.—A mixture of 40 g. of methylpropenepolysulfone and 150 cc. of 10% sodium hydroxide solution was heated to boiling. Within fifteen minutes over 35% of the theoretical amount of methylpropene was liberated. The olefin was identified as the dibromide, b. p. 148–149°. Sodium sulfite was produced in large quantities, but no other hydrolysis products were isolated.

1-Pentenepolysulfone.—A mixture of 35 g. of 1-pentenepolysulfone and 100 cc. of 20% sodium hydroxide solution was heated under a reflux condenser. The polysulfone dissolved in a short time producing a red-colored solution. No 1-pentene was regenerated. After about fifteen minutes a small amount of oily material separated on the surface of the solution. However, no definite products were isolated from the amount of material which was available.

Undecylenyl Alcohol Polysulfone.—Undecylenyl alcohol and sulfur dioxide combine very easily under the general conditions mentioned above, and the paraldehyde can be omitted from the reaction mixture without affecting the yield of product. The polysulfone is at first a jelly-like mass, but soon turns to a semi-transparent, crumbly substance which is insoluble in all common organic solvents, and is also insoluble in dilute aqueous alkalies. The product darkened at 330°, but did not appear to soften or liberate gas.

Anal. Calcd. for $(C_{11}H_{22}SO_3)_n$: C, 54.26; H, 9.86. Found: C, 55.91, 55.54; H, 8.99, 9.19.

The product was converted to a chloroacetyl derivative, but the properties were not changed in any noticeable fashion.

Anal. Calcd. for $(C_{11}H_{21}OCOCH_2ClSO_2)_n$: Cl, 11.4. Found: Cl, 10.8, 10.5.

1-Heptyne Polysulfone.—When 1-heptyne and sulfur dioxide were allowed to react in the presence of 3% hydrogen peroxide and paraldehyde, a 50–60% yield of a polymer was obtained after three days. The product was soluble in acetone and insoluble in alcohol, ether and cold dilute sodium hydroxide solution. It melted at 160–169°.

Anal. Calcd. for $(C_7H_{12}SO_2)_n$: C, 52.5; H, 7.50; S, 20.00. Found: C, 52.38, 52.32; H, 7.55, 7.62; S, 19.5, 19.4.

Summary

1. Methylpropene, 1-pentene, 2-pentene, 1-nonene, 3-cyclohexylpropene and 3-methylcyclohexene give polysulfones by the addition of sulfur dioxide. These polysulfones are all neutral products and the first five of them have alcohol groups at the ends of the chains. Evidence has been obtained to indicate that 1-pentenepolysulfone is degraded with alkali in a manner which is like that reported for propylenepolysulfone, whereas the methylpropene and 2-pentene derivatives are degraded more nearly after the manner of the cyclohexene derivative. The molecular weights of these polysulfones are in the range of 100,000 to 200,000.

2. Highly substituted olefins do not add sulfur dioxide under the experimental conditions used in our work.

3. Polysulfones have been obtained from 1-heptyne and from undecylenyl alcohol. No evidence of addition of sulfur dioxide to typical olefins containing chloro, cyano, phenolic hydroxyl, aldehydo, carboethoxy, carboxyl or salt of carboxyl groups could be obtained.

URBANA, ILLINOIS RECEIVED AUGUST 16, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF NEBRASKA]

Arsenicals Containing the Furan Nucleus. II. Action of Chlorine. Some Substituted Furan Arsenicals

BY WESLEY G. LOWE[1] AND CLIFF S. HAMILTON

The action of chlorine on furyldichloroarsine, difurylchloroarsine and trifurylarsine in chloroform or carbon tetrachloride solution leads in every instance to the formation of 2-chlorofuran tetrachloride. This reaction can be carried out at room temperature or by introducing dry chlorine gas into a chloroform solution of the arsenical at −78° followed by evaporation of the solvent at room temperature. 2-Chlorofuran, prepared from Hill's 5-chloropyromucic acid[2] by decarboxylation in aqueous mercuric chloride,[3] adds four atoms of chlorine under the same conditions and the 2-chlorofuran tetrachloride thus obtained is identical with that prepared from the furan arsenicals.

In agreement with the observation made by Hill and Hartshorn[4] that 2,5-dibromofuran tetrabromide in alcoholic potassium hydroxide solution loses two molecules of hydrogen bromide to yield tetrabromofuran, we have found that from a similar solution of 2-chlorofuran tetrachloride 40% of the total chlorine can be precipitated with silver nitrate, indicating the loss of two molecules of hydrogen chloride and the formation of a trichlorofuran. The action of aqueous silver nitrate on an alcoholic solution of 2-chlorofuran tetrachloride is complex, varying conditions of temperature and acidity leading to a precipitation of 60, 70 and 75% of the total chlorine as silver chloride. Hydrolysis of the symmetrical molecule, 2,5-dibromofuran tetrabromide, involves a loss of five-sixths of the total bromine yielding bromomaleic acid as a final product.[4] This stepwise loss of chlorine is the same for chlorofuran tetrachloride prepared by either of the methods mentioned and is further proof of identity of structure.

Efforts to isolate a second product from the chlorination of furyldichloroarsine were unsuccessful. However, in each of six chlorinations of difurylchloroarsine it was possible to isolate a white solid which on exposure to air gave off hydrogen chloride gas. This compound was not identified as such, but on hydrolysis with cold water it yielded difurylarsinic acid which was purified by crystallization from hot water. Although it is not necessary to fractionate difurylchloroarsine to purity before chlorination in order to obtain this acid, efforts to prepare it from the mixture of arsenicals before distillation were unsuccessful. The acid, when pure, is stable to air and light, but it is more sensitive to sulfuric acid than is furoic acid and can be detected in very dilute solution by the formation of a dark ring at the water–sulfuric acid interface.

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[1] Parke, Davis and Company Fellow.

[2] Hill and Jackson, *Proc. Am. Acad. Arts Sci.*, **24**, 320 (1889).

[3] Gilman and Wright, THIS JOURNAL, **55**, 3302 (1933).

[4] Hill, *Ber.*, **16**, 1132 (1883); Hill and Hartshorn, *ibid.*, **18**, 449 (1885).

Trifurylarsine dichloride was prepared in small yields by slow evaporation of a chloroform or ether solution of chlorinated trifurylarsine. It was obtained as large diamond-shaped transparent crystals, stable in air, but readily hydrolyzed in a water–alcohol solution. Neither trifurylarsine dichloride nor difurylarsinic acid reacted with mercuric chloride in alcoholic solution to form 2-chloromercurifuran as does trifurylarsine.[5] This fact, in view of the results that have been obtained on mercuration of benzene arsenicals,[6] makes it appear that the substitution of arsenic by mercury on aromatic nuclei is a property of trivalent but not of pentavalent arsenic.

In the chlorination of furan arsenicals, three separate reactions are involved: (1) the oxidation of trivalent arsenic, (2) the saturation of the furan nucleus and (3) the scission of the carbon–arsenic bond. Since these could occur in any order, there are six possible courses for the total reaction. The isolation of difurylarsinic acid and trifurylarsine dichloride eliminates two of these since scission of the carbon–arsenic bond cannot, therefore, occur first. Against the probability of scission occurring at the second step, it has been noted that the removal of arsenic from an aromatic nucleus by means of chlorination is not accomplished at the temperature here employed,[7] and that removal of arsenic from an aliphatic radical by this means occurs only after the arsenic has been oxidized. Consequently it is most probable that scission of the carbon–arsenic bond occurs only after the nucleus has been saturated and the arsenic oxidized. Von Baeyer[8] has shown that loss of arsenic from methyltetrachloroarsine occurs at −10°. However, the results of these chlorinations are best explained by assuming that both of the reactions involving scission of the carbon–arsenic bond as the final step occur simultaneously. In other words, the oxidation of the furan nucleus and trivalent arsenic are essentially competitive in nature. Consequently it has not been found possible by means of controlled chlorination of difurylchloroarsine to preclude the formation of either 2-chlorofuran tetrachloride or difurylarsinic acid; both products always appear together. In view of these circumstances the usefulness of chlorination as a general method for preparing various furylarsonic and difurylarsinic acids is limited by the ease of chlorination of substituted furan nuclei. In addition to its failure to produce furylarsonic acid from furyldichloroarsine, repeated applications of the method to di-5-chlorofurylchloroarsine failed to lead to the synthesis of di-5-chlorofurylarsinic acid. This latter result is in accord with our observation that under similar conditions 2-chlorofuran adds chlorine more readily than does furan itself.

Tri-5-chlorofurylarsine and tri-5-bromofurylarsine were prepared by arsenation of 5-chloro-2-chloromercurifuran and 5-bromo-2-chloromercurifuran in benzene solution. The former arsenical was separated by fractional distillation and the latter by fractional crystallization. Both of these compounds are crystalline solids. An attempt was made to prepare tri-5-iodofurylarsine from 5-iodo-2-chloromercurifuran. The arsenation proceeded with great ease, but the resulting mixture of arsenicals was so unstable to the action of air that separation of its components was abandoned.

A study of the action of alcoholic mercuric chloride on these substituted trifurylarsines was made. It was found that although the arsenic can be replaced by mercury to yield the original mercurical, the action is less complete than was observed in the case of trifurylarsine itself.[5] The order of ease of substitution of arsenic by mercury in these arsenicals is: trifurylarsine, tri-5-chlorofurylarsine, tri-5-bromofurylarsine. Since this reaction is characteristic of aromatic nuclei, the aromaticity of furan is lessened by the presence of halogen in the α-position.

Experimental

2-Chlorofuran Tetrachloride.—*Method 1.*—Two grams of furyldichloroarsine, difurylchloroarsine, trifurylarsine or a mixture of these arsenicals was dissolved in 10 cc. of chloroform, the solution chilled by immersing in a bath of solid carbon dioxide and ether and chlorine passed in slowly. Chlorination was continued until on allowing a sample of the solution to warm to room temperature bubbles of chlorine gas were observed to form. The solution was then placed in an evaporating dish and allowed to stand in the open until the chloroform had evaporated. The viscous oil remaining was steam distilled until no more droplets passed over, collected with a small pipet, and dried by allowing to stand in a desiccator; yield 20%.

Method 2.—Six grams of 2-chlorofuran was dissolved in 20 cc. of chloroform, chilled and chlorinated as described above, the chloroform removed by evaporation and the product steam distilled; yield 3 g. The low yields result from the hydrolysis of the oil during steam distillation.

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(5) Lowe and Hamilton, THIS JOURNAL, **57**, 1081 (1935).

(6) German Patent 272,289; *Chem. Zentr.*, I, 1469 (1914).

(7) Michaelis, *Ber.*, **10**, 622 (1887).

(8) Von Baeyer, *Ann.*, **107**, 274 (1858).

2-Chlorofuran tetrachloride is slightly yellow and has a pungent, penetrating odor, d^{25}_4 1.620.

Anal. Calcd. for $C_4H_3OCl_5$: Cl, 72.57. Found: Cl, 72.48, 72.06.

Reactions of 2-Chlorofuran Tetrachloride.—1. To 20 cc. of saturated alcoholic solution of potassium hydroxide was added approximately 60 mg. of 2-chlorofuran tetrachloride. A bright orange coloration appeared which faded while a precipitate of potassium chloride separated. After fifteen minutes the solution was diluted with water, made acid with nitric acid and silver nitrate added. The precipitated silver chloride was dried at 135° and weighed.

Anal. Calcd. for 40% of 72.57: Cl, 29.03. Found: Cl, 29.51, 29.40.

2. Approximately 50 mg. of 2-chlorofuran tetrachloride was placed in 15 cc. of alcohol and made slightly acid with nitric acid. Aqueous silver nitrate was added and a precipitate was observed to form gradually. The precipitation was complete at the end of twelve hours.

Anal. Calcd. for 60% of 72.57: 43.54. Found: (average of four determinations) Cl, 42.98.

3. Approximately 50 mg. of 2-chlorofuran tetrachloride was placed in 15 cc. of alcohol, made slightly acid with nitric acid and heated to boiling. When the precipitate had coagulated, it was filtered, dried and weighed.

Anal. Calcd. for 70% of 72.57: 50.80. Found: Cl, 50.75, 51.05.

4. The filtrate from the above determination was made strongly acid with nitric acid and boiled until brown fumes appeared. The coagulated precipitate was dried and weighed, the weight of this precipitate added to that found in the previous determination and per cent. of chlorine determined on the basis of this sum.

Anal. Calcd. for 75% of 72.57: 54.52. Found: Cl, 53.87, 53.87.

Difurylarsinic Acid.—Thirty-eight grams of 2-chloromercurifuran, 12 g. of arsenic trichloride, and 50 cc. of benzene was refluxed for three hours. The fraction containing difurylchloroarsine was obtained as described in a previous paper,[5] no attempt being made to purify it by further fractionation. This fraction was dissolved in 20 cc. of chloroform, the solution chilled in a bath of solid carbon dioxide and ether, and chlorine introduced slowly. From time to time a sample was removed and allowed to evaporate. When the amount of white solid formed on evaporation was a maximum, the chlorination was stopped and the entire solution evaporated by allowing to stand at room temperature in an evaporating dish. The crystals were washed three times with dry ether to remove the arsenic trichloride and 2-chlorofuran tetrachloride present and allowed to stand overnight in water. The crystals were washed with cold water, dried at room temperature and analyzed. Further purification can be effected by recrystallization from hot water. The acid is soluble in alcohol and glycol; yield, 1.1 g. or 8% of the total furan present in the mercurial; m. p. 138°.

Anal. Calcd. for $(C_4H_3O)_2AsO_2H$: As, 31.00; neut. equiv., 242. Found: As, 31.10, 31.00; neut. equiv., 228.

Trifurylarsine Dichloride.—The ether washings from the above preparation were placed in a beaker and allowed to stand overnight. A heavy oil remained in which transparent, diamond-shaped crystals were present. These were picked out and washed with ligroin, yield 0.25 g. In alcoholic solution the chlorine present in this compound was precipitable with silver nitrate; m. p. 132°.

Anal. Calcd. for $(C_4H_3O)_3AsCl_2$: As, 21.60; Cl, 20.44. Found: As, 21.47; Cl, 20.29.

5-Chloro-2-chloromercurifuran.—This compound was prepared from 5-chloropyromucic acid[2] by boiling a solution of its sodium salt with an equivalent amount of mercuric chloride, using the directions given by Gilman for the preparation of substituted 2-chloromercurifurans.[3] The mercurial was obtained in 65% yield and no other product was formed. It was purified by recrystallization from hot alcohol, m. p. 181°.

Anal. Calcd. for $C_4H_2OHgCl_2$: Hg, 59.42; Cl, 21.03. Found: Hg, 59.02; Cl, 21.13.

Tri-5-chlorofurylarsine.—Forty-three grams of 5-chloro-2-chloromercurifuran, 16 g. of arsenic trichloride and 100 cc. of benzene was refluxed for thirty minutes. The precipitated mercuric chloride was filtered off and the benzene removed from the filtrate by distillation. When the temperature of the distilling vapors reached 85° distillation was continued using a water pump until the excess arsenic trichloride was removed. The arsenicals were then twice distilled at 1 mm., the distillate being separated into two equal fractions in the second distillation. Decomposition during distillation was slight as compared with that observed in the distillation of unsubstituted arsenicals. An analysis for arsenic and chlorine indicated that the first fraction contained impure di-5-chlorofurylchloroarsine, a slightly green liquid. The second fraction on standing solidified to a white solid; total yield of arsenicals, 6 g., or 20–25%.

The trichlorofurylarsine was obtained from the second fraction by fractional crystallization from ether in the form of fine white needles, m. p. 63°.

Anal. Calcd. for $(ClC_4H_2O)_3As$: As, 19.74. Found: As, 19.54, 19.60.

No attempt was made to purify the first fraction. Chlorination failed to form di-5-chlorofuryl arsinic acid but yielded an arsenic-free highly chlorinated oil so readily decomposed during steam distillation that no analysis was attempted. Its odor, ease of hydrolysis and loss of chlorine in the presence of silver nitrate, indicated that it was probably 2,5-dichlorofuran tetrachloride.

Tri-5-bromofurylarsine.—Forty-two grams of 5-bromo-2-chloromercurifuran, 10 g. of arsenic trichloride and 100 cc. of benzene was refluxed for thirty minutes and the mercuric chloride, benzene and arsenic trichloride removed from the arsenicals as described above. After removal of the arsenic trichloride, the mixture on cooling set to a black mass in which crystals were plainly visible. On dissolving in ether and allowing to evaporate the oily constituents formed a ring at the edge of the dish and were absorbed in filter paper. By repeating this treatment four times the tri-5-bromofurylarsine was obtained as white, beautifully formed needle-shaped crystals; yield 8 g., 40%, m. p. 106°.

Anal. Calcd. for $(BrC_4H_2O)_3As$: As, 14.60; Br, 46.76. Found: As, 14.76; Br, 46.64.

Mercuration of Tri-5-chlorofurylarsine.—One-half gram of tri-5-chlorofurylarsine, 1.1 g. of mercuric chloride and 10 cc. of alcohol were heated to boiling and set aside for fifteen minutes. On the addition of water a white precipitate formed which contained 13% arsenic. Repeated crystallization from hot alcohol gave a 15% yield of 5-chloro-2-chloromercurifuran, m. p. 179–180°.

Mercuration of Tri-5-bromofurylarsine.—Mercuration of this material was attempted by the method above, the same ratio of molecular concentrations of reactants being employed. On addition of water tri-5-bromofurylarsine was precipitated almost unchanged. The experiment was repeated, water being added to the alcohol to the point where precipitation was just avoided. Boiling was continued for fifteen minutes. On cooling and adding water a precipitate was obtained which on recrystallization from water–alcohol gave a 7% yield of 5-bromo-2-chloromercurifuran, m. p. 178°.

Summary

Chlorination of furyldichloroarsine, difurylchloroarsine and trifurylarsine yields 2-chlorofuran tetrachloride in all cases. Stepwise loss of chlorine from this compound has been described. Difurylarsinic acid has been prepared by hydrolysis of a chlorination product of difurylchloroarsine and trifurylarsine dichloride has been isolated. Chlorination of furyldichloroarsine and di-5-chlorofurylchloroarsine in an effort to form furylarsonic acid and di-5-chlorofurylarsinic acid has given negative results. The chlorination of furan arsenicals is regarded as competitive oxidation of arsenic and the furan nucleus.

The preparation of some substituted furan arsenicals has been described, and a study of the action of mercuric chloride on tri-5-chlorofurylarsine and tri-5-bromofurylarsine indicates that the aromaticity of the furan nucleus is less in these compounds than in trifurylarsine itself.

LINCOLN, NEBRASKA RECEIVED JULY 29, 1935

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

The Addition of Chloroform and Bromoform to *p*-Chlorobenzaldehyde

BY JOSEPH W. HOWARD

Introduction

The fact that benzaldehyde is one of the few aldehydes to which chloroform and bromoform will add forming the corresponding trichloromethyl and tribromomethyl carbinols,[1] has led the author to undertake a study of these additions with substituted benzaldehydes.

A study of this reaction with *o*-chlorobenzaldehyde has been recently reported.[2] The present investigation was made with *p*-chlorobenzaldehyde.

Experimental Part

Preparation of Trichloromethyl-*p*-chlorophenylcarbinol.—To a mixture of 46 g. of freshly distilled *p*-chlorobenzaldehyde and 60 g. of dry chloroform was added with constant stirring 4 g. of powdered potassium hydroxide over a one-hour period. The mixture was allowed to stand for at least three hours, ether was added and the resultant mixture filtered. The ether and excess chloroform were distilled off. The residue was steam distilled to remove *p*-chlorobenzaldehyde and *p*-chlorobenzoic acid. The non-volatile portion was extracted with ether, the ether extract washed with 2% sodium hydroxide solution and dried over sodium sulfate. The ether was distilled off and the carbinol removed by distillation under diminished pressure. It came over at 187–188° at 26 mm. The yield was 20 g. of d^{20}_{20} 1.523.

Anal. Calcd. for $C_8H_6OCl_4$: Cl, 54.58. Found: Cl, 54.64.

This carbinol is insoluble in water but readily soluble in ethyl alcohol, methyl alcohol, benzene, acetone, ether, chloroform, carbon tetrachloride and carbon bisulfide.

Preparation of Tribromomethyl-*p*-chlorophenylcarbinol.—The above procedure was followed with the substitution of 130 g. of bromoform for 60 g. of chloroform. This compound boils at 198–200° at 19 mm. It solidified readily on cooling and was recrystallized from 95% ethyl alcohol. The yield was 25 g.; m. p. 90–91°.

Anal. Calcd. for $C_8H_6OClBr_3$: Cl, 9.01; Br, 60.96. Found: Cl, 9.05; Br, 60.86.

This carbinol differs in solubility from the trichloromethyl-*p*-chlorophenylcarbinol in that it is only very sparingly soluble in ethyl and methyl alcohols.

Preparation of the Esters

The esters of trichloromethyl-*p*-chlorophenylcarbinol were prepared as follows: the acetate by heating with acetic anhydride at 150–160° for three hours, the propionate with propionic anhydride at 170–180° for three hours and the butyrate with butyryl chloride at 120–130° for three hours. The usual procedure of the Schotten–Baumann reaction was used in preparing the benzoate with benzoyl chloride. The acetate was recrystallized from 75% acetic acid, the propionate and benzoate from 95% ethyl alcohol. The butyrate remained a viscous oil even after long standing.

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(1) Jocicz, *Chem. Centr.*, **68**, I, 1013 (1897); Siegfried, *ibid.*, **70**, I, 606 (1899); Howard, THIS JOURNAL, **47**, 455 (1925); **52**, 5059 (1930).

(2) Howard and Castles, *ibid.*, **57**, 376 (1935).

The average yield of all of these esters was 85%.

ESTERS OF TRICHLOROMETHYL-*p*-CHLOROPHENYLCARBINOL

		M. p., °C.	Formula	Analyses for Cl, % Calcd.	Found
1	Acetate	120–121	$C_{10}H_8O_2Cl_4$	46.98	47.18
2	Propionate	71–72	$C_{11}H_{10}O_2Cl_4$	44.89	45.17
3	Benzoate	128–129	$C_{15}H_{10}O_2Cl_4$	38.98	38.87

The butyrate boils at 172–173° at 6 mm., d^{20}_{20} 1.331. The butyrate is insoluble in water but readily soluble in ethyl alcohol, methyl alcohol, benzene, acetone, ether, chloroform, carbon tetrachloride and carbon bisulfide. The other esters differ from this in that they are only sparingly soluble in ethyl and methyl alcohols.

A number of attempts were made to make these same esters of tribromomethyl-*p*-chlorophenylcarbinol using the same reagents and experimental conditions but the carbinol always came through unchanged. Attempts were also made to prepare the acetate by heating with acetyl chloride at 60–70° for three hours and the benzoate by heating with benzoic anhydride at 180–190° for five hours. The results here were also negative.

Summary

Trichloromethyl-*p*-chlorophenylcarbinol and its acetic, propionic, butyric and benzoic esters have been prepared and studied. The corresponding tribromo carbinol was prepared but it does not form these esters under the same experimental conditions.

MISSOULA, MONTANA RECEIVED SEPTEMBER 17, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Natural and Synthetic Rubber. XV. Oxygen in Rubber

BY THOMAS MIDGLEY, JR., A. L. HENNE, A. F. SHEPARD AND MARY W. RENOLL

The harmful effects of oxygen on rubber have long been known, and the formation of peroxides during milling has been qualitatively demonstrated.[1] However, quantitative measurements of the oxygen have never been made, and the nature of the oxygen compounds has not been investigated.

Rubber frequently has been analyzed by combustion and the ratio of the carbon percentage to the hydrogen percentage has invariably been found to correspond closely to a $(C_5H_8)_n$ formula. However, it does not follow that such is the formula of rubber. In every instance, the total of the carbon and the hydrogen content has fallen short of 100%. The deficiency is very small, especially in the case of pure rubber, but it invariably exists. The best analyses available, those of the Bureau of Standards,[2] done on highly purified, and on recrystallized rubber, show a deficiency of 0.3%. This cannot be accounted for entirely by contamination of the samples, nor can the combustion be assumed to be that inaccurate. It is logical to regard this deficiency as the oxygen and nitrogen content of the sample.

In the present work, the quantity of oxygen present in rubber samples has been measured by means of the combustion method described by the Bureau of Standards; an effort has been made to determine the type of oxygen present and to study the progressive oxidation of rubber. The technique of the Bureau has been altered in only two details: (1) a Jena combustion tube was substituted for the Pyrex tube, to prevent sintering at the high temperature used to burn out the last traces of carbon; (2) weighings were improved to ±0.00002 g.

Procedure

Sol rubber was prepared and purified by fractional precipitation[3] until it contained only 0.007 ± 0.0003% of nitrogen by Nessler titration. A sample of this rubber was analyzed by combustion to determine the H/C ratio and the oxygen and nitrogen content by deficiency. Another sample of the same specimen was treated with methylmagnesium iodide and the resulting methane measured to determine the amount of active hydrogen. The amount of carboxylic or ketonic groups present was investigated by treating a third sample with thionylmagnesium iodide, purifying the reaction product and analyzing it for sulfur.[4] The data are listed in Tables I and II together with the results of the same methods used on purified sodium rubber and on the degraded products of both.

Discussion of the Results

The striking fact shown by the tables is that pure synthetic rubber is oxygen free, while natu-

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(1) Busse, *Ind. Eng. Chem.*, **24**, 140 (1932).

(2) Smith, Saylor and Wing, *Bur. Standards J. Research*, **10**, 479–92 (1933).

(3) Midgley, Henne and Renoll, THIS JOURNAL, **53**, 2733 (1931).

(4) Midgley, Henne, Shepard and Renoll, *ibid.*, **56**, 1325 (1934).

TABLE I

ANALYSIS OF RUBBER BY COMBUSTION

Calcd. for $(C_5H_8)_n$, %	H, 11.84	C, 88.16	H/C = 0.13436
Synthetic rubber, found	11.82, 11.83 and 11.83	88.17, 88.17 and 88.17	.1342
Natural rubber, found	11.86 and 11.86	88.07 and 88.07	.1346

Basis of Calculation: C = 12.0048, H = 1.0081 and O = 16.0000.

Note: The samples of natural rubber contained 0.007% N.

TABLE II

NATURAL RUBBER (SOL RUBBER)

(Nitrogen content = 0.007%)

Material	Analyses, %				Oxygen content measured by		Mol. wt.
	Ash	C	H	H/C	Combustion	Active H	cryoscopy
Original	0.01	88.07	11.86	0.1346	0.06	0.028	∞
Milled 1.5 hours	.065	87.71	11.79	.1344	.44	.095	∞
Degraded 1 day	.02	87.58	11.75	.1342	.65	.16	∞
Degraded 7 days	.02	82.45	11.05	.1340	6.48	1.51	4400
SYNTHETIC RUBBER							
Original	0.00	88.17	11.83	0.1342	0.00	0.00	∞
Degraded 1 day	.01	88.14	11.83	.1342	.02	.00	∞
Degraded 11 days	.01	85.43	11.47	.1343	3.09	.91	∞
Degraded 18 days	.03	84.73	11.34	.1338	3.90	1.49	8100
Degraded 31 days	.00	79.40	10.60	.1335	10.00	2.88	4300

ral rubber purified to the same extent by the same procedure contains oxygen; this oxygen is associated with an appreciable amount of active hydrogen while CO groups or oxygen of a peroxide nature are practically absent. Consequently, the experimental results may be interpreted as establishing the presence of an hydroxyl group in what has heretofore been called a hydrocarbon.

In view of the fact that oxygen is measured by deficiency, and its order of magnitude is very small, it is proper to question the significance of the experimental results.

First, may not the deficiency, as determined by the combustion, be purely an experimental error in the case of undegraded rubber?

This objection is refuted by the fact that a sample of sodium rubber has been repeatedly analyzed in the same apparatus and manner to give zero deficiency within the probable limits of experimental error.

Second, may not all of the oxygen found in undegraded rubber be attributed to an unremoved impurity?

Such an assumption is refuted by the fact that purified natural rubber gels when it is treated with a Grignard reagent; this is a test for combined oxygen in rubber, as previously shown.[5]

Third, could the combined oxygen be the result of slight degradation during fractionation? This is unlikely because synthetic rubber, which degrades quite easily, was subjected to the same method of purification, yet remained free of oxygen.

Fourth, is the combined oxygen a natural part of the rubber molecule or is it the result of slight oxidation between the time the latex left the tree and the time fractionation started?

The present results are only conclusive for the particular sample used. This sample was taken from the center of a bale of sprayed latex rubber and showed no visible signs of oxidation such as could be seen at the surface of the bale. Similar samples had been investigated previously by fractionation and no evidence of degradation had been found. It is probable, therefore, that the combined oxygen is a part of the rubber molecule occurring in nature.

Irrespective of its origin or significance, combined oxygen has been demonstrated to be present in the natural rubber investigated.

Quantitative Value of the Data

No quantitative significance is attached to any minor variation of the data except for the original undegraded sample of natural rubber and the oxygen-free synthetic; hence, this part of the discussion is confined to these two.

The values selected for the atomic weights of hydrogen and carbon are important and affect the results. The latest reported values by Aston,

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(5) Midgley, Henne and Shepard, THIS JOURNAL, **56**, 1156 (1934).

namely, 1.0081 for hydrogen and 12.0048 for carbon, have been used in the calculations.

The deficiency of the natural rubber analysis is determined as 0.06%. This value includes the combined oxygen of the rubber and all the oxygen and nitrogen of the impurities present. The samples contained 0.007% of nitrogen. Previous experience with the fractionation of rubber has shown that the nitrogen impurities which are soluble in benzene and alcohol mixtures are easily eliminated but that an insoluble nitrogenous material collects in a gel phase. By degenerating the gel rubber this impurity may be collected. It contains two atoms of oxygen for each atom of nitrogen and behaves as an amino acid. It is almost certain that this impurity is the source of the nitrogen found, hence the total nitrogen and oxygen external from the rubber molecule itself becomes 0.023%. This leaves the combined oxygen as 0.042%.

The results of the treatment with thionyl Grignard were of no significance. The method is no more accurate than the values obtained. And even though these values were other than experimental error, they still would not represent any more oxygen than that available for this reaction in the nitrogen impurity. If there is any ketone, aldehyde or carboxyl oxygen present in the original L. S. rubber, this investigation fails to disclose it.

The hydroxyl oxygen, as disclosed by active hydrogen measurements, is more reliable. This method gives closely checking results. Blanks indicate a high accuracy for acids but a slightly low value for alcohols. If allowance is made for the active hydrogen present in the nitrogen impurity, considered as an amino acid, the final value becomes (0.028 − 0.008) = 0.02%. This value should be looked upon as possibly somewhat low, as the evidence thus developed points to the rubber molecule being an alcohol.

The value of 0.04% of oxygen as measured by combustion seems somewhat in discrepancy with the value of 0.02% as measured by active hydrogen determination, but a critical study of the possible errors involved in both methods by no means precludes the probability that the true value for the oxygen lies between these two and that hydroxylic oxygen was the only kind of oxygen present in the samples. By computing the molecular weight corresponding to the assumed presence of only one atom of oxygen in each rubber molecule, it is found that 0.04% of oxygen corresponds to a molecular weight of 40,000, while 0.02% corresponds to 80,000 (or 585 and 1170 isoprene units, respectively). This is in substantial harmony with the mol. wt. of 53,000, as determined by sulfur addition,[4] and suggests that the rubber molecule is a high molecular weight member of a pseudo homologous series occurring in nature, starting with geraniol and increasing by isoprene units to rubber.

One definite discrepancy with respect to present-day conceptions of the rubber molecule exists in the data. This is the abnormally high H/C ratio. Experience with the analysis indicates that this ratio is accurate to within ±0.0001. The theoretical H/C ratio for C_5H_8 with C as 12.0048 and H as 1.0081 is 0.13436. The indicated ratio for the original natural rubber is 0.1346. This is in perfect agreement with the value reported by the Bureau of Standards[2] and is 0.00024 too great, or 0.18% in excess, or one extra hydrogen atom for each 70 isoprene units. This is too small a number of isoprene units for it to be an end-group hydrogen. Likewise, if impurities are assumed to be responsible, a deficiency of 0.18% is required to account for it as water, 0.14% as alcohol or 0.75% of a non-volatile paraffinic hydrocarbon must be present, none of which fits the other data and/or the present accepted theories about the rubber molecule.

Oxidation Data

The data presented relative to the oxidation of rubber are to be taken as merely a preliminary study of the application of the analytical methods used to the problem of the chemistry of the oxidation of rubber. The results are, however, significant. As rubber undergoes oxidation, either by milling or exposure to oxygen and sunlight, the following events occur. The H/C ratio decreases, the combined oxygen increases, the active hydrogen increases and the molecular weight (measured by cryoscopy in benzene) decreases. The thionyl Grignard results still lack significance.

In addition to the data reported, the following experiment was performed. A fresh sample of heavily oxidized rubber was placed in a sealed tube and heated for several hours. Oxygen gas was evolved, the combined oxygen decreased to about half of its original value, the active hydrogen decreased slightly, the H/C ratio decreased and, judging by appearance, the molecular weight had greatly decreased.

These observations and data are sufficient to suggest several deductions as to the probable course of events.

1. Oxygen attaches to the rubber molecule in some peroxide linkage.
2. This linkage rearranges to an OH group with the liberation of O.
3. Some of the OH groups join with H and are eliminated as H_2O; hence the lowering of the H/C ratio.
4. The molecule is ruptured during or as the result of one of the above events.

Experimental

Combustion.—The apparatus developed by the Bureau of Standards[2] was used with the following alterations. A Jena Supremax tube was welded to a large Pyrex slip-joint at one end, and this joint was used without lubricant to connect to the purifying train. All combustions were done in air. Generally a platinum boat was used, but undegraded natural rubber was burned without a boat.

Preparation of the Samples.—Sol rubber samples were obtained by fractional precipitation, handled and stored as previously described.[3] The synthetic rubber samples were prepared from purified isoprene by polymerization over Na–K, *in vacuo*. Polymerization was so rapid that cooling was needed to prevent explosions.

Degradation.—Rubber cement (5% in benzene) was placed in an oxygen-filled round-bottom flask, and exposed to sunlight at room temperature. Dry oxygen was fed periodically to make up for the amount used.

Active Hydrogen Determination.—The apparatus was made of sealed Pyrex glass (see Fig. 1), the reaction chamber (a) being an ordinary 300-cc. Kjeldahl flask; the buret (b) was about 7 cc. in capacity and was kept at a known temperature by means of a water circulation jacket.

The reagents used were:

(1) Rubber cement in C. P. benzene. This benzene, which is also used as a wash liquid, must be run as a blank to determine its methane liberation value.

(2) Methylmagnesium iodide in butyl ether, of approximately 1.5 molecular concentration. This reagent is rid of all incidental gases by evacuation and is kept in sealed ampoules containing 7-cc. portions until it is ready to be used. One ampoule is used for each determination.

(3) C. P. triphenylcarbinol, for standardization.

Procedure.—Fill the buret completely with mercury; close the stopcock (c); evacuate the flask completely through (a); place a quantity of rubber cement in (a), such that it will generate from 1.5 to 3.5 cc. of methane; suck it into the flask, and wash (a) with C. P. benzene several times, until the total volume in the flask is about 200 cc. Heat cautiously with a small flame, while evacuating steadily through (a), and shaking vigorously, until the volume is reduced to about 50 cc.; close (b) in such a manner that a small amount of benzene distillate remains above it as a seal. Place the batch of methylmagnesium iodide in (a); reduce it to about one-half of its volume by cautious evacuation, in order to remove any possible gases; allow this reagent to be sucked into the flask, closing (b) just in time to retain a small portion above it as a seal. Heat the mixture cautiously, while shaking frequently; this causes the methane to collect in the side-arm, from where it can be drawn into the buret, together with a small amount of benzene. Close (c), and allow the flask to cool slightly; then reheat with shaking. By watching the ring of benzene condensation rising in the side arm, it is possible to ascertain whether or not more methane is being liberated. Usually two or three successive heatings are sufficient, after which pure benzene reaches the buret. The amount of gas in the buret is then measured, corrected for standard conditions, for benzene vapor and for the previously determined blank.

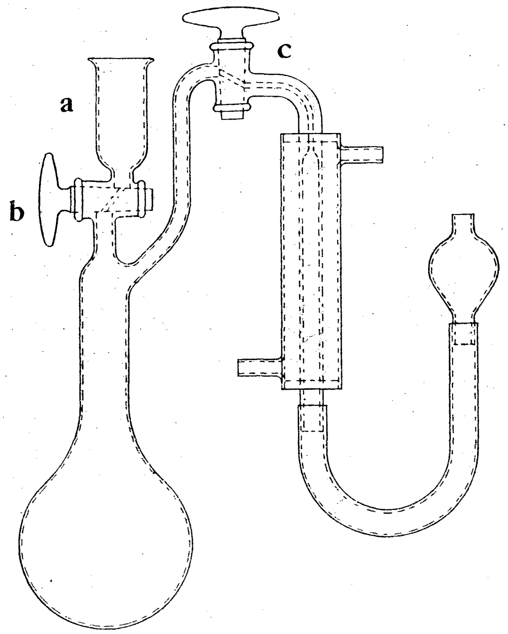

Fig. 1.

ANALYSIS OF TRIPHENYLCARBINOL

Sample, g.		0.0322	0.0370
Methane, cc.	Calcd.	2.77	3.19
	Found	2.53	3.14

Summary

It has been shown that natural rubber contains oxygen, while synthetic rubber is oxygen free. This oxygen appears to be of an hydroxylic type, and its quantity corresponds to about one hydroxyl group for each one thousand isoprene units of the rubber molecule.

Rubber has been allowed to oxidize and a mechanism is proposed to interpret the quantitative data recorded.

MIDGLEY FOUNDATION
COLUMBUS, OHIO

RECEIVED JULY 1, 1935

[CONTRIBUTION NO. 27 FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Action of Nitric Acid on a Bituminous Coal

BY B. JUETTNER, R. C. SMITH AND H. C. HOWARD

Bituminous coals can be converted almost completely into soluble products by treatment with nitric acid, under such conditions that great internal structural changes probably do not occur. A study of the character of the reaction and the nature of the products formed is of importance from the standpoint of our knowledge of the nature of these coals. Previous work[1] has been limited almost entirely to a study of the action of nitric acid on lignites and brown coals.

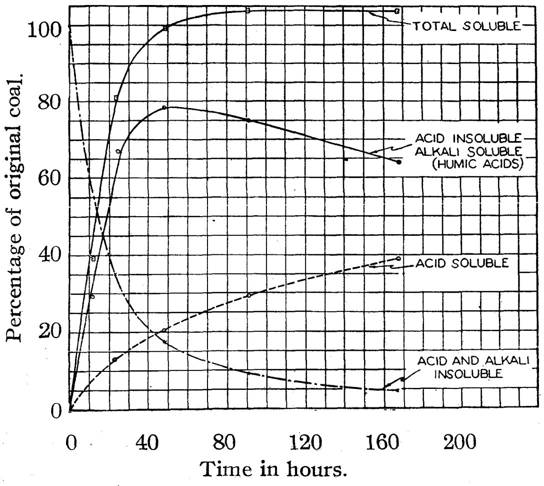

Fig. 1.—Yields of products of the reaction of 1 *N* nitric acid on coal as a function of time.

A preliminary study of the effect of acid concentration on the yield of soluble products, as a function of time showed that even with concentrations as low as one normal, five days' refluxing resulted in conversion of all but a small fraction of the original weight of the Pittsburgh seam coal used[2] into acid or alkali soluble products. At the end of an equal time with 0.1 *N* acid a residue of insoluble material of approximately 46% remained. Since a concentration of one normal appeared to be near the lower limit at which reasonably rapid reaction rates could be obtained, this concentration was chosen for detailed investigation.

Nature of the Reaction

The rates of formation of the products of the reaction, other than gaseous, are shown in Fig. 1. Acid-soluble products increase continuously with time, acid-insoluble, alkali-soluble, the so-called regenerated "humic acids," reach a maximum at about forty-eight hours and then decrease, presumably due to the fact that they are transformed to acid solubles more rapidly than they are formed from the coal. The total soluble material remains quite constant after the initial stages of the reaction are complete, since the principal reaction in the later stages is transformation of humic acids to soluble acids, with apparently little weight change, the decrease in weight due to loss of carbon dioxide during the transformation being approximately balanced by the increased oxygen content of the soluble acids formed.

The distribution of carbon and nitrogen in the oxidation products in a five- and a fifty-two-day oxidation is shown in Table I. It is evident that the reaction is chiefly an oxidation, since such a large fraction of the nitrogen in the nitric acid consumed appears as nitric oxide. The nitrogen in the organic acids decreases with time. Such behavior would be expected if a part of the nitrogen is held at first as isonitroso groups, as Fuchs[3] has suggested, which are removed by hydrolysis during the later stages of the oxidation. Transformation of the carbon of the humic acids to soluble acids with concomitant formation of carbon dioxide as the oxidation proceeds is also shown.

TABLE I

DISTRIBUTION OF CARBON AND NITROGEN IN REACTION PRODUCTS

	5-Day oxidation, %		52-Day oxidation, %	
	C	N	C	N
Humic acids	67.6	9.2	15.0	0.8
Soluble acids	9.2	4.5	33.8	3.1
Carbonic acid	14.4	..	36.2	...
Nitric oxide		82.5		102.0

The work on carbon balances was necessarily done in a closed system. In other oxidations carried out with free access of air to the system it was found that rates of formation of the various

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(1) Schellenberg, *Brennstoff-Chem.*, **2**, 386 (1921); Tropsch and Schellenberg, *Ges. Abhandl. Kenntnis Kohle*, **6**, 225 (1921); Strache-Lant, "Kohlenchemie," Akademische Verlagsgesellschaft, Leipzig, 1924, p. 308; Fuchs, *Brennstoff-Chem.*, **9**, 178 (1928); Fuchs and Stengel, *ibid.*, **10**, 303 (1929); *Ann.*, **478**, 267 (1930).

(2) Described in detail in *Bur. Mines, Tech. Paper*, 525 (1932).

(3) Fuchs, "Chemie der Kohle," Verlag Julius Springer, Berlin, 1931, p. 202.

products were approximately the same as in the absence of air, but determination of nitric acid consumed showed that only about one-fourth as much nitric acid was required. The lower oxides of nitrogen first formed in the reaction are evidently converted, in the presence of air, to nitric acid. This indicates the possibility of carrying out such an oxidation with air, using a relatively small amount of oxides of nitrogen as carrier.

Oxidations were also carried out on the residue from a 260° benzene pressure extraction of this coal[4] and on the "cokes" from its thermal decomposition in a molecular still.[5] Acid-soluble products and humic acids were obtained from the oxidation of the extraction residue as in the oxidation of the original coal. The rate of oxidation, however, was considerably greater, as can be seen by comparison with Table I, a five-day oxidation of the residue yielding 57% of the carbon as humic acids, 13.7% as soluble acids, and 22.2% as carbon dioxide. The reaction products from oxidation of the cokes were not examined in detail, but it was found that in the oxidation of cokes prepared up to about 440°, the yield of soluble products was the same as for the original coal within the limits of error in the analytical method. In Fig. 2, yields of soluble oxidation products from the cokes, determined by difference, gas evolution and tar recovered during the vacuum carbonization, have been plotted. Gas evolution is in terms of pressure in the system at a constant rate of evacuation. The strong initial gas evolution at approximately the same temperature at which the coke residue begins to show resistance to oxidation would seem to indicate some fundamental change in the "coal molecule" over this temperature interval. Tar formation, on the contrary, appears to be relatively independent of any critical range.

Nature of the Products

If the oxidation proceeds for only a few days the chief product is, of course, the dark brown, colloidal humic acids. These regenerated humic acids are similar in composition and general properties to those extracted directly from peat and brown coal. They contain carboxyl and hydroxyl groups, but the latter in definitely smaller proportions than has been reported for humic acids from other sources. For acids from typical German brown coals,[6] the ratio of hydroxyl to carboxyl is given as 1.2, 3.9 and 2.6; for acids[7] from an Italian lignite and a peat 0.87; for those[8] from an Ontario lignite, 2.0; and for acids[8] prepared from sucrose, 1.0. The corresponding figure for the acids from this coal is 0.3 to 0.4.

As in the case of humic acids from other sources,[9] only from a half to two-thirds of the oxygen in these acids can be accounted for in specific groups (see Table II); the balance probably is in ether linkages. The amount of this oxygen of unknown form corresponds approximately to the oxygen of the original coal, thus indicating the presence of a relatively stable oxygen-containing unit both in the coal and in the acids regenerated from it.

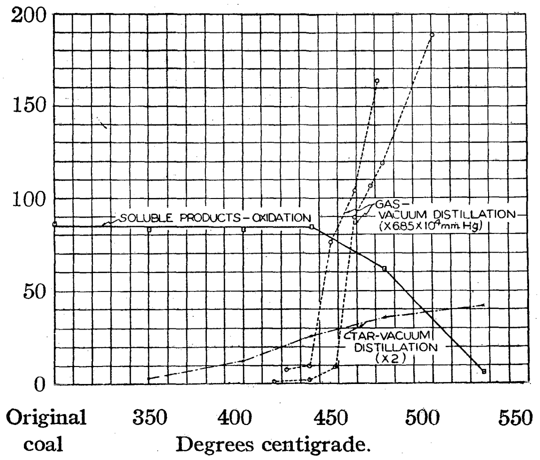

Fig. 2.—Yields of soluble oxidation products from the cokes, gas evolution and tar formation during vacuum pyrolysis as a function of temperature.

If the oxidation is carried on for several weeks, water-soluble, non-volatile acids to the extent of 35–40% of the weight of the coal can be recovered, forming a pale yellow to orange-red, amorphous, highly hygroscopic mass. These acids are lower in carbon and higher in oxygen than the humic acids, the average empirical composition for typical preparations, calculated on the basis of six carbon atoms, being $C_6H_{3.6}O_{4.8}$ for the former, and $C_6H_{3.8}O_{2.2}$ for the latter. A comparison of typical preparations of the two kinds of acids is made in Table II. The soluble acids are definitely smaller in molecular and equivalent weights, contain on the average only small amounts of

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(4) Asbury, *Ind. Eng. Chem.*, **26**, 1301 (1934).

(5) Juettner and Howard, *ibid.*, **26**, 1115 (1934).

(6) Fuchs, Ref. 3, p. 197.

(7) Ubaldini and Siniramed, *Ann. chim. appl.*, **23**, 585 (1933).

(8) Plunguian and Hibbert, THIS JOURNAL, **57**, 528 (1935).

(9) Fuchs, Ref. 3, p. 121.

hydroxyl, and nearly all the oxygen found by ultimate analysis can be accounted for in carboxyl groups. We have observed that whether the attack on coal be made by hydrogenation or oxidation, soluble, crystallizable or distillable products are obtained only when this non-determinable oxygen is largely eliminated, thus indicating the importance of the role played by this element in the coal polymer.

TABLE II

PROPERTIES OF HUMIC AND SOLUBLE ACIDS

	Humic acids	Soluble acids
Molecular weight	200–300	120–140
Equivalent weight	233	68
Carboxyl oxygen, %	13.7	47
Hydroxyl oxygen, %	2.2	<1
O in functional groups, %	15.9	47
Total O (by combustion), %	29	49

The presence in the soluble acids of mellitic and benzene-pentacarboxylic acids was shown by isolation of their methyl esters. The amount of ester recovered was in each case less than 1% of the weight of the coal. German workers,[10] by oxidation of brown and bituminous coals, with oxygen under pressure and with nitric acid, obtained similar soluble acids from which they isolated various benzene carboxylic acids from benzoic to mellitic. The maximum yield of pure benzenoid acids reported was 10.4 g. per 100 g. of coal. Bone[11] and his co-workers state that alkaline permanganate oxidations of English bituminous coals yield 39–46% of the carbon as "crude benzenoid" acids, approximating the tricarboxylic in composition and corresponding to 65–81 g. of crude acids per 100 g. of coal. No figures are given on the actual quantity of pure acids isolated.

It was recognized that the isolation, in good yields, of the individual benzenoid acids from a mixture of the twelve possible, constituted a very difficult problem, hence some more general criterion of the benzenoid nature of these products was sought. Since they all contain the benzene ring as a nucleus, decarboxylation followed by recovery of the benzene formed appeared suitable.[12] Fischer's[13] method of heating the sodium salts with water to high temperatures under pressure was studied with the following known acids: benzoic, the three phthalics, and one each of the tri and tetra acids and the penta. With small samples, $^1/_{16}$ mole, recoveries ranged from 56% with iso-phthalic to 73% with benzoic. With a 1 mole sample of benzoic acid the recovery of benzene was 94%. Application of this method of decarboxylation to the soluble acids obtained in our work yielded approximately 10 cc. of steam-volatile hydrocarbons per 100 g. of acids, corresponding to 9 g. per 100 g. of coal oxidized to soluble acids. Fractionation of these hydrocarbons yielded 40% boiling in the range of benzene, 78–81°, of refractive index 1.496 at 25°. Solid hydrocarbons denser than water appeared in the higher fractions, indicating the presence of aromatic nuclei more complex than the benzene ring. This material contained diphenyl, which also appeared, in small amounts, in the decarboxylation of the known benzenoid acids, and presumably is the result of secondary reactions of the benzene. The residue in the bomb after a decarboxylation smelled strongly of cresol and of aromatic organic bases, and about 2.5% of a tarry residue was recovered by extraction with ether. If all the steam-volatile hydrocarbons are assumed to be benzenoid, approximately one-tenth of the carbon in the coal oxidized to soluble acids was recovered in the form of C_6 rings.

The gas, approximately 20 liters of which was recovered per 100 g. of acids, consisted of 25% methane, 60% hydrogen, and small amounts of ethane and unsaturates. The presence of considerable amounts of the lower aliphatic hydrocarbons and hydrogen, in the gases from decarboxylation, would indicate the presence of aliphatic acids such as oxalic, malonic and succinic, which were, however, not found; hence it appears these gaseous products must have come from the thermal decomposition of acids of more complex nucleus.

Experimental

Determination of Yields of Oxidation Products.—For determination of the rates of formation of the non-volatile oxidation products, 0.5-g. samples of 200 mesh coal[2] were refluxed with 100 cc. of 1 *N* nitric acid in 250-cc. round-bottomed Pyrex flasks connected to water condensers by ground joints. At the end of the determined period the contents of the flask were filtered through weighed Jena fritted glass crucibles with asbestos pads. The insoluble material was thoroughly washed with 1 *N* nitric acid, filtrate and washings evaporated to dryness on the water-

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[10] For a review see Horn, *Brennstoff-Chem.*, **10**, 362 (1929).

[11] Bone, Parsons, Sapiro and Groocock, *Proc. Roy. Soc.* (London), **A148**, 521 (1935).

[12] Kerkovius and Dimroth [*Ann.*, **399**, 120 (1913)] recovered benzene, naphthalene and fluorene by heating the barium salts of acids formed by oxidation of charcoal with fuming nitric acid.

[13] Fischer and Schrader, *Ges. Abhandl. Kenntnis Kohle*, **5**, 307 (1922); Schrader and Wolter, *ibid.*, **6**, 79 (1923); Schrader and Friedrich, *ibid.*, **6**, 108 (1923).

bath in weighed porcelain dishes and finally dried at 110° and weighed. This material constituted the yellowish-orange soluble acids. The acid-insoluble material in the Jena crucibles was dried at 110°, weighed, and then thoroughly washed with cold concentrated ammonium hydroxide. By this means the dark brown, acid-insoluble, alkali-soluble humic acids were extracted. This extraction, however, was never entirely complete; air oxidation continuously formed traces of soluble products during the extraction operation. The acid and alkali insoluble material remaining in the Jena crucibles was dried again at 110° and the weight of humic acids determined by difference. In the experiments on the oxidation of the cokes, the same method was used as for coal, except acid and alkali soluble products were removed in one step by treatment with concentrated ammonium hydroxide, followed by centrifuging and filtration, and the insolubles determined at once by drying the insoluble residue at 110°. Total soluble material was then obtained by difference. In all cases duplicate determinations were carried out, and the agreement was usually within 5 parts per 100.

In those experiments where gaseous products were recovered, to obtain carbon and nitrogen balances, oxygen was completely eliminated from the system by evacuation followed by flushing with nitrogen. The tube for collection of gas samples was sealed directly to the top of the reflux condenser and delivered through the usual U bend immersed in mercury, into mercury filled gas sampling tubes. No attack on the mercury was observed as long as oxygen was carefully excluded. Analyses of gaseous products were made in an Orsat apparatus using standard methods for carbon dioxide, unsaturates, carbon monoxide, hydrogen and methane. Nitric oxide was absorbed in freshly prepared acidified ferrous sulfate.[14] Tests were made for condensable hydrocarbons and nitrous oxide by passage of the gas through a liquid nitrogen trap before absorption in the ferrous sulfate. Negligible amounts of material condensed.

Molecular and Equivalent Weights.—Molecular weights were determined cryoscopically by a technique similar to that already described,[15] the only modification being the use of an atmosphere of dry nitrogen above the fused catechol during the measurements. Equivalent weights were determined electrometrically, using the antimony electrode,[15] and also by the method of Ubaldini and Siniramed,[7] in which the humic acid reacts with a mixture of calcium acetate and carbonate and the evolved carbon dioxide is absorbed and weighed. The latter gave somewhat higher values and the agreement between duplicate determinations was less satisfactory. For a typical regenerated humic acid, values of 233 ± 2 were obtained electrometrically, and 251 ± 4 by the Italian workers' method.

Carboxyl and Hydroxyl Groups.—Carboxyl oxygen was calculated from the equivalent weights. Hydroxyl groups were determined by exhaustive methylation followed by alkaline hydrolysis of the ester methoxyl and a volumetric microdetermination[16] of the unhydrolyzable methoxyl. Several methods of methylation were employed; diazomethane, dimethyl sulfate plus 40% alkali, and Waliaschko's[17] procedure of rubbing the potassium salt in a mortar with dimethyl sulfate. The last gave the highest results, both for total methoxyl and ether methoxyl. Hydroxyl groups in humic acids can also be estimated indirectly by the difference between the carboxyl content, calculated from equivalent weights, and the total acidity carboxyl plus phenolic hydroxyl, determined by the method of Ubaldini and Siniramed.[7] Two determinations for oxygen in hydroxyl in a typical humic acid preparation gave an average of 3.4% by this difference method, compared with an average of 2.2% determined by methylation and hydrolysis.

Examination of the Soluble Acids.—To obtain sufficient amounts of the soluble acids to attempt the isolation of individual compounds, larger quantities of coal were oxidized. In order to avoid handling large volumes the ratio of coal to acid was considerably increased, up to about 7 g. per 100 cc. of acid, and the nitric acid concentration maintained by the addition of fresh acid when required, as determined by periodic titration with standard alkali of small aliquots from the reaction mixture. After a suitable period of oxidation, thirty to sixty days, the insoluble material was separated by sedimentation and filtration and washed with water until peptization started. Filtrate and washings were concentrated to a small volume on the water bath at pressures of 10 to 20 mm. and finally freed completely of nitric and other volatile acids by prolonged evacuation at 50°, using a Megavac pump behind a liquid nitrogen trap. In two experiments of thirty-two days' duration, 33 and 34 g. of acid solubles per 100 g. of coal were recovered. The dried, ground acids were exhaustively extracted in a Soxhlet with ether, acetone and finally methyl alcohol. Approximately 40% of the material did not dissolve. Methylation of the soluble acids with an ether solution of diazomethane, in the usual manner, followed by distillation in a molecular fractioning still, up to bath temperatures of 300°, yielded 10.8 g. of distillable esters per 100 g. of coal. No pure compounds have yet been isolated from these mixed esters.

The esters of mellitic and benzene-pentacarboxylic acids were isolated as follows: 100 g. of the dried, ground acids was treated with 1 liter of concentrated ammonium hydroxide at 0° for an hour. The insoluble ammonium salts were filtered off and treated with an excess of barium hydroxide solution, at the boiling point, until all ammonia was displaced. The barium salts were filtered off, the acids liberated with dilute sulfuric acid, using brom thymol blue indicator, were separated, methylated with diazomethane and the esters fractionated as before. From the fraction evaporating at a bath temperature of 220–300°, pressure of about 1 micron, 1 g. of the methyl ester of mellitic acid, m. p. 187.4°, and 0.2 g. of the benzenepentacarboxylic methyl ester, m. p. 147.9°, were isolated. *Anal.* Hexamethyl mellitate. Calcd.: C, 50.71; H, 4.23. Found: C, 50.68; H, 4.26. Pentamethyl ester of benzenepentacarboxylic acid. Calcd.: C, 52.18; H, 4.34. Found: C, 52.34; H, 4.69. The identity of the penta compound was confirmed by a mixed melting point with the ester prepared by the action of ethereal diazomethane on a sample of Eastman benzenepentacarboxylic acid. The appearance of the penta acid along with the mellitic was

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(14) Moser, *Z. anal. Chem.*, **64**, 81 (1924).

(15) Smith and Howard, THIS JOURNAL, **57**, 512 (1935).

(16) Vieböck and Brecher, *Ber.*, **63**, 3207 (1930).

(17) Waliaschko, *Arch. Pharm.*, **242**, 242 (1904).

unexpected, since it is only the latter which forms an insoluble ammonium salt. It is probable that the amount of the penta acid recovered represents only a small fraction of that present.

Decarboxylation.—One hundred grams of the dried acids, 200 g. of sodium hydroxide, and 100 cc. of water were placed in a 1-liter American Instrument Company bomb furnished with a nickel liner. The temperature was raised to 450° in about four hours, maximum pressure 3800 lb. After cooling, and withdrawal of a gas sample, the pressure head of the bomb was replaced by a head carrying a delivery tube for attachment to a water condenser and an inlet for steam. The steam-volatile hydrocarbons, after passage through the water condenser, were collected over a strong calcium chloride solution acidified with hydrochloric acid, and measured in a small buret calibrated to 0.05 cc. After further drying over anhydrous calcium chloride the hydrocarbons were fractionated through a 51-cm. vacuum jacketed column.

The volume of gaseous products formed in the decarboxylation was calculated from the pressure and volume of the system and their composition determined in an Orsat apparatus by standard methods.

Acknowledgment.—The authors are indebted to F. C. Silbert and T. B. Smith for determinations of ultimate composition, and to J. M. Scott for gas analyses.

Summary

The action of dilute (1 N) nitric acid in converting bituminous coal into soluble products has been shown to be chiefly an oxidation. The yield of humic acids reaches a maximum in a few days, while that of the soluble acids increases slowly with time. If the reaction is carried out in the presence of air, only about one-fourth as much nitric acid is consumed as in its absence.

The residue from the benzene pressure extraction of this coal oxidizes more rapidly than the original coal. Oxidation of the cokes obtained by thermal decomposition of the coal in vacuum shows no difference from the original coal with cokes up to about 440°. Cokes prepared above this temperature show markedly greater resistance to oxidation. It has been pointed out that this temperature coincides with that at which gas evolution becomes rapid.

Determinations of ultimate composition and functional groups on both types of acids formed in this oxidation show the regenerated humic acids to contain markedly less hydroxyl than is reported for other humic acids, while the soluble acids contain negligible amounts. In the humic acids only approximately half the oxygen determined by ultimate analysis can be accounted for in functional groups, while in the soluble acids only small amounts of oxygen are thus unaccounted for. The presence, in the soluble acids, of benzenepentacarboxylic and mellitic acids was shown by isolation of their esters. Of the carbon of the coal which was oxidized to soluble acids, approximately one-tenth was recovered as steam-volatile, aromatic hydrocarbons, by decarboxylation. The presence of acids more complex than the benzene carboxylics is indicated.

PITTSBURGH, PENNA. RECEIVED SEPTEMBER 9, 1935

NOTES

Decomposition of *p*-Iodoaniline

BY F. B. DAINS, R. Q. BREWSTER AND JOHN A. DAVIS

A sample of *p*-iodoaniline was prepared and carefully purified by one of us.[1]

The product stood for three years in a glass-stoppered bottle (hence a limited supply of air) in semi-diffused light, at room temperature; it had then changed to a black liquid, which was found to contain a trace of free iodine and a small amount of aniline. Further examination showed the presence of 2,4-diiodoaniline and unchanged *p*-iodoaniline. The *p*-iodoaniline was removed as its hydrochloric acid salt by extraction of the liquid with hot, dilute acid. The salt crystallized from the solution as it cooled and the free base was liberated with alkali and recrystallized from ligroin, b. p. 90–100° (m. p. 62°). The 2,4-diiodoaniline was extracted from the acid insoluble residue with hot alcohol leaving a black insoluble mass, some 80 g., which was not identified. Dark needles of the 2,4-diiodoaniline crystallized from the alcohol as it cooled. These, when recrystallized from ligroin, gave a light tan colored product (m. p. 95°). In all, 95 g. of 2,4-diiodoaniline

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(1) R. Q. Brewster, "Organic Syntheses," John Wiley and Sons, Inc., New York City, 1931, Vol. 11, p. 62.

and about twice this amount of unchanged *p*-iodoaniline were obtained from approximately 400 g. of crude material.

UNIVERSITY OF KANSAS
LAWRENCE, KANSAS

RECEIVED JULY 1, 1935

The Reaction of Ethylene Oxide with Acetylenic Grignard Reagents

BY JAMES P. DANEHY, RICHARD R. VOGT AND J. A. NIEUWLAND

Recently the preparation of certain acetylenic alcohols by the action of ethylene oxide on acetylenic Grignard reagents has been reported.[1,2] We can now report in a quantitative manner the products obtained from this reaction.

Two moles (192 g.) of heptyne-1 was transformed into the Grignard reagent, treated with a slight excess of ethylene oxide (90 g.) and subsequently hydrolyzed; on fractional distillation under diminished pressure 65 g. of heptyne-1, 95 g. of ethylene bromohydrin and 60 g. of 3-nonyn-1-ol were obtained. The Grignard reagents of hexyne-1 and phenylacetylene when treated with ethylene oxide give analogous products in substantially the same percentage yields.

(1) Faucounau, *Compt. rend.*, **199**, 605 (1934).

(2) Danehy, Vogt and Nieuwland, THIS JOURNAL, **56**, 2790 (1934).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NOTRE DAME
NOTRE DAME, INDIANA

RECEIVED JULY 1, 1935

The Fries–Rosenmund Rearrangement of N-Acetylcarbazole[1]

BY ERICH MEITZNER

3-Acetylcarbazole, in yields not stated, has been prepared by Plant and Williams[2] by heating N-acetylcarbazole with aluminum chloride. Since their method proved to be unsatisfactory, the rearrangement was carried out with nitrobenzene as solvent. With this modification in the conditions, 3-acetylcarbazole may be obtained in yields of 50 to 60%, together with tarry products, carbazole, and the hitherto unknown 1-acetylcarbazole.[3] The complexity of the process is a serious drawback to its use for large scale preparations of 3-acetylcarbazole.

The structure of 1-acetylcarbazole was demonstrated by converting the compound by potassium hydroxide fusion into the known carbazole-1-carboxylic acid.[4] The detection of 1-acetylcarbazole among the reaction products completes the parallelism of this rearrangement to that of acyl phenols to *p*- and *o*-hydroxy ketones.

Experimental

Rearrangement of N-Acetylcarbazole.—Twenty-one grams of N-acetylcarbazole was dissolved in 125 cc. of nitrobenzene, 15 g. of aluminum chloride added (water cooling) and the mixture was allowed to stand for fifteen to twenty hours. The observance of this delay is important, because immediate heating results in increased formation of tar. The mere standing at room temperature does not effect the conversion, however, as was shown by the quantitative recovery of carbazole when the mixture was worked up according to the process described below. The mixture was then heated in an oil-bath to 110–125° for thirty minutes, decomposed with ice, and the nitrobenzene distilled off with steam. The solidified residue was filtered, dried and dissolved in boiling ethyl alcohol. After filtration from an insoluble residue, the solution was evaporated to small bulk. About 12–13 g. of crude 3-acetylcarbazole (m. p. 155–160°) separated at this point. This product was purified by recrystallization from toluene, or sublimation at 170–180° and 10^{-2} mm. It forms snow white prisms, m. p. 167–168°. (3-N-Diacetylcarbazole melts at 156°; Plant and Williams, 153°.) The mother liquors were evaporated and the residue, after removal of some nitrobenzene, distilled at 170° and 10^{-2} mm. The distillate consisted of 3- and 1-acetylcarbazoles, carbazole and a yellow compound which proved to be *m*-dinitrobenzene, undoubtedly present as an impurity in the nitrobenzene used. This mixture was distilled at 130° and 10^{-2} mm.

The residue consisted chiefly of 3-acetylcarbazole, while the distillate was largely a mixture of 1-acetylcarbazole and carbazole, with a small amount of dinitrobenzene deposited farthest from the source of heat. The mixture of 1-acetylcarbazole and carbazole was sublimed at 110°, 10^{-2} mm., and the fine white sublimate of carbazole separated mechanically from the yellowish prisms of 1-acetylcarbazole. The sublimation and separation was repeated and the products recrystallized from ethyl alcohol.

1-Acetylcarbazole crystallizes in fine white needles of m. p. 136°.

Anal. Calcd. for $C_{14}H_{11}ON$: C, 80.35; H, 5.30. Found: C, 80.52; H, 5.41.

1-Acetylcarbazole oxime, white silky needles, m. p. 179–180°.

Anal. Calcd. for $C_{14}H_{12}ON_2$: C, 74.96; H, 5.40. Found: C, 74.59; H, 5.33.

The action of equivalent amounts of acetyl chloride and carbazole under the above conditions yields the same

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(1) The work reported in this paper is part of a unification of effort by a number of agencies having responsibility for the solution of the problem of drug addiction. The organizations taking part are: The Rockefeller Foundation, the National Research Council, the U. S. Public Health Service, the U. S. Bureau of Narcotics, the University of Virginia and the University of Michigan.

(2) Plant and Williams, *J. Chem. Soc.*, 1142 (1934).

(3) In a communication [*ibid.*, 743 (1935)] appearing after the completion of this work, Plant, Rogers and Williams describe the use of nitrobenzene for the rearrangement, but do not mention the formation of 1-acetylcarbazole.

(4) Ciamician and Silber, *Gazz. chim. ital.*, **12**, 272 (1882).

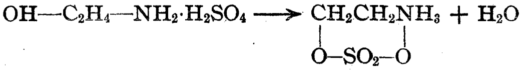
products, with a somewhat higher formation of tarry products.

UNIVERSITY, VIRGINIA RECEIVED AUGUST 9, 1935

The Preparation of Ethylene Imine from Monoethanolamine

BY HENRY WENKER

In view of the readiness with which compounds containing a β-aminoethyl group can be obtained from ethylene imine, a method may be of interest by which 80 g. of this base can be prepared conveniently in the laboratory in one day from inexpensive commercial material. The process consists, firstly, in preparing β-aminoethyl sulfuric acid[1,2] by thermic dehydration of monoethanolamine acid sulfate according to the equation



$$OH{-}C_2H_4{-}NH_2\cdot H_2SO_4 \longrightarrow \begin{array}{l} CH_2CH_2NH_3 + H_2O \\ \;|\qquad\;\;| \\ O{-}SO_2{-}O \end{array}$$

secondly, in distilling this compound with alkali.

An equimolar mixture of monoethanolamine and sulfuric acid is heated rapidly over a free flame until, at a temperature of about 250°, charring begins, necessitating the end of the operation. Only 75% of the mole of water indicated by the formula can be expelled since, irrespective of the rate of heating, the product begins to turn brown rapidly when this degree of dehydration has been reached. As much as 10 moles—610 g., of monoethanolamine and 1020 g. of 96% sulfuric acid—may be used for one operation. On cooling, the thin, clear brown liquid solidifies to a hard, white crystalline cake. It is ground in a mortar with one-half its weight of 60% ethanol, filtered by suction and washed with ethanol; yield, 100 g. per mole of starting material or 71%. It is convenient to dilute both components with their own weight of water previous to mixing, and then to boil off the excess of water.

282 grams of β-aminoethyl sulfuric acid is distilled with 880 g. of 40% caustic soda solution from a 3000-cc. flask. Shortly before the boiling point is reached, a reaction occurs which keeps the mixture boiling for several minutes; during this time, heating must be discontinued. When the reaction ceases, heating is resumed and a total of 240 cc. is distilled over. One distillation requires about forty-five minutes. On addition of potassium hydroxide to the distillate, 65 cc. of base separates; this is dried repeatedly with potassium hydroxide, then with sodium, and finally fractionated. The use of an efficient distilling column is recommended since the crude base contains higher boiling by-products; yield, 23 g. of ethylene imine boiling at 55–56.5° or 26.5%.

ELIZABETH, N. J. RECEIVED JULY 29, 1935

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(1) Gabriel, *Ber.*, **21**, 1056, 2667 (1888).

(2) Fraenkel and Cornelius, *ibid.*, **51**, 1660 (1918).

An All-Glass Valve

BY JOHN WILLARD

An all-glass valve for use in systems where stopcocks are objectionable is illustrated in Fig. 1. It is easily constructed and may be opened and closed by merely heating a quartz tube which surrounds a fine Pyrex capillary. It is particularly useful for admitting a corrosive but thermally stable gas from a reservoir to a reaction.

The tube D is of quartz, about 6 mm. in diameter. Part C is a quartz-to-Pyrex graded seal and the portion of the device above C is of Pyrex. E is a fine Pyrex capillary. The outlet A is connected to a gas reservoir and the outlet B to an evacuated system to be filled from the reservoir.

A small flame from a hand torch applied to the quartz near the tip of the capillary, when there is only a few mm. greater pressure on the A side than on the B side, will cause the capillary to blow out without affecting the quartz. When pressure has been equalized the capillary may be sealed again by similar application of heat. Repeated openings and closings of the valve may be carried out without difficulty if the capillary is long and fairly small even though it may stick to the side of the quartz tube. During an investigation in this Laboratory this device has been in constant use for several months. As many as twenty fillings have been made with it before it was necessary to seal in a new Pyrex capillary.

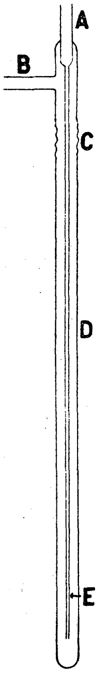

Fig. 1.

Alyea[1] has developed a valve which is similar in purpose to the one here described but which is made completely of Pyrex glass. It is opened by the use of a magnetic pellet and closed by sealing off the outer tube and the capillary together. Other types of greaseless valves are described by

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(1) Alyea, THIS JOURNAL, **52**, 1937 (1930).

Bodenstein,[2] Ramsperger,[3] and Sutton and Mayer.[4] For many purposes the valve described here is more desirable than any of these because it combines ease of construction with ease of operation.

[2] Bodenstein, *Z. physik. Chem.*, **B7**, 387 (1930).

[3] Ramsperger, *Rev. Sci. Inst.*, **2**, 738 (1931).

[4] Sutton and Mayer, *J. Chem. Phys.*, **3**, 20 (1935).

CONTRIBUTION FROM THE
LABORATORY OF PHYSICAL CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

RECEIVED AUGUST 22, 1935

Periodic Classification of the Rare Earths

BY HERMAN YAGODA

Brauner's[1] distribution of the rare earths in the periodic system, Fig. 1, has the disadvantage of placing several of the members into groups where the other elements are chiefly of an amphoteric or acidic nature. Pearce[2] has criticized the classification on the ground that the periodicities observed by Brauner are not connected with the rest of the system. The tendency of these elements to form stable trivalent compounds seems to mask the underlying fact that the properties, of their other valence states, are a periodic function of the atomic number.

Groups	I	II	III	IV	V	VI	VII
8th series	Cs 55	Ba 56	**La 57**	**Ce 58**	**Pr 59**	**Nd 60**	**Il 61**
9th series	**Sm 62**	**Eu 63**	**Gd 64**	**Tb 65**	**Dy 66**	**Ho 67**	**Er 68**
10th series	**Tm 69**	**Yb 70**	**Lu 71**	Hf 72	Ta 73	W 74	Re 75

Fig. 1.

Thus, cerium and terbium are located in the fourth group in agreement with the tetravalence exhibited in their higher oxides CeO_2 and Tb_4O_7. Praseodymium forms two higher oxides, Pr_6O_{11} and PrO_2 in which, according to Prandtl,[3] the metal has a valence of five, in harmony with the position of the element in the fifth group. Again, of all the rare earths only europium[4] and ytterbium[5] form difficultly soluble bivalent sulfates and both elements are allocated to the second group along with the alkaline earths. Evidence for the division of the metals into three series is seen in the variation of the molecular volume of the oxides, Fig. 2, the curve[5a] showing distinct maxima at both samarium and thulium, the initial members of the ninth and tenth series.

If the classification has real significance it should be possible to predict the properties of the rare earth ions in those valency states corresponding with their position in the groups. Thus, Sm^+ and Tm^+ should form difficultly soluble chloroplatinates, Ce^{++++} and Tb^{++++} phosphates, that are insoluble in mineral acids,[5b] in the same way that Eu^{++} and Yb^{++} are now known to form insoluble sulfates.

Molecular volume of the rare earth oxides (R_2O_3).

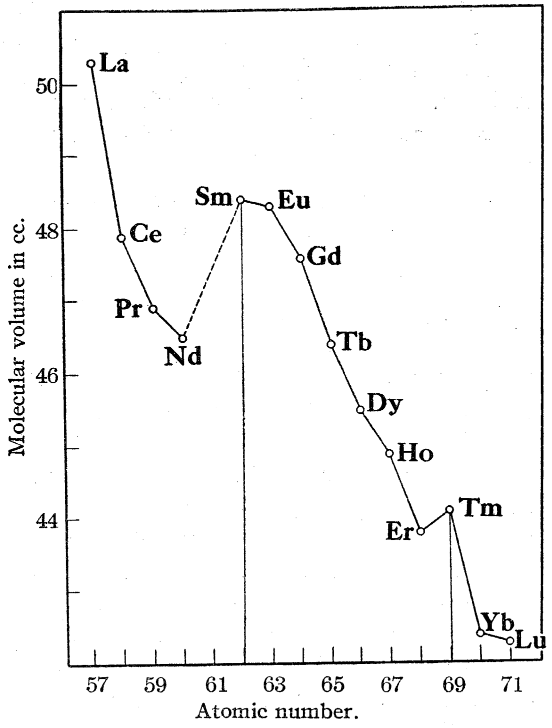

Fig. 2.

Recent investigations[6] reveal that samarium possesses radioactive properties of the same order of magnitude as potassium and rubidium the only elements which exhibit natural radioactivity outside of the members of the three radioactive series.[7] If Brauner's classification of the rare earths is correct, the radioactivity of samarium would seem to indicate that the tendency for nuclear instability in the case of atoms of low atomic weight is centered in the first periodic group. Von Hevesy examined all the members of the rare earths with

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[1] B. Brauner and E. Švagr, *Collection Czechoslov. Chem. Comm.*, **4**, 49, 244 (1932).

[2] D. W. Pearce, *Chem. Rev.*, **16**, 135 (1935).

[3] W. Prandtl and K. Huttner, *Z. anorg. Chem.*, **149**, 235 (1925).

[4] L. F. Yntema, THIS JOURNAL, **52**, 2782 (1930); P. W. Selwood, *ibid.*, **57**, 1145 (1935).

[5] R. W. Ball and L. F. Yntema, *ibid.*, **52**, 4264 (1930); J. K. Marsh, *J. Chem. Soc.*, 1972 (1934); W. Prandtl, *Z. anorg. Chem.*, **209**, 13 (1932).

[5a] The molecular volumes were derived from density measurements recorded by von Hevesy in his "Seltenen Erden von Standpunkte des Atombaues," Berlin, 1927, p. 53. The molecular weights were computed from the International Atomic Weights of 1935.

[5b] Cerium can be separated electrolytically from nitric acid solutions as ceric phosphate [J. W. Neckers, THIS JOURNAL, **50**, 955 (1928)].

[6] G. von Hevesy and M. Pahl, *Nature*, **130**, 846 (1932); M. Curie and F. Joliot, *Compt. rend.*, **198**, 360 (1934).

[7] "Radiation from Radioactive Substances," Rutherford, Chadwick and Ellis, Cambridge, 1930, p. 541.

the exception of illinium and thulium and concluded that samarium was the only one of the group whose radioactivity persisted after purification.[8] As thulium is classified in the first group, it also may possess radioactive properties of a magnitude comparable with that of samarium. Hence, a study of the radioactivity of thulium preparations is well worth investigating.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY,
NEW YORK CITY

RECEIVED JULY 16, 1935

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[8] G. von Hevesy and M. Pahl, *Nature*, **131**, 434 (1933); *ibid.*, *Z. physik. Chem.*, **A169**, 147 (1934).

COMMUNICATIONS TO THE EDITOR

ATTEMPTED PREPARATION OF VANILLOYLFORMIC ACID

Sir:

In an attempt to repeat the oxidation of apocyanin to vanilloylformic acid with nitrobenzene in alkaline solution as described by H. O. Mottern [THIS JOURNAL, 56, 2107 (1934)] no action whatever was observable under the conditions described by the author. Nitrobenzene was recovered quantitatively from the reaction mixture and neither aniline nor azobenzene was detectable by qualitative means.

Difficulty was also experienced in repeating the author's description of the preparation of apocyanin by means of the Fries reaction. The aluminum chloride double compound with guaiacol acetate is quite solid at the temperatures described (0–5°). Before a third of the required amount of aluminum chloride has been added, the mass is so hard as to be impenetrable to a stirring rod, making it impossible to incorporate the balance. The apocyanin used was prepared by the method for low temperature Fries isomerizations described by Baltzly and Bass [*ibid.*, **55**, 4293 (1933)] which differs from the authors in the use of nitrobenzene as a solvent.

FARMINGDALE, L. I. W. E. BARCH

RECEIVED MARCH 12, 1935

NOTE BY THE EDITOR

After the receipt of this Communication a repetition of the oxidation of apocyanin to vanilloylformic acid with nitrobenzene in alkaline solution as described by H. O. Mottern was attempted by a member of the Editorial Board and independently by the Director of Research of a firm manufacturing vanillin on a large scale. Both were unsuccessful; their concordant conclusion is expressed by the latter's statement: "The synthesis of vanillin cannot be carried out following the disclosures of the paper published in THIS JOURNAL, 1934, page 2107."

OCTOBER 10, 1935 ARTHUR B. LAMB, *Editor*

THERMAL DECOMPOSITION OF $CrO_4 \cdot 3NH_3$

Sir:

Some unusual observations recently made in this Laboratory, and which we hope to study in greater detail, should prove of considerable general interest. While attempting the preparation of the tetroxide of chromium, CrO_4, by deammonating $CrO_4 \cdot 3NH_3$ (I) [made according to Riesenfeld, *Ber.*, **38**, 4070 (1905)], the following was noted. (1) Compound (I) loses practically no ammonia upon standing for four months over concentrated sulfuric acid *in vacuo* and at room temperature. (2) If the pressure in a tube containing some (I) is reduced to less than 1 mm. and the tube, still attached to the vacuum line, is immersed in a bath whose temperature may be controlled, a vigorous reaction ensues at 120 ± 10°. Particles of (I) become incandescent and dart about in spectacular fashion. The action is reminiscent of the thermal decomposition of ammonium dichromate and also of certain models that have been constructed to portray molecular motion in gases. (3) The solid residue of the above mentioned decomposition of (I) is composed of microscopic, elongated square prisms of black $CrO_3 \cdot NH_3$ (II). Analysis of (II) for ammonia was made by distilling into standard acid and for chromium by forming lead chromate. The results for samples of (II) obtained from two different experiments are:

Cr found		NH_3 found	
44.50%	Run 1	14.45%	Run 1
44.39		14.47	
44.47	Run 2	14.49	Run 2
Mean 44.46		Mean 14.47	

Cr calcd., 44.44 NH_3 calcd., 14.55

This compound has not been reported previously and unlike the parent substance gives no test for the peroxide group. (4) The presence of small amounts of impurities has a marked influence upon the rate of decomposition of (I), in some cases increasing it to the point of explosive violence (danger!). In some of our experiments (I) was purposely left impure and may have contained ammonium chromate, dichromate or perchromate. (5) The reaction does not proceed under the conditions mentioned in (2) if carried out in the dark or near-dark. Radiation, in or near the visible, is apparently essential to start the reaction. (6) If the starting pressure in the tube be approximately 1 cm., (I) decomposes in the same scintillating manner as under (2) but the product gives the peroxide test and its composition is variable (37–38% Cr, 21–22% NH_3), lying between that of (I) and (II). It probably consists of a mixture of the latter two. (7) The density of (II) is 2.073 g./cc. at 23.5°. It is practically insoluble in carbon tetrachloride, stable in air under ordinary conditions, and hydrolyzed in water. It detonates in the neighborhood of 200° in the atmosphere, leaving Cr_2O_3.

It is interesting to note that (II) may be formulated as a partial dehydration product of ammonium dichromate: $(NH_4)_2Cr_2O_7 = 2CrO_3 \cdot NH_3 + H_2O$, and that neither ammonium dichromate nor chromate shows any sign of reaction under the conditions mentioned in (2).

DEPARTMENT OF CHEMISTRY
WASHINGTON SQUARE COLLEGE
NEW YORK UNIVERSITY
NEW YORK, N. Y.
WILLIAM F. EHRET
ARTHUR GREENSTONE

RECEIVED JULY 30, 1935

THE PHOTOLYTIC AND THERMAL DECOMPOSITION PRODUCTS OF AZOMETHANE. THERMAL REACTION RATES IN QUARTZ, 260 TO 290°

Sir:

Pressure readings at room temperature, −78.5 and −183° at various stages of decomposition of initially pure azomethane show that (1) upon complete decomposition the pressure is approximately double the initial pressure of azomethane; (2) the ratio of the pressure increase at room temperature to the pressure of "permanent" gases formed by the reaction however, diminishes from a value of at least two, in the initial stages, to unity at complete decomposition. A plausible assumption to explain these facts is that the products include, with nitrogen, other "permanent" gases consisting largely of methane. This tentative conclusion is being tested by chemical analysis.

The above observations hold for both photochemical decomposition at 30° and for thermal decomposition at 300°. The course of the thermal reaction at 300° was unaffected by mercury vapor at a pressure of 100 mm. approximately, when this was intentionally introduced.

The thermal reaction rates in quartz fit the unimolecular formula, like Ramsperger's, but our rate constants are roughly half as great as his. The decomposition in Pyrex is being investigated.

The ten-degree temperature coefficient from the dark reaction rates at 260, 270, 280 and 290° is 2.9, in agreement with that of Ramsperger, and apparently affected but little by the presence of mercury vapor.

MALLINCKRODT CHEMICAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS
LAWRENCE J. HEIDT
GEORGE S. FORBES

RECEIVED SEPTEMBER 25, 1935

SEPARATION OF GUANIDINE AND METHYLGUANIDINE BY MEANS OF BETA-NAPHTHALENESULFONYL CHLORIDE

Sir:

In a study of the relation of simple and substituted guanidines to health and disease, occasion came to separate guanidine from methylguanidine. Finding the benzenesulfonyl derivatives, prepared by Ackermann [*Z. physiol. Chem.*, **47**, 366 (1906); **48**, 382 (1906)] unsuitable for the differential precipitation of these guanidines, recourse was had to beta-naphthalenesulfonyl chloride, which was found to give hitherto undescribed derivatives of guanidine and methylguanidine, suitable for the separation of these substances from each other and from other closely related compounds.

Experimental. Di-(β-naphthalenesulfonyl)-guanidine.—To one mol. of guanidine carbonate (1.5 g.) dissolved in 10 cc. of water was added 1.0

cc. of 5 *N* sodium hydroxide. Beta-naphthalenesulfonyl chloride, somewhat in excess of 2 mols. (4.5 g.), was dissolved in 10 cc. of ether, the two solutions were mixed and shaken thoroughly in a separatory funnel. After standing for five minutes, the heavy white precipitate was filtered off and washed with alcohol and ether. The yield was 4.4 g. or 93%. Upon crystallization from hot water, slightly acidified with hydrochloric acid, long, saber-shaped crystals separate rapidly. Similarly shaped but slightly shorter crystals are deposited from hot 95% alcohol. Both sets of crystals melted at 204–206° (uncorrected) apparently without decomposition. After cooling they can be melted again over a broader range, 200–206°. Hydrolysis by 20% hydrochloric acid yields beta-naphthalenesulfonic acid and free guanidine. *Analysis.* Calcd. for $C_{21}H_{17}N_3O_4S_2$: N, 9.56; S, 14.59. Found: N, 9.34; S, 14.47. The desiccator-dried sample contained two moles of water of crystallization, easily removed by heating at 105° in an oven. At 24° 100 cc. of water dissolves 9.0 mg.

Beta-naphthalenesulfonylmethylguanidine.—The procedure used for the guanidine compound yielded no insoluble complex with methylguanidine. A precipitate was obtained with higher alkalinity and a longer period of shaking. One mole of methylguanidine hydrochloride (110 mg.) was dissolved in water and added to a solution of 1 mol. of beta-naphthalenesulfonyl chloride (230 mg.) dissolved in 10 cc. of ether. The mixed solutions were shaken in a separatory funnel after the addition of 2.5 cc. of 5 *N* sodium hydroxide. Shaking was repeated at intervals of five minutes, for half an hour, and the mixture was then allowed to stand overnight. The white crystalline precipitate was removed, washed with alcohol and ether, and dried in a desiccator. The yield was 171 mg. or 65%. Upon crystallization from hot water, slightly acidified with hydrochloric acid, long, slightly curved, branching needles separated rapidly. Similarly shaped crystals are deposited from alcohol. The compound has a greater solubility in alcohol than the guanidine derivative; melting point, 101–102° (uncorrected). *Analysis.* Calcd. for $C_{12}H_{13}N_3O_2S$: N, 15.97; S, 12.18. Found: N, 15.19; S, 12.02. At 24° 100 cc. of water will dissolve 21 mg. Hydrolysis by 20% hydrochloric acid yields beta-naphthalenesulfonic acid and free methylguanidine.

Guanidine yields a di-acylated product whereas the methylguanidine derivative is mono-acylated.

Attempts to prepare insoluble beta-naphthalenesulfonyl derivatives of creatine, creatinine, glycocyamine and glycocyamidine were unsuccessful.

Fifty mg. each of the hydrochlorides of guanidine and methylguanidine were dissolved in 5 cc. of water. With use of beta-naphthalenesulfonyl chloride and a little alkali, the first precipitate was the guanidine complex, rather pure. With increase in alkali, a mixture was obtained readily fractionated and with more alkali and longer standing, the approximately pure methylguanidine complex was obtained. From the original mixture 90% of the guanidine was recovered and with no further attention to maximal yields 45% of the methylguanidine.

CHEMO-MEDICAL RESEARCH INSTITUTE
GEORGETOWN UNIVERSITY W. C. HESS
WASHINGTON, D. C. M. X. SULLIVAN

RECEIVED SEPTEMBER 30, 1935

NEW BOOKS

Les Carotenoïdes des Animaux. (Animal Carotenoids). By EDGAR LEDERER. Hermann et Cie., Éditeurs, 6 Rue de la Sorbonne, Paris, France. 62 pp. 17 × 25.5 cm. Fr. 15.

This supplements the author's "Les Carotenoides des Plantes," which appeared last year, and resembles it in format, style, typography, etc. In the former volume, the classification of the subject matter was primarily chemical. In the present one, it is zoölogical. Its four chapters discuss (I) Carotenoids of the vertebrates, (II) Carotenoids of the invertebrates, (III) Specific animal carotenoids (asteric and salmenic acids, actinioerythryin, astacin, glycymerin and pectenoxanthin), and (IV) biochemical and biological questions.

The author pays a graceful and well-merited tribute to Palmer's classical book on "Carotinoids and Related Pigments" (Am. Chem. Soc. Monograph Series, Chemical Catalog Co., Inc., New York City, 1922), which he says that he is endeavoring to bring more nearly up to date for the animal carotenoids.

Thanks to the labors of Willstätter, Karrer, Kuhn, Von Euler, Zechmeister and their associates, the chemistry of the phytocarotenoids has been remarkably elucidated within the last year or two. Our knowledge, however, of those carotenoids which are peculiar to the animal kingdom is still meager and often but superficial. In addition to the researches of Karrer, Kuhn and von Euler, Lederer, Lönnberg and Willstaedt have made valuable contributions in this group.

The carotenoids which are peculiar to animals are found chiefly in the invertebrates. Those occurring in the vertebrates are generally only the phytocarotenoids ingested with the food. An admirable résumé is presented of the occurrence of the carotenoids in animals, how various groups of vertebrates differ in the particular carotenoids they store, where they store them and the role they play in the living organism.

The few polyene pigments peculiar to animals are described in detail, together with information as to where they are found in the invertebrates and their possible function there.

The book should be of especial value to those interested in the biological and biochemical problems of the carotenoid field.

MARSTON TAYLOR BOGERT

The Structure and Composition of Foods. Volume II. Vegetables, Legumes, Fruits. By ANDREW L. WINTON, Ph.D., and KATE BARBER WINTON, Ph.D. John Wiley and Sons, Inc., 440 Fourth Ave., New York, 1935. xiv + 904 pp. 303 figs. 15.5 × 24 cm. Price, $15.00.

This is the second volume in the series that is being written and illustrated by these authors, the first volume having appeared in 1932. The second volume is divided into two major parts, I, Vegetables, and II, Fruits. Part I is further subdivided into the sections: mushrooms; root vegetables; tuber, corm and rhizome vegetables; leaf and stem vegetables; flower vegetables; and fruit and seed vegetables. In each of these sections the material is arranged by botanical families, and under these, in turn, by genera and species. Part II, Fruits, is also arranged by families, some thirty-five being listed in the table of contents.

An introduction of twenty-four pages has been included, which contains a discussion of the chemical constitution of the principal constituents of vegetables and fruits including proteins, acids, carbohydrates, pectins, pigments and vitamins. In view of the rapid progress that is now being made in the chemistry of these substances, this portion of the book may be out of date long before the remainder has ceased to be a wholly satisfactory source of data.

The Wintons have followed much the same general plan of organization in this volume as in the earlier book. Common and botanical names head each subdivision followed by common names in several foreign languages. Usually a brief historical treatment of the origins and uses of the food in question is followed by a discussion of its macroscopic and microscopic structure. Over 300 figures have been included in this connection. These are the authors' original work, and most of them are here presented for the first time.

Then follows in each case a discussion of the chemical composition of the food. This includes not only the conventional proximate analysis, but in addition, specific constituents are often listed, described and the percentages present (when known) are recorded. In the instance of certain of the more common and important foods, the changes in composition during growth, storage and processing are also included.

The book is a veritable storehouse of useful facts, gathered by a thorough combing of the literature. Many of the latest papers, published during the present calendar year, have been consulted and mentioned in the text, which is thus up to date. The material is rendered the more useful and available by an extensive index which includes common and botanical names of the foods, foreign names and constituents.

C. H. BAILEY

Autenrieth–Rojahn, Qualitative chemische Analyse. (Autenrieth–Rojahn, Qualitative Chemical Analysis.) By DR. C. A. ROJAHN, Martin Luther University, Halle-Wittenberg. Third, revised edition. Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany, 1935. vii + 233 pp. 12 figs. 16 × 24 cm. Price, RM. 10.

This book has three parts: (I) A Systematic Scheme of Analysis; (II) Reactions of Cations and Anions, and (III) General Part (Theoretical Chemistry).

Part I (67 pages) contains a brief discussion of various types of tests useful in Qualitative Analysis. This general discussion is followed by an outline giving a scheme for the systematic separation of the cations. Mercury falls in the copper group and magnesium with the alkali metals. Superscripts refer to subsequent notes on the reactions and procedures.

Part II (90 pages) gives a selected group of reactions for each ion. The style of presentation is similar to the corresponding part of the well-known text by Treadwell and Hall.

Part III (90 pages) gives in very brief and concise form a review of the entire field of inorganic chemistry. A few of the topics included in this review are: atomic theory, Prout's theory, atomic structure, gas laws, heat of fusion, osmosis, electrolytic dissociation, hydrolysis, thermochemistry, equilibrium constants, catalysis, double salts, complex ions, Werner's theory, stereochemistry of complex compounds. Colloid chemistry, oxidation and reduction, and oxidizing and reducing agents, are put under separate headings following the general review.

C. R. CONARD

Gmelins Handbuch der anorganischen Chemie. (Gmelin's Handbook of Inorganic Chemistry.) Edited by R. J. MEYER. Eighth edition. System-Number 53, **Molybdenum.** Issued by the Deutsche Chemische Gesellschaft. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 9, Germany, 1935. 393 pp. 17 × 25 cm. Price, RM. 64.

This volume recounts the physical properties and the chemical behavior of elementary molybdenum and of the compounds of molybdenum with other elements of smaller "system-numbers." This includes all the non-metals, chromium and all the metals of the 0 to 5th group of the Periodic Table other than copper, silver and gold.

Molybdenum has in recent years become an important industrial metal and the up-to-date information which this volume affords particularly as regards its physical properties and the complex compounds of molybdic acid is especially welcome.

The collaborators with the Editor, R. J. Meyer, in the preparation of this volume, which appears to maintain the high standards of its predecessors, were Ellen Schön, Emma Haller, Max du Maire, Gertrud Pietsch-Wilke, Karl Becker, Ortwin von Deines. The literature has been covered through 1934.

ARTHUR B. LAMB

Toxikologische Mikroanalyse. Qualitative Mikrochemie der Gifte u. a. gerichtlich-chemisch wichtiger Stoffe. (Qualitative Microchemistry of Poisons and Other Compounds of Medico-legal Importance.) By Dr. L. ROSENTHALER, Professor at the University of Berne. Verlag von Gebrüder Borntraeger, Schöneberger Ufer 12a, Berlin W 35, Germany, 1935. viii + 368 pp. 173 figs. 16.5 × 25.5 cm. Price, RM. 25.50; bound, RM. 28.

The term poison is usually applied to substances which are injurious in comparatively small doses. The toxicologist must, therefore, often work with very small amounts of material and his results are qualitative rather than quantitative. The present volume treats of poisons only from the qualitative standpoint.

Microsublimation, microdistillation and microextraction, important procedures in detecting small amounts of poisons, are discussed in detail.

Seventy-six pages are devoted to inorganic poisons: chlorine in water, chlorates, bromine, fluorides, nitrites, phosphorus, hydrogen sulfide, selenium compounds, carbon monoxide, arsenic and antimony compounds, ammonia in the air, lead (Fairhall's methods) in blood, urine and various organs; copper, manganese, mercury, thallium, bismuth, etc.

One hundred and twenty-seven pages are devoted to non-alkaloidal organic poisons: methanol and ethanol (including Gettler's methods), aldehydes, phenols, organic acids and their esters, cyanogen compounds; halogen derivatives ("Avertin," chloral hydrate, etc.); thyroxin; barbiturates (fourteen pages), anilin derivatives, saccharin, organic arsenic derivatives (arsphenamine, etc.).

One hundred and twenty-one pages are devoted to alkaloids, glucosides and similar compounds.

Methods for the detection of blood and semen are also discussed.

There are 170 excellent figures of crystals.

REID HUNT

Neuere massanalytische Methoden. (New Methods of Volumetric Analysis.) By Dr. E. BRENNECKE, Prof. Dr. K. FAJANS, PROF. DR. N. H. FURMAN and PRIV.-Doz. Dr. R. LANG. Foreword by Prof. Dr. W. Böttger. Ferdinand Enke Verlag, Hasenbergsteige 3, Stuttgart-W, Germany, 1935. xi + 211 pp. 15 figs. 16.5 × 25 cm. Price, RM. 18; bound, RM. 19.80.

This publication is the 33rd volume in the series of monographs on Analytical Chemistry founded by B. M. Margosches. The present volume was edited by Wilhelm Böttger and contains six sections. These cover some of the more recent activities in analytical chemistry, each chapter being the work of a specialist in the field under discussion.

Chapter I (19 pages) on the Elimination of Titration Errors in Acid and Alkali Titrations, Chapter IV (21 pages) on Chromous Solutions as Reducing Agents in Volumetric Analysis, and Chapter V (44 pages) on Oxidation-Reduction Indicators were prepared by Erna Brennecke.

Chapter II (23 pages) on Ceric Sulphate as an Oxidation Agent in Volumetric Analysis is the work of N. Howell Furman.

Chapter III (52 pages) on Iodate and Bromate Methods and Bromometric Titrations According to Manchot are presented by Rudolf Lang, and Chapter VI (47 pages) on Adsorption Indicators in Precipitation Titrations was written by K. Fajans.

The monograph has been especially prepared for the purpose of inducing a wider appreciation of these methods, and of their applications in analytical chemistry. This aim has been well met, and the monograph should appeal to all analysts who desire concise summaries of the information that is available to date on the subjects that are covered, or who wish to consider possible applications of the methods in the fields of analysis in which they are working.

G. E. F. LUNDELL

Einführung in die Lehre von den Kolloiden. (**Introduction to the Study of Colloids.**) Edited by Prof. Dr. H. Bechhold, Frankfurt a. M. Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany, 1934. vii + 160 pp. 86 figs. 16 × 23.5 cm. Price, RM. 9; bound, RM. 10.

This introductory text of about 150 pages constitutes a novelty in colloid literature, because separate chapters are written by seven different authorities from three countries. It records in revised form a series of lectures given under Bechhold's auspices at the Institute of Colloid Research, Frankfurt a. M., before a general audience.

Instructors in this subject will read the book with curiosity to see what is considered worthy of mention in this brief treatment, and also to observe the attitude taken by the writers toward important questions.

The chapters include an Introduction by Bechhold, preparations by Schwarz, kinetic theory by Hock, surface phenomena by Heymann, properties other than electrical or optical by Hock, electrical properties by Heymann, separation and purification by Erbe, optical properties by Hauser and x-ray results by Brill. An author and a subject index are provided and there are a few references to journal literature. Most of the chapters end with a list of books dealing with the subject. These are mostly (and naturally), but not all, in the same language as the introductory text itself. This book is a valuable and thoroughly modern addition to any colloid library.

James W. McBain

Inorganic Colloid Chemistry. Volume II. By Harry B. Weiser, Professor of Physical Chemistry at the Rice Institute. John Wiley and Sons, Inc., 440 Fourth Avenue, New York, 1935. xi + 429 pp. 70 figs. 15.15 × 23.5 cm. Price, $4.75.

The first volume of this Treatise dealing with The Colloidal Elements was reviewed last year (Vol. **56**, p. 1254). This second volume supersedes the author's well-known "The Hydrous Oxides" of ten years ago, which has been rewritten and completely revised for the purpose. Professor Weiser is not only producing a readable and authoritative treatise on inorganic colloid chemistry by making a comprehensive survey of the materials in this field, but he is furthering the advance of the subject itself by his clear and critical review of relevant theory and its applications.

The author appears justified in his hope that it will prove useful as a reference work alike to those interested in pure science and those concerned with its industrial applications, and as a text for the study of colloidal phenomena in their relation to this class of inorganic compounds.

James W. McBain

A Course in Inorganic Preparations. By William Edwards Henderson, Professor of Inorganic Chemistry, and W. Conard Fernelius, Assistant Professor of Inorganic Chemistry, The Ohio State University. McGraw-Hill Book Company, Inc., 330 West 42d Street, New York City, 1935. xviii + 188 pp. 24 figs. 14 × 21 cm. Price, $2.50.

This book is intended as a laboratory text for advanced and graduate students of chemistry. In it is described the preparation of over a hundred inorganic compounds, which require the use of fairly simple apparatus and readily obtainable chemicals. In part I (55 pages) the preparations are classified according to the method to be employed; such as crystallization, distillation, electrolytic and others. Part II (97 pages) is concerned with the preparation of types of compounds; for example, binary, intermetallic, oxyacidic, thio salt, oxychloride, to mention only a few. Finally part III goes into the subject of colloids, and after describing preparations illustrating general methods, such things as gels, rhythmic bands and emulsions are taken up with three or more examples of each. In all cases the experimental procedures are described clearly and in some detail. At the end of each exercise are given helpful references to easily available Journals and books, especially those in English. No problems or questions are given, and the amount of theory included is small.

The exercises in part I illustrating general methods are, on the whole, well chosen. The classification of preparations in part II according to types of compounds has its advantages, and certainly the student must learn what the known types are, at some stage or other. But this classification is easily understood and would come more naturally in an elementary course. It seems to us that a classification according to types of reactions, or the rows or groups in the periodic system would be more instructive. The latter would lead to a more extensive knowledge of the chemistry of all the elements, as well as pave the way for the introduction of the elements of atomic and molecular structure. In the former it is natural to emphasize equilibria and thermodynamics. It is true that the body of chemical facts included in the book is considerable, and this is highly desirable; but the principles set forth are few and seem too elementary for advanced students.

It is probably true that freshmen and sophomores find a course in preparations helpful and even stimulating, but when they become juniors, seniors or graduates it is high time for them to realize that the unknown things in chemistry far outnumber the known. Accordingly, at this stage they could be given experimental problems which would lead to the discovery of something new, or would result in providing numerical data of interest and importance. The preparation of the substances needed for the problems would give the knowledge and technique which the experiments in the book under review aim to give. The book might well serve as a handy guide for the preparation of the required substances. But as such, and even for the purposes of a more routine course for advanced students, the number of preparations should be increased and greater variety introduced. As it now stands crystallization and precipitation methods are over-emphasized in the book.

We didn't look for errors in printing. Errors in fact and reasoning are few. The first sentence in the first new paragraph on page 5 is confusing and lacks content. In the last paragraph but one, on page 144, a roughly correct conclusion is drawn, but the thermodynamic reasoning used is wrong.

Our views on advanced courses being what they are, we can hardly recommend the book as a text for more advanced and graduate students. For a course in inorganic preparations of the conventional type, it should prove quite satisfactory. It would also serve as a very useful reference book in courses conducted along somewhat different lines.

DON M. YOST

Die organischen Katalysatoren und ihre Beziehungen zu den Fermenten. (Organic Catalysts and their Relation to Enzymes.) By DR. WOLFGANG LANGENBECK, Professor at the University of Greifswald. Verlag Julius Springer, Linkstrasse 23–24, Berlin W. 9, Germany. 112 pp. 6 figs. 16.5 × 24.5 cm. Price, RM. 7.50.

Enzymes, in the past, have been considered as "vital forces," as "active colloids," or as a new and unknown class of chemical compounds, and have only recently been shown to belong to the general class of proteins. Since the enzymes possess very marked properties not exhibited by other proteins they must possess special chemical structure. What this structure is remains to be determined. Professor Langenbeck points out that there are, in general, two methods of determining structure—degradation into known compounds, and synthesis of compounds of known structure having the same properties as other enzymes. The latter method is that chosen by Professor Langenbeck and the present volume summarizes the results of his work.

The author evidently considers enzymes as examples of homogeneous catalysis and his models thus differ from earlier ones, such as Bredig's, which were colloidal.

The guiding principle has been to start with a compound having slight catalytic activity and to form a series of substituted derivatives. These derivatives having higher activity than the original compound were then further substituted. In this way the activity has been increased in a remarkable way so that, in the case of carboxylase models, the most active substitution product was 4000 times as active as the original compound, methyl amine. The activity of this "synthetic enzyme" is of the same order of magnitude as that of crystalline pepsin. Heavy metal catalysis concerned with oxydase and catalase activity, the catalytic activity of hemin, dehydration of amino acids, and carboxylases have been studied in this way.

The group considered to be responsible for the activity is defined as that group which reacts directly with the substrate. This definition is useful and, in the case of the models, quite definite although in the case of enzymes there is, as yet, no conclusive evidence of such a direct reaction between enzyme and substrate. Substituted groups which affect the "active group" are called "activating" groups. This is also a useful term although, strictly speaking, all atoms in the molecule must affect the activity to some extent.

Theoretically, it should eventually be possible to predict in advance what the effect of any given group should be, just as it is now possible to make predictions as to the effect of substitution on the color of dyes. This will require the preparation of a very large series of derivatives, as Professor Langenbeck clearly realizes. Such a series of compounds should be of the greatest importance for the elucidation of the general theory of homogeneous catalysis as well as for the special case of enzymes.

A study of the reaction kinetics of these models has led to a very interesting equation for enzyme reactions which has the same form as the well-known Michaelis and Menten equation. It differs from the latter in that the reaction between enzyme and substrate (in hydrolytic reactions) is assumed to give rise at once to one of the products, while the enzyme remains combined with the other reaction product. This complex then breaks down, liberating the enzyme.

The book contains detailed description of laboratory technique, as well as the theoretical results, and is a decided addition to the literature of catalysis in general and enzymes in particular.

JOHN H. NORTHROP

BOOKS RECEIVED

September 15, 1935–October 15, 1935

HENRY B. BULL. "The Biochemistry of the Lipids." Burgess Publishing Company, 426 South Sixth St., Minneapolis, Minn. 127 pp. $3.25.

HORACE G. DEMING AND SAUL B. ARENSON. "Exercises in General Chemistry and Qualitative Analysis." Fourth edition, rewritten and revised. John Wiley and Sons, Inc., 440 Fourth Ave., New York. 326 pp. $1.80.

WILLIAM T. HALL. "Treadwell–Hall Analytical Chemistry. Vol. II. Quantitative Analysis." Eighth edition. John Wiley and Sons, Inc., 440 Fourth Ave., New York. 858 pp. $6.00.

CARL OPPENHEIMER. "Die Fermente und ihre Wirkungen." Supplement, Lieferung 1. W. Junk Verlag, Scheveningsche Weg 74, The Hague, Holland. 160 pp. $6.80.

WOLFGANG OSTWALD. "Metastrukturen der Materie." Sonderausgabe aus den *Kolloid-Beiheften*. Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 16 pp. RM. 0.80.

W. A. ROTH AND K. SCHEEL. "Landolt–Börnstein Physikalisch-chemische Tabellen." Fünfte umgearbeitete und vermehrte Auflage. Dritten Ergänzungband, erster Teil. Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany. 734 pp. RM. 81.

JULIUS RUSKA, Editor. "Das Buch der Alaune und Salze." Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 35, Germany. 126 pp. RM. 15.

WILLIAM A. WATERS. "Physical Aspects of Organic Chemistry." George Routledge & Sons, Ltd., Broadway House, 68–74 Carter Lane, Ludgate Hill, London E. C. 4, England. 501 pp. 25s./–.

ARNOLD WEISSBERGER AND ERICH PROSKAUER. "Organic Solvents. Physical Constants and Methods of Purification." Translated from the German by Randal G. A. New. Oxford University Press, 114 Fifth Ave., New York. 212 pp. $5.00.

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[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORY OF THE NEW YORK STATE AGRICULTURAL EXPERIMENT STATION]

The Influence of Neutral Salts on the Optical Rotation of Gelatin. III. Effect of the Halides of Lithium, Sodium, Rubidium and Cesium[1]

BY D. C. CARPENTER AND F. E. LOVELACE

Previous communications[2] from this Laboratory have shown that in the case of the halides of potassium, the customary Hofmeister series for anions is observed in their effect on the optical rotation of gelatin held at a constant *p*H on the alkaline side of the isoelectric point. When other uni-univalent salts of potassium[3] are examined, the effect on the rotation is represented by a typical Hofmeister series arranged as follows—$KCNS > KI > KClO_3 > KNO_3 > KBr > KCl$, CH_3COOK, C_2H_5COOK and HCOOK. For uni-bivalent salts we have the series $K_2SO_4 > (COOK)_2 > K_2CrO_4$.

In the work herein reported we have examined the effect of the halides of the other alkali metals to find whether the effect of the halides is a general one and to ascertain the magnitude of the effect of the alkali metal.

Materials and Method

The halide salts used in the experiments to be described were recrystallized several times from water and were either oven dried at 104° for several days or in the case of salts crystallizing as hydrates, dried *in vacuo* over anhydrous phosphorus pentoxide for several days.

The gelatin was the same sample of calfskin gelatin that had been used in previous work. It was de-ashed by electrodialysis and further purified and dehydrated by the method described by Sheppard.[4] A 1.4% stock solution of this purified calfskin gelatin was prepared by swelling 14 g. (dry weight) in water for several hours, warming to 50° for "solution" to take place and cooling to 30°. Before making the volume up to 1000 cc. a measured quantity of 0.1 *N* lithium, sodium, rubidium or cesium hydroxide was added to adjust the *p*H of the gelatin solution to approximately 6.3. The gelatin content of this stock solution was determined by drying a known volume of solution to constant weight at 104° and correcting for the weight of alkali metal contained therein.

In preparing the various solutions for observation of the rotation, varying amounts of the pure anhydrous salts were weighed into a series of small weighed flasks and 25-cc. portions of the stock gelatin solution (*p*H 6.3) added. The total weight of solution in each flask was then brought to 50 g. by adding carbon dioxide-free distilled water. As some of the salts were extremely hygroscopic, precautions were taken in weighing and transferring and in many cases the salt concentration was determined by titrating portions of the prepared solutions with 0.1 *N* silver nitrate solution.[5] To obviate any deleterious effects on the gelatin due to the heat evolved when certain of the anhydrous salts dissolved in water, the flasks were cooled at 0° during this operation. The salt concentration was calculated to a molal basis. From each flask of a series for a given salt, a 200-mm. polarizing tube was filled. It was found advantageous to coat each end of the polarizing tube with vaseline before adjusting the cover glass and to permit a small

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[1] Approved by the Director of the New York State Agricultural Experiment Station for publication as Journal Paper No. 96. Abstracted from a thesis presented to the Graduate School of Cornell University by F. E. Lovelace in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Carpenter, *J. Phys. Chem.*, **31**, 1873 (1927).

[3] Carpenter and Kucera, *ibid.*, **35**, 2619 (1931).

[4] Sheppard, Sweet and Benedict, THIS JOURNAL, **44**, 1857 (1922).

[5] The writers wish to acknowledge their indebtedness to the General Electric Company of Schenectady, N. Y., for placing at their disposal a quantity of rubidium and cesium compounds from which the salts used herein were prepared.

air bubble to remain in the tube to obviate strains within the gels, which otherwise would lead to erratic polariscope readings. The polarizing tubes were then placed in the constant-temperature bath at 0.5 ± 0.02° to come to equilibrium. A constant rotation was usually reached after five days, but the readings recorded in the tables for 0.5° were obtained after seven days so as to insure the attainment of equilibrium in all cases.

After a series of readings was completed at 0.5° the tubes were allowed to warm to room temperature and were then placed in the constant-temperature bath at 40° for half an hour for equilibrium to be established before polarizing at this higher temperature. Equilibrium is practically reached after fifteen minutes at 40°.

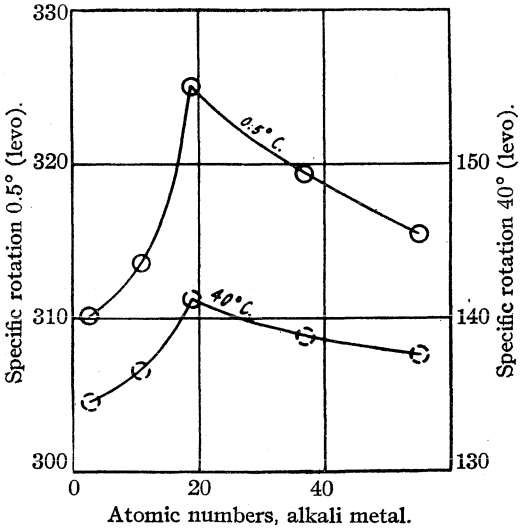

Fig. 1.—Specific rotation of alkali gelatinates.

The pH of the solutions was determined by the quinhydrone electrode, being set up as half cells against a standardized 0.1 N calomel electrode at 25° with a saturated potassium chloride solution as junction. The pH was calculated from the relation $pH = (0.3614 - E)/0.0591$ disregarding corrections for junction potential and for any effect the high salt concentrations may have had upon the quinone–hydroquinone equilibrium within the cell. The pH measurements were made primarily to show that the pH was fairly constant. We have shown before[6] that between pH 6 and 7 the change in rotation at 0.5° caused by increase in pH is not greater than 2%, and as all of our measurements fall well within this limit, pH can have no great effect on our results.

Density determinations were made of all solutions at 25° in a carefully calibrated pycnometer. For the purpose of calculation in this and subsequent articles it is assumed that the density at 0.5 and 40° is the same as that at 25°. The actual error will not be large if this assumption is made and in many cases the density at 0.5° is not experimentally attainable by pycnometer as the solutions are gels.

Specific rotation was calculated from the equation $[a] = (a \times 100)/(l \times d \times p)$ where a is the angle measured, l the length of tube in decimeters, p the grams of gelatin in 100 g. of solution and d the density of the solution. A Schmidt and Haensch triple field polarimeter was used throughout.

Discussion and Conclusions

In Table I are given the data for the specific rotation of the gelatinates of the various alkali metals without added halide salts, and in Fig. 1 these data are shown graphically. It will be seen that the effect of the alkali metal ion on the rotation of gelatin is of minor importance but that the rotation increases with increase in atomic number to a maximum value (potassium) and thereafter decreases. This decrease appears to be connected with the appearance of the shell of eighteen electrons in rubidium and the decrease becomes further augmented with cesium where an additional shell of eighteen electrons is present. Inasmuch as the ratio $[a]^{0.5}_D/[a]^{40}_D$ is practically constant for all of the alkali gelatinates, it is concluded that the effect of temperature on configuration of the gelatin molecule as shown by the rotation, is alike for all of the alkali gelatinates at pH 6–7 and that they are of analogous structure.

Table I

Specific Rotation of Alkali Gelatinates

Alkali metal	Atomic no.	pH	Levo degrees $[\alpha]^{0.5}_D$	Levo degrees $[\alpha]^{40}_D$	$\frac{[a]^{0.5}_D}{[\alpha]^{40}_D}$
Li	3	6.31	310.2	134.6	2.304
Na	11	6.30	313.6	136.6	2.295
K	19	6.36	325.0	141.2	2.301
Rb	37	6.24	319.4	138.8	2.301
Cs	55	6.38	315.1	137.6	2.290

Razukin[7] found that the specific rotation of lithium, sodium and potassium proteinates increased in magnitude with the atomic weight of the metal ion, the order of magnitude of the effect being K > Na > Li. Darmois[8] has found a similar effect on the rotation of tartrates. In the case of the alkali gelatinates we find the magnitude of the rotation to be given by the order K > Rb > Cs > Na > Li at 0.5 and 40°.

As to the effect of neutral salts on the specific rotation of gelatin, our data are recorded in Table II. To present our results clearly and at the same time with economy of space we have shown the results with the lithium halides in Fig. 2. Similar curves are obtained for the halides of each of the alkali metals. In Fig. 3 are collected to-

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(6) Carpenter, Dahlberg and Hening, *Ind. Eng. Chem.*, **20**, 397 (1928).

(7) Razukin and Logunova, *J. Russ. Phys.-Chem. Soc.*, **47**, 1059 (1915); Razukin and Brando, *ibid.*, **48**, 269 (1916); Razukin, *ibid.*, **48**, 265 (1916).

(8) Darmois, *Trans. Faraday Soc.*, **26**, 384 (1930).

TABLE II

INFLUENCE OF SALTS ON OPTICAL ROTATION OF GELATIN AT pH 6–7

Soln. no.	Molality of salt soln.	pH 25°	Wt. gelatin per 100 g. solvent, g.	Density, 25°	$[\alpha]_D^{0.5}$ Levo degrees	$[\alpha]^{40}_D$ Levo degrees
Lithium Chloride						
1	0.00	6.31	0.7674	1.0021	310.2	134.6
2	.62	6.32	.7673	1.0187	307.1	130.3
3	.93	6.48	.7673	1.0255	296.7	128.4
4	1.29	6.47	.6343	1.0361	287.6	123.3
5	1.87	6.52	.7673	1.0480	268.0	121.9
6	2.10	6.01	.7673	1.0577	252.6	119.5
7	2.49	6.61	.7674	1.0634	228.5	117.0
8[a]	2.76	6.53	.7673	1.0752	201.8	115.8
9[a]	2.89	5.99	.7673	1.0777	183.8	113.7
10[a]	3.11	6.59	.7673	1.0843	149.0	113.6
11[a]	3.49	6.80	.7673	1.0941	123.9	116.1
12[a]	3.89	6.79	.7673	1.0995	112.0	108.5
Lithium Bromide						
1	0.00	6.31	0.7674	1.0021	310.2	134.6
2	.59	6.63	.7673	1.0405	297.5	127.1
3	.90	6.53	.7673	1.0608	288.1	125.3
4	1.13	6.33	.7674	1.0770	272.8	124.6
5	1.22	6.50	.7678	1.0825	265.4	123.8
6	1.41	6.25	.7673	1.0953	244.7	120.0
7	1.55	6.53	.7678	1.0973	229.4	120.1
8[a]	1.69	6.33	.7673	1.1179	189.2	116.0
9[a]	1.73	6.49	.7673	1.1196	181.0	116.4
10[a]	1.92	6.57	.7673	1.1343	141.3	115.5
11[a]	2.23	6.28	.7674	1.1602	121.3	110.1
12[a]	2.84	6.30	.7673	1.2091	109.4	104.0
13[a]	3.38	5.81	.7673	1.2564	102.2	97.5
Lithium Iodide						
1	0.00	6.31	0.7674	1.0021	310.2	134.6
2	.58	6.29	.7673	1.0619	278.0	125.2
3	.61	6.62	.7673	1.0654	275.2	122.3
4[a]	.90	6.38	.7673	1.0962	225.3	119.5
5[a]	.91	6.21	.7673	1.0979	220.1	118.7
6[a]	1.21	6.37	.7673	1.1321	134.7	112.2
7[a]	1.52	6.23	.7673	1.1715	115.1	107.9
8[a]	1.76	6.26	.7673	1.2093	109.4	105.1
9[a]	2.40	6.15	.7674	1.2950	102.1	94.1
Sodium Chloride						
1	0.00	6.30	0.7730	1.0023	313.6	136.6
2	0.67	6.30	.7730	1.0303	308.9	128.0
3	1.01	6.32	.7730	1.0441	306.1	125.8
4	1.34	6.26	.7731	1.0582	303.1	119.2
5	1.68	6.13	.7730	1.0734	297.7	119.3
6	2.02	6.27	.7730	1.0875	286.1	115.4
7	2.69	6.23	.7731	1.1174	276.1	108.8
8[a]	3.35	6.17	.7697	1.1482	246.1	110.9
9[a]	4.21	6.23	.7731	1.1883	204.7	94.2
Sodium Bromide						
1	0.00	6.30	0.7730	1.0023	313.6	136.6
2	0.65	6.33	.7744	1.0558	305.2	130.5
3	1.00	6.17	.7730	1.0842	293.5	123.6
4	1.34	6.17	.7730	1.1182	279.4	120.1
5	1.68	6.25	0.7745	1.1516	245.6	116.0
6[a]	2.10	6.22	.7745	1.1937	182.8	111.4
7[a]	2.41	6.47	.7132	1.2274	145.1	106.5
8[a]	2.69	6.07	.7730	1.2601	114.5	102.4
9[a]	3.34	6.00	.7698	1.3410	95.4	91.1
10[a]	4.20	6.02	.7744	1.4638	82.9	82.5
Sodium Iodide						
1	0.00	6.30	0.7730	1.0023	313.6	136.6
2	.35	6.31	.7730	1.0437	300.7	129.9
3	.67	6.27	.7745	1.0847	277.3	124.5
4	.85	6.36	.7730	1.1095	253.0	120.2
5[a]	1.03	6.16	.7730	1.1308	208.2	115.3
6[a]	1.10	6.11	.7745	1.1445	191.2	118.5
7[a]	1.18	5.93	.7731	1.1526	161.6	111.7
8[a]	1.25	6.19	.7730	1.1672	141.9	110.3
9[a]	1.34	6.14	.7744	1.1813	129.0	109.3
10[a]	1.68	5.94	.7745	1.2370	105.9	99.9
11[a]	2.01	5.90	.7731	1.2942	98.4	95.7
12[a]	2.58	5.68	.7731	1.4065	86.0	84.1
13[a]	3.02	5.58	.7744	1.5132	76.8	74.7
14[a]	3.30	5.68	.7745	1.5862	70.4	68.8
Rubidium Chloride						
1	0.00	6.24	0.7902	1.0026	319.4	138.8
2	0.67	6.18	.7906	1.0647	307.1	126.5
3	1.34	6.18	.7668	1.1318	294.4	117.5
4	1.68	6.06	.7668	1.1748	287.0	114.9
5	2.01	6.04	.7667	1.2101	279.2	113.2
6	2.58	5.98	.7667	1.2687	265.3	105.4
7	3.02	5.87	.7636	1.3428	247.2	99.5
Rubidium Bromide						
1	0.00	6.24	0.7902	1.0026	319.4	138.8
2	.48	6.28	.7903	1.0662	307.4	131.1
3	.88	6.39	.7902	1.1252	293.0	125.4
4	1.29	6.14	.7902	1.1926	270.2	121.6
5	1.50	6.24	.7902	1.2295	245.5	114.3
6[a]	1.69	6.09	.7902	1.2645	224.3	113.6
7[a]	1.86	6.20	.7903	1.2993	196.7	111.0
8[a]	2.09	6.01	.7903	1.3466	159.7	111.4
9[a]	2.22	6.16	.7903	1.3734	137.7	105.5
10[a]	2.40	6.02	.7904	1.4179	119.6	102.6
11[a]	2.80	5.77	.7904	1.5244	100.0	96.3
Rubidium Iodide						
1	0.00	6.24	0.7902	1.0026	319.4	138.8
2	.48	6.09	.7904	1.0849	297.9	128.9
3[a]	.88	5.84	.7903	1.1639	236.5	117.4
4[a]	1.08	5.88	.7648	1.2034	182.5	118.4
5[a]	1.19	5.95	.7649	1.2289	151.6	117.5
6[a]	1.29	5.99	.7903	1.2623	125.8	112.8
7[a]	1.69	5.74	.7903	1.3701	103.9	102.6
8[a]	2.09	5.58	.7903	1.4948	94.4	94.0
9[a]	2.36	5.50	.7904	1.5934	88.5	88.1
Cesium Chloride						
1	0.00	6.38	0.7582	1.0022	315.1	137.6
2	.50	6.42	.7581	1.0706	307.0	130.5
3	1.00	6.27	.7581	1.1467	295.3	126.5
4	1.50	6.09	.7432	1.2303	283.3	120.8
5	2.00	6.12	.7581	1.3400	265.8	114.7
6	2.50	6.12	.7581	1.4582	243.8	109.0

TABLE II (*Concluded*)

Soln. no.	Molality of salt soln.	pH 25°	Wt. gelatin per 100 g. solvent, g.	Density, 25°	$[\alpha]_D^{0.5}$ Levo degrees	$[\alpha]^{40}_D$ Levo degrees
			Cesium Bromide			
1	0.00	6.38	0.7582	1.0022	315.1	137.6
2	.47	6.21	.7582	1.0833	305.0	132.1
3	.91	6.24	.7582	1.1771	289.6	123.8
4	1.29	6.16	.7582	1.2678	265.8	118.1
5	1.45	5.88	.7581	1.3095	249.8	117.4
6[a]	1.68	5.87	.7581	1.3707	218.0	113.0
7[a]	1.87	5.82	.7566	1.4384	189.3	107.0
8[a]	2.13	6.00	.7582	1.5286	145.8	106.1
			Cesium Iodide			
1	0.00	6.38	0.7582	1.0022	315.1	137.6
2	.33	6.34	.7581	1.0641	304.5	131.0
3	.64	6.31	.7581	1.1283	279.0	125.1
4	.80	6.17	.7581	1.1886	249.7	119.3

[a] Solutions did not gel at 0.5°. All others were solid gels at 0.5°.

gether graphs for all of the salts reported in this investigation.

It is obvious from the data and graphs that the principal effect of neutral salts of the uni-univalent type is due to the anion of the added salt. The magnitude of the effect produced by iodides is greater than the effect produced by the bromides, which in turn is greater than the effect produced by chlorides. This order is the same at both temperatures for all of the alkali halides, but the effect on the rotation of gelatin is of much greater magnitude at low temperatures. We therefore conclude that, contrary to the views of Loeb,[9] there is a Hofmeister series for the anions, namely, I > Br > Cl, with all the halide salts of the alkali metals.

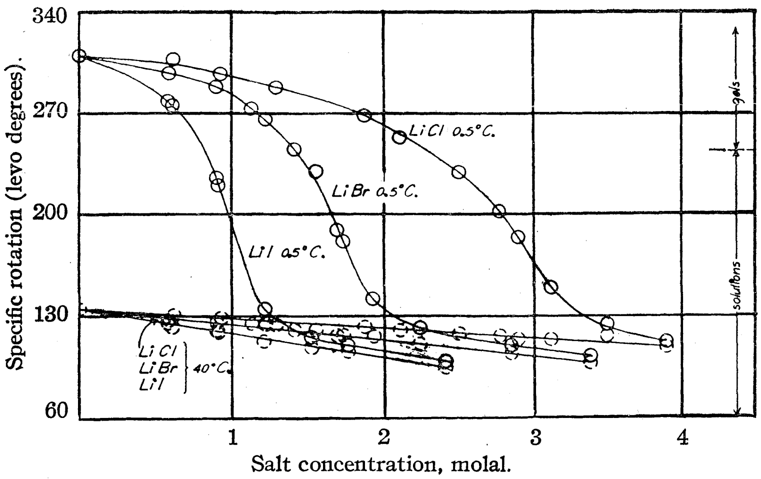

Fig. 2.—Influence of lithium halides on the specific rotation of gelatin.

The data show that there is a very minor effect on the specific rotation of gelatin due to the cation alone, when the alkali metal halides are added. This is more apparent in the case of the chlorides than with the bromides or iodides. The magnitude of this effect can be shown by the following series, Li > Cs > Rb > Na when the concentration of added salt becomes fairly high. The order of this series is practically the same, regardless of the anion in combination with the alkali metal ion, until very high concentrations of bromide and iodide are reached. At this point a slight change in the order occurs.

In experiments which largely concerned the influence of chlorides of various metals on the optical rotation of neutral asparagine, J. Liquier-Milward[10] found that among the alkali metals, the influence was greatest for the metal ion having the smallest radius (LiCl > NaCl > KCl). On account of the fact that no changes in rotation were observed on adding neutral salts to acid solutions of asparagine and none were found with dextrorotatory alanine, (which is largely in the zwitterion form), she ascribed the effect of salts on rotation to a polarization of the asparagine molecule into the zwitterion form. In short she believed the effect of added salt was to produce the zwitterion type of molecule. In acid solutions the NH_2 group is bound to acid and the presence of zwitterion is probably negligible. This fact in any case indicates that the NH_2 group is involved in whatever change in constitution occurs.

Linderstrøm-Lang and Kodama[11] found that the solubility of casein in dilute hydrochloric acid decreased with increasing salt concentration, while Sörensen and Sladek[12] found that the solubility of casein in dilute sodium hydroxide solution *increased* with increasing sodium chloride concentration until the salt concentration was about twice normal. A further increase in salt concentration reduced the solubility of the casein.

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(9) Loeb, "Proteins and the Theory of Colloidal Behavior," The Macmillan Co., New York City, 1922.

(10) Liquier-Milward, *Ann. Physik*, **7**, 121 (1927); *Trans. Faraday Soc.*, **26**, 390 (1930).

(11) Linderstrøm-Lang and Kodama, *Compt. rend. trav. lab. Carlsberg*, **16**, No. 1 (1925).

(12) Sörensen and Sladek, *ibid.*, **17**, No. 14 (1929).

These last authors concluded that compound formation had taken place between the casein and salt or one of the latter's ions.

As regards solubility of proteins in salt solutions, we have found with gelatin an effect similar to that noted by Sörensen and Sladek for casein. The gelatin–salt mixtures we have used pass from solid gels to fluids at a point where the specific rotation reaches −250°. This critical rotation value is a measure of "solubility" in our experiments. This indicates that the solubility of gelatin has been increased by the addition of salts and that the increase is largely dependent on the halide part of the salt present. The above view is understood not to exclude possible interaction between the ions and solvent and the idea of salting out coefficients.

Carpenter and Kucera[3] called attention to the fact that compounds of the zwitterion type NH_3^+–R–COO$^-$, on account of their electric charges, should suffer a diminution of activity on adding neutral salts and that their solubility should be increased. They suggested that compounds of the type NH_3I–R–COONa might be formed as the result of the operation of electrostatic forces in which the properties of the zwitterion entirely disappeared and in which the activity coefficient of the salt presumably would be considerably less. It is expected that with a linkage of nitrogen to halogen the NH_3I–R–COONa type of compound would be ionized completely into I$^-$ and NH_3–R–COONa$^+$ ions, with the protein bound to the metal as a complex.

It is pointed out that to maintain in solution a structure of the NH_3^+–R–COO$^-$ type it is necessary to assume that a large number of the fields of force associated with the two charged regions mutually form a closed field. Consequently although the zwitterion structure looks as if it were a highly reactive form, capable for instance of forming molecular chains through the operation of electrostatic forces, the fact that this is not the case can only mean that the electrified regions have been largely mutually neutralized. The effect of increase in temperature or the addition of neutral salts might easily be that of opening up the force fields around both electrified regions, so that polymerization of the molecule would be possible. If the polymer had a chain structure NH_3^+–R–COO–NH_3–R–COO$^-$ it is obvious that this would be only the first step toward the formation of a huge chain. Lewis[13] in experimenting on the possible polymerization of glycine, found that a dipolymer was formed in a measurable amount and he concluded that higher polymers were unlikely. The fact that the polymerization only goes as far as the double molecule with simple amino acids suggests that the formation of a ring structure is involved which would appear to be a more stable form on account of the relative absence of free force fields. It is assumed that this reaction would be reversible and that while polymerization due to heat or salts would proceed rapidly, the depolymerization reaction, on the other hand, would proceed much slower due to the greater stability of the ring structure. In the case of the simplest species of casein[14] we have found that heating to 40° while the protein was dissolving in buffer solution changed the molecular weight from around 96,000 to 188,000, an almost exact doubling of the molecular weight. It is possible that gelatin behaves in a similar way in which case, as a choice between the two alternate hypotheses to account for the great change in rotation of gelatin, we would favor that of polymerization to a ring structure.

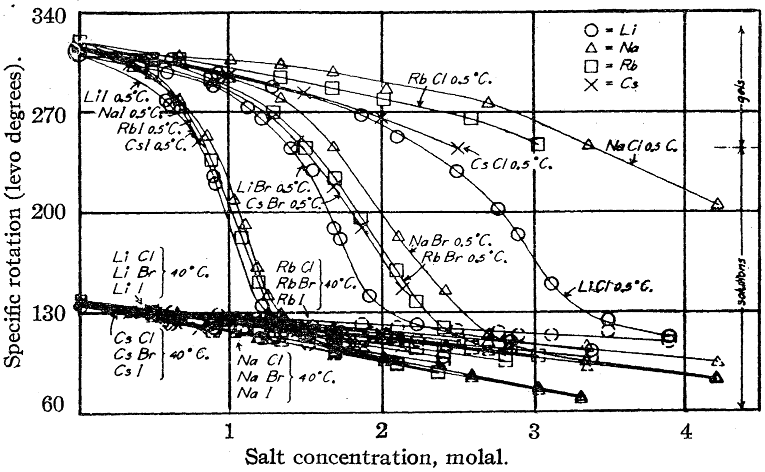

Fig. 3.—Influence of alkali halides on the specific rotation of gelatin.

Summary

The influence of the halides of lithium, sodium, rubidium and cesium on the specific rotation of gelatin at 0.5 and 40° has been examined over the

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[13] Lewis, *Chem. Rev.*, **8**, 151 (1931).

[14] Svedberg, Carpenter and Carpenter, THIS JOURNAL, **52**, 241 and 701 (1930).

solubility range of the respective salts. The results confirm our earlier conclusions that there is a definite Hofmeister series of anions (I > Br > Cl) in their effects on the optical rotation of gelatin. There is also a definite Hofmeister series for cations (Li > Cs > Rb > Na) but the effects of cations are much less in magnitude than those of the anions.

In the absence of added salts, the optical rotation of the gelatinates of the alkali metals increases slightly with atomic number to a maximum rotation with potassium, after which the rotation slightly decreases.

GENEVA, N. Y. RECEIVED JULY 5, 1935

[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORY OF THE NEW YORK STATE AGRICULTURAL EXPERIMENT STATION]

The Influence of Neutral Salts on the Optical Rotation of Gelatin. IV. Rotatory Dispersion of Gelatin in Sodium Iodide Solutions[1]

BY D. C. CARPENTER AND F. E. LOVELACE

Despite the large amount of work on the rotatory dispersion of optically active substances there has been comparatively little done on the proteins. Hafner[2] discussed briefly the measurements he made at four different wave lengths in the visible on serum albumin and serum globulin. Hewitt[3] studied several proteins, making measurements at four wave lengths in the visible. Hewitt confined himself to graphing the reciprocal of the specific rotation against the square of the wave lengths and obtained straight lines which showed only that the dispersion may be expressed by a single term of Drude's equation $[\alpha]_\lambda = \sum \frac{k_n}{\lambda^2 - \lambda_0^2}$. From Hewitt's work one would conclude that absorption bands somewhere below 2700 Å. governed the rotatory dispersion of proteins.

Hansen[4] investigated the rotatory dispersion of egg albumin as influenced by protein concentration, concentration of ammonium sulfate added, *p*H and temperature. Hansen was the first investigator to calculate dispersion constants from his data. He concluded that λ_0 was largely independent of *p*H, temperature and concentration of added salt and protein, while k varied under most experimental conditions.

The rotatory dispersion of gliadin has been studied by Haugaard and Johnson[5] at three different wave lengths and by Wiles and Gortner[6] at six wave lengths. In the former paper the workers recognized that the presence of lithium chloride, as well as changes in *p*H, greatly influenced the rotations. They pointed out that the effect of lithium chloride might be due to complex salt formation or to changed conditions of dissociation of the protein or to a combination of these effects. However, their data were more or less fragmentary and evaluation of the dispersion constants was not attempted. Other alkali halides, potassium iodide, potassium bromide and sodium chloride were used by Wiles and Gortner, who confined themselves to showing that a linear relation existed between the reciprocal of the observed rotations and the square of the wave lengths used.

The purpose of the present investigation was to study the rotatory dispersion of gelatin in sodium iodide solutions, primarily to ascertain the cause of the rapid decrease in rotation experienced with iodide salts at low temperatures.

Experimental

In the present work the specific rotations of gelatin solutions at 0.5 and 40° were measured at five different wave lengths in the visible spectrum, *viz.*: red lithium line, λ = 6707.86 Å.; sodium D line, λ = 5892.617 Å. (optical mean); yellow mercury line, λ = 5780.13 Å. (optical mean); green mercury line, λ = 5460.73 Å.; and the deep blue mercury line, λ = 4358.34 Å. A quartz mercury arc lamp was used as the source for all mercury lines and an electric arc between carbons the cores of which were filled with powdered sodium glass or lithium carbonate was the source of the sodium and lithium lines, respec-

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[1] Approved by the Director of the New York State Agricultural Experiment Station for publication as Journal Paper No. 97. Abstracted from a thesis presented to the Graduate School of Cornell University by F. E. Lovelace in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Hafner, *Biochem. Z.*, **166**, 424 (1925).

[3] Hewitt, *Biochem. J.*, **21**, 216 (1927).

[4] Hansen, *Compt. rend. trav. lab. Carlsberg*, **16**, No. 10 (1927).

[5] Haugaard and Johnson, *ibid.*, **18**, No. 2 (1930).

[6] Wiles and Gortner, *Cereal Chem.*, **11**, 36 (1934).

TABLE I

SPECIFIC ROTATION OF GELATIN SOLUTIONS CONTAINING SODIUM IODIDE AT 0.5° FOR DIFFERENT WAVE LENGTHS OF LIGHT

Soln.	Concn. of NaI, molal	Density at 25°	*p*H	Levo degrees									
				λ6707.86 Å.		λ5892.617 Å.		λ5780.13 Å.		λ5460.73 Å.		λ4358.34 Å.	
				(*a*)	[α]	(*a*)	[α]	(*a*)	[α]	(*a*)	[α]	(*a*)	[α]
1	0.000	1.0023	5.95	3.83	248.01	5.14	332.84	5.38	348.38	6.15	398.24	10.86	703.23
2	.350	1.0436	6.02	3.89	241.95	5.23	325.30	5.47	340.23	6.26	389.36	11.04	686.67
3	.851	1.1011	5.88	3.31	195.09	4.45	262.29	4.65	274.07	5.32	313.56	9.39	553.46
4	1.001	1.1316	5.99	2.89	165.78	3.89	223.13	4.07	233.46	4.65	266.73	8.20	470.36
5	1.121	1.1484	5.96	2.48	140.15	3.33	188.18	3.48	196.66	3.98	224.91	7.02	396.72
6	1.251	1.1676	5.87	2.10	116.74	2.84	157.88	2.96	164.55	3.38	187.89	5.97	331.87
7	2.001	1.2940	5.85	1.63	81.76	2.19	109.85	2.29	114.87	2.62	131.42	4.62	231.74
8	2.578	1.4097	5.64	1.58	72.74	2.12	97.60	2.22	102.21	2.54	116.19	4.48	206.25
9	3.295	1.5824	5.63	1.46	59.89	1.96	80.40	2.05	84.09	2.35	96.39	4.15	170.23

TABLE II

SPECIFIC ROTATION OF GELATIN SOLUTIONS CONTAINING SODIUM IODIDE AT 40° FOR DIFFERENT WAVE LENGTHS OF LIGHT

Soln.	Concn. of NaI, molal	Density at 25°	*p*H	Levo degrees									
				λ6707.86 Å.		λ5892.617 Å.		λ5780.13 Å.		λ5460.73 Å.		λ4358.34 Å.	
				(*a*)	[α]	(*a*)	[α]	(*a*)	[α]	(*a*)	[α]	(*a*)	[α]
1	0.000	1.0023	5.95	1.71	110.73	2.30	148.94	2.41	156.06	2.75	178.07	4.86	314.71
2	.350	1.0436	6.02	1.69	105.12	2.27	141.19	2.38	148.03	2.72	169.18	4.80	298.55
3	.851	1.1011	5.88	1.66	97.84	2.23	131.44	2.33	137.33	2.67	157.37	4.71	277.61
4	1.001	1.1316	5.99	1.66	95.22	2.23	127.92	2.34	134.23	2.67	153.15	4.72	270.74
5	1.121	1.1484	5.96	1.65	93.24	2.22	125.46	2.32	131.11	2.66	150.32	4.69	265.04
6	1.251	1.1676	5.87	1.64	91.16	2.20	122.30	2.31	128.41	2.64	146.76	4.65	258.49
7	2.001	1.2940	5.85	1.59	79.75	2.14	107.34	2.24	112.36	2.56	128.41	4.52	226.73
8	2.578	1.4097	5.64	1.55	71.36	2.09	96.22	2.18	100.37	2.50	115.10	4.40	202.57
9	3.295	1.5824	5.63	1.45	59.48	1.95	79.98	2.04	83.68	2.34	95.98	4.13	169.41

tively. To eliminate all lines but the desired wave length the light was passed through either appropriate Corning glass filters or through a glass absorption cell 1 cm. thick containing an appropriate dye solution or through both of these as required to give monochromatic light before entering the polariscope. The filters employed were as follows: Li red line, Corning Red G5 + alkaline solution containing brom thymol blue in cell; Na D line, Corning Green G701C1 + saturated alcoholic solution of Sudan IV in cell; Hg yellow line, Corning Yellow G34-O through which green and blue Hg lines do not pass; Hg green line, aqueous solution of "Light Green SF" dye, 0.1575 gm. per liter, in cell; Hg blue line, Corning Blue G585 through which yellow and green lines do not pass. To ascertain the wave lengths actually transmitted in each case, the light which reached the eyepiece of the polariscope was checked with a spectroscope.

The procedure for preparation of solutions and for measurement of rotations, density, *p*H, etc., was the same as has been described before.[7] The gelatin concentration of these solutions was 0.7704 g. per 100 g. of solution.

Discussion and Conclusions

In Tables I and II are given our data for 0.5 and 40°, respectively, for the various wave lengths employed. In Figs. 1 and 2 these data are shown graphically, plotting the reciprocal of specific rotation against the squares of the wave lengths at which these rotations were obtained. It is seen that the relationship is linear, which means that a single-term Drude equation will adequately express our results. Each straight line on these graphs represents the rotatory dispersion of a gelatin solution containing a definite quantity of sodium iodide.

It will be seen in both graphs that each straight line cuts the *x*-axis at the same point. This point represents λ^2_0 and graphically locates the absorption band of gelatin at 2200 Å. The same numerical value for λ_0 was obtained by solving our data by the method employed by Lowry and Owen.[8] So far as can be found in the visible spectrum the rotatory dispersion of gelatin dissolved in sodium iodide solutions obeys a single term of Drude's law.

That gelatin has a tremendous absorption in the neighborhood of 2200 Å. was observed in this Laboratory several years ago (D.C.C.). Although the head of the absorption band for gelatin could not be definitely determined, the graph of the extinction coefficient for gelatin (curve 2) is

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(7) Carpenter and Lovelace, THIS JOURNAL, **57**, 2337 (1935).

(8) Lowry and Owen, *Trans. Faraday Soc.*, **26**, 371 (1930).

shown in Fig. 3. In this figure we have also plotted the absorption spectrum of sodium iodide (curve 1) recalculated from the data of Fromherz and Menschick.[9] The head of the absorption band for aqueous sodium iodide is located at 2225 Å. from these data. While the head of the absorption band for gelatin was not definitely determined it seems safe to say that the absorption is very great in the neighborhood of 2200 Å., which agrees with the position of the band calculated from our dispersion data.

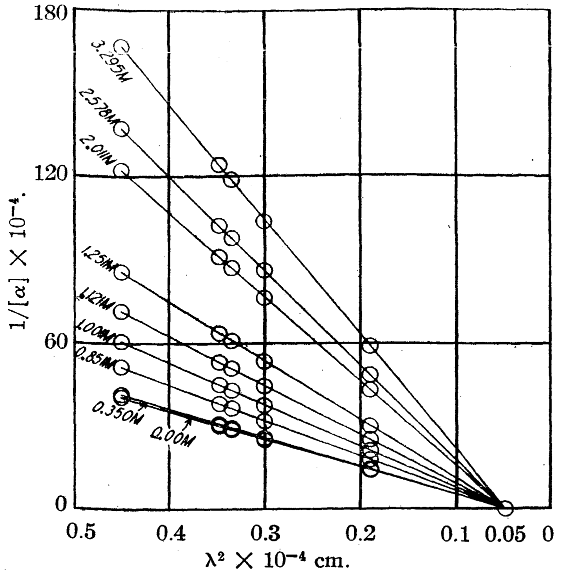

Fig. 1.—Graph of reciprocal of specific rotation *versus* wave length squared at (0.5°).

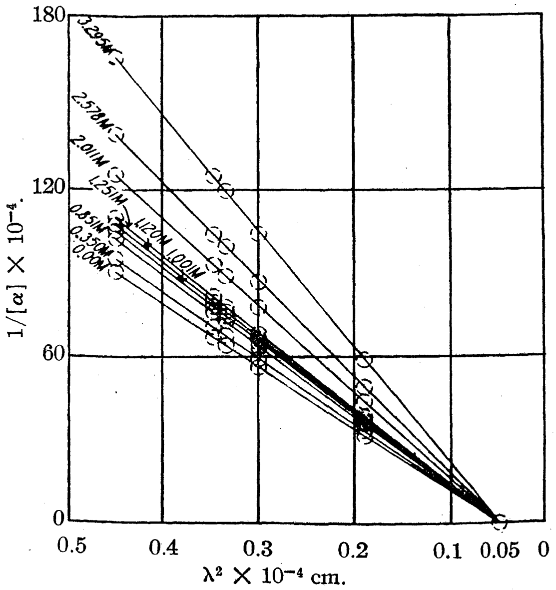

Fig. 2.—Graph of reciprocal of specific rotation *versus* wave length squared at (40°).

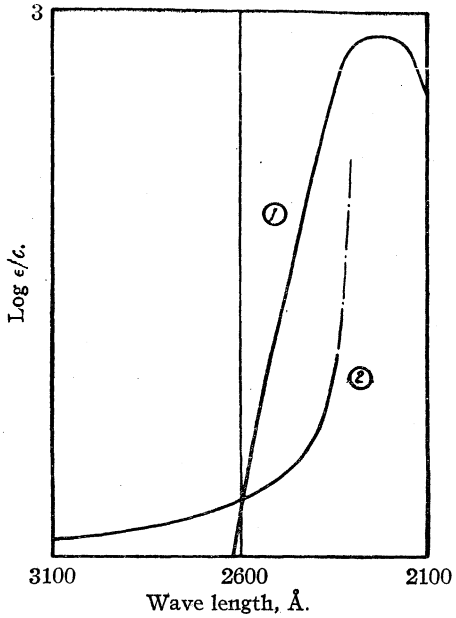

Fig. 3.—Extinction coefficient of aqueous gelatin (2) and sodium iodide solutions (1).

The values of k, numerator in the Drude equation, were calculated for each concentration of sodium iodide and appear in Table III and are graphed in Fig. 4. At 40° the k values bear a linear relation to the concentration of sodium iodide as given by the equation

$$k_{40^\circ} = 44.5170 - 6.220C_{\mathrm{NaI}} \qquad (1)$$

At 0.5° the curve for the k values is made up of two parallel straight lines at the extreme ends as salt concentration is varied, united by a curve which resembles the general type of curve representing a dissociation or association process. In the straight line portion of the curve the k values bear the relation to salt concentration given by the equation

$$k_{0.5^\circ} = 46.3300 - 6.7605C_{\mathrm{NaI}} \qquad (2)$$

and in the rapidly changing part of the curve

$$C_{\mathrm{NaI}} = \frac{1}{2.66} \log \left(\frac{a}{1-a}\right) - \log (1/K) \qquad (3)$$

where a represents the fraction dissociated as shown by the change in magnitude of the dispersion constants $k_{0.5^\circ}$. In Table III are given the a values for the dissociated fraction and the calculated values obtained for log $(1/K)$. The latter agree very well with one another and indicate a mean value of 0.9983.

It is obvious that there will be a log $(1/K)$ value that will be characteristic for iodide and which

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(9) Fromherz and Menschick, *Z. physik. Chem.*, **B7**, 439 (1930).

will be different in magnitude but equally characteristic for bromides, etc. It is seen from the graphs in the previous paper[7] that the log $(1/K)$ values are approximately 1.0 for iodides, 1.8 for bromides and 3.7 for chlorides (LiCl). The factor $^1/_{2.66}$ preceding the dissociation term regulates how rapidly the dissociation takes place. The numerical value of this factor increases in going from iodides to chlorides, approaching unity in the latter case.

Inasmuch as the rotatory dispersion constants for gelatin at 0.5° in the presence of salts follow a dissociation equation, it is concluded that the transformation from what we have hitherto designated as the "gel" form of gelatin to the "sol" form, is a process of dissociation or association of the gelatin molecule.

TABLE III

ROTATORY DISPERSION CONSTANTS AT 0.5 AND 40°

Soln.	Concn. NaI (molal)	$k_{0.5°}$	a	Log $(1/K)$	$k_{40°}$
1	0.000	99.5410	..	...	44.517
2	.350	97.2054	..	...	42.243
3	.851	78.3378	0.291	0.997	39.281
4	1.001	66.6307	.492	.999	38.278
5	1.121	56.2071	.675	1.004	37.495
6	1.251	46.9638	.830	0.993	36.611
7	2.011	32.8214	..	...	32.074
8	2.578	29.1903	..	...	28.702
9	3.295	24.0540	..	...	23.929

$k_{0.5°} = 46.3300 - xC_{\text{NaI}}$ where $x = 6.7605$
$k_{40°} = 44.5170 - xC_{\text{NaI}}$ where $x = 6.220$
mean log $(1/K) = 0.9983$

By the method of determinants, Lucas[10] has developed a formulation from which the number of optically active species in a system may be determined. Lucas' relation is based on the assumption that the active species have different dispersion constants and, of course, would only apply to systems satisfying this requirement. In the case of two active components the equation takes the form

$$k = \left[\frac{[a]_1 - [a]_2}{[a]_1 - [a]_n}\right]_{\lambda_a} = \left[\frac{[a]_1 - [a]_2}{[a]_1 - [a]_n}\right] = \left[\frac{[a]_1 - [a]_2}{[a]_1 - [a]_n}\right]_{\lambda_c} \text{etc.} \quad (4)$$

where $[a]_1$, $[a]_2$ and $[a]_n$ represent the specific rotations of the active material in a related series (with a given salt) at wave lengths λ_a, λ_b, λ_c, etc. In applying Lucas' equation a series of any two pairs may be selected for comparison. If a constant is obtained for different wave lengths λ_a, λ_b, λ_c, etc., it is good evidence that two optically active components and only two are present.

TABLE IV

CALCULATION OF THE LUCAS CONSTANT FOR GELATIN–SODIUM IODIDE SYSTEM CONTAINING TWO OPTICALLY ACTIVE COMPONENTS (0.5°)

Combination[a]	λ6708 Å.	λ5892 Å.	λ5780 Å.	λ5461 Å.	λ4358 Å.
1–2/1–9	0.0322	0.0298	0.0308	0.0294	0.0316
1–3/1–9	.286	.278	.281	.280	.280
1–4/1–9	.437	.434	.434	.435	.438
1–5/1–9	.573	.573	.570	.574	.575
1–6/1–9	.697	.693	.695	.696	.696
1–7/1–9	.883	.883	.883	.883	.884
1–8/1–9	.931	.931	.931	.934	.932

[a] The numbers in this column refer to corresponding soln. no. in Table I.

We have applied Lucas' method of analysis to our data for the rotation of gelatin at 0.5° and the results are given in Table IV. In the column headed "Combination" is given the combination of specific rotations employed in the various calculations of k, the numbers 1, 2, 3, 4, etc., referring to the same gelatin solutions as given in Table I. It is obvious from the calculated values of the Lucas constant for the five wave lengths, for the systematic series of combinations employed, that a constant is actually obtained for any combination (within the probable error of polariscope readings) as is required for a mixture of two optically active substances. Any other combination that might be chosen would give a similar constancy for the Lucas constant. We therefore conclude that at 0.5° gelatin is converted from one optically active form to another by the action of neutral salt. There appear to be only two optically active species present. This is entirely in harmony with our foregoing conclusion that the two forms are closely related

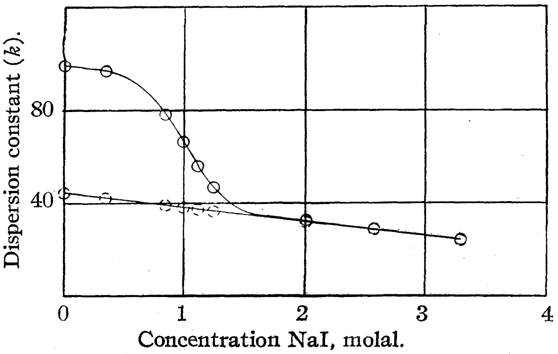

Fig. 4.—Rotatory dispersion constant of gelatin in sodium iodide solutions at 0.5 and 40°.

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(10) Lucas, *Ann. phys.*, [10] **9**, 381 (1928); *Trans. Faraday Soc.*, **26**, 418 (1930).

to each other, one being a dissociated (or associated) form of the other and also that the associated form is likely a polymer of a ring type resulting from the mutual electrostatic neutralization of zwitterion structures.

Summary

The rotatory dispersion of gelatin has been examined in various concentrations of sodium iodide at 0.5 and 40°, at five different wave lengths in the visible spectrum.

A single term Drude equation was shown to express the experimental results. From calculations it was shown that an absorption band at 2200 Å. governed the dispersion. Absorption spectrum data showed that gelatin has a high absorption in this region.

The rotatory dispersion constants of gelatin at 40° follow the linear equation $k_{40°} = 44.5170 - 6.220C_{\mathrm{NaI}}$.

The rotatory dispersion constants at 0.5° were found to be expressed by the sum of two equations

$$C_{\mathrm{NaI}} = \frac{1}{2.66}\log\left(\frac{a}{1-a}\right) - \log\left(\frac{1}{K}\right)$$

and the linear equation

$$K_{0.5°} = 46.3300 - 6.7605C_{\mathrm{NaI}}$$

It was concluded that the linear effect of salt concentration on the dispersion constant was due probably to a shift in the association of the solvent (hydrol–polyhydrol equilibrium) or an association between solvent and salt, and that the much greater effect of added salt at 0.5° was due to a dissociation or association of the gelatin molecule.

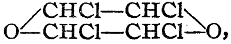
Based on the formulation of Lucas, it was shown that two and only two optically active species exist in gelatin solutions or gels.

GENEVA, N. Y. RECEIVED JULY 5, 1935

[CONTRIBUTION FROM THE DAIRY CHEMISTRY LABORATORY OF THE NEW YORK STATE AGRICULTURAL EXPERIMENT STATION]

The Catalytic Chlorination of Dioxane[1]

BY J. J. KUCERA AND D. C. CARPENTER

According to recent investigations,[2] 1,4-dioxane and 2,3-dichlorodioxane on chlorination without catalysts give poor yields of the tetrachlorodioxanes and particularly of the symmetrical isomers  $O\langle{}^{\mathrm{CHCl-CHCl}}_{\mathrm{CHCl-CHCl}}\rangle O$, which are valuable because of their quantitative yield of glyoxal on hydrolysis. Since preliminary experiments with copper, iron, manganese, nickel, tin and iodine chlorides showed that the two latter substances catalyzed the chlorination most vigorously, we have carried out carefully chlorinations using them.

Technical dioxane was purified by distillation, crystallization and a final distillation over sodium. The purified dioxane boiled at 101.5–101.7° and melted at 11°. The usual method of chlorination was employed, the amount of chlorine absorbed being calculated from the increase in weight of the reaction vessel.

Starting with 78.5 g. of dioxane and chlorinating at a temperature of 90°, a yield of 96.6% of the 2,3-dichlorodioxane was obtained, both with stannic chloride (added as 1 g. of $SnCl_2$) and with iodine chloride (added as 1 g. of I) catalyst. The amount of decomposition was negligible. This yield is considerably greater than that (69%) previously reported in the absence of a catalyst.[3]

In the chlorination of 47 g. of the 2,3-dichlorodioxane at 145° using stannic chloride as a catalyst (added as 0.5 g. of $SnCl_2$), the following unsymmetrical tetrachlorodioxanes were obtained: 37 g., b. p. 96° at 14 mm., and 1 g., m. p. 57–58°, together with symmetrical tetrachlorodioxanes: 12 g., m. p. 70° and 6 g., m. p. 143°. This corresponds to a total yield of 83% and a 32% yield of the symmetrical tetrachlorodioxanes. In the run with iodine chloride (added as 1 g. of I) as a catalyst at 145°, and starting with 81.8 g. of 2,3-dichlorodioxane, 68 g. of the unsymmetrical tetrachlorodioxane b. p. 96° at 14 mm., and 2 g., 21 g. and 10 g. of the symmetrical isomers melting respectively at 60, 70 and 143° were obtained. This corresponds to a total yield of 85% and a 33% yield of the symmetrical isomers. In

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(1) Approved by the Director of the New York Agricultural Experiment Station for publication as Journal Paper No. 98.

(2) Butler and Cretcher, THIS JOURNAL, **54**, 2987 (1932); Christ and Summerbell, *ibid.*, **55**, 4547 (1933); Baker, *J. Chem. Soc.*, 2666 (1932).

(3) Böeseken, Tellegen and Henriquez, *Rec. trav. chim.*, **50**, 909 (1931).

corresponding runs without catalysts total yields of 83 and 33% of the symmetrical isomers were obtained. These experiments show that these catalysts have no influence on either the total yield or the total yields of the symmetrical isomers. This is presumably due to the fact that because of the more elevated temperature required for this reaction, the stannic chloride and the iodine monochloride are volatilized and lost from the reaction mixtures despite the presence of a condenser.

Summary

Iodine and tin chlorides are suitable catalysts for the chlorination of dioxane to 2,3-dichlorodioxane, the yield being almost quantitative. Their use is not adapted to the further chlorination of 2,3-dichlorodioxane to tetrachlorodioxane on account of the high temperatures required for the latter reaction at ordinary pressures. The yields of the various tetrachlorodioxanes produced have been recorded.

Geneva, New York Received July 5, 1935

[Contribution from the Chemical Department, University of Toronto]

The Sourness of Acids

By R. M. Beatty[1] and L. H. Cragg

Many attempts have been made in the past to relate the sourness of acids to various other properties such as their hydrogen-ion concentration, normality, vapor pressure, surface tension, etc., but with little success. A fairly complete survey of the literature up to the year 1926 was made by Dietzel.[2] Several important papers were missed in that discussion and further work has been done on the subject since 1926.[3]

In a preliminary paper, F. B. Kenrick[4] showed that the proportion of a phosphate buffer required to bring the *p*H of various acids of the same molar concentration to a fixed value of about 5 is roughly proportional to the sourness of the various acids alone, the sourness being defined as the normality of the hydrochloric acid solution of equal sourness. From this work it appeared that the sourness of an acid might be determined roughly by titration with a phosphate buffer to the shade of bromcresol green indicator corresponding to *p*H 5. To obtain the relative sourness of the acids Kenrick made use of the table of threshold values given by Paul and Bohnen (see Dietzel[2]) and assumed on the basis of a few experiments that the relative sourness of equimolar solutions was roughly independent of the concentration.

The present research was undertaken to test (a) the validity of this assumption, and (b) the accuracy of the conclusion drawn from the preliminary experiments. The *p*H's and total phosphate concentrations of the buffers used were within the ranges of the values possessed by most physiological fluids, such as saliva and blood serum.

Procedure

Equally sour solutions of various acids were prepared and the *p*H's of these solutions with addition of varying proportions of buffer were determined.

In all experiments (with the exception of those in section 2) hydrochloric acid was used as the standard and each of the other acids was altered in concentration until it had the same sourness as the hydrochloric acid.

The following precautions were taken in tasting the solutions in order to make the comparisons as accurate as possible.

(a) The nose was closed by a pair of balance forceps to prevent the interference of odors.

(b) For the more dilute acids 20 cc. of solution was taken into the mouth for each test and between each the mouth was rinsed with distilled water; in the case of acids which were sour enough to "set the teeth on edge" the tongue was dipped into a crucible of the liquid.

(c) In the final comparisons the effect of personal equation was reduced by placing the solutions in two tubes indistinguishable except for a hidden marking, and recording the decisions before re-identifying the tubes. These comparisons were continued until after seven tests there was no definite preponderance of choice of one as the sourer.[5]

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[1] Holder of a Bursary from the National Research Council of Canada, 1931.

[2] Dietzel, *Kolloid-Z.*, **40**, 174 (1926).

[3] Special reference might be made to the following: Corin, *Arch. biol.*, **8**, 121 (1888); Becker and Herzog, *Z. physiol. Chem.*, **52**, 496 (1907); Liljestrand, *Arch. neerland. physiol.*, **7**, 532 (1922); Taylor, *Protoplasma*, **10**, 98 (1930).

[4] F. B. Kenrick, *Trans. Roy. Soc. Can., III*, [3] **25**, 227 (1931).

[5] Opinions as to the sourness of an acid vary slightly but definitely from one taster to another; consequently, although with accumulated experience (Cragg) small differences such as that between values for acetic acid equisour to 0.0025 *M* HCl (0.0070 in 3b and 0.0065 in 1) can now be reduced, it has been thought advisable to confine the data to the observations of one individual (Beatty in 1931).

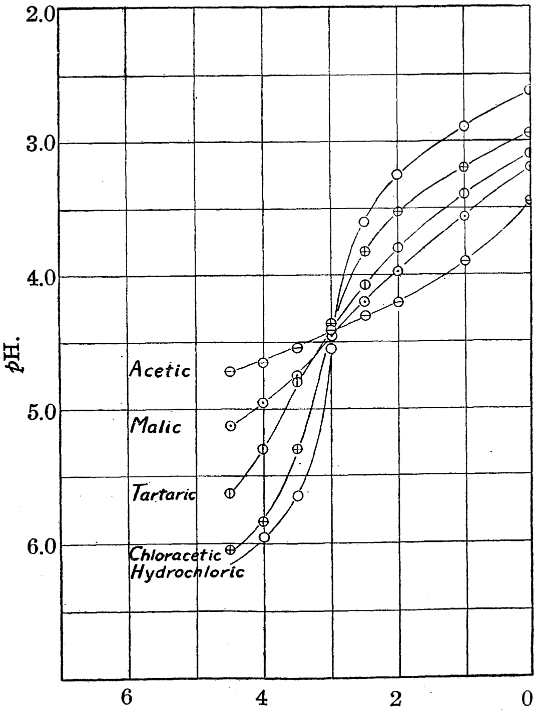
The pH's of the various solutions were determined electrometrically with a Leeds and Northrup potentiometer and a cell of the type

Hg/HgCl, KCl (satd.)/acid solution + quinhydrone/Pt

In some of the experiments a gold electrode was used; it was found that platinum and gold gave the same results, but the platinum required cleaning less frequently.

Experimental Results

1. Various Acids.—Solutions of chloroacetic, tartaric, acetic and malic acids were adjusted by dilution to a sourness equal to that of 0.0025 *M* hydrochloric acid (*M* = moles per liter). These solutions were titrated with a phosphate buffer of pH 6.9, made up as follows: 3.240 g. of sodium dihydrogen phosphate $NaH_2PO_4 \cdot H_2O$, 0.480 g. of disodium hydrogen phosphate $Na_2HPO_4 \cdot 12H_2O$, 10 cc. of approximately normal sodium hydroxide solution, made up to one liter with distilled water. The results are given in Fig. 1.

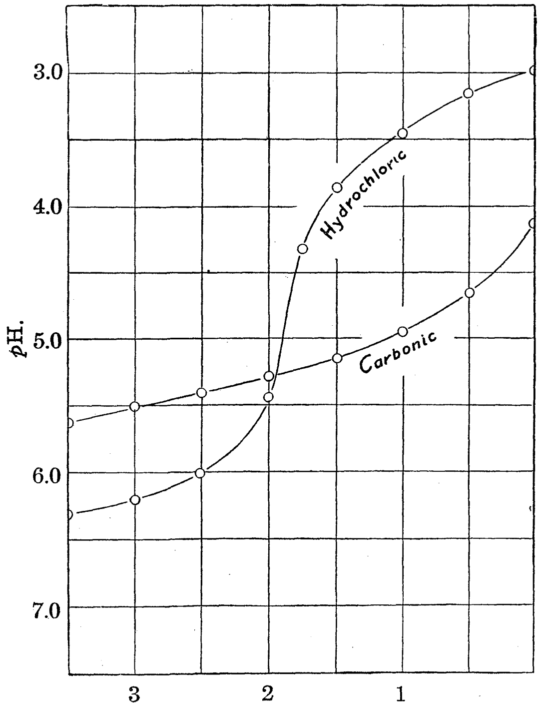


Cc. of buffer (pH 6.9) added to 15.0 cc. of acid.

Fig. 1.—Concentration *M*: hydrochloric, 0.0025; chloroacetic, 0.0028; tartaric, 0.0016; malic, 0.0021; acetic, 0.0065.

2. Saturated Carbon Dioxide Solution.—When comparing hydrochloric acid and carbon dioxide solutions it was found advantageous to adjust the concentration of the hydrochloric acid solution. As the very peculiar taste of carbon dioxide solutions made comparison difficult, attempts were made to imitate the prickling sensation by adding thymol, chloroform, capsicum, oil of cloves, etc., to the hydrochloric acid. Although the prickling could be duplicated to a certain extent in this way, it was found that the sensation gradually increased in intensity so that when enough of the substance in question was added to imitate the immediate sensation characteristic of carbon dioxide solution, the liquid in a few seconds became too painful to retain in the mouth; when less was added the effect was too slow in coming. Attempts to imitate this sensation by supersaturating the hydrochloric acid with nitrous oxide were also unsuccessful. Finally, however, 0.0013 *M* hydrochloric acid was chosen as having about the same sourness as a saturated solution of carbon dioxide (0.0361 *M* from solubility data). The buffer used was the same as in section 1.

The results are shown in Fig. 2. Each point on the curve for carbonic acid was determined with a freshly made solution.



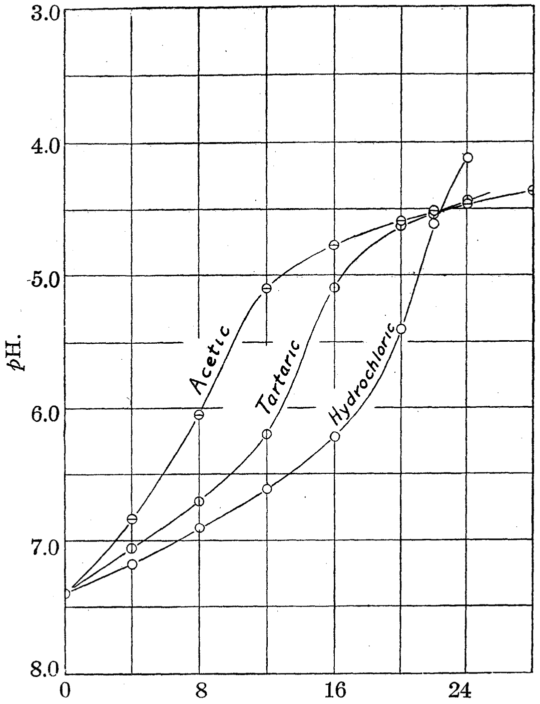
Cc. of buffer (pH 6.9) added to 15.0 cc. of acid.

Fig. 2.—Concentration *M*: hydrochloric, 0.0013; carbonic, 0.0361.

3. Equisour Acid Solutions at Various Concentrations.—In these experiments equisour hydrochloric, acetic and tartaric acid solutions (representative of strong and weak monobasic acids and dibasic acids, respectively) were used with a buffer of pH 7.4, ten times as dilute as that of section 1.[6]

In each set of experiments the concentrations of acetic and tartaric acids were chosen so that the acids were equisour to the hydrochloric acid used in that set. The acids were added to a measured volume of buffer.

The results are summarized in Figs. 3a, b, c, d and e.

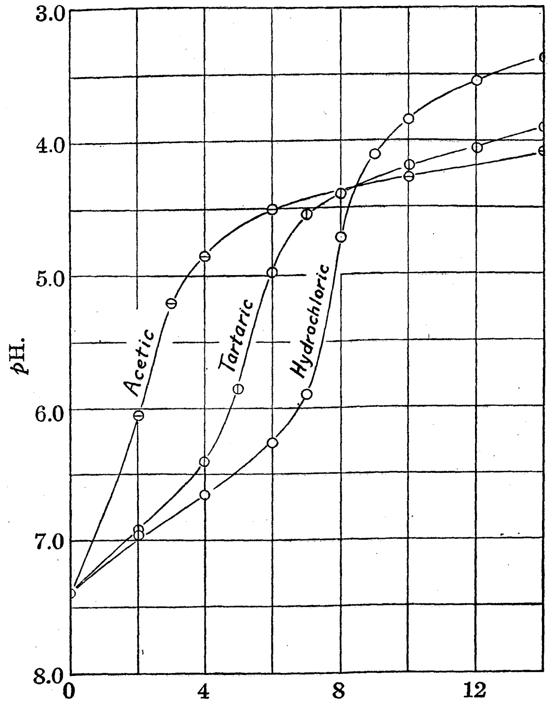


Cc. of acid added to 10.0 cc. of buffer.

Fig. 3(a).—Concentration M: hydrochloric, 0.0010; tartaric, 0.0006; acetic, 0.0022.

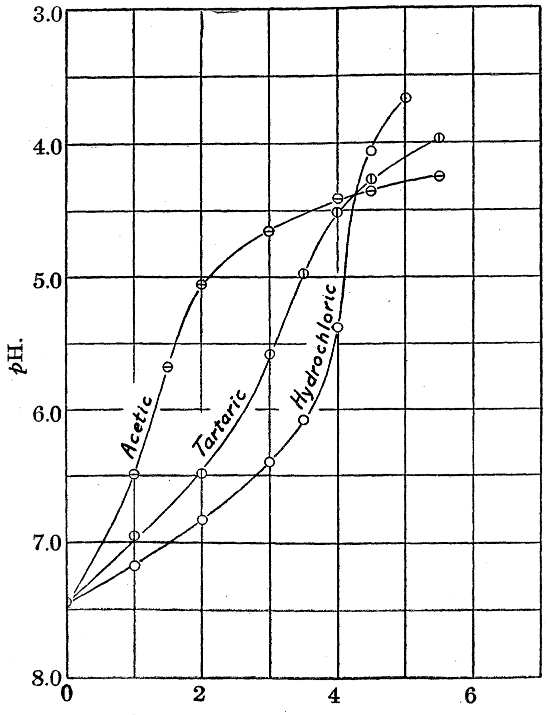
Discussion

When 0.0025 M hydrochloric acid and the various equisour acid solutions are titrated with buffer of pH 6.9, the titration curves cross at a pH of 4.40 to 4.45 (see Fig. 1), *i. e.*, it requires the same amount of buffer to bring the pH of the different acids to pH 4.4. The position of this point is not affected by moderate changes in the pH and concentration of the buffer, for from Fig. 3b the curves still cross at pH 4.4 when acids of the same concentration as were used in section 1 are titrated with a buffer ten times as dilute and with a pH of 7.4. Furthermore, its position is constant even when the concentrations



Cc. of acid added to 10.0 cc. of buffer.

Fig. 3(b).—Concentration M: hydrochloric, 0.0025; tartaric, 0.0016; acetic, 0.0070.



Cc. of acid added to 10.0 cc. of buffer.

Fig. 3(c).—Concentration M: hydrochloric, 0.0050; tartaric, 0.0030; acetic, 0.0140.

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[6] 0.3240 g. of $NaH_2PO_4 \cdot H_2O$, 0.0480 g. of $Na_2HPO_4 \cdot 12H_2O$, and 2.0 cc. of approximately normal NaOH solution, all made up to one liter with distilled water.

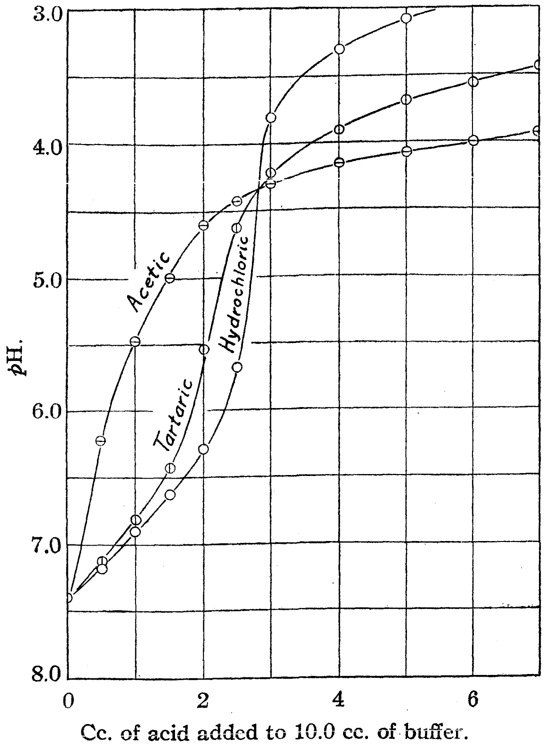

Fig. 3(d).—Concentration *M:* hydrochloric, 0.0075; tartaric, 0.0043; acetic, 0.024.

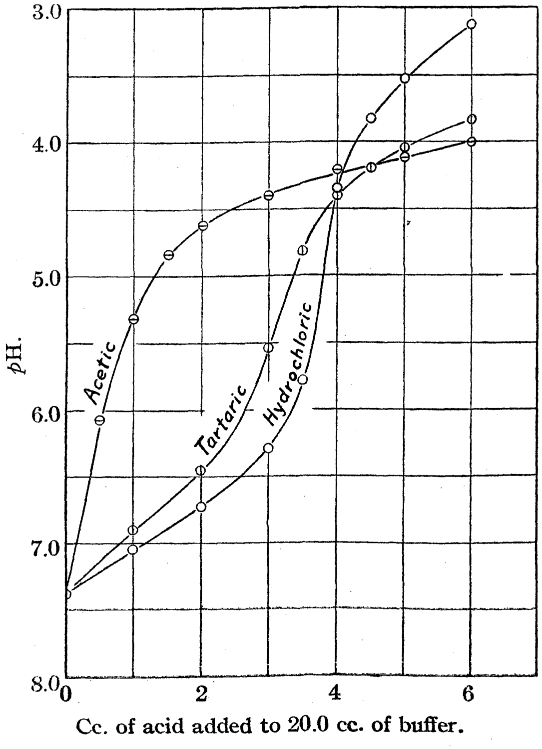

Fig. 3(e).—Concentration *M:* hydrochloric, 0.0100; tartaric, 0.0055; acetic, 0.045.

of the acids used are varied over almost the whole range of taste perception (see Table I).

TABLE I

Fig. no.	Concn. of HCl (standard), *M*	*p*H at intersection
3a	0.0010	4.5
3b	.0025	4.4
3c	.0050	4.4
3d	.0075	4.4
3e	.0100	4.2–4.4[a]

[a] The unpleasant sensation caused by acids of this concentration in the mouth makes judgment uncertain and it is very difficult to make an accurate comparison with the tongue dipping into the liquid.

It will be noted that the titration curves for hydrochloric acid and equisour carbon dioxide solution do not cross at *p*H 4.4, but at 5.3. We do not know whether this deviation indicates an exception to the rule or is due to the difficulty in tasting carbon dioxide solutions referred to in Section 2.

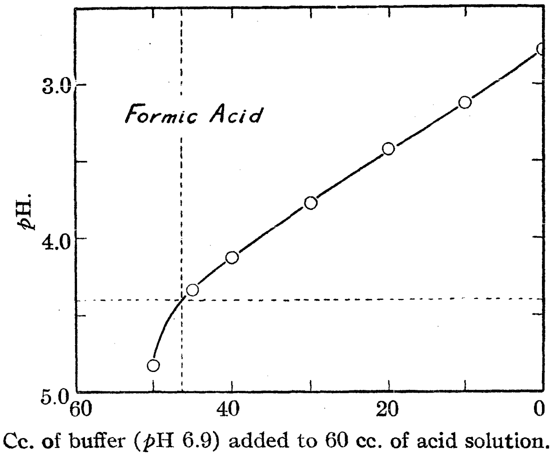

Fig. 4.

These results show the very considerable degree of accuracy of the statement that the volume of buffer required to bring a given volume of an acid to a *p*H of 4.4 (Kenrick said "about 5") is proportional to its sourness. This is illustrated for acetic, tartaric and hydrochloric acids in Table II.

Acids more sour than 0.0100 *M* hydrochloric and less sour than 0.0010 *M* hydrochloric[7] cannot be compared by taste measurements, so that these results cover the whole range of measurable sour taste. They may be summed up by the formula $S = x/470$, where S is the sourness of the acid and x is the volume in cc. of the buffer required to bring 1 cc. of the acid to *p*H 4.4.

(7) Paul and Bohnen (see Dietzel[2]) consider this the threshold value for hydrochloric acid.

TABLE II

Fig. no.	Concentration, M Acetic	Concentration, M Tartaric	Sourness = normality of equisour HCl, M	Vol. buffer to bring 1 cc. acid to pH 4.4 Calcd. from figs.	Vol. buffer / Sourness
	M = moles per liter				
3a	0.0022	0.0006	0.0010	0.463	46 × 10
3b	.0070	.0016	.0025	1.18	47
3c	.0140	.0030	.0050	2.35	47
3d	.024	.0043	.0075	3.54	47
3e	.045	.0055	.0100	5.0 approx.	50[a]

[a] When checking the pH curves of 3e it was found that it required 4.15 cc. of buffer to bring 20 cc. of 0.0100 M hydrochloric acid to pH 4.4 rather than 4.0 cc., thus making the constant 480 approximately. The curves however still did not cross at a common point. This was attributed to the difficulty of making taste comparisons at this concentration. After trying acetic acid solutions of various concentrations, it was estimated that a solution 0.0038 M would give a titration curve crossing at pH 4.4, approximately. It is interesting to note that when plotted on Fig. 5, this point gives a continuation of the curve for acetic acid more similar in shape to that for tartaric acid.

Since it has been shown that changing the concentration and pH of the buffer within certain limits does not affect the validity of this relation the formula can be extended to take account of small variations in the buffer used; thus $S = x/K$ where K is a constant characteristic of the buffer.

Example: To Measure a Sourness by Titration.—Formic acid was chosen because it had not been used in the preceding experiments. The constant K for the buffer of pH 6.9 used in Sec. 1 can be calculated from the results in Fig. 1: $S = 0.0025$, $x = 3/15$ and therefore $K = x/S = 80$.

A formic acid solution (0.0090 M) was titrated with the buffer of pH 6.9 with the results shown in Fig. 4. From this curve it is seen that 60 cc. of acid required 46.5 cc. of buffer, and $S = 46.5/(60 \times 80) = 0.0097$.

The actual sourness of this formic acid solution was measured by Beatty in 1931 and found to be 0.0100. Thus even for a sourness as high as 0.0100, the two values agree to within 3%.

These results also enable us to verify the assumption that the relative sourness of equimolar solutions is independent of concentration. Fig. 5 is plotted from the data of 3a, b, c, d and e. The curves give the sourness of acetic and tartaric acids at various molar concentrations. It is obvious that if these curves were straight lines the assumption would be exactly true. As it is the curves differ very little from straight lines up to a sourness of 0.0075, beyond which tasting becomes difficult. The assumption is therefore approximately true over the whole range of accurate tasting.

This research was carried out at the suggestion and under the direction of Dr. F. B. Kenrick.

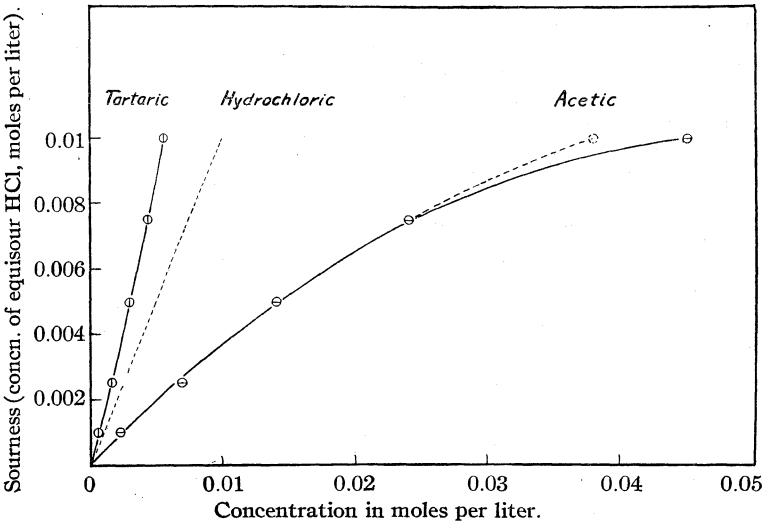

Fig. 5.—Sourness of acetic and tartaric acid solutions (Beatty).

Summary

The sourness of a solution being defined as the normality of an equally sour hydrochloric acid, it has been established for several typical acids that the sourness of an unbuffered acid solution is expressed by x/K, where x is the volume of a phosphate buffer required to bring a unit volume of the acid to a pH of 4.4 and K is a constant characteristic of the buffer used.

This relation has been verified for buffers of pH from 6.9 to 7.4 and of total concentration of anhydrous sodium phosphates from 0.04 to 0.35% by weight—within which ranges most physiological liquids lie.

TORONTO, ONTARIO, CANADA RECEIVED APRIL 30, 1935

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

The Sensitized Decomposition of Hydrogen with Electrons of Controlled Energy

BY GEORGE GLOCKLER AND LLOYD B. THOMAS[1]

I. Introduction

The use of electrons of known energy as activating agents for chemical reactions has been studied by one of us[2,3] in the case of hydrogen and oxygen. In this paper we wish to report further experiments on the decomposition of hydrogen in the presence of mercury using electrons of controlled speed as activating agents. This reaction is the analog of the Cario and Franck[4] experiment substituting for the incident radiation (λ = 2537 Å.) electrons of definite voltage. The general basis of studying such electron activated reactions is to elucidate mechanisms for such reactions as are produced in electric fields (ozonizers) and by alpha particles[5] and to compare reactions activated by various agents.

The photosensitized decomposition of hydrogen can be described best by the steps

$$h\nu\ (2537\ \text{Å.}) + \mathrm{Hg}(6^1\mathrm{S}_0) \longrightarrow \mathrm{Hg}(6^3\mathrm{P}_1)$$
$$\mathrm{Hg}(6^3\mathrm{P}_1) + \mathrm{H}_2(^1\Sigma_g^+) \longrightarrow 2\mathrm{H(atoms)} + \mathrm{Hg}(6^1\mathrm{S}_0)$$
$$2\mathrm{H(atoms)} + \mathrm{CuO(solid)} \longrightarrow \mathrm{H_2O(liq.)} + \mathrm{Cu(solid)}$$

The last reaction simply serves as a means of removing hydrogen atoms so that the whole process may be followed by a pressure decrease. From this photochemical reaction one would predict that the corresponding electron-activated reaction should be

$$\mathrm{E}^-(4.9\ \text{e.v.}) + \mathrm{Hg}(6^1\mathrm{S}_0) \longrightarrow \mathrm{Hg}(6^3\mathrm{P}_1)$$
$$\mathrm{Hg}(6^3\mathrm{P}_1) + \mathrm{H}_2(^1\Sigma_g^+) \longrightarrow 2\mathrm{H(atoms)} + \mathrm{Hg}(6^1\mathrm{S}_0)$$
$$2\mathrm{H(atoms)} + \mathrm{CuO(solid)} \longrightarrow \mathrm{H_2O(liq.)} + \mathrm{Cu(solid)}$$

Electrons of 4.9 e. v. energy should dissociate hydrogen molecules in the presence of mercury vapor. Since it is known that electrons in the absence of mercury atoms must have 11.7 e. v. energy[2,6] before they can dissociate molecular hydrogen, it should be easy to detect the effect of mercury atoms on the decomposition of hydrogen when induced by electrons. The pressure decrease should happen at 4.9 instead of 11.4 volts.

The results of the experiments described in this paper are not in accordance with this prediction. We find that *at low pressures (H_2 at 0.02 mm. and Hg at 0.002 mm.) decomposition starts at 7.7 volts.* The reasons for this difference will be given below.

II. Experimental Procedure and Results

The apparatus used is shown in Fig. 1. The experimental tube used is the sixth one developed in this work. The earlier ones were discarded for various reasons. They are described in detail elsewhere.[1] It is important in this work to produce a copious stream of electrons from a filament of as low a temperature as can be attained. The filament must not heat up the copper oxide surface. A hot copper oxide surface would readily be reduced by molecular hydrogen, entailing a large background of pressure drop, which would be very undesirable. The filament was made of nickel, oxide covered (9 mm. long, 0.5 mm. wide and about 0.1 mm. thick) and required only 1.5 amperes heating current. The filament drop was less than 0.4 volt so that less than 0.6 watt was consumed. Since only the central portion of the filament was hot enough to emit electrons, it delivered electrons of nearly uniform velocity. The electron current to the plate was of the order of 50 microamperes depending on the accelerating voltage. Since very little heat is evolved by a filament of this kind no large background of pressure drop was observed and the Pirani gage showed very little zero drift, *i. e.*, pressure drop at "zero" accelerating voltage. The wire of the Pirani gage was a tungsten filament 5 cm. long and 0.025 mm. thick. The glass tube carrying this wire concentrically was of 8 mm. inside diameter. A six-volt storage battery connected in series with a milliammeter and a dial resistance box (10,000 ohms) heated the gage to a dull red heat. The fall of potential over the Pirani wire is balanced by the potentiometer using a moderately sensitive galvanometer (5.68×10^4 cm. divisions per volt) with telescope and scale. The rate of pressure change is measured by the rate of drift of the galvanometer. The potentiometer is not read but is used as a convenient means of bringing the galvanometer to the desired position on the scale. If the tungsten wire is allowed to cool or to run a long time without heating strongly its resistance drops markedly so that it cools below red temperature. As adsorbed gases are driven from the filament the wire will assume its original condition. After baking the tube out and setting the apparatus in operation, it required at least two days to reach steady conditions. Even during the calibration measurements some adsorption of gas is noted for the ascending and descending portions of the curves for hydrogen (Fig. 1) do not coincide, but the difference is noted to be very small. A mixture of krypton and hydrogen was also studied and it is seen that the slope of the curve is the same in pure hydrogen or in mixtures containing various amounts of krypton. Kryp-

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(1) This article is based upon a thesis presented to the Faculty of the Graduate School of the University of Minnesota by Lloyd B. Thomas in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Glockler, Baxter and Dalton, THIS JOURNAL, **49**, 58 (1927).

(3) Glockler and Wilson, *ibid.*, **54**, 4544 (1932).

(4) Cario and Franck, *Z. Physik*, **11**, 161 (1922).

(5) S. C. Lind, "The Chemical Effects of Alpha Particles and Electrons," Chemical Catalog Co., New York City, 1928, second edition.

(6) Hughes and Skellett, *Phys. Rev.*, **30**, 11 (1927).

ton was more convenient to use than mercury as foreign gas. Dividing the slope of the pressure *versus* voltage curve by that of the deflection *vs.* voltage curve gives the pressure change per scale division. The former value for hydrogen is 0.480 mm. Hg/volt and the latter is 5.68×10^4 cm./volt so that the sensitivity of the Pirani gage is 8.45×10^{-6} mm. pressure change per cm. scale deflection. In order to determine the validity of this calibration it was checked by an entirely different method. A certain pressure of krypton was led into the apparatus and its volume was reduced by allowing a mercury column to rise in one of the cut-off tubes. The galvanometer deflection was observed for the two positions of the mercury column. The agreement was very good with the deflection predicted from the compression, the slope of the curve (Kr) and the galvanometer sensitivity.

It was found that a well baked out tube would adsorb the water formed during the reaction so that liquid air was not necessary for the removal of the reaction product, although it was used in some of the runs. Hydrogen was introduced through a palladium tube in the usual manner. The applied voltage was read on a "Jewel" precision voltmeter. The volume of the reaction tube to the mercury cut-off was 77.9 cc. The plate galvanometer had a current sensitivity of 3.81×10^{-8} amp./cm. on shunt 1.0 and one-tenth and one-hundredth of this value on shunts 0.1 and 0.01.

It is desired to determine the number of hydrogen molecules decomposed per electron passing between the filament and plate as a function of the energy of the electrons. This relationship may be calculated from the following four readings taken at a series of accelerating potentials: the accelerating voltage as registered by the precision voltmeter, the drift of the galvanometer in the Pirani circuit, the time over which the drift is measured and the current which reaches the plate. From the pressure decrease, the volume of the tube (77.9 cc.) and the temperature (298°), the number of hydrogen molecules disappearing per minute may be calculated.

The detailed calculations and data can be found in another place.[1] The results are shown in Fig. 3 and Table I. The experimental values of the electron energies needed to cause the decomposition of hydrogen with and without mercury atoms as sensitizers are found to be 7.77 and 11.86 e. volts. These values must be corrected for the initial velocity of the electrons.

Initial Velocity Correction.—A variety of methods was tried to determine the initial velocity of the electrons as they leave the filament. The most satisfactory results are obtained by the use of the excitation potential or term value of the ${}^3\Sigma_g^+$ state of hydrogen. This value is known from spectroscopic studies[7–9] to be 11.72 e. volts. On this basis then the correction is 0.14 e. v. and the non-sensitized decomposition happens at 11.72 ± 0.22 e. v. This value is higher than the earlier results[2,6] by 0.28 e. v. Since the spectroscopic term is more accurate than the values based on any current-potential experiment, the present figure is greatly to be preferred. It is well known that the matter of obtaining velocity corrections in an unambiguous manner is difficult. We have studied five different methods of obtaining the initial velocity correction. They gave values which would lower the result (11.86 e. v.) by 0.4 to 1.0 e. volt. However, every method has its drawbacks. Either a foreign gas or a gas mixture (H_2 and He or H_2 and Hg) has to be employed or the method depends on some complicated use of current-potential relations. After an extended and time-consuming study of the situation, we came to the conslusion that the use of the spectroscopic term value of ${}^3\Sigma_g^+$ of hydrogen was the most satisfactory way of eliminating the initial velocity correction of the electrons.

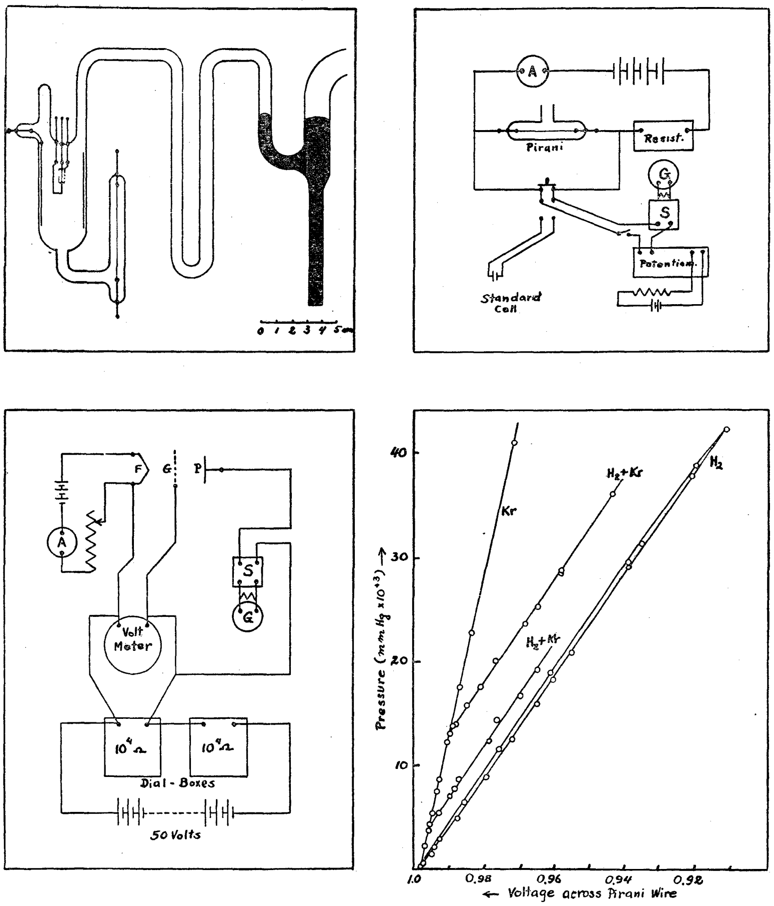

Fig. 1.—Apparatus: reaction tube; Pirani gage; electrical connections for reaction system and Pirani gage calibration curves.

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(7) O. W. Richardson, "Molecular Hydrogen and Its Spectrum," Yale University Press, New Haven, Conn., 1934, p. 327.

(8) W. Jevons, "Band Spectra of Diatomic Molecules," The University Press, Cambridge, England, 1932, p. 268.

(9) R. S. Mulliken, "Interpretation of Band Spectra," Part III, *Review of Modern Physics*, **4**, 1 (1932).

TABLE I

SUMMARY OF EXPERIMENTAL RESULTS: NON-SENSITIZED AND MERCURY SENSITIZED DECOMPOSITION OF HYDROGEN

Run	Pressure, mm. Hg × 10^3 H_2	Hg	Beginning of pressure drop, volts (uncorr.)
1	4.6		12.12
2	11.3		12.08
3	10.4		12.02
4	11.2		11.69
5	12.7		11.65
6	27.8		11.58
			11.86 ± 0.22
7	2.1	1.85	8.24
8	5.9	1.85	7.46
9	10.3	1.90	7.70
10	15.4	2.00	7.44
11	25.2	2.30	7.44
12	47.3	2.20	7.68
13	6.2	1.70	7.86
14	11.7	1.85	7.76
15	17.3	1.60	7.84
16	34.3	1.60	8.24
			7.77 ± 0.23

III. Discussion of Results

The Non-Sensitized Reaction.—The higher energy states of hydrogen molecules which need to be considered in the interpretation of these experiments are given in Table II and Fig. 2.

TABLE II

ENERGY STATES OF HYDROGEN MOLECULE

State	Term-values (zero vibration)	Excitation potential (Franck–Condon)	Possible transition
$(1s^2)\ {}^1\Sigma_g^+$	Zero		
$(2p)\ {}^3\Sigma_u^+$	Repulsive	8.5–10.4	Two H atoms
$(2p)\ {}^1\Sigma_u^+$	11.12 e. v.	11.4–12.6	Radiation
$(2p)\ {}^3\Pi_u$	11.72 e. v.	11.7–13.0	Metastable H_2
$(2s)\ {}^3\Sigma_g^+$	11.73 e. v.	11.6–12.4	Continuum + 2H
$(2p)\ {}^1\Pi_u$	12.22 e. v.	12.2–13.6	Radiation
$(2s)\ {}^1\Sigma_g^+$	12.25 e. v.	12.0–13.4	Metastable H_2

Electrons can transfer normal hydrogen molecules into the various excited states shown above.[10] If the excited state is an odd singlet state then the excited molecule can return to normal with emission of radiation. Such transitions will lead to chemical action with only low probability for it would mean that the excited molecule during its short life will either have to make an impact with another normal molecule or the wall in order that decomposition occurs. The chance for reactions of the type

$$H_2({}^1\Sigma_u^+) + H_2({}^1\Sigma_g^+) \longrightarrow \text{H atoms etc.}$$
$$H_2({}^1\Pi_u) + H_2({}^1\Sigma_g^+) \longrightarrow \text{H atoms etc.}$$

most likely is much smaller than the return to the normal state with radiation

$$H_2({}^1\Sigma_u^+) \longrightarrow H_2({}^1\Sigma_g^+) + h\nu\ (1109.3\ \text{Å.})$$
$$H_2({}^1\Pi_u) \longrightarrow H_2({}^1\Sigma_g^+) + h\nu\ (1009.5\ \text{Å.})$$

If the life of an excited hydrogen molecule is of the order of 10^{-7} seconds it can readily be calculated that it will make only very few collisions (0.01) during its life. At 0.01 mm. pressure, its collision diameter would have to be many times the kinetic theory diameter of the normal molecule in order that these states would be involved in the reaction. It can also readily be shown that the average excited molecule cannot reach the wall of the reaction tube during its life. It would appear then that the excited states ${}^1\Sigma_u^+$ and ${}^1\Pi_u$ do not contribute to the chemical reaction.

The repulsive state ${}^3\Sigma_u^+$ could be reached by impact with electrons having 8.5 or 10.5 e. v. energy or any value between these limits (Franck–Condon principle). However no such transfer is observed and we conclude that this step is of very low probability

$$H_2({}^1\Sigma_g^+) + E^-(8.5 - 10.5\ \text{e. v.}) \longrightarrow \text{No reaction}$$

The last excited state mentioned in **Table II**, $(2s)\,{}^1\Sigma_g^+$ with a term value and excitation potential of 12.25 e. v. is higher than two other states which appear to contribute to reaction. The state appears to have the desired property of a long life, for it cannot combine with any lower triplet nor singlet state and hence is metastable. It should contribute to reaction when the impinging electrons reach the appropriate energy.

The most likely states which are responsible for the initial pressure decrease in our reaction are the states $(2p)^3\Pi_u$ and $(2s)^3\Sigma_g^+$. Being triplet states they cannot combine with the normal state which is a singlet state and hence they cannot radiate and return to normal. Nor can the state ${}^3\Pi_u$ interact with the repulsive triplet state ${}^3\Sigma_u^+$ on account of the "odd-even" selection rule. Hence this state ($(2p)^3\Pi_u$) is metastable. Hydrogen molecules in this state should readily reach the wall and there react with the copper oxide, reducing it. But the ${}^3\Sigma_g^+$ state also should be involved in the chemical reaction. While it can radiate the continuum[11,12] when the molecule goes to the repulsive state it also produces two hydrogen atoms of high kinetic energy which should readily reduce copper oxide producing a

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(10) Condon and Smyth, *Proc. Nat. Acad. Sci.*, **14**, 871 (1928).

(11) Winans and Stueckelberg, *ibid.*, **14**, 867 (1928).

(12) Finkelnburg and Weizel, *Z. Physik*, **68**, 577 (1931).

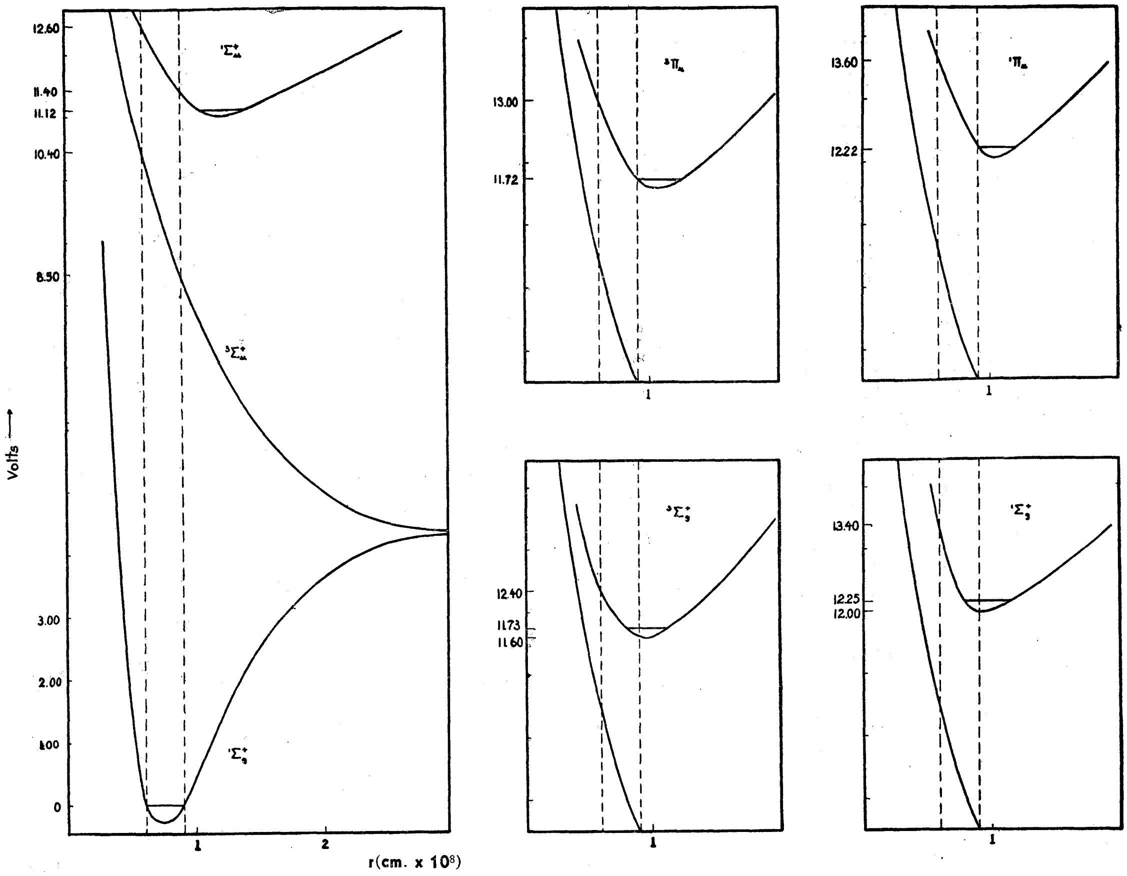

Fig. 2.—The one and two quantum states of hydrogen molecule.

pressure drop under our experimental conditions. The reactions taking place are

$$H_2(^1\Sigma_g^+) + E^-(11.72 \text{ e. v.}) \longrightarrow H_2(^3\Pi_u) + E^-(\text{zero e. v.})$$
$$H_2(^3\Pi_u) + CuO(\text{solid}) \longrightarrow H_2O(\text{liq.}) + Cu(\text{solid})$$

and

$$H_2(^1\Sigma_g^+) + E^-(11.73 \text{ e. v.}) \longrightarrow H_2(^3\Sigma_g^+) + E^-(\text{zero e. v.})$$
$$H_2(^3\Sigma_g^+) \longrightarrow H_2(^3\Sigma_u^+) \longrightarrow 2H \text{ atoms} + \text{Kin. Energy} + \text{continuum}$$
$$2H \text{ atoms} + CuO(\text{solid}) \longrightarrow H_2O(\text{liq.}) + Cu(\text{solid})$$

No choice is possible between these two reaction mechanisms. Both should happen. They have nearly the same electron energy and their excitation potentials are nearly the same. Hence it appears reasonable to consider 11.72 e. v. to be the voltage for onset of pressure drop. We calculate the initial velocity correction to be 11.86 − 11.72 = 0.14 e. v. as was noted above.

A change in slope in the curves (*M/E vs.* electron speed) is noticeable at about 15.5 e. v. Ionization is known to set in at this voltage. The slope decreases, showing lessened probability for reaction. When ions are produced their recombination is necessarily involved in the reaction mechanism. At the low pressures used such recombination between hydrogen mole ions and electrons would be very infrequent and reaction of the cluster type[5] would not happen readily. The reaction observed is most likely due to excited states which are still produced with some probability even at voltages somewhat higher than their term values. Hydrogen mole ions might be thought of as ionic catalysts. However, they would not be expected to attract greatly hydrogen molecules of small polarizability nor would these molecules be greatly distorted in the field of the ion. Hence at low pressures of hydrogen ionization does not produce increased chemical action.

The Mercury Sensitized Reaction.—From Table I it is seen that the presence of mercury lowers the voltage at which reaction sets in from 11.86 to 7.77 e. v. (uncorr.). Applying the correction just determined we find that the mercury-sensitized reaction occurs at 7.77 − 0.14 = 7.63 e. v. and not at 4.86 e. v. as might be predicted from the photosensitized reaction. It must mean that at low pressures the 6^3P (4.9 e. v.) state of mercury is inefficient in producing reaction. The energy states of the mercury atom which must be considered in the interpretation of the experimental results are the following: $6^3P_0(4.64)$, 6^3P_1 (4.86), $6^3P_2(5.43)$, $6^1P_1(6.67)$, $7^3S_1(7.69)$ and 7^1S_0 (7.86) e. v.

Since the metastable states of mercury 6^3P_0 and 6^3P_2 do not assist the reaction, we must suppose that the efficiency of their direct production by electron impact is small. If they are produced then mercury atoms in these metastable states should be able to transfer energy to hydrogen molecules by collisions of the second kind with consequent dissociation. That these two metastable states are indeed much less readily produced by electron impact can be seen from current-potential curves obtained by Franck and Einsporn[13] and Foard.[14] The 6^3P_1(4.9 e. v.) state, however, is not metastable and hence can return to normal with emission of 2537 Å. Hence this state will only be efficient if the excited mercury atoms during their short life can make a sufficient number of impacts with hydrogen molecules. At low enough hydrogen and mercury pressures an insufficient number of mercury atoms may be created and not enough impacts may happen to produce a measurable pressure change. We believe that these conditions are maintained in our experiments. Similarly therefore the states 6^1P_1(6.67 e. v.) and 7^1S_0(7.86 e. v.) are inefficient. The only remaining state is the term 7^3S_1(7.69 e. v.). While it also will radiate to the three ^3P states, only two of these are metastable and will have a sufficiently long life to interact with hydrogen molecules in accordance with the following reaction mechanism.

$$E^-(7.7\text{ e. v.}) + \text{Hg}(6^1S_0) \longrightarrow \text{Hg}(7^3S_1) + E^-(0\text{ e. v.})$$
$$\text{Hg}(7^3S_1) \longrightarrow \text{Hg}(6^3P_{0,2}) + h\nu\ (5461\text{ or }4047\text{ Å.})$$
$$\text{Hg}(6^3P_0) + H_2(^1\Sigma_g^+) \longrightarrow 2\text{H(atoms)} + \text{Hg}(6^1S_0) + 0.3\text{ e. v. K. E.}$$
$$\text{Hg}(6^3P_2) + H_2(^1\Sigma_g^+) \longrightarrow 2\text{H(atoms)} + \text{Hg}(6^1S_0) + 1.1\text{ e. v. K. E.}$$
$$2\text{H(atoms)} + \text{CuO(solid)} \longrightarrow H_2\text{O(liq.)} + \text{Cu(solid)}$$

It is seen that the term value (7.69 e. v.) of the 7^3S_1 state of mercury is closer to our experimental onset voltage (7.63 e. v.) than any other possible term value and the above mechanism affords a reasonable picture of the steps leading to reaction.

There have been mentioned in the literature[13,15] some energy states of the mercury atom which do not fit into the spectroscopic set of term values. These states were found by critical potential methods. The values of interest here are 7.1 and 7.45 e. v. We have not involved these states in our considerations of a reaction mechanism for the sensitized reaction because we feel that they are not close enough to our experimental value for the beginning of the reaction. Similarly we have excluded the possible formation of mercury hydride in a triple collision which might happen at 7.05 e. v.[9]

$$E^-(7.05\text{ e. v.}) + \text{Hg}(6^1S_0) + H_2(^1\Sigma_g^+) \longrightarrow \text{HgH}(^2\Pi) + \text{H atom} + E^-(0)$$

However the formation of mercury hydride may be involved in the reaction

$$\text{Hg}(6^3P_0) + H_2(^1\Sigma_g^+) \longrightarrow \text{HgH}(^2\Sigma^+) + \text{H atom} + 0.67\text{ e. v. K. E.}$$
$$\text{Hg}(6^3P_2) + H_2(^1\Sigma_g^+) \longrightarrow \text{HgH}(^2\Sigma^+) + \text{H atom} + 1.43\text{ e. v. K. E.}$$

We see that greater amounts of kinetic energy are liberated when mercury hydride molecules are involved. On the well-known principle that collisions of the second kind happen with greatest probability when the amount of energy going to kinetic energy is smallest, it is seen that the $^3P_0$ state is more likely to lead to reaction.

The 7^3P States of Mercury.—From Fig. 3 we can see that there is a change in slope at about 8.5 e. v. in the curve (*M/E vs.* voltage). This kink would indicate a new process becoming of importance. Indeed we notice that the 7^3P states of mercury atom have the term values 8.57, 8.61 and 8.78 e. v. We therefore interpret the reaction in the following way.

$$E^-(8.57\text{ e. v.}) + \text{Hg}(6^1S_0) \longrightarrow \text{Hg}(7^3P_0) + E^-(0\text{ e. v.})$$
$$\text{Hg}(7^3P_0) \longrightarrow \text{Hg}(7^3S_1) + h\nu\ (13951\text{ Å.})$$
$$\text{Hg}(7^3S_1) \longrightarrow \text{Hg}(6^3P_{0,2}) + h\nu\ (5461\text{ or }4047\text{ Å.})$$
$$\text{Hg}(6^3P_0) + H_2(^1\Sigma_g^+) \longrightarrow 2\text{H(atoms)} + \text{Hg}(6^1S_0) + 0.3\text{ e. v. K. E.}$$
$$\text{Hg}(6^3P_2) + H_2(^1\Sigma_g^+) \longrightarrow 2\text{H(atoms)} + \text{Hg}(6^1S_0) + 1.1\text{ e. v. K. E.}$$
$$2\text{H(atoms)} + \text{CuO(solid)} \longrightarrow H_2\text{O(liq.)} + \text{Cu(solid)}$$

The mercury atoms reach the metastable states by two radiative transitions. We have not looked for the radiations involved for the presence of the filament makes the discovery of a faint radiation a matter of great difficulty.

However, we have been able to explain the reactions studied on the basis of the energy level

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(13) Franck and Einsporn, *Z. Physik*, **2**, 18 (1920).

(14) Foard, *Phys. Rev.*, **35**, 1186 (1930).

(15) Messenger, *ibid.*, **28**, 962 (1926).

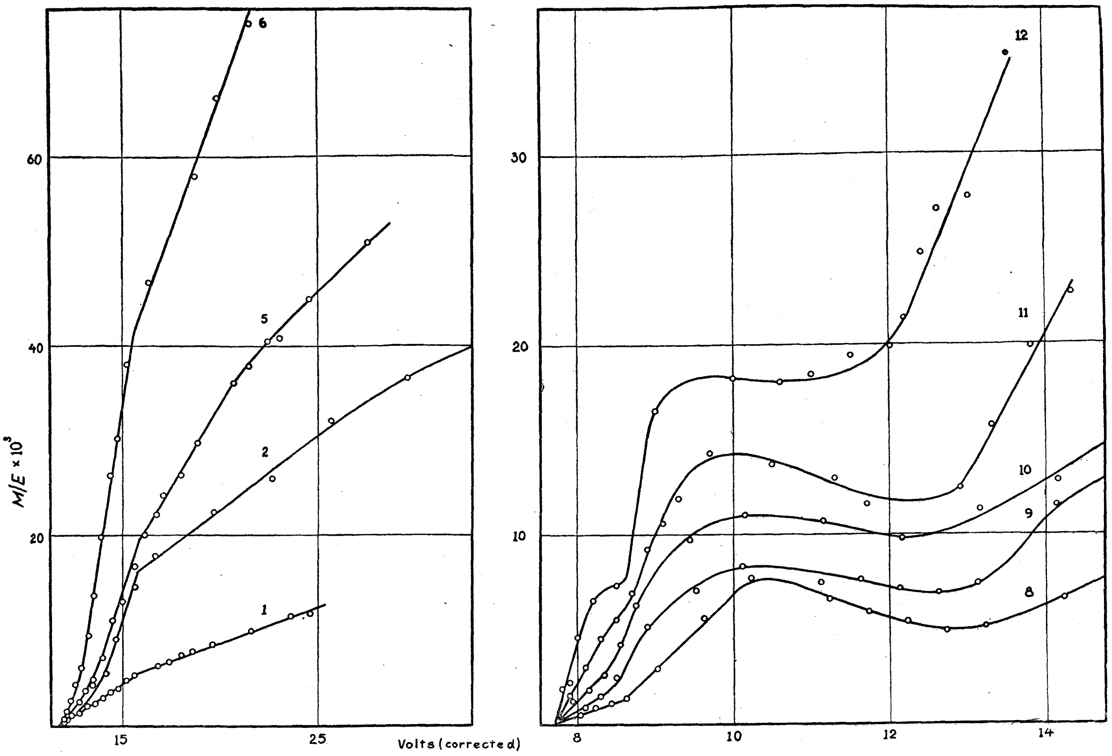


Fig. 3.—Molecules of hydrogen reacting per electron as a function of electron speed; non-sensitized and sensitized by mercury atoms.

diagrams of the substances involved. While we hope to deal with more complicated cases later, we expect to study next the effects of increasing pressure for the case reported here. At higher mercury and hydrogen pressures onset of reaction should appear at 4.9 e. v., corresponding to the original Cario–Franck experiment.

Abstract

Hydrogen molecules have been dissociated by electrons of known speed using mercury atoms as a sensitizing agent. These reactions are analogous to the photochemical decomposition of hydrogen using $\lambda = 2537$ Å. and mercury (Cario and Franck experiment). From the photochemical case one would predict that 4.9 e. v. electrons should initiate the mercury-sensitized reaction; while without a sensitizer electrons must possess 11.7 e. v. energy. In the present experiment it is found that at low pressures (H_2 at 0.02 mm. and Hg at 0.002 mm.) the short-lived radiative states of mercury (4.9 and 6.7 e. v.) and the well-known metastable states ($6^3P_{0,2}$) are not efficient or are too short-lived to cause reaction. However, electrons of 7.7 e. v. energy can cause dissociation of hydrogen in the presence of mercury. The sequence of reaction is

$$E^-(7.7\text{ e. v.}) + Hg(6^1S_0) \longrightarrow Hg(7^3S_1) + E^-(\text{zero e. v.})$$

$$Hg(7^3S_1) \longrightarrow Hg(6^3P_{0,2}) + h\nu \text{ (5461 or 4047 Å.)}$$

$$Hg(6^3P_{0,2}) + H_2(^1\Sigma_g^+) \longrightarrow 2H(\text{atoms}) + Hg(6^1S_0)$$

$$2H(\text{atoms}) + CuO(\text{solid}) \longrightarrow H_2O(\text{liq.}) + Cu(\text{solid})$$

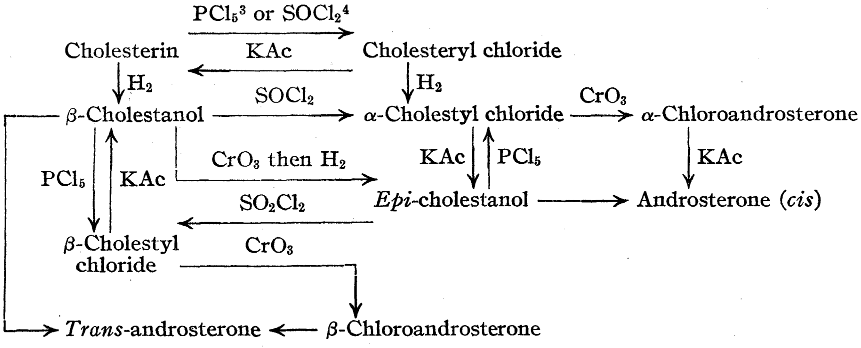
MINNEAPOLIS, MINN. RECEIVED AUGUST 20, 1935

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE AND THE PARKE, DAVIS RESEARCH LABORATORIES OF DETROIT, MICHIGAN]

Androsterone and Related Sterols

BY RUSSELL E. MARKER, FRANK C. WHITMORE AND OLIVER KAMM

In the preparation of androsterone and other physiologically active compounds it is often necessary to change the —OH in the sterols from the *trans-* into the *cis*-form. This was shown by Ruzicka[1] and co-workers in the preparation of *trans* and *cis* androsterone in which they showed that the *cis*-form which is the natural androsterone (*epi*-OH) had about seven times the activity of the *trans* derivative. This conversion into the *epi*-form was brought about by first reducing cholesterin to beta-cholestanol. This was oxidized to beta-cholestanone which was then reduced by hydrogen in butyl ether at 70° according to the method of Vavon and Jakubowicz.[2] This reaction requires two catalytic reductions and an oxidation, which due to the small solubility of the compounds and the large amount of platinum oxide catalyst necessary, is very expensive and time-consuming. To overcome this, advantage is taken of the following scheme to produce the *epi*-form of the sterols in quantity. Also conversion of the *cis*-form back into the *trans*-form can be brought about by these reactions.



When cholesterol is treated with either phosphorus pentachloride or thionyl chloride cholesteryl chloride is formed. This on hydrolysis gives cholesterol with the —OH unchanged. However, if cholesteryl chloride is reduced with platinum oxide and hydrogen, α-cholestyl chloride is formed which on hydrolysis then gives the —OH in the *cis*-form. In the first case there was no Walden inversion in the final product, whereas in the reduced product a Walden inversion occurred in one of the steps.

Whereas when cholesterol is treated with either phosphorus pentachloride or thionyl chloride the same chloride is formed, if beta-cholestanol is treated with thionyl chloride it gives beta-cholestyl chloride and when treated with thionyl chloride alpha-cholestyl chloride. A Walden inversion occurs in one of the halogenations and not in the other. The same is true for *epi*-cholestanol. When this is treated with phosphorus pentachloride it gives alpha-cholestyl chloride but when treated with thionyl chloride it gives beta-cholestyl chloride.

In the hydrolysis of the various chlorides, alpha-cholestyl chloride gives *epi*-cholestanol while beta-cholestyl chloride gives beta-cholestanol.

When alpha-cholestyl chloride is oxidized it gives alpha-chloroandrosterone which apparently is identical to the chloride produced by Butenandt and Dannenbaum[5] by the reduction of an unsaturated chloro ketone isolated from urine. This chloro ketone on hydrolysis gives androsterone. α-Chlorocholanic acid is isolated as a by-product of this oxidation. Since this work was completed Ruzicka and co-workers[6] have prepared α-chloroandrosterone from *epi*-cholestanol.

The authors wish to express their thanks to The Parke, Davis Laboratories, Detroit, Mich., for a grant making this work possible.

Experimental

Cholesteryl Chloride.—This was prepared both by the method of Mauthner[3] by the use of phosphorus pentachloride on cholesterol and by the method of Diels and Blumberg[4] by the action of thionyl chloride on cholesterol. Mixed melting points showed the two products to be identical, m. p. 95° (uncorr.).

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[1] Ruzicka, *Helv. Chim. Acta*, **17**, 1395 (1934).

[2] Vavon and Jakubowicz, *Bull. soc. chim.*, [4] **53**, 584 (1933).

[3] Mauthner, *Monatsh.*, **15**, 87 (1894).

[4] Diels and Blumberg, *Ber.*, **44**, 2848 (1911).

[5] Butenandt and Dannenbaum, *Z. physiol. Chem.*, **229**, 192 (1934).

[6] Ruzicka and co-workers, *Helv. Chim. Acta*, **18**, 998 (1935).

α-Cholestyl Chloride.—(1) By reduction of cholesteryl chloride. Fifty grams of cholesteryl chloride was dissolved in 500 cc. of ether and 2 g. of platinum oxide and 10 cc. of glacial acetic acid added. The product was shaken for one hour with hydrogen at 45 pounds pressure. Although reduction was complete in fifteen minutes it was shaken for one hour. The product was crystallized from acetone; m. p. 112° (uncorr.).

(2) By the action of phosphorus pentachloride on *epi*-cholestanol. Five grams of *epi*-cholestanol, m. p. 185°, was added to 2.5 g. of phosphorus pentachloride and ground in a mortar until a paste was obtained. This was added to water and boiled for thirty minutes. The product was extracted with ether and crystallized twice from alcohol–ether, then three times from acetone; m. p. 112° (uncorr.). Mixing with α-cholestyl chloride prepared by the first method gave no depression in the melting point.

(3) By the action of thionyl chloride on beta-cholestanol. Five grams of beta-cholestanol was added to 5 g. of thionyl chloride. The product was let stand overnight, then poured into a 2% sodium hydroxide solution. It was extracted with ether, then crystallized twice from alcohol–ether and three times from acetone; m. p. 112° (uncorr.). Mixed with α-cholestyl chloride prepared by the two previous methods it showed no depression in the melting point, whereas when mixed with pure beta-cholestyl chloride it gave a depressed melting point of 75–80°; yield, 4 g.

Anal. Calcd. for $C_{27}H_{47}Cl$: C, 79.7; H, 11.7. Found: C, 79.9; H, 11.8.

Beta-Cholestyl Chloride.—(1) By the action of phosphorus pentachloride on beta-cholestanol. This was prepared according to the method described by Ruzicka and co-workers[1] giving a product melting at 102–103° (uncorr.) after crystallizing from acetone. Mixture with α-cholestyl chloride gave a depression to 78–83°.

2. By the action of thionyl chloride on *epi*-cholestanol. Three grams of *epi*-cholestanol was treated with 5 cc. of thionyl chloride and let stand at 40° overnight. This was shaken with 2% sodium hydroxide, extracted with ether, crystallized first from alcohol–ether, then from acetone; m. p. 102–103° (uncorr.). Mixture with beta-cholestyl chloride showed no depression, whereas mixture with α-cholestyl chloride gave a depression to 78–80°.

Anal. Calcd. for $C_{27}H_{47}Cl$: C, 79.7; H, 11.7. Found: C, 79.5; H, 11.9.

Hydrolysis of α-Cholestyl Chloride.—One gram of α-cholestyl chloride was added to 10 g. of potassium acetate in 20 cc. of valeric acid. The product was refluxed for thirty hours, then alkali added. The neutral product was extracted with ether, then boiled with alcoholic potassium hydroxide for two hours. The alcohol was distilled off and the product extracted with ether. This was treated with norit and the product crystallized from alcohol; m. p. 185–186°. Mixed with *epi*-cholestanol prepared by the method of Vavon and Jakubowicz,[2] it showed no depression in melting point. Mixture with beta-cholestanol gave a depression of the melting point to 131°.

Anal. Calcd. for $C_{27}H_{48}O$: C, 83.4; H, 12.5. Found: C, 83.6; H, 12.5.

Hydrolysis of Beta-Cholestyl Chloride.—Three grams of beta-cholestyl chloride was hydrolyzed as described for α-cholestyl chloride. The product was crystallized from alcohol four times; m. p. 139°. Mixture with beta-cholestanol showed no depression in melting point, whereas mixture with *epi*-cholestanol gave a melting point of 116°.

Anal. Calcd. for $C_{27}H_{48}O$: C, 83.4; H, 12.5. Found: C, 83.3; H, 12.7.

α-Chloroandrosterone.—A total of 700 g. of α-cholestyl chloride was oxidized in 100-g. quantities; one hundred grams of the chloride was added to 3.5 liters of glacial acetic acid and heated to 95°. A solution of 250 g. of chromic oxide in 175 cc. of water and 400 cc. of glacial acetic acid was slowly run in over a period of four hours. It was then heated an additional ten hours on a steam-bath with stirring. The acetic acid from the seven oxidations was evaporated *in vacuo* and the residue dissolved in water and ether. The ether extract was washed with water and then treated with a 10% sodium hydroxide solution by shaking. An insoluble sodium salt of α-chlorocholanic acid precipitated. This was extracted with ether and the ether distilled to one liter. Two liters of alcohol was added and the remainder of the ether distilled off. On cooling the unoxidized chloride precipitated out. This was filtered off, washed with cold alcohol and dried at 100°; 310 g. of unchanged chloride was obtained. This was again oxidized in 100-g. quantities, and the total alcoholic filtrates evaporated to dryness on a steam-bath. The residue was then steam distilled to remove volatile ketones. The neutral oil was dissolved in 400 cc. of alcohol, filtered and 44 g. of semicarbazide hydrochloride and 53 g. of sodium acetate added. The product was heated for thirty minutes then put in a refrigerator for two days. The crystalline material was filtered, washed with ether and boiled with water. It was filtered again and washed with cold alcohol then ether; m. p. of crude material 272–273° (dec.). This was crystallized several times from alcohol–chloroform; m. p. 279–281° (dec.); yield, 9.2 g. and 4 g. additional with a slightly lower decomposition point recovered from the alcohol.

Four grams of the semicarbazone was added to 200 cc. of 75% alcoholic solution of hydrochloric acid. This was refluxed for three hours, neutralized and evaporated to one-third. The product was extracted with ether, treated with norit and recrystallized from methyl alcohol and finally from hexane, m. p. 170–171° (uncorr.).

Anal. Calcd. for $C_{19}H_{29}OCl$: C, 73.9; H, 9.5. Found: C, 74.0; H, 9.7.

α-Chlorocholanic Acid.—The insoluble sodium salt from the oxidation of α-cholestyl chloride was filtered, washed with dilute alkali, extracted with ether, then treated with hydrochloric acid. The oily material was extracted with ether and crystallized from acetone; m. p. 174–175°.

Anal. Calcd. for $C_{24}H_{39}O_2Cl$: C, 73.0; H, 10.0. Found: C, 73.2; H, 10.1.

We wish to thank Dr. F. W. Breuer for the micro-analyses on the compounds reported in this paper.

Summary

A method of converting *cis*-OH sterols into the *trans*-OH form, and the *trans* back into the *cis*

has been established. α-Chlorocholestane has been oxidized to produce α-chloroandrosterone and α-chlorocholanic acid.

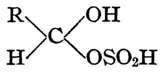
STATE COLLEGE, PA. RECEIVED AUGUST 26, 1935

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

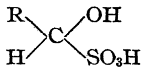
The Constitution of the Bisulfite Addition Compounds of Aldehydes and Ketones

BY WALTER M. LAUER AND CARL M. LANGKAMMERER

Since the discovery of the first aldehyde and ketone bisulfite addition compounds[1] many difficulties have been encountered in attempting to decide between the α-hydroxysulfite ester formula (I) and the α-hydroxysulfonic acid formula (II) for these compounds.



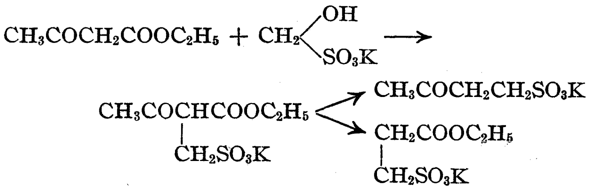
I



II

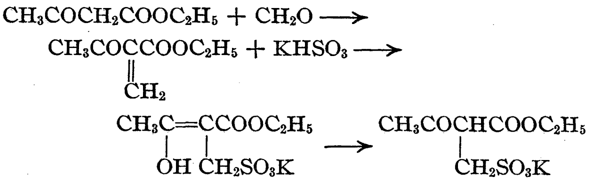
Each structure had its proponents[2] and the problem apparently was solved many years ago with the preparation of a "hydroxymethane sulfonic acid" which was not identical with formaldehyde bisulfite.[3] Since then additional "α-hydroxysulfonic acids" have been prepared;[4] they too differed from the corresponding bisulfite addition products. It is natural, therefore, that formation of the α-hydroxynitriles upon treatment of the bisulfite addition compounds with potassium cyanide came to be regarded as characteristic of the –O–SO_2H group.[5] These views were current until the time of the exemplary investigations of Raschig and Prahl.[6] These investigators were able to show that the "hydroxymethane sulfonic acid" obtained by Müller on sulfonating methyl alcohol was actually symmetrical acetone disulfonic acid, formed by the sulfonation of acetone present in the methyl alcohol of that early date. The "hydroxymethane sulfonic acid" described by Glimm and by Reinking, Dehnel and Labhardt as the product of the action of sulfuric acid on methyl alcohol was demonstrated to be an isomer, methyl hydrogen sulfate. Likewise, the "α-hydroxyisopropyl sulfonic acid," $(CH_3)_2C(OH)SO_3H$, which Schroeter prepared by the hydrolysis of the diphenyl ester of dimethylmethionic acid, $(CH_3)_2C(SO_2OC_6H_5)_2$, and which was not identical with the acetone bisulfite addition compound, was shown to be the methyl ether of this sulfonic acid.

After thus removing much of the evidence which was damaging to the α-hydroxysulfonic acid structure (II), Raschig and Prahl submitted the reaction



$$CH_3COCH_2COOC_2H_5 + CH_2{<}^{OH}_{SO_3K} \longrightarrow$$
$$\underset{CH_2SO_3K}{CH_3COCHCOOC_2H_5} \begin{matrix} \nearrow CH_3COCH_2CH_2SO_3K \\ \searrow \underset{CH_2SO_3K}{CH_2COOC_2H_5} \end{matrix}$$

as indicative of structure II, since the cleavage products were definitely sulfonic acids. However, these investigators[7] were not unmindful of the possibility of intermediate formation of methylene-acetoacetic ester with subsequent 1,4-addition of potassium bisulfite but their evidence led them to regard this as unlikely.



$$CH_3COCH_2COOC_2H_5 + CH_2O \longrightarrow$$
$$\underset{CH_2}{\underset{\|}{CH_3COCCOOC_2H_5}} + KHSO_3 \longrightarrow$$
$$\underset{OH\ CH_2SO_3K}{CH_3C{=}CCOOC_2H_5} \longrightarrow \underset{CH_2SO_3K}{CH_3COCHCOOC_2H_5}$$

Backer and Mulder[8] a short time ago have introduced independent evidence for the hydroxysulfonic acid structure, for the compound $NH_2CH_2SO_3H$ (or $NH_3^+CH_2SO_3^-$) obtained by treating formaldehyde bisulfite with ammonia contains a carbon–sulfur linkage since treatment with nitrosyl chloride yields chloromethane sulfonic

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[1] Redtenbacker, *Ann.*, **65**, 37–43 (1848); Tilley, *ibid.*, **67**, 105–15 (1848); Bertagnini, *ibid.*, **85**, 179–196, 268–288 (1853); Limpricht, *ibid.*, **93**, 238–242 (1855).

[2] Mendeleff, *ibid.*, **110**, 241 (1859); Schiff, *ibid.*, **210**, 123 (1881); Eibner, *ibid.*, **316**, 89 (1901).

[3] Müller, *Ber.*, **6**, 1031 (1873); Glimm, "Inaug.-Diss.," Freiburg, 1902; Reinking, Dehnel and Labhardt, *Ber.*, **38**, 1069 (1905).

[4] Schroeter, *Ann.*, **418**, 161–257 (1919); *Ber.*, **59**, 2341–2343 (1926); *ibid.*, **61**, 1616–1627 (1928).

[5] Knoevenagel, *ibid.*, **37**, 4059–4065 (1904).

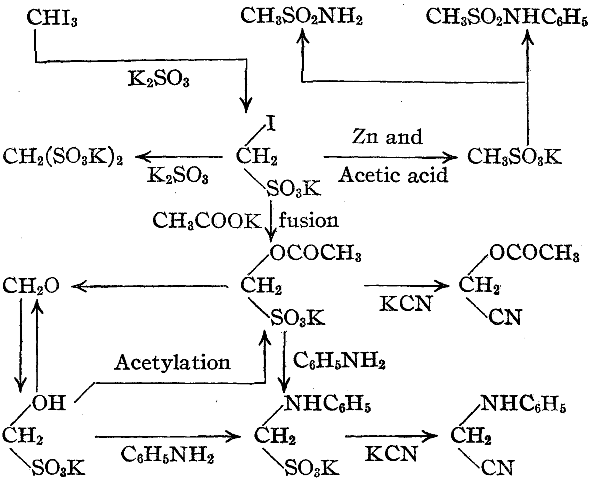
[6] Raschig and Prahl, *Ber.*, **59**, 859–865 (1926); *Ann.*, **448**, 265–312 (1926); *Ber.*, **59**, 2025–2028 (1926); *ibid.*, **61**, 179–189 (1928).

[7] See also Schroeter, *Ber.*, **61**, 1621 (1928).

[8] Backer and Mulder, *Rec. trav. chim.*, **52**, 454–468 (1933); *ibid.*, **53**, 1120–1127 (1934).

acid. In spite of this excellent evidence for structure II, it was thought desirable[9] to add still further and, if possible, equally conclusive proof.

The following series of reactions, which needs but little explanation, has been carried out.



Iodomethane sulfonic acid is definitely a sulfonic acid since it can be transformed into methionic acid and methane sulfonic acid. Fusion (*ca.* 200°) of this compound with potassium acetate and acetylation of the formaldehyde bisulfite addition compound each yields acetoxymethane sulfonic acid. The identity of these two preparations has been demonstrated. This evidence, in conjunction with that submitted by other investigators, supplies ample proof of the hydroxymethane sulfonic acid structure for formaldehyde bisulfite and makes it unnecessary to resort to a "polymolecule formula," (R_2CO), (SO_2), (HOH), of the type suggested by Schroeter.

Experimental

Potassium Iodomethane Sulfonate.—Since the preparations of the salts of iodomethane sulfonic acid are described only in patent literature[10] the details of procedure are included here.

Ninety-five grams (0.6 mole) of potassium sulfite was dissolved in 450 cc. of water in a 1-liter round-bottomed flask and 78.8 g. (0.2 mole) of freshly recrystallized iodoform added so that the iodoform formed a layer above the water. The reaction mixture was refluxed for a period of three to four hours until practically all of the iodoform and methylene iodide had disappeared. After filtering the solution it was evaporated to dryness on a steam-cone. (Blowing a stream of compressed air over the beaker shortens considerably the length of time required for this operation.) The dry solid was extracted with methyl alcohol at room temperature. One extraction with 300 cc. followed by two extractions with 200 cc. of methyl alcohol is sufficient to remove almost all of the inorganic iodide. The residue was then treated with 800 cc. of boiling 80% ethyl alcohol and filtered. The cooled filtrate yielded 38.0 g. (73%) of shiny, white plates which were washed with absolute alcohol and ether and then air dried.

Anal. Calcd. for CH_2ISO_3K: K, 15.03. Found: K, 14.95, 15.05.

The sodium salt was prepared in a similar way; however, in this case it is not necessary to remove the sodium iodide. The evaporated reaction mixture is extracted directly with 300 cc. of 90% ethyl alcohol; yield, 68%.

Anal. Calcd. for $CH_2ISO_3Na \cdot H_2O$: K, 8.78; H_2O, 6.68. Found: K, 8.78; H_2O, 7.16.

Potassium Acetoxymethane Sulfonate (a) from Potassium Iodomethane Sulfonate.—After refluxing potassium acetate and potassium iodomethane sulfonate in aqueous solution for fifteen hours no iodide ion had formed. However, when 10.4 g. (0.04 mole) of potassium iodomethane sulfonate and 5 g. (0.05 mole) of potassium acetate were ground in a mortar and heated to 200–205° in a Wood's metal-bath and held there for an hour with stirring the mass liquefied. The reaction was maintained at this temperature for two and one-half hours. After cooling to room temperature the mass was chipped out of the flask and ground. The solid was extracted with two 200-cc. portions of methyl alcohol and then with one 100-cc. portion, all at room temperature. The methyl alcohol extracts were evaporated to dryness and then dissolved in 100 cc. of water. Titration of a 10-cc. portion with silver nitrate showed that 92% of the iodine in the original compound had been changed to iodide ion.

The solid remaining after the methyl alcohol extraction was treated with 400 cc. of boiling 95% ethyl alcohol. The cooled filtrate produced 1.03 g. of solid. A second extraction yielded 0.55 g. of the same material, yield 20.5%.

Anal. Calcd. for $C_3H_5O_5SK$: K, 20.35. Found: (for 1.03-g. fraction) K, 20.07, 20.11; (for 0.55-g. fraction) K, 20.09.

Potassium Acetoxymethane Sulfonate (b) from the Potassium Bisulfite Addition Compound of Formaldehyde.—Treatment of the potassium bisulfite addition compound of formaldehyde with acetic anhydride according to the procedure of Raschig and Prahl[11] yielded a product the potassium content of which was somewhat too high for potassium acetoxymethane sulfonate. Recrystallization lowered the percentage of potassium but it was still higher than theory. The substance was prepared in the following way.

Twenty grams of the potassium bisulfite addition compound of formaldehyde (K, 26.15; calcd., 26.04) was added to a 200-cc. round-bottomed flask containing 100 cc. of acetic anhydride and 10 cc. of glacial acetic acid. After twenty minutes of refluxing *with constant shaking* the flask was filled with a mass of crystals. Filtered, washed with

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[9] See for example D. Gibson, *Chem. Rev.*, **14**, 431–457 (1934).

[10] German Patents 532,766, 535,652, 546,354, 551,145, 564,211, 562,501; British Patents 353,477, 369,473; French Patents 708,270, 40,169; U. S. Patents 1,842,626, 1,867,793; *Industria chimica*, **7**, 714 (1932).

[11] Raschig and Prahl, *Ann.*, **448**, 305 (1926).

absolute alcohol, followed by ether and then dried, the solid weighed 20.0 g. (75%). The potassium content of the crude product was 20.77%. The solid was recrystallized from 95% alcohol; approximate solubility hot, 0.55 g. per 100 cc. of 95% ethyl alcohol; cold, 0.07 g. per 100 cc. of 95% ethyl alcohol. In larger amounts the substance can be recrystallized satisfactorily from 80% alcohol.

Anal. Calcd. for $C_3H_5O_5SK$: K, 20.35. Found: (for various fractions) K, 20.34, 20.38, 20.17, 20.33.

Comparison of the Potassium Acetoxymethane Sulfonate Prepared by the Two Methods.—The decomposition temperature of the first preparation is 239–245°; that of the second 243–246°. A mixture of the two substances decomposes at 240–246°.

Dr. E. B. Sandell of the division of analytical chemistry of the University of Minnesota kindly submits the following crystallographic comparison. Both substances recrystallized from 95% alcohol form plates and flattened prisms which are anisotropic and exhibit parallel extinction. The index of refraction corresponding to light vibrating parallel to the long direction of the prisms is 1.491 ± 0.002, whereas the index most often exhibited crosswise is 1.521 ± 0.003 *in both samples.*

Potassium Methionate from Potassium Iodomethane Sulfonate.—Twenty-six grams (0.1 mole) of potassium iodomethane sulfonate and 47.5 g. (0.3 mole) of potassium sulfite were dissolved in water and diluted to 500 cc. Placed in a 1-liter round-bottomed flask under a reflux condenser the reaction mixture was heated on a steam-bath. At approximately twenty-four hour intervals 10-cc. portions were removed and extracted with methyl alcohol. The alcoholic extract was evaporated and the resulting solid titrated with silver nitrate solution using eosin as an indicator. At the end of twenty-four hours, 34.3% reaction; forty-eight hours, 49.3%; seventy-two hours, 65.0%; ninety-six hours, 68.8%; one hundred and twenty hours, 76.8%; one hundred and forty-four hours, 87.3%; one hundred and sixty-eight hours, 87.0%. The solution was then evaporated to 150 cc., cooled and the solid filtered off. Recrystallized from 125 cc. of hot water this yielded 15.50 g. of air-dried potassium methionate.

Anal. Calcd. for $CH_2O_6S_2K_2$: K, 30.99. Found: K, 30.91.

A further crop of 3.7 g. potassium methionate was obtained by working up the filtrates; total yield, 19.2 g. (84.6%).

Potassium Methane Sulfonate from Potassium Iodomethane Sulfonate.—Twenty-six grams (0.1 mole) of potassium iodomethane sulfonate, 20 g. of glacial acetic acid and 25 g. of zinc dust were placed in 380 cc. of 50% alcohol and refluxed for two and one-half hours. The excess zinc dust was filtered off and the solution evaporated to 200 cc. The zinc sulfide formed on saturating the solution with hydrogen sulfide was filtered off and the filtrate evaporated to dryness. An extract with 150 cc. of methyl alcohol was discarded. The remaining solid was recrystallized from 150 cc. of 80% ethyl alcohol; total yield (3 crops), 9.8 g. (73%).

Anal. Calcd. for CH_3SO_3K: K, 29.14. Found: K, 28.90.

The amide prepared in the customary manner melted at 89–90°.[12] The sulfonanilide melts at 102–103°.[13]

Acetoxyacetonitrile from Potassium Acetoxymethanesulfonate.—19.2 g. of potassium acetoxymethanesulfonate (0.1 mole) and 6.5 g. (0.1 mole) of potassium cyanide were dissolved in 50 cc. of water and allowed to stand at room temperature for thirty minutes. An oil formed on the surface and was extracted with ether (200 cc.) and the ether extract dried over anhydrous sodium sulfate. The ether was removed on a water-bath and the oil remaining distilled: 105–178°, 1.65 g.; 178–179°, 1.70 g.; total yield 33.9%; after redistillation $n^{20}{}_D$ 1.4040°. Henry[14] reports a boiling point of 179–180° and $n^{20}{}_D$ 1.4107 for acetoxyacetonitrile prepared by the action of potassium acetate on chloracetonitrile.

Potassium Anilinomethane Sulfonate from Potassium Acetoxymethane Sulfonate.—3.84 g. (0.02 mole) of potassium acetoxymethane sulfonate and 40 cc. of aniline were refluxed until the reaction mixture set almost to a solid mass. The flask was cooled to room temperature and an equal volume of absolute alcohol added. The solid after filtration weighed 3.88 g. (85%). Recrystallized from methyl alcohol it analyzed for potassium anilinomethane sulfonate.

Anal. Calcd. for $C_7H_8O_3NSK \cdot H_2O$: H_2O, 7.41; K, 16.07. Found: H_2O, 6.79; K, 16.31.

Treatment with potassium cyanide yielded an oil which was presumably anilinoacetonitrile. Since difficulty was experienced in crystallizing this oil a small part of it was converted to phenylglycine the melting point (124–126°) of which was not depressed on adding authentic phenyl glycine.

Hydrolysis of Potassium Acetoxymethane Sulfonate.—One gram of potassium acetoxymethane sulfonate was dissolved in 25 cc. of water in a 50-cc. distilling flask, 1 cc. of concentrated sulfuric acid was added and the solution distilled slowly into 1 g. of dimethyl dihydroresorcinol dissolved in 75 cc. of water. A precipitate was formed which melted below the melting point of dimethyl dihydroresorcinol. After filtering off this solid the filtrate was treated with potassium bicarbonate and the precipitate recrystallized from a small amount of acetone. The melting point and mixed melting point with a sample of formaldehyde dimethone melting at 191–192°, was 191–192°.

The authors gratefully acknowledge a grant from the Graduate School Fund of the University of Minnesota, which made this work possible.

Summary

It has been shown that the bisulfite addition compound of formaldehyde and presumably all aldehyde and ketone bisulfites are salts of α-hydroxysulfonic acids, $R_2C(OH)SO_3Me$.

MINNEAPOLIS, MINN. RECEIVED SEPTEMBER 12, 1935

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[12] Duguet [*Rec. trav. chim.*, **21**, 76 (1902)] reports 90° for the melting point of methyl sulfonamide.

[13] Duguet, *loc. cit.*, reports 99° for the melting point of methyl sulfonanilide.

[14] Henry, *Rec. trav. chim.*, **24**, 169 (1905).

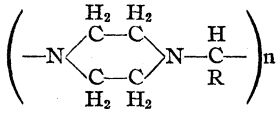
[CONTRIBUTION FROM THE ORGANIC CHEMICAL LABORATORY OF THE UNIVERSITY OF FLORIDA]

Derivatives of Piperazine. VIII. Condensation with Aldehydes

BY W. T. FORSEE, JR., AND C. B. POLLARD

The literature reveals very few data on reactions between piperazine and aldehydes and this small amount of published work is somewhat contradictory. Experimental evidence has failed to establish a basis for predicting the type of compound expected when an aldehyde is condensed with piperazine.

In this investigation piperazine was condensed with formaldehyde, acetaldehyde, butyraldehyde, benzaldehyde, salicylaldehyde, *p*-tolylaldehyde and *o*-chlorobenzaldehyde. With two exceptions, data indicate compounds of the structure



The structure of the products from acetaldehyde and butyraldehyde have not yet been determined. Formaldehyde and piperazine[1] gave the same product as was obtained from methylene iodide and piperazine. Benzaldehyde and piperazine[2] gave the same product as was obtained from benzal chloride and piperazine. These reactions and the analyses show these condensation products to be a N,N′-bis-piperazylalkylmethane type of compound. However, the molecular structure might be one of any number of polymers. Since these compounds are practically insoluble in all solvents and are unstable at temperatures near the melting points, a molecular weight determination by ordinary methods was impossible. Purification was accomplished by using highly purified reagents and washing the products repeatedly with several solvents.

In order to block the possibility of polymerization, N-monophenylpiperazine was condensed with various aldehydes. Compounds of the N-bis-(N′-phenylpiperazyl)-alkylmethane type were obtained from formaldehyde, acetaldehyde, benzaldehyde, *p*-tolylaldehyde and anisaldehyde. N-Monophenylpiperazine with formaldehyde[3] gave the same compound as was obtained from N-monophenylpiperazine and methylene iodide.

Properties of the compounds obtained from piperazine are shown in Table I. Table II gives

TABLE I

YIELDS, PROPERTIES AND COMPOSITION OF PIPERAZINE DERIVATIVES

	Compound	Formula	Yield, %	M. p., °C.	Analyses, % N Found	Calcd.
1	Methylene piperazine	$(—NC_4H_8N·CH_2—)_n$	97	Not under 300	28.51	28.57
1	From methylene iodide		98	Not under 300	28.67	28.57
2	Benzylidene piperazine	$(—NC_4H_8N·CH(C_6H_5)—)_n$	98	270 (dec.)	16.12	16.09
2	From benzal chloride		46	265 (dec.)	15.93	16.09
3	*o*-Hydroxybenzylidene piperazine	$(—NC_4H_8N·CH(C_6H_4·OH)—)_n$	44	210 (dec.)	14.70	14.73
4	*p*-Methylbenzylidene piperazine	$(—NC_4H_8N·CH(C_6H_4·CH_3)—)_n$	90	275 (dec.)	15.12	14.88
5	*o*-Chlorobenzylidene piperazine	$(—NC_4H_8N·CH(C_6H_4·Cl)—)_n$	95	240 (dec.)	13.37	13.42
6	*p*-Methoxybenzylidene piperazine	$(—NC_4H_8N·CH(C_6H_4·OCH_3)—)_n$	85	290 (dec.)	13.72	13.72

TABLE II

YIELDS, PROPERTIES AND COMPOSITION OF N-MONOPHENYLPIPERAZINE DERIVATIVES

	Compound	Formula	Yield, %	M. p., °C.	Analyses, % N Found	Calcd.
1	N-Bis-(N′-phenylpiperazyl)-methane	$C_6H_5·NC_4H_8N·CH_2·NC_8H_4N·C_6H_5$	79	123–124	16.58	16.66
1	From methylene iodide		24	123–124	16.74	16.66
2	N-Bis-(N′-phenylpiperazyl)-ethane	$C_6H_5·NC_4H_8N·CH(CH_3)·NC_4H_8N·C_6H_5$	25	121–123	15.82	16.00
3	N-Bis-(N′-phenylpiperazyl)-phenylmethane	$C_6H_5·NC_4H_8N·CH(C_6H_5)·NC_4H_8N·C_6H_5$	90	125–126	13.54	13.59
4	N-Bis-(N′-phenylpiperazyl)-*o*-methylphenylmethane	$C_6H_5·NC_4H_8N·CH(C_6H_4·CH_3)·NC_4H_8N·C_6H_5$	83	144–144.5	13.29	13.13
5	N-Bis-(N′-phenylpiperazyl)-*o*-methoxyphenylmethane	$C_6H_5·NC_4H_8N·CH(C_6H_4·OCH_3)·NC_4H_8N·C_6H_5$	67	135–136	12.67	12.66

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[1] Herz, *Ber.*, **30**, 1584 (1897).

[2] Schmidt and Wichmann, *ibid.*, **24**, 3237 (1891).

[3] Prelog and Blazik, *Coll. Czech. Chem. Comm.*, [2] **6**, 549 (1934).

the data for those obtained from N-monophenylpiperazine.

All of the condensation products are readily decomposed by acids. In contrast to the products from piperazine those from N-monophenylpiperazine were readily crystallized from appropriate solvents.

All of the condensation products were prepared by reacting the amine with the aldehyde either in the absence or presence of a solvent. The method recommended by Cummings, Hopper and Wheeler[4] was used in all reactions which involved alkyl halides.

Summary

It has been shown that when aldehydes react with piperazine or N-mono-substituted piperazines, one molecule of the aldehyde reacts with two amino groups and a molecule of water is eliminated.

[4] Cummings, Hopper and Wheeler, "Synthetic Organic Chemistry," p. 294.

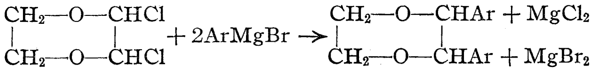
GAINESVILLE, FLORIDA RECEIVED AUGUST 22, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Studies in the Dioxane Series. II. Aryl Substituted Dioxanes Synthesis of *p*-Dioxene[1]

BY R. K. SUMMERBELL AND L. N. BAUER

The preparation of 2,3-diphenyl-1,4-dioxane by the reaction of 2,3-dichloro-1,4-dioxane with phenylmagnesium bromide was described by Christ and Summerbell.[2]



$$\begin{array}{l} CH_2—O—CHCl \\ | \qquad\quad | \\ CH_2—O—CHCl \end{array} + 2ArMgBr \rightarrow \begin{array}{l} CH_2—O—CHAr + MgCl_2 \\ | \qquad\quad | \\ CH_2—O—CHAr + MgBr_2 \end{array}$$

The same method of synthesis has been satisfactorily applied to a number of aryl substituted dioxanes.

Although two 2,3-disubstituted dioxanes may be predicted from theory, only one was obtained in each case. In a repetition of the 2,3-diphenyl-1,4-dioxane synthesis, a yield of 80% of the previously described material was obtained, and attempts to isolate a second disubstituted dioxane were unsuccessful. The high yield of a single product in this case, and the failure to obtain two isomers in any of the experiments described in this paper, may be taken to indicate that the 2,3-dichloro-1,4-dioxane used was a pure compound, rather than a mixture of *cis* and *trans* isomers.

The reaction of benzylmagnesium chloride with dichlorodioxane might give an *o*-tolyl derivative.[3] As only a small amount of phthalic acid was obtained on permanganate oxidation of the reaction product, there is very little, if any, of this type of rearrangement. Further work on high molecular weight residues must be carried out to explain all that takes place in this reaction.

In an attempt to extend this method of synthesis to alkyl substituted dioxanes, only small yields of dimethyl, diethyl and dibutyl-1,4-dioxanes were obtained. The yields were so small that a discussion of their properties will be withheld, pending the outcome of experiments now under way on modifications of procedure designed to increase the yield and hence the material available for investigation.

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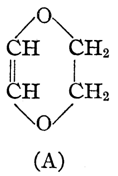
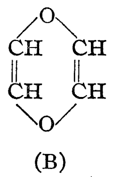
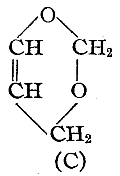
[1] The name 1,4-(or *p*-)dioxene for a new compound (A) described in this paper requires explanation. It follows logically from 1,4-dioxane, the preferred name [Patterson, THIS JOURNAL, **55**, 3911 (1933)] of the fully hydrogenated analog. It might be called 2,3-dihydro-1,4-dioxin since dioxin has been proposed [Widman, *Ber.*, **42**, 3269 (1909)] to represent the least hydrogenated member. Unfortunately for the logic involved, dioxin turns out to be either $C_4H_4O_2$ or $C_4H_6O_2$ depending on whether 1,4-dioxin (B) or 1,3-dioxin (C) is being considered.



(A)



(B)



(C)

(See *Chem. Abs.*, **28**, 8219 (1934) for both structures.) It is incredible that two related non-isomeric substances of known structures should needlessly be assigned the same name.

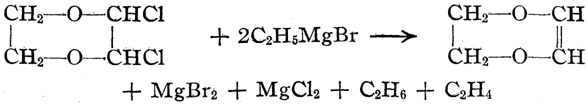
The logical name for (C) is 1,3-dioxene. Instead of 1,4-dioxin, the name dioxadiene is proposed for (B). The name is simple, informative, and free from an ambiguous past.

This plan applies equally well for the sulfur analogs: dithiane, dithiene, oxathiane and oxathiene. The last two names are preferable to thioxane and thioxene since, according to the rules of numbering ring systems, the oxygen should be numbered one; thus 1,4-oxathiane, etc. We acknowledge assistance in this formulation from E. J. Crane and A. M. Patterson, members of the A. C. S. committee on nomenclature.—C. D. HURD, C. M. SUTER AND R. K. SUMMERBELL.

[2] Christ and Summerbell, THIS JOURNAL, **55**, 4547 (1933).

[3] Gilman and Kirby, *ibid.*, **54**, 345 (1932); John R. Johnson, *ibid.*, **55**, 3029 (1933); and earlier work to which these articles contain references.

The chief product in the reaction of methyl, ethyl, and butylmagnesium bromides with 2,3-dichlorodioxane was *p*-dioxene.



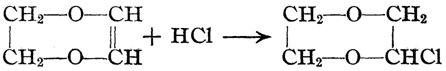
$$\begin{array}{l}CH_2\text{—}O\text{—}CHCl\\ |\qquad\quad |\\ CH_2\text{—}O\text{—}CHCl\end{array} + 2C_2H_5MgBr \longrightarrow \begin{array}{l}CH_2\text{—}O\text{—}CH\\ |\qquad\quad \|\\ CH_2\text{—}O\text{—}CH\end{array}$$
$$+ MgBr_2 + MgCl_2 + C_2H_6 + C_2H_4$$

The identity of this compound was proved by: (a) analysis and molecular weight determinations; (b) ozonization and identification of the expected products, formic acid and ethylene glycol; and (c) addition of chlorine to form the known 2,3-dichloro-1,4-dioxane.

The chief hydrocarbon products of the reaction are as represented in the equation above, although there was produced also a small amount of a saturated hydrocarbon of higher molecular weight, probably butane.

Dioxene adds bromine very readily to form 2,3-dibromo-1,4-dioxane. This compound had previously been described in a very impure liquid state by Tellegen.[4] As we obtained it, it is an unstable solid, constantly evolving hydrogen bromide. It reacts with phenylmagnesium bromide to yield 2,3-diphenyl-1,4-dioxane, thus indicating its structure.

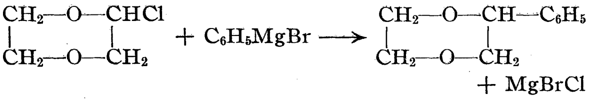
Hydrogen chloride also adds to the double bond of *p*-dioxene to give monochloro-*p*-dioxane. The chlorine atom of the latter compound, being alpha to an oxygen atom, should be reactive, and



$$\begin{array}{l}CH_2\text{—}O\text{—}CH\\ |\qquad\quad \|\\ CH_2\text{—}O\text{—}CH\end{array} + HCl \longrightarrow \begin{array}{l}CH_2\text{—}O\text{—}CH_2\\ |\qquad\quad |\\ CH_2\text{—}O\text{—}CHCl\end{array}$$

thus the compound should be a valuable intermediate for the sythesis of monosubstituted *p*-dioxanes.

Monochloro-*p*-dioxane does react with phenylmagnesium bromide to give phenyl-*p*-dioxane.



$$\begin{array}{l}CH_2\text{—}O\text{—}CHCl\\ |\qquad\quad |\\ CH_2\text{—}O\text{—}CH_2\end{array} + C_6H_5MgBr \longrightarrow \begin{array}{l}CH_2\text{—}O\text{—}CH\text{—}C_6H_5\\ |\qquad\quad |\\ CH_2\text{—}O\text{—}CH_2\end{array}$$
$$+ MgBrCl$$

The isolation of monochloro-*p*-dioxane is of peculiar interest, in that it has never been isolated in the direct chlorination[5] of *p*-dioxane. The failure to isolate monochloro-*p*-dioxane is easy to understand from its properties, for it is unstable at room temperature, and would be much less stable at the usual temperature of chlorination. If one assumes that the addition of hydrogen chloride to *p*-dioxene is reversible, one has a satisfactory picture of a mechanism for the chlorination of 1,4-dioxane to give 2,3-dichloro-1,4-dioxane. Probably monochloro-*p*-dioxane is first formed. It readily loses hydrogen chloride to give *p*-dioxene, which, in turn, adds a molecule of chlorine to give 2,3-dichloro-1,4-dioxane. The addition of chlorine to a double bond would probably give chiefly one isomer, whereas chlorination of the two carbon atoms independently would give a mixture of isomers. The 2,3-dichloro-1,4-dioxane obtained by us seems to be a pure compound and not a mixture of isomers.

Further work on the role of this compound in the chlorination of dioxane and its use in synthesis is contemplated and under way at the present time.

Experimental

A. General.—As the procedure was in all cases similar to that previously described,[6] only notes on important details, analysis, etc., will be given here. Grignard reagents were prepared with at least five moles of ether for each mole of freshly distilled halide. They were titrated[7] by the method of Gilman.

The 2,3-dichloro-1,4-dioxane was prepared by chlorinating[8] 632 g. of purified 1,4-dioxane which melted at 11–12.5° for sixteen hours at 90° with mechanical stirring. The product was obtained in 61% yield, m. p. 28–30°; b. p. 85° (15 mm.).

Molecular weights were determined by the lowering of the melting point of camphor.[9,10]

B. 2,3-Diphenyl-1,4-dioxane.[11]—The synthesis of this compound was repeated in order to determine accurately the yield on a run of moderate scale, and to furnish material for a more intensive search for an isomeric 2,3-diphenyldioxane.

Phenylmagnesium bromide was prepared in the usual manner, using the following quantities of materials: 701 g. of bromobenzene, 108 g. of magnesium, and 2300 cc. of anhydrous ether; yield of Grignard reagent, 4.27 moles or 95.7%. The entire preparation, a large excess, was treated with 167.6 g. (1.067 mole) of 2,3-dichloro-1,4-dioxane. Hydrolysis of the reaction product was carried out with dilute sulfuric acid. The ether layer was fractionally distilled, the major part of high boiling material distilling at 185–187° (13 mm.). After recrystallizing seven times from ligroin in an effort to separate any foreign

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[4] Tellegen, Dissertation, "Dioxaan en derivaten," Delft, Holland, Oct., 1934, Chap. II.

[5] Böeseken, Tellegen and Henriquez, *Rec. trav. chim.*, **50**, 909 (1931); THIS JOURNAL, **55**, 1284 (1933); Butler and Cretcher, *ibid.*, **54**, 2987 (1932); Summerbell and Christ, *ibid.*, **54**, 3777 (1932); **55**, 4547 (1933); Baker, *J. Chem. Soc.*, 2666 (1932); Baker and Shannon, *ibid.*, 1598 (1933); Kucera and Carpenter, Organic Chem. Division, American Chemical Society, New York, April, 1935.

[6] Christ and Summerbell, THIS JOURNAL, **55**, 4547 (1933).

[7] Gilman, Wilkinson, Fishel and Meyers, *ibid.*, **45**, 150 (1923); Gilman, Zoellner and Dickey, *ibid.*, **51**, 1576 (1929).

[8] Böeseken, Tellegen and Henriquez, *Rec. trav. chim.*, **50**, 909 (1931).

[9] Rast, *Ber.*, **55**, 1051 (1922).

[10] Smith and Young, *J. Biol. Chem.*, **75**, 289 (1927).

[11] This experiment and several of the analyses were performed by Mr. Maxwell Pollack.

material, 205 g. of 2,3-diphenyl-1,4-dioxane melting at 49–50° was obtained. The yield is 80%. No isomeric substance was found in the mother liquors.

C. **New Symmetrical 2,3-Diaryl-1,4-dioxanes.**—Other new symmetrical 2,3-diaryl-1,4-dioxanes were prepared and analyzed as shown in Tables I and II.

The smaller yields are due partially to smaller scale experiments.

TABLE I

SYMMETRICAL 2,3-DIARYL-1,4-DIOXANES

Substituents	Yields, RMgX	in % Dioxane	M. p., °C. (corr.)	Mol. wt. Found	Calcd.
o-Tolyl	95	61	105.7–106.2	268	268
m-Tolyl	85	51	84.2	270	268
p-Tolyl	89	72	56–57.2	259	268
p-ClC_6H_4	93	49	152–153	304	309
p-Anisyl	85	67	79–80.2	299	300
α-Naphthyl	98	53	vitreous[a]	351	340
Xenyl[b]	59	..	144.5–146	394	392
Benzyl[c]	91	22	62.2	266	268

[a] Observed b. p. 255–258° (3–4 mm. (uncorr.)).

[b] Part of product lost in purification.

[c] A viscous, sirup-like mass remaining in the distilling flask which would not distil below a bath temperature of 300° at a pressure less than 1 mm. has not been investigated. Permanganate oxidation [Gilman and Kirby, THIS JOURNAL, 54, 345 (1932)] of the 2,3-dibenzyldioxane gave a large quantity of benzoic acid and only traces of phthalic acid, indicating very little rearrangement to the *o*-tolyl derivative. The small yield is doubtless connected with the low yields of aliphatic dioxanes prepared by this method. They are being investigated.

TABLE II

Substituents	Formula	Analyses, % Calcd. C	H	Found C	H
o-Tolyl	$C_{18}H_{20}O_2$	80.60	7.46	80.55	7.49
m-Tolyl	$C_{18}H_{20}O_2$	80.60	7.46	80.76	7.44
p-Tolyl	$C_{18}H_{20}O_2$	80.60	7.46	80.39	7.30
p-ClC_6H_4	$C_{16}H_{14}O_2Cl_2$	Cl, 22.98		23.04	
p-Anisyl	$C_{18}H_{20}O_4$	72.00	6.67	72.20	6.69
α-Naphthyl	$C_{24}H_{20}O_2$	84.71	5.58	84.19	5.68
Xenyl	$C_{28}H_{24}O_2$	85.71	6.12	85.35	6.18
Benzyl	$C_{18}H_{20}O_2$	80.60	7.46	80.46	7.58

Several of the aryl disubstituted dioxanes form picrates. Use was made of this fact in obtaining solid 2,3-*p*-ditolyl-1,4-dioxane. The reaction product was a very viscous liquid which, however, formed a solid picrate. On treatment of this picrate with alkali, a solid was obtained which was used to seed the main mass of material, which then solidified; m. p. of picrates: *m*-ditolyldioxane, 91–92°; *p*-ditolydioxane 96.5°; *p*-dianisyldioxane, 107–108°; α-dinaphthyldioxane, 166–167°.

D. **Preparation of *p*-Dioxene.**—2,3-Dichloro-1,4-dioxane (2.43 moles) dissolved in 500 cc. of anhydrous ethyl ether was added over a period of four hours to 4.85 moles of ethylmagnesium bromide. The heat evolved resulted in gentle refluxing. After standing for twenty hours, the reaction product was hydrolyzed with an excess of water at 0°. The ether layer was separated, dried over anhydrous sodium sulfate, and fractionated by distillation in a 50-cm. vacuum-jacketed column containing a nichrome wire coil. Two chief products were obtained: (a) 140.5 g. of a liquid which was light greenish-yellow in color immediately after distillation, but which turned colorless on standing, b. p. 94.5° (754.3 mm.); (b) 22.3 g. of a colorless liquid having the odor of green willow bark, b. p. 164–175° (747.9 mm.). This compound is evidently an impure sample of 2,3-diethyldioxane. It is being investigated.

During the addition of 2,3-dichloro-1,4-dioxane to ethylmagnesium bromide, copious quantities of gas were evolved. The small yield of the expected product made the identification of this gas of interest. A similar run was made, and a sample of the evolving gas collected. This gas was analyzed by absorption and combustion.[12,13] Of 91.8 cc. of gas, 44.5 cc. was absorbed by 96% sulfuric acid. Combustion of the saturated remainder showed *n*, the number of carbon atoms, to be 2.13, 2.14. The analysis then corresponds to 48.5% unsaturated hydrocarbon, probably ethylene, 48.2% ethane, and 3.4% butane. The butane may have been the result of a side reaction of the original Grignard reagent synthesis. The principal course of the reaction must have followed the equation given in the theoretical part.

E. Properties and Structure of *p*-Dioxene

(a) **Properties.**—Fraction (a) of the above was again distilled; b. p. 94.2° (749.9 mm.); $d^{20}{}_4$ 1.083; $n^{22.5}{}_D$ 1.4375; $n^{25}{}_D$ 1.4362.

Anal. Calcd. for $C_4H_6O_2$: R_L[14] 21.38; mol. wt., 86; C, 55.81; H, 6.98. Found: R_L, 20.99; mol. wt., 89.9[15] 90.6;[16] C, 55.94; H, 7.11.

(b) **Ozonization.**—Pure dioxene (4.55 g.) was dissolved in 80 cc. of carbon tetrachloride and placed in a flask surrounded by ice. Over a period of eight and one-half hours, 0.03 cu. meter of pure dry oxygen was run through an ozonizer and bubbled through the solution. The ozonide thus formed was hydrolyzed with water at the temperature of a steam-bath for two hours. Titration with 0.4554 *N* potassium hydroxide required 194.6 cc., indicating a yield of 83.7% of formic acid. The solution of the potassium salt was evaporated, and the presence of the formate ion proved by reaction of a portion of the neutral potassium salt with 0.005 mole of *p*-bromophenacyl bromide.[17] The *p*-bromophenacyl ester of formic acid, m. p. 140°, mixed m. p. 140°, was obtained.

To prove that ethylene glycol was also a product of ozonization and hydrolysis, the solution obtained by neutralization was treated with benzoyl chloride in the presence of an excess of potassium hydroxide. An excellent yield of the dibenzoate of ethylene glycol resulted, m. p. 70°, mixed m. p. 70°.

F. Reaction of 2,3-Dichlorodioxane with other Alkylmagnesium Halides

(a) **Methylmagnesium Bromide.**—The reaction of 2,3-dichlorodioxane with methylmagnesium bromide was

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[12] Gas analyses in this paper by Mr. E. Field.

[13] Lunge and Ambler, "Technical Gas Analysis," Gurney and Jackson, London, 1934.

[14] R_L, the molecular refractivity. The formula of Lorentz and Lorenz was used.

[15] Method of Dumas.

[16] Method of Victor Meyer.

[17] Hurd and Christ, THIS JOURNAL, **57**, 2007 (1935).

carried out as described for the reaction with ethylmagnesium bromide. The chief product isolated was *p*-dioxene.

(b) **Butylmagnesium Bromide.**—The reaction of 0.573 mole of 2,3-dichlorodioxane with 1.146 mole of *n*-butylmagnesium bromide was carried out as described for ethylmagnesium bromide. A yield of 38.8 g. (78.7%) of crude *p*-dioxene was obtained. A small fraction, 2.5 cc. boiling at 122.5–125° (746.7 mm.), n^{20}_D 1.3985, was probably *n*-octane. Another fraction, 2.5 g., b. p. 120–122° (16–17 mm.), is probably 2,3-dibutyl-1,4-dioxane and will be investigated when more material is available.

The gases evolved during the reaction were condensed in a solid carbon dioxide trap. A portion was allowed to distil and analyzed. The sample analyzed 46.3% saturated, butane, and 53.7% soluble in 82% sulfuric acid, butylene.

G. Addition of Chlorine to *p*-Dioxene.—*p*-Dioxene (23.27 g. or 0.271 mole) was dissolved in pure carbon tetrachloride. Fifteen and three-tenth grams of chlorine gas mixed with dry nitrogen was dried over anhydrous magnesium perchlorate, and passed into the vigorously stirred solution at 0° during a period of four hours. The reaction product was fractionated, and 22.7 g. of a liquid boiling at 85° (15 mm.) (2,3-dichloro-1,4-dioxane) was obtained; yield, 53.4%. The product was positively identified by reaction of a portion with *o*-tolylmagnesium bromide to form 2,3-*o*-ditolyl-1,4-dioxane, m. p. 106–107°.

H. The Addition of Bromine to *p*-Dioxene.—To 4.29 g. (0.05 mole) of *p*-dioxene dissolved in 15 cc. of dry carbon tetrachloride was added 7.97 g. (0.05 mole) of bromine dissolved in 25 cc. of dry carbon tetrachloride. During the dropwise addition of the latter, which took one hour, the reaction mixture was stirred vigorously and the temperature maintained at 0°. The carbon tetrachloride was evaporated by decreasing the pressure (26–15 mm.) and white crystals formed. Recrystallization from dry ether gave 11.3 g. of a product that softened at 64° and melted at 69–70°; yield 92.2%. The crystals were soluble in ether, carbon tetrachloride, dioxane, and water, but not readily so in petroleum ether. They may be kept in an evacuated (approx. 15 mm.) desiccator for several days, but on exposure to the atmosphere, hydrogen bromide is continuously evolved and a dark brown oil eventually results.

Anal. Calcd. for $C_4H_6O_2Br_2$: Br, 65.00. Found: Br, 63.60, 63.22.

A sample which had stood for two days in a vacuum desiccator showed a slight lowering of melting point and gave 63.06% of bromine. The continually decreasing bromine content serves to explain why all of the analyses are below theoretical.

Since these analyses were only moderately satisfactory, it seemed desirable to prepare a derivative that would prove whether or not the above crystals were 2,3-dibromodioxane; 22.6 g. of the compound was prepared as described above, dissolved in 50 cc. of anhydrous ether, and added over a period of an hour to an ether solution of phenylmagnesium bromide (0.20 mole). The reaction mixture was cooled to 0°, hydrolyzed with water and dilute sulfuric acid, and the ether layer separated. On distillation, 13 g. of a colorless oil, b. p. 185–189° (11–12 mm.), resulted. On crystallization of this oil from petroleum ether, 12.4 g. of 2,3-diphenyldioxane, m. p. 49°, mixed m. p. 49°, was obtained; yield, 56.2%.

I. Addition of Hydrogen Chloride to *p*-Dioxene. (Monochloro-*p*-dioxane.)—It was observed that much heat is evolved when dry hydrogen chloride is passed into *p*-dioxene. As one of the reactions that may be postulated would indicate the unknown monochloro-*p*-dioxane, the following experiment was carried out in an attempt to isolate this compound.

p-Dioxene (6.5 g. or 0.076 mole) was cooled to 0°. Hydrogen chloride was slowly bubbled through the *p*-dioxene with stirring at 0°. Immediate fractionation yielded 6.6 g. of a product, b. p. 59° (17 mm.). Approximately 1 g. of a tarry residue remained. Redistillation gave a b. p. of 62–63° (14 mm.); d^{20}_{20} 1.276.

Anal. Calcd. for $C_4H_7O_2Cl$: Cl, 28.94. Found: Cl, 26.84.

An experiment using ether as a solvent failed to give as good a yield as the above procedure.

In yet another experiment, bismuth trichloride was used as a catalyst, with rather surprising results. To 12.04 g. (0.14 mole) of *p*-dioxene was added 0.0135 g. (0.0001 mole) of bismuth trichloride. Dry hydrogen chloride was passed in for thirty minutes as the liquid was agitated, the temperature being maintained at 0°. The reaction product became light brown to orange in color. Less than 1 cc. distilled at 12–13 mm. when the temperature of the bath surrounding the distilling flask was raised to 275°. The material remaining in the distilling flask became a dark colored tarry residue. It is probably a polymer of *p*-dioxene, and is being further investigated.

Monochloro-1,4-dioxane is a colorless liquid. It constantly loses hydrogen chloride, and on standing for a few minutes becomes yellow. Within a week it changes to a black, viscous tar. Analyses other than those given above on freshly distilled material gave 25.66% Cl and 27.62% Cl compared with the calculated value of 28.94% Cl. Evidently the compound decomposes to such an extent that a satisfactory analysis is impossible; however, the identity of the compound was proved by the following experiment.

J. Monophenyl-*p*-dioxane.—A Grignard reagent was prepared by reaction of 19.28 g. (0.126 mole) of bromobenzene with 3.064 g. (0.126 mole) of magnesium, using 75 cc. of dry ether.

Freshly prepared monochloro-*p*-dioxane (7.31 g. or 0.06 mole) was dissolved in 10 cc. of dry ether and added to the agitated Grignard reagent at such a rate that the vigorous reaction resulted in a gentle refluxing of the solvent. Hydrolysis was carried out with water and dilute sulfuric acid at 0°. The ether layer upon evaporation yielded 4.8 g. of crystals, m. p. 45–46°. Recrystallization of the product from either alcohol or petroleum ether gave a melting point of 46°; yield, 49%.

Alkaline permanganate oxidation of the monophenyl-*p*-dioxane prepared above gave benzoic acid, proving a phenyl radical attached to carbon. The identity of the benzoic acid was ascertained by the formation of the *p*-toluidide, m. p. 156.5–157°.

Anal. Calcd. for $C_{10}H_{12}O_2$: mol. wt., 164.1; C, 73.13; H, 7.37. Found: mol. wt., 175;[18] C, 73.43; H, 7.36.

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[18] Mol. wt. by Rast camphor method.

Conclusions

1. A number of 2,3-diaryl-1,4-dioxanes have been synthesized for the first time.
2. The reaction of alkylmagnesium halides with 2,3-dichloro-1,4-dioxane produces *p*-dioxene, a new compound, of which the structure has been proved.
3. The reactions of *p*-dioxene have been studied.
4. Monochloro-*p*-dioxane has been obtained for the first time, and a mechanism for the chlorination of dioxane proposed.
5. Monophenyl-*p*-dioxane has been prepared.
6. The work is being continued.

EVANSTON, ILLINOIS RECEIVED JULY 29, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

The Identification of Phenols with 2,4-Dinitrochlorobenzene

BY R. W. BOST AND FRANK NICHOLSON

Although numerous reagents have been proposed for the identification of phenols,[1-5] nevertheless serious objections may be raised against most of them. The method of Koelsch[5] is perhaps the best but many of his derivatives melt so close together that identification is difficult, whereas the *o*- and *p*-nitrophenols were not obtained.

The value of 2,4-dinitrochlorobenzene as a reagent for the identification of mercaptans has been shown in previous communications.[6,7] Since the reactions of mercaptans and phenols are similar in many respects, it seemed desirable to study the usefulness of 2,4-dinitrochlorobenzene as a reagent for phenols. In a few cases 2,4-dinitrophenyl ethers occur in the literature and in such cases the melting points and literature references are given in the table. In cases where discrepancies occur between the melting points of those reported in the literature and of those obtained in our study, analyses were made and herein recorded.

Procedure

0.01 Mole of the phenol is added to 0.01 mole of sodium hydroxide dissolved in 5 cc. of water. The resulting solution of sodium phenolate is added to 0.01 mole of 2,4-dinitrochlorobenzene dissolved in 30 cc. of ethyl alcohol (95%). In some cases with difficultly soluble compounds more alcohol must be added to keep the substance in solution. The solution at this point is always highly colored. In most cases it turns dark red in color; however in some cases it is almost black. The solution is then heated under reflux on a steam-bath until the red color is discharged and a copious precipitate of salt appears. (Usually one-half hour is sufficient.) The reaction mixture is diluted with an equal part of water whereupon the 2,4-dinitrophenyl ether is precipitated, then filtered, washed with water and finally recrystallized from alcohol. As a rule one recrystallization is sufficient.

Discussion of Results

There are times when a precipitate occurs at the point when the aqueous solution of the phenolate is added to the alcoholic solution of the reagent. This precipitate is not to be confused with the precipitate of salt which appears after heating for some time. It has been shown[8] that 2,4-dinitrochlorobenzene forms addition products with certain phenols, and apparently the precipitate first formed in our work is of such a nature, since it contains both nitrogen and chlorine. Upon heating, it loses chlorine as well as its color, and sodium chloride is precipitated.

The 2,4-dinitrophenyl ethers which were obtained are easily purified, highly crystalline, and possess sharp melting points widely enough separated to ensure identification. An exception is noted only in the case of derivatives of 2,4-dibromophenol and 2,4,6-tribromophenol, which have the same melting point. However, in this case, the original phenols melt 56° apart. With the exception of the derivatives of thymol, carvacrol and hexylresorcinol, all are precipitated from the reaction mixture as solids. The reagent is superior to the isocyanates in that the presence of water in the phenol does not interfere with the formation of the derivative. The melting points are high enough so that very few are obtained as oils, again indicating the superiority of the reagent. 2,4-Dinitrochlorobenzene is more stable than both

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(1) Herzog, *Ber.*, **40**, 1831 (1907).

(2) Reid, THIS JOURNAL, **39**, 304 (1917); Lyman and Reid, *ibid.*, **42**, 615 (1920).

(3) Brown and Kramers, *J. Am. Pharm. Assoc.*, **11**, 607 (1922).

(4) French and Wertel, THIS JOURNAL, **48**, 1736 (1926).

(5) Koelsch, *ibid.*, **53**, 304 (1931).

(6) Bost, Turner and Norton, *ibid.*, **54**, 1985 (1932).

(7) Bost, Turner and Conn, *ibid.*, **55**, 4456 (1933).

(8) Buehler, Hisey and Wood, *ibid.*, **52**, 1939 (1930).

2,4-DINITROPHENYL ETHERS

Phenol	Color	Crystal form	M. p., °C. Obsd.	M. p., °C. Lit.	Analyses, % N Calcd.	Analyses, % N Found
Phenol[a]	Faint yellow	Fine needles	69	70	10.76	10.62
o-Cresol	Faint yellow	Prisms	90		10.22	10.03
m-Cresol	Pale greenish-yellow	Prismatic needles	74		10.22	10.45
p-Cresol[b]	Faint yellow	Flat needles	93.5	93	10.22	10.08
Thymol	Faint yellow	Prismatic needles	67		8.85	8.57
Guaiacol	Faint yellow	Prismatic needles	97		9.65	9.40
α-Naphthol	Pale yellow	Very fine needles	128		9.03	9.12
β-Naphthol[c]	Colorless	Hair-like needles	95	95	9.03	8.93
p-Hydroxydiphenyl	Faint greenish-yellow	Needles	118		8.33	7.92
Resorcinol[d]	Buff	Granular	194	184	12.67	13.00
Eugenol[e]	Yellow	Very fine needles		114–115		
Isoeugenol[e]	Sulfur yellow	Needles	130	129–130		
Vanillin[e]	Colorless	Needles		131		
o-Nitrophenol[f]	Buff	Granular	142	119	13.81	14.00
m-Nitrophenol[g]	Light yellow	Prismatic needles	138	136	13.81	13.81
p-Nitrophenol	Light yellow	Fine needles	120	114	13.81	14.08
2-Chloro-5-hydroxytoluene	Faint greenish-yellow	Needles	112		9.07	8.80
o-Iodophenol	Faint yellow	Small plates	95		7.22	7.01
					Analyses, % halogen	
o-Chlorophenol	Faint greenish-yellow	Needles	99		12.04	11.85
m-Chlorophenol	Faint yellow	Needles	75		12.04	11.90
p-Chlorophenol	Light yellow	Small needles	126		12.04	12.11
2,4-Dichlorophenol	Faint yellow	Very short needles	119		21.87	21.72
2,4,6-Trichlorophenol	Pale yellow	Rhombic crystals	136		29.26	29.40
o-Bromophenol	Faint greenish-yellow	Small prisms	89		23.58	23.20
p-Bromophenol	Faint yellow	Fine needles	141		23.58	23.70
2,4-Dibromophenol	Pale yellow	Fine needles	135		38.28	38.48
2,4,6-Tribromophenol	Faint greenish-yellow	Long needles	135		48.26	48.10
p-Iodophenol[h]	Light yellow	Needles		156		

[a] Willgerodt, *Ber.*, **12**, 764 (1879); Cook, THIS JOURNAL, **32**, 1291 (1910). [b] Cook, *ibid.*, **32**, 1289 (1910). [c] Ernst, *Ber.*, **23**, 3429 (1890). [d] Nietzki and Schundelen, *ibid.*, **24**, 3586 (1891). [e] Einhorn and Frye, *ibid.*, **27**, 2457 (1894). [f] Willgerodt and Huetlin, *ibid.*, **17**, 1765 (1884). [g] German Patent 28,053 (1914); *Chem. Zentr.*, **86, I**, 74 (1915). [h] Willgerodt and Weigand, *Ber.*, **42**, 3764 (1909).

the isocyanates and the nitroacyl halides and possesses an advantage in this respect. The procedure is simple and requires no special degree of skill. Good results may be obtained in the hands of a beginner.

Summary

1. 2,4-Dinitrochlorobenzene reacts with phenols forming highly crystalline stable solids, easily purified, and possessing sharp melting points.

2. The procedure is simple and requires no unusual of technique.

3. Derivatives of twenty-eight phenols are given.

CHAPEL HILL, NORTH CAROLINA

RECEIVED AUGUST 12, 1935

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

Studies on the Polymethylbenzenes. XIII.[1] Mercuration

BY LEE IRVIN SMITH AND F. LOWELL TAYLOR[2]

Direct mercuration is a characteristic substitution reaction of aromatic hydrocarbons which has not been studied previously in the series of the polymethylbenzenes. In the study reported in this paper, six polymethylbenzenes, namely, mesitylene, pseudocumene, durene, isodurene, prehnitene, and penta-methylbenzene were mercurated and the acetoxymercuri-, halogenomercuri-, and bis-arylmercury derivatives were prepared and characterized.

Michaelis[3] treated bromomesitylene and 5-bromopseudocumene with sodium amalgam in xylene, and obtained the corresponding bis-arylmercury compounds; from the latter he prepared arylmercuric halides by the action of mercuric halides. Whitmore[4] and his students mercurated mesitylene directly with mercuric acetate, but they did not report the properties of acetoxymercurimesitylene. Jacobsen[5] obtained bis-(pentamethylphenyl)-mercury when he attempted to prepare pentamethylbenzoic ester from bromopentamethylbenzene, chloroformic ester and sodium amalgam.

The polymethylbenzenes were mercurated by mercuric acetate in methanol solution. Pentamethylbenzene, durene, and mesitylene gave good yields of monoacetoxymercuri derivatives; pseudocumene and prehnitene formed considerable amounts of diacetoxymercuri derivatives. Pseudocumene mercurated first in the 5-position; the position of the second mercury atom in the diacetoxymercuri compound was not determined. Acetoxymercuriisodurene was most conveniently prepared from the fraction of b. p. 79–91° (15 mm.) obtained by direct methylation of xylene. Most of the durene was removed from this fraction by filtration at −10°, and the filtrate then contained about 90% of isodurene.[6] Since acetoxymercuriisodurene was more soluble than acetoxymercuridurene in alcohol, the two compounds were separated by crystallization. This procedure avoided the time consuming preparation of pure isodurene. Samples of acetoxymercuriisodurene prepared from the mixture of hydrocarbons and from pure isodurene had the same melting point; the melting point of the substance was depressed by acetoxymercuridurene.

Chloro-, bromo- and iodomercuri derivatives of the hydrocarbons were prepared from the acetoxymercuri compounds by metathesis, since the halides were less soluble than the acetates. Likewise, since the bis-(polymethylphenyl)-mercury compounds were less soluble than the iodomercuri compounds, they were prepared from the iodo compounds by the action of sodium iodide.[4] Iodomercuripentamethylbenzene could not be prepared from the acetate because even less than one mole of sodium caused the formation of bis-(pentamethylphenyl)-mercury.

The mercury compounds which were previously unknown are listed in the tables, with melting points and analytical data.

Experimental Part

Mercuration.—The hydrocarbons were dissolved in five volumes of methanol, and a mole of mercuric acetate was introduced. Enough acetic acid was added to prevent hydrolysis of the mercury salt[7,8] and the solutions were refluxed. Mercuration of durene, mesitylene and pentamethylbenzene required five to seven days for completion. Isodurene, prehnitene and pseudocumene were allowed to react for only twenty to forty hours because of the formation of large amounts of diacetoxymercuri derivatives. The procedures for isolation of the products were determined by the solubilities. The following specific conditions were used in the preparation of the individual compounds.

Acetoxymercuripentamethylbenzene was insoluble in the hot reaction mixture; the product was filtered and crystallized from chloroform; m. p. 180°; yield 80%.

Acetoxymercuridurene was soluble in the hot reaction mixture; the solution was filtered from the insoluble diacetoxymercuridurene and cooled. The crude product (m. p. 152–156°, yield 60%) was crystallized from methanol (solubility, 12 g. per 100 cc. at the b. p.; 3 g. per 100 cc. at 0°). The melting point of the pure substance was 158–159°.

Acetoxymercurimesitylene was soluble in the cold reaction mixture. The solution was filtered from diacetoxymercurimesitylene and then diluted with water. The oil[9]

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[1] Paper XII, THIS JOURNAL, **57**, 1293 (1935).

[2] Abstracted from the thesis of F. Lowell Taylor, presented to the Graduate School of the University of Minnesota, in partial fulfilment of the requirements for the Ph.D. degree, March, 1935.

[3] Michaelis, *Ber.*, **28**, 588 (1895).

[4] Whitmore and Sobatzki, THIS JOURNAL, **55**, 1128 (1933); Whitmore and Beattie, *ibid.*, p. 1567.

[5] Jacobsen, *Ber.*, **22**, 1220 (1889).

[6] Smith and Cass, THIS JOURNAL, **54**, 1611 (1932).

[7] Maynard, *ibid.*, **46**, 1510 (1924); **54**, 2118 (1932).

[8] Mercuric oxide (1 mole) and acetic acid (2 moles) were often substituted for the mercuric acetate.

[9] The oil was a strong vesicant.

TABLE I

ACETOXYMERCURI-POLYMETHYLBENZENES, $RHgOCOCH_3$

Parent hydrocarbon[a]	M. p., °C.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Mercury Calcd.	Mercury Found
Pentamethylbenzene	180	$C_{13}H_{18}O_2Hg$	38.35	37.9	4.46	4.49		
Durene (1, 2, 4, 5)	158–159	$C_{12}H_{16}O_2Hg$	36.67	36.5	4.11	4.57	51.1	50.6
Isodurene (1, 2, 3, 5)	108	$C_{12}H_{16}O_2Hg$	36.67	35.6	4.11	4.4	51.1	51.2
Prehnitene (1, 2, 3, 4)	147	$C_{12}H_{16}O_2Hg$	36.67	36.2	4.11	4.4		
Mesitylene (1, 3, 5)	102–103	$C_{11}H_{14}O_2Hg$					53.0	52.0
Pseudocumene[b] (1, 2, 4)	145–147	$C_{11}H_{14}O_2Hg$					53.0	53.2

[a] The figures denote the positions of the methyl groups. [b] Acetoxymercuri group in the 5-position.

TABLE II

HALOGENOMERCURI-POLYMETHYLBENZENES

Parent hydrocarbon	X	Solvent	M. p., °C.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Pentamethylbenzene	Cl	$CHCl_3$	205	$C_{11}H_{15}HgCl$	34.45	34.2	3.96	4.12
	Br	$CHCl_3$	195–196	$C_{11}H_{15}HgBr$	30.87	30.4	3.54	3.6
Durene	Cl	$CHCl_3$	188–189	$C_{10}H_{13}HgCl$	32.51	32.3	3.55	3.93
	Br	$CHCl_3$–MeOH	174	$C_{10}H_{13}HgBr$	29.01	28.8	3.17	3.39
	I	$CHCl_3$–MeOH	161–162	$C_{10}H_{13}HgI$	26.05	26.2	2.84	3.37
Isodurene	Cl	$CHCl_3$–MeOH	174	$C_{10}H_{13}HgCl$	32.51	32.2	3.55	3.84
	Br	$CHCl_3$–MeOH	160	$C_{10}H_{13}HgBr$	29.01	28.7	3.17	3.54
	I	$CHCl_3$–MeOH	163–164	$C_{10}H_{13}HgI$	26.05	25.8	2.84	3.12
Prehnitene	Cl	$CHCl_3$	216–217	$C_{10}H_{13}HgCl$	32.51	32.2	3.55	3.88
	Br	$CHCl_3$	213–214	$C_{10}H_{13}HgBr$	29.01	28.6	3.11	3.3
	I	$CHCl_3$	200	$C_{10}H_{13}HgI$	26.05	25.7	2.84	3.29

TABLE III

BIS-(POLYMETHYLPHENYL)-MERCURY COMPOUNDS, R_2Hg

Derivative of	M. p., °C.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Mercury Calcd.	Mercury Found
Pentamethylbenzene	278[a]	$C_{22}H_{30}Hg$	53.35	53.1	6.11	6.29		
Durene	242–243	$C_{20}H_{26}Hg$	51.41	50.5	5.61	5.9	43.0	42.5
Isodurene	217–218	$C_{20}H_{26}Hg$	51.41	49.6	5.61	5.8	43.0	42.4
Prehnitene	200	$C_{20}H_{26}Hg$	51.41	50.3	5.61	5.7	43.0	41.4

[a] Jacobsen, *loc. cit.* reported the m. p. as 266°.

which separated did not crystallize until unchanged mesitylene had been removed by steam distillation. Crystallization from methanol gave the pure substance; m. p. 102–103°; yield 30%.

Acetoxymercuriisodurene also separated as an oil[9] when the reaction mixture was diluted with water, but the substance solidified after it was washed by decantation and cooled. It was crystallized from 75% alcohol (warmed only to 60°). The yield of the product, m. p. 108°, was 30%, when prepared from either pure isodurene or the mixture of tetramethylbenzenes ("durene filtrate").

Acetoxymercuriprehnitene was soluble in the hot reaction mixture. The solution was filtered from insoluble diacetoxymercuriprehnitene, cooled, and diluted with water. The substance crystallized from methanol in radial needles, m. p. 147°; yield 15%.

5-Acetoxymercuripseudocumene was isolated in the same manner as the prehnitene derivative; the substance was crystallized from 95% ethanol; m. p. 145–147°; yield 30%.

Crude acetoxymercuri derivatives were recovered by dilution of the alcoholic filtrates with water. The filtrates were then treated with salt or hydrochloric acid to remove the remainder of the organomercury compounds by precipitation as chloromercuri derivatives. The final filtrates from the reaction mixtures were treated with sulfide to recover mercury.

Halogenmercuri Compounds.—The halides were prepared as follows: the acetoxymercuri compounds were dissolved in chloroform, alcohol or a mixture of the two solvents. Hydrochloric acid, sodium bromide or sodium iodide, respectively, was dissolved in aqueous alcohol and added to the solutions of the mercury compounds. The precipitates were filtered, washed and crystallized. The solvents which were used for the individual substances are listed in Table II.

It was necessary to use less than one equivalent of sodium iodide in the preparation of iodomercuripolymethylbenzenes in order to prevent formation of bis-arylmercury compounds. Despite that precaution, the product from acetoxymercuripentamethylbenzene was a mixture of iodomercuripentamethylbenzene and bis-(pentamethylphenyl)-mercury. Separation of the two substances by crystallization was impossible. Mercuric iodide was formed, which indicated that the iodomercuric compound in solution was converted to the bis-aryl compound by heat alone.

Bis-arylmercury Compounds.—The iodomercuri derivatives were precipitated from alcoholic solutions of the acetates and, without purification, were digested for several hours in alcohol with four moles of sodium iodide.[10] The substances were crystallized from chloroform. Diduryl mercury was prepared also by reduction of the acetate with sodium stannite.[7,11] The method was unsatisfactory because separation of the product from finely divided mercury was difficult.

Analyses.—Furter[12] demonstrated that mercury causes low analytical values for carbon. However, satisfactory carbon and hydrogen analyses of most of the mercury compounds were obtained by the semi-micro method with a Pregl universal filling in the combustion tube when precautions were taken. The substances were covered with cupric oxide and burned in an oxygen stream which had half the usual velocity. Silver foil was used in the tip of the combustion tube to collect free mercury. Silver was not very satisfactory for the purpose, but gold was not available.

Mercury analyses, in the absence of halogens, were made by titration with potassium thiocyanate after the organic material had been destroyed by hot concentrated nitric acid and permanganate.[13]

Summary

1. The mercuration of six polymethylbenzenes (mesitylene, pseudocumene, durene, isodurene, prehnitene and pentamethylbenzene) has been studied.

2. A number of related mercury derivatives have been prepared from each of the primary products of mercuration.

3. Twenty new organomercury compounds have been described.

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[10] Steinkopf and Baumeister, *Ann.*, **403**, 50 (1914); Whitmore, *et al., loc. cit.;* Johns and Hixon, *J. Phys. Chem.*, **34**, 2218 (1930); THIS JOURNAL, **52**, 2820 (1930); **56**, 1333 (1934).

[11] Dimroth, *Ber.*, **35**, 2032, 2853 (1902); *ibid.*, **54**, 1504 (1921).

[12] Furter, *Mikrochem.*, **9**, 27 (1931); see also Hernler, *ibid.*, Pregl Festschrift, 154 (1929); Verdino, *ibid.*, **6**, 5 (1928); Grignard and Abelmann, *Bull. soc. chim.*, [4] **19**, 25 (1916).

[13] Tabern and Shelberg, *Ind. Eng. Chem., Anal. Ed.*, **4**, 401 (1932).

MINNEAPOLIS, MINN. RECEIVED JULY 26, 1935

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

Organic Flocculating Agents in the Quantitative Precipitation of Zinc Sulfide[1]

BY JOHN R. CALDWELL AND HARVEY V. MOYER

Comprehensive reviews of proposed methods for the precipitation of zinc sulfide are to be found in the comparatively recent publications of Jeffreys and Swift,[2] J. N. Frers,[3] and Mayr.[4]

Practically all of the efforts made to obtain the precipitate in a suitable physical form are based on three general procedures: (a) precipitation from hot solution; (b) salting-out with a large excess of some neutral salt; (c) maintenance of a low *p*H value by means of buffers. It is a well-recognized fact that in the early stages of precipitation most sulfides exist as hydrosols, and the formation of an insoluble precipitate depends to a large extent on the rate of transformation from sol to flocculent state. This transformation may be promoted by the presence of finely divided solid matter as demonstrated by Kolthoff[5] and by Frers.[3]

Recently we have found that certain organic substances may be used to alter the nature of analytical precipitates.[6,7] It seemed quite probable that flocculation of colloidal zinc sulfide could be induced by a somewhat similar procedure. The coagulation of precipitates by means of small concentrations of organic substances has been reported frequently by colloid chemists. Contrary to the ordinary behavior, certain hydrophilic colloids such as agar-agar, gelatin, gum arabic, etc., will not stabilize suspensoid sols if present in minute traces, but will bring about complete and rapid flocculation. This phenomenon, called sensitization, has been known for many years, but apparently never before has been applied to analytical chemistry. A brief review of recent colloid literature furnished ample indication that this field offers attractive possibilities for further investigation.

Rossi and Scandallari[8] showed that minute quantities of gelatin brought about rapid coagulation of sulfur sols. Chaudhury[9] reported that sols of ferric hydroxide and arsenic trisulfide were sensitized and flocculated by methyl alcohol,

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 89th meeting of the American Chemical Society, New York City, April 22 to 26, 1935.

[2] Jeffreys and Swift, THIS JOURNAL, **54**, 3219 (1932).

[3] J. N. Frers, *Z. anal. Chem.*, **95**, 1–36 (1933).

[4] Mayr, *ibid.*, **96**, 273 (1934).

[5] Kolthoff, *J. Phys. Chem.*, **36**, 549 (1932).

[6] Caldwell and Moyer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 38 (1935).

[7] Caldwell, THIS JOURNAL, **57**, 96 (1935).

[8] Rossi and Scandallari, *Ann. chim. appl.*, **23**, 67 (1933).

[9] Chaudhury, *J. Phys. Chem.*, **32**, 1481 (1927).

ethyl alcohol, pyridine, urea and glycerol. Gelatin was used to flocculate sols of antimony trisulfide[10] while gum arabic had a similar effect on arsenic trisulfide and manganese dioxide sols.[11] Ghosh and Dhar[12] demonstrated that gelatin and tannin rapidly flocculated sols of ferric hydroxide and arsenic trisulfide. Weiser showed that certain organic compounds not only brought about rapid flocculation of arsenic trisulfide and ferric hydroxide sols, but also reduced the amount of adsorbed ions carried down by the precipitate.[13]

A review of the literature revealed that at least two attempts have been made to flocculate zinc sulfide precipitates by a mechanism similar to those just described. K. Bornemann[14] passed hydrogen sulfide into a zinc solution containing soldium bisulfite and buffered with ammonium acetate. He claimed that the colloidal sulfur formed in the reaction helped to coagulate the zinc sulfide. More recently, Hibbard,[15] in a procedure for the microdetermination of zinc as the sulfide, added talc to the solution in order to promote flocculation.

With the object of developing an improved method for precipitation of zinc sulfide, a systematic study was made of the effect of various hydrophilic colloids on the coagulation of the freshly formed precipitate.

Materials

Standard Zinc Solution.—Zinc ammonium sulfate was prepared by mixing concentrated solutions of C. P. ammonium sulfate and C. P. zinc sulfate. The zinc ammonium sulfate crystals which separated from solution were recrystallized twice. A solution was prepared containing approximately 5 mg. of zinc per ml. and was standardized by precipitating the zinc in 50 ml. as sulfide from a sulfate buffered solution according to the directions of Jeffreys and Swift[2] and also from chloroacetic acid–sodium acetate buffered solutions according to the procedure of Mayr.[4] In all cases the zinc sulfide was ignited to the oxide in an electric muffle at a temperature of 1000° as recommended by Hillebrand and Lundell.[16] The temperature of ignition was measured with a thermocouple. Of eight determinations, the extreme values were 0.3163 and 0.3155 g. of zinc oxide, the average being 0.3160 g.

Sulfates of Other Metals.—Reagent grade sulfates of nickel, cobalt and manganese were dissolved and filtered before use. Chromium, aluminum and iron were used in the form of their potassium alums.

Organic Materials, Gums, Soaps, etc.—No attempt was made to determine the purity of these materials and they were used without further treatment. Low-ash gelatin (0.03%) was purchased from the Eastman Kodak Co.

Experimental Work

Three hundred milliliters of a solution containing 0.25 g. of zinc as the sulfate and 6–8 g. of ammonium sulfate was used as the starting point for the tests. Two general plans were followed: (a) the substance to be tested was added to this solution and hydrogen sulfide passed in for fifteen to twenty minutes; (b) hydrogen sulfide was passed in for fifteen to twenty minutes and the test material was added slowly with stirring in the form of a dilute aqueous or alcoholic solution. Both methods were carried out at room temperature. Among the agents used were gelatin, agar-agar, gum ghatti, gum tragacanth, gum arabic, casein, egg albumin, sucrose, saponin, various soaps, and mixtures of these.

It was found that gelatin (0.5 to 2.0 mg.) and agar-agar (2 to 5 mg.) produced the desired effect. When added to the solution either before or after precipitation with hydrogen sulfide, these two agents caused instantaneous and complete flocculation of the zinc sulfide. Gelatin was chosen as the more suitable flocculating agent, because it can readily be obtained practically ash-free.

Further experimental work was carried out at higher dilutions and it was found that 0.05 mg. of gelatin would give a pronounced flocculation in volumes up to 500 ml. This is a dilution of one to ten million and the sensitivity is comparable to that of precipitin reactions with immune sera used in bacteriological work. If several milligrams of egg albumin was added to the solution before precipitation, the sensitivity of the gelatin was increased until it gave flocculation in dilutions of one:one hundred million.

Procedure for Quantitative Precipitation of Zinc Sulfide.—The procedure finally adopted for quantitative precipitation of zinc is based essentially on conventional methods. A solution free of chlorides, containing approximately 0.25 g. of zinc and 6 to 8 g. of ammonium sulfate is diluted to 250 to 300 ml. and made just acid to methyl orange. A rapid stream of hydrogen sulfide is passed through the solution for thirty minutes at room temperature. Five to 10 ml. of a 0.02% solution of gelatin is added with rapid stirring and the precipitate is allowed to settle. The most satisfactory gelatin for the purpose is a low-ash product containing less than 0.1% ash. A few drops of oil of wintergreen will preserve a dilute solution for several months. An instantaneous and complete flocculation of the colloidal precipitate takes place upon the addition of the gelatin, and if 10 to 20 mg. of gelatin is added, the flakes of precipitate are so large that they cling together and tend to slow up filtration. After fifteen minutes' standing, the supernatant liquid is practically clear, and may be decanted from the precipitate. The precipitate is easily washed by decantation and distilled water may be used as there is no peptizing action. In about 100 precipitations, a clear filtrate was always obtained when Schleicher and Schull blue-band filter paper was used.

The gelatin is adsorbed completely on the precipitate as shown by negative protein color tests on the filtrate,

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(10) Meneghetti, *Bull. soc. ital. biol. sper.*, **3**, 779 (1928).

(11) A. S. Mennon, *Kolloid-Z.*, **38**, 242 (1926).

(12) Ghosh and Dhar, *ibid.*, **41**, 229 (1927).

(13) Weiser, *J. Phys. Chem.*, **28**, 1253 (1924).

(14) K. Bornemann, *Z. anorg. Chem.*, **82**, 216 (1913).

(15) P. L. Hibbard, *Ind. Eng. Chem., Anal. Ed.*, **6**, 423 (1934).

(16) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929.

It was found that this quantity of gelatin (1 to 2 mg.) does not interfere with the ferrocyanide volumetric determination of zinc.

If iron is present, it is better to wash with hydrogen sulfide water to keep the iron in a reduced state.

Quantitative Experiments.—Fifty milliliters of standard zinc solution, equivalent to 0.3160 g. of zinc oxide, precipitated according to the procedure outlined above, gave this weight of zinc oxide after ignition at 1000° with deviations of +0.6, −0.3, −0.4, +0.1, +0.3 mg.

Separation of Zinc from Iron, Nickel, Cobalt, Manganese, Aluminum, Chromium.—Table I summarizes the results obtained when zinc sulfide was precipitated in the presence of other metals. In each case, the precipitate was ignited to the oxide and analyzed for the contaminating metal. The iron was reduced with sulfur dioxide and the sulfur dioxide removed with carbon dioxide before saturation with hydrogen sulfide. This step was necessary, as the *p*H of the solution allows the formation of a small amount of ferric hydroxide before reduction of iron by hydrogen sulfide is complete. Iron in the ignited precipitate was determined colorimetrically as ferric thiocyanate. Manganese was determined colorimetrically as permanganate after oxidation with potassium periodate. Nickel was determined with dimethylglyoxime. Cobalt was determined colorimetrically by dissolving the precipitate in concentrated hydrochloric acid and comparing with standards prepared in the same way. For aluminum and chromium, the precipitate was dissolved in hydrochloric acid and the solution made just basic to methyl red with ammonia. No precipitate appeared with aluminum, and a trace of precipitate was formed with chromium.

Table I

Precipitation in Presence of Other Metals

Volume 250 to 300 ml. containing 6 to 8 g. of $(NH_4)_2SO_4$. Zinc equivalent to 0.3160 g. of ZnO, and 0.25 g. of other metal present.

Other metal	Other metal in ZnO ppt., mg.	Ignited ppt., g.	Dev. from std., g.
Ni	Less than 0.1	0.3157	−0.0003
	Less than .1	.3157	− .0003
Mn	0.1	.3164	+ .0004
	.1	.3158	− .0002
Al	Less than 0.1	.3163	+ .0003
	Less than .1	.3160	± .0000
Co	5.8	.3236	+ .0076
	7.0	.3258	+ .0098
Cr	0.1	.3162	+ .0002
	.1	.3159	− .0001
Fe	.3	.3166	+ .0006
	.2	.3164	+ .0004

If zinc sulfide is precipitated in the presence of small concentrations of certain aldehydes, practically no cobalt is carried down. A new separation of zinc and cobalt based on this principle will be described in a later paper.

As a final test of the method, zinc ore No. 2a from the Bureau of Standards was analyzed according to the procedure outlined by Lord and Demorest.[17] The only departures from the original procedure were a reprecipitation of cadmium sulfide, and the use of 2 mg. of gelatin as a flocculating agent. The average of four determinations was 30.45% of zinc, while the value given by the Bureau was 30.53%.

Precipitation in Solution Buffered with Chloroacetic Acid–Sodium Acetate.—When it is necessary to precipitate zinc in the presence of alkaline earth metals, it is not permissible to use a sulfate buffer. Mayr[4] has proposed a chloroacetic acid–sodium acetate buffer for this purpose. It is also possible to make a separation from iron without preliminary reduction, as the *p*H is sufficiently low (2.8) to hold ferric iron in solution. Excellent results were obtained when this method was used together with flocculation by gelatin. Mayr recommends a wash solution consisting of the diluted buffer saturated with hydrogen sulfide, but when the precipitate has been flocculated by 1–2 mg. of gelatin, distilled water may be used and no peptization occurs. Satisfactory separations from all metals but cobalt were obtained.

Other Applications.—Further applications of this principle are now being investigated, and preliminary experiments on the precipitation of other sulfides, ammonium phosphomolybdate, certain fluorides, and the hydrous oxides indicate a promising field for future research.

Summary

A new method for flocculating certain colloidal precipitates is proposed. It has been found that gelatin (0.5 to 2 mg.) and agar-agar (2 to 5 mg.) will produce instantaneous and complete flocculation of 0.3 g. zinc sulfide in 300 ml. of solution. Precipitations are made at room temperature, and the solution may be filtered within fifteen minutes after precipitation. Satisfactory separations from all metals but cobalt are obtained, and the precipitate may be washed with cold distilled water.

Columbus, Ohio Received May 18, 1935

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[17] Lord and Demorest, "Metallurgical Analysis," McGraw-Hill Book Company, Inc., New York, 1924.

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

A Separation of Zinc from Cobalt Based on a New Method for Reducing Post-Precipitation[1]

BY JOHN R. CALDWELL AND HARVEY V. MOYER

At the present time there is no method described in the literature that will give a quantitative separation of zinc sulfide from cobalt in one precipitation. The zinc sulfide always carries down an appreciable quantity of cobalt, and several reprecipitations must be made. Our observations, as well as those of Jeffreys and Swift,[2] indicate that this contamination has a mechanism similar to that described by Kolthoff for the post-precipitation of zinc on copper sulfide.[3]

Recent work published by us has shown that the presence of certain hydrophilic colloids and of some organic compounds exerts a profound influence upon the physical nature of precipitates.[4,5,6] It seemed probable that this principle could be used to reduce post-precipitation and co-precipitation in standard sulfide precipitations.

When zinc sulfide is contaminated with cobalt it is colored green, and the depth of color indicates approximately the relative amount of cobalt carried down.

Two general classes of material were investigated: (a) protective colloids such as agar-agar, gum arabic, egg albumin, etc., were used with the possibility that they might be preferentially adsorbed in place of the hydrogen sulfide and thus reduce the concentration of hydrogen sulfide at the surface of the zinc sulfide particles; (b) organic compounds capable of reacting with hydrogen sulfide were investigated with the expectation that if they were absorbed on the precipitate they might reduce the concentration of hydrogen sulfide below the precipitation value. Among the compounds used for this purpose were alcohols, ketones, aldehydes, nitro compounds, amines, aromatic nitro acids, unsaturated compounds and others.

Materials

Standard Zinc Sulfate Solution.—The preparation of this solution was described in an earlier paper.[6] It was equivalent to 0.3160 g. of zinc oxide per 50 ml.

Cobalt Sulfate.—A C. P. grade was dissolved and filtered before use. It contained no zinc.

Organic Compounds, Gums, Colloids, etc.—A large number of organic compounds and hydrophilic colloids were used in the investigation. No attempt was made to secure these in a purified condition except in those cases discussed in detail below.

Experimental Work

The substance to be tested was added to 300 ml. of solution containing 0.25 g. of zinc, 0.50 g. of cobalt and 6 to 8 g. of ammonium sulfate. Hydrogen sulfide was passed in for thirty minutes at room temperature, the precipitate flocculated by gelatin,[6] and filtered off. The cobalt content was then determined by comparison with known standards. The amount of cobalt in the standards had been determined colorimetrically by dissolving a precipitate of the same color in hydrochloric acid, and comparing with known amounts of cobalt chloride dissolved under the same conditions. This method was suitable for quantities of cobalt ranging from 0.1 to about 20 mg.

It was found that certain aldehydes would greatly reduce the amount of cobalt carried down. The aldehydes tested were benzaldehyde, cinnamic aldehyde, propionaldehyde, paraldehyde, acetaldehyde, furfural, heptaldehyde, isoamyl aldehyde, *m*-nitrobenzaldehyde, anisaldehyde, crotonaldehyde, chloral, piperonal, paraformaldehyde, glucose, butyraldehyde, formaldehyde and acrolein. Some of the aldehydes were very effective in preventing post-precipitation of cobalt, but they formed troublesome resins which interfered with filtration, or in some cases they prevented complete precipitation of the zinc. It was found that acrolein was best suited for the purpose. It was very effective in small concentrations, did not form a resin readily, and allowed complete precipitation of the zinc.

Freshly distilled acrolein was used for some of the quantitative determinations, but it was found that the liquid part of an old, partly polymerized product was just as effective. For convenience in handling, an aqueous solution containing 4 ml. of acrolein per 100 ml. of water was prepared. About 10 mg. of hydroquinone and 1 drop of concentrated hydrochloric acid were added per 100 ml. of solution to inhibit polymerization. This solution retained its activity for several weeks.

Quantitative Procedure.—The quantitative procedure adopted for precipitation of zinc sulfide in the presence of cobalt is but slightly different from conventional methods. The *p*H of a chloride-free solution containing 0.25 g. of zinc and cobalt up to 0.5 g. is adjusted until the hydroxides just remain in solution, then 6 to 8 g. of ammonium sulfate is added. The total volume is brought to 250 to 300 ml., and 0.2 ml. of acrolein is added. A rapid stream of hydrogen sulfide is passed in at room temperature for thirty minutes. Five to 10 ml. of a 0.02% gelatin solution is added[6] and the precipitate is filtered off after fifteen to

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 89th meeting of the American Chemical Society, New York City, April 22 to 26, 1935.

[2] Jeffreys and Swift, THIS JOURNAL, **54**, 3219 (1932).

[3] Kolthoff, *J. Phys. Chem.*, **36**, 549 (1932).

[4] Caldwell and Moyer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 38 (1935).

[5] Caldwell, THIS JOURNAL, **57**, 96 (1935).

[6] Caldwell and Moyer, *ibid.*, **57**, 2372 (1935).

twenty minutes' standing. Cold distilled water is used to transfer and wash the precipitate. In some cases, the filtrate develops a faint white turbidity after standing. This is due to the formation of a small quantity of resinous acrolein–hydrogen sulfide reaction product. If the filtrate is to be used for further analysis, it is strongly acidified and boiled down to about one-third of its original volume. This treatment will drive out most of the acrolein, and if any still remains, it will appear as small yellow flakes which are readily filtered off.

Quantitative Experiments.—Solutions containing 50 ml. of standard zinc solution, 0.5 g. of cobalt and 6 to 8 g. of ammonium sulfate were precipitated according to the procedure outlined above. When no acrolein was present, 6 to 10 mg. of cobalt was carried down. When 0.2 ml. of acrolein was added before precipitation, the precipitate contained from 0.2 to 0.4 mg. of cobalt. Four determinations using acrolein yielded weights of zinc oxide that deviated by +0.6, ±0.0, +0.1 and +0.3 mg. from the standard value of 0.3160 g. If more than 0.3 ml. of acrolein was used for 0.25 g. of zinc, there was some resin formation and filtration was retarded.

Kolthoff[3] showed that an increase in temperature caused an increase in the amount of zinc post-precipitated with copper sulfide. We found the same general rule to hold with cobalt and zinc. Acrolein proved to be very effective in preventing post-precipitation in hot solution. Solutions having the composition described above were heated for thirty minutes on a boiling water-bath after precipitation. When 0.20 ml. of acrolein was present, the precipitates contained 0.4 to 0.5 mg. of cobalt. In controls containing no acrolein, more than 30 mg. of cobalt was carried down.

If the solution containing zinc and cobalt is first heated to boiling, and hydrogen sulfide then passed in, the effect of acrolein is not so pronounced, and several milligrams of cobalt is carried down. This may be due to the possibility that acrolein is not so readily adsorbed from hot solution.

Precipitation in Chloroacetic Acid–Sodium Acetate Buffer.—For procedures where it is undesirable to have sulfates in the solution, Mayr[7] has proposed the use of a chloroacetic acid–sodium acetate buffer. He reported satisfactory separations from all metals but cobalt. Good separations were obtained with the use of acrolein, when precipitation was carried out at room temperature. The results are summarized in Table I.

TABLE I

PRECIPITATION IN SOLUTION BUFFERED WITH CHLOROACETIC ACID–SODIUM ACETATE

Total volume 250 ml. containing 15 ml. 2 *N* monochloroacetic acid, 15 ml. of 1 *N* sodium acetate, and 0.2 ml. of acrolein. Zinc equivalent to 0.3160 g. of ZnO. Precipitate flocculated by gelatin.

Other metal present in solution, g.	Wt. other metal found in ppt., mg.	Ignited ppt., g.	Dev. from std. soln. value, g.
0.25 Fe .25 Co	[a] [a]	0.3159	−0.0001
.25 Fe .25 Co	[a] [a]	.3158	− .0002
.50 Co	0.3	.3162	+ .0002
.50 Co	.3	.3161	+ .0001

[a] Not determined.

From the table, it is evident that this procedure gives satisfactory separations from cobalt, and from mixtures of iron and cobalt.

Theoretical Discussion.—Although a number of aldehydes were effective in reducting post-precipitation, there seemed to be a high degree of specificity in the case of acrolein that made it far superior to all others tried. A probable explanation of the effect may be based on Kolthoff's theory of post-precipitation. He showed that certain organic compounds containing sulfur were adsorbed by cupric sulfide precipitates and reduced the concentration of hydrogen sulfide at the surface. The action of aldehydes in general, and of acrolein in particular, apparently goes one step farther. They not only are readily adsorbed by the sulfide precipitate, but they also react rapidly with the hydrogen sulfide on the surface and reduce its concentration below the precipitation value. A survey of the organic literature shows that in general aldehydes will react with hydrogen sulfide under the above conditions to give various types of polymerized thioaldehydes.[8,9,10]

Microscopic examination of the precipitate shows that a distinct alteration in the nature of the surface has taken place. The reaction is apparently confined mainly to the surface of the particles, because there is very little decrease in hydrogen sulfide concentration in the solution itself.

It is planned to continue this study as applied to the post-precipitation of zinc on copper sulfide.

Acknowledgment

We wish to take this opportunity to express our appreciation to Professors C. E. Boord and W. R. Brode for their generosity in supplying us with a large number of aldehydes and other organic compounds used in this research. We also wish to acknowledge the kind assistance of Mr. G. R. Owens who furnished the acrolein, and of Mr. C. M. Hull who supplied a quantity of propionaldehyde.

Summary

If zinc sulfide is precipitated in the presence of small concentrations of certain aldehydes, particularly acrolein, the amount of cobalt carried down

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(7) Mayr, *Z. anal. Chem.*, **96**, 273 (1934).

(8) Klinge, *Ber.*, **9**, 1893 (1876).

(9) Baumann, *ibid.*, **22**, 1035, 2605 (1889).

(10) Wörner, *ibid.*, **29**, 139 (1896).

is greatly reduced. This makes it possible to separate zinc and cobalt by one precipitation. Experimental evidence indicates that acrolein reacts with hydrogen sulfide on the surface of the zinc sulfide particles, thereby reducing post-precipitation.

COLUMBUS, OHIO RECEIVED MAY 18, 1935

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

The Accuracy of the Titration of Thiocyanate with Mercuric Mercury

BY I. M. KOLTHOFF AND J. J. LINGANE

In a previous paper[1] it was shown that in the direct and the reverse titration of silver with thiocyanate nearly theoretical results are obtained, slight deviations being found as a result of side reactions occurring during the reaction of the silver and thiocyanate ions. It was thought of interest to test the accuracy of the titration of mercuric mercury with thiocyanate and the reverse titration, especially since it had been shown that the end-point could be determined with great precision. The titrations were made potentiometrically and also with ferric iron as indicator.

Materials and Apparatus

Pure potassium thiocyanate prepared as described in a previous paper[1] was used.

Mercury.—The metal was purified in the usual manner by bubbling hot air through it for several hours, followed by washing with dilute nitric acid and distillation in vacuum.

Mercuric Thiocyanate.—The salt was precipitated from a dilute potassium thiocyanate solution by adding a slight excess of mercuric nitrate solution. The crystalline precipitate was washed thoroughly with water, and was then recrystallized from a large volume of hot water.

Mercury Electrode.—The electrode shown in Fig. 1 was specially designed for this work, the electrode mercury being contained in the conical cup. Electrical connection between the mercury cup and the mercury column in the stem was made by means of a platinum wire, sealed solidly in the neck connecting the cup and stem. The cup had a diameter of 1 cm. at the top and was filled with pure mercury so that the level of the latter was slightly above the rim of the cup. The stem was filled with ordinary mercury, into which the copper wire potentiometer lead dipped.

This electrode was much more convenient than the conventional type, prepared by electrodeposition of mercury on a platinum electrode, and it eliminates the trouble of frequent replating necessary with the latter type.

Standard Solutions.—Standard stock solutions of potassium thiocyanate were prepared by weight according to the technique already described.[1] Standard mercuric nitrate solutions were prepared by dissolving carefully weighed samples (corrected to vacuum) of the pure metal in a moderate excess of 6 *N* nitric acid, boiling to remove oxides of nitrogen, and diluting to a known weight. This solution was *ca.* 0.4 *N* (0.2 molar) by weight, and was *ca.* 0.02 *N* in free nitric acid. An exactly 0.05 *N* solution, for the finish of the titrations, was prepared by dilution of a weighed portion of the stock mercuric nitrate solution in a calibrated flask.

The total operative error involved in the preparation of the standard stock solutions (weighing materials and solutions) was probably less than 0.005%. The solutions were stored in the all-glass storage flasks previously described.[1]

Procedure and Results of the Titrations

The general procedure of the titrations was as follows. A suitable portion of one of the stock solutions (*ca.* 50 g. of the potassium thiocyanate solution or 25 g. of the mercuric nitrate solution) was weighed into a 250-cc. beaker from a weight buret and diluted to 100-125 cc., with addition of sufficient nitric acid to make its concentration 0.1 *N* at the end of the titration. The mercury electrode, stirrer and salt bridge were then placed in the solution and the titrating solution was added from a weight buret with thorough stirring, until the measured e. m. f. indicated that either a slight excess or a slight deficiency had been added. The titration was then finished with the appropriate dilute solution from a calibrated 5-cc. microburet. The end-point was located in the usual way from the maximum in $\Delta E/\Delta V$. The final volume at the end of the titration was about 200 cc.

Titrations were made both at room temperature (*ca.* 23°) and at 0°, the titration beaker being placed in a jar of cracked ice for the latter titrations. Titration at 0° is preferable to titration at room temperature because the maximum in $\Delta E/\Delta V$ at the end-point is much more pronounced (change in solubility and dissociation with temperature). This is illustrated in Fig. 2, in which the data, in the region of the equivalence point, have been plotted for two typical titrations at 23 and at 0°.

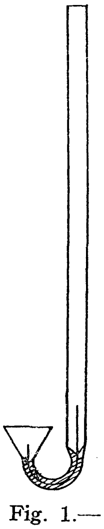

Fig. 1.—Mercury electrode for potentiometric titrations.

Steady e. m. f. readings are obtained very quickly throughout the entire course of the titration, which is a marked advantage of the thiocyanate–mercury titration over the thiocyanate–silver titration.

The results obtained in ten titrations, given in Table I, have been expressed in terms of the ef-

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[1] I. M. Kolthoff and J. J. Lingane, THIS JOURNAL, **57**, 2126 (1935).

TABLE I

COMPARISON OF POTASSIUM THIOCYANATE AGAINST MERCURY

	Conditions	Effective strength of KCNS, %
1	$Hg(NO_3)_2$ to KCNS at R.T.; final titration with dilute $Hg(NO_3)_2$	99.93
2	As (1)	99.93
3	As (1)	99.94
4	As (1), except final titration with dilute KCNS	99.96
5	As (1), except titration at 0°	99.95
6	As (5)	99.95
7	As (5)	99.98
8	KCNS to $Hg(NO_3)_2$ at 0°; final titration with dilute $Hg(NO_3)_2$	100.02
9	As (8) except final titration with dilute KCNS	100.05
10	As (9)	100.04

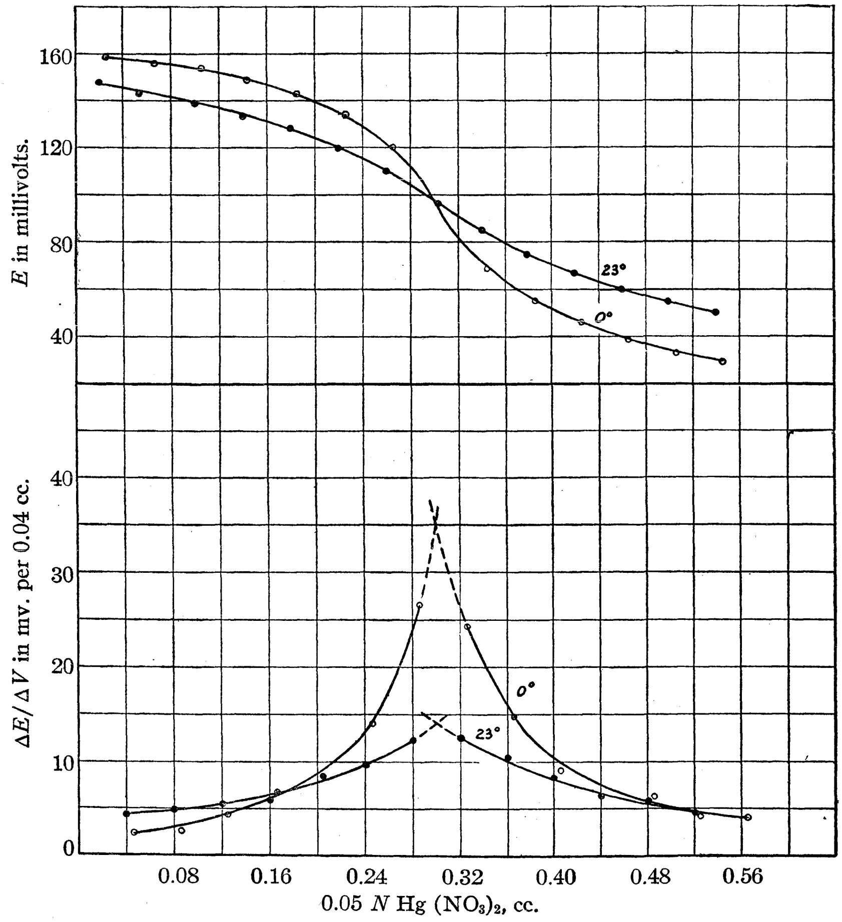


Fig. 2.—Curves of final titration of thiocyanate with mercuric nitrate in region of equivalence point at 0° and at 23°.

fective strength of the potassium thiocyanate. In view of the careful technique employed in the comparisons, the total operative errors, including preparation of stock solutions, weighing portions of the solutions for titration and location of the exact equivalence point, were probably less than 0.01%.

In the first four titrations the standard mercuric nitrate solution was added to the potassium thiocyanate solution and the titrations were made at room temperature. In the first three titrations a slight deficiency of the mercuric nitrate was added and the titration was finished with the dilute mercury solution; in the fourth trial a slight excess of the mercuric nitrate solution was added and the excess was titrated back with the dilute thiocyanate solution. The remaining six titrations were all made at 0°. In experiments 5–7, the mercuric nitrate solution was added to the potassium thiocyanate solution, but in the last three trials the reverse order of precipitation was employed.

The visual Volhard method for locating the end-point was compared with the potentiometric method as follows. The suspension remaining from a potentiometric titration, which contained a slight known excess of mercuric nitrate, was transferred to a glass-stoppered flask and after adding 2 cc. of saturated ferric alum as indicator, the solution was cooled to 12°[2] and titrated with the dilute thiocyanate solution to the appearance of the first reddish-brown coloration.

A comparison flask was prepared which contained the same quantity of recrystallized mercuric thiocyanate and the same concentration of nitric acid, potassium nitrate and ferric alum at 12° as the solution titrated. In this way the end-point could be determined to within about 0.07 cc. of 0.01 *N* thiocyanate solution in a volume of 200 cc. corresponding to a titration error of 0.01%.

[2] I. M. Kolthoff and L. H. van Berk, *Z. anal. Chem.*, **71**, 339 (1927).

In these titrations it was found that the Volhard end-point came 0.02% later than the potentiometric end-point, with respect to thiocyanate, or in other words, the effective strength of the potassium thiocyanate by the Volhard method was 0.02% less than the effective strength by the potentiometric method.

Discussion of Results

The data in Table I show that the reaction between mercuric mercury and thiocyanate is not exactly stoichiometric. When the mercury solution was added to the thiocyanate the effective strength of the potassium thiocyanate was found to be 99.94% at 25° and 99.96% at 0°. However, when the titration was carried out in the reverse way an effective strength of 100.03% was found at 0°. Although the deviation from the theoretical value is within the limits of an accurate analytical determination, it is greater than corresponds to the experimental error. The deviation found indicates that in the reaction between mercuric mercury and thiocyanate slight side reactions occur similar to those in the thiocyanate–silver titration.[1]

By using the same technique described in the latter case we were able to detect small, but definite, quantities of fixed ammonia in the supernatant solutions after precipitation, whereas no trace of ammonia could be detected in the original mercuric nitrate and potassium thiocyanate solutions, or in any of the reagents and water used.

The presence of ammonia in the final solutions is definite proof that side reactions, probably involving the intermediate formation of cyanic acid and its subsequent decomposition to ammonium ion and carbon dioxide, take place during the precipitation of mercuric thiocyanate.

The occurrence of these side reactions is a serious objection to the use of potassium thiocyanate as a primary standard substance in mercurimetry, in extremely precise work. However, the errors caused by the side reactions are small (−0.05 to +0.05%, depending on the order of precipitation), so that the salt should be a useful standard substance in work not requiring an accuracy better than ±0.05%.

Acknowledgment.—We wish to express our appreciation to the Graduate School of the University of Minnesota for financial assistance during the course of the work described in this paper.

Summary

1. The effective strength of potassium thiocyanate as found by titration with mercuric mercury solution depends upon the order of precipitation, being an average of 99.95% when the mercury is added to the thiocyanate solution and 100.03% when the reverse order of precipitation is used. The effective strength is 0.02% lower by the visual Volhard method than by the potentiometric method when the solution at the end-point has a temperature of 12°.

2. The slight deviations from the theoretical value are attributed to the occurrence of side reactions; the presence of ammonium ion was detected in the solution at the end of the reaction.

3. In the potentiometric titration a much sharper break is found at 0° than at room temperature.

4. Potassium thiocyanate can be recommended as a standard substance in mercurimetry for work not requiring an accuracy greater than ±0.05%.

MINNEAPOLIS, MINN. RECEIVED SEPTEMBER 25, 1935

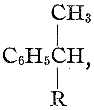
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Oxidation in the Benzene Series by Gaseous Oxygen. V. The Oxidation of Tertiary Hydrocarbons

BY H. N. STEPHENS AND FELICIANO L. RODUTA[1]

It has been shown by one of us[2] that alkyl benzenes are slowly oxidized at the α-carbon atom at 100°. If at least two hydrogen atoms are attached to this carbon atom an aldehyde or ketone is formed and the oxidation is completely inhibited by excess water. If two alkyl groups and only one hydrogen atom are attached to the α-carbon atom a ketone is formed, through the loss of one of the alkyl groups, and the oxidation is not inhibited by water. The absence of inhibition by water in the latter type of hydrocarbon was previously established only in the cases of cumene and cymene but in the present paper a similar behavior is shown for methylethylphenyl-, methylpropylphenyl-, methylbutylphenyl-, methyldiphenyl-, and triphenylmethane. One further example of a secondary hydrocarbon, diphenylmethane, was included as a control and in conformity with previous experience its oxidation was completely inhibited by water.

Inhibition by water has been ascribed to a reversible elimination of water in the decomposition of a primary oxidation product. The failure of water to inhibit the oxidation of tertiary hydrocarbons therefore implies that in this case there is no such reversible decomposition. This may find explanation in the fact that the formation of a molecule of water from one of a primary addition product of oxygen and tertiary hydrocarbon would require the contribution of one of the hydrogen atoms from an alkyl group. The resulting alkylene residue then must drop off if a ketone, which is always the observed product, is formed. The loss of a carbon atom attendant upon the elimination of water may so reduce the probability of reversal of this step by excess water that no observable inhibition results.

It has been found that hydrocarbons of the type  $C_6H_5\overset{CH_3}{\underset{R}{C}}H$, in which R is ethyl, *n*-propyl, or *n*-butyl, lose the larger group, and acetophenone was the only ketone that could be identified. The absence of the alternative ketone was checked very carefully in the case of methylethylphenylmethane by oxidizing 100 g. of the hydrocarbon at a temperature higher than usual (140°). In 7.5 g. of crude ketone obtained from the oxidation no propiophenone could be detected and it appears quite safe to say at least that acetophenone constitutes well over 90% of the total ketone formed. On the basis of the above mechanism this would indicate that the larger alkyl group is involved in the elimination of water from the primary oxidation product. Such behavior is strongly reminiscent of the dehydration of the phenyldialkylcarbinols, which apparently involves the larger alkyl group exclusively.[3] Triphenylmethane distinguishes itself from all other examples studied by having no alkyl group to participate in the elimination of water. The only products identified in this case were benzophenone and phenol.

Experimental Part

Materials and Apparatus.—The hydrocarbons listed below were oxidized in 15 to 25-g. samples for periods varying between fourteen and twenty-nine days in the absence of water and between thirty-one and thirty-four days in the presence of an equal weight of water. Oxidation was carried out in a specially constructed flask, by bubbling oxygen slowly through the hydrocarbon. The flask was sealed to a tall reflux condenser and enclosed in a vapor-bath for maintaining constant temperature. Boiling pentanol-2 (b. p. 119°) was used in this bath for oxidations in the absence of water and boiling water for oxidations in the presence of water. The following is a description of the hydrocarbons employed.

1. Methylethylphenylmethane, from Friedel and Crafts reaction; b. p. 173–174°, n^{25}_D 1.4863.
2. Methyl-*n*-propylphenylmethane, from Friedel and Crafts reaction; b. p. 191–192°, n^{25}_D 1.4902.
3. Methyl-*n*-butylphenylmethane, from Friedel and Crafts reaction; b. p. 206–207°, n^{25}_D 1.4902.
4. Methyldiphenylmethane, from paraldehyde and concd. H_2SO_4; b. p. 267–269°, n^{25}_D 1.5702.
5. Triphenylmethane, from Kahlbaum; m. p. 90°.
6. Diphenylmethane, from Friedel and Crafts reaction; b. p. 258–259°, n^{25}_D 1.5649.

It has been emphasized in previous papers that oxidations of the alkyl benzenes proceed very slowly at temperatures of the order of 100°. It is desirable, however, to keep

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[1] This paper is based largely on the Master's Thesis of Roduta, Minnesota, 1931.

[2] Stephens, THIS JOURNAL, **48**, 1824, 2920 (1926); **50**, 2523 (1928).

[3] Tiffeneau, *Ann. chim. phys.*, [8] **10**, 362 (1907); Auwers and Eisenlohr, *J. prakt. Chem.*, [2] **82**, 96 (1910).

the temperature as low as possible in order to avoid excessive secondary reactions. Therefore, it follows that, within a reasonable time, only small amounts of oxidation products will be obtained. In the present investigation, as in previous ones, no attempt was made (except in one case) to carry the oxidation any further than was necessary to yield readily identifiable amounts of products. When the dry hydrocarbons were used the yields of ketones were approximately 0.5 to 1.5 g. In the presence of water the amounts were smaller, due to the lower temperature. Although the yields of ketone are of no particular significance it was considered very important to establish the presence or absence of other early oxidation products. To this end we made a careful search in each case for alcohols, but with consistently negative results.

The ketone was identified in each case as the dinitrophenylhydrazone and the identity of these derivatives with specimens prepared from pure ketones was established by mixed melting points. In addition to ketone there was always formed an appreciable amount of soft reddish-brown or dark brown resin with no simple empirical composition. These obviously arise essentially from further oxidation of the ketones, as the oxidation of acetophenone itself yields a product similar to those from hydrocarbons which give acetophenone.

The ketones obtained from the respective hydrocarbons were

Methylethylphenylmethane—acetophenone
Methyl-*n*-propylphenylmethane—acetophenone
Methyl-*n*-butylphenylmethane—acetophenone
Methyldiphenylmethane—benzophenone
Triphenylmethane—benzophenone
Diphenylmethane—benzophenone (no oxidation in the presence of water).

In order to make sure that we had not missed the alternative ketones, propio-, butyro- and valerophenone which might have been formed from the first three hydrocarbons, we oxidized 100 g. of methylethylphenylmethane for ninety days at 140°. On fractional distillation we obtained 7.5 g. of crude ketone which was cut into 4 fractions of 1.7, 4.1, 0.6 and 0.8 g. (residue). The dinitrophenylhydrazones of fractions 1, 2 and 3, without recrystallization, melted at 230–238, 235–238 and 234–238°, respectively. The derivative from acetophenone melts at 237.5–238.5°. The whole of the last fraction was treated with dinitrophenylhydrazine and yielded 0.2 g. of derivative which, after extracting with boiling ligroin and recrystallizing from a mixture of alcohol and chloroform, melted at 174–180°. A mixture of this material with the dinitrophenylhydrazone of propiophenone (m. p. 190–191.5°) melted at 169–172°. From these facts it is obvious that propiophenone was present, if at all, in only very small amount. It might be mentioned that 4.2 g. of benzoic acid was obtained in this particular experiment. This arises from further oxidation of acetophenone, as it was found that 198 g. of the latter, oxidized at the same temperature (140°) for six days, yelded 1.9 g. of benzoic acid. Benzoic acid had not previously been detected in the oxidations at lower temperatures.

Accompanying the ketone there ought to appear in each case some product corresponding to the alkyl radical which has been eliminated. It has been shown that cumene and cymene yield formic acid if oxidation is carried out at 80°. Similarly 12 g. of methyldiphenylmethane, oxidized at 80–85° in the presence of water for thirty days, gave a strongly acid water layer in which formic acid was recognized by the mercuric oxide test. In oxidations involving elimination of alkyl radical with two or more carbon atoms we have had great difficulty in obtaining a satisfactory identification of the corresponding acids. In the oxidation of methyl-*n*-butylphenylmethane, for example, the presence of butyric acid was indicated by the odor but we were unable to obtain a pure derivative. The second oxidation product of triphenylmethane, however, was readily identified as phenol. The crude product from 15 g. of hydrocarbon, oxidized at 119° for twenty-one days, was extracted with 80% alcohol, and on distilling the residue from this solution under reduced pressure a mass of colorless crystals collected in the condenser. On dissolving a few of these crystals in dilute acetic acid and adding bromine water a copious precipitate of tribromophenol (m. p. 92°) was obtained. Triphenylcarbinol was searched for with negative results.

The writers wish to acknowledge assistance from Messrs. D. Tenenbaum and J. R. Vincent in part of this work, the assistance being made available through a grant from the Graduate School.

Summary

Results obtained from a study of the oxidation of several tertiary hydrocarbons show that oxidation always takes place at the α-carbon atom and that the reactions are not inhibited by water.

MINNEAPOLIS, MINN.

RECEIVED MARCH 25, 1935

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 491]

The Effect of Wave Length on the Iodine-Sensitized Decomposition of Ethylene Iodide in Carbon Tetrachloride Solution

BY ROSCOE G. DICKINSON AND NELSON P. NIES

The present work was undertaken primarily in order to obtain a partial answer to the question as to what extent iodine atoms are produced by the absorption of radiation by iodine in carbon tetrachloride solution when the radiation is of longer wave length than that of the band convergence of gaseous iodine. The absorption spectrum of gaseous iodine in the visible is continuous for wave lengths below 4989 Å. and shows many fine lines at longer wave lengths. In a well-known paper, Franck[1] has considered absorption in the continuous region to produce dissociation into a normal ($^2P_{3/2}$) and metastable ($^2P_{1/2}$) iodine atom, and absorption in the discontinuous to produce electronically excited molecules. These views, aside from their agreement with the dissociation energy of iodine, have received support from experiments[2] showing the disappearance of fluorescence when the wave length of the exciting light is decreased into the continuous; and further support from experiments[3] showing the presence of atomic absorption lines in strongly illuminated iodine vapor. Atomic absorption experiments in the presence of argon[4] showed iodine-atom formation even when the gas was illuminated with wave lengths longer than 5100 Å.; apparently the excited iodine molecules were dissociated by collisions with argon. For iodine in carbon tetrachloride solution, similar information does not exist, but use has been made of photochemical methods.

The decomposition of ethylene iodide in carbon tetrachloride solution has been found to be sensitized to visible radiation by iodine[5] and a chain mechanism has been proposed which is essentially a catalysis of the decomposition by iodine atoms. For this solution reaction, relative values of quantum yields have been measured[6] using both radiation corresponding to the continuum of the gas and radiation corresponding to the region of discontinuous absorption. For the wave length 4358 Å. the quantum yields measured were five to six times as great as those for the wave length 5461 or for the lines at 5770 and 5790. From these facts it was concluded that the excited iodine molecules produced by the absorption of the green or yellow lines, under the conditions of the experiments usually gave up their energy without dissociating.

This conclusion, however, has seemed to us not justified. The reaction in question is one whose rate is proportional to the square root of the intensity of illumination.[5] With a reaction of this type if two experiments were to be made with different wave lengths but with the same concentrations, the same intensities (using einsteins), and substantially complete absorption in each case, then even though the two wave lengths were equally effective in dissociating the absorber, the rates of reaction could be different in the two experiments if the absorption coefficients for the two wave lengths were different; indeed, with properly stirred solutions, the rates should be inversely proportional to the square roots of the absorption coefficients.[7]

The available measurements[8] of the absorption coefficient of iodine in carbon tetrachloride solution show much higher values in the green than in the blue so that, qualitatively, smaller quantum yields in the green than in the blue are to be expected. Unfortunately, however, the published data concerning the quantum yields are insufficiently detailed to permit satisfactory recalculation. We have accordingly attempted to measure the dependence of this reaction rate on the wave length under appropriate conditions, and have measured the absorption coefficients at the temperatures of interest.

Materials.—The carbon tetrachloride was purified by the treatment described by Polissar.[9] The ethylene iodide was prepared as described by Mooney and Ludlam,[10] and contained a small amount of free iodine. A weighed amount was dissolved in a weighed amount of the purified carbon tetrachloride. In most of the experiments the iodine concentration was increased by adding iodine which

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[1] J. Franck, *Trans. Faraday Soc.*, **21**, 536 (1925).

[2] Dymond, *Z. Physik*, **34**, 553 (1925).

[3] L. A. Turner and E. W. Samson, *Phys. Rev.*, **37**, 1023 (1931).

[4] L. A. Turner and E. W. Samson, *ibid.*, **37**, 1684 (1931).

[5] Schumacher and Wiig, *Z. physik. Chem.*, **B11**, 45 (1930).

[6] Schumacher and Stieger, *ibid.*, **B12**, 348 (1931).

[7] See A. J. Allmand, *J. Chem. Soc.*, 1557 (1929).

[8] Gillam and Morton, *Proc. Roy. Soc.* (London), **A124**, 604 (1929); Getman, THIS JOURNAL, **50**, 2883 (1928).

[9] Polissar, *ibid.*, **52**, 956 (1930).

[10] Mooney and Ludlam, *Proc. Roy. Soc. Edinburgh*, **49**, 160 (1929).

had been resublimed from potassium iodide. The free iodine was determined by titration with thiosulfate freshly diluted to 0.00544 *N* and the ethylene iodide concentration calculated.

Apparatus.—A diagram of the experimental arrangements is shown in Fig. 1. The reaction vessel was a Pyrex cylinder 4.0 cm. in diameter and 2.1 cm. in internal length between the plane ends; an accessory bulb provided a free gas space of 25 cc. Since uniformity of concentration of the reactants throughout the solution was desired, the cell was provided with a magnetically operated glass spiral plunger which kept in operation throughout the illumination. The volume of stirrer glass in the light beam was 0.15 cc.; the error in rate caused by its presence is estimated to be 0.8% at most and usually much less. In each experiment the cell was filled with 28.0 cc. of solution (measured at room temperature) and sealed off. It was found imperative to avoid decomposition of carbon tetrachloride during the sealing-off process; this was accomplished, as shown by blank experiments, by sweeping any liquid as well as vapor from the side tube with a stream of air and sealing quickly before more vapor could diffuse into the side tube.

The thermostat was so constructed that the reaction cell could be placed in a small closed air space which was provided with double windows and surrounded by the vapor of boiling liquid except at the ends and top. The reaction cell was heated in the dark to approximately the right temperature; it was then transferred to the thermostat (a dim red room light was used) and was left for twenty minutes before illumination. During illumination stray light was avoided by the use of a cylindrical shield at the window near A and by closing with a black shutter the window near B. After illumination the cell was rapidly cooled to room temperature in the dark. The titration occurred in light; but since the temperature coefficient of the reaction is fairly large (1.6 for 10°) little reaction resulted here.

The light source was a quartz mercury arc; the source was defined by a hole 1.1 cm. in diameter. The light was filtered through 1 cm. of 10% $CuCl_2 \cdot 2H_2O$ solution to remove infra-red and red, and through suitable Corning glass filters to isolate the desired mercury lines. All filter combinations were examined spectroscopically. With the filter for 4358, only this line and its immediate weak neighbors were appreciably transmitted; in particular, the line 4916 and the lines near 4050 and shorter were absent from a plate showing reversal of 4358. The filter for 5461 gave a radiation contaminated by less than 1% of the yellow lines. That for 5770 and 5790 gave a radiation contaminated by less than 0.5% of the green line.

With the aid of the lenses and the 3.5-cm. diaphragm at A, the beam was adjusted so that all of it passed through the reaction solution and remained substantially constant in diameter in so doing. The lens at B threw on the face of a Moll microthermopile an image of the diaphragm A. The thermopile elements were situated at the center of this image whose diameter was 31 mm. The thermostat was mounted on tracks and could be removed entirely from the light beam.

The reaction was followed by measuring the iodine concentration. Before and after illumination, 5 cc. of the reaction mixture at room temperature was pipetted into slightly acidified potassium iodide solution and titrated with thiosulfate.

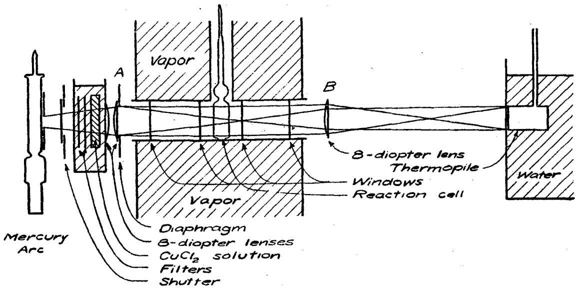

Fig. 1.—Vapor-thermostat and optical arrangements. The thermostat was removable from the light beam for measurement of incident intensity. The window near B was closed by a shutter (not shown) during reaction.

Absorption Coefficients.—The absorption coefficients of iodine solutions at various wave lengths were determined by measuring: (1) the transmission τ_0 of the thermostat with the reaction cell in place and containing only carbon tetrachloride; (2) the transmission τ of the thermostat with a known iodine solution in the cell. The coefficients α' were then calculated from the equation

$$\alpha' = \frac{1}{(I_2)l} \log_e \frac{\tau_0}{\tau}$$

where (I_2) is the concentration of iodine in moles per kilogram of solution, and l is the inside thickness of the cell (2.1 cm.). These and the coefficients α, calculated with concentrations in moles per cc., are given in Table I.[11] Although these absorption coefficients were determined in pure carbon tetrachloride solution, the small effect of non-polar solvents on the molal absorption coefficients of the halogens makes it unlikely that the values are unsuitable for use in solutions containing mol fractions of ethylene iodide of 0.01 or less.

Treatment of Reaction Rate Data.—From the work of Schumacher and Wiig,[5] we have taken the local rate of photochemical reaction in any illuminated element of the solution to be given by

$$d(I_2)/dt = k(I_{abs.})^{1/2}\,(C_2H_4I_2) \qquad (1)$$

where $(I_{abs.})$ is the local rate of absorption of radiation in einsteins × cc.$^{-1}$ × sec.$^{-1}$. This assumption receives *a posteriori* justification in the present work. The average rate in a solution of

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[11] The thermal expansion of the solution was assumed equal to that for pure carbon tetrachloride. The density of carbon tetrachloride was taken as 1.59 g./cc. at 22°; 1.48 at 76.6°; and 1.45 at 99°.

TABLE I

ABSORPTION COEFFICIENTS OF IODINE IN CARBON TETRACHLORIDE SOLUTION

	4358 Å.		5461 Å.		5770 and 5790 Å.	
T., °C.	(I_2) (moles/kg.) × 10^4	α'	(I_2) (moles/kg.) × 10^4	α'	(I_2) (moles/kg.) × 10^4	α'
22	8.94	242	0.70	2620	3.05	1050
	12.00	239	1.50	2520	4.27	1040
	15.45	248	2.56	2570	7.48	1010
	16.45	240	3.00	2510		
	Mean α'	242	Mean α'	2560	Mean α'	1030
	Mean α	1.52 × 10^5	Mean α	1.60 × 10^6	Mean α	6.49 × 10^5
76.6	11.90	250	1.08	2450	3.05	1170
	17.00	248	1.54	2430	4.27	1170
	23.75	247	2.15	2380	7.48	1160
	Mean α'	248	Mean α'	2420	Mean α'	1170
	Mean α	1.68 × 10^5	Mean α	1.64 × 10^6	Mean α	7.32 × 10^5
99	7.72	247	0.70	2420		
	9.84	250	0.90	2460		
	10.45	245	1.40	2412		
	19.85	248	1.80	2420		
	Mean α'	247	Mean α'	2430		
	Mean α	1.70 × 10^5	Mean α	1.68 × 10^6		

volume v and thickness l illuminated by a parallel beam of cross-section a, is then given by

$$\frac{d(I_2)}{dt} = \frac{2kI_0^{1/2}(C_2H_4I_2)\,a}{\alpha^{1/2}(I_2)^{1/2}\,v}\,(1 - \sqrt{\tau}) \qquad (2)$$

Here I_0 is the intensity of radiation incident on the solution in einsteins × cm.$^{-2}$ × sec.$^{-1}$; and τ is the transmission $e^{-\alpha(I_2)l}$ of the solution. In obtaining (2) it is assumed that: (a) the concentrations of the reactants are maintained uniform throughout the solution; (b) Beer's law applies; (c) the rate in one element of solution is unaffected by the intensity prevailing in neighboring elements.

With constant incident intensity, values of the specific rate constant k may be obtained from equation (2)

$$k = \frac{\alpha^{1/2}\,v}{2I_0^{1/2}\,a\,\Delta t}\int_{c_1}^{c_2}\frac{(I_2)^{1/2}\,d(I_2)}{(1-\sqrt{\tau})\,(C_2H_4I_2)} \qquad (3)$$

where Δt is the time of illumination and c_1 and c_2 are the values of (I_2) just before and after illumination. We have calculated the specific rate constant in arbitrary units k_a using the equation

$$k_a = \frac{1}{\lambda^{1/2}\,G^{1/2}\alpha'\,\Delta t}\int_{y_1}^{y_2}\frac{y^{1/2}\,dy}{(1-e^{-y/2})\left(S - \dfrac{y}{\alpha' l}\right)} \qquad (4)$$

In equation (4), $G^{1/2}$ is the mean of the square roots of the corrected galvanometer deflections, λ is the wave length (used to obtain proportionality to einsteins), y is equal to $\alpha'(I_2)l$ and S is the total concentration of iodine (free and combined). Since the value of the integrand may be calculated for any stated value of y, we have approximated the integral using Simpson's rule;[12] this is convenient since the integrand often remains fairly constant over a considerable range of values of y.

TABLE II

SPECIFIC RATE-CONSTANT DETERMINATIONS

$(C_2H_4I_2)_0$ (moles/kg.) × 10^3	$(I_2)_0$ (moles/kg.) × 10^3	$(I_2)_f$ (moles/kg.) × 10^3	$G^{1/2}$ cm$^{1/2}$	Δt min.	τ_0	τ_f	k_a × 10^6
Wave length 4358 Å., temperature 76.6°							
33.1	0.81	1.59	2.28	225.5	0.66	0.44	4.37
66.2	1.02	2.15	1.31	270.5	.59	.33	4.12
66.2	1.02	3.25	2.54	245.5	.59	.18	3.82
66.2	1.08	1.97	2.51	116.3	.57	.36	4.04
66.2	1.08	2.19	2.66	241.0	.57	.32	2.27[a]
66.2	1.10	2.28	2.75	138.5	.57	.30	4.01
58.7	2.48	3.09	3.19	61.0	.27	.20	4.01
58.7	2.50	3.82	3.11	128.0	.27	.14	4.16
							Mean 4.08
Wave length 5461 Å., temperature 76.6°							
58.7	0.357	1.38	5.29	60.0	0.16	0.0$_3$92	3.75[b]
58.7	.360	1.63	4.50	90.0	.16	.0$_3$26	3.78
58.7	.258	1.72	3.98	116.5	.27	.0$_3$16	3.87
58.7	.357	1.78	5.19	90.0	.16	.0$_3$12	3.78
58.7	.258	1.94	4.47	125.5	.27	.0$_4$54	3.78
33.1	.81	2.09	3.42	252.0	.016	.0$_3$24	3.66
66.2	1.02	2.65	2.26	257.5	.0$_2$56	.0$_5$15	3.73
66.2	1.02	2.82	3.95	154.0	.0$_2$56	.0$_6$6	4.04
							Mean 3.80
Wave length 5770 and 5790 Å, temperature 76.6°							
60.8	0.440	1.40	3.12	91.5	0.34	0.033	3.48
60.8	.445	1.65	2.66	132.5	.34	.018	3.55
60.8	.445	2.01	2.73	183.5	.34	.0074	3.29
66.2	.870	2.73	2.90	186.0	.12	.00125	3.49
66.2	1.49	3.71	3.54	181.5	.026	.0$_3$11	3.88
							Mean 3.54
Wave length 4358 Å., temperature 99°							
58.7	0.068	0.89	2.58	60.0	0.97	0.67	14.6
58.7	1.72	3.33	2.70	60.0	.41	.18	13.2
58.7	1.72	3.56	3.09	60.0	.41	.16	13.2
							Mean 13.7
Wave length 5461 Å., temperature 99°							
58.7	0.068	1.25	4.36	30.0	0.71	0.0018	10.9
58.7	.068	1.77	2.77	30.0	.71	.0$_3$12	11.9
58.7	.068	1.49	3.70	40.0	.71	.0$_3$53	10.7
58.7	.428	1.99	3.88	45.0	.12	.0$_4$42	11.6
58.7	.428	2.15	4.36	45.0	.12	.0$_4$19	11.6
							Mean 11.3

[a] Not included in the mean. [b] Stirrer not operated.

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(12) See, for example, E. B. Wilson, "Advanced Calculus," 1912, Ginn and Co., Boston, p. 77.

The results of the measurements and calculations of k_a are given in Table II. The measurements at 76.6° are more extensive than those at 99° and are more reliable because of smaller uncertainty arising from thermal reaction. Since the mechanisms of the thermal and photochemical reactions are probably not independent, it is doubtful whether the results would be improved by subtraction of the thermal from the combined rates; at 76.6° thermal reaction would amount to 0.5 to 3% of the combined reaction in the present experiments, and at 99° from 3 to 10%. No correction for thermal contribution to the reaction during illumination has been applied; but for the experiments at 99° the initial iodine concentrations have been corrected (by separate blank experiments) for thermal reaction previous to the beginning of illumination. At the close of illumination the solution was quickly cooled. The results show that at either temperature there is only a small decrease of k_a with increasing wave length.

Discussion.—It is possible to draw conclusions from the comparative constancy of k_a with wave length without making detailed representations as to the complete mechanism of the reaction. This may be especially important since the possible effect of oxygen has not been investigated, and air was present in these experiments. Since it is probable that blue light dissociates iodine molecules, and since the empirical rate expression is of the same form for all visible wave lengths investigated, we may assume simply that light brings about reaction through dissociation of iodine molecules, either directly or on collision subsequent to absorption; and, further, that at a point in a solution of given composition the local rate of reaction is dependent only on the rate at which iodine atoms are produced by light regardless of the wave length that produces them. This rate of production of iodine atoms by light is $2\beta(I_{\text{abs.}})$ where β is the fraction of the absorbed quanta which result in dissociation (and may depend on λ). From the empirical result $\mathrm{d}(\mathrm{I}_2)/\mathrm{d}t = k(I_{\text{abs.}})^{1/2} f(c\ldots)$, where $f(c\ldots)$ depends only on the composition but where k may depend on the wave length, it may readily be shown that $\mathrm{d}(I_2)/\mathrm{d}t = \beta^{1/2}(I_{\text{abs.}})^{1/2}k' f(c\ldots)$ where k' is independent of the wave length.

For two different wave lengths it is evident that $\beta_1/\beta_2 = k_1^2/k_2^2$. The data of Table II give the result that at 76.6°, $\beta_{5461}/\beta_{4358} = 0.87$ and $\beta_{5780}/\beta_{4358} = 0.75$. On the assumptions made it appears, then, that wave lengths corresponding to discontinuous absorption in gaseous iodine are little less effective than those corresponding to continuous absorption in producing dissociation in carbon tetrachloride solution.

Absolute Values of the Rate Constants.—Although not essential to the examination of wave length effect, we have made an approximate determination of the absolute value of the k of equation 1 using equation 3. For this purpose, the units employed throughout were moles, einsteins, centimeters and seconds. The determination involved: (a) calibration of the thermopile against a Bureau of Standards carbon filament lamp; (b) corrections for reflection at various windows (multiple reflections were ignored); (c) examination, with the aid of the thermopile, of the distribution of intensity across the beam at the position of the cell and at the diaphragm A; (d) determination of the relative galvanometer deflections with the thermopile in the position shown and with it at the center of A. From this calibration it was found that the effective value of $aI_0^{1/2}$ in ergs$^{1/2}$ × cm. × sec.$^{-1/2}$ was given by 87.1 $G^{1/2}$. These values of k, expressed in einsteins$^{-1/2}$ × cm.$^{3/2}$ × sec.$^{-1/2}$ are: at 76.6°, 0.42 for 4358, 0.39 for 5461, 0.37 for 5780; and at 99°, 1.4 for 4358, and 1.2 for 5461 Å. The radiation measurements and corrections should be good to 20% or better.

Quantum yields, calculated as moles of iodine formed per quantum absorbed in the whole experiment, are, of course, quite variable. The first two experiments of Table II, for example, give the values 2.9 and 8.8, respectively, while the twelfth gives 0.96.

Summary

The dependence on wave length of the rate of iodine-sensitized decomposition of ethylene iodide in carbon tetrachloride solution has been reexamined. In view of the lack of proportionality between rate and intensity, absorption coefficients have been measured and special attention has been given to the distribution of intensity through the solutions. The wave lengths used were 4358, 5461, and 5770 and 5790 Å.; for these three radiations the relative values of the rate-constant at 76.6° have been found to be 1:0.931:0.867. The results indicate that light corresponding to continuous absorption in gaseous iodine is slightly

more effective in bringing about dissociation of iodine in the solution than light corresponding to the discontinuous absorption, but that the difference is not large. Absolute values of the empirical specific rate constant have been measured.

PASADENA, CALIFORNIA RECEIVED AUGUST 17, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Determination of the Zirconium–Hafnium Ratio[1]

BY GRANT WERNIMONT[2] AND THOMAS DE VRIES

The optical rotation of solutions containing potassium tartrate along with various amounts of zirconium or hafnium oxychloride has been studied by de Boer and Emmens.[3] They found that the effect of zirconium was somewhat less than that of hafnium and suggested that the polariscope might be used for determining zirconium–hafnium ratios. This paper describes such a procedure in which the fluorides were used.

Experimental

The rotation measurements were made with a Schmidt and Haensch No. 52b, Lippich type polarimeter using sodium D light from a monochromator.

Three samples of zirconium oxide were prepared (one by the method of Drophy and Davy[4] to remove completely small amounts of hafnium) from C. P. zirconium salts which were shown to contain no iron or titanium.

Measurement of Rotation Change.—To measure the rotation change, zirconium oxide samples were weighed into platinum crucibles, dissolved in 5 ml. of 50% hydrofluoric acid, evaporated to dryness on the steam-bath and the residues taken up with a little water. The solutions were transferred to volumetric flasks, 10 ml. of approximately 20% tartaric acid solution (about 14 millimoles) and 10 ml. of six normal potassium hydroxide were added along with sufficient water to make 50 ml. of solution. Blank solutions containing no zirconium were also prepared.

The rotations of the solutions and blank were determined in 2-dm. tubes, the differences being taken as the rotation change. When the weight of zirconium oxide was plotted against rotation change, a straight line resulted (Fig. 1). The equation for this is $\Delta\alpha_{Zr} = 5.37W_{Zr}$ where W_{Zr} is the grams of ZrO_2 and $\Delta\alpha_{Zr}$ is the corresponding rotation change in degrees. Twenty-six points ranging from 0.1017 to 1.002 g. of oxide were used to fit the equation. The maximum deviation of calculated rotation change from the observed value was 0.09° and the average of all deviations was 0.04°.

When less than 0.3 g. of ZrO_2 was present in solution, these results are in good agreement with those of de Boer and Emmens but when more than this amount of zirconium was present, the values found by de Boer and Emmens were less than those found in this investigation.

As the molecular ratio of tartrate to zirconium approached or became greater than two to one, the observed values were less than the calculated values. Therefore care must be taken that the ratio of tartrate to zirconium (and hafnium) is greater than two to one in the final solutions.

Hafnium salts, free from zirconium, were not available in this Laboratory; hence it was necessary to use the values of de Boer and Emmens for the rotation of hafnium tartrate solutions. Their results give a straight line (Fig. 1) and were fitted to the equation $\Delta\alpha_{Hf} = 1.16W_{Hf}$.

Calculation of Zirconium–Hafnium Ratios.—A convenient method of evaluating the ratio of hafnium to zirconium was devised by using the linear equations to derive a general expression for the relation between mole ratio, rotation change and weight of zirconium–hafnium oxide present in solution. The following equation was obtained

$$\frac{N_{Hf}}{N_{Zr}} = 0.5851 \times \frac{5.37W - \Delta\alpha}{\Delta\alpha - 1.16W}$$

where W is the grams of mixed oxides present in 50 ml. of test solution and $\Delta\alpha$ is the corresponding rotation change measured in a 2-dm. tube using sodium D light.

Preparation of Zirconium–Hafnium Oxide Samples for Analysis.—Two oxide samples were prepared from two fractions of a series of

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[1] Abstracted from a thesis submitted by Grant Wernimont to the Graduate School of Purdue University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1934.

[2] Present address, Eastman Kodak Company, Rochester, N. Y.

[3] De Boer and Emmens, *Rec. trav. chim.*, **49**, 955 (1930).

[4] Drophy and Davy, *Phys. Rev.*, **25**, 882 (1925).

fractional precipitations as follows. Five grams of the zirconium–hafnium phosphate mixture was dissolved in 50% hydrofluoric acid. The solution was filtered into cold 5% potassium hydroxide and the hydroxides were washed by decantation until free from phosphate.

The supernatant liquid was decanted and enough cold 10% sulfuric acid added to double the volume of the remaining mixture, which was then stirred and allowed to stand until the hydroxides had dissolved. Eight grams of tartaric acid was added, the solution was made alkaline with ammonia, saturated with hydrogen sulfide and the sulfide precipitate was filtered off. The filtrate was acidified, boiled and the zirconium and hafnium precipitated in the cold with a 6% cupferron solution. The precipitate was washed, dried and ignited to the oxide.

This procedure can be used quite generally to prepare samples of the mixed oxides for analysis with the polariscope. Titanium is not removed by the procedure but it was known to be absent from our samples. It should be noted that the incomplete removal of substances which have an effect on the rotation of the reference tartrate solution, makes the ratio of hafnium to zirconium appear to be less than it actually is.

Table I summarizes the results of the analysis of the two samples of mixed oxides. Three different weights of Sample No. 1 gave almost a straight line when plotted (Fig. 1). The ratios found by this method are in reasonable agreement with ratios found by the other methods indicated.

TABLE I

MOLE RATIO OF UNKNOWN MIXTURES OF ZIRCONIUM AND HAFNIUM

Sample	Expt.	Grams of oxide	Rotation change	Mole ratio Hf/Zr This method	Mole ratio Hf/Zr Other methods
1	a	0.207	0.74°	0.43	0.45 (density of mixed oxides)
	b	.408	1.46	.43	
	c	.607	2.22	.40	
2	a	.635	2.79	.18	0.15 (spectroscopic method)

Millimoles of $H_6C_4O_6$ = 14.8; millimoles of KOH = 63.3; total volume of solutions = 50.0 ml.

The method is not thought to be more accurate than other methods which have been used for determining the zirconium–hafnium ratio. Of course it is not to be compared with a careful atomic weight determination. It is rapid and therefore convenient for following fractional separations of hafnium from zirconium.

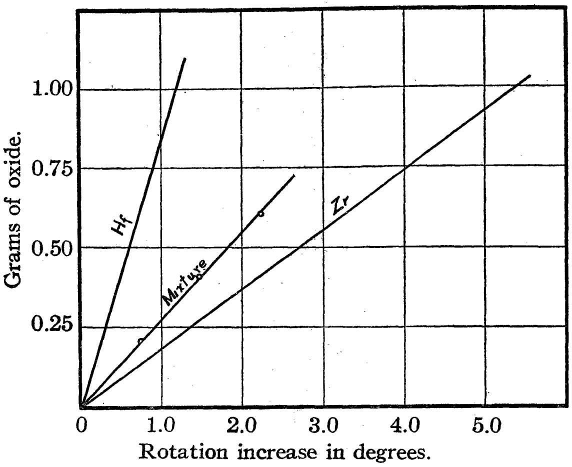

Fig. 1.

Summary

The optical rotation of basic tartrate solutions containing various amounts of zirconium have been measured and compared with the values obtained by de Boer and Emmens.

A procedure has been described for the rapid preparation of samples of zirconium–hafnium oxide suitable for analysis with the polariscope.

An equation has been given which may be used to calculate the mole ratio of hafnium to zirconium in mixtures of the two when the effect of a known weight of the mixed oxides on the rotation of certain reference tartrate solutions has been measured.

The mole ratios of two samples of zirconium–hafnium oxide have been determined and compared with the mole ratios found by other methods.

LAFAYETTE, INDIANA RECEIVED JUNE 11, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE FRUIT PRODUCTS LABORATORY, UNIVERSITY OF CALIFORNIA]

The Kinetics of the Auto-oxidation of Catechol in the Presence of Several Foreign Substances

BY G. E. K. BRANCH AND M. A. JOSLYN

It is well recognized that many auto-oxidations are inhibited by small quantities of foreign substances.[1-5] As a rule this process destroys the inhibitor and its action is temporary. This phenomenon is readily explained only on the assumption of a chain mechanism for the auto-oxidation, and the existence of a typical temporary inhibition is one of the best indications for a chain mechanism for a thermal auto-oxidation.

Since we had studied the kinetics of the absorption of oxygen by moderately alkaline solutions of catechol[6] it seemed desirable to find out whether or not the reaction involved a chain mechanism. With this in view we measured the rate of auto-oxidation of catechol in the presence of a number of foreign substances. During these investigations we observed certain peculiarities in the behavior of catechol in the presence of small quantities of pyrogallol, hydroquinone, or resorcinol, which led us to investigate the auto-oxidation when a large proportion of catechol was replaced by one of these phenols.

Experimental

The experimental procedure was essentially that used for pure catechol.[6] The rates of absorption of oxygen were measured by changes in pressure at constant volume; the solutions were buffered by the mixture of KH_2PO_4 and K_2HPO_4 obtained on addition of catechol to 0.8 *M* K_2HPO_4; and the *p*H values of the solutions were obtained with a glass electrode. The solution was shaken sufficiently vigorously to maintain it saturated with oxygen. During each individual experiment the concentration of catechol and the pressure of oxygen were practically constant as the total amount of oxygen absorbed was small with respect to both the oxygen and the catechol in the reaction vessel. The only variation from our previous procedure was that the foreign substances were added to the catechol solutions, or to the phosphate buffer when some reaction in the catechol solution was expected. In our search for inhibitors the foreign substances were all 0.001 *M* and the catechol 0.1 *M*. In experiments with large quantities of foreign phenols, the total phenol concentration was maintained at 0.1 *M* but the proportion of catechol was varied.

The rates are expressed in cc. of oxygen at 25° and 1 atmosphere absorbed by 125 cc. of solution. The average error in the measurements is 7%, most of which is due to error in *p*H measurement. An effect of less than 10% is not considered as significant.

Data and Discussion

Effects of Small Quantities of Foreign Substances.—Under the conditions of our experiments, when pure catechol solutions are used, about 20 cc. of oxygen can be absorbed without the rate decreasing by more than 10%. This approximately constant rate is that of the first measurable step in the reaction between oxygen and catechol.

When the foreign substance is not oxidized specifically faster than catechol, the rate of absorption is also practically constant, and may be faster, slower or equal to that characteristic of pure catechol, according as the foreign substance acts as a catalyst, or an inhibitor or is without action on the absorption of oxygen by catechol.

When the foreign substance is oxidized specifically much faster than catechol, its concentration is reduced to practically zero before that of catechol has been affected greatly, for the foreign substances were always added in quantities very small with respect to catechol. The foreign substances were added in quantities equivalent to about 3 cc. of oxygen in a reaction in which one molecule of oxygen reacts with one of the foreign substance. The result is that the absorption rate changes at the beginning of the experiment but becomes approximately constant before the end. When the products of the oxidation of the foreign substance are without action on the absorption of oxygen by catechol, the approximately constant final rate is that of pure catechol, and may be recognized as such. In these cases the initial rate is slower or faster than the final rate according as the foreign substance is an inhibitor or accelerator of the auto-oxidation of catechol. A foreign substance that absorbs oxygen independ-

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(1) Hans L. J. Bäckström, THIS JOURNAL, **49**, 1460 (1927).

(2) Hubert N. Alyea and Hans L. J. Bäckström, *ibid.*, **51**, 90 (1929).

(3) W. P. Jorissen and A. H. Belinfante, *Rec. trav. chim.*, **48**, 711 (1927).

(4) Charles Moureu and Charles Dufraisse, *Chem. Rev.*, **3**, 113 (1927); *J. Soc. Chem. Ind.*, **47**, 891 (1928).

(5) N. A. Milas, *J. Phys. Chem.*, **33**, 1204 (1929); THIS JOURNAL, **52**, 739 (1930); *Chem. Rev.*, **10**, 296 (1932).

(6) M. A. Joslyn and G. E. K. Branch, THIS JOURNAL, **57**, 1779 (1935).

ently of catechol, and at a specific rate ten times as fast as that of the auto-oxidation of catechol, would behave like an accelerator that is oxidized specifically much faster than catechol.

When the foreign substance is itself without action on the absorption of oxygen by catechol but is readily oxidized to a catalyst or inhibitor, the absorption starts at the rate characteristic of catechol but changes to that of a catalyzed or inhibited reaction. This final rate may be approximately constant if the product reaches a steady state concentration before the discontinuation of the experiment. This phenomenon is not restricted to substances that are rapidly auto-oxidized, for its oxidation may be induced by that of catechol. Resorcinol is an example of such a case. Catalytic or inhibitory actions of less than 10%, and independent absorptions of oxygen by the foreign substances less than ten times the specific rate of that by catechol are not observable in our experiments as they are indistinguishable from experimental fluctuations.

The data obtained are summarized in Table I, which shows the initial and final rates, the *p*H values, and the rate in pure catechol at the same *p*H values. This table shows examples of all the cases discussed above, excepting that of an inhibitor that is formed during the reaction.

TABLE I

OXYGEN ABSORPTION BY CATECHOL IN THE PRESENCE OF FOREIGN SUBSTANCE

Foreign substance	*p*H	Initial rate	Final rate	Rate in pure catechol
Ammonium chloride	8.3	3.4	3.4	3.3
Arsenious acid	8.3	2.8	2.8	3.3
Benzidine HCl	8.35	3.5	3.5	3.7
Cysteine HCl	8.3	0.1	3.2	3.3
Cystine	8.3	3.3	3.3	3.3
Gallic acid	8.3	3.8	3.8	3.3
Glycine	8.3	3.3	3.3	3.3
Hydroquinone	8.2	2.6	3.5	2.6
Indigo carmine	8.3	3.2	3.2	3.3
Maleic acid	8.3	3.1	3.1	3.3
Methylene blue	8.3	3.3	3.3	3.3
o-Aminophenol·HCl	8.3	0.8	3.2	3.3
p-Aminophenol·HCl	8.3	4.1	4.1	3.3
p-Hydroxybenzoic acid	8.3	3.3	3.3	3.3
Phenol	8.2	2.3	2.3	2.6
Picric acid	8.3	2.4	2.4	3.3
Potassium cyanide	8.3	3.3	3.3	3.3
Potassium iodide	8.2	2.4	2.4	2.6
Potassium sulfite	8.3	0.2	3.1	3.3
Potassium thiocyanate	8.3	3.2	3.2	3.3
Pyrogallol	8.2	4.8[a]	2.4	2.6
Resorcinol	8.2	2.7	3.6	2.6
Salicylic acid	8.3	3.2	3.2	3.3
Sodium phosphate	8.3	3.3	3.3	3.3
Tyrosine	8.3	3.2	3.2	3.3
Urea	8.3	3.3	3.3	3.3

[a] This is strictly a maximum rate, as in the first few seconds the rate is sensibly that for pure catechol.

It is evident that most of the substances tested had practically no effect on the rate of oxygen absorption. Of the substances which maintained a steady rate, three, namely, arsenious acid, phenol and picric acid, exhibited a slight inhibition and two, gallic acid and *p*-aminophenol, showed slight catalytic action.

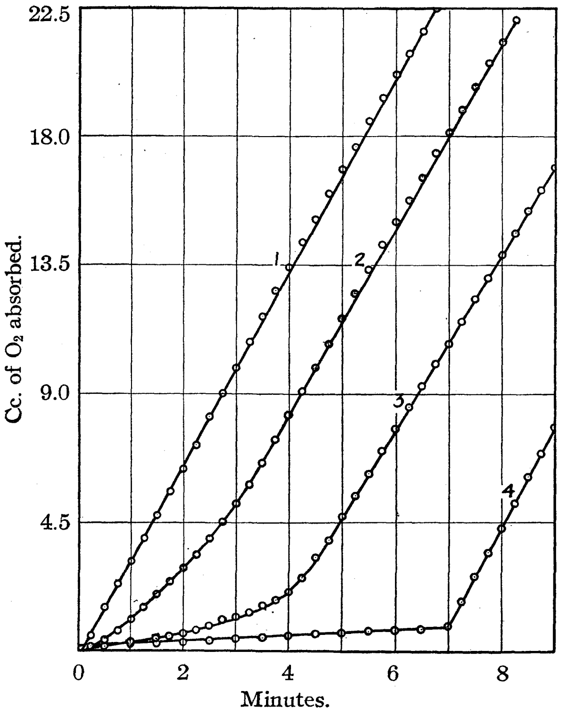

Fig. 1.—Rate of oxygen absorption by catechol at *p*H 8.3 in presence of: 1, no added substance; 2, *o*-aminophenol; 3, potassium sulfite and 4, cysteine hydrochloride.

It is evident from the data summarized in Table I and presented in more detail in Fig. 1 that *o*-aminophenol, cysteine and potassium sulfite are definite inhibitors for the reaction. The curves show reactions that are slow at first, but after a period rapidly change to the normal rates. This phenomenon is characteristic of an inhibited reaction in which the inhibitor is destroyed either in the act of inhibition or by the products of oxidation or both. This indicates that the absorption of oxygen by moderately alkaline solutions of catechol has a chain mechanism.

We have shown previously that the rate law for the oxidation of catechol in the range of *p*H value 6.5 to 10 is given by

$$V \propto (\text{cat}^-)(O_2)\ C/(C + A)$$

where C is the total concentration of catechol—being the sum of the concentration of dissociated and undissociated molecules—and A some constant. The kinetics can be accounted for on the assumption that "catechol," oxygen and the monovalent ion function in chain initiating and chain continuing processes and that "catechol" and solvent function in chain breaking processes.

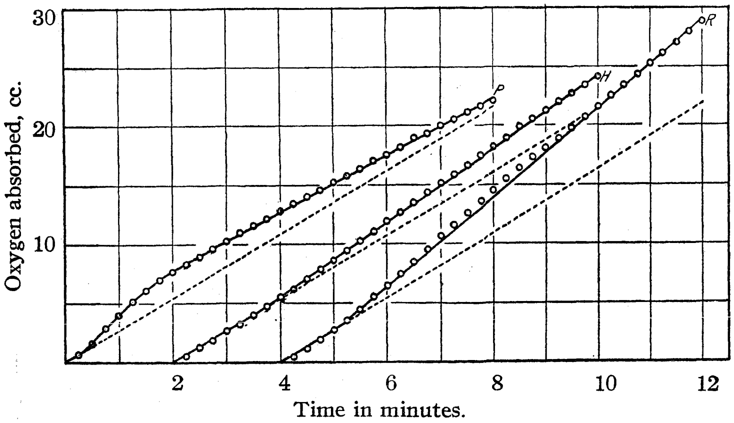

Fig. 2.—Rate of oxygen absorption by catechol in presence of small quantities of pyrogallol (P), hydroquinone (H) and resorcinol (R) at *p*H 8.3. The abscissas of the curves for H and R are displaced 2 and 4 minutes, respectively, to the right. The dotted lines show the rate in pure catechol.

The term "catechol" as used above refers to both the undissociated molecule and its ions. The constant A is the ratio of the specific rate of the chain breaking process of the solvent to that of catechol.

This mechanism also explains why so few of the chosen substances acted as inhibitors. For catechol is its own inhibitor, and the foreign molecule must compete in the chain breaking process with a hundred molecules of catechol.

The inhibition of cysteine is of special interest. Assuming that one molecule of oxygen can destroy four molecules of cysteine, about 0.75 cc. is sufficient to remove the cysteine added. After the absorption of 1 cc. of oxygen the cysteine is removed, as is shown by the appearance of the normal rate. This leads to the conclusion that cysteine is an extremely effective inhibitor and must almost completely *remove the chain character of the reaction.* This conclusion is further confirmed by the extremely sharp break in the cysteine curve between the inhibited and the normal absorption. The inhibited reaction is about 0.03 times the normal rate, and the length of the normal chain may be estimated as between 30 to 60 links.

Small amounts of pyrogallol, hydroquinone and resorcinol after an initial period in which they exerted practically no effect (which extends for about fifteen seconds for pyrogallol, one minute for resorcinol and one and three-fourths minutes for hydroquinone) appreciably increased the rate of oxidation of catechol (see Fig. 2). This increase in rate is maintained over more than five minutes by hydroquinone and resorcinol but the maximum rate reached in thirty seconds in pyrogallol is reduced in about two minutes to that of catechol alone.

Effect of Pyrogallol, Hydroquinone and Resorcinol in Large Quantities.—The rates of oxygen absorption by mixtures of catechol and pyrogallol, hydroquinone or resorcinol in which the mole fraction of the foreign phenol varied from 0 to 1.0 but at constant concentration of total phenol (0.1 *M*) are shown in Figs. 3 and 4.

It is seen from the data presented in Fig. 3, that pyrogallol and hydroquinone act as catalysts for the oxidation of catechol. But the type of catalysis is peculiar. Pyrogallol–catechol and hydroquinone–catechol mixtures oxidize at much faster rates than would be possible if the components of the mixture oxidized at rates independent of each other. In both mixtures a molal fraction of 0.2 of the more reactive phenol produces an oxygen absorption almost as fast as that of the more reactive phenol by itself. One way of explaining this phenomenon is to assume that either phenol can continue or break the chain initiated by either activated phenol. Then neglecting the chain breaking effect of the solvent

$$V = k_1C\,\frac{a_{11}C + a_{12}P}{b_{11}C + b_{12}P} + k_2P\,\frac{a_{12}C + a_{22}P}{b_{12}C + b_{22}P}$$

where V is rate; C and P the respective concentrations of catechol and pyrogallol or hydroquinone; a the rate constant for the chain continuing process, the subscript 11 referring to the chain initiated by C and continued by C, and 12 to the chain initiated by C and continued by P, etc.; b the rate constant for the chain breaking process; and k_1 and k_2 the rate constants for the chain initiating processes for catechol and pyrogallol or hydroquinone, respectively. If the more reactive phenol is specifically much more efficient in both continuing and breaking the chains begun by either phenol, *i. e.*, $a_{12} > a_{11}$, $b_{12} > b_{11}$, $a_{22} > a_{21}$ and $b_{22} > b_{21}$, then

$$V = k_1 \frac{a_{12}}{b_{12}} C + k_2 \frac{a_{22}}{b_{22}} P \text{ (approx.)}$$

even when P is small with respect to C. If $k_1(a_{12}/b_{12})$ is approximately equal to $k_2(a_{22}/b_{22})$, the rate of oxidation of the mixtures of pyrogallol or hydroquinone and catechol is approximately that of the more reactive phenol of the same total concentration

$$V = k_2(a_{22}/b_{22})(P + C) \text{(approx.)}$$

The above explanation necessitates that the more reactive phenol be used up at a faster specific rate than catechol, so that when the concentration of the more reactive phenol is very small, its concentration would decrease appreciably while but little oxygen is absorbed. This would result in an observable decrease of the rate to that of pure catechol. This is true for molal fractions of 0.01 pyrogallol but is not true for hydroquinone at this concentration.

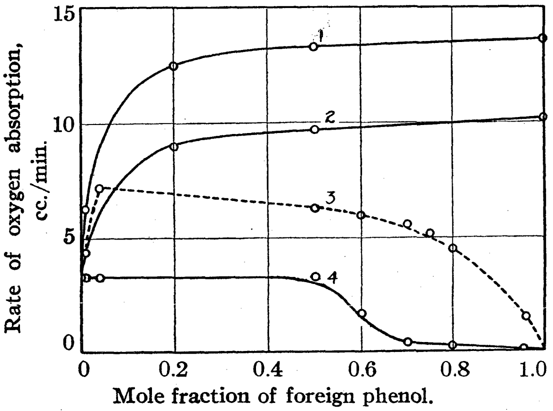

Fig. 3.—Rate of oxygen absorption at pH 8.3 by mixtures of catechol and the following phenols: 1, pyrogallol; 2, hydroquinone; 3, 4, resorcinol. Curve 3 is for first constant rates and curve 4 for initial rates. The pH values of the solutions were between 8.2 and 8.3. The rates are corrected to pH 8.3 on the assumption that the rates change with pH in the same way for the mixtures as for pure catechol. The error introduced cannot be significant.

Another possible explanation is as follows. Let us assume that chains of activated pyrogallol are longer than those of activated catechol; that any chain may be continued or broken by either phenol; that the length of the chain depends chiefly on the nature of the activated phenol and less on the nature of the phenol acted upon; and that a chain begun as an activated catechol chain may be converted into an activated pyrogallol chain, or *vice versa*. If chains are initiated at approximately equal rates by catechol or pyrogallol, the rate of oxygen absorption in a mixture depends chiefly on the relative proportions of catechol and pyrogallol chains, but owing to the chain exchanging process this proportion is not that of the phenols in the mixture. Should the change of activated catechol to activated pyrogallol be specifically faster than the reverse process, then the pyrogallol chains would predominate and the rate approximate that of pure pyrogallol even when catechol is in excess.

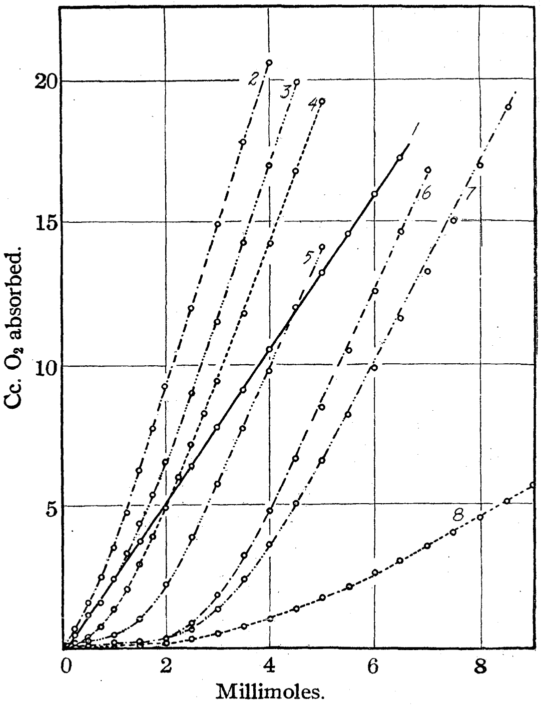

Fig. 4.—Rate of oxygen absorption at pH 8.2 by mixtures of catechol and resorcinol having the following mole fractions of resorcinol: 1, 0.0; 2, 0.04; 3, 0.5; 4, 0.6; 5, 0.7; 6, 0.75; 7, 0.8; 8, 0.96. The rate for pure resorcinol was measured as 0.0038 cc. of oxygen per minute at pH 8.3.

In this explanation of the phenomenon, the rate of oxidation of the more reactive phenol may, but need not, be specifically faster than that of catechol in mixtures of the two. It is therefore applicable to both pyrogallol and hydroquinone and is to be preferred.

When small quantities of pyrogallol or hydroquinone are used the initial rate is that of pure catechol and the catalysis does not show itself until a certain lapse of time (see Fig. 2). This would suggest that the chain exchanging process on which the catalysis depends occurs with an intermediate product of the oxidation of pyrogallol or hydroquinone, such as a deactivated peroxide. When larger quantities of pyrogallol or hydroquinone are used, the necessary intermediate is formed so quickly that the induction period is not noticeable.

The ideas presented may be clarified by the following mechanism for the delayed and limited catalysis of the oxidation of catechol by hydroquinone or pyrogallol provided the reader realizes that the formulation is schematic. In this formulation A refers to catechol, B to the more active phenol and activated molecules are starred. Initiation, continuation and termination of chains by B and termination of chains by the solvent have been omitted for the sake of brevity.

1. $A + O_2 + OH^- \longrightarrow AO_2^{-*}$ (chain initiating)
2. $AO_2^{-*} + A \longrightarrow AO_2 + A^{-*}$ (chain continuing)
3. $A^{-*} + O_2 \longrightarrow A^*O_2^-$
4. $AO_2^{-*} + A \longrightarrow AO_2 + A^-$ (chain breaking)
5. $AO_2^{-*} + B \longrightarrow BO_2 + A^{-*}$ (reaction upon which 6 must wait)
6. $BO_2 + A^{-*} \longrightarrow B^{-*} + AO_2$ (chain exchanging)
7. $B^{-*} + O_2 \longrightarrow BO_2^{-*}$
8. $BO_2^{-*} + A \longrightarrow B^{-*} + AO_2$ (continuing new chain)
9. $BO_2^{-*} + A \longrightarrow B^- + AO_2$ (breaking new chain)

Now if the specific rate of 6, k_6, is greater than that of 4, k_4, the chains in solution tend to become B chains as reaction progresses. Furthermore if $k_8/k_9 > k_2/k_4$ the new chains will be longer than the old.

In mixtures of catechol with small quantities of pyrogallol, the pyrogallol is used up specifically faster than is catechol and the rate soon becomes that for pure catechol; whereas, in mixtures of catechol and small quantities of hydroquinone, the maximum rate is maintained for a long time, showing that the composition of the mixture does not change much, the catechol and hydroquinone being oxidized at rates approximately proportional to their concentrations. Apparently, then, the essential difference between the behavior of pyrogallol–catechol and hydroquinone–catechol mixtures lies in the fact that pyrogallol is acted upon by the activated chains specifically faster than is hydroquinone. This is borne out by the longer induction period with hydroquinone.

The resorcinol–catechol mixtures, as seen in Fig. 3, differ from those of pyrogallol–catechol or hydroquinone-catechol in two important respects. In the first place, the induction periods, observable only when small concentrations of pyrogallol or hydroquinone are used, exist in all proportions of resorcinol to catechol and may last for a considerable duration of time. Secondly, the steady rates that are obtained eventually are higher than those obtained with either phenol alone. We have included, therefore, in Fig. 4 two curves for resorcinol, one for that of the steady rates and the other that for initial rates. But as the initial rates are often very slow the points on that curve are somewhat dubious.

The curves for the catechol–resorcinol mixtures are similar to those given by an inhibitor which is used up during the reaction, except that the final rate obtained is faster than that for catechol. It, therefore, is possible that we may be dealing with an auto-catalyst, resorcinol and small quantities of an inhibitor introduced with the resorcinol. The curve for the steady rates would not be affected by the introduced impurity but the curve of the initial rates would be that for reactions inhibited by an impurity. To test this we subjected the resorcinol to prolonged oxidation (about six hours) but the increase in the rate of absorption of oxygen which would be expected after the destruction of the inhibitor was not observed. The amount of oxygen absorbed in this test (over 1 cc.) was sufficient to have produced a marked increase in the rate of oxygen absorption by a catechol–resorcinol mixture. The experiment is not absolutely conclusive because it is possible that the oxidation of the inhibitor could be induced by that of catechol but not by that of resorcinol. However, we shall discuss the behavior of the catechol–resorcinol mixtures on the assumption that no inhibiting impurity was introduced with resorcinol.

The simplest explanation of the curve for the steady rates is that a rapidly oxidized intermediate is formed in the induced oxidation of resorcinol. This intermediate (probably a polyhydroxybenzene) acts like pyrogallol or hydroquinone in producing longer chains than those characteristic of either catechol or resorcinol. The curve is more complex than that for either pyrogallol–catechol or hydroquinone–catechol mixture because it is the result of the action of three components instead of two.

In the initial stages of the reaction we are dealing with the oxidation of mixtures of catechol and resorcinol before the resorcinol has been oxidized to the more active intermediate. The initial rates may be compared to those obtained in mixtures of pyrogallol or hydroquinone with catechol except that in catechol–resorcinol mixtures, catechol is the more instead of less active phenol. When mixtures of hydroquinone and catechol are oxidized there is a lag in the reaction during which the rate approximates that of the less reactive phenol followed by a steady rate approximating that of the more reactive phenol. This lag can be observed only when the time necessary for the formation of an intermediate in an amount sufficient to produce the steady rate is appreciable. This time varies inversely with the product of the concentration of the more reactive phenol by the true initial rate. Because of the fast initial rate in hydroquinone–catechol mixtures, this lag is observable only when small quantities of hydroquinone are present. The plot of observed initial rates against composition shows a double inflection as we pass from compositions in which the lag is observable to those in which it is not. The inflections for the hydroquinone–catechol mixtures occur very near to the axis representing 100% catechol. In the more inactive mixtures of catechol and resorcinol the inflections occur at about 50 mole per cent. of catechol.

The curve of the initial rates of oxygen absorption by catechol–resorcinol mixtures is therefore a combination of two phenomena. With high concentrations of catechol the measured initial rate is that characteristic of the mixture which has absorbed sufficient oxygen to give the maximum rate obtainable in absence of the formation of the more reactive intermediate from resorcinol. With smaller quantities of catechol the measured initial rate is approximately that of a mixture which has not absorbed sufficient oxygen to permit the change from the shorter resorcinol chains into the longer catechol chains.

Although it is thus apparent that the behavior of resorcinol–catechol mixtures can be explained in accordance with the general theory for pyrogallol or hydroquinone and catechol mixtures, the measurements seem to indicate an additional inhibitory action of resorcinol. This inhibition is shown in both the initial and steady-state rates obtained. The initial rates with small quantities of catechol are decidedly lower than those that would be expected for the same concentration of catechol in the absence of resorcinol, using the equation $V \propto [C^2/(C + A)]$. The steady-state rates obtained with large quantities of resorcinol are definitely lower than those with small quantities. This could be due either to inhibition by resorcinol or to the active intermediate being produced only in the induced oxidation of resorcinol. Inhibition by resorcinol would result if chains are shorter when they oxidize resorcinol than when they oxidize catechol, pyrogallol or hydroquinone.

At *p*H 8.3 the rate of absorption of oxygen by resorcinol (0.0038 cc./min.) is much slower than the rate of absorption by catechol inhibited by cysteine (0.1 cc./min.). If we accept the conclusion that in the cysteine inhibited reaction the chain is very short, the chain initiating reaction must be much slower for resorcinol than for catechol.

Acknowledgment.—We take this opportunity to thank Mr. Leo A. Joslyn for his aid in making the rate measurements.

Summary and Conclusions

1. The effect of a large number of foreign substances on the rate of oxygen absorption by catechol was studied. Most of these had little effect but cysteine, potassium sulfite and *o*-aminophenol behaved as genuine inhibitors destroyed during the reaction. Hydroquinone, resorcinol, pyrogallol, gallic acid and *p*-aminophenol appreciably increased the rate of oxygen absorption.

2. The oxidation of mixtures of catechol with pyrogallol or hydroquinone was studied at constant concentration of total phenol but varying proportions of the two phenols. The chief effect of pyrogallol or hydroquinone was to increase the rate of the reaction to almost that of pure pyrogallol or hydroquinone, respectively, over wide ranges of concentration of the latter. This is explained on a chain mechanism by the introduction of a chain exchanging process wherein a chain initiated by one phenol is convertible into a chain characteristic of the other.

3. In the presence of resorcinol, the initial rates are smaller than those of catechol alone, but these rates then increase until they are considerably greater than the rate for pure catechol.

This has been explained on the assumption that resorcinol is an inhibitor whose oxidation is induced by that of catechol to form poly-hydroxylbenzenes whose effects are similar to those of pyrogallol or hydroquinone.

BERKELEY, CALIFORNIA RECEIVED SEPTEMBER 24, 1935

[CONTRIBUTION FROM SIR JOHN CASS TECHNICAL INSTITUTE]

The Reaction between Diphenylchloromethane and Ethyl Alcohol

BY F. G. KNY-JONES AND A. M. WARD

The results of a study of the rate of displacement of chlorine from diphenylchloromethane in ethyl alcoholic solution, obtained by Norris and Morton[1] differ in a number of respects from those obtained by one of us.[2]

Norris and Morton determined the velocity of the displacement from measurements of changes in the conductance of ethyl alcoholic solutions of the chloro compound, and concluded that the reaction is reversible, $CHPh_2Cl + EtOH$ (excess) $\rightleftharpoons CHPh_2OEt + HCl$, the direct reaction proceeding, under their experimental conditions, from 84.3 to 94.6% toward completion (Norris and Morton, Table IV, p. 1801); the factors which influenced this variation were not discussed, and the values of k for the postulated reverse reaction varied from 0.0015 to 0.0230. Ward[2] did not detect the reverse reaction in his kinetic study, which was based upon titration with alcoholic alkali of the hydrogen chloride formed. We did not obtain evidence of the reverse reaction by titrating alcoholic hydrogen chloride solutions of the final products.

Norris and Morton[1] (p. 1802) were unable to verify experimentally the calculated value for the reverse reaction and recorded but one experiment to show that the reaction was reversible; in this they passed hydrogen chloride into a solution of diphenylmethyl ethyl ether, dissolved in a mixture of dry benzene and petroleum ether, to which calcium chloride was added to remove the ethyl alcohol formed. The fact that they obtained diphenylchloromethane under these conditions does not afford any proof, however, of reversibility under the conditions of the kinetic experiments.

The velocity coefficients obtained by Ward (*e. g.*, $k = 0.00341$, 0.00349) are considerably higher than those of Norris and Morton ($k = 0.00281$ to 0.00310), which are higher also than those of Norris and Banta ($k = 0.00266$).[3] The values of k for the forward reaction were found to increase rapidly with increase in the water content of the alcohol, and the differences in the three sets of results may well be due to varying small amounts of water in the alcohol. According to Norris and Morton[1] (Table V, p. 1801) the extent of the reverse reaction diminished with increasing concentrations of water present. The equilibrium constant (K) for the reactions

$$CHPh_2Cl + EtOH \text{ (excess)} \rightleftharpoons CHPh_2OEt + HCl$$

is given by

$$K = \frac{k_1}{k_2} = \frac{[CHPh_2OEt][HCl]}{[CHPh_2Cl]}$$

where k_1 is the velocity coefficient of the forward reaction, k_2 that of the reverse reaction, and equilibrium concentrations are shown in square brackets. If the initial and equilibrium concentrations in g./mole/liter of diphenylchloromethane are C and $(1 - \alpha)C$, under the conditions of Norris and Morton's experiments $k_1/k_2 = \alpha^2C/(1-\alpha)$. The percentage conversions, calculated from their data (Table V), are shown.

Water, % by weight	0.15	0.58	1.07
Formality of $CHPh_2Cl$	.0990	.1191	0.1065
$k_1 \times 10^5$	316	358	407
$k_2 \times 10^4$	26	12	9
Conversion, %	93.0	96.3	97.8

Even if some 0.5% of water were present, about 4% of chloro compound should therefore be unchanged.

The failure to detect the reverse reaction in Ward's experiment might be due (1) to continued hydrolysis during the titrations, which were carried out by addition of alcoholic sodium hydroxide to a sample of the reaction mixture. Norris and Morton[1] (p. 1802), in checking results obtained by their conductivity method, added the reaction mixture to ice-cold water, removed cloudiness by means of carbon bisulfide, and then

(1) Norris and Morton, THIS JOURNAL, **50**, 1795 (1928).

(2) Ward, *J. Chem. Soc.*, 2285 (1927).

(3) Norris and Banta, THIS JOURNAL, **50**, 1804 (1928).

titrated; (2) to water present in the alcohol, which was dried over lime, but the densities of the solvents used were not measured.

Further experiments, therefore, were carried out in which the alcohol used was purified by heating with quicklime and calcium, and fractionated (d^{20}_4 0.78940; Osborne, McKelvy and Bearce[4] give d^{20}_4 0.78934; the latter corresponds with Norris and Morton's value, d^{25}_4 0.78506). Diphenylchloromethane was prepared as previously,[5] and chlorine was determined by dissolving a sample in alcohol and titrating with sodium hydroxide, with warming, until displacement was complete.

Experiments were carried out by dissolving a known weight of chloro compound in the purified alcohol at 25.0°, adjusting the total volume to 250 ml., and leaving in the thermostat for two days; 50-ml. samples were then (1) titrated directly with standard alcoholic sodium hydroxide (approx. $N/20$); (2) added to about 200 ml. of ice-cooled water, free from carbon dioxide, and titrated with standard aqueous sodium hydroxide (approx. $N/20$); (3) added to 200 ml. of ice-cooled water, containing some 50 ml. of carbon bisulfide; the acidity of the mixture was previously removed by means of dilute sodium hydroxide. The mixture was well shaken, and then titrated as in (2). Phenolphthalein was used throughout as indicator.

RESULTS OF EXPERIMENTS

Chloro compound, g.		5.0014	4.7940	5.3020	8.1916
Chlorine, %		17.44	17.44	17.50	17.50
Titers, ml. $N/20$	(1)	98.3	93.7	104.3	161.3
	(2)	98.3	93.4	104.3	161.6
	(3)	98.1	93.2	104.5	161.3
Calcd. titer, x% displ.	$x = 100$	98.2	94.2	104.6	161.5
	$x = 94.6$	92.9	89.1	98.9	152.8
	$x = 84.3$	82.8	79.4	88.1	136.1

The end-points in procedures (1) and (2) were generally discharged by boiling; the further additions of $N/20$ alkali, necessary to produce permanent end-points after boiling, in the four series of experiments were

(1)	0.21	0.13	0.34	nil.	ml.
(2)	0.32	0.50	0.04	0.33	ml.

These results confirm that displacement was complete in the two processes.

The foregoing experiments, standing alone, do not disprove the findings of Norris and Morton concerning reversibility for the equilibrium position may be so rapidly displaced under the conditions of titration that any remaining chloro compound is completely hydrolyzed. It must be borne in mind, however, that hydroxyl ions are not effective in this hydrolysis, which depends upon a slow ionization of the diphenylchloromethane. To obtain evidence on this, three experiments were carried out.

(1) Diphenylchloromethane (about 0.5 g.) was dissolved in dry ethyl alcohol (about 50 ml.) at 17° and at once titrated with alcoholic sodium hydroxide ($N/20$) in presence of phenolphthalein. Good end-points were obtained.

Time after mixing, min.	1/2	2	3	6	13
Titer (total), ml.	0.10	0.26	0.34	0.78	1.49

The temperatures at which the solutions were titrated can be considered to approximate to room temperature, and as the time of titration did not exceed three to five minutes, any displacement error would not have exceeded about 0.5 ml. This is very much smaller than the differences required from Norris and Morton's equilibrium values.

(2) Diphenylchloromethane (about 0.5 g.) was dissolved in ethyl alcohol (50 ml.), at once added to about 200 ml. of ice-cold water, and titrated at the times shown, against $N/20$ aqueous sodium hydroxide.

Time, min.	1	2	5	12
Titer, ml.	4.40	5.57	6.27	7.63

The rapidity of reaction of the aqueous alcoholic emulsion was much too great to allow any deduction to be drawn concerning the possible equilibrium, the difference between the titers for complete and 94.6% displacement being of the same order as the above titration values, after two minutes.

(3) The experiment was as in (2), but the alcoholic solution was added to ice-cold water containing carbon bisulfide, previously neutralized.

Time, min.	1/2	2	9	15
Titer, ml.	1.45	1.55	1.95	2.20

These results, showing an initial rapid reaction, followed by a slow change, indicate that rapid displacement of halogen takes place before the compound is extracted by the carbon bisulfide, but that afterward the reaction is slow.

The foregoing results show that titration with alcoholic alkali is the most satisfactory titration

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[4] Osborne, McKelvy and Bearce, *Bull. Bur. Stand.*, **9**, 245 (1913).

[5] Ward, *J. Chem. Soc.*, 2288 (1927).

technique for arriving at the displacement figure and no evidence is obtained by titration methods for reversibility.

Summary

1. Norris and Morton, from conductance measurements, considered the reaction between diphenylchloromethane and ethyl alcohol to be reversible. Ward, by a titration method, found the reaction to be irreversible.

2. The titration method has now been examined in greater detail. No evidence is obtained for reversibility.

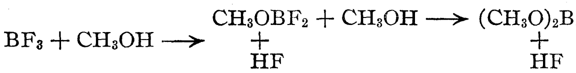
SIR JOHN CASS TECHNICAL INSTITUTE
LONDON, ENGLAND
RECEIVED APRIL 18, 1935

[CONTRIBUTION NO. 47 FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

A New Method for the Preparation of Alkoxyboron Halides and their Reaction with Metals

BY CORLISS R. KINNEY, H. THERON THOMPSON AND LEE C. CHENEY

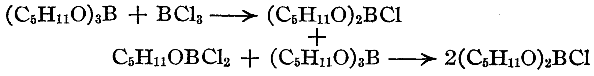
Alkoxyboron halides were first prepared by Gasselin[1] in 1894 by the action of methyl alcohol on boron trifluoride.



$$\mathrm{BF_3 + CH_3OH \longrightarrow \underset{HF}{\underset{+}{CH_3OBF_2}} + CH_3OH \longrightarrow \underset{HF}{\underset{+}{(CH_3O)_2BF}}}$$

In 1932 Bowlus and Nieuwland[2] observed that alcohols higher than methyl or ethyl did not produce fluoro esters, but a complex hydrocarbon mixture. The chloro esters were first investigated by Ramser and Wiberg[3] and later by Wiberg and Sütterlin[4] who prepared the methyl and ethyl derivatives from the corresponding alcohols or ethers and boron trichloride.

Preliminary experiments on the action of metals on diethoxyboron chloride indicated that larger groups would be desirable; consequently diisoamyloxyboron chloride was prepared and studied. The substance was prepared first using Wiberg and Sütterlin's method, but the yield was not satisfactory. Several attempts were made to prepare the substance from triisoamyl borate and dry hydrogen chloride, thionyl chloride, and phosphorus pentachloride[5] but the desired product was not obtained. With boron trichloride, however, the chloro ester was obtained and in much increased yields.



$$\mathrm{(C_5H_{11}O)_3B + BCl_3 \longrightarrow \underset{C_5H_{11}OBCl_2}{\underset{+}{(C_5H_{11}O)_2BCl}} + (C_5H_{11}O)_3B \longrightarrow 2(C_5H_{11}O)_2BCl}$$

Diisoamyloxyboron chloride did not react with "molecular silver" at room temperature, but did react readily with sodium or zinc when warmed. The reaction was exothermic and became violent unless cooled. Unexpected gaseous products were observed even at 70° in a benzene solution. The gas contained hydrogen chloride and probably isoamylene and hydrogen. The liquid product did not react with water to form hydrogen, indicating that $(C_5H_{11}O)_2BNa$ or possibly $(C_5H_{11}O)_2BB(OC_5H_{11})_2$ was absent. On distillation only triisoamyl borate and boric anhydride were obtained.

The reaction was obviously complex and involved secondary reactions. Without doubt the sodium removed the chlorine atom and the resulting radical, instead of combining with another of its kind, decomposed into an isoamyl radical and isoamyl metaborate.

$$\mathrm{(C_5H_{11}O)_2BCl + Na \longrightarrow (C_5H_{11}O)_2B\text{—} + NaCl}$$
$$\mathrm{(C_5H_{11}O)_2B\text{—} \longrightarrow C_5H_{11}OBO + C_5H_{11}\text{—}}$$

The unsaturated hydrocarbon gas and the hydrogen are accounted for by the decomposition of the isoamyl radical into isoamylene and nascent hydrogen, and the hydrogen chloride by the action of the hydrogen on another molecule of the chloro ester.

$$\mathrm{C_5H_{11}\text{—} \longrightarrow C_5H_{10} + H}$$
$$\mathrm{(C_5H_{11}O)_2BCl + H \longrightarrow (C_5H_{11}O)_2B\text{—} + HCl}$$

Finally, the isolation of triisoamyl borate and boric anhydride are to be expected because the attempt to isolate a metaborate by fractional distillation always results in the orthoborate and boric anhydride.

Experimental Part

The Reaction of Diethoxyboron Chloride with Metals.—Diethoxyboron chloride reacted readily with sodium or dry zinc dust when warmed slightly. Gases were evolved and a liquid product distilling between 110 and 150° was

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[1] Gasselin, *Ann. chim. phys.*, [7] **3**, 83 (1894).

[2] Bowlus and Nieuwland, THIS JOURNAL, **54**, 2017 (1932).

[3] Ramser and Wiberg, *Ber.*, **63**, 1136 (1930).

[4] Wiberg and Sütterlin, *Z. anorg. allgem. Chem.*, **202**, 1 (1931).

[5] Schiff, *Ann. Suppl.*, **5**, 154 (1867).

obtained. The yield amounted to practically one-third the weight of chloro ester taken. Assuming that one molecule of the ester yields one third of a molecule of triethyl borate, the crude yield was 93%. Upon redistillation more than 75% of the product distilled between 112 and 114°, the boiling point of triethyl borate at 640 mm. The residue was boric anhydride.

The Preparation of Diisoamyloxyboron Chloride.—Upon adding dry isoamyl alcohol to boron trichloride dissolved in dry chloroform and cooled to −20°, a yield of only 15% of diisoamyloxyboron chloride was obtained. On the other hand, by mixing triisoamyl borate with boron trichloride in the ratio of two moles to one, allowing the mixture to stand for twenty-four hours and then fractionating, a yield of 45% was obtained. The yield was not increased by allowing the mixture to stand for a longer time or by heating it in a sealed tube to 100° for eleven hours. The compound distilled at 110 to 115° at 14 mm. pressure. The substance was analyzed by decomposing a weighed sample with water and titrating the hydrochloric and boric acids produced, using methyl orange and phenolphthalein as indicators.

Anal. Calcd. for $(C_5H_{11}O)_2BCl$: Cl, 16.1; B, 4.9. Found: Cl, 15.9; B, 4.9.

The Reaction of Diisoamyloxyboron Chloride with Metals.—Diisoamyloxyboron chloride reacted vigorously with sodium or zinc dust when warmed. In order to avoid excessive decomposition the reaction was carried out in a dry benzene solution. Twenty-two grams (0.1 mole) of the chloride was dissolved in 75 cc. of benzene dried over sodium and 4.5 g. of sodium shavings added. The flask was equipped with a reflux condenser to which a tube was attached to carry the evolved gases through a wash bottle containing water and then through another bottle containing a carbon tetrachloride solution of bromine. Upon heating the flask to 70° the sodium reacted slowly and bubbles of gas were evolved. The gas turned the water acidic in the first bottle and a test for chloride ion with silver nitrate was positive. On the other hand, a test for borate ion with turmeric paper was negative. After passing through the water the gas had an odor similar to that of gasoline, burned with a sooty flame and when passed into the bromine solution rapidly decolorized it. The residual gas was odorless and burned with a pale blue flame similar to that of hydrogen.

The reaction mixture was heated until no chlorine could be detected in the benzene solution, a period of seven hours being required. The dark red solution was filtered from the solid residue which dissolved completely in water leaving no residue of amorphous boron. Thirty grams of the total of seventy-five grams of the solution was treated with water in an apparatus designed to detect the liberation of gas, but none was evolved. The remainder of the solution was fractionated twice and 6.6 g. of pure triisoamyl borate boiling at 245 to 250° at 640 mm. pressure and 2.0 g. of boric anhydride were obtained.

Summary

1. Diisoamyloxyboron chloride has been prepared.

2. Dialkoxyboron halides react with metals forming extensive decomposition products.

SALT LAKE CITY, UTAH RECEIVED MAY 29, 1935

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

The Thermal Equilibrium of the Cis–Trans Isomers of Dichloroethylene at High Temperatures

BY WILLIAM MARONEY

In the investigation of the thermal and photochemical equilibria of the *cis–trans* isomers of dichloroethylene, Olson and Maroney[1] were limited by decomposition reactions to temperatures below 350°. In the present study, the temperature range has been extended to 975° by using a flow method and low pressures.

The method of preparing the materials and the method of analysis are the same as those described in the previous paper.

The experimental method consisted in passing mixtures of known composition of the gaseous isomers through a heated reaction tube, and finding the change in composition due to the thermal isomerization. The reaction tube used at 825° was a section of quartz tubing, 4.5 mm. inside diameter and the portion heated, 17 cm. long. The heating element was wound in five sections. The current through each section could be regulated separately. The temperature was measured by five thermocouples, one for each section. The reaction tube used at 975° was made in a similar manner. The inside diameter of the tubing was 2.5 mm., the heated portion, 12 cm. long. Three heating units and three thermocouples were used. It was found that the length and bore of the tubes employed could be changed without altering the values found for the equilibrium composition.

The pressure at each end of the reaction tube was measured by sulfuric acid manometers. Since the manometers were about 20 cm. from the

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[1] A. R. Olson and William Maroney, THIS JOURNAL, **56**, 1320 (1934).

ends of the reaction tube, the pressure which they recorded was only approximately that at the ends of the tube.

In making a run, the vapor from a mixture of the isomers in the liquid state contained in a glass storage bulb was allowed to flow through the reaction tube at a definite rate, controlled by a Fowler[2] gas leak and a streaming manometer. The reaction products were frozen out in a liquid air trap, from which they could be removed for analysis. The composition of the samples used in the runs was varied sufficiently so that the equilibrium was approached from both sides.

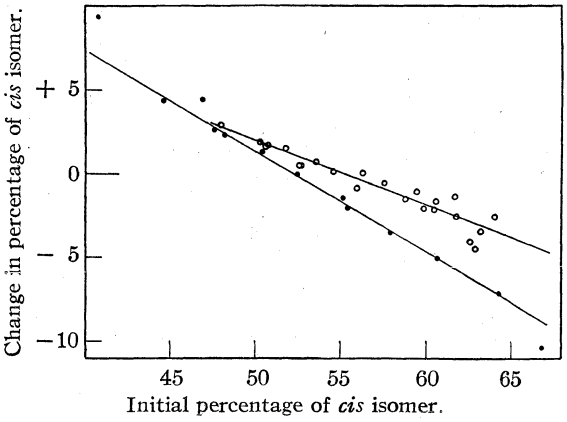

Fig. 1.—●, 975°; ○, 825°.

The two lines in Fig. 1 were obtained by plotting the change in the percentage of the *cis* isomer during a run against the initial percentage of that isomer. The composition corresponding to the point of zero change is the composition of the equilibrium mixture. The second and third columns of Table I give the average values of the pressures at the ends of the reaction tube as measured by the manometers. The values for the composition of the thermal equilibrium mixtures given in the next column are from Fig. 1.

TABLE I

Temp., °C.	Pressure, mm. Hg Input	Output	% *cis* at equil.
975	7.5	0.30	52.3
825	11.2	.34	55.1

In calculating ΔH, the heat of transition, Olson and Maroney[1] used the approximate equation $N_{trans}/N_{cis} = e^{-\Delta H/RT}$ because the possible errors in the equilibrium constants were so large compared to the change in the equilibrium constant for the fifty-degree change in temperature. If we now combine the present equilibrium constants with those given by Olson and Maroney and use the exact equation

$$\Delta H = \log \frac{K_1}{K_2} \times 4.58 \frac{T_1T_2}{\Delta T}, \text{ we get}$$

$$\Delta H_{300-975°} = 725 \text{ cal.}, \quad \Delta H_{350-875°} = 510 \text{ cal.}$$

the average of which agrees almost exactly with the value $\Delta H_{300°} = 600$ cal. given by Ebert and Büll.[3]

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(2) R. D. Fowler, *Rev. Sci. Inst.*, **6**, 26 (1935).

(3) Ebert and Büll, *Z. physik. Chem.*, **A152**, 451 (1931).

BERKELEY, CALIFORNIA RECEIVED SEPTEMBER 23, 1935

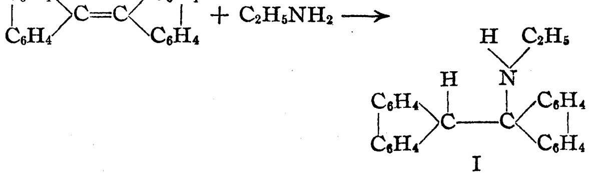
[CONTRIBUTION FROM THE FERTILIZER INVESTIGATIONS UNIT OF THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

Interaction of Amines and Ammonia with Dibiphenyleneethylene

BY L. A. PINCK AND GUIDO E. HILBERT

With the aim of obtaining more information that might aid in elucidating the mechanism of the interaction between 9-fluorylamine and dibiphenyleneethylene in liquid ammonia which gives as end-products 9-iminofluorene and dibiphenyleneethane,[1] and in order to test the suspected similarity of the double bond in dibiphenyleneethylene to an ethylenic linkage adjacent to an activating group, as carbonyl or cyano,[2] we have been led to investigate the action of amines on dibiphenyleneethylene.

It has now been found that dibiphenyleneethylene combines easily at room temperature with ethylamine, methylamine or dimethylamine to give 1-ethylamino (I), 1-methylamino (II) and 1-dimethylaminodibiphenyleneethane, respectively.



$$(C_6H_4)_2C{=}C(C_6H_4)_2 + C_2H_5NH_2 \longrightarrow (C_6H_4)_2CH{-}C(NHC_2H_5)(C_6H_4)_2$$

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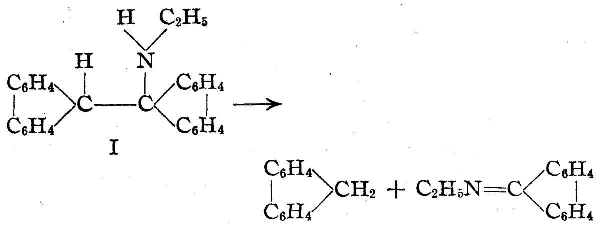
(1) Pinck and Hilbert, THIS JOURNAL, **54**, 710 (1932).

(2) Lapworth and McRae, *J. Chem. Soc.*, **121**, 2741 (1922), and Kolker and Lapworth, *ibid.*, **127**, 307 (1925), have suggested that the properties of an ethylenic linkage, which is in the α,β-position with respect to a carbonyl group, are intermediate to those of a normal ethylenic linkage and those of the carbonyl group.

As the rate of addition of these amines to the double bond is relatively rapid, the slow side reactions which occur subsequent to the formation of the amine, are of minor significance and depress the yield of the primary product only slightly below that required by theory. However, in the interaction of benzylamine or ammonia with dibiphenyleneethylene the rate of addition of the base to the unsaturated grouping is so slow that the secondary reactions assume a major role. These reactions are favored by elevated temperatures and 1-benzylaminodibiphenyleneethane (III) can be prepared in fair yield only by carrying out the reaction (several months for completion) at room temperature. When ammonia is used as the basic reactant, only secondary products can be isolated from the reaction mixture. In contrast to the behavior of the above amines, diethylamine, triphenylmethylamine or aniline do not react under conditions which are generally more favorable than those used for the other amines. The comparative data obtained indicate that the rate of addition of amines to dibiphenyleneethylene is in the order $CH_3NH_2 > C_2H_5NH_2 > (CH_3)_2NH > C_6H_5CH_2NH_2 > NH_3 > (C_2H_5)_2NH$ or $C_6H_5NH_2$. Such data as are available in the literature point to the same order of addition of amines to α,β-unsaturated acids. It is interesting to note that although II readily forms an acetyl derivative, I and III fail to react when subjected to the usual acetylation procedures. All three amines however interact with nitrous acid to give nitroso derivatives. Additional evidence indicating the presence of the –NH– grouping in I, II and III was secured by Dr. Wulf and Mr. Liddel of the spectroscopic section of this Laboratory by a study of the infra-red absorption spectra in the region 1.65–1.45 μ; the molal absorption area ($cm.^{-1}$) was found to be 7, 9 and 8, respectively. The –NH– absorption per molecule is thus somewhat lower than has yet been experienced with the rather large and varied group of organic –NH– compounds which they have investigated.[3]

These amines are quite sensitive to thermal conditions and the nature of the decomposition is influenced by the character of the medium in which they are dissolved. In alcohol at 100° the dismutation of I yields fluorene and 9-ethyliminofluorene exclusively. But in ethylamine a different type of scission leading to the formation of dibiphenyleneethane and ethylideneimide also occurs. Because of the high temperature and the length of time required to effect a reaction between ammonia and dibiphenyleneethylene, the primary product formed, 1-aminodibiphenylenethane, does not survive and only the secondary products, fluorene and 9-iminofluorene are found in the reaction mixture.



Although there are numerous examples of the facile combination of ammonia or amines with unsaturated acids or related compounds in which the double bond is in the α,β-position to form the respective β-amino or β-substituted amino acids,[4] the only investigation other than the work reported here on the combination of amines with the ethylenic linkage of unsaturated hydrocarbons appears to be that of Hickinbottom.[5,6] The employment of a promoter (amine hydrochloride) in the examples studied by Hickinbottom obscures the mechanism of the reaction and it is by no means certain, in view of the type of catalyst used, that the reaction product was not formed indirectly.[7] On the other hand, the combination of amines with dibiphenyleneethylene is effected in the absence of any promoter and would thus seem to allow of no other interpretation than that of direct addition of the amine to the ethylenic linkage.

Although general experience in the past[8] would have seemed to indicate that there is an abrupt change in the reactivity of ethylenic linkages in unsaturated hydrocarbons as compared to those in unsaturated α-carbonyl compounds toward

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[3] Liddel and Wulf, THIS JOURNAL, **55**, 3574 (1933); Wulf and Liddel, *ibid.*, **57**, 1464 (1935).

[4] See Phillippi and Galter [*Monatsh.*, **51**, 253 (1929)] for an extensive survey of this subject.

[5] Hickinbottom, *J. Chem. Soc.*, 2646 (1932); 319 and 1981 (1934).

[6] It is interesting to note that calculations assuming the validity of the Nernst approximation formula indicate that the reaction of ethylene and ammonia to give ethylamine is thermodynamically possible.

[7] A discussion of the nature of the reaction was postponed by Hickinbottom in order to test experimentally the various hypotheses that might be proposed to account for the reaction. As the aromatic amine hydrochlorides, which were used as catalysts, are appreciably dissociated at the temperatures at which these reactions were carried out, it seems to us quite possible that the formation of the amines was dependent on the prior addition of hydrogen chloride to the double bond.

[8] Lapworth and McRae *J. Chem. Soc.*, **121**, 2741 (1922); Kolker and Lapworth, *ibid.*, **127**, 307 (1925).

certain reagents as amines, hydrogen cyanide, diethyl malonate, etc., our work shows that the properties of the double bonds, even in unsaturated hydrocarbons, when the appropriate groups are attached, can approach in similarity those of the unsaturated linkage in the grouping —CH=CHCO—. The natural inference is that the electronic configuration of the double bond in dibiphenyleneethylene is more like that of the ethylenic linkage with an adjacent carbonyl group than that of the normal type in ethylene. This suggests the possible interaction of dibiphenyleneethylene with other reagents that are generally considered to be specific for compounds containing the group —CH=CHCO—. Moreover, in view of the activating influence of the biphenylene group upon a double bond, one might expect a like effect upon the methylene group in fluorene and its derivatives and this seems to be substantiated by the remarkable parallelism of many of its reactions, although the rates are much slower, with those of the methylene group in a compound such as diethyl malonate.

We wish to express our appreciation to Dr. R. T. Milner and Mrs. M. S. Sherman for the recorded microanalyses.

Experimental

Interaction of Dibiphenyleneethylene with Ammonia.—A mixture of 1 g. of dibiphenyleneethylene and 15 cc. of liquid ammonia was heated in a sealed tube at 65° for three weeks. At the end of this time it was apparent that the red ethylene compound was completely altered. After opening the tube, the ammonia was removed and the residue triturated with dry ether. The fraction insoluble in ether weighed 0.5 g. and melted at 295°; it was crystallized from acetone and separated as colorless prisms; m. p. 300°.[9] Treatment of the ether extract with dry hydrogen chloride precipitated the orange colored hydrochloride of 9-iminofluorene, yield 0.40 g.; m. p. 303° (dec.).[10] The hydrochloride was converted into the free base which was crystallized from hexane; yellow needles; m. p. 123°; m. p. when mixed with 9-iminofluorene unchanged.

Anal. Calcd. for $C_{13}H_9N$: C, 87.11; H, 5.06; N, 7.82. Found: C, 87.22; H, 5.25; N, 7.81.

The ether filtrate from 9-iminofluorene hydrochloride was concentrated to dryness; 0.07 g. of fluorene was removed by sublimation; m. p. 114°; the m. p. when mixed with fluorene was unchanged.

1-Ethylaminodiphenyleneethane (I).—Two grams of dibiphenyleneethylene in 10 cc. of ethylamine reacted completely in two days when heated at 65°. Excess ethylamine was removed by distillation, the residue dissolved in dry benzene and 1-ethylaminodibiphenyleneethane precipitated as the hydrochloride; m. p. 210–215° (dec.). This was converted to the free base, which was crystallized from a benzene–alcohol solution; it separated as colorless prisms melting at 165°; yield 65% of the theoretical. It is soluble in benzene, hot hexane and slightly soluble in alcohol.

Anal. Calcd. for $C_{28}H_{23}N$: C, 90.04; H, 6.21; N, 3.75; mol. wt., 373. Found: C, 89.86; H, 6.39; N, 3.73; mol. wt., 369.

From the benzene–hydrogen chloride filtrate there were isolated small amounts of the secondary products fluorene (sublimation) and dibiphenyleneethane. As is shown below these products originated from a relatively slow degradation of I in ethylamine and obviously for the preparation of it in good yield excessive heating and a delay in working up the reaction mixture is to be avoided.

The picrate crystallized from an alcoholic acetone solution; yellow diamond-shaped prisms; m. p. 228° (dec.).

Anal. Calcd. for $C_{34}H_{26}N_4O_7$: C, 67.76; H, 4.35; N, 9.30. Found: C, 67.86; H, 4.50; N, 9.19.

The nitroso derivative was prepared by treating a solution of the amine in acetic acid with an aqueous solution of sodium nitrite. It separated from an acetone–alcohol solution as pale yellow rhombic crystals melting at 217°; very soluble in acetone and slightly soluble in alcohol and ether; the yield was practically quantitative.

Anal. Calcd. for $C_{28}H_{22}N_2O$: C, 83.55; H, 5.51; N, 6.96. Found: C, 83.98; H, 5.47; N, 6.98.

This, as well as the other nitroso derivatives, did not respond to the Liebermann nitrosoamine test, which is based on the nitrous acid formed in the scission of the —N—N— linkage. The negative test in these particular compounds may be accounted for by the preferential rupture of the —C—N— linkage[11] to form methyldiazonium hydroxide, which would decompose and liberate nitrogen. It is noteworthy that the nitrosoamine when treated with concentrated sulfuric acid immediately generated considerable gas. When warmed, the brown colored acid mixture turned to a red solution and this on dilution with water deposited red flocks suggestive of dibiphenyleneethylene. An oxdiazolidine structure has also been considered for the nitroso compound but this possibility was definitely excluded since a carbon tetrachloride solution showed no —NH— absorption in the region 1.65–145 μ.

Dismutation of 1-Ethylaminodibiphenyleneethane.—A solution of 2 g. of 1-ethylaminodibiphenyleneethane in 20 cc. of absolute ethyl alcohol was heated at 100° for ten days. After concentrating the alcoholic solution, the yellow sirupy residue was dissolved in hexane and treated with dry hydrogen chloride, yielding 0.90 g. of a pale peach-colored precipitate. The residue obtained by concentrating the filtrate was sublimed *in vacuo;* yield 0.81 g. of a yellow colored sublimate, that consisted mainly of fluorene contaminated with some fluorenone, which was probably formed by the hydrolysis of a portion of the imide. The fluorenone was separated from fluorene by converting it to the difficultly soluble fluorenone ketazine (0.10 g.; m. p. 267°).[12] Fluorene was recovered from the

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(9) Evidence concerning the structure and the mechanism of the formation of this compound is the subject of a further investigation.

(10) All melting points are corrected.

(11) Kharasch and Howard [This Journal, **56**, 1370 (1934)] showed that triphenylmethylamine is hydrolyzed by acid.

(12) Taipale, *Ber.*, **63**, 243 (1930).

filtrate and identified; yield, 0.67 g. The hydrochlorides representing the basic fraction were treated with liquid ammonia and the mixture concentrated. The residue was extracted with hexane and the extract concentrated to a yellow sirup (9-ethyliminofluorene). This was hydrolyzed to fluorenone; yield 0.31 g. In another experiment the amine (0.5 g.) was degraded and the 9-ethyliminofluorene isolated as the picrate by adding an alcoholic solution of picric acid to the reaction mixture; yield 0.20 g.; m. p. 204° (dec.), m. p. 205° (dec.) when mixed with the specimen obtained below.

Anal. Calcd. for $C_{21}H_{16}N_4O_7$: C, 57.79; H, 3.70; N, 12.86. Found: C, 58.03; H, 3.81; N, 12.94.

The decomposition of 1-ethylaminodibiphenyleneethane was also studied in ethylamine in order to gain information concerning the origin of the fluorene and dibiphenyleneethane that were isolated as by-products in the interaction of ethylamine with dibiphenyleneethylene. 1-Ethylaminodibiphenyleneethane (1 g.) was heated in ethylamine (15 cc.) in a sealed tube at 85° for several days. The ethylamine was removed from the reaction mixture, the residue dissolved in benzene and the bases separated by means of hydrogen chloride. From the filtrate there was isolated 0.18 g. of dibiphenyleneethane and 0.15 g. of fluorene. Attempts to ascertain the nature of the basic fragment resulting simultaneously with dibiphenyleneethane were not successful and this is not surprising, since the initial product to be expected, ethylideneimine[13] would subsequently either suffer polymerization or react with the medium to yield ethylideneethylamine.

9-Ethyliminofluorene was prepared for purposes of comparison with the product obtained above. A solution of 1.3 g. of 9-iminofluorene[14] and 20 cc. of ethylamine was heated at 55° for eighteen hours and gradually assumed a pale green color. The ethylamine was removed and the yellow sirup was placed in an evacuated desiccator containing sulfuric acid; it did not crystallize and slowly developed a greenish color. It was converted to the *picrate* which separated from a solution of nitrobenzene and alcohol as orange needles; m. p. 206° (dec.).

Anal. Calcd. for $C_{21}H_{16}N_4O_7$: C, 57.79; H, 3.70; N, 12.86. Found: C, 58.00; H, 3.90; N, 12.86.

The low yield, 0.57 g., of the imide picrate is significant and may be accounted for by isomerization of the imide during its preparation as it is a prototropic system.[15]

1-Methylaminodibiphenyleneethane.—The reaction between dibiphenyleneethylene (2 g.) and methylamine at room temperature was complete in one day. The reaction product was crystallized from hexane; yield 1.55 g.; m. p. 151°.

Anal. Calcd. for $C_{27}H_{21}N$: C, 90.22; H, 5.89; N, 3.90. Found: C, 90.41; H, 5.92; N, 3.98.

The acetyl derivative separated as colorless plates from alcohol; m. p. 232°.

Anal. Calcd. for $C_{29}H_{23}NO$: C, 86.75; H, 5.78; N, 3.49. Found: C, 86.66; H, 5.80; N, 3.40.

The nitroso derivative crystallized from alcohol as long prisms melting at 203°. It was soluble in hot carbon tetrachloride and separated with one molecule of solvent of crystallization.

Anal. Calcd. for $C_{27}H_{20}N_2O \cdot CCl_4$: CCl_4, 28.38. Found: CCl_4 (loss *in vacuo*), 28.65. Calcd. for $C_{27}H_{20}N_2O$: C, 83.47; H, 5.19; N, 7.22. Found: C, 83.48; H, 5.20; N, 7.39.

1-Dimethylaminodibiphenyleneethane crystallized from a solution of alcohol containing 20% benzene as colorless distorted hexahedra; m. p. 215° (dec., red liquid).

Anal. Calcd. for $C_{28}H_{23}N$: C, 90.04; H, 6.21; N, 3.75. Found: C, 89.88; H, 6.44; N, 3.85.

Reaction of Dibiphenyleneethylene with Benzylamine.—A mixture of 5 g. of dibiphenyleneethylene and 20 cc. of benzylamine was kept in a sealed tube for about six months, when it was evident that no more of the unsaturated hydrocarbon was present. The supernatant liquid was decanted from the precipitated dibiphenyleneethane (0.80 g.) and transferred into one leg of a two-legged tube. The benzylamine was distilled under diminished pressure from one portion of the tube which was immersed in boiling water, to the other which was cooled by an acetone–carbon dioxide mixture. The residue was triturated with a small quantity of cold alcohol and dried; yield 4.62 g. 1-Benzylaminodibiphenyleneethane was purified by crystallizing first from a solution of 1 part benzene and 4 parts alcohol and then from propyl alcohol; short stout prisms; m. p. 168°.

Anal. Calcd. for $C_{33}H_{25}N$: C, 91.04; H, 5.79; N, 3.17. Found: C, 91.00; H, 5.84; N, 3.27.

The hydrochloride could be recrystallized from benzene; m. p. 215–218°.

Anal. Calcd. for $C_{33}H_{26}NCl$: N, 2.97; Cl, 7.51. Found: N, 3.04; Cl, 7.40.

The nitroso derivative separated from a solution of acetone and alcohol as stubby prisms melting at 217–218°.

Anal. Calcd. for $C_{33}H_{24}N_2O$: C, 85.31; H, 5.21; N, 6.03. Found: C, 85.68; H, 5.42; N, 6.28.

An attempt to prepare the methiodide was unsuccessful.

When a solution of dibiphenyleneethylene (5 g.) in benzylamine (10 cc.) was heated at 100° the reaction was completed in six days. From the reaction mixture there were isolated dibiphenyleneethane (2.2 g.), fluorene (0.05 g.), an unidentified hydrocarbon (1.0 g., small colorless plates from xylene; m. p. 318° (decomp. to red melt). *Anal.* Found: C, 94.43; H, 5.49), 1-benzylaminodibiphenyleneethane and an unidentified base[16] crystallized from alcohol; m. p. 90°.

Anal. Calcd. for $C_{21}H_{22}N_2$: C, 83.43; H, 7.33; N, 9.24. Found: C, 83.67; H, 7.24; N, 9.19. Hydrochloride, m. p. 212°. *Anal.* Calcd. for $C_{21}H_{24}N_2Cl_2$: C, 67.19; H, 6.45; N, 7.47. Found: C, 67.23; H, 6.42; N, 7.27.

Dismutation of 1-benzylaminodibiphenyleneethane was effected by heating 1 g. in 20 cc. of absolute ethyl alcohol in a sealed tube at 100° for ten days. Fluorene (0.25 g.), small quantities of fluorenone and benzaldehyde[17] and a few milligrams of an unidentified product, which separated

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[13] Strain, THIS JOURNAL, **54**, 1221 (1932).

[14] Pinck and Hilbert, *ibid.*, **56**, 490 (1934).

[15] Ingold and Wilson, *J. Chem. Soc.* 1493 (1933).

[16] Compare with the benzyldiaminostilbene of Japp and Moir, *J. Chem. Soc.*, **77**, 608 (1900).

[17] Fluorenone and benzaldehyde were formed by hydrolysis of the basic fraction indicative that some isomerization of 9-benzyliminofluorene had taken place; see Ingold and Wilson, *J. Chem. Soc.*, 1493 (1933).

from benzene–alcohol as colorless prisms melting at 202°, were isolated.

Anal. Found: C, 88.40; H, 5.64.

Summary

Dibiphenyleneethylene combines with ethylamine, methylamine and dimethylamine with facility at room temperature to give the corresponding substituted 1-aminodibiphenyleneethane derivatives. These products are quite labile and readily suffer dismutation to give fluorene and the substituted 9-iminofluorenes. The addition of benzylamine and ammonia to the ethylenic linkage was relatively sluggish, and in the reaction involving the latter only the secondary products fluorene and 9-iminofluorene were obtained. With the possible exception of the recent work of Hickinbottom this appears to be the first case reported of the addition of amines to an unsaturated hydrocarbon containing an olefin double bond.

WASHINGTON, D. C. RECEIVED AUGUST 8, 1935

[CONTRIBUTION NO. 48 FROM THE CHEMICAL LABORATORY, UNIVERSITY OF UTAH]

The Direct Carboxylation of Carbon Compounds. III. The Free Energy of Benzoic Acid at 522°K.

BY W. D. BONNER AND C. R. KINNEY

Two papers dealing with the direct carboxylation of carbon compounds have been published from this Laboratory.[1] The theme of these two papers was that carboxylic acids may be produced directly from carbon compounds and carbon dioxide through the formation of an equilibrium gas mixture at high temperature and pressure. A catalyst always was present to facilitate the establishment of this equilibrium. The yields, except for one or two instances, were small. Furthermore, as stated in the first paper, an approximate calculation of the free energy showed that equilibrium probably lay well to the left in the reaction $C_6H_6 + CO_2 \longrightarrow C_6H_5COOH$. Since, however, it did not seem possible to make a more precise free energy calculation, and as carboxylic acids certainly were obtained, albeit in small amounts, there seemed no reason for withholding the data from publication. Recently we have been able to calculate a more acceptable free energy value, and to arrive at a plausible reason for the observed formation of carboxylic acids.

Free Energy Calculations

For the reaction $C_6H_6(g) + CO_2(g) \longrightarrow C_6H_5CO_2H(l)$ we find that $\Delta F^0_{298} = 4300$ cal.[2] However, we wish to know ΔF^0 at 522°K.

The free energy of formation of benzene at any temperature T is given by the relation[3]

$$\Delta F^0_T = 24{,}400 + 19.6T \ln T - 0.013T^2 - 87.0T$$

Therefore, $\Delta F^0_{522} = 39{,}600$ cal. In a similar manner the free energy of formation of carbon dioxide at 522° is[4] $\Delta F^0_{522} = -94{,}263$. For benzoic acid a corresponding equation does not appear in the literature. Parks and Huffman[5] give for the reaction

$$7C + 3H_2 + O_2 \longrightarrow C_6H_5CO_2H(l);\quad \Delta F^0_{298} = -59{,}160$$

ΔH_{298} (benzoic acid solid) as $-93{,}210$ cal. and the heat of fusion of benzoic acid at the melting point as 4140. Putting the general free energy equation into the form

$$\Delta F^0_T = \Delta H^0 - \Delta C_P\, T \ln T + IT$$

we can evaluate these quantities one by one, and finally arrive at a value of ΔF^0_{522} for benzoic acid. $\Delta C_P = C_P$ (products) $- C_P$ (reactants) $= C_P$ (benzoic acid) $- C_P(7C, 3H_2, O_2)$. Using available heat capacity data[6] we find ΔC_P between 25 and 249.2° to have an average value of 17.9 cal. per mole.

Using the value of ΔH_{298} (benzoic acid solid) already referred to, and assuming C_P (benzoic acid liquid) to be the same below as above the melting point, we calculate ΔH_{298} (benzoic acid liquid) $= -90{,}927$ calories. Then, since $\Delta H_T = \Delta H_0 + T\Delta C_P$, it follows that $\Delta H_0 = -90{,}927 - 17.9(298) = -96{,}261$ cal. The integration constant I, then is

$$I = \frac{\Delta F^0{}_{98} - \Delta H_0 + \Delta C_P T \ln T}{T} = \frac{-59{,}160 + 96{,}261 + 17.9(298)\ (5.697)}{298} = 226.5$$

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(1) Kinney and Langlois, THIS JOURNAL, **53**, 2189 (1931); Kinney and Ward, *ibid.*, **55**, 3796 (1933).

(2) Parks and Huffman, "Free Energies of Some Organic Compounds," A. C. S. Monograph No. 60, pp. 47 and 233.

(3) Parks and Huffman, *loc. cit.*, p. 93.

(4) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., N. Y., 1923, p. 576.

(5) Parks and Huffman, *loc. cit.*, pp. 134, 135.

(6) Parks and Huffman, *loc. cit.*, pp. 45, 46; "International Critical Tables," Vol. V, pp. 104, 110.

Substituting these and the value of ΔF^0_{298} into the free energy equation we get ΔF^0_{522} (benzoic acid) $= -36{,}491$ cal. From this it follows that the free energy of formation of benzoic acid from benzene and carbon dioxide at 522°K. is 18,172 cal. The equilibrium constant for this reaction is calculated, from the relationship $-\Delta F^0 = RT \ln K$, to be $K = 10^{-7.63}$.

It can be shown readily that this value will not be much affected by an increase of pressure of the order of 35 atmospheres. It is evident that in the reactions studied by Kinney and his students, the equilibrium amounts of carboxylic acids cannot account for the quantities actually found. The most plausible explanation, it seems to us, is that the zinc oxide of their oxide catalyst was slowly converted into the zinc salt of a carboxylic acid, and in this way appreciable amounts were built up in their apparatus. This would account also for the observation that fresh catalysts were always most effective and that the catalyst became almost inactive by the third usage.

This emphasizes the fact that catalysts may not always be purely catalysts, but that small amounts of products may result from direct chemical action with the catalyst or with one of its constituents. In such cases free energy data if available are of great value.

We acknowledge indebtedness to Professor George S. Parks for criticizing the preliminary calculations, and to Dr. Lyman G. Bonner for rechecking the final ones. The latter also has made a precise calculation of the free energy of benzoic acid at the boiling point, using complete heat capacity equations. This calculation, however, differs from ours by less than 0.5%.

SALT LAKE CITY, UTAH RECEIVED JULY 29, 1935

[CONTRIBUTION FROM THE UNIVERSITY OF AKRON]

Binary Systems of p-Dichlorobenzene with Diphenyl, Naphthalene and Triphenylmethane

BY ROSS E. MORRIS AND WALTER A. COOK

Schröder[1] some years ago showed that p-dibromobenzene forms an almost perfect solution with benzene. The purpose of this investigation was to find the nature of solutions of p-dichlorobenzene with various aromatic hydrocarbons. Those chosen were diphenyl, naphthalene and triphenylmethane. These solutions have not been previously investigated.

In the following report the solubilities, eutectic temperatures and eutectic compositions are compared with values calculated for perfect solutions from the equation given by Washburn[2]

$$\mathrm{d}T_f = \frac{RT_f^2}{\Delta H_f}\frac{\mathrm{d}N}{N}$$

where T_f is the freezing point of the solution, ΔH_f is the heat of fusion of the crystals separating from the solution at the freezing point, R is the gas constant and N is the mole fraction of the component which crystallizes at the freezing point. The values for ΔH_f are given in Table I.

Materials.—Commercial naphthalene and p-dichlorobenzene were purified by distillation until no further changes in melting points were observed. Eastman C. P. grade of diphenyl and triphenylmethane were purified by recrystallization, the former from alcohol and the latter from acetone, and dried *in vacuo*. The melting points of the purified materials are compared with the "International Critical Tables" values in Table II.

TABLE I

HEAT OF FUSION ΔH_f

	G. cal./mole	Ref.
p-Dichlorobenzene	$-10{,}250 + 94.07T - 0.1511T^2$	3
Diphenyl	$-11{,}240 + 112.8T - 0.2835T^2 + 0.0002568T^3$	4
Naphthalene	$+4265 - 26.31T + 0.1525T^2 - 0.0002140T^3$	4
Triphenylmethane	$-9230 + 66.35T - 0.07324T^2$	4

The agreement in melting points is good except in the case of triphenylmethane. The "I. C. T." value is undoubtedly too low for this compound.

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[1] Schröder, *Z. physik. Chem.*, **11**, 449 (1893).

[2] Washburn, "Principles of Physical Chemistry," McGraw-Hill Book Co., Inc., New York City, 1921, p 202.

(3) Calculated from specific heat and heat of fusion data given in "International Critical Tables," Vol. V, p. 132.

(4) Calculated from specific heat and heat of fusion data given by Spaght, Thomas and Parks [*J. Phys. Chem.*, **36**, 882 (1932)].

TABLE II

	Melting point, °C.	
	Our material	“I. C. T.”
p-Dichlorobenzene	53.2	52.9
Diphenyl	69.1	69.0
Naphthalene	80.0	80.1
Triphenylmethane	93.2	92.5

Smith and Andrews[5] in their careful work on the heat capacity and melting point of triphenylmethane found 93.1° by thermometer, which is in good agreement with our value.

Experimental.—Temperatures were measured with short stem Anschütz precision thermometers. Two thermometers were used, covering the ranges −13 to 60° and 38 to 110°, respectively. Each was 155 mm. over-all length and contained an enclosed white glass scale which was divided in 0.2° unit. With the aid of a magnifying glass the thermometers could be read accurately to 0.05°. Both were compared with a thermometer standardized by the Bureau of Standards. With these thermometers there was no correction for emergent stem because the entire thermometer was enclosed with the melt.

Weighed samples in test-tubes (22 mm. in diameter) were placed in larger test-tubes which were immersed in a water-bath. The melt was allowed to cool with the bath, the difference in temperature between the melt and bath never amounting to more than three degrees. The melt was well stirred with a glass stirrer having a ring at the bottom encircling the thermometer. When supercooling occurred the highest temperature attained after crystallization started was taken as the melting point. This temperature could be checked to within 0.2°. Supercooling never amounted to more than 0.5°.

TABLE III

p-DICHLOROBENZENE–DIPHENYL

Mole per cent. *p*-Dichlorobenzene	Initial cryst. *T*, °C.	Final solidification *T*, °C.
0.0	69.1	69.1
5.0	66.3	
10.6	63.2	
17.7	58.7	
29.2	50.8	26.6
37.9	44.1	26.8
44.0	39.1	26.8
48.0	35.0	26.8
54.0	29.4	27.0
57.5E	26.9	26.9
63.0	30.8	27.1
69.0	35.2	27.0
78.8	41.2	
84.9	45.0	
93.1	49.4	
100.0	53.2	53.2

TABLE IV

p-DICHLOROBENZENE–NAPHTHALENE

Mole per cent. *p*-Dichlorobenzene	Initial cryst. *T*, °C.	Final solidification *T*, °C.
0.0	80.0	80.0
10.6	73.8	
18.2	68.9	
30.8	59.7	
37.8	53.7	30.0
44.7	47.3	
49.0	43.3	30.2
53.1	38.5	30.1
59.1	31.6	30.0
60.6E	30.2	30.2
63.2	30.9	30.2
63.9	31.1	30.1
65.2	31.8	30.0
69.9	35.6	30.2
77.1	40.0	30.0
88.1	46.4	
95.0	50.5	
100.0	53.2	53.2

TABLE V

p-DICHLOROBENZENE–TRIPHENYLMETHANE

Mole per cent. *p*-Dichlorobenzene	Initial cryst. *T*, °C.	Final solidification *T*, °C.
0.0	93.2	93.2
5.1	90.3	
12.2	86.1	
18.6	82.0	
28.1	75.9	
36.6	69.3	
43.1	64.0	
50.1	57.1	35.7
57.3	50.0	35.9
62.4	43.7	35.9
65.9	39.3	35.7
68.5E	35.9	35.9
80.2	42.2	35.8
87.0	46.1	
93.9	49.8	
100.0	53.2	53.2

The procedure of projecting back the cooling curve of the two-phase system to intersect with the liquid cooling curve and taking the point of intersection as the melting point has been used frequently in work of this type.[6] However, in this investigation we found that this procedure was inapplicable, especially at low temperatures and high concentrations of one of the constituents. The ring stirrer became caked with crystals so that uniform stirring could not be obtained and therefore the heat transfer was affected. Taylor and Rinkenbach[7] experienced the same difficulty

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[5] Smith and Andrews, THIS JOURNAL, **53**, 3644 (1931).

[6] Bell and Sawyer, *Ind. Eng. Chem.*, **11**, 1025 (1919); Lee and Warner, THIS JOURNAL, **55**, 209 (1933).

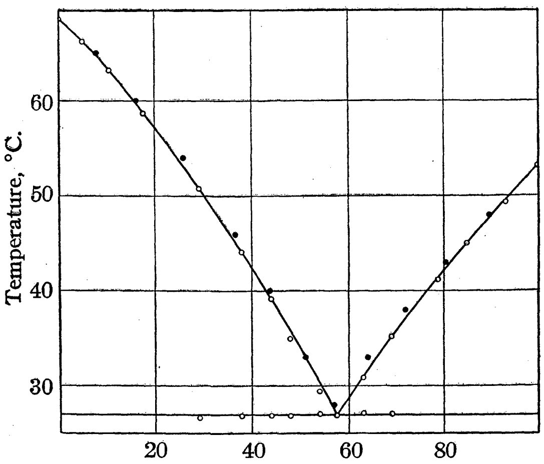
[7] Taylor and Rinkenbach, *ibid.*, **45**, 44 (1923).

TABLE VI

	p-Dichlorobenzene with Diphenyl	Naphthalene	Triphenylmethane
Eutectic temperature, °C.			
Ideal	27.5	32.0	34.9
Found	26.9	30.2	35.9
Difference	−0.6	−1.8	−1.0
Eutectic composition Mole fraction *p*-dichlorobenzene			
Ideal	0.563	0.625	0.670
Found	.575	.606	.685
Difference	−.012	−.019	−.015

in their work on the solubility of trinitrotoluene in carbon tetrachloride.

Results and Discussion.—The data obtained are given in Tables III, IV and V, and the freezing point–composition diagrams are shown in Figs. 1, 2 and 3. The ideal solubilities calculated from the above equation are shown by the filled circles in the figures. A comparison of the ideal eutectic compositions and temperatures is presented in Table VI.

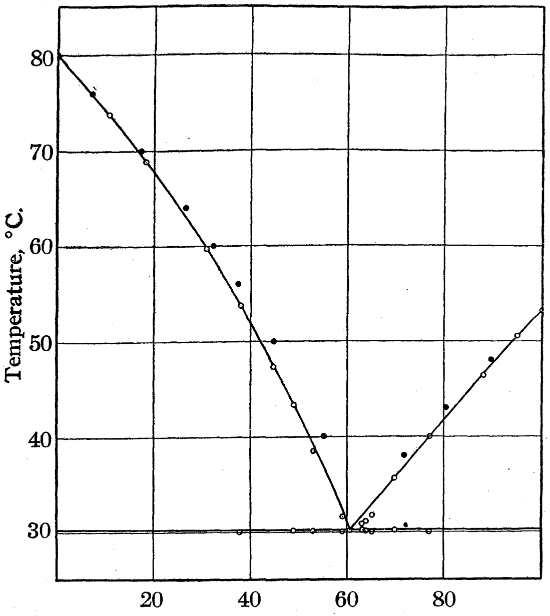


Mole per cent. of *p*-dichlorobenzene.

Fig. 1.—*p*-Dichlorobenzene–diphenyl.

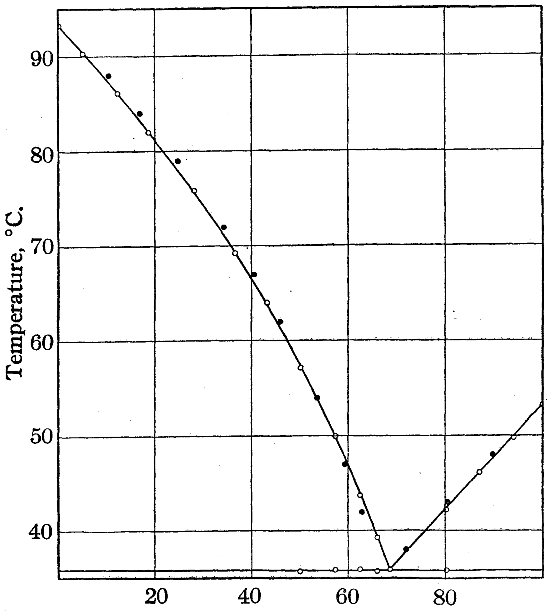
One may conclude that these three binary systems show a fairly close approach to ideal properties.

Although *p*-dichlorobenzene is non-polar, the presence of the chlorine atoms in the molecule evidently influences the properties of the latter sufficiently to make its solution with hydrocarbons somewhat less perfect than mixtures of hydrocarbons. For example, Lee and Warner[8] have shown that diphenyl, dibenzyl and naphthalene form practically perfect solutions among themselves.



Mole per cent. of *p*-dichlorobenzene.

Fig. 2.—*p*-Dichlorobenzene–naphthalene.



Mole per cent. of *p*-dichlorobenzene.

Fig. 3.—*p*-Dichlorobenzene–triphenylmethane.

We wish to thank Professor D. E. Anderson for the use of his laboratory and the Goodyear Tire and Rubber Co. for standardizing the thermometers in their laboratories.

Summary

1. The system *p*-dichlorobenzene with diphenyl shows a simple eutectic at 26.9° and 57.5 mole per cent. *p*-dichlorobenzene, with naphthalene a simple eutectic at 30.2° and 60.6

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[8] Lee and Warner, THIS JOURNAL, **57**, 318 (1935).

mole per cent. *p*-dichlorobenzene, and with triphenylmethane a simple eutectic at 35.9° and 68.5 mole per cent. *p*-dichlorobenzene.

2. Solubilities, eutectic temperatures and eutectic compositions in each of the three binary systems are a close approach to those calculated for ideal solutions.

AKRON, OHIO RECEIVED AUGUST 30, 1935

[CONTRIBUTION FROM THE JARVIS CHEMICAL LABORATORY OF TRINITY COLLEGE]

Equilibrium in the System, Lithium Phthalate–Phthalic Acid–Water

BY STERLING B. SMITH, WILLIAM A. STURM AND EDWARD C. ELY

Introduction

The use of acid phthalates as standards in volumetric analysis has become widespread during the past twenty years. Both the potassium and the sodium acid salts are used. Their use was first suggested by Dodge[1] and by Hendrixson.[2] A phase rule study of the system potassium phthalate, phthalic acid and water has been made by Smith,[3] and the system sodium phthalate, phthalic acid and water by Smith and Sturm.[4] It is possible that the acid phthalates of other alkali metals could be used for similar purposes and it is with this point in mind that an investigation of the solubility relations in the system lithium phthalate, phthalic acid and water has been undertaken.

Experimental Part

Materials and Methods.—Phthalic acid was prepared by crystallizing from aqueous solution sublimed phthalic anhydride obtained from the Eastman Kodak Co.

Lithium phthalate was prepared by neutralizing in aqueous solution an equivalent weight of phthalic acid with C. P. lithium carbonate. The resulting solution was boiled to drive off carbon dioxide, evaporated to a small volume and allowed to crystallize. The resultant crystals of lithium phthalate were filtered on a Büchner funnel and dried in the air. The composition of this salt was found by analysis to be $2Li_2C_8H_4O_4{\cdot}3H_2O$.

Lithium acid phthalate, while not a component of this system, appears as one of the important solid phases and is used in the preparation of mixtures for analysis. This salt as will be apparent later cannot be crystallized from aqueous solution at room temperature and was prepared by adding less than the equivalent weight of phthalic acid to each equivalent of lithium phthalate prepared as above, and allowing the acid salt to crystallize from a solution of lithium phthalate.

Solubilities were determined by analyzing solutions obtained by rotating for a minimum of twenty-four hours mixtures of the three components in an electrically controlled thermostat. At zero degrees the temperature was maintained constant by the use of ice and a small amount of salt. Temperature variations were within ±0.1°. When equilibrium was attained, the mixtures were allowed to settle and samples for analysis removed from the clear supernatant liquid by means of a pipet. At elevated temperatures the pipet was previously warmed to prevent crystallization during the sampling. When necessary, to prevent entrance of solid phase into the pipet, a small plug of cotton was placed in a short length of rubber tubing slipped over the end of the pipet.

Phthalic acid was determined by titration with alkali using phenolphthalein as the indicator. Lithium phthalate was determined by conversion into lithium sulfate with sulfuric acid and evaporating to dryness. The excess sulfuric acid was removed by ignition in a stream of ammonia. Water was determined by difference.

In making up the original mixtures, wherever possible the salts were used which exist as solid phases after equilibrium has been reached. The composition of the solid phases was determined by the analysis of wet residues according to Schreinemakers.[5] Because of the viscosity of many of the solutions, no attempt was made to determine their density.

Experimental Results.—Isotherms at 0, 25 and 50° have been completed. Compound formation takes place at all these temperatures. The solubility isotherms at these temperatures consist of three intersecting curves, representing isothermally univariant equilibrium between the solutions and one solid phase, and two isothermally invariant points where two solid phases are in equilibrium with the solutions. Inasmuch as no new solid phases appeared and the same solid phases remained at these three temperatures, no further isotherms were completed.

Experimental results are given in Table I. The symbol "P" is used here as in previous work to designate the phthalate radical, $C_8H_4O_4$. The figures representing the composition of the solutions at the isothermally invariant points are the average of several closely agreeing results.

The Acid Salt.—The composition of the acid salt, $LiHP{\cdot}2H_2O$, is most important as it is this material that has possibilities as a standard in volumetric analysis. The composition of this salt has been determined both graphically and by analysis. The extrapolated tie lines at each

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[1] F. D. Dodge, *J. Ind. Eng. Chem.*, **7**, 29 (1915).

[2] W. S. Hendrixson, THIS JOURNAL, **37**, 2352 (1915).

[3] S. B. Smith, *ibid.*, **53**, 3711 (1931).

[4] S. B. Smith and W. A. Sturm, *ibid.*, **55**, 2414 (1933).

[5] Schreinemakers, *Z. physik. Chem.*, **11**, 76 (1893).

temperature intersect at a point closely representing this composition. Calculating the composition of the solid phase by the algebraic extrapolation of tie lines according to Hill and Ricci,[6] it was found that in no case did the calculated composition vary from the theoretical by more than 0.72%, with an average deviation of 0.33%.

TABLE I

SOLUBILITY DATA

Point in figs.	Solution % H_2P	Solution % Li_2P	Wet residues % H_2P	Wet residues % Li_2P	Solid phases
		Temperature, 0°			
A	0.30	None	...	...	H_2P
	1.47	1.62	92.47	0.78	H_2P
	1.97	2.28	92.39	.43	H_2P
	2.63	3.41	95.10	.67	H_2P
	3.92	5.83	98.64	.48	H_2P
	5.58	11.06	88.13	1.86	H_2P
	7.45	16.55	92.74	2.18	H_2P
	8.67	20.39	94.29	1.89	H_2P
B	9.61	22.45	71.14	13.48	H_2P; $LiHP\cdot 2H_2O$
			39.65	32.39	H_2P; $LiHP\cdot 2H_2O$
	8.36	24.18	...	...	$LiHP\cdot 2H_2O$
	7.15	26.09	...	...	$LiHP\cdot 2H_2O$
	6.18	27.37	38.67	41.70	$LiHP\cdot 2H_2O$
	4.15	32.40	...	...	$LiHP\cdot 2H_2O$
	3.46	36.25	38.26	42.56	$LiHP\cdot 2H_2O$
	2.84	40.55	...	...	$LiHP\cdot 2H_2O$
	2.81	45.06	39.10	42.76	$LiHP\cdot 2H_2O$
C	2.81	45.75	20.96	63.08	$LiHP\cdot 2H_2O$; $2Li_2P\cdot 3H_2O$
	1.27	45.41	0.82	72.04	$2Li_2P\cdot 3H_2O$
D	None	45.37	...	...	$2Li_2P\cdot 3H_2O$
		Temperature, 25°			
E	0.68	None	...	...	H_2P
	3.34	3.22	83.43	0.69	H_2P
	4.59	5.07	66.61	1.31	H_2P
	6.97	8.87	...	...	H_2P
	8.15	10.55	73.25	3.78	H_2P
	10.56	14.56	76.21	4.35	H_2P
	11.38	16.10	71.54	4.99	H_2P
	13.32	19.39	75.56	5.76	H_2P
	15.85	23.40	88.87	4.32	H_2P
F	16.34	24.25	82.61	6.01	H_2P; $LiHP\cdot 2H_2O$
			53.53	28.73	H_2P; $LiHP\cdot 2H_2O$
	14.01	25.56	...	...	$LiHP\cdot 2H_2O$
	11.39	28.23	...	...	$LiHP\cdot 2H_2O$
	9.08	32.36	...	...	$LiHP\cdot 2H_2O$
	7.79	34.07	38.34	42.64	$LiHP\cdot 2H_2O$
	7.56	35.17	35.89	42.37	$LiHP\cdot 2H_2O$
	6.51	38.13	...	...	$LiHP\cdot 2H_2O$
	5.25	44.55	33.70	42.80	$LiHP\cdot 2H_2O$
G	5.20	45.19	26.00	50.70	$LiHP\cdot 2H_2O$; $2Li_2P\cdot 3H_2O$
			7.38	67.64	$LiHP\cdot 2H_2O$; $2Li_2P\cdot 3H_2O$
	3.60	45.15	0.99	76.24	$2Li_2P\cdot 3H_2O$
	2.38	45.17	0.48	75.01	$2Li_2P\cdot 3H_2O$
H	None	45.20	...	...	$2Li_2P\cdot 3H_2O$
		Temperature, 50°			
I	1.75	None	...	...	H_2P
	4.75	3.28	92.46	0.75	H_2P
	6.81	5.30	95.31	.70	H_2P
	11.48	10.80	87.16	.95	H_2P
	15.29	15.28	87.94	2.73	H_2P
	20.21	21.36	83.81	4.18	H_2P
J	24.00	26.69	70.87	17.79	H_2P; $LiHP\cdot 2H_2O$
			46.04	36.42	H_2P; $LiHP\cdot 2H_2O$
	21.78	28.29	38.07	40.50	$LiHP\cdot 2H_2O$
	18.92	30.05	...	...	$LiHP\cdot 2H_2O$
	16.47	32.57	35.92	41.00	$LiHP\cdot 2H_2O$
	15.07	34.77	...	...	$LiHP\cdot 2H_2O$
	12.42	39.32	34.21	42.45	$LiHP\cdot 2H_2O$
	10.51	44.10	34.17	42.49	$LiHP\cdot 2H_2O$
K	9.97	46.01	30.15	50.46	$LiHP\cdot 2H_2O$; $2Li_2P\cdot 3H_2O$
			13.97	71.20	$LiHP\cdot 2H_2O$; $2Li_2P\cdot 3H_2O$
	9.44	46.00	3.01	72.43	$2Li_2P\cdot 3H_2O$
	6.40	46.00	2.49	70.52	$2Li_2P\cdot 3H_2O$
	3.72	46.01	...	...	$2Li_2P\cdot 3H_2O$
L	None	46.08	...	...	$2Li_2P\cdot 3H_2O$

A sample of the acid salt was carefully prepared by adding solid lithium phthalate and phthalic acid to a solution of lithium phthalate, the proportions being arbitrarily selected, as will be apparent. The mixture was rotated in the thermostat at 25° for sixty hours and then allowed to settle. The composition of the liquid phase was found by analysis to be H_2P = 7.32% and Li_2P = 35.27%, represented by a point in approximately the middle of the line representing the composition of all solutions in equilibrium with the acid salt as solid phase. The residue was quickly centrifuged and analyzed, giving the data: H_2P = 39.22%, Li_2P = 43.80%, H_2O by difference = 16.98%. The percentage composition

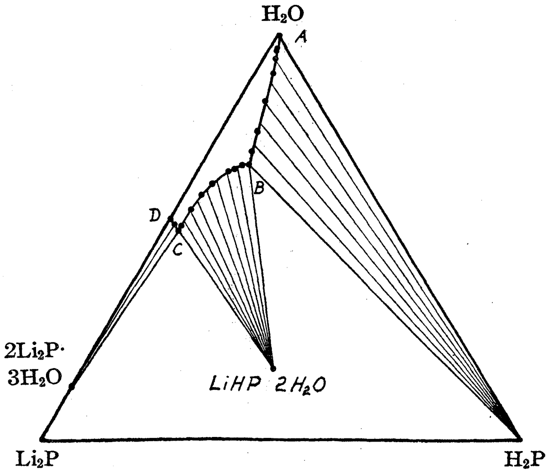

Fig. 1.—Temperature, 0°.

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(6) Hill and Ricci, THIS JOURNAL, 53, 4306 (1931).

corresponding to the formula $LiHP \cdot 2H_2O$ is $H_2P = 39.91\%$, $Li_2P = 42.77\%$, $H_2O = 17.32\%$.

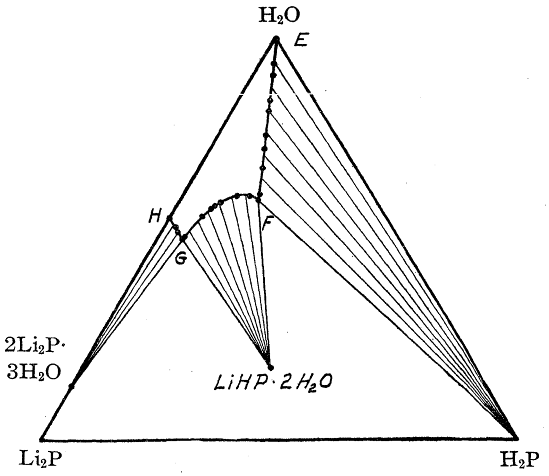

Fig. 2.—Temperature, 25°.

Discussion of Results

In order that a salt shall be crystallizable from aqueous solution at a given temperature, it is necessary that a straight line on the triangular diagram for that temperature, drawn from the apex, representing pure water, to that point on the diagram representing the composition of the salt in question, shall pass through the line representing the composition of all solutions in stable equilibrium with that salt as the solid phase.

Inspection of Fig. 3 shows that such a line would pass directly through the isothermally invariant point, "J." This means that at 50° lithium acid phthalate cannot be purified by crystallization from aqueous solution if the impurity is phthalic acid. Such procedure would result in the deposition of both salts. If the impurity were lithium phthalate, purification would result from recrystallization. At temperatures below 50°, Figs. 1 and 2, this reference line crosses the line representing the composition of all solutions in stable equilibrium with phthalic acid as the solid phase. Purification by recrystallization from aqueous solution at temperatures below 50° is obviously impossible.

It is apparent that the isothermally invariant point representing the composition of solutions in stable equilibrium with the two solid phases, phthalic acid and lithium acid phthalate, is working toward the right side of the diagram and approaches the above mentioned reference line as the temperature increases. In order to determine whether or not it has moved sufficiently so that our reference line crosses the line representing the composition of all solutions in stable equilibrium with lithium acid phthalate as the solid phase, a few experiments were carried out at 60°.

The composition of the solution in equilibrium with solid phthalic acid and solid lithium acid phthalate at this temperature was found to be $H_2P = 27.31\%$ and $Li_2P = 28.05\%$. This point has now moved across our reference line, showing the acid salt, $LiHP \cdot 2H_2O$, to be crystallizable from aqueous solution at 60°.

Lithium acid phthalate might therefore be purified by recrystallization from aqueous solution for use as a volumetric standard provided the crystallization were carried out at a temperature not less than 60°. Owing to the high cost of lithium salts as well as to the fact that recrystallization must be carried out at a high temperature resulting in large losses, it is doubtful that lithium acid phthalate will be added to our list of volumetric standards.

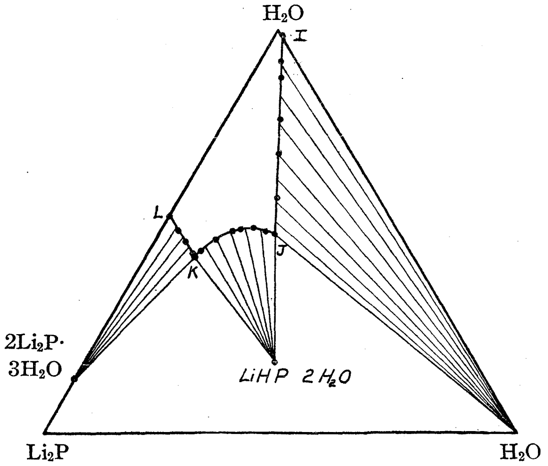

Fig. 3.—Temperature, 50°.

Summary

1. The solubility relations in the ternary system, lithium phthalate, phthalic acid and water at 0, 25 and 50° have been determined.

2. Compound formation has been found to take place at all of these temperatures.

3. The composition of this compound has been shown to be $LiHC_8H_4O_4 \cdot 2H_2O$.

4. It has been shown that this acid salt is crystallizable from aqueous solution at temperatures not lower than 60°.

HARTFORD, CONNECTICUT RECEIVED AUGUST 23, 1935

[CONTRIBUTION FROM THE INSTITUTE OF ANALYTICAL CHEMISTRY OF CHARLES UNIVERSITY]

Volumetric Determinations in Strongly Alkaline Solutions. III. The Titration of Thallium and Cerium with Hypobromite

BY O. TOMÍČEK AND M. JAŠEK

In the preceding communications of this series,[1,2] the results of titrations with ferricyanide were given. In the present paper new titrations with hypobromite are described. This reagent has already been used for the determination of ammonia, ammonium salts and urea,[3] for the determination of arsenites,[4] iodides,[5] thiocyanates,[6] and thiosulfates.[5,7]

Applying the potentiometric control, we have repeated the mentioned determinations[8] and also tried the possibility of the titration of yet other reduction–oxidation systems. Efforts to bring about a direct oxidation of plumbous, ferrous and chromic salts were without success. However, cerous salts could be titrated in a way analogous to that which has been described for the use of ferricyanide.[9] Such a titration with hypobromite proceeds very slowly and is not very satisfactory, while that of thallous salts (in the form of sulfate, carbonate, chloride or nitrate) is quick and complete. As thallous salts, especially the carbonate and sulfate, are easily prepared in a pure and well-defined state, they can be recommended as starting substances for the standardization of hypobromite solutions; thallous carbonate has already been employed as an acidimetric standard.[10]

A second reason for the advisability of thallous salts as starting substances for the direct standardization of solutions of alkali hypobromites is the fact that the accuracy of the determination is not so much dependent upon the basicity of the solution as in the case of arsenite solutions, which would otherwise be most suitable.

Materials and Apparatus

Solution of Sodium Hypobromite (in Some Cases the Potassium Salt).—About 0.05 *M* sodium hypobromite [potassium hypobromite] was prepared as follows. To an aqueous solution of *ca.* 0.5 *M* sodium [potassium] hydroxide of usual purity, which is cooled by freezing mixture of salt and ice to −4°, is added chemically pure bromine (8 g. per liter). The solution is well mixed and then left in the freezing mixture for two hours in the dark. After twelve more hours its titer was determined. The solution which has a yellow to greenish-yellow color was always stored in a bottle of dark hard glass in a cool place. Even hypobromite solutions, which were prepared with the utmost care, contain bromide and bromate ions (and sometimes perhaps also traces of bromite). For the direct titration in alkaline solutions only the hypobromite content is of significance. The standardization is made with arsenite or thallous salt as described below. The total oxidizing capacity of the solution (equal content of $BrO^- + BrO_3^-$) is determined, if desired, best by introducing the hypobromite solution in a solution of potassium iodide, which has been acidified with sulfuric acid; the titration then is carried out with thiosulfate. The solutions of hypobromite are not very stable; it is therefore advisable to check their titer before and after each series of experiments. For instance, the titer of a solution *ca.* 0.05 *M* sodium hypobromite and *ca.* 0.5 *M* sodium hydroxide was unchanged for a month; after three months it fell 16.7% and after six months 30.2%.

Solution of Arsenite (0.05 *M*).—It was prepared from chemically pure arsenic trioxide by the usual method.[11]

Thallous Salts and their Solutions.—For their preparation were used anhydrous, chemically pure thallous salts, which had been dried at 100° to constant weight, *viz.*, thallous sulfate (Tl_2SO_4) and thallous carbonate (Tl_2CO_3). To prepare a 0.025 *M* standard solution, 5.860 g. of thallous carbonate or 6.311 g. of thallous sulfate was weighed out exactly, then dissolved by warming and after cooling made up to 500 cc. Such a solution is very stable and does not change its titer even after many months. The other solutions were furthermore controlled by titrating with exactly standardized potassium ferricyanide.[1]

For the determination of cerium, a solution of cerous chloride, free from other earths, had been prepared; its titer was determined with 0.1 *M* ferricyanide solution.[9]

All other salts and reagents used were of average purity.

The apparatus and the calibrated vessels were the same as described in the previous communication.[1] In cases where oxidation by atmospheric oxygen did not interfere, the solution was stirred by an electrical stirrer without passing any carbon dioxide. The titration vessels were of hard glass throughout.

Titration of Thallium

The titrations were carried out as follows. To 25 cc. of the 0.025 *M* solution of thallous sulfate were first added

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[1] O. Tomíček and F. Freiberger, THIS JOURNAL, **57**, 801 (1935).

[2] O. Tomíček and J. Kalný, *ibid.*, **57**, 1209 (1935).

[3] P. Artmann and A. Skrabal, *Z. anal. Chem.*, **46**, 5 (1907).

[4] I. M. Kolthoff and A. Laue, *ibid.*, **73**, 177 (1928).

[5] H. H. Willard and F. Fenwick, THIS JOURNAL, **45**, 631 (1923).

[6] J. Golse, *Bull. Soc. Pharmacol.*, **66**, 139 (1928), and **67**, 226 (1929).

[7] I. M. Kolthoff and N. H. Furman, "Potentiometric Titrations," John Wiley and Sons, Inc., 440 Fourth Ave., New York City, 1931, 2d ed., p. 311.

[8] The results of these experiments will be given elsewhere later.

[9] O. Tomíček, *Rec. trav. chim.*, **46**, 410 (1925).

[10] R. Hac and K. Kámen, *Coll. Czechoslovak Chem. Comm.*, **4**, 145 (1932).

[11] I. M. Kolthoff, "Die Massanalyse," II, Verlag Julius Springer, Berlin, 1931, 2d ed., p. 379.

various quantities of sodium or potassium hydroxide. Then the solution was titrated sometimes in an atmosphere of carbon dioxide and sometimes open to the air with *ca.* 0.05 *M* sodium hypobromite solution, which had been standardized with arsenite simultaneously under the same conditions.

It was found unnecessary to work in an atmosphere of carbon dioxide. The liquid, which at the beginning remained clear even after the addition of sodium hydroxide, became turbid at once after the first drops of the hypobromite were added, forming a precipitate of thallium hydroxide. If the solution is stirred vigorously, this precipitate does not at all delay the quick attainment of a stable potential, and thus does not interfere with the exact course of the titration. A few results of many experiments are compiled in the following tables. It may be seen that the most suitable alkalinity is that when the reaction liquid at the end of titration is 1.5 to 2 *M* sodium hydroxide. Under these conditions, the inflection potential lies at +0.05 volt against the saturated calomel electrode. The drop in potential is considerable and well recognizable, and a stable potential is quickly attained also in the neighborhood of the equivalent point. With increasing concentration of hydroxide, this jump in potential is somewhat smaller. It is advisable to clean the indicating platinum electrode before each titration by washing with hydrochloric acid and burning in the flame. The course of a titration may be seen from Fig. 1.

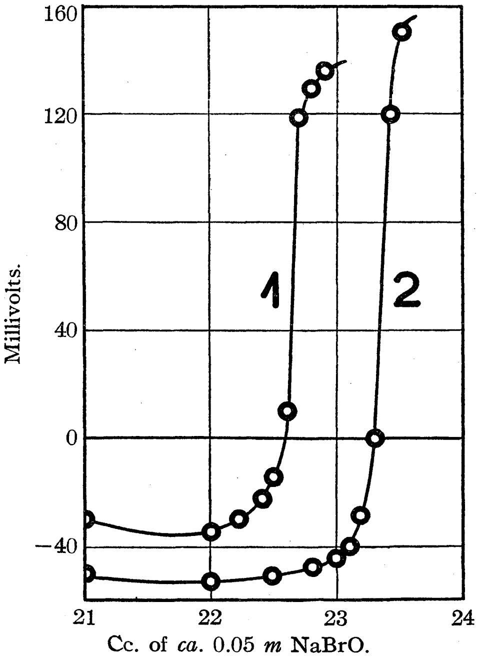

Fig. 1.—The titration curves of thallous salts by hypobromite: Curve 1, the titration of thallous carbonate in 3 *M* NaOH. Curve 2, the titration of thallous sulfate in 2.5 *M* NaOH.

The following experiments show that thallous nitrate also may be titrated in the same way: 0.2358 and 0.4510 g. of thallous carbonate were treated with a few drops of dilute nitric acid until the evolution of carbon dioxide ceased; the resulting solution was diluted with water and then treated as in the preceding experiments. It was found that the presence of nitrate ions did not interfere at all. The amount of *ca.* 0.05 *M* sodium hypobromite spent was as follows: 14.95 cc. (calcd. 15.00 cc.) and 28.75 cc. (calcd. 28.70 cc.).

TABLE I

TITRATION OF 25.00 CC. 0.025 *M* Tl_2CO_3 AND 0.025 *M* Tl_2SO_4

Basicity of titration, *M*		*Ca.* 0.05 *M* NaBrO for 25.00 cc. of		
Beginning	End	0.05 *M* Na_3AsO_3	0.025 *M* Tl_2CO_3	
0.5	0.5	30.15	29.73	29.73
1.0	0.8	30.20	29.90	29.90
2.0	1.5	30.05	30.07	30.07
3.0	2.5	29.95	30.07	30.07
4.0	3.5	29.80	30.07	30.07
			0.025 *M* Tl_2SO_4	
0.5	0.5	23.15	22.95	22.95
1.0	0.8	23.25	22.95	22.93
2.0	1.5	23.05	22.95	22.95
3.0	2.5	22.95	22.95	22.95
4.0	3.5	22.75	22.95	23.00

TABLE II

TITRATION OF VARIOUS QUANTITIES OF 0.025 *M* Tl_2SO_4

0.025 *M* Tl_2SO_4, cc.	Basicity of titration, *M*		*Ca.* 0.05 *M* NaBrO, cc.		
	Beginning	End	Calcd.	Used	
5.00	2.0	1.9	3.73	3.75	3.73
10.00	2.0	1.8	7.45	7.43	7.45
20.00	2.0	1.65	14.90	14.85	14.90
50.00	2.0	1.5	37.25	37.20	37.30

Also the reverse titration of hypobromite with a solution of thallous salts is possible, but is of less importance due to the readiness with which it is oxidized by air. It is of no particular interest to study the interference of easily oxidizable cations as the main purpose of these investigations was to prove that thallous salts are very suitable for the standardization of hypobromite solutions.

For the standardization of *ca.* 0.025 *M* hypobromite solution a thallium salt is therefore quite suitable, in accordance with the equations

$$Tl_2CO_3 + 2NaBrO + 2NaOH + 2H_2O = 2Tl(OH)_3 + 2NaBr + Na_2CO_3$$

$$Tl^+ + BrO^- + OH^- + H_2O = Tl(OH)_3 + Br^-$$

Either 0.025 *M* solution of thallous sulfate or carbonate may be used in the standardization, or 0.25-g. portion of salt may be weighed out, dissolved in about 20 cc. of water, with warming if necessary. The cool solution is then diluted with concd. sodium or potassium hydroxide in such amount that the final solution (50–75 cc.) is 2–3 *M* in base. This solution is titrated with the unknown hypobromite to the maximum of inflection, according to the procedure already described.

Determination of Cerium

Preliminary experiments to titrate cerous salts with hypobromite in a solution which had been made alkaline with sodium or potassium hydroxide gave no satisfactory results. However, a cerous salt solution (either the chloride or sulfate) to which so much potassium carbonate had been added that it contained 20 to 30% of potassium carbonate at the end of the titration could be titrated with hypobromite, if the atmospheric oxygen was removed from the solution by passing carbon dioxide or nitrogen (free from oxygen) through it. The reaction liquid remains clear and becomes yellow in color after the addition of hypobromite. Yet the attainment of stable potentials is extremely slow and could not be accelerated by changes of temperature or any addition of catalyzers. It is, therefore, of advantage to obtain an idea as to the position of the maximum by a preliminary titration. For the proper titration almost the whole amount of necessary hypobromite is added at once and only the remaining few tenths cc. are used to accomplish the titration. On the whole the procedure is the same as has been described[9] for the much quicker and thereby much more satisfactory titration of cerous salts with ferricyanide. The inflection potential under the given conditions is 0.10 volt against the saturated calomel electrode.

Experiments.—20.00 cc. of *ca.* 0.1 *M* cerous chloride solution required for a titration 19.13 and 19.13 cc. of 0.1 *M* ferricyanide. The same quantity of cerous chloride required 19.20, 19.13, 19.04 and 19.09 cc. of the 0.05 *M* solution of hypobromite.

Summary

1. A new and simple titration of thallous salts with hypobromite has been described. It is very suitable for the standardization of hypobromite solutions by using thallous carbonate or sulfate as standard.

2. Also cerous salts can be titrated with hypobromite in 20 to 30% solution of potassium carbonate from which the atmospheric oxygen has been removed. However, the titration with ferricyanide is to be preferred.

PRAGUE, CZECHOSLOVAKIA RECEIVED JULY 26, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF ROCHESTER]

Photochemical Investigations. II. The Photochemical Decomposition of Ethylene Iodide in Solutions of Carbon Tetrachloride[1]

BY ROBERT E. DERIGHT AND EDWIN O. WIIG

The thermal decomposition of ethylene iodide in solutions of carbon tetrachloride was found by Polissar[2] to consist of two parts, the ordinary and that catalyzed by iodine. Arnold and Kistiakowsky[3] found similar reactions to occur in the gas phase. The iodine photosensitized decomposition in solutions of carbon tetrachloride was found by Schumacher and Wiig[4] to be a chain reaction propagated by iodine atoms. It was thought that an investigation of the decomposition brought about by light absorbed by the ethylene iodide itself might give some insight into the mechanism of the decomposition and the manner in which the iodine is split off the ethylene iodide.

Experimental Details

Preparation and Purification of Materials.—The carbon tetrachloride was purified by the method used by Polissar.[2] Only the middle fraction from the last distillation was retained. The ethylene iodide was prepared from pure ethylene and iodine[5] and purified by recrystallization from dry ether. Attempts to prepare ethylene iodide by bubbling ethylene into concentrated solutions of iodine in carbon tetrachloride gave negligible yields. Uranyl sulfate and oxalic acid were purified in the manner described by Leighton and Forbes.[6]

The decomposition of ethylene iodide was followed by titrating the liberated iodine with *N*/200 solutions of sodium thiosulfate and of iodine. The relative strength of these solutions was checked frequently, the normality of the iodine being determined by titration against potassium permanganate solutions, the titer of which against sodium oxalate remained constant over long periods.

Apparatus and Procedure.—The reaction cell was cylindrically shaped with optically plane windows. The cell, made from fused quartz with fused seams, was 40 mm. in diameter and 35 mm. in length and was filled with 37 cc. of solution by means of a 12-mm. tube located near the rear window. In the experiments with the uranyl sulfate–oxalic acid solutions a stirrer was inserted through this tube. This cell was immersed in a thermostat, provided with a fused quartz window, in which the temperature of the water was regulated to ±0.03°.

The light source was a vertical Uviarc quartz mercury vapor lamp operated on 120 volt d. c. The lamp was rigidly mounted and the voltage carefully controlled so that the intensity was constant over long periods. A large crystalline quartz monochromator (f:1.9) with collimator and exit slits of 1.50 and 1.05 mm., respectively, was adjusted with the aid of a Beck fluorescent spectroscope to give the maximum intensity of light of the wave length desired. In all experiments, except those used to evaluate

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[1] Presented at the New York meeting of the American Chemical Society, April, 1935.

[2] Polissar, THIS JOURNAL, **52**, 956 (1930).

[3] Arnold and Kistiakowsky, *J. Chem. Phys.*, **1**, 166 (1933).

[4] Schumacher and Wiig, *Z. physik. Chem.*, **11B**, 45 (1930).

[5] Semenoff, Jahresberichte über die Fortschritte der Chemie, 1864. p. 483.

[6] Leighton and Forbes, THIS JOURNAL, **52**, 3139 (1930).

the photosensitized reaction, light of λλ303 and 313 mμ was used. Photographs of this light overexposed thirty times showed only traces of longer wave lengths. The light intensity was measured by means of a linear thermopile of the Coblentz type. The thermopile was calibrated after each experiment against a standard lamp which had been compared with Radiation Standard C-67 calibrated by the Bureau of Standards. A resistance pattern of the type described by Leighton and Leighton[7] was used to decrease the deflections of the galvanometer. The solutions of ethylene iodide were prepared by adding weighed amounts to carbon tetrachloride contained in a volumetric flask. These solutions were prepared in artificial light to prevent decomposition and could be stored indefinitely in the dark. The cell was filled, allowed to come to the temperature of the thermostat, and then exposed to the light when the lamp had reached a steady state. At the end of an experiment the cell was cooled to room temperature and two 15-cc. samples pipetted into 100-cc. portions of distilled water. Enough sodium thiosulfate was added to give *ca.* 10 cc. excess. The flask was then shaken thoroughly and slowly back titrated with iodine solution.

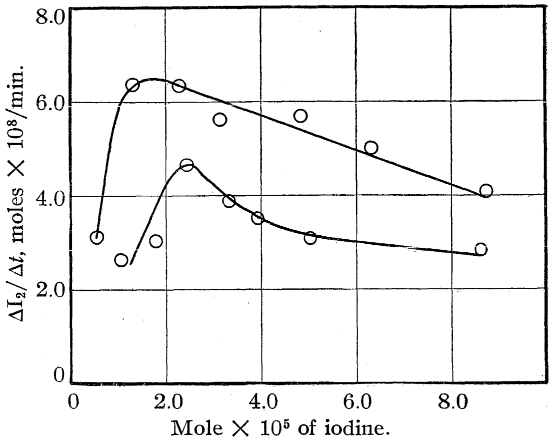

Fig. 1.—The rate of decomposition of ethylene iodide: upper curve, Table I; lower curve, Table II.

Results

Absorption Spectrum.—The absorption spectra of solutions of ethylene iodide in carbon tetrachloride were obtained by photographing the light from impregnated carbon arcs which had passed through the reaction cell filled with solutions containing 0.5, 1.0 and 2.0 g. (1.79, 3.57 and 7.14 × 10^{-3} mole) of ethylene iodide per 50 cc. of carbon tetrachloride. The photographs were made with a large Hilger spectrograph, employing a method described by O'Brien.[8] Absorption was found to begin at a wave length of 360 mμ. The 303 and 313 mμ Hg lines were strongly absorbed. The intensity of this light transmitted by various solutions of ethylene iodide and of iodine was measured with the thermopile. The iodine absorbed weakly in this region. These data were then used to obtain absorption coefficients which could be used to calculate the partition of the light at any time in an experiment.

Rate of Reaction.—A series of experiments was carried out for various lengths of time. The temperature of the thermostat in these experiments was 25°. The data are shown in Table I.

TABLE I

THE RATE OF DECOMPOSITION OF ETHYLENE IODIDE FOR VARIOUS LENGTHS OF TIME

Molarity of ethylene iodide 0.0357

Time, min.	Total I_2 mole × 10^5	ΔI_2 mole × 10^5	$\frac{\Delta I_2 \times 10^3}{\Delta t}$	$\frac{\Sigma \Delta I_2 \times 10^3}{\Sigma \Delta t}$
180	0.57	0.57	3.15	3.15
300	1.33	.76	6.35	4.43
450	2.28	.95	6.33	5.07
600	3.12	.84	5.60	5.20
900	4.82	1.70	5.67	5.36
1200	6.32	1.50	5.00	5.27
1800	8.76	2.44	4.07	4.87

Two similar series of experiments were performed outside the thermostat. The light was first passed through 1 cm. of 0.0055 and 0.0147 molar solutions of iodine in carbon tetrachloride contained in a filter cell. These data are shown in Table II.

TABLE II

THE RATE OF DECOMPOSITION CAUSED BY LIGHT PASSED THROUGH AN IODINE FILTER

Molarity of ethylene iodide 0.0357

I_2 in filter cell, molar	Time, min.	Total I_2 moles × 10^5	ΔI_2 Moles × 10^5	$\frac{\Delta I_2 \times 10^3}{\Delta t}$
0.0357	390	1.03	1.03	2.64
	638	1.78	0.75	3.02
	780	2.44	.66	4.65
	1005	3.31	.87	3.87
	1175	3.91	.60	3.53
	1540	5.03	1.12	3.07
	2805	8.63	3.60	2.85
0.0147	540	1.17	1.17	2.16
	720	1.66	0.49	2.72
	1380	3.91	2.25	3.41

The data from Tables I and II are shown graphically in Fig. 1.

It is apparent that in every case, despite changes in intensity and passage of the light beam through solutions of iodine, the rate increased to a maximum and then fell slowly. These facts preclude the possibility that the increase was due to absorption by the iodine of light of longer wave

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(7) Leighton and Leighton, *J. Phys. Chem.*, **36**, 1882 (1932).

(8) O'Brien, *Bull. Am. Phys. Soc.*, Feb. 10 (1932).

length. The increase was much larger than the experimental error.

Effect of Concentration.—The effect of varying the initial concentrations of ethylene iodide, iodine and ethylene in experiments performed outside the thermostat is shown in the following tables.

TABLE III

THE EFFECT OF THE INITIAL CONCENTRATION OF ETHYLENE IODIDE ON THE RATE OF DECOMPOSITION OF ETHYLENE IODIDE

$C_2H_4I_2$ molar	Time, min.	Total I_2 moles $\times 10^5$	ΔI_2 moles $\times 10^5$	$\frac{\Delta I_2 \times 10^3}{\Delta t}$
	300	1.24	1.24	4.13
0.0357	600	2.89	1.65	5.50
	945	5.50	2.61	7.57
	300	1.28	1.28	4.27
0.0714	603	2.86	1.58	5.21
	936	5.47	2.61	7.84
	300	1.23	1.23	4.10
0.143	660	3.14	1.91	5.31
	960	6.03	2.89	9.63

TABLE IV

THE EFFECT OF THE INITIAL CONCENTRATION OF IODINE ON THE RATE OF DECOMPOSITION OF ETHYLENE IODIDE

Molarity of ethylene iodide, 0.0357

Time, min.	Mole $\times 10^5$ iodine added initially	Total mole $\times 10^5$ dec.	Mole $\times 10^7$ dec. per min.
600	0	3.12	0.520
620	0.87	3.09	.498
600	2.72	2.75	.458
603	3.26	2.62	.436
600	4.17	2.56	.427
607	7.52	2.46	.405
600	10.78	2.40	.400

TABLE V

THE EFFECT OF ETHYLENE ON THE RATE OF DECOMPOSITION OF ETHYLENE IODIDE

Molarity of ethylene iodide, 0.0357

Ethylene added	Time, min.	Total mole $\times 10^5$ dec.	Mole $\times 10^7$ dec. per min.
Yes	615	2.94	0.478
Yes	660	3.30	.500
No	600	2.89	.482

These data show that increasing the concentration of the ethylene iodide appears to increase the rate of decomposition slightly. Small initial concentrations of ethylene had no measurable effect on the rate while increasing amounts of iodine caused successively larger decreases in the rate of decomposition.

Effect of Intensity.—The light absorbed was varied thirty fold. These results are shown in Table VI. The rate of decomposition was approximately proportional to the energy absorbed throughout the range investigated.

TABLE VI

THE RATE OF DECOMPOSITION OF ETHYLENE IODIDE FOR VARIOUS LIGHT INTENSITIES ABSORBED

Molarity of ethylene iodide, 0.0357

Reaction ratio	1.71	1.74	2.01	1.91	1.93
Intensity	1.83	1.83	1.91	1.91	1.91
Moles decompd.	1.03	1.87	1.35	2.23	2.36
Reaction ratio	2.32	2.50	2.10	28.7	28.5
Intensity ratio	2.38	2.38	2.38	28.4	28.4
Moles decompd.	1.17	1.66	3.91	0.44	0.43

Effect of Temperature.—Measurements of the rates of decomposition at 20 and 30° showed only very slight effects of temperature so that some of the preceding experiments, as already indicated, were not carried out in the thermostat. Raising the temperature to 50°, however, resulted in a measurable increase in the rate as shown in the following table.

TABLE VII

THE EFFECT OF TEMPERATURE ON THE RATE OF DECOMPOSITION OF ETHYLENE IODIDE

Molarity of ethylene iodide, 0.0357

Temp., °C.	Time, min.	Total mole $\times 10^5$ dec.	Mole $\times 10^7$ dec. per min.
25	720	3.64	0.506
50	615	3.75	.610
50	618	3.71	.601

Using these data and additional data at 25° from Table I, the ratios of the times necessary for equal amounts of decomposition were determined. The decomposition which occurred in 615 minutes at 50° required 694 minutes at 25° or a ratio of 1.13. The corresponding temperature coefficient for 10° is 1.05. It is to be noted that the thermal reaction which is responsible for this temperature coefficient accounts for only a part of the total reaction.

Evaluation of the Photosensitized Reaction.—Since Schumacher and Wiig[4] found the iodine photosensitized decomposition of ethylene iodide to be a chain reaction and since iodine, a product of the photodecomposition, absorbs slightly light of the wave lengths used here, experiments were carried out to determine whether the acceleration observed could be accounted for by a sensitized reaction. The yield at λλ436 and 465 mμ, where ethylene iodide does not absorb and iodine absorbs strongly, was determined under our experimental conditions. Assuming the same quantum efficiency at the shorter wave lengths and calculating the partition of light of these wave lengths between iodine and ethylene iodide, the maximum possible effect of the photosensitized reaction was found to be less than 2–3% of the observed increase in rate at any time.

Determination of the Quantum Yield.—The quantum measurements were made outside the thermostat but the variation of room temperature was less than ±1°. The lamp voltage was carefully controlled and the intensity measured frequently as described previously. The experiments with the uranyl sulfate–oxalic acid actinometer were carried out under identical conditions. Assuming a quantum yield[6] of 0.561 at λ313 mμ the following transmission factors for the rear window of the cell and optical system were obtained: 1.480, 1.481, 1.490 and 1.511, or an average of 1.490. The results of the quantum measurements are given in Table VIII.

TABLE VIII

THE DETERMINATION OF THE QUANTUM YIELD FOR THE DECOMPOSITION OF ETHYLENE IODIDE

Molarity of ethylene iodide, 0.0357

Time, min.	Mole × 10^5 dec.	Molecules × 10^{19} dec.	Quanta × 10^{19} absorbed	Quantum yield
600	1.29	0.78	1.10	0.71
600	1.35	.82	1.11	.74
900	2.00	1.21	1.62	.75
900	2.23	1.35	1.67	.81
960	2.36	1.43	1.77	.81

Discussion

The mechanism of the photochemical decomposition of ethylene iodide is probably given by the equations

$$C_2H_4I_2 + h\nu \longrightarrow C_2H_4I + I \qquad (1)$$
$$C_2H_4I_2 + I \rightleftharpoons C_2H_4I + I_2 \qquad (2) \text{ and } (3)$$
$$C_2H_4I \rightleftharpoons C_2H_4 + I \qquad (4) \text{ and } (5)$$
$$I + I \longrightarrow I_2 \qquad (6)$$

Light of the wave lengths used supplies more than enough energy to break the carbon–iodine bond so that reaction (1) is possible. The remaining equations have been suggested previously in connection with the formation,[9] thermal decomposition[3,9] and the photosensitized decomposition[4] of ethylene iodide. Some calculations by Narayanmurti[10] based on the mechanism for the last-mentioned reaction indicate that the theoretical and observed rates are in excellent agreement. Reactions analogous to (2) through (5) have been suggested in connection with the photosensitized decomposition of dibromotetrachloroethane.[11] With reasonable simplifying assumptions these reactions lead to the rate equation

$$-d(C_2H_4I_2)/dt = I_{\text{abs.}}/[1 + (k_3/k_4)\,(I_2)]$$

This is in agreement with the experimental results except that it does not account for the increase in the decomposition rate observed when only small amounts of iodine have been formed. The initial increase in rate might be due either to a decrease in the concentration of an inhibitor or to some unknown reaction involving perhaps C_2H_4I or I_3. The carbon tetrachloride was carefully purified but air was not removed or excluded from the reaction mixture. That oxygen may have an inhibiting effect has been found in somewhat similar reactions.[12] The amount of iodine formed at the maximum (Fig. 1) is less than the solubility of oxygen in carbon tetrachloride, so that inhibition by oxygen is a possibility. Unfortunately no experiments were performed to test this.

In the early stages of an experiment reaction (3) would be of no importance because of the low iodine molecule concentration. As the concentration of iodine builds up, however, reaction (3) will predominate over (2), since their energies of activation are 1.8 and 11.8 cal., respectively.[13] This explains the retarding effect of iodine.

The quantum yield experiments give an average value of 0.76 but the measurements include the period in which the reaction rate is rising. If the yield is calculated for the period of six-hundred to nine-hundred minutes in Table VIII, a value of 0.86 is obtained. The light intensities employed in the experiments in Table I may be estimated quite readily. The quantum yields corresponding to those energies are 0.54 at the beginning, 1.10 at the maximum and 0.70 at the end of the measurements. The value to be assigned to the quantum efficiency of the primary process depends upon the interpretation of the initial increase in reaction rate.

The value of the quantum yield for the primary photo-process is of interest in connection with theories of photochemical reactions in solution. In a recent paper, Franck and Rabinowitsch[14] discuss the photochemistry of reactions in solution. They compare reactions in solution with the bet-

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(9) Shumacher, THIS JOURNAL, **32**, 3132 (1930).

(10) Narayanmurti, *J. Ind. Chem. Soc.*, **12**, 173 (1935).

(11) Carrico and Dickinson, THIS JOURNAL, **57**, 1343 (1935).

(12) Dickinson and Leermakers, *ibid.*, **54**, 3852 (1932); Chapman, *ibid.*, **56**, 818 (1934); Bauer and Daniels, *ibid.*, **56**, 2014 (1934).

(13) Sherman and Sun, *ibid.*, **56**, 1096 (1934).

(14) Franck and Rabinowitsch, *Trans. Faraday Soc.*, **30**, 120 (1934).

ter known gas reactions and point out three effects which are of importance in the former. (1) There is a certain time lag between the absorption of light and the decomposition of the molecule. The large number of collisions with solvent molecules makes deactivation possible during this interval. (2) Similarly, since all collisions of reaction products would be triple collisions, secondary recombination would be enhanced. (3) If the decomposition yields atoms or radicals these would lose their excess kinetic energy by collision before going much more than the length of a molecular diameter and if they were still close together they would undergo primary recombination. All of these effects would decrease the quantum yield but the third would be of greatest importance. Hence, they conclude that for all reactions involving atoms or radicals the primary quantum yield should be definitely less than one. Furthermore, light of shorter wave length should cause the decomposition products to leave with greater kinetic energy; they should travel further before losing their kinetic energy and primary recombination would be decreased. Thus light of shorter wave length should produce a greater quantum yield. The photodecomposition of ethylene iodide would seem to proceed by atoms and radicals. If the low yield at the beginning of an experiment is not due to inhibition, then the present results would tend to substantiate the theory of Franck and Rabinowitsch.

Without citing any evidence, Emschwiller[15] states that when solutions of ethylene iodide are exposed to polychromatic ultraviolet light the primary decomposition products are ethylene and iodine. Such a simple mechanism cannot account for the retardation of the reaction rate observed in our experiments, since union of ethylene and iodine proceeds too slowly at room temperatures. The mechanism suggested here follows from related studies on the decomposition of ethylene iodide. With polychromatic light the ethylene iodide photodecomposition is quite likely complicated by the iodine photosensitized decomposition, which would increase the difficulty of interpreting the results.

The study of the photodecomposition of the halogen addition products of ethylene is being continued in this Laboratory. It is also planned to extend the investigations to the gaseous reactions.

Summary

The apparent quantum yield for the photodecomposition of ethylene iodide in carbon tetrachloride solutions by light of wave lengths 303 and 313 mμ was found to be 0.76. This includes both the photo- and any subsequent thermal reactions. A mechanism involving a primary dissociation into C_2H_4I and atomic iodine has been suggested. The rate equation based on this mechanism is in agreement with the data obtained. A further study of this reaction should be of interest in connection with the Franck and Rabinowitsch theory of photochemical reactions in solution.

ROCHESTER, NEW YORK RECEIVED AUGUST 12, 1935

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[15] Emschwiller, *Compt. rend.*, **199**, 854 (1934).

[CONTRIBUTION FROM RESEARCH AND DEVELOPMENT LABORATORIES, UNIVERSAL OIL PRODUCTS COMPANY]

Reaction of Paraffins with Aromatic Hydrocarbons (Destructive Alkylation)[1]

BY ARISTID V. GROSSE AND V. N. IPATIEFF

We have recently described the catalytic reaction of saturated hydrocarbons with olefins.[2] We have also found that paraffins can react with aromatic hydrocarbons in the presence of catalysts under mild conditions. The reaction consists in the splitting of the paraffin into a lower molecular weight paraffin and an olefin "in statu nascendi," which immediately alkylates the aromatic hydrocarbon. The general reaction proceeds according to the equation

$$\underset{\text{Paraffin}}{C_{(m+n)}H_{2(m+n)+2}} + \underset{\text{Aromatic hydrocarbon}}{C_xH_{2x-6}} \xrightarrow{\text{Catalyst}} \underset{\text{Lower molecular paraffin}}{C_nH_{2n+2}} + \underset{\text{Alkyl-aromatic hydrocarbon}}{C_xH_{2x-5}\cdot C_mH_{2m+}}$$

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[1] Presented before the Organic Division of the 90th meeting of the American Chemical Society at San Francisco on August 21, 1935.

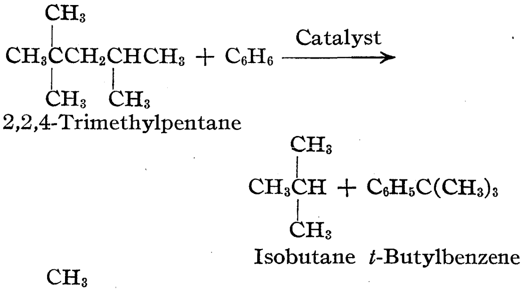
[2] V. N. Ipatieff and A. V. Grosse, THIS JOURNAL, **57**, 1616 (1935).

This reaction may be appropriately termed destructive alkylation.

The reaction was first discovered in the case of an octane (2,2,4-trimethylpentane) and benzene, and will be described in detail here. The same reaction takes place with *other aromatic* hydrocarbons, for instance, with toluene and the xylenes, and with *other paraffins*, for instance, *n*-heptane, hexanes and pentanes.

The reaction between 2,2,4-trimethylpentane and benzene was studied in the presence of aluminum chloride, zirconium chloride, boron fluoride and magnesium chloride. In the last two cases there is no reaction, and both hydrocarbons remain unchanged.

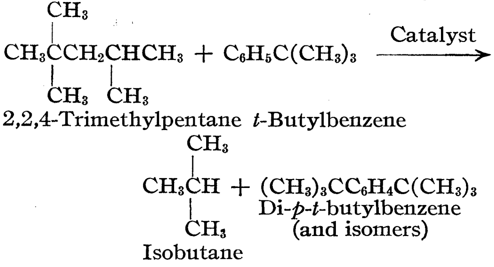
In the presence of aluminum chloride and zirconium chloride, the following reactions take place



$$CH_3C(CH_3)_2CH_2CH(CH_3)CH_3 + C_6H_6 \xrightarrow{\text{Catalyst}} CH_3CH(CH_3)CH_3 + C_6H_5C(CH_3)_3 \quad (1)$$

2,2,4-Trimethylpentane

Isobutane *t*-Butylbenzene



$$CH_3C(CH_3)_2CH_2CH(CH_3)CH_3 + C_6H_5C(CH_3)_3 \xrightarrow{\text{Catalyst}} CH_3CH(CH_3)CH_3 + (CH_3)_3CC_6H_4C(CH_3)_3 \quad (2)$$

2,2,4-Trimethylpentane *t*-Butylbenzene

Isobutane Di-*p*-*t*-butylbenzene (and isomers)

The octane can be *practically completely* converted into isobutane and the *t*-butylbenzenes. With aluminum chloride, the reaction takes place at 25–50° and ordinary pressure during about four hours; with zirconium chloride, at a temperature of 50–75° during about four hours. These chlorides act as real catalysts, since one molecule of each of them can convert at least twenty molecules of the octane. Hydrogen chloride is added in each case to promote the action of the chlorides. The aluminum chloride and also zirconium chloride partly combine with the aromatic hydrocarbons forming the well-known pasty or liquid brown-red addition compounds of Gustavson.[3]

Experimental Part

(1) Reaction of 2,2,4-Trimethylpentane with Benzene in the Presence of Aluminum Chloride

The reaction was carried out at atmospheric pressure in a three-necked glass flask fitted with (a) a stirrer, (b) a separatory funnel, (c) a reflux condenser with an outlet tube and (d) a gas inlet tube for nitrogen and dry hydrogen chloride from a cylinder.

The gas from the outlet tube of the condenser passed through two dry ice receivers, Nos. 1 and 2, at −78°, a mercury manometer, a safety bottle and a graduated gas holder. A known quantity of the aluminum chloride was placed in the flask. Before starting the reaction, the whole apparatus was flushed out with oxygen-free nitrogen and then the benzene and octane were poured in through the separatory funnel.

From the start of the experiment, dry hydrogen chloride gas was bubbled through the liquid reagents until saturation, a few bubbles being added from time to time during the course of the reaction. The reaction proceeded at room temperature (20°) with evolution of condensable gas and the formation of a dark brown lower layer which quite rapidly increased in quantity. After about one hour the temperature of the reaction vessel was slowly increased to 50° by placing it in a water-bath. After a total reaction time of four and one-half hours, the reaction was stopped.

The Products of the Reaction and their Identification.—The reaction products consisted of (a) gases (condensable and uncondensable at −78°), (b) a clear, water-white upper layer and (c) a dark brown lower layer.

In one typical experiment, the amounts of reagents used and the products obtained after the completion of the reaction, were as follows:

BEFORE REACTION		Grams
Aluminum chloride (9.4 g. or 0.0705 mole reacted, 8.8 g. recovered unchanged)		18.2
Hydrogen chloride		≃ 0.3
2,2,4-Trimethylpentane (very pure, n^{20}_D 1.3922), 1.40 moles		160.1
Benzene (very pure), 1.63 moles		127.3
Total		305.9
AFTER REACTION		
Uncondensable gas (at −78°) = 800 cc.		
Condensable gas (at −78°):		
Receiver 1		69.77
Receiver 2		0.0
Upper layer		202.5
Lower layer:		
Unreacted AlCl$_3$,	8.8	32.6
Reacted AlCl$_3$,	9.4	
Hydrocarbons,	14.4	
Losses		1.0
Total		305.9

(a) **Gases.**—The condensable gas at −78° (dry ice) was analyzed by low-temperature Podbielniak distillation and contained 64.7 g. of isobutane, 4.7 g. of pure benzene and only traces (≃0.3 g.) of propane and pentanes. The

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[3] Gustavson, *J. prakt. Chem.*, [2] **34**, 161–177 (1883), [2] **68**, 209–234 (1903); [2] **72**, 57–79 (1905); *Compt. rend.*, **136**, 1065 (1903); **140**, 940 (1905).

TABLE I

UPPER LAYER

(Octane + Benzene + Aluminum Chloride)

Charge = 241 cc. = 192 g.; d^{20}_4 = 0.796; n^{20}_D = 1.4663

Frac.	B. range at 752 mm.	Vol., cc.	Wt., g.	% of total	Density g./cc. at °C.	n^{20}_D	% Paraffins[a]	Remarks
1	71.0– 80.0	13.0	10.7		0.8198 at 22.5	1.4659	18.5	Index of residual paraffins n^{20}_D 1.3966
2	80.0– 81.5	78.5	64.9		0.8275 at 22.5	1.4711	17.9	n^{20}_D 1.3920; odor of isooctane; boiling at 99°
3	81.5–168.0	27.5	21.0		0.7635 at 22.4	1.4332	Ab. 45.0	n^{20}_D 1.3938; odor of isooctane
4	168.0–169.0	73.0	63.1	34.0	0.8644 at 22.7	1.4916	None	
5	169.0–192.0	less 0.5	≃0.2		....	....	..	
6	192.0–216.0	34.5	30.2		0.8751 at 22.6	1.4949	Less than 2.0	These 2% had n^{20}_D 1.4879 and reacted with nitrating mixture
Bottoms	> 216.0	≃3.0	≃2.5			1.5267	Less than 2.0	
Losses			≃0.0					
Total			192.0					

[a] The paraffins remained after the aromatics were absorbed by shaking (in a volume ratio of 1:1) first with 100% sulfuric acid, second with 7% or 15% free SO_3–H_2SO_4, until the residual hydrocarbon gave no reaction with nitrating mixture.

isobutane was very pure; it had a constant boiling point of −10.2° at 760 mm. pressure and the theoretical molecular weight when determined by Stock's gas balance.

The uncondensable gas (800 cc.) was nitrogen, displaced by isobutane from the reaction flask.

(b) **Upper Layer.**—After washing with water and drying, the upper layer was subjected to a high temperature Podbielniak distillation. The distillation curve is shown on Diagram 1; the properties of the fractions are given in Table I. All fractions were water-white and stable to potassium permanganate solution and therefore free from olefins; all reacted with nitrating mixture and therefore contained aromatic hydrocarbons. The principal products of the reaction are present in fractions 4 and 6, since fractions 1, 2 and 3 contain pure unreacted benzene and isooctane.

From the data of Table I it can be seen that fraction 4 consists of a very pure aromatic hydrocarbon (or mixture of closely boiling isomers), and fraction 6 is also practically free from paraffins.

TABLE II

	Bromide from fraction 4	Bromo-*t*-butylbenzene[4]
Boiling point at 740 mm., °C.	230–231	230
Melting point, °C.	+19	+14
Bromine, %	36.8 (Parr bomb)	37.5
Index of refraction, n^{20}_D	1.5290	..
Density, d^{15}_4	1.2519	1.2572
Appearance	White needles	White needles

Investigation of Fraction 4.—The composition of this fraction corresponds to an alkyl-benzene of the formula $C_{10}H_{14}$. *Anal.* Calcd.: C, 89.48; H, 10.52. Found: C, 89.39, 89.49; H, 10.60, 10.59.

By bromination in the presence of iron powder, it was practically quantitatively converted into a monobromine derivative which proved to be identical with bromo-*t*-butylbenzene described by Schramm[4] as seen from the data of Table II.

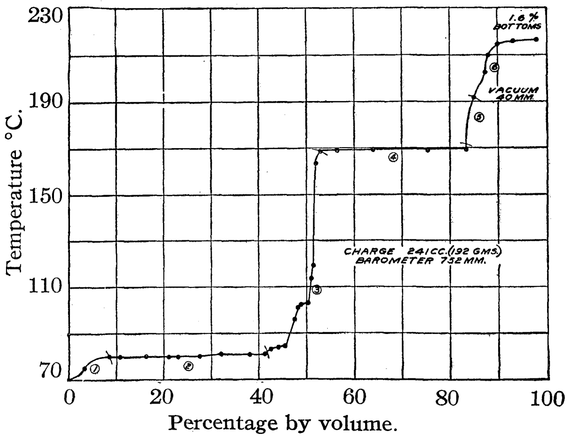

Fig. 1.—High temperature Podbielniak distillation.

For further identification this hydrocarbon was sulfonated and the sulfonic acid, obtained quantitatively, converted into a phenol. The barium salt of the acid (proved later to be *p*-*t*-butylbenzene sulfonic acid) was fractionally crystallized; all fractions were identical proving the homogeneity of our hydrocarbon.

The potassium salt (obtained through double decomposition with potassium sulfate) was melted with potassium hydroxide at 280–350° in a copper dish. The phenol, ob-

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(4) Schramm, *Monatsh.*, 9, 846 (1888).

tained in nearly quantitative yields, proved to be identical with *p*-*t*-butylphenol by comparing the data of Table III.

TABLE III

	Phenol from fraction 4	*p*-*t*-Butylbenzene[5]
Melting point, °C.	98.5 (sharp)	98.5
Sublimation point	About 100°	Around 100°
Appearance	White long silky needles	White long needles
Mixed melting point	No depression	

These results, together with its physical properties as shown in the following table, leave no doubt but that our hydrocarbon is *t*-butylbenzene.

	Hydrocarbon from fraction 4	*t*-Butylbenzene
Boiling point at 760 mm., °C.	169	169
Melting point. °C.	Below −50	
Density, d^{20}_4	0.8665	0.8671
Index of refraction, n^{20}_D	1.4910	1.4925
% C	89.49	89.48
% H	10.59	10.52
Monobromide from	Identical (see Table II)	
Phenol from	Identical (see Table III)	

Investigation of Fraction 6.—On cooling well-developed spears or needles appeared, which when recrystallized from methanol melted at 76°, and on mixing with pure di-*p*-*t*-butylbenzene (1:1) showed no depression and can be therefore identified with it. Its quantity corresponded to ≃40% of the fraction, the remainder being composed in all probability of the *o*- and *m*-isomers.

(c) **Investigation of the Lower Layer.**—This layer represents a deep red liquid which is much more mobile than the lower layer in ethylene polymerization.[6] It contained, besides unreacted aluminum chloride, addition compounds of aluminum chloride with hydrocarbons and hydrogen chloride. Water easily decomposed these compounds into a water-white hydrocarbon layer and an acid solution of aluminum chloride.

The hydrocarbons were fractionated; fractions below 200° (about 60% of the layer) contained only benzene and mono-*t*-butylbenzene. Fractions from 200–300° (E. P.) decolorized permanganate solution rapidly and contained unsaturated hydrocarbons, which in all probability retarded the continued activity of aluminum chloride.

(2) Reaction of 2,2,4-Trimethylpentane with Benzene in the Presence of Zirconium Chloride

This reaction was carried out in a rotating autoclave (volume, 750 cc.), the chemicals being placed in a glass liner, at a temperature of 50° for one and one-half hours and at 75° for two hours, the maximum pressure increasing to 7 kg./sq. cm. The balance of reagents used and the products obtained are given below.

BALANCE OF PRODUCTS

Bomb evacuated to 4 mm. before HCl addition; reaction products collected in same apparatus as with $AlCl_3$.

BEFORE REACTION

		Grams
Benzene (c. p., Na dry)		63.01
2,2,4-Trimethylpentane (purest, n^{20}_D 1.3922)		78.52
$ZrCl_4$		16.73
HCl		≃ 8.00
Total		166.0

AFTER REACTION

Uncondensable gas = 0.0 cc.		0.00
HCl (in NaOH scrubbers)		4.00
Condensable gas at −78°		41.63
Upper layer		82.50
Lower layer	hydrocarbon part and HCl	21.28
	$ZrCl_4$	16.73
Total		166.0

The liquefied gas contained 40.4 g. of isobutane and 1.2 g. of benzene. The isobutane was absolutely pure.

The water-white upper layer was fractionated with a high temperature Podbielniak column, the results obtained being given in Table IV.

There was obtained, just as in the case of aluminum chloride, mono-*t*-butylbenzene and di-*t*-butylbenzenes (only the para compound was isolated in the pure state), and some unreacted benzene and octane.

TABLE IV

Charge = 89 cc. = 72.5 g.

Frac.	B. range, °C., at 750 mm.	Vol., cc.	Wt., g.	n^{20}_D	d^{20}_4	% Aromatics	Remarks
1	79– 84	27.5	23.4	1.4790	0.8495	86, balance is octane	Benzene and 14% octane (n^{20}_D 1.3945)
2	84–169	9.0	7.7	1.4790	0.8526	≃90	
3	169–170	28.5	24.7	1.4930	0.8673	100	Pure *t*-butylbenzene
4	170–224	11.0	9.6	1.4944	0.8735		Some di-*p*-*t*-butylbenzene
5	224–256	5.5	4.9	1.5025	....		About 50% of fraction-pure di-*p*-*t*-butylbenzene (m. p. 76°)
Bottoms	>256	2.0	1.7	....	....		
Losses			0.5				
Total			72.5				

All fractions were stable to permanganate solution.

The lower layer is very mobile, dark brown in color and very similar to the aluminum chloride layer. Dilute cold

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(5) Senkowski, *Ber.*, **23**, 2417 (1890).

(6) V. N. Ipatieff and A. V. Grosse unpublished results.

hydrochloric acid decomposes it rapidly, giving liquid hydrocarbons and a zirconium oxychloride solution. These hydrocarbons consisted of benzene, *t*-butylbenzene and some partly unsaturated, in all probability polynuclear, hydrocarbons.

(3) Reaction of 2,2,4-Trimethylpentane with Benzene in the Presence of (a) Magnesium Chloride ($MgCl_2$) and (b) Boron Fluoride (BF_3)

There was no reaction in the presence of magnesium chloride and hydrogen chloride at 200° and a pressure of 20 atmospheres during twenty hours. Boron fluoride, promoted by nickel and water, effected no reaction at 55° during four hours in a nickel-lined autoclave.

Summary

A new reaction between paraffins and aromatic hydrocarbons in the presence of catalysts has been described. It consists in the formation of a lower molecular weight paraffin and an alkylated aromatic hydrocarbon, for instance, 2,2,4-trimethylpentane reacts with benzene, giving isobutane and mono- and di-*t*-butylbenzenes.

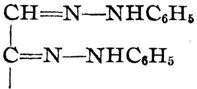
RIVERSIDE, ILL. RECEIVED AUGUST 19, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, COLUMBIA UNIVERSITY]

The Constitution of Osazones[1]

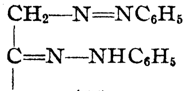
BY LEWIS L. ENGEL[2]

The first suggestion that the Fischer formula for the osazones[3] does not give an adequate explanation of their behavior was made by Zerner and Waltuch,[4] who observed a small but unmistakable mutarotation of the phenylosazones of *l*-arabinose and *l*-xylose in alcoholic pyridine solution. Later, Levene and LaForge[5] confirmed these findings and extended them to the phenylosazones of *d*-glucose, *d*-altrose, *d*-galactose and *d*-gulose. The first observation of the mutarotation of an osazone formed from a secondary hydrazine was made by Votoček and Valentin,[6] who reported that the methylphenylosazone of fructose shows a large mutarotation in methyl alcoholic solution. As an explanation for mutarotation, Zerner and Waltuch suggested that the classical osazone structure (I) was present in equilibrium with the isomeric azo-form (II). The finding of Votoček and Valentin, however, seems to exclude this explanation, since fructose methylphenylosazone possesses no hydrogen capable of migrating in this manner. The present author has been unable to confirm this result of Votoček and Valentin, but has found other evidence which conflicts with the hypothesis of Zerner and Waltuch.



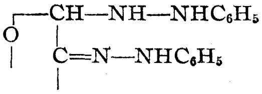
$$\begin{array}{l}\mathrm{CH{=}N{-}NHC_6H_5}\\ |\\ \mathrm{C{=}N{-}NHC_6H_5}\\ |\end{array}$$

(I)



$$\begin{array}{l}\mathrm{CH_2{-}N{=}NC_6H_5}\\ |\\ \mathrm{C{=}N{-}NHC_6H_5}\\ |\end{array}$$

(II)



$$\begin{array}{ll}\ulcorner & \mathrm{CH{-}NH{-}NHC_6H_5}\\ \mathrm{O} & |\\ | & \mathrm{C{=}N{-}NHC_6H_5}\\ & |\end{array}$$

(III)

Haworth[7] has suggested that if one of the phenylhydrazine groups in an osazone be assumed to exist as a phenylhydrazino group attached to a cyclic sugar (III), mutarotation could be explained as being due to a shift from the α-form to the β-form. It is also possible that the mutarotation of osazones may be due to partial hydrolysis in solution. In order to test these views it is necessary to ascertain, first, whether the osazones are cyclic compounds; second, whether the nature of the attachment of the sugar to phenylhydrazine is such that hydrolysis will take place under the conditions of the mutarotation experiments; and third, whether the mutarotation is affected by factors which should affect the equilibrium.

It was hoped that the question of the ring could be settled by a study of the methylation products of glucose phenylosazone, but unexpected difficulties were encountered. Methylation by a number of methods was attempted but in no case was it possible to obtain homogeneous crystalline products. Methylation in dioxane with dimethyl sulfate and alkali yielded sirupy products with methoxyl contents ranging from 16.3

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[1] This work was aided by a grant from The Chemical Foundation, Inc.

[2] William J. Gies Fellow, 1933–34; Columbia University Fellow, 1934–35. This report is from a thesis submitted by L. L. Engel in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

[3] Fischer, *Ber.*, **20**, 821 (1887).

[4] Zerner and Waltuch, *Monatsh.*, **35**, 1025 (1914).

[5] Levene and LaForge, *J. Biol. Chem.*, **20**, 429 (1915).

[6] Votoček and Valentin, *Coll. Czech. Chem. Comm.*, **3**, 432 (1931).

[7] Haworth, "Constitution of Sugars," Edward Arnold, London, 1929, p. 7.

to 22.6% and crystalline mixtures having methoxyl contents ranging from 14.1 to 20.7%. Basic products, comprising N-methylated osazones and methylphenylhydrazine, were always formed. Methylation of partially methylated material with methyl iodide and silver oxide or carbonate led to slight increase in methoxyl content, but considerable decomposition occurred. Neither methylation of partially acetylated glucose phenylosazone with dimethyl sulfate and alkali, nor treatment of a partially methylated sirup with sodium–potassium alloy followed by treatment with dimethyl sulfate, led to satisfactory results. Methylation of fructose methylphenylosazone by the liquid ammonia technique of Muskat[8] led to cleavage of the N–N linkages instead of methylation of the hydroxyl groups. The only crystalline product isolated was trimethylphenylammonium iodide. The question of ring structure could thus not be solved by methylation experiments. However, light has recently been thrown on it by the observation of Bergmann and Grafe[9] that the compound IV displays a large and rapid mutarotation in pyridine, the rotation changing from +226 to +311° in three hours. The possibility that this change may be due to deacetylation is excluded by the fact that the deacetylated compound has a lower initial rotation and mutarotates downward.

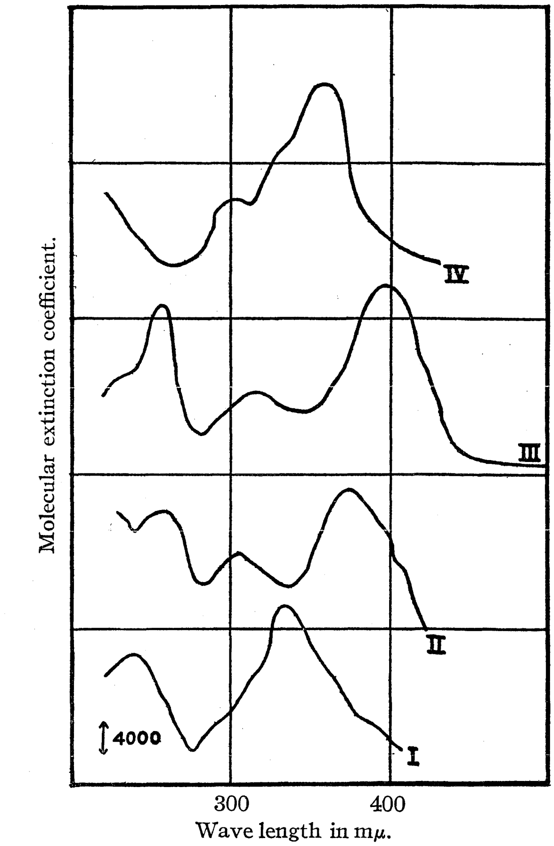
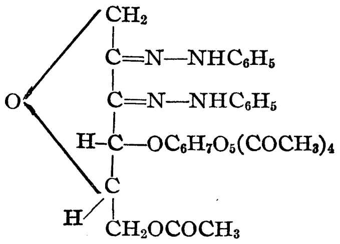


Fig. 1.—Absorption spectra of osazones. Curve I. Fructose methylphenylosazone. Curve II. Glucose phenylmethylphenylosazone. Curve III. 3, 4, 6-Trimethylglucose phenylosazone. Curve IV. Dimethylglyoxal phenylosazone. Each curve is displaced vertically by 20,000 units to avoid confusion of lines.



(IV)

Attention was turned to the study of the absorption spectra of osazones and their derivatives. The earliest measurements on this class of compounds were made by Baly, Tuck, Marsden and Gazdar.[10] The results (Table I, Fig. 1) obtained by the present author, which are in fairly good agreement with some of the findings of these investigators, indicate that the absorption spectra of the osazones studied can be divided very sharply into two classes: one class consisting of the sugar osazones and their derivatives, and the other, the osazones of simple α-keto-aldehydes and α-diketones. The compounds of the second class studied in the present investigation were the phenylosa-

TABLE I

ABSORPTION OF PHENYLOSAZONES

Compound	Maxima			Minima		
Glycerose phenylosazone	250	318	381		281	335
Lactose phenylosazone	253	310	392		281	342
Lactose phenylosazone anhydride	256	310	398		282	342
Galactose phenylosazone	254	312	390		280	344
Monoacetonegalactose phenylosazone	256	313	390		280	348
3,4,6-Trimethylglucose phenylosazone	256	315	396		281	344
Tetraacetylglucose phenylosazone	256	312	392		280	327
Tetrabenzoylglucose phenylosazone			388			322
Xylose phenylosazone	256	315	390		282	332
Methylglyoxal phenylosazone		300	361		273	310
Dimethylglyoxal phenylosazone		302	357		266	310
Glucose phenylmethylphenylosazone	258	305	374	239	282	336
Methylated glucose phenylosazone	258	304	376	240	282	340
Fructose methylphenylosazone	238	335			276	
Tetraacetylfructose methylphenylosazone	244	337			277	

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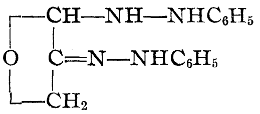
[8] Muskat, THIS JOURNAL, **56**, 693, 2449 (1934). The author wishes to express thanks to Dr. Muskat for his kindness in making available and demonstrating the use of his apparatus.

[9] Bergmann and Grafe, *J. Biol. Chem.*, **110**, 173 (1935).

[10] Baly, Tuck, Marsden and Gazdar, *J. Chem. Soc.*, 1572 (1907).

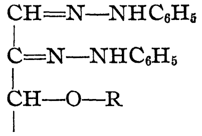
zones of methylglyoxal and dimethylglyoxal (diacetyl), which have almost identical absorption spectra. Sugar osazones show among themselves an equally marked resemblance in absorption characteristics. In the case of tetrabenzoylglucose phenylosazone the four benzoyl groups are undoubtedly responsible for the intense absorption in the region of shorter wave length.

The substantial coincidence of the absorption spectra of all the sugar osazones, including glycerose phenylosazone, indicates their structural similarity. In the cyclic formula of Haworth the conjugated system $—N=\overset{|}{C}—\overset{|}{C}=N—$, presumably strongly chromophoric, is replaced by the grouping $—\overset{|}{N}—\overset{|}{C}—\overset{|}{C}=\overset{|}{N}$, which would be expected to absorb far less strongly. Application of the Haworth formula to glycerosazone would lead to the inherently improbable structure



This four-membered ring cannot exist in 3,4,6-trimethylglucose phenylosazone, the absorption characteristics of which coincide with those of the phenylosazones of glucose and glycerose.

The grouping responsible for the specific absorption of the sugar osazones may therefore be represented by V, in which R may be hydrogen,

(V) 

$$\begin{array}{l} CH=N—NHC_6H_5 \\ | \\ C=N—NHC_6H_5 \\ | \\ CH—O—R \\ | \end{array}$$

alkyl or acyl. The difference between the absorption spectra of sugar osazones on the one hand, and the osazones of simple α-diketones on the other, is ascribable to the presence on carbon atom 3 of the oxygen atom which functions as an auxochrome.

It is interesting to note the coincidence of the absorption spectrum of one of the crystalline methylation products of glucose phenylosazone (m.p. 130° (corr.), OCH_3, 20.4%) with that of the mixed osazone, glucose phenylmethylphenylosazone (Fig. 1). The absorption characteristics of these compounds differ quite markedly from those of fructose methylphenylosazone (Fig. 1). Acetylation of the latter compound leads to a tetraacetate, the absorption spectrum of which is closely similar to that of the parent compound.

Evidence that the attachment of the hydrazine group in osazones is of such a nature that it may be split off under the conditions which obtain during mutarotation has been accumulating for some time. In an extended study, Votoček and Vondracek[11] found that the phenylhydrazine group in the sugar phenylhydrazones and osazones readily could be replaced by another hydrazine group. In the case of the osazones, they found that either one or both of the hydrazine groups could be replaced by the entering hydrazine. In the case of the condensation products of glucose with phenylhydrazine and methylphenylhydrazine, they prepared both isomeric mixed osazones in pure form. They carried out the reactions at water-bath temperature; the present author has found that certain of them can be conducted at room temperature. If fructose methylphenylosazone is allowed to stand in methyl alcoholic solution for two weeks with two moles of *p*-nitrophenylhydrazine, the mixed osazone, glucose *p*-nitrophenyl-methylphenylosazone crystallizes out. Similarly, fructose methylphenylosazone in contact with phenylhydrazine yields glucose phenylmethylphenylosazone.

This type of reaction is characteristic of the condensation products of carbonyl compounds with nitrogenous bases in general. Phenylhydrazones can be reversibly converted to oximes,[12,13,14] semicarbazones[15] and azines.[16]

The carbohydrate residue in an osazone or hydrazone may similarly be replaced by another carbonyl compound, as in the most commonly employed method of preparing a free sugar from a hydrazone, or an osone from an osazone.

All of these reactions suggest that hydrolysis may occur in solution even when the compound is not subjected to the influence of a competing hydrazine or carbonyl compound.

If mutarotation is partly or wholly ascribable to the establishment of an equilibrium between the osazone and its hydrolysis products, it should be possible to influence its course by the addition of one of the components of the system. Experimentally, it is easiest to measure the effect of phenylhydrazine since it is optically inactive and readily obtainable in the pure state. The rota-

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[11] Votoček and Vondracek, *Ber.*, **37**, 3848 (1904).

[12] Just, *ibid.*, **19**, 1205 (1886).

[13] Pechmann, *ibid.*, **20**, 2539 (1887).

[14] Fulda, *Monatsh.*, **23**, 907 (1902).

[15] Knöpfer, *ibid.*, **31**, 87 (1910).

[16] Knöpfer, *ibid.*, **30**, 29 (1909).

tion of 3,4,6-trimethylglucose phenylosazone in alcoholic pyridine was found to change from −48.8 to +61.5° in one hundred and eight hours. In the presence of phenylhydrazine (16.3 moles of phenylhydrazine per mole of osazone) the rotation changed from −50.6 to +30.0° in one hundred and fifty-five hours (Fig. 2). The addition of phenylhydrazine, therefore, has the effect which it would be expected to have if it were one of the components of a system approaching equilibrium.

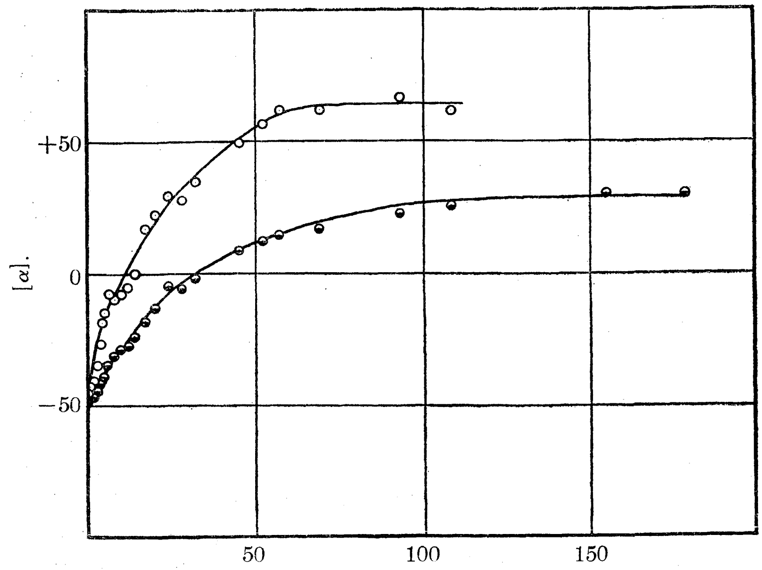

Fig. 2.—Mutarotation of 3,4,6-trimethylglucose phenylosazone. ○—3,4,6-Trimethylglucose phenylosazone in 1 : 1 95% alcohol-pyridine. ◐—3,4,6-Trimethylglucose phenylosazone and phenylhydrazine in 1 : 1 95% alcohol-pyridine (16.3 moles of phenylhydrazine per mole of osazone).

Experimental

Methylation of Glucose Phenylosazone.—Of many experiments, only one will be described in detail. To a suspension of 50 g. of the osazone in 250 cc. of dioxane were added, in twenty portions of each, 500 cc. of methyl sulfate and 1500 cc. of 30% sodium hydroxide at 50–55°. Stirring was continuous throughout the addition, which occupied five hours. The temperature was then raised to 65° for half an hour. The dioxane layer, in which all of the methylated osazone had dissolved, was evaporated to dryness under reduced pressure; the residue dissolved in 50% alcohol was held at 0° for a week. The solid which separated was fractionally crystallized from mixtures of ethyl acetate and petroleum ether and from aqueous alcohol of various concentrations. Four crystalline but apparently inhomogeneous, fractions were obtained:

(1) M. p. 102–105° (corr.); CH_3O, 14.24%
(2) M. p. 110° (corr.); CH_8O, 15.3%
(3) M. p. 106–108° (corr.); CH_3O, 18.66%
(4) M. p. 110–116° (corr.); CH_3O, 20.67%

In another similar experiment, the crude product was dissolved in ether and shaken repeatedly with 0.1 *N* hydrochloric acid. The neutral fraction, which formed the principal product, contained 16.3% of methoxyl. The basic fraction was separated into two fractions by shaking an ethereal solution with 5% acetic acid. That extracted by acetic acid consisted mainly of methylphenylhydrazine; the *p*-nitrobenzal derivative had a m. p. 135.5° (corr.), unaltered on admixture of an authentic sample. The fraction soluble in hydrochloric acid but insoluble in acetic acid was a yellow sirup which possessed an absorption spectrum identical with that of fructose methylphenylosazone. An authentic sample of the latter was also found to be soluble in 0.1 *N* hydrochloric acid.

Replacement of Methylphenylhydrazine by Phenylhydrazine in Fructose Methylphenylosazone.—Two-tenth gram (0.52 millimole) of fructose methylphenylosazone and 0.2 cc. (1.95 millimoles) of phenylhydrazine were dissolved in methyl alcohol and the solution made up to 25 cc. After standing at room temperature for a week, pale yellow needles separated out. After recrystallization from 50% alcohol they melted at 192–193° (corr.). Glucose methylphenyl-phenylosazone is reported to melt at 192°.[11]

Anal. Calcd. for $C_{19}H_{24}N_4O_4$: C, 61.3; H, 6.45. Found: C, 60.82; H, 6.50.

Replacement of Methylphenylhydrazine by *p*-Nitrophenylhydrazine in Fructose Methylphenylosazone.—A mixture of 0.5 g. (1.3 millimoles) of fructose methylphenylosazone and 0.4 g. (2.6 millimoles) of *p*-nitrophenylhydrazine was dissolved in methyl alcohol and diluted to 25 cc. After standing for two weeks, the orange needles were filtered off, washed with methyl alcohol and recrystallized from dilute ethyl alcohol. The product was glucose methylphenyl-*p*-nitrophenylosazone, m. p. 223.5–224.5° (corr.).

Anal. Calcd. for $C_{19}H_{25}N_5O_6$: N, 16.79. Found: N, 16.86.

Monoacetone Galactose Phenylosazone.—To a suspension of 5 g. of galactose phenylosazone in 200 cc. of acetone 10 g. of phosphorus pentoxide[17] was added in small portions with stirring over a period of one hour, keeping the temperature at 0°. Stirring was continued for two hours more and the solution was filtered and washed with saturated potassium carbonate. The acetone was evaporated under reduced pressure and the residue taken up in warm ethyl acetate. The product crystallized on the addition of ligroin to the dried solution. After recrystallization, once from 95% alcohol and once from ether and petroleum ether, monoacetone galactose phenylosazone was obtained as yellow needles, m. p. 183.5–184.5° (corr.).

Anal. Calcd. for $C_{21}H_{26}N_4O_4$: N, 14.08. Found: N, 14.14.

3,4,6-Trimethylglucose Phenylosazone Hydrate.—Trimethyl inulin was prepared by the method of Haworth

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(17) Smith and Lindberg, *Ber.*, **64**, 505 (1931).

and Streight.[18] Acid hydrolysis[19] yielded 3,4,6-trimethylfructofuranose which was converted to the osazone.[20] For the mutarotation and absorption spectrum measurements, the osazone was recrystallized three times from petroleum ether containing a trace of ether and three times from dilute alcohol; m. p. 81–82° (corr.).

Glycerose Phenylosazone.—To a mixture of 264 g. of diacetin, 149.4 g. of $Na_2Cr_2O_7 \cdot 2H_2O$ and 450 cc. of glacial acetic acid, a solution of 227.4 g. of sulfuric acid in 375 cc. of acetic acid was added with stirring over a period of eight hours at 20–25°. Then 55.5 g. of hydrated sodium acetate was added and the solution stirred for two hours. The precipitate was filtered off and washed with acetic acid. The filtrate and washings were evaporated to dryness under reduced pressure, the residue was taken up in ether, washed thoroughly with saturated sodium chloride, dried over sodium sulfate and distilled under reduced pressure. The fraction boiling at 130–150° (8 mm.) was redistilled, yielding 111.3 g. (b. p. 134–136° at 8 mm.) of a liquid.

That dihydroxyacetone diacetate was the principal constituent was demonstrated by the preparation of the 2,4-dinitrophenylosazone of monoacetylglyceraldehyde by warming 0.5 g. with 0.6 g. of 2,4-dinitrophenylhydrazine in 25 cc. of hot glacial acetic acid on the steam-bath for a half hour. The product, crystallized once from absolute alcohol and once from glacial acetic acid, formed yellow needles, m. p. 196–197° (corr.).

Anal. Calcd. for $C_{17}H_{14}N_8O_{10}$: N, 22.86. Found: N, 22.93.

Three and one-half grams of crude dihydroxyacetone diacetate was dissolved in 15 cc. of water and 5 cc. of 28% ammonia by warming on the steam-bath. The solution was cooled, treated with 6 cc. of glacial acetic acid and 6.5 g. of phenylhydrazine, and then warmed on the steam-bath for fifteen minutes, after which it was diluted with water and chilled. The product was filtered off and recrystallized once from 50% alcohol and once from benzene; m. p. 130° (corr.).

Tetrabenzoylglucose Phenylosazone.—This compound was prepared by the method of Fischer and Freudenberg[21] and was obtained as an amorphous solid, m. p. 100–110°, which decomposed at 125° (corr.).

Anal. Calcd. for $C_{46}H_{38}N_4O_8$: N, 7.24. Found: N, 7.20. $[\alpha]^{24}_D$ $-16.5°$, for $c = 0.606$ in *s*-tetrachloroethane.

$[\alpha]^{24}_D$ $+20.7°$, for $c = 0.435$ in a mixture of 1.5 parts 95% ethyl alcohol and 1 part pyridine. After forty-eight hours this value fell to +17.2°. Fischer and Freudenberg found $[\alpha]^{20}$ $-12.16°$ in *s*-tetrachloroethane (Welsbach light).

Acetylation of Glucose Phenylosazone.—Two grams of glucose phenylosazone was suspended in a mixture of 8 cc. of acetic anhydride and 20 cc. of pyridine. On heating to 50° for one hour the osazone dissolved, giving a dark orange solution which was poured into ice-water and allowed to stand overnight. The brown gum crystallized partly after standing for several weeks. It was washed repeatedly with 50% alcohol on a centrifugal filter until microscopic examination showed it to consist entirely of yellow needles. The product was dried *in vacuo;* m. p. 102–104° (corr.); $[\alpha]^{25}_D$ $-58.5°$, for $c = 0.431$ in 95% alcohol.

Anal. Calcd. for tetraacetylglucose phenylosazone, $C_{26}H_{30}N_4O_8$: C, 59.25; H, 5.86; N, 10.64. Found: C, 59.33; H, 5.60; N, 10.73.

Acetylation of Fructose Methylphenylosazone.—Fructose methylphenylosazone was acetylated as in the preceding description. The product, after one recrystallization from 95% alcohol, was obtained in orange-yellow needles, m. p. 126–127° (corr.); $[\alpha]^{27}_D$ $-184.8°$, for $c = 0.403$ in 95% alcohol.

Anal. Calcd. for tetraacetylfructose methylphenylosazone, $C_{28}H_{34}N_4O_8$: C, 60.62; H, 6.18; N, 10.11. Found: C, 60.62; H, 7.24; N, 10.09.

The author wishes to express his gratitude to Professor Hans T. Clarke for the guidance and encouragement he has given throughout the course of this research.

Conclusions

1. The spectral absorption characteristics of the sugar osazones are practically identical and in concord with the structure originally suggested by Fischer.

2. The bis-phenylhydrazones of methylglyoxal and dimethylglyoxal have practically coincident absorption curves; the differences from those of the sugar osazones are ascribable to the presence in the latter of an oxygen atom on the neighboring carbon atom.

3. Osazones are readily susceptible to hydrolysis under mild conditions; the mutarotation of sugar osazones appears to depend upon the establishment of an equilibrium between them and their hydrolysis products.

NEW YORK, N. Y. RECEIVED JULY 27, 1935

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[18] Haworth and Streight, *Helv. Chim. Acta*, **15**, 609 (1932).

[19] Haworth, Hirst and Percival, *J. Chem. Soc.*, 2384 (1932).

[20] Haworth and Learner, *ibid.*, 619 (1928).

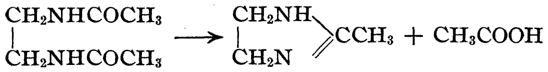
[21] Fischer and Freudenberg, *Ber.*, **46**, 1116 (1913).

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

Some Alkyl-glyoxalidines[1]

BY HENRY C. CHITWOOD AND E. EMMET REID

In 1875 Ladenburg[2] distilled *o*-phenylenediamine with acetic acid and obtained ethenylphenylenediamine. Hofmann[3] distilled diacetylethylenediamine in a current of hydrogen chloride and got μ-methyl-glyoxalidine.



$$\begin{array}{l} CH_2NHCOCH_3 \\ | \\ CH_2NHCOCH_3 \end{array} \longrightarrow \begin{array}{l} CH_2NH \\ | \\ CH_2N \end{array} \!\!> CCH_3 + CH_3COOH$$

Ladenburg[4] prepared the same compound by distilling a mixture of ethylenediamine hydrochloride with two moles of sodium acetate. The ethyl and propyl derivatives have also been made.[3,4,5]

The present investigation was undertaken to improve the method of preparation, to prepare some of the higher members of the series, and to obtain more knowledge of the physical and pharmacological properties of the alkyl-glyoxalidines.

We were unable to obtain glyoxalidine itself from diformylethylenediamine but have greatly improved the method of preparing its methyl derivative, obtaining a 68% yield as compared with 11 and 8% by following Hofmann and Ladenburg. It is a curious fact that the above reaction can be carried out by heating the diacetylethylenediamine alone or with such diverse reagents as hydrogen chloride, caustic soda, magnesia, magnesium, zinc and sodium. As acetic acid is one of the products of the reaction, the use of acid-binding materials seemed desirable. Such materials did improve the yields, magnesium giving the best.

Methyl-glyoxalidine is a strong base, melting at 105° and boiling at 198–200°. It is very soluble in water, alcohol and chloroform, less so in benzene, carbon tetrachloride and petroleum ether. It is readily brominated in cold chloroform solution, forming the hydrobromide of the monobrominated base. The bromine is probably attached to a nitrogen, since it is readily eliminated by boiling with water with the regeneration of the original base. It was hoped that it could be split off as hydrobromic acid leaving methylglyoxaline but this could not be effected. Methylglyoxalidine when heated with an aqueous alkali is hydrolyzed back to ethylenediamine. Attempts to hydrogenate or dehydrogenate it were unsuccessful. It readily forms complexes with salts of silver, copper and cobalt. When it is added to a solution of a cupric salt, copper hydroxide is precipitated and then redissolved, giving a dark blue solution. A solution of the base dissolves cobalt carbonate. It dissolves freshly precipitated silver chloride but the solution is not stable.

The alkyl-glyoxalidines, methyl to undecyl, have been prepared by heating the corresponding diacylethylenediamines with sodium or magnesium, the lower ones distilling out while the higher ones were extracted from the mass after heating. The octyl, decyl and undecyl were prepared in a molecular still. The bases were taken up in hydrochloric acid, liberated with alkali, extracted with benzene, dried over solid caustic potash and distilled *in vacuo*. The lower members of the series are hygroscopic and very soluble in water, giving strongly basic solutions. This solubility decreases with the lengthening of the alkyl side chain; the undecyl is practically insoluble in water. All dissolve in hydrochloric acid to give well-defined salts. The hydrochlorides of the three highest give soapy solutions in water. All are very soluble in alcohol and moderately so in benzene but only slightly soluble in ether or petroleum ether. The lower ones are best purified by distillation, the higher ones by recrystallization from benzene with the addition of petroleum ether. They are best identified by their picrates, which are readily formed by adding a saturated aqueous picric acid solution to solutions of the bases or of their salts. Their gold or platinum double salts are formed when the hydrochlorides of the bases are added to solutions of the metal chlorides. The gold salts were analyzed by simple ignition as recommended by Hofmann and by Klingenstein.

The necessary diacyl derivatives of ethylenediamine were prepared by heating the acids or their ethyl esters with ethylenediamine. Their solubility in water decreases rapidly as we go up

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(1) From the Ph.D. dissertation of H. C. Chitwood, June, 1934.

(2) Ladenburg, *Ber.*, **8**, 677 (1875).

(3) Hofmann, *ibid.*, **21**, 2332 (1888).

(4) Ladenburg, *ibid.*, **27**, 2952 (1894).

(5) Klingenstein, *ibid.*, **28**, 1173 (1895).

the series, the diheptoyl and higher being quite insoluble. With increasing size of the alkyls they become less soluble in alcohol and more so in ethyl acetate. They are best recrystallized from mixtures of these three solvents.

The melting points of the bases, their picrates and the diacylethylenediamines from which they were prepared are given in Table I.

TABLE I

MELTING POINTS OF THE DIACYL DERIVATIVES OF ETHYLENEDIAMINE, THE ALKYLGLYOXALIDINES AND THEIR PICRATES. ANALYSES OF GOLD DOUBLE SALTS

R	Melting points, °C. $(RCONHCH_2)_2$	$RC_3H_5N_2$	Picrate	Gold salt % of gold Calcd.	Found
Methyl	175.6	105.0	205	46.49	46.55
Ethyl	191.4	38.1	137.1	45.01	45.15
Propyl	192.0	35.3	129.0	43.62	43.60
Butyl	184.2	41.0	125.8	42.30	42.38
Amyl	178.5	33.8	128.4	41.07	41.04
Hexyl	173.0	46.2	...	39.90	39.95
Heptyl	171.0	60.0	104.8	38.80	38.66
Octyl	167.0	52.1	...	37.76	38.65
Nonyl	164.6	71.4	122	36.77	36.76
Decyl	160.8	79.5	82.0	35.84	35.83
Undecyl	158.8	79.8	61.5	34.95	35.08

The picrates of the hexyl and octyl derivatives could not be made to crystallize. The melting points of the diamine derivatives show slight alteration from 5 to 11 while those of the alkyl-glyoxalidines alternate from 2 to 9 but show a reversal of the alternation at the hexyl.

Pharmacological. — Methyl-glyoxalidine, known also as lysidine, has been considered as a solvent for uric acid.[4] In friendly coöperation, the pharmacological properties of it and of the next four members of the series have been studied by Dr. David I. Macht who reports as follows.

Aqueous solutions of the compounds were tested on seedlings of *Lupinus albus*, goldfish, tadpoles, mice, rabbits and cats. Contrary to the usual pharmacological experience, the toxicity of the five compounds decreased with the increase in length of the alkyl radical. Goldfish and tadpoles survived in solutions of 1:5000 but succumbed in the order named when placed in solutions of 1:1000. Ten milligrams of the methyl compound, administered intraperitoneally, killed mice, but the higher members of the series were not so toxic. Phytotoxic indices also showed that the latter were less poisonous for plants. Half a gram per kilo of any one of these compounds, given by stomach, was not toxic for rabbits and did not impair their kidney function. The methyl compound, however, increased the acidity of the urine. Ten milligrams injected intravenously in cats under ether, produced a transient fall in blood pressure but little effect on the respiration.

Experimental

The best method of preparing methyl-glyoxalidine so far found is to heat 30 g. of diacetylethylenediamine with 5 g. of magnesium powder in a flask in a solder-bath at 270° for seventy-five minutes. The hydrogen that is evolved helps carry over the product. Some acetone was noticed. Solid potassium hydroxide is added to the distillate with boiling benzene. The reaction flask is rinsed with hot benzene. The benzene solutions are united and dried over solid caustic potash, decolorized with active charcoal, filtered and evaporated to 30 cc. On cooling the methyl-glyoxalidine crystallizes out. A second crop of crystals may be obtained by concentrating the mother liquor and adding petroleum ether; yield 12.7 g. or 68%.

In comparative experiments the yields obtained were:

Ladenburg's method	8.0%
Hofmann's method	11.4
Simple dry distillation	24.6
Distillation with sodium hydroxide	22.3
Heating with sodium	39.3
Heating with zinc	43.4
Heating with magnesium	68.0
Heating with magnesium oxide	44.0
Ethylenediamine and acetic acid	19.1
Monoacetylethylenediamine hydrochloride with sodium hydroxide	26.2

Various other methods were tried, such as distilling diacetylethylenediamine under reduced pressure or dropping it in small portions into a heated flask, but without any improvement.

The higher homologs were all prepared from the diacylethylenediamines by distilling with sodium or magnesium, or by refluxing the diamides with the metal and extracting the bases with benzene. In most cases the product was dissolved in benzene, decolorized by activated carbon, dried over potassium hydroxide and purified by vacuum distillation. When very small amounts of materials were used, as in making the octyl, decyl and undecyl glyoxalidines, the reactions were effected in a molecular still. The bases were extracted from the distillate by dilute hydrochloric acid, precipitated by addition of alkali, extracted with hot benzene and redistilled. Table II gives a summary of experiments on the production of the glyoxalidine homologs.

The diacyl derivatives of ethylenediamine as intermediates in the preparation of the bases can be made by heating ethylenediamine with the ethyl esters, although the lower members are conveniently obtained on refluxing ethylenediamine with the free acids. The solubility in water decreases abruptly in going up the series, the diheptoyl and higher derivatives being quite insoluble. They are increasingly soluble in ethyl acetate and decreasingly soluble in alcohol, and may be recrystallized from solutions in appropriate mixtures of ethyl acetate and alcohol, on cooling the solutions and on addition of one or the other of these liquids. Diformylethylenediamine closely resembles granular sugar in appearance. The diacetyl derivative crystallizes in beautiful large white prisms, while the others, due to their abrupt change in solubility on cooling, usually come down as fine light crystals.

TABLE II

PREPARATION OF ALKYL-GLYOXALIDINES

	Ethylenediamine deriv.	Wt. used	Metal	Wt.	T., °C.	Press., mm.	Time, hours	Wt. of product, g.	Yield
I	Diacetyl	30	Mg	5	270	at.	1.25	12.7	68
II	Dipropionyl	20	Mg	1.5	300	at.	5	5.2	46
III	Dibutyryl	20	Mg	1.2	330	at.	1.25	5.5	49
IV	Divaleryl	10	Mg	0.5	290	125	2.5	1.5	27
V	Dicaproyl	4	Mg	.2	190	75	1.75	0.7	34
VI	Diheptoyl	12	Mg	.5	300	at.	7	.1	1.7
VII	Dicaprylyl	1.7	Na	.1	270	at.	1	.4	47
VIII	Dipelargonyl	0.7	Na	.2	250	2	..	.08	21
IX	Dicapryl	5.5	Mg	.5	300	at.	6	.015	5.6
X	Diundecylyl	0.9	Na	..	300	10	..	.10	22
XI	Dilauroyl	1.6	Na	..	300	2	0.5	.20	24

Reactions of Methyl-glyoxalidine.—To 5 g. of the base dissolved in chloroform was added a solution of bromine in the same solvent, with shaking and cooling, until the color remained. The heavy yellow precipitate was filtered off, washed with chloroform and dried in a vacuum desiccator. The yield was 11.9 g. or 82%. Analysis gave 65.23% of bromine; calculated for $C_4H_7N_2Br \cdot HBr$, 65.53. The product appears to be the hydrobromide of the brominated base.

Summary

The method of preparing methyl-glyoxalidine has been improved. Its homologs with normal alkyls have been made up to the undecyl. Their pharmacological properties have been determined.

BALTIMORE, MARYLAND RECEIVED SEPTEMBER 30, 1935

[CONTRIBUTION FROM THE HALL LABORATORY OF CHEMISTRY, WESLEYAN UNIVERSITY]

The Omega-Benzyl Derivatives of Acetophenone and their Reduction Products

BY G. ALBERT HILL AND A. J. COFRANCESCO

Although Haller and Bauer were not the first to prepare omega benzylated acetophenones, no earlier investigator produced these substances by the use of sodamide.[1,2] They did not, however, make tribenzylacetophenone. From our experience[3] with omega benzylated pinacolones, it was believed that tribenzylacetophenone could be synthesized by the sodamide method. As a consequence, it was decided that the preparation of the series of omega, mono-, di- and tri-benzyl acetophenones should be undertaken. Furthermore, it was decided to parallel our earlier investigation of the benzylpinacolone derivatives and to prepare, in addition to the ketones, their oximes, the corresponding carbinols and their phenylurethans, and also the hydrocarbons resulting from the replacement of each of the ketone oxygen atoms by two atoms of hydrogen.

Some trouble was experienced because the solvents employed in the ketone syntheses, ether, benzene, and toluene, seemed to form additive compounds with the first products of the reactions, the sodium derivatives of acetophenone, of monobenzylacetophenone, and of dibenzylacetophenone, respectively. This effect increased the viscosity of the systems to an extraordinary degree, making thorough mixing and temperature control difficult. These factors markedly affect the success of a given synthesis and may lead to the decomposition of the desired product when that has been formed.

Monobenzylacetophenone was prepared from sodamide, acetophenone, and benzyl chloride, in toluene, since the above-mentioned difficulties were minimized in this medium. Though odorless at first, the ketone developed fragrance on standing. This was probably caused by oxidation and splitting, an effect which is known to occur with dibenzyl ketone.[4] No attempt was made to isolate or to identify the odorous substances. With hydroxylamine, the ketone yielded a crystalline oxime.[5]

The secondary alcohol derived from monobenzylacetophenone had already been prepared

(1) Haller and Bauer, *Ann. chim.*, [8] **28**, 398 (1931).

(2) Haller and Bauer, *Bull. soc. chim.*, **31**, 1077 (1922).

(3) Hill and Bruce, THIS JOURNAL, **52**, 347 (1930).

(4) Fortey, *J. Chem. Soc.*, **75**, 871 (1899).

(5) Perkin and Stenhouse, *ibid.*, **59**, 1008 (1891).

by reduction with sodium and alcohol,[6] and also catalytically.[7] The ketone was reduced in this Laboratory by the older methods and by Hartung's[8] which had not been reported previously. Contrary to expectations, this method did not yield the hydrocarbon, for reduction stopped at the alcohol stage. The phenylurethan obtained from this product melted at 86°. Straus and Grindel reported a melting point of 83—84°.

Monobenzylacetophenone, previously reduced to 1,3-diphenylpropane, only by catalytic means,[7] in this investigation was reduced by the action of red phosphorus and hydriodic acid in a heated sealed tube.[9] It is significant that neither Clemmensen's[10] nor Hartung's method accomplished the desired result.

Dibenzylacetophenone was formed simultaneously with the monobenzyl compound. Its purification was complicated by a tendency to yield intractable condensation products if the temperature were too high or if the vacuum were not sufficiently low. Although the earlier investigators were unable to prepare its oxime, this compound was finally obtained.

The corresponding alcohol, 1,3-diphenyl-2-benzylpropanol-1,[11] had not been prepared before by the reduction of this ketone. Sodium and alcohol sufficed to bring about the desired transformation. This alcohol readily yielded a phenylurethan.

Dibenzylacetophenone was reduced to a hydrocarbon by the method involving hydriodic acid and red phosphorus. The product, so synthesized, has already been reported.[12] In the reduction of dibenzylacetophenone, as in the case of the monobenzyl ketone, Clemmensen's method failed completely; Hartung's gave only the secondary alcohol.

Tribenzylacetophenone was prepared from dibenzylacetophenone. Despite strenuous efforts, all attempts to isolate its oxime were uniformly unsuccessful. It is believed that steric hindrance is the cause of these negative results.

The corresponding carbinol, 1,3-diphenyl-2,2-dibenzylpropanol-1, was easily formed from the ketone by the use of sodium and absolute alcohol. Attempts to purify the product, a gummy mass, by vacuum distillation, always failed because of resinification. The carbinol was separated from the unchanged ketone by taking advantage of its greater solubility in ethyl alcohol. All efforts to prepare a phenylurethan invariably came to nought.

Tribenzylacetophenone was not affected when subjected to the reducing action of Hartung's or of Clemmensen's method. Heating in a sealed tube with red phosphorus and hydriodic acid brought about the desired result, the formation of 1,3-diphenyl-2,2-dibenzylpropane, tetrabenzylmethane. This hydrocarbon had previously been prepared by treating appropriate Grignard reagents with certain organic halides.[13,14] However, the yields never approached those obtained in this investigation.

The consistent failure of the Clemmensen method to reduce the ketones of this series, and the analogous derivatives of pinacolone, previously reported, seems sufficiently interesting to merit further study.

In the experimental part only the reactions leading to new products or to considerably improved yields of known compounds will be reported.

It is a pleasure to acknowledge the assistance given us by W. F. Bruce and R. W. Ehlers in certain preliminary work in the synthesis of tribenzylacetophenone. Without the financial aid afforded by the Atwater Fund this investigation could not have been undertaken.

Experimental

Dibenzylacetophenone Oxime.—Five grams of ketone was dissolved in 75 cc. of 95% ethyl alcohol. An excess (3 g.) of hydroxylamine hydrochloride and 2 g. of potassium hydroxide in 3 cc. of water were added. The system was refluxed vigorously for ninety-six hours. Water, sufficient to dissolve the potassium salt, was added and the solution extracted with ether. After drying with anhydrous sodium sulfate, the ether solution was distilled. The white crystalline residue was recrystallized from 95% ethyl alcohol, in which any unchanged ketone dissolved readily. The oxime melted at 157°.

Anal. Calcd. for $C_{22}H_{21}ON$: N, 4.45. Found: N, 4.50.

Phenylurethan of 1,3-Diphenyl-2-benzylpropanol-1.—Three grams of the alcohol was dissolved in 3 cc. of dry toluene; 2 g. of phenyl isocyanate was added and the solution kept at 40° for fourteen hours. The white, crystalline solid which settled out was recrystallized from 95% ethyl alcohol. The melting point was 185°.

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[6] Dieckmann and Kämmerer, *Ber.*, **39**, 3049 (1906).

[7] Straus and Grindel, *Ann.*, **439**, 294 (1924).

[8] Hartung, THIS JOURNAL, **53**, 2248 (1931).

[9] Lautemann, *Ann.*, **310**, 322 (1863).

[10] Clemmensen, *Ber.*, **46**, 1841 (1913).

[11] Tiffeneau and Lévy, *Bull. soc. chim.*, [4] **39**, 780 (1926).

[12] Hill, Little, Wray, Jr., and Trimbey, THIS JOURNAL, **56**, 911 (1934).

[13] Schmerda, *Monatsh.*, **30**, 387 (1909).

[14] Trotman, *J. Chem. Soc.*, **127**, 88 (1925).

Anal. Calcd. for $C_{29}H_{27}O_2N$: N, 3.32. Found: N, 3.35.

Tribenzylacetophenone.—160 g. of dibenzylacetophenone was dissolved in twice its volume of toluene, 400 cc. Cooling occurred as solution progressed. Twenty-three grams of sodamide of the necessary high quality was finely pulverized and placed in a three-necked flask equipped with a condenser, a mercury-seal stirrer, and a dropping funnel. The ketone solution was introduced dropwise during two hours while the mixture was stirred and refluxed. At the end of the two-hour period, the system became purple and ammonia was evolved very rapidly. The reaction was continued for eighteen hours. Seventy-four grams of benzyl chloride, b. p. 176–178°, was then introduced at a rate of three or four drops a second. Heating and stirring were continued for twenty-four hours more. By the end of this period the purple color had given place to yellowish-brown. The flask was cooled, 250 cc. of water was added and the toluene layer separated. It was washed with water, dilute hydrochloric acid, and again with water, dried with calcium chloride and distilled on a steam-bath under slightly reduced pressure. The crude ketone which crystallized was filtered and washed with 50 cc. of methyl alcohol in which tribenzylacetophenone is but very slightly soluble, whereas the dibenzyl compound is soluble. The product, recrystallized from toluene, melted at 127–128°. The average yield of crude crystals was 135–140 g., about 68%. The unused dibenzylacetophenone was recovered. Neither the use of a larger proportion of sodamide nor longer heating had a material effect in increasing the output.

Anal. Calcd. for $C_{29}H_{26}O$: C, 89.23; H, 6.67; mol. wt., 390. Found: C, 89.24, 89.17; H, 6.74, 6.77; mol. wt. (ebullioscopic method with benzene), 383, 380.

1,3-Diphenyl-2,2-dibenzylpropanol-1.—Five grams of tribenzylacetophenone was dissolved in 400 cc. of absolute alcohol. As rapidly as possible, 50 g. of sodium was added to the solution. When the vigor of the reaction had abated, the system was heated and refluxed for half an hour, then 200 cc. of water was added to the cooled contents of the flask. The gummy organic product was heated repeatedly with portions of hot ethyl alcohol which removed the carbinol, but had little effect on any unchanged ketone. Evaporation of the alcohol yielded 2 g. of a very viscous, light yellow liquid which decomposed when heated even under a low pressure. Two grams of ketone was recovered.

When a similar experiment was conducted with isoamyl alcohol as the medium, there resulted in addition to the oil, mentioned above, a solid which, after treatment with acetone and finally with toluene, was found to be tetrabenzylmethane.

Anal. Calcd. for $C_{29}H_{28}O$: C, 88.77; H, 7.14; mol. wt., 392. Found: C, 88.73, 88.75; H, 7.06, 7.08; mol. wt. (Rast method), 383, 384.

Tetrabenzylmethane.—Four grams of tribenzylacetophenone was heated for twenty-four hours at 200° in a sealed tube with 4 g. of red phosphorus and 80 cc. of 47% hydriodic acid. The cooled tube was opened and the contents extracted with toluene. This solution was washed with aqueous potassium hydroxide and with water, and then dried with calcium chloride. Removal of the toluene left a gummy white mass which upon repeated crystallization from ethyl alcohol gave 0.5 g. of large diamond-shaped crystals melting at 164°. The yield is 13%.

Anal. Calcd. for $C_{29}H_{28}$: C, 92.55; H, 7.45; mol. wt., 376. Found: C, 92.50; H, 7.38; mol. wt. (Rast method), 374.

Summary

1. Tribenzylacetophenone has been produced by a sodamide synthesis.
2. Certain derivatives of the omega-benzylacetophenones, analogous to a series of omega-benzylpinacolone derivatives, have also been prepared.

MIDDLETOWN, CONN. RECEIVED OCTOBER 2, 1935

[CONTRIBUTION FROM THE RESEARCH LABORATORY, UNITED STATES STEEL CORPORATION]

A Useful Integrated Form of the Equation for Calculating Change of Equilibrium with Temperature

BY J. B. AUSTIN

There are a number of thermodynamic equations expressing the change of equilibrium with temperature which have the general form

$$\mathrm{d} \ln f/\mathrm{d}T = \Delta H/RT^2 \qquad \text{I}$$

where f is the equilibrium constant, vapor pressure, solubility, or some other similar quantity which characterizes a state of equilibrium, ΔH is the molar heat effect for the reaction in question at the absolute temperature T, and R is the gas constant. If ΔH is assumed constant with T, this equation integrated between T' and T gives

$$\ln f'/f = \frac{\Delta H}{R}\left(\frac{T'-T}{T'T}\right) \qquad \text{II}$$

This relation, according to which $\ln f'/f$ is a linear function of $1/T$, has proved very useful as an aid in the critical examination of experimental observations, and even as a basis for estimating values of f'/f from ΔH (or conversely) when no direct measurement is available. The ease with which it can be applied, however, can be considerably increased in a number of cases, particularly in condensed systems, by a simple transformation into an approximate form which holds over a restricted temperature range. Thus, the approximate equation shows: (1) that experimental values of f, whatever it may be, when plotted against T on double logarithmic coördinates should fall on a straight line; (2) that if we plot on double logarithmic coördinates, not T directly but a "reduced" temperature—that is, if the actual absolute temperature is divided by a suitable reference temperature, such as the melting point of the solvent in considering solubility the data for all substances which have the same entropy change in the given reaction (in the case of solubility, the same entropy of melting) fall on the same straight line; and (3) that these relations hold in many cases even if ΔH varies with T, so long as this variation is effectively linear over the temperature range considered. The transformed equation also leads directly to the useful empirical rules of Ramsay and Young and of Dühring.

The Generalized Transformation

The transformation employed can be applied directly to many forms of equation I integrated on the assumption that ΔH is constant, but since the results are identical with those obtained on the basis of the general postulate that ΔH varies linearly with T, the discussion is confined to the latter case. If in equation I we put $\Delta H = \Delta H_0 + AT$ and integrate, we have

$$\ln f'/f = \frac{\Delta H_0}{RT'}\left(\frac{T'-T}{T}\right) + \frac{A}{R}\ln\frac{T'}{T} \qquad \text{III}$$

Now if we set $T'/T = X$, the quantity $(T' - T)/T$ in III is equal to $(X - 1)$ which is the first term in a well-known series expansion of $\ln X$[1] which is convergent for values of X between 0 and 2. For values of X not much different from unity, which covers nearly all the practical applications of such an equation, the higher terms of the series are negligible compared to the first one, *i. e.*, $(X - 1)$; hence for $(X - 1)$ we may substitute $\ln X$, on which basis we get the equivalent equations

$$\left.\begin{aligned} \ln f'/f &= \frac{\Delta H_0 + AT'}{RT'}\ln\frac{T'}{T} = \frac{\Delta H'}{RT'}\ln\frac{T'}{T} && \text{(a)} \\ \ln f'/f &= \frac{\Delta H'}{RT'}\ln T' - \frac{\Delta H'}{RT'}\ln T && \text{(b)} \\ f'/f &= \left(\frac{T'}{T}\right)^{\Delta H'/RT'} && \text{(c)} \end{aligned}\right\} \quad \text{IV}$$

where $\Delta H'$ is the heat effect at T'.

The magnitude of the error introduced by the substitution of $\ln T'/T$ for $(T' - T)/T$ is indicated by a comparison of some typical values as given in Table I. The first two columns contain values of $(T' - T)/T$ and $\ln T'/T$, respectively; the third and fourth give values of f'/f calculated from the first two columns on the basis that $\Delta H'/RT' = 10$, which is a fair average of values likely to be used in applying the equation. It is apparent that the error in this case is relatively small for values of $(T' - T)/T$ less than 0.100. If $\Delta H'/RT'$ is smaller, the error is less; if greater, the error is larger. It should be noted that since the approximation is valid for small values of $(T' - T)$—that is, when $(X - 1)$ is not far from unity—the condition for convergence of the series is fulfilled.

Applications

I. Solubility Relations in Ideal Solutions

A Complete Immiscibility in Solid Phase.—Since there are a number of advantages deriving from the use of the approximate equation in specific applications, a number of examples will be considered. The first is that of the lowering of the freezing point of an ideal solution from which one component separates as a pure phase on cooling; that is the components are completely miscible in the liquid but completely immiscible in the solid. Under these conditions $\Delta H' = \Delta H_m$ the heat of fusion of the solvent, T' is the melting temperature of the pure solvent, and $f = N_2$, the mole fraction of solvent in the liquid at T. Obviously $f' = N'_2 = 1$, hence equation IV may be written in the equivalent forms

$$\left.\begin{aligned} \ln N_2 &= \frac{\Delta H_m}{RT_m}\ln T/T_m && \text{(a)} \\ \log N_2 &= \frac{\Delta H_m}{RT_m}\log T - \frac{\Delta H_m}{RT_m}\log T_m = \\ &\qquad \frac{\Delta H_m}{RT_m}\log T + \text{const.} && \text{(b)} \\ N_2 &= (T/T_m)^{\Delta H_m/RT_m} = (T_m/T)^{-\Delta H_m/RT_m} = \\ &\qquad \text{const. } T^{\Delta H_m/RT_m} && \text{(c)} \end{aligned}\right\} \quad \text{V}$$

Table I

Comparison of Values of f'/f Calculated from $\dfrac{T'-T}{T}$ and from $\ln T'/T$

$\dfrac{T'-T}{T}$	$\ln T'/T$	f'/f calcd. from $\Delta H'/RT' = 10$ $(T'-T)/T$	$\ln T'/T$	Difference, %
0.010	0.0100	0.904	0.904	0
.0200	.0199	.818	.819	+ 0.12
.0500	.0488	.606	.613	+ 1.1
.0750	.0724	.472	.484	+ 2.5
.1000	.0954	.367	.385	4.9
.2000	.1830	.135	.160	11.0

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[1] See, for example, Hudson, "The Engineers Manual," John Wiley and Sons, Inc., New York, 1917, p. 35.

Equation V shows that if we plot N_2 against T/T_m on double log paper, the data for all ideal solutions in the same solvent should fall on the same straight line; moreover, that these straight lines all radiate from a single point ($N_2 = 0$, $T/T_m = 1$) and that for any solvent the angle between its characteistic line and the temperature axis depends only on the magnitude on $\Delta H_m/RT_m$. Consequently, by plotting a few guiding lines for integral values of $\Delta H_m/RT_m$ or $\Delta H_m/T_m$, the line for any given solvent can be quickly and easily drawn, provided, of course that ΔH_m and T_m are known. On the other hand ΔH_m, if not known, can be rapidly estimated by plotting the available data for appropriate solutions and drawing the best straight line through them. It should be noted that $\Delta H_m/RT_m$ is $1/R$ times the entropy of melting of the pure solvent, which is approximately the same for many chemically related substances; hence, when plotted in this way, the straight lines for many related substances as solvents coincide, a fact which is useful in estimating solubility in the absence of any direct measurement of N_2 or ΔH_m.

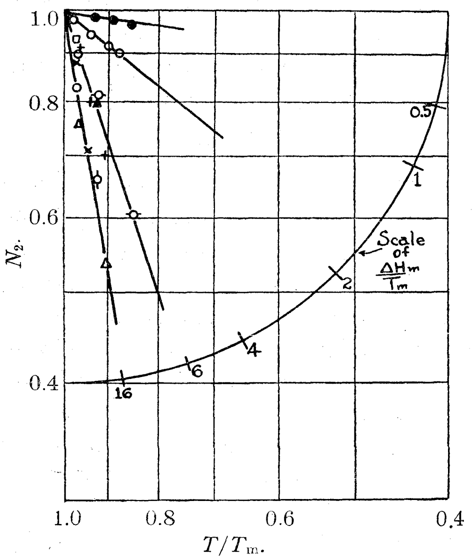

Fig. 1.—Solubility relations in systems with immiscibility in the solid phase plotted on double log coördinates using a reduced temperature according to eq. Va. Solid lines are calculated from heat of melting of solvent (component *italicized*): △, *anorthite*-diopside; □, *NaCl*-$Na_2Cr_2O_7$; ⦶, *diopside*-anorthite; ▲, *NaCl*-CsCl; ×, *diopside*-albite; -○-, *NaCl*-Na_2SO_4; ○, *magnesium*-nickel; +, *NaF*-NaCl; ●, *iron*-iron carbide.

In order to illustrate the usefulness of these relations a few typical data have been plotted in this manner in Fig. 1. The solutions selected are all high temperature systems—metals, fused salts and silicates—because they cover a relatively wide range of values of $\Delta H_m/T_m$; but the method applies equally well to any substantially ideal solution. It should be noted that the condition for proper application of the equation is met in that the value of T/T_m is never far from unity, even though a relatively wide range of temperature is included.

The points on the lowest line are for three silicate solutions taken from Bowen's study of the system diopside ($CaO\cdot MgO\cdot 2SiO_2$)–anorthite[2] ($CaO\cdot Al_2O_3\cdot 2SiO_2$)–albite ($Na_2O\cdot Al_2O_3\cdot 6SiO_2$). Following Bowen the molecular weights are taken as 217, 278 and 263, respectively. The full line is the calculated curve based on the directly determined heat of fusion of anorthite (105 cal. per gram).[3] It is evident that the solubility data are in excellent accord with the values calculated from ΔH_m for anorthite. Since anorthite and diopside are very similar, this agreement indicates that the entropy of melting of silicates of this type is very nearly the same and is close to 16 e. u.

The next curve compares the experimental data for four fused salt solutions, as given in "International Critical Tables" (Vol. IV), with the line calculated from the entropy of fusion of sodium chloride. Not only do the points for three solutions in sodium chloride as solvent fall on the line but those for a solution of sodium chloride in sodium fluoride come very close to it, indicating again that the behavior of solutions in related solvents can be represented by a single line with ample accuracy for many practical purposes.

The third line represents the solubility of nickel in magnesium as determined by Hanson and Payne,[4] compared with the solubility calculated from the entropy of fusion of magnesium. In this case it was demonstrated by direct measurement that the maximum solid solubility of nickel in magnesium is of the order of 0.1% so that the system closely approaches the ideal case of zero solid solubility. It should be noted that the entropy of fusion of magnesium is practically 2, which is a good average for that of most elements; hence $\Delta H_m/RT_m$ is close to one, which greatly simplifies the calculations.

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(2) N. L. Bowen, *Am. J. Sci.*, **40**, 161 (1915).

(3) Vogt, "Das Silikatschmelzlösungen," Vol. II Videnskabs.-Selskabets Skrifter, I Math. naturv. Klasse, 1904, No. I.

(4) Hanson and Payne, *J. Inst. Metals*, **54**, advance copy (1934).

The uppermost curve in Fig. 1 gives the effect of carbon (Fe_3C) on the $\alpha \longrightarrow \gamma$ transformation temperature of iron, as taken from Sato[5] and is included, first because it shows that the equation applies to solid solutions and solid transformations as well as to liquid solutions and melting; and second because it is a good example of a transformation which has a very small entropy change (0.2 e. u.).

In Fig. 2, the data for the silicates have been plotted directly on double-log paper. The heat of fusion calculated from the slope of these curves is: for anorthite, 39,900 cal. per mole (107.5 cal. per gram) in good agreement with the directly determined value (105 cal. per gram); for diopside 20,000 cal. per mole or 93 cal. per g. in satisfactory agreement with the experimental value (approximately 100 cal./g.).[3]

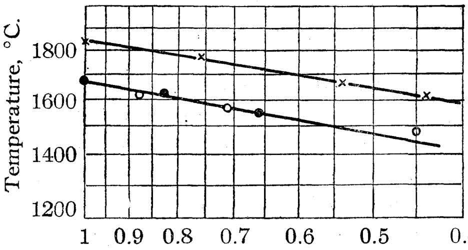

Fig. 2.—Solubility relations in some silicate systems plotted on double logarithmic coördinates according to eq. Vb. The solvent is the component *italicized.* ○, *Diopside*-anorthite; ●, *diopside*-albite; ×, *anorthite*-diopside.

Equation Vc is especially interesting because it shows that *the addition of a given mole fraction of solute lowers the (absolute) melting point of all solvents of related composition, i. e., those for which* $\Delta H_m/T_m$ *is the same, by the same percentage;* or *the solubility of a given solute at an absolute temperature which is a given fraction of the melting temperature is the same for all such solvents.* In other words, if N_2, the mole fraction of solvent, is plotted against T/T_m on rectangular coördinates, a single solubility curve is obtained for all ideal solutions in a given solvent, or for all ideal solutions in which the solvents have the same entropy of melting, thus providing a convenient way of representing a large number of data on a single curve or family of curves. An illustration of this method of plotting is given in Fig. 3.

It should be noted that the conclusion given in italics in the preceding paragraph is a rule for solutions exactly analogous to the rule of Ramsay and Young for vapor pressures which, as will be shown later, can be derived in the same way as equation Vc. It also leads to a rule for solutions analogous to the Dühring rule for vapor pressure. Thus if we plot the temperature at which a given substance has a given solubility in one solvent as ordinate and the temperature at which it has the same solubility in a "related" solvent (one whose entropy of melting is the same, or nearly the same) as abscissa, the experimental points should fall on a straight line whose slope is the ratio of the melting temperatures of the solvents.

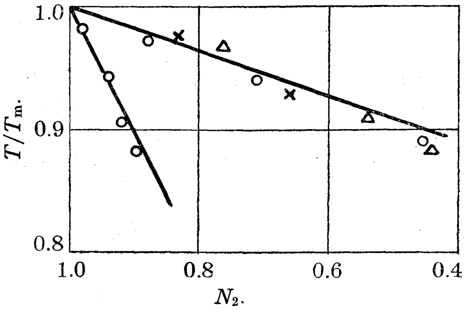

Fig. 3.—Solubility relations plotted on Cartesian coördinates using a reduced temperature according to eq. Vc. The solid lines are calculated from the heat of fusion of the solvent which is the component *italicized:* ×, *Diopside*-anorthite; ○, *diopside*-albite; △, *anorthite*-diopside; ●, *magnesium*-nickel.

It is also obvious that equation Vc in the form N_2 = const. $T^{\Delta H_m/RT_m}$ where the constant is $(T_m)^{-\Delta H_m/RT_m}$, enables one to draw in the actual solubility curve on linear coördinates with very little effort. Furthermore, the equation in this form demonstrates the factors which govern the shape of the solubility curve when plotted as N_2 against T. Clearly, when $\Delta H_m/RT_m = 1$ the solubility curve is a straight line between ($N_2 = 1$, $T = T_m$) and ($N_2 = 0$, $T = 0$); when $\Delta H_m/RT_m > 1$ the curve lies above this straight line and is concave to the N_2 axis, and when $\Delta H_m/RT_m < 1$ the curve is below the straight line and is convex to the composition axis. These relations, illustrated schematically by the curves in Fig. 4, are easily checked by considering a specific example. If $\Delta H_m/RT_m = 2$ equation Vc is a parabola passing through the origin ($N_2 = 0$, $T = 0$) and the melting point ($N_2 = 1$, $T = T_m$) and is symmetrical about the N_2 axis; whereas if $\Delta H_m/RT_m = 0.5$,

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(5) Sato, *Tech. Repts. Tohôku Imperial Univ.*, **8**, 27 (1928).

the curve passes through the same two points but is symmetrical about the T axis at the $N_2 = 0$ side. Actually the equation would not hold over this range, but it does hold as N_2 approaches unity and in this region has the same form as if it were valid to $N_2 = 0$. It is concluded, therefore, that if the entropy of melting is close to 2, as it is for most of the elements, the solubility curve is substantially a straight line; if it is greater than 2, the curve is concave to the composition axis; if it is less than 2, the curve is convex to this axis, and in each of the last two cases the curvature becomes less as N_2 approaches unity. From this reasoning it is clear that if the curvature of the solubility line changes sign, then ΔH has changed in such a way that $\Delta H_m/RT_m$ has passed from its initial value through unity. These points are illustrated by Fig. 5, which shows data for three types of solution plotted as N_2 against T.

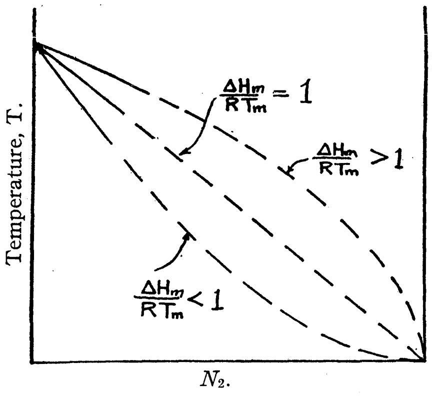

Fig. 4.—Schematic chart showing the relation between the entropy of melting and the curvature of the solubility line in a system in which there is no solid solubility.

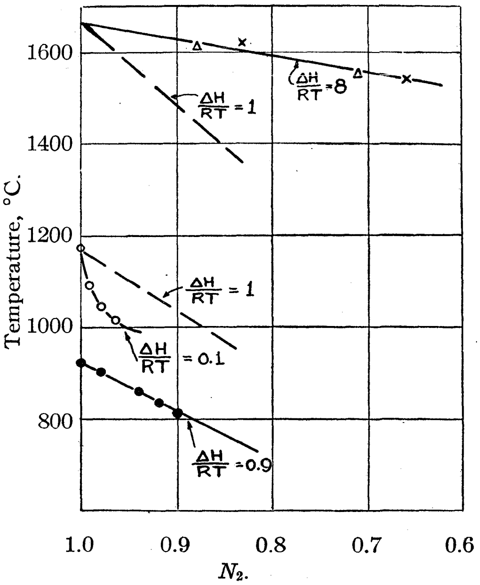

Fig. 5.—Chart illustrating the relation between the entropy of melting and curvature of the solubility line. △, *Diopside*–albite; ×, *diopside*–anorthite; ○, *iron*–iron carbide; ●, *magnesium*–nickel.

There is another interesting transformation which can be applied to equation V. It is a well-known fact that the value of $-\ln X$ approaches $(1 - X)$ as X approaches unity; hence, as N_2 approaches unity, that is, in a dilute solution, $-\ln N_2$ can be replaced by $(1 - N_2)$ or N_1, the mole fraction of solute in the liquid at T. On this basis we have

$$dN_1/dT = -\Delta H_m/RT^2 \qquad \text{VI}$$

which is the van't Hoff freezing point equation for dilute solutions. By the methods already indicated this becomes

$$\left.\begin{aligned} N_1 &= \frac{\Delta H_m}{RT_m}\ln\frac{T_m}{T} = -\frac{\Delta H_m}{RT_m}\ln T/T_m && \text{(a)}\\ N_1 &= -\frac{2.3\,\Delta H_m}{RT_m}\log T + \text{const.} && \text{(b)}\\ T &= T_m\,e^{-N_1T_mR/\Delta H_m} = T_m\,e^{-aN_1} && \text{(c)}\end{aligned}\right\}\ \text{VII}$$

In this case plotting on semi-logarithmic coördinates gives a straight line. The advantages of these equations for dilute solutions are in general those mentioned for equation V and need not be discussed in detail again. Data for the silicates and for magnesium which have been plotted on this basis are shown in Fig. 6.

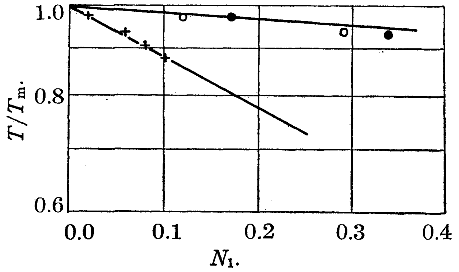

Fig. 6.—Solubility relations in some high temperature systems plotted on semi-logarithmic coördinates using a reduced temperature according to eq. VIIa. ×, *Magnesium*–nickel; ○, *diopside*–albite; ●, *diopside*–anorthite.

Case 2. Miscibility in the Solid Phase.—The second general case to be considered is that of a system showing solubility of the components in the solid phase (or in the low temperature form in the case of a solid transformation). In this case $\ln N_2$ is replaced by $\ln N_l/N_s$ where N_l and N_s are the mole fractions of solvent in the liquid and solid, respectively,[6] and we have

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[6] The solvent is taken as the component whose heat of melting and melting temperature are used, usually the component present in the largest concentration.

$$\left.\begin{aligned}
\ln N_l/N_s &= \frac{\Delta H_m}{RT_m}\ln T_m/T = \\
&\qquad -\frac{\Delta H_m}{RT_m}\ln T/T_m && \text{(a)}\\
\log N_l/N_s &= -\frac{\Delta H_m}{RT_m}\log T + \text{const.} && \text{(b)}\\
N_l/N_s &= \left(\frac{T}{T_m}\right)^{-\Delta H_m/RT_m} = \\
&\qquad \text{const. } T^{-\Delta H_m/RT_m} && \text{(c)}
\end{aligned}\right|\ \text{VIII}$$

These equations are entirely analogous to equations V, and show that by plotting N_l/N_s against T/T_m or against T directly on double log paper, a straight line having the slope $\Delta H_m/RT_m$ should be obtained. Equation VIIIa shows that the lines again radiate from a common point, as is evident from Fig. 7 which shows a few typical data plotted in this manner. The lowest curve is for anorthite-rich solutions of albite and anorthite,[2] and the middle one is for the albite-rich end of this system plotted so as to fall on the graph instead of above it as it normally would. The uppermost curve shows the ratio N_l/N_s at the eutectic temperature of each of a series of aluminum alloys.[7] The full lines are those calculated from the directly-measured heat of fusion while the dashed line (for albite) is the best straight line through the data. The entropy of fusion of albite is considerably lower than that of anorthite, indicating that $\Delta H_m/RT_m$ does not have the same value for all silicates; nevertheless, the agreement demonstrated previously between the entropy of fusion of diopside and anorthite, which are closely related chemically, suggests that the silicates can be classified into a small number of groups, the members of each group having the same entropy. The comparison of silicates emphasizes that Fig. 1 is nothing more than a special case of Fig. 7—the value of N_s being unity in the former. The data of Fig. 1 can therefore be plotted on Fig. 7, and the lines for anorthite and diopside would coincide. The uses of equation VIIIb are apparent and need no further discussion.

While the equations as given are derived for melting phenomena, it is obvious that they apply equally well to the boiling point of solutions of a volatile solute in a volatile solvent. Thus by making ΔH_m the heat of vaporization, T_m the boiling point and changing N_l and N_s to N_v and N_l, the mole fractions of solvent in vapor and liquid, respectively, we get

$$\left.\begin{aligned}
\ln N_v/N_l &= \frac{\Delta H_v}{RT_v}\ln\frac{T_v}{T} = -\frac{\Delta H_v}{RT_v}\ln T/T_v && \text{(a)}\\
\log N_v/N_l &= -\frac{\Delta H_v}{RT_v}\log T + \text{const.} && \text{(b)}\\
N_v/N_l &= (T/T_v)^{-\Delta H_v/RT_v} = \\
&\qquad \text{const. } T^{-\Delta H_v/RT_v} && \text{(c)}
\end{aligned}\right\}\ \text{IX}$$

Since these equations are precisely analogous to equations VIII whose application has been considered, no further discussion is needed, except to state that for a non-volatile solvent, $N_v = 1$ and the equations simplify to the form analogous to equation V.

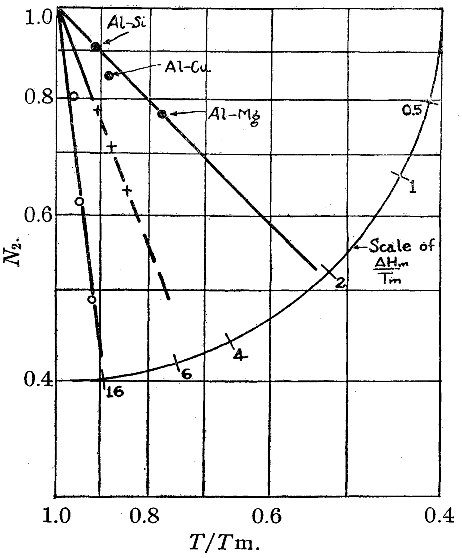

Fig. 7.—Solubility relations on systems having solid solubility, plotted on double logarithmic coördinates using a reduced temperature according to VIIIa. The solid lines are calculated from the heat of melting of the solvent which is the component *italicized:* ○, *Anorthite–albite*; +, *albite*–anorthite; ●, *aluminum* alloys at eutectic temp.

Other Applications.—In a purely formal way the approximate equations are valid for any quantity whose variation with temperature is given by equation I, and apply therefore to the equilibrium constant of a reaction, vapor pressure, dissociation pressure or electron emission. Actually, the change in these quantities with temperature is such that the restriction of keeping T'/T less than 1.2 imposes a serious limitation so that the equations are useful in only a few special cases.

There are, however, certain interesting aspects of the equations for some of these quantities, particularly the one for vapor pressure. Thus, if f' in IVc is the vapor pressure at T' of a liquid

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(7) Fink and Freche, *Trans. A. I. M. M. E.*, **111**, 304 (1934).

whose normal boiling point is T, it follows that for "related liquids," *i. e.*, those whose entropy of vaporization is the same, at the same vapor pressure

$$T_1/T_2 = T_1'/T_2' = \text{constant}$$

which is the empirical rule of Ramsay and Young.

Dühring's rule also follows from IVc, for considering a given pressure we write

$$\left(\frac{T_1'}{T_1}\right)^{\Delta H_1'/RT_1'} = \left(\frac{T_2'}{T_2}\right)^{\Delta H_1'/RT_2'}$$

and for "related liquids"

$$T_1' = T_1/T_2T_2' = \Delta H_1'/\Delta H_2' \times T_2'$$

which is the equation for the Dühring line. It also indicates that the slope of the Dühring line is the ratio of the absolute boiling temperatures or the heat of vaporization of the liquids chosen.

It is also possible to give some basis to Guldberg's empirical rule that for many liquids the normal boiling point is two-thirds of the absolute critical temperature. Thus, denoting the values of the quantities at the boiling point and critical point by the subscripts b and c, it can be shown on the basis of IVc that $T_b/T_c = (^1/P_c)^{-\Delta H_b/RT_b}$. Since P_c for most liquids is of the order of magnitude of 60 atmospheres, and by Trouton's rule, $-\Delta H_b/RT_b = -11$, the ratio T_b/T_c is roughly 0.7.

Summary

By a simple transformation the equations relating the change of solubility with temperature can be changed into an approximate form which is in many cases more convenient for interpolation or extrapolation than the original equations. Thus it is shown that experimental values of these quantities fall on a straight line when plotted against the temperature, or the reduced temperature, on double logarithmic coördinates. The approximate equation for vapor pressure leads directly to the rules of Ramsay and Young and of Dühring.

KEARNY, NEW JERSEY RECEIVED JULY 13, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ST. JOHN'S UNIVERSITY]

The Formation and Composition of Lithium Aluminate

BY HAROLD A. HORAN AND JOHN B. DAMIANO

Introduction

According to Allen and Rogers,[1] an insoluble aluminate of lithium is formed when aluminum is dissolved in a solution of lithium hydroxide. Analysis of the air-dried substance for alumina and water led them to assign the formula, $LiH(AlO_2)_2 \cdot 5H_2O$. As a result of conductometric measurements on the saturated solution of the substance, similarly prepared, Prociv[2] concluded lithium and aluminum were present in the ratio of 0.8Li:2Al, which, he says, is an atomic ratio of approximately 1Li:2Al. According to him lithium aluminate may also be precipitated by the addition of a solution of lithium hydroxide to a solution of an aluminum salt or by adding a solution of a lithium salt to a solution of an alkali aluminate. On ignition, he claims, the compound is converted into $Li_2O \cdot 2Al_2O_3$. Dobbins and Sanders[3] describe the formation of lithium aluminate by the addition of dilute ammonia to a solution containing a lithium and an aluminum salt, in the presence of phenolphthalein as an indicator. However, they claim the compound contains lithium and aluminum in atomic ratio of 2Li:5Al and, as a result of a series of ignitions assign the formula, $2Li_2O \cdot 5Al_2O_3$, for the ignited product.

Thus there is disagreement as to the composition of lithium aluminate prepared by different methods. This might be attributed to a variation of conditions, *i. e.*, alkalinity, relative ionic concentrations or temperature, in the different methods used. Concerning temperature, Allen and Rogers[1] and Heyrovsky[4] suggest precipitation at low temperatures, (near 0°), to prevent decomposition of the aluminate.

Since the compound has not been extensively studied, this investigation was undertaken in order, (1) to determine conditions for the precipitation of lithium aluminate from a solution of an aluminum salt, (2) to determine, by analytical means, the atomic proportions of lithium to aluminum in the substance precipitated, (3) to

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[1] Allen and Rogers, *Am. Chem. J.*, **24**, 304 (1900).

[2] Prociv, *Collection des Travaux Chimique de Tchecoslovaquie*, **1**, 95 (1929).

[3] Dobbins and Sanders, THIS JOURNAL, **54**, 178 (1932).

[4] Heyrovsky, *J. Chem. Soc.*, **117**, 1013 (1920).

determine the behavior of the substance on ignition.

Materials

Aluminum Ammonium Sulfate.—The C. P. substance was recrystallized twice from water. Solutions were made up and standardized by the oxine method.[5]

Acetic Acid.—A good grade, practically free of nonvolatile matter, was used.

Ammonia.—This was freshly distilled and made up to approximately 0.5 molar concentration.

Ammonium Acetate.—An approximately 2 molar solution was prepared by mixing the proper amounts of acetic acid, ammonia and water.

8-Hydroxyquinoline.—This was the Eastman Kodak Co. product.

Lithium Chloride.—This was purified by the usual method of precipitating the carbonate and evaporation with hydrochloric acid. An approximately 5% solution was made up and standardized by evaporating a known volume to dryness, in the presence of a little sulfuric acid, gently igniting and weighing the residue.

Experimental

To solutions containing known amounts of aluminum and having volumes of 100 cc., lithium chloride solution was added in amounts to provide an excess (approx. 10%), over the calculated amount, assuming for calculations 1Li:2Al. The solutions were cooled to approximately 5° and maintained at that temperature until after filtration. Dilute ammonia was added, with stirring, to effect precipitation. The amounts added varied in several cases. In some, just enough was added to give the solution a faint yellow color in the presence of neutral red as an indicator. In others, phenolphthalein was used as an indicator and a faint pink color established, while still in others a deep pink color was established by the addition of larger amounts of ammonia. The precipitates which formed were allowed to settle, filtered and washed with cold water (approx. 5°), until washings showed no test for chlorides with silver nitrate solution. To ensure proper washing and prevent "channeling" the precipitates were stirred while washing. The precipitates were analyzed as outlined below.

Another series of precipitations was carried out in solutions where the amounts of aluminum were held constant and the lithium chloride added was varied over a considerable range. Dilute ammonia was added to these solutions, in the presence of phenolphthalein, until the solutions had a definite pink color. The solutions and precipitates were handled as described above.

For the analyses of the freshly precipitated aluminates, most of the precipitate was washed from the paper, with water, into a clean beaker. The filter paper was then boiled up with sulfuric acid (1:6) to dissolve the remaining aluminate, and extracted several times with small portions of boiling water. The sulfuric acid solution and water extractions were filtered into the beaker containing the bulk of the precipitate, which dissolved upon heating. The solution was diluted to 100 cc. with water and almost neutralized with ammonia. The aluminum was then determined by the oxine[5] method. To recover the lithium sulfate, the filtrate and washings were carefully evaporated in platinum to approximately 10 cc. Concentrated nitric acid was added, in small increments, while the evaporation was continued. After destruction of most of the ammonium salt, acetic acid and organic matter, the solution was evaporated to incipient dryness. The residue was transferred with hot water to a platinum crucible. The crucible and contents were heated in an air-bath until dry. The excess sulfuric acid was carefully expelled and the crucible heated to constant weight at about 600°. Several blanks were run on solutions containing the same amounts of aluminum but no lithium. The lithium sulfate weights were then corrected. These corrections never amounted to more than 0.6 mg. The residues from the blank determinations revealed a trace of aluminum, probably due to the solubility of the quinolate.

The results of the two series of analyses are given in Tables I and II. The lithium–aluminum ratios are also given.

TABLE I

Expt.	Al_2O_3 (taken), g.	Al_2O_3 (found), g.	Li_2SO_4 (found), g.	Li/Al
1	0.0987	0.0982	0.0519	0.490
2	.0987	.0983	.0516	.488
3	.0987	.0984	.0522	.492
4	.1043	.1038	.0540	.483
5	.1043	.1041	.0544	.485
6	.1043	.1039	.0547	.489
7	.0554[a]	.0551	.0286	.487
8	.0554[a]	.0548	.0290	.491
9	.1264[b]	.1262	.0670	.492
10	.1264[b]	.1260	.0674	.494
11	.1407[b]	.1402	.0748	.494
12	.1407[b]	.1403	.0743	.491
13	.1562[b]	.1556	.0827	.490
14	.1635[b]	.1630	.0860	.488
15	.1635[b]	.1627	.0854	.487

Expts. 1, 6, 7, 10, 11, 15 were done using neutral red as an indicator. Expts. 2, 4, 12, 14, were done using phenolphthalein as an indicator until a faint pink color resulted. Expts. 3, 5, 8, 9, 13, were done using phenolphthalein as an indicator until a very deep pink color resulted.

[a] The volume of the solution for analysis was 60 cc.

[b] Aliquot portions sufficient to give approximately 0.1 g. of Al_2O_3 per 100 cc. were taken for analysis.

TABLE II

Expt.	Al_2O_3 (taken), g.	Li_2SO_4 (taken), g.[a]	Al_2O_3 (found), g.	Li_2SO_4 (found), g.	Li/Al
16	0.1043	0.0735	0.1040	0.0542	0.485
17	.1043	.1508	.1039	.0545	.487
18	.1264[b]	.0735	.1262	.0670	.492
19	.1264[b]	.1053	.1258	.0667	.490
20	.1264[b]	.1800	.1257	.0666	.490
21	.1407[b]	.0817	.1402	.0748	.494
22	.1407[b]	.1800	.1403	.0740	.490

[a] Actually LiCl, but calculated as Li_2SO_4. [b] Aliquot portions sufficient to give approximately 0.1 g. of Al_2O_3 per 100 cc. were taken for analysis.

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[5] Kolthoff and Sandell, THIS JOURNAL, **50**, 1900 (1928).

Several samples were precipitated using various amounts of lithium chloride solution and varying the alkalinity over the range indicated above. They were filtered, washed and transferred to silica crucibles. The precipitates were dried and the paper burned off at a low temperature. The temperature was gradually increased, the final ignitions to constant weight being made in a muffle at about 1050°. Some of the results are given in Table III. The calculated values, using formulas $Li_2O \cdot 2Al_2O_3$ and $2Li_2O \cdot 5Al_2O_3$ are also given.

TABLE III

Expt.	Al_2O_3 (taken), g.	Ignited residue, g.	$Li_2O \cdot 2Al_2O_3$ (calcd.), g.	$2Li_2O \cdot 5Al_2O_3$ (calcd.), g.
23	0.1154	0.1317	0.1324	0.1289
24	.1154	.1318	.1324	.1289
25	.1154	.1320	.1324	.1289
26	.0987	.1130	.1132	.1103
27	.0987	.1127	.1132	.1103
28	.0554	.0631	.0636	.0619
29	.0554	.0632	.0636	.0619

Expts. 25, 29 were done using neutral red as an indicator. Expts. 23, 24, 27 were done using phenolphthalein as an indicator until a faint pink color resulted. Expts. 26, 28 were done using phenolphthalein as an indicator until a very deep pink color resulted.

Discussion

The results in Table I show that within limits of experimental error the same results are obtained whether the solution is made faintly or definitely alkaline (*p*H 7.5–10.5). Thus there is no need for careful adjustment of alkalinity as suggested by Dobbins and Sanders.[3] Large excess of hydroxide should be avoided, as this causes slow solution of the precipitate.

As shown in Table II, the lithium chloride concentration has been varied over a considerable range without effect on the composition of the precipitate. It is not desirable to have too large a concentration of lithium chloride present, since this would entail prolonged washing of the precipitates to render them free of the excess, with consequent losses due to solubility and hydrolysis.

The lithium sulfate values given in Tables I and II are slightly lower than predicated by a 1Li:2Al ratio. This is undoubtedly due to loss of lithium in the solution and washings, for we have found more than traces removed if the washing is prolonged. The values are higher by some 25% than demanded by a 2Li:5Al ratio, making certain that the components are not present in that ratio.

In Table III the weights of the ignited residues, though slightly lower than expected, indicate that the ignition product is better represented by the formula $Li_2O \cdot 2Al_2O_3$ than by $2Li_2O \cdot 5Al_2O_3$. The percentage differences are only some 2.5% and, were it not for the large differences in lithium sulfate values mentioned above, one might not be justified in assigning a ratio of 1Li:2Al.

In assigning a 2Li:5Al ratio, Dobbins and Sanders[3] were led to this conclusion by (1), a series of ignitions of precipitates formed in solutions containing known amounts of aluminum and (2), Prociv's 0.8Li:2Al ratio, determined conductometrically. Concerning the first, it should be pointed out that precipitations and washings were made at room temperature where losses due to decomposition and solubility probably amount to at least 1%. In addition, no analysis of un-ignited precipitates was made prior to assignment of the formula. These points are important since the percentage difference in the weight of an ignited residue as calculated by one formula and the other is only 2.5%. Concerning Prociv's value, it is according to himself only approximate. It is an isolated value and not the result of a series of measurements. Other values obtained by Prociv[2] were quite close to a 1Li:2Al ratio.

Conclusions

1. An insoluble aluminate of lithium is precipitated, practically quantitatively, when a solution of an aluminum salt containing sufficient lithium salt, is made alkaline with ammonia.

2. Analysis shows that the substance contains lithium and aluminum in atomic ratio of 1Li:2Al.

3. Upon ignition at a high temperature the substance becomes constant in weight. The weight of the residue, obtained from a precipitate containing a known amount of aluminum, suggests the formula $Li_2O \cdot 2Al_2O_3$ for the residue.

BROOKLYN, N. Y. RECEIVED APRIL 26, 1935

[CONTRIBUTION FROM THE JARVIS CHEMICAL LABORATORY OF TRINITY COLLEGE]

Purification and Physical Properties of Organic Compounds. X. The Freezing Point Diagram for the System Acetanilide–Propionanilide[1]

BY EVALD L. SKAU AND LOUIS F. ROWE

In 1923 Hurd[2] isolated a white crystalline substance composed of propionanilide and acetanilide and concluded that in spite of the sharp melting point and apparent homogeneity of its long needle-like crystals it was not a compound but a mixture. Gilbert and Clarke[3] constructed the freezing point diagram of this binary system by a slightly modified Beckmann method and concluded that a compound crystallized from mixtures containing between 43 and 58 mole per cent. of propionanilide. Due to the unreliability of the Beckmann method for determining binary freezing points[4] it was thought desirable to reconstruct the diagram using a static method.

Materials.—Eastman Kodak Co. products were purified by repeated recrystallization from acetone. Their freezing points were determined by means of heating curves in an apparatus described elsewhere.[5] The curves showed that each still contained a trace of impurity.

Method.—The sample weighing from 1 to 3 g. was sealed in a glass tube (12 mm. diameter and 1 mm. wall thickness) extreme precautions being taken to avoid any overheating. The sample tube was fastened to the arm of an electric bell and vigorously agitated in a 2-liter water or glycerol bath. A 17-ohm nichrome filament wound around a Pyrex U-tube and connected to a lighting circuit through an 80-ohm Vitrohm rheostat controlled the temperature of the bath. A stream of bubbles released below the heater wires circulated the liquid. The temperature of the bath was measured by means of a carefully calibrated thermometer with 0.1° graduations. This type of thermostat was very easy to manipulate from one constant temperature to another and the temperatures in various parts of the bath differed by less than 0.1°.

The freezing point was determined by finding two temperatures, 0.2° or less apart, such that at the lower temperature a few crystals[6] persisted during thirty minutes of agitation and at the higher temperature the sample became completely liquid. The average of these two temperatures was taken as the freezing point of the sample after stem-emersion and calibration corrections had been made.

Results and Discussion

The results are given in Table I and are compared graphically in Fig. 1 with those previously obtained by the Beckmann method. Table I gives the equilibrium temperatures between the melt and the stable crystalline phases. For compositions up to and including 46.00% the crystalline phase is acetanilide (flakes), between 49.95

TABLE I

BINARY FREEZING POINT DATA FOR ACETANILIDE AND PROPIONANILIDE

Mole % of propionanilide	Equilibrium temp., °C.	Mole % of propionanilide	Equilibrium temp., °C.
0.00	114.1	51.48	79.8
10.31	107.9	51.68	79.6
22.76	100.5	51.79	79.6
30.19	95.1	53.40	80.0
39.25	87.9	54.86	80.1
39.30	87.7	56.57	81.35
41.15	86.5	56.95	81.6
41.82	86.0	57.09	82.0
45.00	83.55	60.83	85.0
46.00	82.4	67.16	88.7
49.95	79.4	79.97	96.5
50.77	79.4	90.19	101.6
50.95	79.5	100.00	105.6

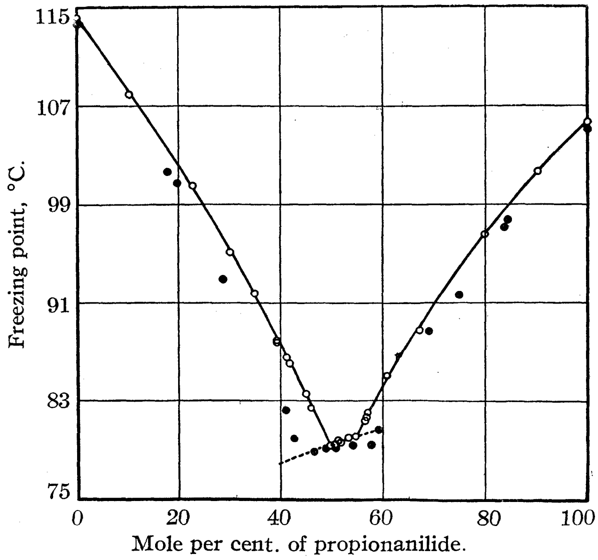

Fig. 1.—Binary freezing point diagram of the system acetanilide–propionanilide: ○, static method; ●, previous authors by Beckmann method; - - - -, unstable equilibrium.

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[1] From part of a thesis submitted by Louis F. Rowe in partial fulfillment of the requirements for a Master of Science Degree at Trinity College, 1933.

[2] Hurd, THIS JOURNAL, **45**, 3095 (1923).

[3] Gilbert and Clarke, *ibid.*, **49**, 2296 (1927);

[4] For an analysis of the magnitude of the errors involved see Skau and Saxton, *J. Phys. Chem.*, **37**, 183 (1933). See also Andrews, Kohman and Johnston, *ibid.*, **29**, 914 (1925); Skau, THIS JOURNAL, **52**, 945 (1930); *J. Phys. Chem.*, **39**, 761 (1935).

[5] Skau, *Proc. Am. Acad. Arts Sci.*, **67**, 551 (1933).

[6] Formed by bringing the very tip of the sample tube containing the liquid at that temperature above the surface and touching it with a cold object.

and 54.86% it is compound (needles), and between 56.57 and 100% it is propionanilide (granules).

The results bear out the fact that the Beckmann method, giving values as it does from 0.5 to 5° too low, is not suitable for determining binary freezing points. It is found that the needle-shaped crystals of the compound are in stable equilibrium with liquid mixtures between about 49.5 and 55 mole per cent. of propionanilide instead of between about 43 and 58 mole per cent. as previously accepted. The 49.5 per cent. composition, freezing at 79.4°, is a eutectic between the compound and acetanilide; and the 55 per cent. point, at 80.1°, is an incongruent melting point for the compound.

An interesting fact was noted in regard to the behavior of mixtures between about 42 and 57 mole per cent. propionanilide but outside the compound region. When the tip of the sample tube containing the supercooled liquid was brought above the surface of the bath and touched with a cool object, needle-shaped crystals were formed. These seemed always to melt rapidly when agitated in the bath unless the temperature was below about 79.5° on the acetanilide side and about 80.2 to 80.5° on the propionanilide side. If the temperature was so regulated that the needles persisted, the liquid became turbid in a few minutes and very soon the characteristic flake-like crystals of acetanilide (or the granular crystals of propionanilide in the case of compositions above 55 per cent.) formed as the needles disappeared. These flakes (or granules) did not then disappear until the melting point represented for this composition in the diagram was reached. It was never found possible to cause the flakes of acetanilide to crystallize out spontaneously even by continued agitation at temperatures between the full line and the dotted line in the figure. This behavior makes it seem probable that Gilbert and Clarke were dealing with the unstable solid phase at either end of the compound region and illustrates an additional source of error involved in the Beckmann method.

The determination of the exact composition of the compound was hindered by the great difficulty of isolating it in a pure state but our results indicate that it is perhaps composed of two moles of propionanilide and one mole of acetanilide. A small crop of the needle-shaped crystals was crystallized from a mixture containing 55 mole per cent. of propionanilide and separated by means of a centrifugal filtration tube.[7] Due to the fact that the temperature range over which the compound forms is so small (0.7°) these crystals were undoubtedly contaminated with a very considerable amount of the eutectic mixture of about 49.5 per cent. composition. Their melting point was 80.2° and after being kept just below this temperature for a few minutes, granular propionanilide crystals formed which did not dissolve until 81.3° had been reached, corresponding to a composition of 56.5 mole per cent. of propionanilide. This also corroborates the fact that the compound has an incongruent melting point.

Grateful acknowledgment is made for grants from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences and from Curtis H. Veeder, of Hartford, which have made this investigation possible.

Summary

The binary freezing point diagram for the acetanilide–propionanilide system has been reconstructed by means of an accurate static method; the Beckmann method for binary freezing point determinations has again been shown to be unreliable. The system shows compound formation with incongruent melting. The compound tends to crystallize out in unstable equilibrium from liquid mixtures near the compound region.

HARTFORD, CONN.

RECEIVED JULY 24, 1935

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[7] Skau and Rowe, *J. Ind. Eng. Chem., Anal. Ed.*, **3**, 147 (1931)

[CONTRIBUTION NO. 359 FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Purification and Physical Properties of Organic Compounds. XII. The Lower Aliphatic Bromides[1]

BY EVALD L. SKAU AND ROGERS MCCULLOUGH

In the course of some rate of reaction work it became necessary to know the densities of certain bromides of the aliphatic series. The data in the literature showed considerable disagreement. Accordingly a number of these bromides were prepared in as pure a form as practicable and their boiling points, densities and freezing points were determined.

Preparation and Purification of the Bromides.—The bromides were all prepared by the action of constant boiling hydrobromic acid of high purity on the corresponding pure alcohols by the method of Norris[2] as modified by McCullough and Cortese.[3] The alcohols were carefully fractionated pure materials boiling over a range of not more than 0.1°. Their purity was checked by density determinations. For the sample of *n*-amyl bromide we are indebted to Dr. Richard H. F. Manske of the Canadian National Research Laboratories, Ottawa.

Each of the bromides was washed repeatedly with constant boiling hydrobromic acid and then dried over anhydrous sodium sulfate or calcium chloride and subjected to systematic fractional distillation through a 180-cm. spiral fractionating column electrically heated and supplied with a still-head for controlling the reflux. The boiling ranges and boiling points recorded in the accompanying table are the values obtained for the best fraction in this distillation. In the case of isopropyl bromide this sample was then fractionally crystallized from its own melt by means of an apparatus to be described in a later communication.

The final step in the purification always consisted of distilling the material in a high vacuum at low temperatures by immersing the receiver in liquid air. One portion of the middle fraction was collected in a freezing point tube and another, for use in the density determination, was collected in a special sample tube. Both were sealed off without admitting air.

Measurement of Physical Constants.—The boiling points except as noted were read by means of Anschütz thermometers totally immersed in the vapors. They were calibrated under the same conditions against standards of the same design certified by the U. S. Bureau of Standards and the Deutsches Reichsanstalt. In the cases of *n*-butyl, *s*-butyl and *n*-amyl bromide, a carefully calibrated copper–constantan thermocouple was used. Correction to 760 mm. was made by use of the temperature–pressure coefficients given in the "International Critical Tables."

The densities were determined by means of a 5-cc. Pyrex Sprengel pycnometer having the arms bent up at an angle of about 20° and provided with tightly fitting ground glass caps. The pycnometer after being rapidly filled from a freshly opened vacuum-sealed ampoule was capped and allowed to remain immersed in the thermostat for at least twenty minutes before the adjustment was made between two scratch marks. The temperature of the thermostat, which was maintained at 25.00 ± 0.01°, was checked by a standard certified Reichsanstalt thermometer which was in turn carefully checked against a platinum resistance thermometer at the ice-point and in a thermostat maintained at 30.000 ± 0.002°. The pycnometer was always allowed to stand inside the balance case for thirty minutes before being weighed with calibrated weights, making correction to vacuum.

The freezing points were determined from both cooling and heating curves,[4] an average being taken of the values obtained by the two methods.

Results and Discussion.—The results obtained are listed in Table I. For comparison with previous values in the literature only those of Timmermans, who with his co-workers has done the most extensive accurate work in this field, have been cited except where more recent accurate determinations have been made.

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(1) The experimental work for this paper was completed in 1928 during the tenure of a National Research Council Fellowship by the Senior Author.

(2) Norris, *Am. Chem. J.*, **38**, 640 (1907).

(3) McCullough and Cortese, THIS JOURNAL, **51**, 225 (1929).

(4) For a description of the freezing point apparatus, its uses in estimating the purity of the sample, and the establishment of the thermometric scale used, see the first two papers of this series: *Proc. Am. Acad. Arts Sci.*, **67**, 551 (1933), and *J. Phys. Chem.*, **37**, 609 (1933).

TABLE I

SOME PHYSICAL PROPERTIES OF THE LOWER ALIPHATIC BROMIDES

	Total b. p. range, °C.	B. p., °C. 760 mm.	B. p., °C., lit.	d^{25}_4	d^{25}_4 lit.[h]	F. p., °C.	F. p., °C., lit.
Ethyl bromide	0.04	38.34	38.40[a]	1.4512	1.45048[a]	−118.9	−119.0[a]
n-Propyl bromide	.05	70.97	71.00[a]	1.3455	1.34305[a]	−109.8	−110.0[a]
Isopropyl bromide	.03	59.41	59.35[b]	1.3063	1.30555[b]	− 90.0	− 89.0[b]
			59.45 ± 0.02[e]				− 88.6, −89.1[e]
n-Butyl bromide	.00	101.26	101.60[a]	1.2686	1.26840[a]	−112.3	−112.4[a,e]
			101.2 ± 0.1[e]		1.2689[f]		−112.7[f]
					1.2685[g]		
Isobutyl bromide	.06	(91.72)	91.40[b]	(1.2480)	1.25715[b]	(−118)	−118.05[e]
			91.1 ± 0.2[e]				
s-Butyl bromide	.04	91.24	91.20[c]	1.2530	1.25363[c]	−112.1	−111.9[c]
							−112.7[f]
n-Amyl bromide	.09	129.6	129.70 ± 0.02[d]	1.2121	1.21091[d]	− 87.9 (stable)	− 95.25[d]
					1.2114[f]	− 94.6 (unstable)	− 88.0[f]

[a] Timmermans and Martin, *J. chim. phys.*, **23**, 747 (1926). [b] Timmermans and Martin, *ibid.*, **25**, 411 (1928). [c] Timmermans and Delcourt, *ibid.*, **31**, 85 (1934). [d] Simon, *Bull. soc. chim. Belg.*, **38**, 47 (1929). [e] Timmermans, *ibid.*, **30**, 62 (1921). Deese, THIS JOURNAL, **53**, 3673 (1931). [g] Bridgman, *Proc. Am. Acad. Arts Sci.*, **68**, 1 (1933). [h] Calculated from the values given for 0, 15 and 30° values except for ref. (*f*).

The boiling point values agree very closely with those of Timmermans and others except in the case of isobutyl bromide which differed by 0.3 to 0.6°.

The density values are slightly higher than those previously reported except in the case of isobutyl and secondary butyl bromides. It was found that the final high vacuum distillation to which all the samples were subjected always raised the density. It should also be pointed out that the method of preparation and purification used avoided the formation of traces of unsaturated compounds and ethers[3] which might be difficult to remove and which would tend to lower the density. The largest discrepancy in density is in the case of isobutyl bromide. This was probably due to the presence of impurities as mentioned below.

The shape of the heating curves indicates that all of the compounds studied were of a high degree of purity[4] with the exception of the secondary butyl bromide, which contained a slight trace of impurity, and the isobutyl bromide. The latter gave very unsatisfactory cooling curves due to sluggish crystallization, and the heating curves indicated the presence of considerable impurity. The actual freezing point obtained was −118.1°, showing acceptable agreement with the best value previously reported, −118.05°, but it is probable that it would be at least 0.5° higher for the pure compound. It seems probable, on the other hand, that the other freezing points do not differ by more than a few tenths of a degree from the correct values for the pure bromides.

There are two solid forms of *n*-amyl bromide, an unstable form, melting at −94.6, and a stable form, melting at −87.9°. The unstable form always appeared when cooling curves were run in the usual way. When kept for some time at a temperature 10 to 20° below its melting point or when suddenly cooled in liquid air the unstable form transformed in the solid state to the stable form with an evolution of heat. It was found possible to get a heating curve on the unstable form immediately after a cooling curve even though the temperature of the sample fell to −102° meanwhile and remained there some twenty minutes. A cooling curve on the stable form was finally obtained on a sample which had been completely transformed in the solid state and then partially melted. This behavior proves that *n*-amyl bromide is dimorphous and further that it is monotropic. It also explains why Simon obtained a freezing point of −95.25° for this compound while Deese[5] obtained −88.0° (see Table I). The former obtained his value by freezing point measurements and the latter by heat content measurements which involved preliminary cooling to much lower temperatures.

An inspection of Table I shows that our freezing points agree acceptably with previous values except in the case of isopropyl bromide and the unstable form of *n*-amyl bromide.

HARTFORD, CONN.

RECEIVED AUGUST 20, 1935

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(5) Deese [THIS JOURNAL, **53**, 3673 (1931)] states that "a transition phenomenon was found to occur at about −113°" but heat content measurements failed to verify the existence of a second solid form.

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Estimation of Transference Numbers in Dilute Solutions from Limiting Ionic Conductances

BY BENTON BROOKS OWEN

While the known transference data of simple strong electrolytes can be reproduced with high precision by the empirical evaluation of a single parameter in the Longsworth[1] equation, or by the adjustment of two parameters in the equation of Jones and Dole,[2] the semi-empirical relation

$$T_+ = T_+^0 + \frac{(2T_+^0 - 1)\beta\sqrt{C}}{\Lambda^0 - (\alpha\Lambda^0 + 2\beta)\sqrt{C}}\left[1 - (1 - \alpha\sqrt{C})\sqrt{2C}\right] \quad (1)$$

permits the estimation of certain transference numbers from limiting conductances alone.[3] This equation is formally equivalent to that of Longsworth, but a comparison of coefficients shows that the parameter, A, which Longsworth evaluated from the transference data for each individual electrolyte, may be replaced by the quantity $-\beta\sqrt{2}(2T_+^0 - 1)/\Lambda^0$, characteristic of the whole group of electrolytes conforming to the Longsworth equation. Although this replacement is accompanied by a loss in precision, there are obvious practical advantages afforded by the gain in generality.

TABLE I

TEST OF EQUATION (1) AT 25°

Electrolyte	Λ^0	$T_+^{0\,a}$	$(T_+(\text{Eq. (1)}) - T_+(\text{Obs.}))10^4$		
HCl	426.17	0.8209	−6	−11	−24
$NaC_2H_3O_2$	90.99	.5507	−1	1	4
NH_4Cl*	149.94	.4909	−3	− 6	−12
KCl	149.86	.4906	0	− 1	2
KI*	150.29	.4892	2	− 1	− 7
KBr*	151.63	.4849	7	2	− 8
NaCl	126.43	.3963	−2	− 8	4
LiCl	115.03	.3364	−6	− 9	5
Concentration (moles per liter), $C =$			0.05	0.1	0.2

[a] $\lambda^0_{Cl^-} = 76.34$.

In Table I are recorded the differences between T_+ calculated by Equation (1) and the smoothed experimental values recently tabulated by Longsworth.[4] The average differences are (with increasing concentration) three, five and eight units in the fourth decimal place of the transference numbers. The maximum individual difference amounts to nearly 0.3%. The necessary values of $\Lambda^0(=\lambda_+^0 + \lambda_-^0)$ and $T_+^0(=\lambda_+^0/\Lambda^0)$ are all computed from the table of limiting ionic conductances given by MacInnes, Shedlovsky and Longsworth,[5] except those indicated with an asterisk. Of these latter, $\Lambda^0(KBr)$ is due to Jones and Bickford,[6] $\Lambda^0(KI)$ to Lasselle and Aston,[7] and $\Lambda^0(NH_4Cl)$ is given by Longsworth.[8] All values have been adjusted to conform to the primary conductance standard of Jones and Bradshaw.[9]

Equation (1) is not in accord with the known transference data for silver and potassium nitrates,[4] for calcium[4] and barium[2] chlorides, and for sodium sulfate.[4] Its failure in this respect is parallelled by that of the Longsworth[1] equation, but the results in Table I indicate that we might confidently expect an accuracy of better than one unit in the third decimal place of the transference number when it is applied to *dilute solutions* ($C < 0.15$ normal) *of uni-univalent electrolytes in which ionic association is negligible.* Precise limiting conductances are already available for a number of electrolytes in this category, including the chlorides, bromides, iodides, acetates, propionates, chloro substituted acetates, etc., of lithium, sodium and potassium. The accuracy to be expected in such calculations for the halides of hydrogen and ammonia, and possibly the hydroxides of the alkali metals, would hardly be better than two or three in the third decimal place of the transference numbers at 0.2 normal, but should improve with dilution, because the equation reduces, in the limit, to the theoretical tangent derivable from the Onsager[10] conductance equation. With proper attention to the above limitations, however, it appears that this equation might have considerable application in problems involving diffusion and liquid junction potentials, and in the determination[11] of the activity coefficients of salts (the bromides and iodides of lithium and sodium, for example) at high dilution.

NEW HAVEN, CONN. RECEIVED AUGUST 27, 1935

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(1) Longsworth, THIS JOURNAL, **54**, 2741 (1932).

(2) Jones and Dole, *ibid.*, **51**, 1073 (1929).

(3) The constants α and β from the Onsager conductance equation[10] will be taken as 0.2277 and 29.93, respectively (25°), in subsequent calculations.

(4) Longsworth, THIS JOURNAL, **57**, 1185 (1935).

(5) MacInnes, Shedlovsky and Longsworth, *ibid.*, **54**, 2758 (1932).

(6) Jones and Bickford, *ibid.*, **56**, 602 (1934).

(7) Lasselle and Aston, *ibid.*, **55**, 3067 (1933).

(8) This value was obtained by extrapolation from 0.01 normal.[4]

(9) Jones and Bradshaw, *ibid.*, **55**, 1780 (1933).

(10) Onsager, *Physik. Z.*, **28**, 277 (1927).

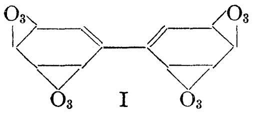
(11) Brown and MacInnes, THIS JOURNAL, **57**, 1356 (1935).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

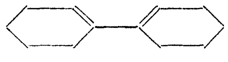
The Ozonation of Certain Hydrogenated Diphenyls

BY C. R. NOLLER AND G. K. KANEKO

During the course of his exhaustive work on the ozonation of organic compounds, Harries found that[1] whereas benzene forms a triozonide in accordance with the Kekulé formula, diphenyl forms only a tetraozonide. He suggested that the tetraozonide had Formula I and that the non-addition of ozone to the double bonds in the 1 and 1′ positions was due to steric hindrance.



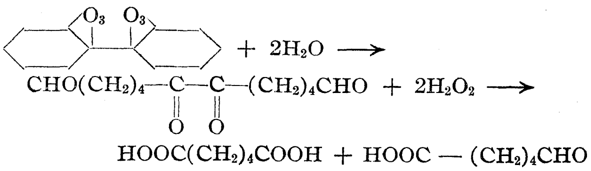
I



II

Because of the difficulty of preparing the tetraozonide, the products formed on decomposition with water have not been identified, but it should be possible to determine whether steric hindrance plays a role by studying compounds such as 1-phenylcyclohexene-1 and dicyclohexenyl-1,1′ (II) in which non-benzenoid double bonds occur in positions similar to those which are supposed to be sterically hindered in benzene.

A review of the literature showed that Brus and Peyresblanques[2] had ozonized 1-phenylcyclohexene-1 and they state that one mole of ozone adds rapidly and quantitatively while benzene adds ozone only slowly. One might be led to believe, however, from the curves given, that the addition was more like that to benzene rather than to an aliphatic double bond. They did not report the decomposition products of the ozonide and it is conceivable as in the case of diphenyl that the ozone is not added to the double bond in the 1- or 1′-position. This work was therefore repeated on 1-phenylcyclohexene-1 and extended to include dicyclohexenyl-1,1′. It was found that phenylcyclohexene adds one mole of ozone as readily as does a simple unsaturated compound such as methyl oleate, and that the ozonide on decomposition with water gives δ-benzoyl-*n*-valeric acid proving that the ozone added to the double bond in the cyclohexene ring. Moreover, dicyclohexenyl-1,1′ was found to add one mole of ozone rapidly while the second double bond added ozone slowly but at a faster rate than benzene. Decomposition of the ozonide did not yield the expected diketo-dibasic acid but adipic acid instead. The reaction may be formulated



$$+ 2H_2O \longrightarrow$$

$$CHO(CH_2)_4—\underset{\underset{O}{\|}}{C}—\underset{\underset{O}{\|}}{C}—(CH_2)_4CHO + 2H_2O_2 \longrightarrow$$

$$HOOC(CH_2)_4COOH + HOOC — (CH_2)_4CHO$$

The aldehyde acid was probably oxidized also to the dibasic acid, due to the exposure to air during the boiling and isolation. Adipic acid could hardly arise from an ozonide other than the diozonide shown and it therefore seems unlikely that steric hindrance, in the sense that there is no room for two ozonide groups to occupy the 1,1′ positions, can account for the non-formation of a diphenylhexaozonide.

During the course of this work the structure of tetrahydrodiphenyl obtained by the reduction of diphenyl with sodium in amyl alcohol[3] also was determined. When diphenyl is reduced by hydrogen in the presence of a nickel catalyst,[4] the products are phenylcyclohexane and dicyclohexyl. This fact led Turner[5] to predict that the tetrahydrodiphenyl of Bamberger and Lodter was a phenylcyclohexene rather than a dicyclohexadiene. Tetrahydrodiphenyl prepared according to the procedure of Bamberger and Lodter was ozonized and found to absorb about 68% of the calculated amount of ozone. Decomposition of the ozonide gave δ-benzoyl-*n*-valeric acid, identical with that obtained from 1-phenylcyclohexene-1. Hence tetrahydrodiphenyl is 1-phenylcyclohexene-1, contaminated with diphenyl or with phenylcyclohexane.

Experimental

Reagents.—1-Phenylcyclohexene-1[6] was prepared by the dehydration of 1-phenylcyclohexanol-1 in 75% yields by distilling 49 g. of the alcohol with 1 g. of potassium bisulfate and 50 cc. of bromobenzene through a 30-cm. Vigreux column as long as water came over (about two hours). The bromobenzene was separated from the distillate and returned to the flask from time to time. Finally all of the bromobenzene was distilled and the product fractionated under a vacuum; b. p. 136–138° (25 mm.).

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(1) Harries and Weiss, *Ann.*, **343**, 337, 374 (1905).

(2) Brus and Peyresblanques, *Compt. rend.*, **190**, 685 (1930).

(3) Bamberger and Lodter, *Ber.*, **20**, 3077 (1887).

(4) Sabatier and Murat, *Compt. rend.*, **154**, 1390 (1912).

(5) Turner, *Rec. trav. chim.*, **48**, 821 (1929).

(6) Sabatier and Mailhe, *Compt. rend.*, **138**, 1321 (1904).

Dicyclohexenyl-1,1′, b. p. 133–135° (23 mm.) was prepared in 68% yields by dehydrating dicyclohexanediol-1,1′[7] using an analogous procedure. The latter compound was prepared in poor yields by following the procedure given in "Organic Syntheses," Coll. Vol. I, p. 448, for pinacol hydrate. This was found to be superior to the sodium reduction method of Zelinsky.[8]

Tetrahydrodiphenyl was prepared by the procedure of Bamberger and Lodter.[3]

Ozonation and Decomposition of the Ozonides.—Oxygen containing 4–5% ozone was passed into a solution of the compound in glacial acetic acid until a sample no longer decolorized a solution of bromine in carbon tetrachloride. To the acetic acid solution of the ozonide was added 25 cc. of water and the solution refluxed for one hour. The acetic acid and water were distilled under reduced pressure and the residue poured into an evaporating dish to solidify. In the cases of phenylcyclohexene and tetrahydrodiphenyl the products were crystallized from ether and melted at 77–78°; the semicarbazones melted at 191–192° and mixed melting points showed no depression. Auwers and Treppmann[9] report the melting point of δ-benzoyl-*n*-valeric acid as 77–78° and the semicarbazone as 187°.

The crude product of the decomposition of the ozonide of dicyclohexenyl-1,1′ was crystallized from ethyl acetate, when it melted at 152–153° and had a neutralization equivalent of 74.6. Adipic acid melts at 153–153.5° and has a neutralization equivalent of 73. A mixed melting point showed no depression.

Summary

1. 1-Phenylcyclohexene-1 adds one mole of ozone to the double bond in the cyclohexene ring and dicyclohexenyl-1,1′ adds ozone to both double bonds. This indicates that steric hindrance in the 1 and 1′ positions is not the factor involved in the failure of diphenyl to form a hexaozonide.

2. Tetrahydrodiphenyl prepared by reducing diphenyl with sodium and amyl alcohol is chiefly 1-phenylcyclohexene-1.

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[7] Wallach and Pauly, *Ann.*, **381**, 112 (1911).

[8] Zelinsky, *Ber.*, **34**, 2801 (1901).

[9] K. v. Auwers and W. Treppmann, *ibid.*, **48**, 1217 (1915).

STANFORD UNIVERSITY, CALIF.

RECEIVED SEPTEMBER 23, 1935

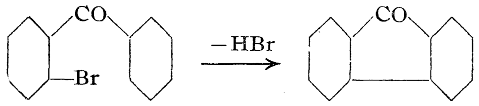
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Higher Benzenoid Hydrocarbons. II. The Isomeric Bromofluorenones[1]

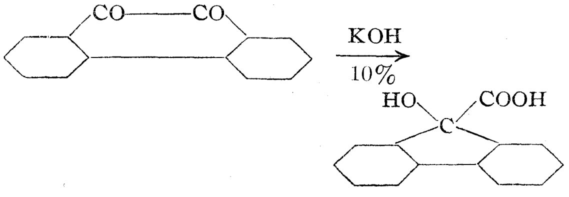
BY HARRY F. MILLER AND G. BRYANT BACHMAN

Of the four possible monobromofluorenones, 2-bromofluorenone is the only one readily available. The preparation of the 4-isomer has never been recorded and the 1- and 3-isomers have been prepared in small quantities only and by way of difficultly accessible intermediates.[2] As a part of our program to elucidate the fundamental chemistry of some of the polycyclic coal tar hydrocarbons it was decided to devise nuclear syntheses for the 3- and 4-bromofluorenones which would make them more readily available and which would serve to establish definitely their structure.

There are five general methods which have been used for the preparation of substituted fluorenones. (1) *Direct substitution.* This serves very well for the preparation of 2-bromo and 2,7-dibromofluorenones. Apparently, however, no other isomers arise in the bromination of either fluorenone or fluorene.[3] (2) *Elimination of hydrogen bromide from substituted o-bromobenzophenones.*



Although this method was used by Montagne to prepare 1- and 3-bromofluorenones, the yields are small and the intermediates difficult to prepare. Furthermore, in view of the high temperatures employed to effect condensation, there is always to be considered the danger of an intramolecular rearrangement. (3) *The rearrangement of phenanthraquinone derivatives.* This is an application of the benzil–benzilic acid rearrangement.



The diphenyleneglycolic acid formed decomposes in the presence of boiling water liberating fluorenone. The method has been used successfully in the preparation of certain nitrofluorenes[4] and of a

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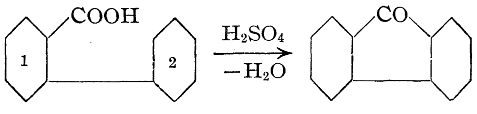
[1] First paper in this series, THIS JOURNAL, **57**, 766 (1935).

[2] Montagne and Van Charante, *Rec. trav. chim.*, **32**, 164 (1913).

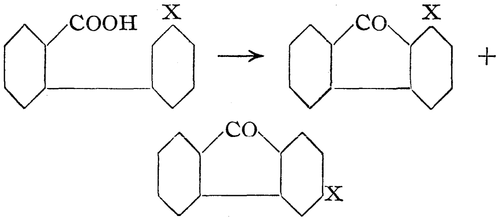
[3] Courtot and Vignati, *Bull. soc. chim.*, [4] **41**, 58 (1927).

[4] Schmidt, *et al.*, *Ber.*, **38**, 3737 (1905); **41**, 3679 (1908).

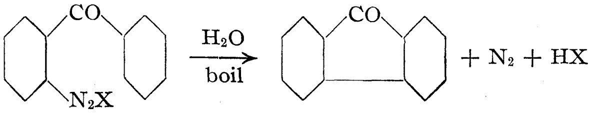
few other fluorene derivatives, but its broader application awaits the further development of phenanthrene chemistry, since in many cases the necessary phenanthraquinones are unknown. The isomeric bromophenanthraquinones have not yet been thoroughly studied. (4) *The dehydration of o-carboxydiphenyl derivatives.* This method is



of particular value in that it gives very high yields as a rule. Applied to the synthesis of substituted fluorenones however it will be noted that the method suffers certain disadvantages if the substituent group is located in the meta position of ring 2. In such cases either one or both of two different isomers may result upon ring closure



Where establishment of structure is being attempted such a mixture might lead to confusion and should be avoided. Furthermore, it has been our experience that mixtures of bromofluorenones are not easily separable. Substituents in ring 1 and in the ortho or para position of ring 2 lead to but one product, however, and since this method is otherwise quite general in its application and relatively simple to apply, it is to be recommended. The above arguments apply to all nuclear fluorenone syntheses in which ring closure of this type occurs. These include methods (2), (4) and (5). *Method* (5) consists in the coupling of diazotized *o*-aminobenzophenone derivatives.[5]



For the present work methods (4) and (5) have been used since they seemed to be most satisfactory from the standpoints of yield, cost, and generality of application. The flow diagram shown in Table I indicates the various steps used for the synthesis of 3- and 4-bromofluorenones. For 3-bromofluorenone the over-all yield from phthalic anhydride (5 steps) was 55%, from anthranilic acid (4 steps) 21%. The 4-bromofluorenone was obtained from bromophthalic anhydride (5 steps) in 25% yield, from *o*-iodobromobenzene and methyl *o*-iodobenzoate (2 steps) in 14% yield. The difficulty of preparing the last two intermediates makes this last synthesis of little practical value. Fortunately 4-bromofluorenone may be obtained more readily by the oxidation of the easily prepared 4-bromofluorene whose synthesis will be described in the succeeding paper.

It should be pointed out that by combinations of the two general methods here used some of the heteronuclear dibromofluorenones could also be prepared. The conversion of the bromofluorenones into the corresponding bromofluorenols and bromofluorenes is described in the succeeding paper.

The Synthesis of 3-Bromofluorenone

2-(4-Bromobenzoyl)-benzoyl Chloride.—The condensation of phthalic anhydride with bromobenzene in the presence of aluminum chloride according to Ullmann and Sone[6] yielded 2-(4-bromobenzoyl)-benzoic acid, m. p. 171–172°, in 83% yields (above authors report 86%). Fifty-three grams of this product, 37 g. of phosphorus pentachloride and 200 cc. of benzene were refluxed until no more hydrogen chloride was evolved. On cooling, the acid chloride separated as white opaque needles; yield 92% theoretical, m. p. 162–163°.

Anal. Calcd. for $C_{14}H_8O_2BrCl$: Br and Cl, 35.66. Found: Br and Cl, 35.48.

2-(4-Bromobenzoyl)-benzamide.—Twenty-five grams of finely powdered acid chloride was added in small portions to 200 cc. of liquid ammonia in a Dewar tube. The mixture was stirred by a stream of air bubbles from a capillary at the bottom of the tube. After the ammonia had evaporated water was added and the residue separated and recrystallized from a mixture of 500 cc. of xylene and 50 cc. of acetone. The amide formed feathery white needles, m. p. 184.5–185.0°, and was obtained in 95% yields.

Anal. Calcd. for $C_{14}H_{10}O_2NBr$: Br, 26.20. Found: Br, 26.05.

2-(4-Toluenesulfonamido)-benzoyl Chloride.—Anthranilic acid was converted into its *p*-toluenesulfonanilide (yield 86%, m. p. 217–218°)[5b] and then into the corresponding acid chloride[7] with phosphorus pentachloride (yield 96%, m. p. 129°). In this latter reaction it was found simplest to use no solvent since the acid is but slightly soluble in benzene and other inert solvents.

2-(4-Bromobenzoyl)-aniline. First Procedure.—Ten grams of 2-(4-bromobenzoyl)-benzamide and 30 cc. of 10% sodium hydroxide solution were made into a thin paste in a mortar. A sodium hypobromite solution was prepared from 15 g. of sodium hydroxide, 13 g. of bromine

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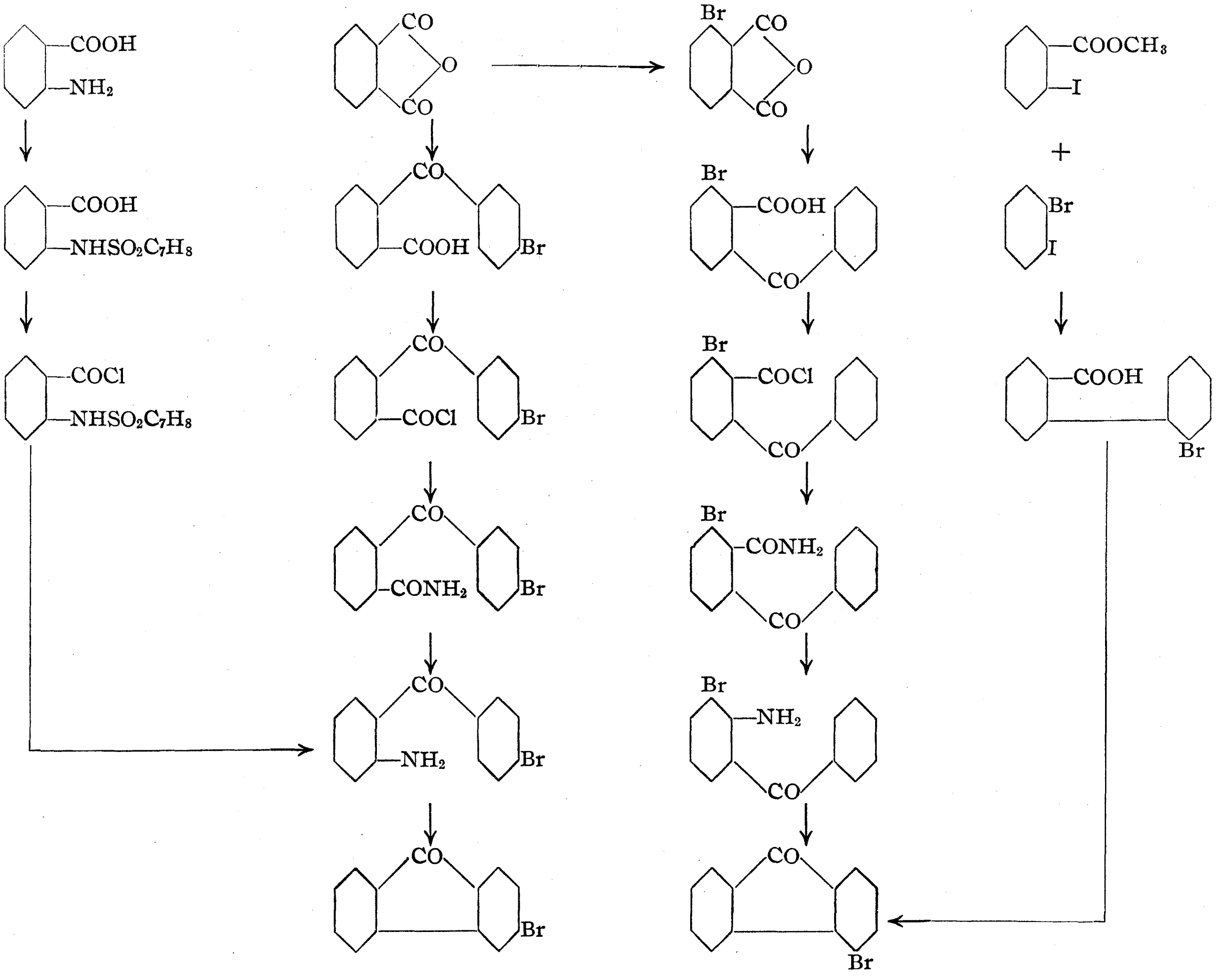
[5] (a) Ullmann and Mallett, *Ber.*, **31**, 1694 (1898); (b) Ullmann and Bleier, *ibid.*, **35**, 4273 (1902).

[6] Ullmann and Sone, *Ann.*, **380**, 337 (1911).

[7] Schroeter and Eisleb, *ibid.*, **367**, 111 (1909).

TABLE I

SYNTHESIS OF 3- AND 4-BROMOFLUORENONES



and 100 cc. of water. The mixture was cooled in an ice-bath and the amide paste added in small portions with vigorous stirring. Most of it dissolved. After standing for one hour in the cold, the solution was filtered, 5 cc. of ethanol added, and the mixture then boiled for one-half hour and allowed to stand for one day. The yellow amine crystallized in a cake and was filtered and dried. It melted at 107–108° and was pure enough for further synthesis. The filtrate was boiled with 20 cc. of saturated sodium bisulfite solution and on cooling deposited 1.5 g. of unchanged amide. On acidification, the second filtrate precipitated 3.9 g. of 2-(4-bromobenzoyl)-benzoic acid. The total yield of amine was 3.8 g. (82.5%, based on the amide used).

Second Procedure.—Fifty-three grams of 2-(4-toluenesulfonamido)-benzoyl chloride was refluxed with 100 g. of bromobenzene until solution took place. One hundred grams of anhydrous aluminum chloride was added to the cooled solution and the mixture warmed on the water-bath, gently at first, and then at the boiling point for eight hours. The mass was cooled, decomposed with ice, water and hydrochloric acid, the water layer decanted, and the pitch-like solid steam distilled to remove excess bromobenzene. The remaining dark solid sulfonamide was too insoluble to be purified by solution in alkali, therefore it was converted directly to the amine. This was done by dissolving the crude product in a mixture of 300 cc. of 90% sulfuric acid and 150 cc. of glacial acetic acid, heating for three hours on the water-bath, and then allowing to stand overnight. The solution was poured into 3 liters of water and filtered. The clear filtrate was neutralized cautiously with concentrated sodium hydroxide. On cooling, bright yellow needles of the amine, melting at 108°, formed. By treating the residue once more with sulfuric acid, as above, a further quantity of amine was obtained; total yield 12.9 g. (28% of theoretical).

Third Procedure. The Oesterlin Reaction.—Oesterlin[8] has proposed a general method for the conversion of carboxy acids into amines directly. In applying this reaction to 2-(4-bromobenzoyl)-benzoic acid the expected synthesis occurred to a very small extent only and the dimorph of the original acid was obtained as the principal product. Eight and seven-tenths grams of acid dissolved in 50 cc. of chloroform was treated with 50 cc. of concd. sulfuric acid, the temperature being maintained at 40–45°. To the mixture was then added in small portions 1.8 g. of

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[8] Oesterlin, *Z. angew. Chem.*, **45**, 536 (1932).

sodium azide. There was a vigorous gas evolution after each addition. The mixture was held at 40° for one hour and then poured into 600 cc. of cold water. The white solid which precipitated was filtered and dried. It weighed 7.3 g., melted at 158°, and proved to be the dimorph of the original acid. After resolidification it melted at 173° and was identical with the original acid. The yellow-colored filtrate was made alkaline with 10% sodium hydroxide. On standing 0.15 g. of 2-(4-bromobenzoyl)-aniline precipitated; yield 1.9%, m. p. 106–107°.

Anal. Calcd. for $C_{13}H_{10}OBrN$: Br, 28.95. Found: Br, 28.77.

3-Bromofluorenone.—To 5 g. of 2-amino-4-bromobenzophenone suspended in 50 cc. of water was added 4 cc. of concentrated sulfuric acid. The amine dissolved in the hot solution, but the amine sulfate quickly precipitated as a fine suspension. This suspension was cooled to 10° and diazotized with 1.3 g. of sodium nitrite in 3 cc. of water. The sulfate first dissolved and the solid diazo compound on warming gradually took on the yellow color characteristic of fluorenones, and, after standing for three hours, was filtered by suction, washed with water and then warmed with 5% sodium hydroxide solution in a beaker, with stirring. The solid was again filtered, washed well with water and air dried. Recrystallization from benzene gave light yellow needles, melting at 162°; total yield 4.3 g. (92% of theoretical).

Anal. Calcd. for $C_{13}H_7OBr$: Br, 30.73. Found: Br, 30.67.

The Synthesis of 4-Bromofluorenone

2-Benzoyl-6-bromobenzoyl Chloride.—To 7.8 g. of 2-benzoyl-6-bromobenzoic acid, prepared from bromophthalic anhydride, benzene and aluminum chloride according to the directions of Stephens,[9] were added 5.5 g. of phosphorus pentachloride and 25 cc. of benzene. The mixture was refluxed for forty-five minutes, then cooled, and 25 cc. of ligroin added. Light brown prisms of the acid chloride, m. p. 119–120°, separated; yield 7.1 g., 85.9%.

Anal. Calcd. for $C_{14}H_8O_2ClBr$: Br and Cl, 35.66. Found: Br and Cl, 35.70.

2-Bromo-6-benzoylbenzamide.—A mixture of 5 g. of 2-benzoyl-6-bromobenzoyl chloride and 15 g. of finely powdered ammonium carbonate was heated until gas evolution began. It was maintained at this temperature with stirring for ten minutes and then cooled. Water was added and the insoluble residue separated, dried and recrystallized from 150 cc. of xylene. The amide formed white matted needles, m. p. 135–140°; yield 4.2 g., 87%.

Anal. Calcd. for $C_{14}H_{10}O_2BrN$: Br, 26.20. Found: Br, 26.09.

2-Bromo-6-benzoylaniline.—Three grams of 2-bromo-6-benzoylbenzamide was subjected to the Hofmann degradation in a manner similar to that used in the preparation of 2-(4-bromobenzoyl)-anilines. On heating to boiling an oily yellow liquid separated which solidified on cooling. Recrystallization from alcohol gave 1.6 g. of the amine, m. p. 128–130°, a 57% yield. Acidification of the filtrate gave 0.8 g. of 2-bromo-6-benzoylbenzoic acid, formed by the hydrolysis of part of the amide.

Anal. Calcd. for $C_{13}H_{10}OBrN$: Br, 28.95. Found: Br, 28.76.

2-Bromo-2′-carboxydiphenyl.—A 500-cc., three-necked flask was fitted with a stirrer, an air condenser, and a 400° thermometer. Fifty-three grams of methyl-*o*-iodobenzoate and 56 g. of *o*-bromoiodobenzene were placed in the flask and the mixture heated to 260° in a Woods metal bath. Sixty grams of copper powder which had been treated as recommended by Kleiderer and Adams[10] was then added over a one-hour period to the vigorously stirred mixture, after which the temperature was raised to 290°, kept there for a further half hour, and then allowed to cool. The voluminous precipitate of copper iodide was extracted with two 150-cc. portions of boiling ethanol, which were combined and evaporated to 100 cc. This solution then was refluxed for eight hours with 500 cc. of 10% sodium hydroxide solution, and cooled. The water layer was filtered and acidified slowly with dilute acetic acid. A precipitate formed on standing which was filtered, redissolved in sodium hydroxide solution, and again precipitated as above with acetic acid. The product so obtained was recrystallized from 80% acetic acid to give 5.7 g. (14% yield) of 2-bromo-2′-carboxydiphenyl, white clumps, which darkened on standing, and melted at 186–187°.

Anal. Calcd. for $C_{13}H_9O_2Br$: Br, 28.84. Found: Br, 28.61.

The combined filtrates, on acidification with dilute hydrochloric acid, gave 15.6 g. of diphenic acid, m. p. 227°.

4-Bromofluorenone. First Procedure.—Two grams of 2-bromo-6-benzoylaniline was added with stirring to 20 cc. of 25% sulfuric acid. The amine sulfate immediately precipitated in a finely divided form. After cooling to 10° diazotization was effected with 1 g. of sodium nitrite dissolved in 3 cc. of water. The precipitate slowly changed to a lighter shade of color. The solution was allowed to warm up to room temperature, and after five hours' standing was heated to boiling. As soon as the precipitate clumped together and turned yellow, the mixture was cooled and the yellow solid filtered, and stirred into 50 cc. of 10% sodium hydroxide solution. The undissolved solid was filtered, washed with water several times, and dried. When recrystallized from benzene, 1.3 g. of 4-bromofluorenone, m. p. 185–187°, was obtained in the form of light yellow clumps. This corresponded to a 70% yield.

Second Procedure.—One gram of 2-bromo-2′-carboxydiphenyl was heated on a steam-bath with 40 cc. of concentrated sulfuric acid for one-half hour. The hot mixture was poured onto 500 cc. of ice and allowed to stand an hour with occasional stirring, after which the yellow solid was filtered with suction and air-dried. Recrystallization from benzene gave light yellow needles, melting at 190–191°; yield quantitative.

Anal. Calcd. for $C_{13}H_7OBr$: Br, 30.73. Found: Br, 30.61.

Summary

1. 3- and 4-bromofluorenones have been prepared by nuclear syntheses and their properties described.

COLUMBUS, OHIO RECEIVED SEPTEMBER 26, 1935

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[9] Stephens, THIS JOURNAL, **43**, 1950 (1921).

[10] Kleiderer and Adams, *ibid.*, **55**, 4225 (1933).

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

The Higher Benzenoid Hydrocarbons. III. The Isomeric Monobromo-9-fluorenols and Monobromofluorenes

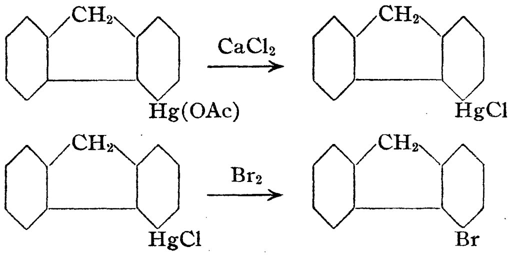
BY HARRY F. MILLER AND G. BRYANT BACHMAN

The reduction of the bromofluorenones with zinc dust and alcoholic ammonia leads to the formation of the corresponding bromo-9-fluorenols in excellent yields. However, the subsequent reduction of these bromofluorenols to bromofluorenes is not always readily accomplished because of the lability of the bromine atoms particularly in the 3-position. We found that with hydriodic acid and phosphorus 3-bromo-9-fluorenol yields fluorene only. Montagne and Moll[1] have also called attention to the ease with which the bromine in this position is removed on reduction with sodium amalgam in boiling alcohol. This lability is rather remarkable in view of the equally great stability of the bromine atom in the 2-position. It was shown previously[2] that 2-bromofluorene either does not yield a Grignard reagent or does so with unusual difficulty. Loevenich, Becker and Schröder[3] have shown that toward potassium phenolate and sodium acetate 2-bromofluorene is only about 50–75% as reactive as bromobenzene and is similar to meso-bromoanthracene in stability. The contrast between 2- and 3-bromofluorenes is reminiscent of the similar contrast in stability offered by 1- and 2-bromonaphthalenes.

Preparation of the bromofluorenes by direct reduction of the bromofluorenones by Clemmensen's method is highly satisfactory even in the case of 3-bromofluorene. Of the five possible monobromofluorenes only two, 2-bromofluorene[4] and 9-bromofluorene[5] have been prepared previously. In the present work 3- and 4-bromofluorenes have been obtained for the first time by reduction methods from the bromofluorenones described in the preceding paper.

Mercuration of Fluorene

Having once established the structure of the isomeric bromofluorenes by nuclear synthesis, it was decided to determine the position or positions in which fluorene mercurates, by heating the hydrocarbon with mercuric acetate and converting the product into one or more bromofluorenes as the case might be. As is well known, the entering mercuric group often attaches itself to a different position than that attacked by other reagents such as the halogens, nitric acid, sulfuric acid, etc. In the case of fluorene all of these latter reagents enter the 2-position first and the 7-position next, so that with bromine for example, the 2- and the 2,7-derivatives only are obtained by direct substitution. Goswami and Das-Gupta[6] report that fluorene reacts with mercuric acetate, but the structure of the product was not elucidated. We find that in the presence of acetic acid fluorene mercurates predominantly in the 4-position. In the absence of solvents some of the 3-isomer is also formed. By treatment of the product with alcoholic calcium chloride and subsequent bromination of the fluorene mercurichloride, good yields of 4-bromofluorene were obtained.



3-Bromofluorene was also prepared by this method.

An interesting point may be raised in view of the above results. Conant and Wheland[7] and others have offered the idea that in the reaction

$$RH + R'Na \longrightarrow RNa + R'H$$

the hydrocarbon RH may be regarded as a very weak acid, which is, however, relatively stronger than R'H for it is able to abstract Na from the salt R'Na. For instance, fluorene is a stronger acid than triphenylmethane, for it abstracts sodium from triphenylmethyl–sodium to form fluoryl-9-sodium. A whole series of compounds in the order of their acidities may be formed by

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(1) Montagne and Moll, *Rec. trav. chim.*, **32**, 164 (1913).

(2) Miller and Bachman, THIS JOURNAL, **57**, 766 (1935).

(3) Loevenich, Becker and Schröder, *J. prakt. Chem.*, **127**, 248 (1930).

(4) Courtot and Vignati, *Bull. soc. chim.*, [4] **41**, 58 (1927).

(5) Wanscherdt, *Ber.*, **59**, 2092 (1926).

(6) Goswami and Das-Gupta, *J. Ind. Chem. Soc.*, **8**, 475 (1931).

(7) Conant and Wheland, THIS JOURNAL, **54**, 1212 (1932).

such competitive reactions. Gilman[8] suggests further that if metalation is a function of relative acidities, then the most acid hydrogen atom in an aromatic compound is that replaced in the metalation reaction. Accordingly, he calls the hydrogen atom in the 4-position in dibenzofuran more acidic than those in the 2- or 3-positions. Such a statement is inapplicable to fluorene, for, if it were true, fluorene should mercurate in the 9-position. It is recognized that the hydrogen atoms in the methylene bridge are very active, as shown by many condensation reactions, by the fact that ethane is liberated from ethylmagnesium bromide to form fluoryl-9-magnesium bromide and by the fact that fluorene will form fluoryl-9-sodium by reaction with sodium triphenylmethyl. Gilman's hypothesis might be modified to state that mercuration may only determine the most acidic hydrogen atom on a truly aromatic hydrocarbon ring.

The Dibromo and Chlorobromofluorenes

By saturating alcoholic solutions of the bromo-9-fluorenols with hydrogen bromide or hydrogen chloride the corresponding *x*-9-dibromo- and *x*-bromo-9-chlorofluorenes were obtained. The properties of these and the other fluorene derivatives prepared are indicated in Table I. Further work on the preparation and reactions of the Grignard reagents of the isomeric bromofluorenes is now under way.

TABLE I

BROMO DERIVATIVES OF FLUORENE

Substance	Cryst. form	Yield, %	M.p., °C.	Anal. for halogen Calcd.	Anal. for halogen Found
2-Bromofluorenol[a]	Fluffy needles	97	130		
3-Bromofluorenol	White plates	85	142–145	30.62	30.45
4-Bromofluorenol	Feathery needles	92	149–150	30.62	30.57
2-Bromofluorene[a]	White plates	82	110		
3-Bromofluorene	Short needles	Quant.	90–91	32.61	32.51
4-Bromofluorene	Needles	80	165	32.61	32.49
2,9-Dibromofluorene	Fluffy needles	Quant.	107.5–108.5	49.34	49.32
3,9-Dibromofluorene	Matted needles	92	124–125	49.34	49.17
4,9-Dibromofluorene	Thick needles	83	194–195	49.34	49.22
2-Bromo-9-chlorofluorene[a]	Long needles	Quant.	102		
3-Bromo-9-chlorofluorene	Fluffy needles	87	116–117	41.28	41.08
4-Bromo-9-chlorofluorene	Matted needles	86	141–142	41.28	41.11

[a] Previously recorded in the literature.

Experimental

Reduction of Bromofluorenones to Bromofluorenols with Zinc and Alcoholic Ammonia.—The reduction of one isomer only will be described since the procedure in all other cases was similar.

Three and five-tenths grams of 4-bromofluorenone, 14 g. of zinc dust, 110 cc. of ethanol and 20 cc. of concentrated ammonium hydroxide were refluxed for one hour and filtered hot. Water was added to precipitate a gelatinous mass of 4-bromofluorenol. This was filtered by suction, pressed down well, and washed with 40% ethanol. After drying and recrystallizing from benzene, 3.2 g. of feathery white needles, m. p. 149–150°, was obtained, a 91.5% yield.

Reduction of Bromofluorenols to Bromofluorenes.—Although 2-bromofluorene is known, its preparation from the corresponding fluorenol has never been recorded.

One gram of 2-bromofluorenol, 1 g. of red phosphorus and 1 g. of iodine were refluxed for two hours in a solution of 20 cc. of glacial acetic acid and 2 cc. of water. The hot solution was filtered and added to 200 cc. of cold water containing 4 cc. of saturated sodium bisulfite solution. The white precipitate which formed was filtered after standing for one hour. Recrystallization from alcohol yielded a pure product melting at 110° alone or when mixed with an authentic sample of 2-bromofluorene. The material weighed 0.75 g., corresponding to an 82% yield.

Reduction of Bromofluorenones to Bromofluorenes.—One gram of 3-bromofluorenone and 20 cc. of ethanol were added portionwise over a three-hour period to a refluxing mixture of 7 cc. of concentrated hydrochloric acid, 3 cc. of water and 25 g. of amalgamated zinc. During this period 10 cc. of concentrated hydrochloric acid also was added portionwise. The mixture was refluxed three more hours, and the liquid portion decanted hot. The zinc was washed with two 5-cc. portions of hot ethanol, and the washings added to the main solution. On cooling short white needles formed, which were recrystallized from hot ethanol. Long white needles formed, melting at 90–91°. The yield was practically quantitative.

Preparation of *x*-9-Dibromofluorenes.—A solution of 3 g. of 3-bromofluorenol in 15 cc. of ethanol was saturated in the cold with dry hydrogen bromide. The mixture was stoppered tightly and left in the ice-bath, which was allowed to warm up overnight. Short stubby needles of 3,9-dibromofluorene formed which, after two days of standing, were filtered at the pump, washed with 50% alcohol, and dried. They melted at 124–125°. A second small crop was obtained by diluting the filtrate with water. The total yield was 3.1 g. (92%).

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[8] Gilman and Young, THIS JOURNAL, **56**, 1415 (1934).

Preparation of *x*-Bromo-9-chlorofluorenes.—Two grams of 4-bromofluorenol was dissolved in 10 cc. of ethanol and saturated in the cold with dry hydrogen chloride. The container was well stoppered and left in the ice-bath, which was allowed to come to room temperature. Unlike the other chlorides, this one precipitated first as an oil, and it was necessary to add a few drops of water to the mixture and place it in an ice-chest to induce it to crystallize. The white matty needles were filtered by suction, washed with 50% ethanol and recrystallized from benzene to give 1.94 g. of white needles melting at 141–142°, an 86% yield.

Mercuration of Fluorene in the Absence of a Solvent.—Eighty-three grams of fluorene was melted in a 2-liter round-bottomed flask and 159 g. of mercuric acetate added as soon as the temperature of the melt reached 125°. By means of an oil-bath the temperature of the melt was raised to 145°, at which point acetic acid began to distil (hood). The melt was held at this temperature for twenty-five minutes, at the end of which time the reaction had ceased, as indicated by the cessation of acetic acid fumes. The mixture was cooled to 110° and 500 cc. of glacial acetic acid added. The fluorene mercuriacetate went into solution easily. The solution was immediately treated with 2500 cc. of a saturated alcoholic calcium chloride solution. The mixed fluorene monomercurichlorides immediately precipitated in a voluminous mass, which was filtered hot and washed with glacial acetic acid, hot benzene, more glacial acetic acid, and finally with water. The air-dried white powder weighed 136 g., a 66% yield. However, 16 g. of pure fluorene was recovered from the filtrate, which raised the yield by difference to 81.4%. The product did not melt below 225°, and was shown to be a mixture of the 3- and 4-isomers in the ratio of approximately 3:1 by conversion of the mixture into the corresponding bromofluorenes and separating by recrystallization. The separation of the mixed mercurichlorides was not attempted due to their insolubility in all solvents tried.

The product obtained did not correspond with that of Goswami and Das-Gupta. These authors describe their unknown fluorene mercurichloride as a light pink solid melting at 130–132° with decomposition.

Bromination of the Mercurated Fluorene Mixture.—Eighty grams of the mixed mercurichlorides, obtained by mercuration of fluorene in the absence of a solvent, was suspended in 150 cc. of glacial acetic acid in a 500-cc. round-bottomed flask. Thirty-two grams of bromine in 25 cc. of glacial acetic acid was added with efficient stirring over a seven-hour period. The mixture was heated to boiling and filtered hot. Hydrogen sulfide was passed into the hot filtrate to remove dissolved mercury compounds, and the mixture was filtered again. As the filtrate cooled, a white crystalline precipitate slowly formed. This was removed by filtration and several more crops obtained by successive evaporation of the solvent. Each crop melted over a wide temperature range. The combined product totalling 35.4 g. (72.2% yield) was added to a mixture of 500 cc. of ligroin and 25 cc. of benzene. This mixture was boiled for five minutes and filtered hot, approximately two-thirds of the solid dissolving. On evaporation of the solvent a white waxy solid was obtained which was recrystallized from 75 cc. of glacial acetic acid. The 22.1 g. (45% yield) of white flaky material so obtained melted at 148–149°, and proved to be 4-bromofluorene. The ligroin insoluble portion was recrystallized twice from glacial acetic acid to give 7.2 g. (14% yield) of 3-bromofluorene, m. p. 88–94°.

Mercuration of Fluorene in Acetic Acid.—Eighty-three grams of fluorene, 159 g. of mercuric acetate and 250 cc. of glacial acetic acid were refluxed for twelve hours. A pink-colored solid settled out during the last six hours. The solution was filtered hot and 250 cc. of a saturated alcoholic calcium chloride solution added with stirring. A pink-colored precipitate formed immediately. This was filtered and washed with glacial acetic acid, hot benzene, glacial acetic acid and finally water. The color was not removed by this treatment. The solid after being air-dried weighed 40 g. (63% yield based on the fluorene used). The product melted at 235–240° with darkening at 165°. It was shown by bromination to be practically pure fluorene-4-mercurichloride.

Bromination of Fluorene-4-mercurichloride.—Forty grams of fluorene-4-mercurichloride suspended in 200 cc. of glacial acetic acid was brominated with 14.5 g. of bromine in 25 cc. of glacial acetic acid during an eight-hour period. The product was isolated as before. All of it melted from 145–148° and recrystallization from acetic acid gave white needles; m. p. 165°; yield 16.1 g. (66%). 4-Bromofluorene also crystallizes occasionally in white plates.

Oxidation of 3- and 4-Bromofluorenes.—In order to establish further the structure of the 3- and 4-bromofluorenes obtained through mercuration, they were converted into the corresponding bromofluorenones by oxidation with sodium dichromate and acetic acid. The products so obtained were identical with the bromofluorenones obtained in the preceding paper by ring closure methods.

Five and six-tenths grams of 4-bromofluorene and 16 cc. of glacial acetic acid were placed in a 120-cc. round-bottomed flask fitted for reflux. The mixture was brought to a vigorous boil and a hot mixture of 20 g. of technical sodium dichromate, 10 cc. of water and 28 cc. of glacial acetic acid was added by means of a dropping funnel over a one-half hour period, in such a manner that no lumps of unreacted material separated. After refluxing vigorously for three hours, the hot material was poured into 200 cc. of ice and water, allowed to stand for two hours, filtered by suction and washed, first with 4% sulfuric acid, and then several times with water. The air-dried material was dissolved in 15 cc. of benzene and left to crystallize. Five and nine-tenths grams (96%) of yellow needles of the ketone was obtained, melting at 185–187°.

Summary

1. The 2-, 3- and 4-monobromo-9-fluorenols and monobromofluorenes have been prepared by the reduction of the corresponding monobromofluorenones.

2. The monobromo-9-fluorenols have been converted into the corresponding *x*,9-dibromofluorenes and *x*-bromo-9-chlorofluorenes.

3. The mercuration of fluorene with mercuric acetate in the presence and in the absence of

a solvent has been studied. The preparation of 3- and 4-bromofluorenes from the resulting fluorene mercury derivatives has been described.

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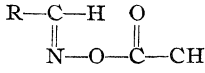
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

The Removal of Hydrogen and Acid Radicals from Organic Compounds by Means of Bases. II. The Removal of Acetic Acid from Acetyl-aldoximes by Alkalies

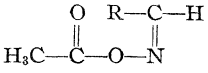
BY CHARLES R. HAUSER AND EARL JORDAN

As part of a general program on the removal of the elements of acids from organic compounds by means of bases it was of interest to study the removal of acetic acid from geometrically isomeric acetyl-aldoximes, (I) and (II).



$$\begin{array}{ccccc} R-C-H & & O & & \\ \| & & \| & & \\ N & -O- & C & - & CH_3 \end{array}$$

(I) *syn* (α)



$$\begin{array}{cccc} & O & & R-C-H \\ & \| & & \| \\ H_3C- & C & -O- & N \end{array}$$

(II) *anti* (β)

It is well known that in the presence of alkali one of these isomers eliminates acetic acid more readily than the other. Indeed, this reaction is used to distinguish a pair of geometrically isomeric aldoximes; the isomer whose acetyl derivative more readily forms nitrile is designated the β-, whereas the other is designated the α-isomer. Formerly, it was assumed that the unstable (β-) acetate had the *syn* configuration simply because the hydrogen atom and acetate group are in closer proximity in (I) than in (II); this view was based presumably on the assumption that the elements of acetic acid were removed simultaneously. At the present time, however, the unstable (β-) acetate is assigned the *anti* configuration (II), whereas the more stable (α-) isomer is assigned the *syn* (I). This view is based on a good deal of experimental evidence[1] accumulated during the past ten years. It is supported also on theoretical grounds on the basis of the hypothesis that, in the formation of nitrile, a proton is removed first by the action of alkali followed by the release of the acetate ion. According to Mills,[2] after the removal of a proton, the movement of the nitrogen nucleus to form the triple bond of the nitrile favors the release of the acetate ion, only in the case of the isomer with configuration (II). It should be pointed out also that the proximity of the acetate group to the hydrogen atom in (I) might offer some steric hindrance to the removal of the proton, thereby hindering the release of the acetate ion and formation of nitrile.

Although the reactions of acetyl aldoximes with alkalies have been studied extensively in connection with the determination of configurations of aldoximes there appears to have been relatively little quantitative work carried out under controlled conditions. In this investigation we have studied these reactions at definite temperatures and in most cases have isolated almost quantitative yields of products. The results are given in the following tables. The melting points of the crude products and those recorded in the literature are listed consecutively following the yields. In most cases the melting points of the crude products were either practically the same as those reported in the literature or were raised to these values after one recrystallization.

Discussion

It is often stated or implied in the literature that acetyl-α-, and acetyl-β-aldoximes react entirely differently toward alkali, that the α- give only oxime, and the β- only nitrile. Recently, however, it has been shown[3] that with sodium hydroxide certain acetyl-β-aldoximes give both nitrile and oxime, the yields of these products being dependent on the temperature, and now it has been found that at the temperature of the boiling water-bath at least certain acetyl-α-aldoximes with alkali give some nitrile in addition to the corresponding oxime.

It can be seen from Table I that, in general, acetyl-β-benzaldoximes with 2 *N* sodium hydroxide gave higher yields of oxime than nitrile at 0°, but greater yields of nitrile at 30°. These results confirm and extend those previously reported.[3]

In Table II are given the yields of products obtained from the reactions of certain acetyl-α-benzaldoximes with 2 *N* sodium hydroxide. It can be seen that at 61–64° the 2-nitro derivative

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[1] For review of evidence, see Freudenberg, *Stereochemie*, **7**, 974–979 (1933); Perkin and Kipping, "Organic Chemistry," Part III, 1934, pp. 661–663.

[2] Mills, *J. Soc. Chem. Ind.*, **51**, 755 (1932).

[3] Hauser and Sullivan, THIS JOURNAL, **55**, 4611 (1933).

TABLE I

PERCENTAGE YIELDS OF PRODUCTS FROM ACETYL-β-BENZALDOXIMES AND 2 *N* SODIUM HYDROXIDE

Acetyl derivative	Temp., °C.	Nitrile Yield, %	Nitrile M. p., °C. Obsd.	Nitrile M. p., °C. Lit.	Acid Yield, %	Acid M. p., °C. Obsd.	Acid M. p., °C. Lit.	Oxime Yield, %	Oxime M. p., °C. Obsd.	Oxime M. p., °C. Lit.	Total, %
4-Nitro-	0	38	139–140	147	13	228	238	45	164	184	96
4-Nitro-	30	1	126–127	147	57	232	238	27	158–160	184	85
3,4-Methylenedioxy-	0	33	85–88	94–95				66	143–145	146	99
3,4-Methylenedioxy-	30	48	93–94	94–95				38	130–132	146	86
4-Methoxy-[a]	0	25	56–57	60				71	131	133	96
4-Methoxy-[a]	30	41	53–54	60	25	180	184	25	61[c]	64	91
4-Methoxy-[b]	30	45	54–55	60	10	171	184	32	63[c]	64	87

[a] The previously reported[3] yields of products from this derivative were: at 0°, nitrile 25%, oxime 63%; at 30°, nitrile 55%, oxime 30%. [b] 0.48 *N* NaOH used. [c] On standing this oxime had changed to the α-isomer.

TABLE II

PERCENTAGE YIELDS OF PRODUCTS FROM ACETYL-α-BENZALDOXIMES AND 2 *N* SODIUM HYDROXIDE

Acetyl derivative	Temp., °C.	Nitrile Yield, %	Nitrile M. p., °C. Obsd.	Nitrile M. p., °C. Lit.	Acid Yield, %	Acid M. p., °C. Obsd.	Acid M. p., °C. Lit.	Oxime Yield, %	Oxime M. p., °C. Obsd.	Oxime M. p., °C. Lit.	Total, %
2-Nitro-	30				9	128–130	148	86	97–98	102	95
2-Nitro-	61–64	24	91–93	109–110	12	148	148	57	99–100	102	93
Blank	61–64				[3 gum]			[93	102	102]	[93]
4-Nitro-	30				2	205	238	95	130	133	97
4-Nitro-	97–100				16	237	238	76	128–129	133	92
Blank	97–100				[5	190–193	238]	[90	130–132	133]	[95]
3-Nitro-	30					Trace		96	122	123	96
3-Nitro-	97–100				11 gum			86	121–122	123	86
2-Chloro-	30				Trace	132	139	97	73–74	75–76	97
2-Chloro-	97–100				25	137	139	74	73–75	75–76	99
Blank	97–100				[5	137	139]	[94	74–75	75–76]	[99]
3,4-Methylenedioxy-	30				Trace			98	108–109	110	98
	97–100				5	220	228	94	108–109	110	99
Blank	97–100				[3	224	228]	[90	109–110	110]	[93]
4-Methoxy-	30				3	145–148	184	94	60–63	64	97
4-Methoxy-	97–100				10	180	184	87	62–64	64	97
Blank	97–100				[3	173–175	184]	[93	62–63	64]	[96]

TABLE III

PERCENTAGE YIELDS OF PRODUCTS FROM THE ACETYL DERIVATIVES OF α- AND β-3,4-$CH_2O_2C_6H_3CH{=}NOH$ AND ALKALIES AFTER CERTAIN TIME INTERVALS

Isomeric form	Alkali	Temp., °C.	Time, min.	Oxime Yield, %	Oxime M. p., °C. Obsd.	Oxime M. p., °C. Lit.	Nitrile Yield, %	Nitrile M. p., °C. Obsd.	Nitrile M. p., °C. Lit.	Recovered acetate Yield, %	Recovered acetate M. p., °C. Obsd.	Recovered acetate M. p., °C. Lit.
α	Aq. NaOH	0	6	4	105–107	110				95	105	105
β	Aq. NaOH	0	6	35	144–146	146	(60% of mixture of acetate and nitrile)					
α	Alc. NaOH	0	3	69	109–110	110						
β	Alc. NaOH	0	3	70	125–129	146						
α	Alc. NaOH	−8	3	53	109–110	110						
β	Alc. NaOH	−8	3	64	145–146	146						
α	Na_2CO_3 (aq. acetone soln.)	0	6	15	110	110						
α	Na_2CO_3 (aq. acetone soln.)	0	60 hrs.	75	109–110	110				13	105	105
β	Na_2CO_3 (aq. acetone soln.)	0	6	12	143–145	146						
β	Na_2CO_3 (aq. acetone soln.)	0	52 hrs.	30	144–145	146	63	92–93	94–95			

TABLE IV

PERCENTAGE YIELDS OF PRODUCTS FROM THE ACETYL-β-BENZALDOXIMES AND 10% AQ. Na_2CO_3

Acetyl derivative	Temp., °C.	Nitrile Yield, %	Nitrile M. p., °C. Obsd.	Nitrile M. p., °C. Lit.	Oxime Yield, %	Oxime M. p., °C. Obsd.	Oxime M. p., °C. Lit.	Total, %
3,4-Methylenedioxy-	0	75	92–93	94–95	21	145–146	146	96
3,4-Methylenedioxy-	30	88	92–93	94–95	9	134–135	146	97
4-Methoxy-	30	86	53–55	60	13	63[a]	64	99

[a] On standing this oxime had changed to the α-isomer.

TABLE V

PERCENTAGE YIELDS OF PRODUCTS FROM ACETYL-α-BENZALDOXIMES WITH 2 N $NaOC_2H_5$ IN ABSOLUTE C_2H_5–OH

Acetyl derivative	Acid Yield, %	Acid M. p., °C. Obsd.	Acid M. p., °C. Lit.	Oxime Yield, %	Oxime M. p., °C. Obsd.	Oxime M. p., °C. Lit.	Total, %
2-Chloro-	2	133	139	66	73–74	75–76	68
3,4-Methylenedioxy-	1	174	228	90	109–110	110	91
4-Methoxy-	Trace			91	63–64	64	91

PERCENTAGE YIELDS OF PRODUCTS FROM ACETYL-α-BENZALDOXIMES WITH 2 N NaOH IN 50% ALCOHOL

Acetyl derivative	Acid Yield, %	Acid M. p., °C. Obsd.	Acid M. p., °C. Lit.	Oxime Yield, %	Oxime M. p., °C. Obsd.	Oxime M. p., °C. Lit.	Total, %
2-Chloro-	3	124	139	94	75–76	75–76	97
3,4-Methylenedioxy-	2	220–221	228	97	109–110	110	99
4-Methoxy-	1	158–160	184	95	61–62	64	96

TABLE VI

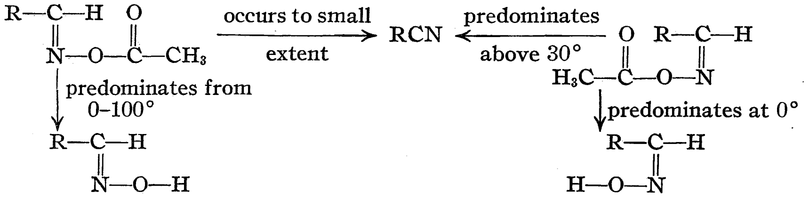
PERCENTAGE YIELDS OF PRODUCTS FROM ACETYL-α-BENZALDOXIMES WITH POTASSIUM AMIDE

Acetyl derivative	Nitrile Yield, %	Nitrile M. p., °C. Obsd.	Nitrile M. p., °C. Lit.	Acid Yield, %	Acid M. p., °C. Obsd.	Acid M. p., °C. Lit.	Oxime Yield, %	Oxime M. p., °C. Obsd.	Oxime M. p., °C. Lit.	Total, %
4-Methoxy-	47	145–147	162[a]	Trace	150–154	184	43	61–62	64	90
3-Nitro-	23	95–97	118	60 gum			8	108–112	123	31
2-Chloro-	80	42	42–43				9	66–68	75–76	89
Blank				[2	gum]		[88	74–75	75–76]	[88]
3,4-Methylenedioxy-	58	85–87	94–95	2	185–187	228	39	110	110	99
Blank				[1	192–193	228]	[96	110	110]	[97]

[a] The corresponding amide was obtained in this case.

gave some nitrile and acid in addition to the corresponding oxime, and at the temperature of the boiling water-bath several of the other acetyl-α-derivatives also gave appreciable yields of the acid. Even at 30° it has been possible to isolate small quantities of acid from the nitro derivatives. Although most of the yield of the carboxylic acid reported in each case in Table II was probably produced by the hydrolysis of the corresponding nitrile formed from the acetyl derivative by elimination of acetic acid, a small percentage of it was apparently produced, directly or indirectly, by a reaction of alkali with the α-oxime which was formed by the hydrolysis of the acetate. The yields of acid obtained from blanks determined with α-oximes are given in brackets in Table II. The actual yields of acid obtained from the acetyl derivatives through the intermediate formation of nitrile may be calculated by subtracting the blanks from the yields reported in this table. The small quantities of acid obtained from the oximes were probably also produced through the intermediate formation of nitrile formed from the oxime by elimination of water.

Since it is unlikely that these acetyl-α-derivatives rearranged[4] to the corresponding β-isomers previous to elimination of acetic acid, these results indicate that acetyl-α- and acetyl-β-benzaldoximes undergo fundamentally the same types of reaction with sodium hydroxide; they form oxime by hydrolysis and nitrile by elimination of acetic acid as represented by the scheme.



The yields of products in each case depend on the relative rates of the two competing reactions. It is obvious that with acetyl-β-aldoximes at 0° the hydrolysis proceeds more rapidly than the elimination of acetic acid, but at 30° or above, the elimination process is more rapid; whereas with the α-isomers,[5] the hydrolysis is more rapid than the elimination reaction even at 100°. At 30°, most acetyl-α-derivatives form an almost negligible yield of nitrile.[6] It is noteworthy that the elimination reaction apparently has a higher temperature coefficient than the hydrolysis.

The fact that at a given temperature the acetyl-β-aldoximes give much higher yields of nitrile, and correspondingly lower yields of oxime than

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(4) It should be pointed out that aldoximes tend to undergo the reverse change in alkaline solution. At 30° β-oximes are relatively stable but at the temperature of the boiling water-bath they are converted within a few hours to the α-isomers and corresponding carboxylic acids.

(5) There is a possibility that at 100° certain α-aldoxime acetates might give more nitrile than oxime.

(6) This is not the case, however, with certain carbethoxy-α-benzaldoximes; at 30°, the 2-nitro derivative gives a higher yield of nitrile than oxime (see following paper).

the α-isomers indicates, that the β-isomers eliminate acetic acid much more rapidly than the α-, or that the latter are hydrolyzed much more readily. Actually, β-3,4-methylenedioxybenzaldoxime acetate undergoes hydrolysis somewhat more rapidly than the corresponding α-isomer; therefore the β-derivative must eliminate the elements of acetic acid much more readily than the α-isomer in order to account for the much higher yield of nitrile produced. From Table III it can be seen that with aqueous[7] or alcoholic sodium hydroxide the β-acetate is hydrolyzed more rapidly than the α-isomer. The 64 and 70% yields of oxime obtained from the β-acetate after three minutes at -8 and 0°, respectively, correspond to practically complete decomposition of this derivative (see Table I). On the other hand, the α-acetate was only 53 and 69% decomposed under the same conditions.[8]

On the basis of the hypothesis proposed for the formation of nitrile it should be expected that the rate of removal of acetic acid from an acetyl aldoxime would be dependent on the activity of the aldehydic hydrogen atom and on the strength of the base used. The activity of the hydrogen atom is apparently dependent on at least two factors, (a) on polarity, as influenced by the presence of so-called negative atoms or groups, and (b) on a steric factor.

Since the acetate group and the aldehydic hydrogen atom are closer in a *syn* acetate (I) than in the *anti* isomer (II), it would appear that the relative unreactivity of the hydrogen atom in the former is at least in part due to a steric factor.

Of the *syn* (α-) acetates studied in this investigation, only the *o*-nitro derivative gave nitrile fairly readily (36% at 61–64°). It is probable that the greater yield of nitrile obtained in this case is due primarily to an increased rate of elimination of acetic acid rather than to a retarded hydrolysis, since the presence of the nitro group in *o*-nitrobenzalchlorimine ($RCH{=}NCl$) greatly facilitates the removal of hydrogen chloride by alkali.[9] Apparently the nitro group in the ortho position in both the aldchlorimine and the acetyl aldoxime greatly enhances the reactivity of the aldehydic hydrogen atom.

It was of interest to study the reactions of acetyl aldoximes with certain other alkaline reagents. Sodium carbonate has often been used instead of sodium hydroxide to distinguish α- and β-isomers;[10] the β- gives mostly nitrile, whereas the α- is either unattacked or is hydrolyzed to the corresponding oxime. Contrary to the results recently reported[11] it has now been found possible to isolate low yields of oxime in addition to high yields of nitrile from the reaction products of certain acetyl-β-benzaldoximes and sodium carbonate. These results are given in Tables III and IV. From Table III it can be seen that, similar to the results obtained with sodium hydroxide, β-3,4-methylenedioxybenzaldoxime acetate is hydrolyzed by excess sodium carbonate in aqueous acetone solution more rapidly than the corresponding α-isomer. After six minutes at 0°, approximately the same yields (12–15%) of oxime were obtained from both isomers. Since a 30% yield of oxime was obtained from the β-acetate on complete decomposition, the 12–15% yield of oxime obtained after six minutes corresponds to approximately 50% decomposition of the β-acetate. On the other hand, the α-acetate was only 12–15% decomposed under the same conditions.

It is to be observed that the yields of oxime obtained with sodium carbonate are much lower, and the yields of nitrile correspondingly higher, than those obtained with sodium hydroxide (see Table I). This rather striking fact suggests that the carbonate ion is capable of removing the elements of acetic acid from β-acetates to form nitrile, but has relatively little if any effect on the hydrolysis, whereas the hydroxyl ion brings about both reactions. The high concentration of carbonate ion and low concentration of hydroxyl ion in the carbonate solution would then cause the elimination reaction to proceed at a relatively rapid rate, and the hydrolysis at a relatively slow rate.

It seemed possible that acetyl-α-aldoximes might form considerable nitrile when treated with

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[7] A part of the difference in rate with aqueous sodium hydroxide might be due to a difference in solubility. Although the α-aldoxime acetate is more soluble in ether or benzene, the β-isomer appears to be more soluble in water. This is being studied.

[8] It is possible that certain α-aldoxime acetates might be hydrolyzed more rapidly than the corresponding β-isomers, but it is not likely that there would be any great difference in their rates.

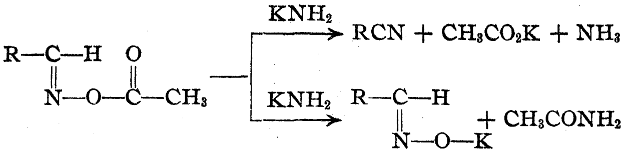
[9] The rates of removal of hydrogen chloride from $RCH{=}NCl$ by alkali in alcoholic solution are in general in the same relative order as the ionization constants of the corresponding acids (RCOOH). In this reaction nitrile is formed almost quantitatively. Hauser, LeMaistre and Rainsford, THIS JOURNAL, **57**, 1056 (1935).

[10] Brady has found that certain acetyl-β-aldoximes are relatively stable in sodium carbonate. See *J. Chem. Soc.*, **117**, 1045 (1920); **123**, 1800 (1923); **125**, 1419 (1924).

[11] It has usually been considered that acetyl-β-aldoximes with sodium carbonate give only nitrile. Also in a recent paper[3] it was reported that it was not possible to isolate oxime from the reaction products of certain acetyl-β-aldoximes and sodium carbonate.

sodium ethylate or potassium amide, which are stronger bases than sodium hydroxide. However, when certain acetyl-α-aldoximes were added to sodium ethylate[12] in absolute alcohol at the refluxing temperature, the sodium salt of the corresponding oxime precipitated almost immediately, very little acid being produced (see Table V). Apparently the rate of the reaction leading to the formation of the oxime (alcoholysis) was more rapid than the elimination reaction.

As was expected the reaction of potassium amide in liquid ammonia with acetyl-α-aldoximes formed considerable nitrile, in addition to the corresponding oxime. The yields of products are given in Table VI. It is probable that the reaction took place as represented by the equations



$$R{-}\underset{\displaystyle N{-}O{-}\underset{}{C}{-}CH_3}{\overset{}{C}}{-}H \quad (\overset{O}{\|}) \longrightarrow \begin{cases} \xrightarrow{KNH_2} RCN + CH_3CO_2K + NH_3 \\ \xrightarrow{KNH_2} R{-}C{-}H\ (=N{-}O{-}K) + CH_3CONH_2 \end{cases}$$

Evidently, the rate of removal of acetic acid from the α-acetate was more rapid than the reaction leading to the formation of oxime (ammonolysis).

Finally, it should be mentioned that the products of reaction of acetyl aldoximes with alkalies at 100° often had the isocyanide odor. However, it has not been possible to isolate an isocyanide; even attempts to obtain a positive test for an isocyanide failed. It is evident, therefore, that the reactions of an acetyl aldoxime with alkali yield not more than a trace if any of an isocyanide (which would be a rearrangement product), but form almost quantitative yields of the non-rearrangement products, nitrile, acid and oxime. According to the mechanism proposed for the formation of nitrile from an acetyl aldoxime, it should not be expected that the elimination of acetic acid would be accompanied by rearrangement of the molecule, since the negative fragment that is formed by the removal of a proton should be stabilized most readily by the release of acetate ion and shift of an electron pair, thus

$$\left(R:\ddot{C}::N:\underset{\cdot\cdot}{\ddot{O}}:Ac\right)^{-} \longrightarrow R:C:::\underset{\cdot\cdot}{N} + :\overset{-}{\underset{\cdot\cdot}{\ddot{O}}}:Ac$$

it should be expected that an electron pair would shift more readily than the group (R).

The Configuration of Aldoximes and their Acyl Derivatives.—In the determination of the configurations of aldoximes no difficulty should be encountered. However, both geometrical isomers should be isolated and their acetyl derivatives treated with alkali under the same conditions, preferably at about 30°. If only one isomer is known its configuration might be determined at least in some cases by comparing the alkaline decomposition products of its acetyl derivative with those of similarly constituted acetyl derivatives which are known in two isomeric forms. Although most acetyl α-benzaldoximes with sodium hydroxide even at the temperature of the water-bath give high yields of oxime and relatively little nitrile or acid, certain other acyl-α-derivatives produce considerable nitrile under the same conditions, and accordingly have been erroneously assigned the β-configuration. Certain of these are discussed in the following paper.

Experimental

Preparation of Acetyl Benzaldoximes.—The acetyl-α-benzaldoximes were prepared by a modification of the method of Brady and Dunn.[13] The pure α-oxime was dissolved in about equal weight of acetic anhydride and the solution allowed to stand at room temperature for five to ten minutes. Sufficient ice and sodium carbonate solution was then added to decompose the excess acetic anhydride and precipitate the α-acetate. The mixture was filtered through a Büchner funnel and the solid washed with cold water until free from the odor of acetic anhydride. After sucking the precipitate practically dry, the α-acetate was dissolved by pouring through the funnel small portions of acetone or alcohol. To this solution was added about 3 volumes of finely crushed ice and the mixture vigorously shaken. The α-acetate separated as small white crystals which were filtered off and dried. In most cases a pure product was obtained by this procedure in 70–80% yields. If the melting points were low, the compound was recrystallized.

The acetyl-β-benzaldoximes were prepared by the method recently described.[3]

Reaction of Acetyl Benzaldoximes with 2 *N* Sodium Hydroxide.—The reactions of acetyl-α-benzaldoximes were carried out usually at 30 ± 0.1° in a thermostat, and at 97–100° in a boiling water-bath; the reactions of the β-derivatives at 0° in an ice-bath and at 30°. The products were filtered through sintered glass crucibles of the Gooch type.

In general, a 1.0-g. sample of acetate was added to 15 cc. of 2 *N* sodium hydroxide which had previously been brought to the desired temperature. For the reactions at 97–100°, the samples were made into pellets and introduced into the hot solution through a short reflux condenser. After the reactions were complete (forty-five to ninety minutes at 97–100°, one to four days at 30° and two to

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[12] In this connection it is of interest to note that Segaller [*J. Chem. Soc.*, **103**, 1430 (1913)] found that more isobutylene was formed from tertiary butyl iodide in the presence of potassium hydroxide than in the presence of sodium ethylate under the same conditions.

[13] Brady and Dunn, *J. Chem. Soc.*, **103**, 1619 (1913).

seven days at 0°), the mixture was filtered and the solution extracted with ether. This procedure removed nitrile. The alkaline solution was then saturated with carbon dioxide to precipitate oxime. After filtering off the oxime and extracting the filtrate with ether, the aqueous solution was acidified with hydrochloric acid to precipitate carboxylic acid. This was filtered off and the solution extracted again with ether. These ether extracts were dried with sodium sulfate and evaporated in tared beakers. Even in cases where no precipitate formed, the solution was extracted with ether. The residue from the first ether extract contained small amounts of oxime and nitrile. These were separated by dissolving the oxime in a small amount of cold alkali. All products were dried, weighed, and their melting points taken. After recrystallization mixed melting points with authentic specimens were determined.

Relative Rates of Hydrolysis of the Acetyl Derivatives of α- and β-3,4-Methylenedioxybenzaldoximes

With Aqueous Sodium Hydroxide.—After a given time the reaction mixture of 15 cc. of 2 *N* sodium hydroxide and 1 g. of the acetate was filtered rapidly with suction and the filtrate saturated with carbon dioxide. The extent of hydrolysis was then calculated from the amount of oxime obtained.

With Alcoholic Sodium Hydroxide.—A 1-g. sample of the acetate was dissolved in 60 cc. of 80% alcohol at 0°, and the solution added to an equal volume of 1.3 *N* sodium hydroxide in the same solvent, also at 0°. After a certain time the solution was poured into an excess of acetic acid containing ice. Most of the alcohol was then quickly evaporated in an air draft and the mixture extracted with benzene, which in turn was extracted with 100 cc. of ice cold 1 *N* alkali to remove the oxime. The oxime was precipitated with carbon dioxide in the usual way. During the extraction of the benzene solution with alkali, a small amount of the unchanged acetate was hydrolyzed. Therefore the extraction process was standardized, each extraction being shaken ten times, using 100 cc. of 1 *N* sodium hydroxide at 0°. Under these conditions 80–90% of the free oxime in the benzene solution was extracted as the sodium salt, whereas when a 0.6-g. sample of either the α- or β-acetate in benzene solution was extracted with alkali under the same conditions only 3–5% of oxime was obtained. The yields of oximes reported in Table III are those obtained as described above minus this blank (3–5%).

In the experiments carried out at −0.8°, 1 g. of the acetate in 80 cc. of 95% alcohol was mixed with an equal volume of 0.6 *N* sodium hydroxide in 95% alcohol.

With Sodium Carbonate.—The sodium carbonate used in this work was prepared from pure sodium bicarbonate. A 1-g. sample of the acetate was dissolved in 60 cc. of acetone at 0°, and added with stirring to 250 cc. of a 2% aqueous sodium carbonate solution also at 0°. A slight turbidity was produced, but no precipitate was formed. After standing at 0° for a certain time the solution was poured into an excess of cold acetic acid and then extracted with benzene. The benzene solution was extracted with ice cold alkali. The oxime was precipitated from the alkaline solution in the usual manner. In cases where some unchanged acetate was present, blanks of 3–5% have been subtracted from the yields of oxime obtained. These are given in Table III.

Reaction of Acetyl-β-benzaldoximes with 10% Sodium Carbonate.—A 1-g. sample of the acetate was added to 15 cc. of a 10% aqueous sodium carbonate solution at 0 or 30°. After three to six days the solid was filtered off. When the filtrate was saturated with carbon dioxide and extracted with ether a very small amount of oxime was obtained. It was shown that the solid consisted mostly of nitrile mixed with a small amount of oxime. When cold sodium hydroxide was poured over the solid the oxime dissolved, leaving the nitrile in the funnel. The oxime was isolated by saturating the alkaline solution with carbon dioxide and extracting with ether.

In order to show that the oxime obtained in this manner had not been produced by the action of the sodium hydroxide on some unchanged acetate, the following experiment was carried out. The solid, obtained after filtering off the carbonate, was dissolved in benzene and the solution extracted with cold alkali. The yield of oxime obtained by saturating the alkaline solution with carbon dioxide was approximately the same as that obtained in the manner described above. It has been shown that even if as much as 0.6 g. of acetate in benzene solution is extracted with alkali in the manner employed yields of oxime of only 3–5% are obtained.

Reaction of Acetyl-α-benzaldoximes with Alkali in Alcoholic Solution.—A 1-g. sample of an acetate was introduced through a reflux condenser into 15 cc. of 2 *N* sodium ethylate in absolute alcohol at the refluxing temperature of the solution. The acetate reacted immediately, forming a precipitate of the sodium salt of the oxime. After refluxing for forty-five minutes the mixture was cooled and an equal volume of water added. After evaporating most of the alcohol in an air draft the products were isolated from the alkaline solution in the usual manner.

The experiment was repeated with 2 *N* sodium hydroxide in 50% alcohol.

Reaction of Acetyl-α-benzaldoximes with Potassium Amide in Liquid Ammonia.—The potassium amide in liquid ammonia was prepared[14] by suspending a rusty nail in a 2 *N* potassium solution in liquid ammonia until the blue color disappeared.

A 1-g. sample of an acetate was dissolved in a minimum of dry ether (20–50 cc.). To this solution was added with rapid shaking, about 50 cc. of the potassium amide solution of liquid ammonia. After the ammonia had evaporated cold water was added and the mixture extracted with ether. The nitrile was obtained by evaporation of the ether solution. The oxime and acid were isolated in the usual manner.

Summary

1. The products of the reactions of certain acetyl-β-benzaldoximes with 2 *N* sodium hydroxide have been determined at 0 and 30°. Both nitrile and oxime were formed at these temperatures, the yields of oxime in most cases predominating at 0°, and those of the nitrile at 30°.

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[14] See Bergstrom and Fernelius, *Chem. Rev.*, **12**, 59 (1933); and Coleman and Maxwell, THIS JOURNAL, **56**, 133 (1934).

2. The products of the reactions of certain acetyl-α-benzaldoximes with 2 N sodium hydroxide have been determined at 30 and 100°. Both nitrile (or the corresponding acid) and oxime were formed at 100°, and in certain cases, even at 30°. With the exception of the o-nitro derivative, the yields of oxime were much greater than those of the acid; at 30°, the yields of acid were extremely small.

3. It has been shown that β-3,4-methylenedioxybenzaldoxime acetate is hydrolyzed somewhat more rapidly than the corresponding α-isomer, but it is probable that there is no very great difference in these rates.

4. It has been concluded that α- and β-aldoxime acetates undergo fundamentally the same types of reaction with alkali; they form oxime by hydrolysis, and nitrile by elimination of acetic acid. They differ primarily in the ease with which they eliminate acetic acid, the β-isomers undergoing this reaction much more readily than the corresponding α-isomers.

5. These results are discussed on the basis of the hypothesis that the formation of nitrile from acetyl aldoximes consists of the removal of a proton by alkali, followed by the release of acetate ion.

6. It has been shown that in the presence of sodium carbonate certain acetyl-β-benzaldoximes give high yields of nitrile and low yields of the corresponding oxime.

7. It has been found that certain acetyl-α-benzaldoximes with potassium amide in liquid ammonia form both nitriles and oxime, the yields of nitrile being greater.

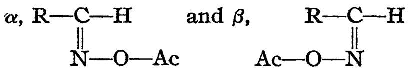
DURHAM, N. C. RECEIVED SEPTEMBER 11, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

The Reactions of Aldoxime Derivatives with Bases. II. The Reactions of Carbethoxy-α-benzaldoximes with Sodium Hydroxide

BY CHARLES R. HAUSER, EARL JORDAN AND RUTH O'CONNOR

In the previous paper[1] it has been shown that the acetyl derivatives of a pair of geometrically isomeric aldoximes



$$\alpha,\ \begin{matrix}\mathrm{R{-}C{-}H}\\ \|\\ \mathrm{N{-}O{-}Ac}\end{matrix}\qquad \text{and } \beta,\ \begin{matrix}\mathrm{R{-}C{-}H}\\ \|\\ \mathrm{Ac{-}O{-}N}\end{matrix}$$

undergo fundamentally the same types of reaction with sodium hydroxide; they form oxime by hydrolysis, and nitrile by elimination of acetic acid. They differ primarily in the ease with which they eliminate the elements of acetic acid, and therefore can be readily distinguished. At 30° the β-isomer gives a high yield of nitrile, whereas the α-isomer gives a high yield of oxime, with only a trace or a very small yield of nitrile. At the temperature of the boiling water-bath, however, certain acetyl-α-benzaldoximes[2] give considerable nitrile or corresponding acid, in addition to the α-oxime. Since the yields of products are dependent upon the relative rates of the two competing reactions it appeared not improbable that certain other acyl-α-derivatives might eliminate the elements of acid sufficiently rapidly, relative to their rates of hydrolysis, to give high yields of nitrile at ordinary temperatures, and if the acyl derivative is known in only one isomeric form it might readily be mistaken for the β-isomer. It seemed worth while therefore to reinvestigate the reactions of alkali with various acyl derivatives prepared from α-aldoximes, especially those that have been assigned the β-configuration. In this paper are reported the results obtained with carbethoxy derivatives, certain of which have been previously assigned the β-configuration.[3]

Experimental

Preparation of the Carbethoxy-α-benzaldoximes.—These compounds were prepared from the α-oxime in cold alkaline solution and ethyl chlorocarbonate (ethyl chloroformate), and recrystallized from acetone, alcohol and water according to the method of Brady and McHugh.[3] The yields were about 70%. The melting points of our

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[1] Hauser and Jordan, THIS JOURNAL, **57**, 2450 (1935).

[2] Acetyl-α-o-nitrobenzaldoxime gives 36% nitrile and acid even at 61–64°.

[3] Brady and McHugh [*J. Chem. Soc.*, **123**, 1190 (1923)] have reported that of fourteen carbethoxy derivatives prepared from α-aldoximes and ethyl chlorocarbonate, ten had the α-configuration, but, contrary to what was expected, four of them (2-nitro-, 4-nitro-, 4-methoxy- and 3,4-methylenedioxybenzaldoxime derivatives), appeared to have the β-configuration since nitrile (or acid) was obtained when they were heated with alkali on the water-bath. They point out that an explanation is required for the formation of β-derivatives from α-oximes in the presence of alkali, especially since, under the same conditions, β-oximes yield nitriles.

TABLE I

PERCENTAGE YIELDS OF PRODUCTS FROM CARBETHOXY-α-BENZALDOXIMES AND 2 *N* SODIUM HYDROXIDE

Carbethoxy derivative	*T*, °C.	Nitrile Yield, %	Nitrile Melting point, °C. Obsd.	Nitrile Melting point, °C. Lit.	Acid Yield, %	Acid Melting point, °C. Obsd.	Acid Melting point, °C. Lit.	Oxime Yield, %	Oxime Melting point, °C. Obsd.	Oxime Melting point, °C. Lit.	Total, %
Benzal-	30				2	110–111	121	92	Oil	35	94
Benzal-	97–100				8	118–120	121	74	Oil	35	82
2-Nitro-	0	30	104–105	109–110	7	120–122	148	34	101–102	102–103	71
2-Nitro-	30	8	108–109	109–110	67	138–139	148	17	101–102	102–103	92
3-Nitro-	30	2	98– 99	118	6	122–124	140	65	120–121	123	73
3-Nitro-	97–100				50	120–122	140	45	120–121	123	95
4-Nitro-	0	3	146–147	147	2	225–227	238	90	129–131	133	95
4-Nitro-	30				8	225–226	238	78	129–131	133	86
4-Nitro-	97–100	40	140	147	8	233–234	238	51	132–133	133	99
2-Chloro-	30				5	118–120	139	94	72– 74	75– 76	99
2-Chloro-	97–100	54	42– 43	42– 43	20	136	139	16	74– 75	75– 76	90
4-Chloro-	30				2	235	236	95	107–108	110	97
4-Chloro-	97–100	81	76– 78	92	2	215–217	236	16	105–106	110	99
2-Methoxy-	30					Trace		80	90– 91	92	80
2-Methoxy-	97–100				12	97–98	98.5	60	91– 92	92	72
4-Methoxy-	30				1	160–162	184	92	63– 64	64	93
4-Methoxy-	97–100				31	175–177	184	52	62– 63	64	83
3,4-Methylene-	30	3	166[a]	166				96	110	110	99
dioxy-	97–100				34	220–221	228	59	108–109	110	93

[a] The corresponding amide was obtained in this case.

TABLE II

PERCENTAGE YIELDS OF PRODUCTS FROM CARBETHOXY-α-BENZALDOXIMES AND POTASSIUM AMIDE IN LIQUID AMMONIA

Carbethoxy derivative	Nitrile Yield, %	Nitrile M. p. °C. Obsd.	Nitrile M. p. °C. Lit.	Oxime Yield, %	Oxime M. p., °C. Obsd.	Oxime M. p., °C. Lit.	Total, %
3-Nitro-	60	100–102	118	3	99–100	123	63
4-Methoxy-	70	53– 55	60	12	58– 60	64	82

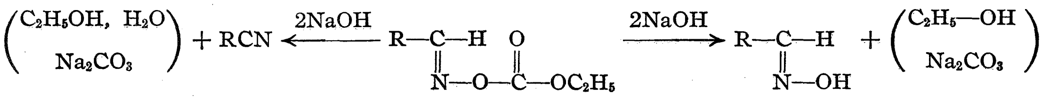
products were the same as those reported by Brady and McHugh. We were not able, however, to isolate the *p*-nitro derivative in two forms. Our product melted 108–109°, agreeing with that of the higher melting α-product reported by these earlier workers.

Reactions of Carbethoxy-α-benzaldoximes with 2 *N* Sodium Hydroxide.—A 1-g. sample of the carbethoxy-α-benzaldoxime was added to 15 cc. of 2 *N* sodium hydroxide at a definite temperature, and after the reaction was complete (usually two to seven days at 30° and one to two hours at 97–100°) the products were isolated according to the method previously used in the study of the reactions of acetyl-α-benzaldoximes with alkali.[1] The results are given in Table I. The melting points of the crude products and those recorded in the literature are listed consecutively following the yields. In most cases the melting points of the crude products obtained were either practically the same as those reported in the literature or were raised to these values after one recrystallization.

Reaction of Carbethoxy-α-benzaldoximes with Potassium Amide in Liquid Ammonia.—The reactions with potassium amide were carried out in a manner similar to that used in the study of the reactions of the acetyl-α-benzaldoximes with this reagent.[1]

Discussion

It can be seen from Table I that nitriles (or the corresponding acids) and α-oximes have been obtained from all of the carbethoxy derivatives. The fact that α-oximes[4] and not their β-isomers,[5] have been obtained by the hydrolysis of the carbethoxy derivatives, shows that these derivatives had also the α- or *syn*[6] configuration. Hence the reactions of carbethoxy-α-derivatives with alkali might be represented as follows



$$\left(\begin{matrix}C_2H_5OH,\ H_2O\\ Na_2CO_3\end{matrix}\right) + RCN \xleftarrow{2NaOH} \begin{matrix}R-C-H\quad O\\ \|\qquad\ \|\\ N-O-C-OC_2H_5\end{matrix} \xrightarrow{2NaOH} \begin{matrix}R-C-H\\ \|\\ N-OH\end{matrix} + \left(\begin{matrix}C_2H_5-OH\\ Na_2CO_3\end{matrix}\right)$$

It can be seen from Table I that at 30° the yields of oxime were much greater than those of

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(4) The configurations of these oximes have previously been established from a study of the reactions of alkali with their acetyl derivatives and with the acetyl derivatives of the corresponding β-isomers. See previous paper.[1]

(5) The hydrolysis of acetyl-β-aldoximes at 30° gives the corresponding β-oximes. The latter in alkaline solution are relatively stable at 30°. Therefore if the carbethoxy derivatives listed in Table I had had the β-configuration, the corresponding β-oximes should have been formed on hydrolysis.

(6) See previous paper[1] for references to the evidence supporting the view that the α-oximes and their derivatives have the *syn* configuration.

nitrile with the exception of the *o*-nitro derivative, which gave considerable nitrile even at 0°. At 97–100°, the yields of nitrile were higher than those obtained at 30°, and in several cases even greater than those of oxime. As with the acetyl derivatives, the elimination reaction appears to have a higher temperature coefficient than the hydrolysis.

It should be pointed out that the yields of nitrile obtained from these carbethoxy derivatives are higher, and those of oxime correspondingly lower, than those obtained from the analogous acetyl-α-aldoximes under the same conditions.[1] Evidently, a carbethoxy-α-aldoxime eliminates the elements of acid to form nitrile more readily, and/or undergoes hydrolysis less rapidly, than the corresponding acetyl-α-derivatives.

In Table II are given the yields of products obtained from the reactions of potassium amide in liquid ammonia with certain carbethoxy-α-derivatives. It can be seen that high yields of nitrile and low yields of oxime were produced.

Summary

1. The relative yields of nitriles and oximes formed in the reactions of carbethoxy-α-benzaldoximes with sodium hydroxide are a function of the temperature.

2. Contrary to the previously accepted view, that certain carbethoxy derivatives of α-benzaldoximes have β-configurations, it has been shown that they are all of the α-type.

3. The carbethoxy-α-benzaldoximes with sodium hydroxide give higher yields of nitrile, and lower yields of oxime, than the corresponding acetyl-α-benzaldoximes.

DURHAM, N. C. RECEIVED SEPTEMBER 11, 1935

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

Dehalogenation of β-Bromo Acids. IV. β-Bromophenylpyruvic Acid

BY BEN SOBIN AND G. BRYANT BACHMAN

In the present work an effort has been made to extend the β-bromo acid synthesis of olefin derivatives to the preparation of ketenes. It seemed probable from previous studies[1] that α-keto-β-bromo acids ought to dehalogenate predominantly as follows

$$\mathrm{RCHBrCOCOOH} \longrightarrow \mathrm{RCH{=}C{=}O} + \mathrm{HBr} + \mathrm{CO_2} \qquad (1)$$

in view of the strongly electronegative character of the α-carbonyl group. In order to test this hypothesis, β-bromophenylpyruvic acid was prepared and its dehalogenation studied under a variety of conditions.

The difficulty of selecting a suitable solvent and a suitable dehalogenating agent for the proposed study was immediately apparent, for no substance could be present at any time which would react with the ketene formed. This of course eliminated a good many common solvents and bases from consideration. At first sight, tertiary amines seemed ideally suited for the purpose both as solvents and as dehalogenating agents. When the reaction was tried, however, with pyridine and dimethylaniline the results were unsatisfactory. Carbon dioxide was evolved as expected but the products were tars which were apparently complex in nature and which contained no ketene.

An endeavor was next made to adapt the method to the synthesis of ketene derivatives. It was hoped that primary or secondary amines either in the presence or absence of other solvents would react to form substituted amides of phenylacetic acid. Here again, however, in addition to carbon dioxide only tars were obtained, and no evidence was found of the presence of simple ketene derivatives. Fortunately, we were able to secure decomposition in the desired manner by simply boiling the bromo acid with water. Carbon dioxide was evolved and phenylacetic acid in 77% yield was recovered from the solution. Furthermore, when an aqueous solution of the acid was shaken with silver oxide the same product was obtained in 94% yields. It is difficult to account for the product formed other than by assuming the intermediate formation of phenylketene which then reacted further with water to form phenylacetic acid.

$$\mathrm{C_6H_5CHBrCOCOOH} \longrightarrow \mathrm{C_6H_5CH{=}C{=}O} + \mathrm{HBr} + \mathrm{CO_2} \qquad (2)$$

$$\mathrm{C_6H_5CH{=}C{=}O} + \mathrm{H_2O} \longrightarrow \mathrm{C_6H_5CH_2COOH} \qquad (3)$$

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[1] Bachman, THIS JOURNAL, **55**, 4279 (1933); Farrell and Bachman, *ibid.*, **57**, 1281 (1935); Alberts and Bachman, *ibid.*, **57**, 1284 (1935).

The above reactions are remarkably sensitive to increases in the hydroxyl-ion content of the solution. With sodium carbonate solution no phenylacetic acid was formed and the principal product consisted of benzoylcarbinol.

$$C_6H_5CHBrCOCOOH \xrightarrow{Na_2CO_3} C_6H_5CHOHCHO + CO_2 + HBr \quad (4)$$

$$C_6H_5CHOHCHO \longrightarrow C_6H_5COCH_2OH \quad (5)$$

The spontaneous rearrangement of mandelic aldehyde to benzoylcarbinol (5) has been previously pointed out by Nef[2] and by others. Evans[3] has shown that benzoylcarbinol undergoes further decomposition in the presence of alkalies to form benzoic acid. This substance was also identified in the reaction product and increased in amount at the expense of the benzoylcarbinol upon prolonged boiling of the reaction mixture.

With sodium bicarbonate which is intermediate in basicity between water and sodium carbonate a 40% yield each of phenylacetic acid and benzoylcarbinol was obtained and a new product as yet unidentified made its appearance in small amounts. It was a bright yellow solid, m. p. 218–219°, which qualitative tests showed to be an alpha hydroxy acid of high molecular weight. It was but slightly soluble in most organic solvents.

In view of the reaction of bromophenylpyruvic acid with water it was decided to attempt the preparation of the ethyl ester of phenylacetic acid by reaction with alcohol. Accordingly a solution of the bromo acid in ethyl alcohol was boiled until no more carbon dioxide was evolved. The product after distillation and saponification yielded a little benzoic acid but no phenylacetic acid. Better success was obtained when an alcoholic solution of the bromo acid was treated with a half molal portion of silver oxide. From the filtrate a 36% yield of ethyl phenylacetate was obtained by distillation.

Further efforts to adapt the dehalogenation of α-keto-β-bromoacids to the synthesis of ketenes and their derivatives are being made.

Experimental

Preparation of β-Bromophenylpyruvic Acid.—To 55 g. of phenylpyruvic acid[4] suspended in 750 cc. of carbon tetrachloride was added slowly with stirring 54 g. of bromine. The solid product was filtered and allowed to stand for two days at the end of which time no more hydrogen bromide was being evolved. The yield was practically quantitative and the product melted at 103–104°. Recrystallization from benzene gave fine yellow needles with the same melting point.

Anal. Calcd. for $C_9H_7O_3Br$: Br, 32.84. Found: Br, 32.84, 32.86.

Conversion of β-Bromophenylpyruvic Acid to Phenylacetic Acid.—Four grams ($^1/_{60}$ mole) of the bromo acid in 50 cc. of water was refluxed one-half hour and the filtered solution extracted with ether several times. The extract yielded 1.3 g. of a product which, after recrystallization from petroleum ether, melted at 76° and was confirmed as phenylacetic acid by a mixed melting point with an authentic sample; yield 77%.

In a similar experiment 2.0 g. of bromo acid dissolved in 50 cc. of water was shaken with 0.9 g. of silver oxide and finally warmed on the steam-bath. After removal of the silver bromide a 94% yield of phenylacetic acid was recovered from the filtrate.

Conversion of β-Bromophenylpyruvic Acid to Ethyl Phenylacetate.—To 24 g. of the bromo acid in 200 cc. of absolute alcohol was added portionwise 11.5 g. of silver oxide. At the end of the initial reaction the mixture was filtered and the filtrate distilled. There was obtained 6 g. (36% yield) of a product (b. p. 120–130° at 20 mm.) which upon saponification yielded phenylacetic acid.

Reaction of β-Bromophenylpyruvic Acid with Other Reagents.—With Aqueous Sodium Carbonate.—A solution of 24 g. of the bromo acid in 40 cc. of 25% sodium carbonate was refluxed for one-half hour. Upon cooling and extracting with ether 5.0 g. of benzoylcarbinol, m. p. 85°, was obtained. The identity of this substance was confirmed by oxidizing it to mandelic acid, m. p. 118°, with cupric acetate by the method of Evans.[3]

The alkaline solution from which the benzoylcarbinol had been extracted was then acidified with dilute hydrochloric acid, extracted with ether, and the ether evaporated. The thick oil which remained was extracted with petroleum ether. Evaporation of the petroleum ether left 3 g. of benzoic acid, m. p. 121°. The amide was also prepared for confirmation and melted at 128°.

With Aqueous Sodium Bicarbonate.—Four grams of the bromo acid was gradually added to 3.5 g. of sodium bicarbonate dissolved in 41 cc. of water, and allowed to stand overnight. Extraction of the alkaline solution with ether, and subsequent evaporation of the ether left 0.5 g. (40% theoretical) of benzoylcarbinol. The solution was then acidified with dilute hydrochloric acid and extracted with ether. Evaporation of the ether left a yellow gummy solid. The solid was extracted with boiling petroleum ether for an hour, and yielded in this way 0.9 g. (40% theoretical) of phenylacetic acid. The yellow residue from the extraction was difficultly soluble in hot benzene, from which on cooling it crystallized as very fine yellow needles. When dry, the powder was found to be highly electrophoric, and to have a melting point of 218–219°. Qualitative tests showed it to be an acid. It gave a yellow color with ferric chloride indicating the presence of an hydroxyl group alpha to a carbonyl. An alcoholic solution decolorized bromine water and potassium permanganate solution. It did not give a phenylhydrazine test. However, it reacted with acetyl chloride to give a derivative melting at 162–163°. The neutralization equivalent was

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[2] Nef, *Ann.*, **355**, 247 (1907).

[3] Evans, THIS JOURNAL, **35**, 125 (1906).

[4] Hemmerlé, *Ann. chim.*, [9] **7**, 229 (1917).

found to be 181 and the molecular weight as determined by the melting point depression of naphthalene as 373. Evidently there were two carboxyl groups in the molecule. The compound was analyzed for carbon and hydrogen. *Anal.* C, 73.1, 73.3; H, 4.4, 4.4. From the carbon and hydrogen analysis and the molecular weight determination the molecular formula of the yellow compound was calculated to be most probably $C_{23}H_{16}O_5$.

With Nitrogen Bases.—Portions of the bromo acid were treated in turn with anhydrous pyridine, aniline, dimethylaniline and diethylamine. In all cases an evolution of carbon dioxide resulted, and considerable heat was evolved. All three amines gave tarry and gummy masses from which the reaction products could not be isolated. With aqueous ammonium hydroxide a dark brown solution was obtained which yielded a little benzoylcarbinol by extraction with ether. Upon acidification a tar precipitated which was almost insoluble in most organic solvents.

Summary

1. The dehalogenation of β-bromophenylpyruvic acid has been studied under a variety of conditions. Evidence has been obtained for the intermediate formation of phenylketene under certain of the above conditions.

2. The possibilities and some of the difficulties of utilizing the dehalogenation of α-keto-β-bromo acids as a new method of synthesis of ketene derivatives have been pointed out.

COLUMBUS, OHIO RECEIVED SEPTEMBER 19, 1935

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

Reactions between Organomercury Compounds and Nitrosyl Compounds[1,2]

BY LEE IRVIN SMITH AND F. LOWELL TAYLOR

The reactions between nitrosyl compounds and organomercury compounds were discovered by Baeyer,[3] who first prepared nitrosobenzene by the action of nitrosyl bromide upon diphenylmercury.[4]

Bamberger[5] studied the reactions between nitrogen oxides and bis-arylmercury compounds. Apparently, he concluded that the action of nitrogen sesquioxide upon organomercury compounds was entirely different from that of nitrogen dioxide. He represented the reaction between nitrogen dioxide and diphenylmercury by equation (1).

$$(C_6H_5)_2Hg + N_2O_4 \longrightarrow C_6H_5HgNO_3 + C_6H_5NO \quad (1)$$

Despite the fact that he also obtained a small quantity of nitrosobenzene by the action of nitrogen sesquioxide, Bamberger represented the reaction between the sesquioxide and diphenylmercury by equation (2).

$$(C_6H_5)_2Hg + 2N_2O_3 \longrightarrow C_6H_5HgNO_3 + C_6H_5N_2NO_3 \quad (2)$$

He ascribed the formation of the nitrosobenzene to the action of nitrogen dioxide formed by dissociation of the sesquioxide. Moreover, nitric oxide did not act upon diphenylmercury, but did act upon nitrosobenzene, *o*-nitrosotoluene, and *p*-bromonitrosobenzene. The corresponding diazonium nitrates were formed (equation 3).

$$C_6H_5NO + 2(NO) \longrightarrow C_6H_5N_2NO_3 \quad (3)$$

In the present work it was found that nitrogen sesquioxide, nitrogen dioxide, and nitrosyl chloride formed nitroso compounds by their action upon organomercury derivatives of polymethylbenzenes. The nitroso group replaced the mercury, which was removed as an inorganic salt. Equations (4) and (5) express the reactions in general forms, where NOX denotes the nitrosyl compounds.[6]

$$R_2Hg + NOX \longrightarrow RHgX + RNO \quad (4)$$
$$RHgX + NOX \longrightarrow HgX_2 + RNO \quad (5)$$

A diazonium nitrate was formed only when a mixture of nitrogen sesquioxide and excess nitric oxide was allowed to act upon a mercury compound. It seemed, then, that the primary reaction (5) between nitrogen sesquioxide and the arylmercury compound was accompanied by a

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[1] Polymethylbenzenes. XIV. Paper XIII, THIS JOURNAL, **57**, 2370 (1935).

[2] Abstracted from the thesis of F. L. Taylor, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the Ph.D. degree, March, 1935.

[3] Baeyer, *Ber.*, **7**, 1638 (1874).

[4] Gilman and Wright [THIS JOURNAL, **55**, 3302 (1933); **56**, 1415 (1934)] treated 2-chloromercurifuran with nitrosyl chloride, but did not isolate a product from the reaction.

[5] E. Bamberger, *Ber.*, **30**, 506 (1897); **32**, 3546 (1899); Kunz, *ibid.*, **31**, 1528 (1898).

[6] If conclusions as to the structures of nitrogen oxides are valid when based upon their reaction products, nitrogen sesquioxide is nitrosyl nitrite and the dioxide is nitrosyl nitrate. See, Wieland, *Ann.*, **328**, 154; **329**, 225 (1903); **340**, 63 (1905); **424**, 71 (1921); *Ber.*, **53**, 210, 1343 (1920); **54**, 1776 (1921); Battegay *et al.*, *Bull. soc. chim.*, **41**, 1336 (1927); **43**, 109 (1928); Reihlen and Hake, *Ann.*, **452**, 47 (1927); Schaarschmidt *et al.*, *Ber.*, **57**, 32, 2065 (1924).

secondary reaction (3) between nitric oxide and the nitroso compound.[7]

The yields which were obtained in preparation of the mercury compounds described in the previous paper and in preparation of the nitroso compounds were sufficient to make the reactions satisfactory for synthesis of the compounds in quantity. The most convenient procedure made use of the reaction between organomercury compounds and nitrosyl chloride. Nitrosyl chloride was prepared in the reaction mixture from ethyl nitrite.[8] Nitrosopolymethylbenzenes are valuable intermediates for preparation of the amino methylbenzenes because the mono-nitro compounds cannot be prepared by direct nitration of the hydrocarbons.[9] The nitroso compounds were characterized by conversion to the known amines and acetamines. Nitrosomesitylene[10] and 5-nitrosopseudocumene[11] were known previously. Both forms of 5-nitrosopseudocumene, the green, labile form, m. p. 45–46°, and the white form, m. p. 65°, were isolated. Nitrosoprehnitene, which has a structure very similar to that of nitrosopseudocumene, was isolated only in a green, stable form, m. p. 72°. The other nitroso compounds resembled nitrosomesitylene in that their melting points were high and their solutions were colorless, or yellow, in the cold but green when dilute or warm. The new nitroso compounds are listed in the table with their melting points and analytical data.

The action of nitric acid upon arylmercury compounds usually causes replacement of the mercury by a nitro group, although the replacement is probably not direct.[4,12] Under certain conditions, nitration of the aryl group in arylmercury compounds may occur without destruction of the carbon–mercury bond.[13]

Nitric acid of specific gravity 1.26 formed nitrodurene and nitroisodurene by action upon the corresponding acetoxymercurimethylbenzenes. Probably the nitroso compounds were formed as intermediates. Nitrodurene and nitroisodurene were prepared also by oxidation of the nitroso compounds with nitric acid (sp. gr. 1.26). The substances are listed in the table.

TABLE I

NITROSO- AND NITRO-POLYMETHYLBENZENES

				Analyses, %			
				Carbon		Hydrogen	
Substance	Yield, %	M. p., °C.	Formula	Calcd.	Found	Calcd.	Found
Nitrosopentamethylbenzene	80	160[a]	$C_{11}H_{15}NO$	74.52	74.2	8.54	8.42
Nitrosodurene	81	160[a]	$C_{10}H_{13}NO$	73.57	73.3	8.03	8.16
Nitrosoisodurene	61	134	$C_{10}H_{13}NO$	73.57	71.5[b]	8.03	7.9[b]
Nitrosoprehnitene	70	72	$C_{10}H_{13}NO$	73.57	73.3[b]	8.03	8.0[b]
Nitrodurene	40	112–113	$C_{10}H_{13}NO_2$	67.00	67.1	7.32	7.49
Nitroisodurene		39	$C_{10}H_{13}NO_2$	67.00	66.7	7.32	7.41

[a] Decomposition, rapid heating; slow heating, m. p. 152–155°. [b] Average of several concordant analyses.

Experimental Part

A. Preparation of Nitrosopolymethylbenzenes

1. **General Method.**—The acetoxymercuri polymethylbenzene (20 g.) was dissolved in chloroform (100 cc.); the solution was cooled in an ice-bath and stirred mechanically. Ethyl nitrite (5 cc.; 1 + mole)[14] was added; this was followed by addition, in one portion, of a mixture of hydrochloric acid (15 cc. concd.; 3 moles) and acetic acid (20 cc.). The fresh precipitates of arylmercuric halides reacted quickly with nitrosyl chloride. The reaction mixtures were stirred for fifteen minutes to one hour. The procedures for isolation of the products are described separately.

2. **Nitrosopentamethylbenzene.**—The reaction mixture was washed with water (mercury salt recovered) and filtered. The precipitate was crude nitroso compound (4.5 g.). The green filtrate, evaporated to 40 cc. and cooled, deposited an additional 4 g. of nitroso compound. The substance was crystallized from chloroform; needles, m. p. 160°; yield, 80%. The melting (decomposition) point depended upon the rate of heating.

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(7) Since nitrosopolymethylbenzenes were formed by the action of either nitrogen sesquioxide or dioxide, it was concluded that the nitrosobenzene found by Bamberger was probably the primary product, and that the diazonium nitrate was formed from nitrosobenzene by the action of nitric oxide (equation 3) which resulted from dissociation of the sesquioxide. If the reaction between nitric oxide and nitrosobenzene were much faster than the reaction between nitrogen sesquioxide and diphenylmercury (equation 4), then most of the nitroso compound would be converted to the diazonium nitrate which Bamberger found. Apparently, the reactivity of mercury derivatives of benzene hydrocarbons toward nitrogen sesquioxide increases with the number of methyl groups attached to the ring; the reverse is true of the nitroso derivatives.

(8) O. Wallach, *Ann.*, **253**, 251 Anm. (1889).

(9) Willstätter and Kubli, *Ber.*, **42**, 4151 (1909); Töhl, *ibid.*, **21**, 904 (1888); see also the previous papers in this series.

(10) (a) V. Pechmann and Nold, *ibid.*, **31**, 561 (1898); (b) Bamberger and Rising, *ibid.*, **33**, 274, 3632 (1900).

(11) Bamberger, *ibid.*, **43**, 1842 (1910).

(12) Hanke, THIS JOURNAL, **45**, 1321 (1923); Dreher and Otto, *Ber.*, **2**, 542 (1869); *Ann.*, **154**, 93 (1870); Henry and Sharp, *J. Chem. Soc.*, 2432 (1926).

(13) Challenger and Rothstein, *ibid.*, 1258 (1934); see also Whitmore and Culhane, THIS JOURNAL, **51**, 602 (1929).

(14) Prepared by the method of Wallach, ref. 8.

Reduction of the nitroso compound by stannous chloride in alcohol and hydrochloric acid gave 6-aminopentamethylbenzene, m. p. 151°; reported m. p. 151–152°[15] and 151°.[16] The amine was acetylated by acetic anhydride. The melting point of acetaminopentamethylbenzene was 211°; reported, m. p., 213°[15] and 212–213°.[16]

3. Nitrosodurene.—The chloroform solution was extracted with water, warmed to dissolve all the product, extracted three more times, treated with 10 cc. of methanol, filtered, concentrated to 50 cc. by distillation, and cooled. The pure white, crystalline product changed to a powder when it was dried in air; m. p. 160° (decomposition, rapid heating); yield, 73%.

The melting point of crude aminodurene obtained by reduction of nitrosodurene was 74–75°. The reported melting points are 75°;[16] after sublimation, 72–73°.[17] The amine was crystallized from 60% methanol; the product, m. p. 71°, was analyzed.

Anal. Calcd. for $C_{10}H_{15}N$: C, 75.40; H, 10.13. Found: C, 75.23, 76.20; H, 9.48, 9.24.

The melting point of acetaminodurene was 207–208°; reported m. p. 207°.[16]

4. Nitrosoisodurene.—After the chloroform solution was washed, it was concentrated to 40 cc., treated with 40 cc. of methanol, distilled until a precipitate formed, cooled and filtered. The melting point of the product was 132°; yield, 61%.

For analysis, 1 g. of nitrosoisodurene was crystallized from 15 cc. of methanol and 5 cc. of benzene. The crystalline product, m. p. 137°, was dried in vacuum for five hours at 55°. It changed to a powder, m. p. 134°. Analyses gave values for carbon which were 2% low. However, when reduced, a liquid amine was formed; reported melting point of aminoisodurene, 14°[18a] and 23–24°.[18b] The melting point of acetaminoisodurene was 215°; reported m. p. 215°,[18b] 210–211°,[19a] 216°,[19b] and 214–215°.[15]

When 1 g. of nitrosoisodurene, m. p. 132°, was crystallized from methanol (10 cc.) and chloroform (3 cc.) the melting point of the product (dried over sulfuric acid) was 138°.

Anal. Found: C, 67.42, 67.35; H, 7.51, 7.54. Calcd. for $C_{10}H_{13}N + CH_3OH$: C, 67.64; H, 8.78.

The compound was not characterized; it was probably an addition product. In solution it behaved as nitrosoisodurene.

5. Nitrosoprehnitene.—The chloroform solution was washed, excess methanol was added, and the solution evaporated nearly to dryness to remove all of the chloroform. The methanol solution was cooled and filtered; the melting point of the product was 72°, yield 35%. Crude material (35%) was obtained from the filtrate. Nitrosoprehnitene (0.7 g.) was crystallized from 3 cc. of methanol and dried over sulfuric acid, m. p. 72°; when dried in vacuum for six hours at 55°, the melting point was 72°. The green solid did not change color during several months.

Reduction formed aminoprehnitene, m. p. 64–65°; reported m. p. 64–66°,[18b] and 70°.[20] The melting point of acetaminoprehnitene was 170–171°; reported m. p. 169.5°[18b] and 172°.[20]

6. Nitrosomesitylene.—The solvent was washed, excess methanol added, and the solution evaporated until the chloroform was removed. The final mixture (75 cc.) was cooled and filtered. The melting point of nitrosomesitylene was 121–122°; yield, 90%; reported m. p. 122°[10b] and 129°.[10a]

7. Nitrosopseudocumene.—The crude substance was obtained by evaporation of the solvent; yield, 68%. The melting point of the green form was 44°; of the white form, 64–65°; recorded m. p., green, 45–46°; white, 65°.[11]

B. Reactions between Nitrogen Oxides and Mercury Compounds

1. Preparation of the Nitrogen Oxides.—The red oxides of nitrogen were prepared by the reaction between nitric acid and copper, in an all-glass apparatus which was connected directly to a reaction flask through the hollow mechanical stirrer.

(a) **Nitrogen Sesquioxide.**—The red oxides were treated with dry nitric oxide until the condensate was converted to blue sesquioxide; the oxide was dried by phosphorus pentoxide.

(b) **Nitrogen Dioxide.**—Dry oxygen was used to oxidize the red oxides to the light yellow dioxide; the dioxide was dried by phosphorus pentoxide.

(c) **Nitric oxide** was prepared from sodium nitrite by the method of Noyes,[21] and dried by passing it through a train of concentrated sulfuric acid and phosphorus pentoxide.

2. Nitrogen Sesquioxide and Acetoxymercuriisodurene.—Acetoxymercuriisodurene (15 g.) was dissolved in 125 cc. of absolute chloroform and the solution was kept at −10°. Nitrogen sesquioxide was distilled into the solution. A voluminous white precipitate (I) formed and then dissolved and left a brown precipitate (II). The precipitate was removed by filtration (filtrate III), washed with absolute chloroform, and dried at 60°; weight 7 g. The material was almost completely soluble in water. The solution contained mercuric and nitrite ions. Values for mercury content of the solid varied from 59 to 70%; calcd. for mercuric nitrite, 68.5% mercury. The substance was evidently impure mercuric nitrite.

The filtrate (III) was treated as described in part A 4. The product was nitrosoisodurene, m. p. 125°; weight, 4 g. (64%).

The white precipitate (I) was removed (in a separate experiment), washed with absolute chloroform, and dried in a desiccator. Values for mercury content were 54 and 58%; calculated for $C_{10}H_{13}HgNO_2$, 52.8%. The substance was probably nitritomercuriisodurene contaminated with mercuric nitrite.

3. Nitrogen Dioxide and Acetoxymercuriisodurene.—The experiment was performed as described in part 2;

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[15] A. W. Hofmann, *Ber.*, **18**, 1822 (1885); Smith and Paden, This Journal, **56**, 2171 (1934).

[16] Willstätter and Kubli, *Ber.*, **42**, 4162 (1909).

[17] Smith and Tenenbaum, private communication.

[18] (a) A. W. Hofman, *Ber.*, **17**, 1913 (1884); (b) Limpach, *ibid.*, **21**, 644 (1888).

[19] (a) Noelting and Baumann, *ibid.*, **18**, 1149 (1885); (b) Liebermann and Kardos, *ibid.*, **47**, 1575 (1914).

[20] Töhl, *ibid.*, **21**, 905 (1888).

[21] W. A. Noyes, This Journal, **47**, 2170 (1925).

dioxide was used instead of sesquioxide. Crude nitrosoisodurene was obtained, m. p. 123°; yield, 4.5 g. (72%).

C. Preparation of Nitrodurene and Nitroisodurene

Oxidation of Nitrosodurene.—A mixture of 2 g. of nitrosodurene and 40 cc. of nitric acid (sp. gr. 1.26) was heated to 70° and shaken for ten minutes. The material was dissolved and nitrogen oxides were evolved. The solution was cooled immediately, poured into 100 cc. of ice and water, and filtered. The product was crystallized from 14 cc. of alcohol; pale yellow prisms, m. p. 112–113°; yield, 0.87 g. (40%). Reduction of nitrodurene formed aminodurene, m. p. 71°.

Acetoxymercuridurene and Nitric Acid.—The mercury compound (11.8 g.) was heated and shaken with 120 cc. of nitric acid (sp. gr. 1.26); the substance was changed to material which floated (probably nitrosodurene). Nitrogen oxides were evolved. At 70°, the material was dissolved within five minutes; the solution was kept warm two minutes longer, then it was poured into ice and water, and filtered. The precipitate was triturated and washed with water, and dried for one day over sulfuric acid. The crude nitrodurene weighed 4.8 g. (89%); m. p. 100–105°.

Oxidation of Nitrosoisodurene.—The substance was oxidized with nitric acid at 70–80°; the oxidation was stopped by dilution with ice and water as soon as the material had dissolved. The diluted mixture was extracted with ether; the ether was washed and evaporated. The residual oil was steam distilled; the yellow oil was removed from the distillate by extraction with ether; the residue from evaporation of the ether was crystallized from methanol at the temperature of liquid air. The product was dried for three days in a desiccator. The melting point of nitroisodurene was 38–39°.

Nitrosoisodurene was oxidized also by nitrogen dioxide. The solvent, absolute chloroform, was heated nearly to the boiling point by the heat of reaction. After action had subsided the chloroform was washed with water and evaporated. The residual oil was steam distilled; the distillate was extracted with ether, the ether was evaporated and the residue crystallized from low boiling petroleum ether. The melting point of nitroisodurene was 39°.

Acetoxymercuriisodurene and Nitric Acid.—The procedure was the same as for the reaction between nitric acid and acetoxymercuridurene. From 4 g. of the mercury compound, there was obtained 1.5 g. (82%) of crude (liquid) nitroisodurene. Further oxidation of nitroisodurene occurred when the reactions were continued too long, or were allowed to proceed at higher temperatures.

Reduction of nitroisodurene formed a liquid amine. The melting point of acetaminoisodurene was 215°.

Summary

1. A method was developed for synthesis of nitroso compounds by the action of nitrosyl chloride upon organomercury derivatives of polymethylbenzenes. Four new nitroso and two new nitro compounds were prepared.

2. The action of nitrogen sesquioxide upon arylmercury compounds, like that of the dioxide, formed nitroso compounds as the primary products.

MINNEAPOLIS, MINNESOTA RECEIVED JULY 26, 1935

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

The Peroxide Effect in the Addition of Reagents to Unsaturated Compounds. X. The Addition of Hydrogen Bromide to Methylacetylene (Allylene)

BY M. S. KHARASCH, J. G. MCNAB[1] AND M. C. MCNAB

Introduction

In previous communications from this Laboratory Kharasch and his collaborators[2] have demonstrated the importance of peroxides in directing the addition of hydrogen bromide to olefinic hydrocarbons, in which the double bond is at the end of the chain. It seemed desirable to extend the investigation to the acetylene series, and so the addition of hydrogen bromide to methylacetylene was studied in some detail.

The experiments of Réboul[3] have previously shown that hydrogen bromide in aqueous solution adds to methylacetylene to yield 2,2-dibromopropane.

Addition of Hydrogen Bromide to Methylacetylene.—We found it expedient, after a few preliminary experiments, to limit our investigation to a study of the final product formed by the addition of two moles of hydrogen bromide to methylacetylene. These experiments were carried out in the presence of peroxides and also *in vacuo* under peroxide-free conditions.

The structure of the molecule first formed, under peroxide-free conditions, by the addition of one mole of hydrogen bromide to methylacetylene, can be inferred readily from a consideration of the products isolated in this investigation, together

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[1] The authors wish to express here their appreciation to the Eli Lilly Company of Indianapolis for support which made this work possible.

[2] Kharasch and co-workers, THIS JOURNAL, **55**, 2468, 2521, 2531 (1933); **56**, 1642 (1934).

[3] Réboul, *Ann. chim.*, [5] **14**, 365 (1878).

TABLE I

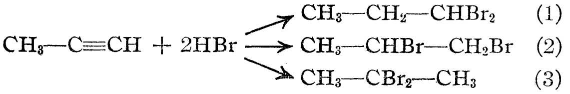
ADDITION OF HYDROGEN BROMIDE TO METHYLACETYLENE

In all experiments 15 g. of methylacetylene and 91 g. of hydrogen bromide were used. The reaction mixture was allowed to stand for four days. The experiments recorded were checked many times. The yields were quantitative (95–100%).

Conditions	B. p., °C.	n^{20}_D	% 1,2-dibromopropane	% 2,2-dibromopropane
No agent added. Vacuum technique	112–115	1.4977	0	100
0.4 g. diphenylamine added to the methylacetylene. Vacuum technique	112–115	1.4977	0	100
0.2 g. thiocresol added to methylacetylene. Vacuum technique	112–115	1.4977	0	100
0.8 g. ascaridole added to methylacetylene, HBr passed in at −33°	139–142	1.5192	100	0
Same as above except vacuum technique used	139–142	1.5193	100	0

with the work on the addition of hydrogen bromide to various bromopropylenes under way in this Laboratory.

From structural considerations, it is obvious that methylacetylene can add two moles of hydrogen bromide to yield three dibromopropanes.



$$CH_3—C≡CH + 2HBr \rightarrow \begin{cases} CH_3—CH_2—CHBr_2 & (1) \\ CH_3—CHBr—CH_2Br & (2) \\ CH_3—CBr_2—CH_3 & (3) \end{cases}$$

In all of our experiments, however, the reaction product proved to be the 2,2-dibromopropane, the 1,2-dibromopropane or a mixture of these two compounds. The possibility of obtaining the 1,1-dibromopropane was not disregarded, but careful analysis of the reaction products (experimental part) revealed none of this compound.

Some of our experimental results are given in Table I. A consideration of these data leaves little doubt regarding the striking effect peroxides exert in governing the direction of the addition. The 2,2-dibromopropane is formed when the reaction is allowed to take place *in vacuo*, and in the absence of any appreciable amounts of peroxides; on the other hand, 1,2-dibromopropane is formed exclusively in the presence of peroxides.

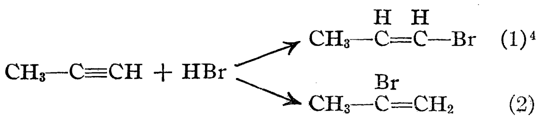
It should be mentioned here that although it is possible to obtain the "abnormal" product (1,2-) in the presence of added peroxides, the system as a whole is not particularly sensitive to traces of peroxides. This of course readily can be predicted from the fact that freshly prepared methylacetylene, or even material three to four days old, does not give a peroxide test, even though no precautions are used to exclude oxygen. Further corroboration of the low susceptibility of the system to the "peroxide effect" is found in the fact that the same product (2,2-dibromopropane) was formed whether the addition was carried out in air, or *in vacuo* or with antioxidants *in vacuo*. In this respect methylacetylene is similar to propylene,[2] and markedly different from halogen ethylenes, which are extremely sensitive even to traces of oxygen and (or) peroxides.

A critical consideration of this addition, in the light of our knowledge of the effect of peroxides on the direction of addition, points to the conclusion that the product of the non-catalyzed first addition of hydrogen bromide to methylacetylene should be 2-bromopropylene.

$$CH_3—C≡CH + HBr \longrightarrow CH_3—CBr=CH_2$$

If the probability of a rearrangement is ignored (and there is not the slightest reason to assume it) then only 2-bromopropylene can yield the 2,2-dibromopropane under peroxide-free conditions. It is to be noted that from the standpoint of the theory developed in our earlier papers,[2] the methyl group and the bromine atom in 2-bromopropylene reinforce each other in their directive effect, an interpretation in strict agreement with the exclusive formation of 2,2-dibromopropane under peroxide-free conditions.

The structure of the bromopropylene formed in the addition of hydrogen bromide to methylacetylene under peroxide conditions, is not deducible from a consideration of our data.



$$CH_3—C≡CH + HBr \rightarrow \begin{cases} CH_3—\overset{H}{C}=\overset{H}{C}—Br & (1)^4 \\ CH_3—\overset{Br}{C}=CH_2 & (2) \end{cases}$$

In the light of our experience, the 1,2-dibromopropane should be the product formed by addition of hydrogen bromide to either (1) or (2) in the presence of peroxides. To check this prediction, the addition of hydrogen bromide to the isomeric bromopropylenes is now under way in our laboratory. However, it is clear that the information thus obtained may not give an unequivocal

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(4) We have purposely omitted in this discussion the probability of formation of the *cis–trans* isomers of 1-bromopropylene, and the possibility of formation of different products due to a difference in the addition to the two stereoisomers. The justification for this omission rests upon our demonstration of the identity of the products formed in the addition of hydrogen bromide to many *cis-trans* isomers [McNab, Doctorate Dissertation, University of Chicago, 1935].

answer regarding the nature of the product when methylacetylene reacts with one mole of hydrogen bromide under peroxide conditions.

An experimental solution of the problem, namely, the actual isolation of the bromopropylene formed under peroxide-catalyzed conditions, is not very easy, because of the number of possible isomers, and particularly because of the greater sensitivity of the bromopropylenes to peroxides, which leads to the formation of large amounts of the 1,2-dibromopropane. A few preliminary experiments have convinced us that both the theoretical and experimental objections to this approach are well justified.

Typical examples of experimental runs are recorded in Table I. It was necessary to depart slightly from the standard Kharasch–Mayo technique in order to effect complete reversal of hydrogen bromide addition through the agency of peroxides. As a rule a tube containing the unsaturated compound was immersed in a bath of carbon dioxide and acetone, ascaridole added and hydrogen bromide bubbled into the mixture. When the required amount of hydrogen bromide had been introduced, the tube was sealed and allowed to stand at room temperature until the addition was complete. However, in the case of methylacetylene, in order to reverse the addition of the halogen acid completely by peroxides, it has been found necessary to pass in the hydrogen bromide at a temperature between −33 and −40°. This is undoubtedly due to the fact that ascaridole is but very slightly soluble in methylacetylene at the temperature of the carbon dioxide–acetone mixture.

Experimental Work

I. Technique of Addition.—The usual Kharasch–Mayo[2] vacuum technique was employed in experiments involving the addition of hydrogen bromide under peroxide-free conditions. Quantitative yields of 2,2-dibromopropane were obtained in each case. In a few experiments using peroxides (ascaridole), the hydrogen bromide was bubbled into the mixture at −78°. Only a partial reversal in the addition was produced. However, it was observed that the ascaridole dissolved but slightly in the unsaturated hydrocarbon at the low temperature. In other experiments the ascaridole–methylacetylene mixture was allowed to stand for one hour in a bath of liquid ammonia (at which temperature the peroxide is appreciably dissolved) and hydrogen bromide introduced at a slow rate. In this case complete reversal was effected, the addition product being exclusively 1,2-dibromopropane.

II. Preparation of Methylacetylene.—Methylacetylene was prepared in 200-g. lots by the action of dimethyl sulfate on a solution of sodium in liquid ammonia according to the method of Meinert and Hurd.[5] From our standpoint this was the best method, since the only impurity, acetylene, is readily removed by careful fractionation in a Davis column. Working with such relatively large quantities of materials, the experimental difficulties in this preparation (which is hard to carry out even on a small scale) were numerous. After some practice, however, we were able to obtain pure methylacetylene in yields of 70–80%. A sample of the product gave no test for peroxides.

III. Analysis and Identification of Products.—The reaction tubes were opened, allowed to stand for one hour to remove excess hydrogen bromide, the product weighed for yield and fractionally distilled three times *in vacuo*. This treatment was followed by washing with sodium bicarbonate solution and water, drying over calcium chloride and careful fractionation. The 1,2- and 2,2-dibromopropanes are distinguishable by their boiling points and can be separated to a large extent by repeated fractionations. Kharasch and Mayo[6] have reported the refractive index, $n^{20}\text{D}$ of 1,2-dibromopropane as 1.5194. We have found the refractive index of 2,2-dibromopropane (not previously reported) to be 1.4977.[7] Under peroxide-free conditions, a yield of 75 g. of product was obtained, all of which boiled in a range of 3° (112–115°). This product is the 2,2-dibromopropane. In the presence of peroxides we obtained 75 g. of product (100% yield) all of which distilled within the range 139–142° (1,2-dibromopropane). The 2,2-dibromopropane was further identified by conversion to acetone. Ten grams of the dibromide and 100 g. of water were heated at 160° for sixteen hours in a sealed tube. The acetone was distilled from the water solution and treated with 2,4-dinitrophenylhydrazine. The melting point of the product thus obtained was that given for the 2,4-dinitrophenylhydrazone of acetone (m. p. 128°). The melting of a sample was not depressed when mixed with a known synthetic sample.

Summary

1. It has been shown that the "normal" addition of hydrogen bromide to methylacetylene produces exclusively 2,2-dibromopropane.

2. Under the influence of added peroxides, hydrogen bromide adds to methylacetylene to give 1,2-dibromopropane.

3. It has been found that the hydrogen bromide must be passed into the methylacetylene, containing the added peroxide at a temperature of −33 to −40° in order to effect a complete reversal of the "normal" addition.

CHICAGO, ILLINOIS RECEIVED OCTOBER 19, 1935

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[5] Meinert and Hurd, THIS JOURNAL, **52**, 4544 (1930).

[6] Kharasch and Mayo, *ibid.*, **55**, 2468 (1933).

[7] This substance was also prepared by us by direct bromination of isopropyl bromide. There was a perfect agreement of physical constants in the products obtained.

The Decomposition of Propane and *n*-Butane at Carbon Filaments

BY LEONARD BELCHETZ[1] AND ERIC K. RIDEAL

In a previous communication[2] it was shown that methylene and ethylene, respectively, were the primary products of the decomposition of methane and ethane at hot carbon surfaces. The methods employed in this work have now been extended to an investigation of the reactions of propane and *n*-butane.

Propane was found by Hague and Wheeler[3] to decompose at 700° mainly to methane and ethylene and to a less extent to hydrogen and propylene, a view supported by the work of Pease.[4]

$$C_3H_8 \longrightarrow CH_4 + C_2H_4 \qquad (1)$$
$$C_3H_8 \longrightarrow H_2 + C_3H_6 \qquad (2)$$

Attempts to distinguish between the primary and secondary reactions by progressively varying the rate of flow of the gas at a given temperature and extrapolating the data obtained were made by Schneider and Frolich,[5] who were able to show that at 725° and one atmosphere pressure, 48% of the reaction proceeded according to (1) and 42%, according to (2). The order of importance of these processes was however reversed at 600°.

In the case of *n*-butane, Hague and Wheeler[3] determined the main reactions at 750° to be

$$C_4H_{10} \longrightarrow C_2H_6 + C_2H_4 \qquad (1)$$
$$C_4H_{10} \longrightarrow CH_4 + C_3H_6 \qquad (2)$$
$$C_4H_{10} \longrightarrow \text{Butylenes} + H_2 \qquad (3)$$

occurring, respectively, to the extent of 40, 35 and 20%. The reaction at 700°, according to Hurd and Spence,[6] occurred in a similar manner, but propylene and methane proved to be the principal products at 600°. Essentially the same conclusions were arrived at by Neauhaus and Marek,[7] who applied the method of Schneider and Frolich[5] for propane to the investigation of the primary decomposition of *n*-butane.

Rice and his co-workers have[8,10] obtained radicals on passing propane and *n*-butane through a hot silica tube at 800°, and on the assumption that methyl and ethyl radicals are produced in the primary rupture of the hydrocarbon chain, have developed a chain mechanism to account for the olefinic products of decomposition.

Experimental.—To avoid as far as possible the occurrence of secondary reactions, the hydrocarbon vapors were passed at a high streaming velocity and low pressure (0.1 mm.) across a heated carbon filament situated 2–3 mm. from a tellurium mirror maintained at 100°, with which any radicals formed could react. These conditions are most favorable for the detection of methylene radicals as the polymer of telluroformaldehyde[9,2] and of methyl radicals as dimethyl ditelluride.[10] Separate experiments under corresponding conditions of temperature and pressure, but in the absence of tellurium, were also performed for the purpose of identifying the olefin products of reaction, these being condensed out together with excess hydrocarbon in a liquid air trap and distilled into a side tube containing bromine. Bromination was allowed to proceed at about −10°, excess of the reagent being avoided.

The Decomposition of Propane on a Carbon Filament.—In experiments performed at 1650°, 1,2-dibromopropane (b. p. 141°) was the only liquid product which could be isolated, while experiments with tellurium indicated that no radicals were being simultaneously produced. These, however, were detected at 1750° at which temperature also it was possible to separate ethylene dibromide (b. p. 132°) from the brominated olefin products.

The action of the products of decomposition at 1750° on hot tellurium gave rise to a small quantity of a yellow solid, finally identified as the polymer of telluroformaldehyde, as well as an orange liquid resembling dimethyl ditelluride. When, however, a boiling point determination of the latter was attempted by the micro method, decomposition of some constituent of the oil to metallic tellurium occurred between 140–160°. The addition of ether to the oil precipitated a yellow solid, which, since it decomposed at about 150° to metallic tellurium, proved to be the methylene–tellurium complex $(TeCH_2)_n$, of Rice

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[1] Emmanuel College (Cambridge) External Research Student and H. B. Webb Gift Research Scholar.

[2] Belchetz and Rideal, THIS JOURNAL, **57**, 1168 (1935).

[3] Hague and Wheeler, *ibid.*, **51**, 378 (1929).

[4] Pease, *ibid.*, **50**, 1779 (1928).

[5] Schneider and Frolich, *Ind. Eng. Chem.*, **23**, 1405 (1931).

[6] Hurd and Spence, THIS JOURNAL, **51**, 3353 (1929).

[7] Neauhaus and Marek, *Ind. Eng. Chem.*, **24**, 401 (1932).

[8] Rice, THIS JOURNAL, **53**, 1959 (1931); *ibid.*, **55**, 3035 (1933); Rice, Johnston and Evering, *ibid.*, **55**, 3529 (1933).

[9] Rice and Glasebrook, *ibid.*, **56**, 2381 (1934).

[10] Rice and Glasebrook, *ibid.*, **56**, 2472 (1934).

and Glasebrook.[9] With cold tellurium mirrors, dimethyl ditelluride and dimethyl telluride only were obtained.

Previous work[2] has shown that unless the accumulation of the non-volatile polymer of telluroformaldehyde on the tellurium acceptor is entirely prevented—this being partially achieved by maintaining the mirror at 100°—reduction of this substance by atomic or hot molecular hydrogen to the methyl tellurides readily ensues. It is believed that the dimethyl ditelluride and dimethyl telluride obtained in these experiments were produced in an analogous manner.

Experiments with Mercury.—If the dimethyl ditelluride isolated in the above experiments was in fact due to methyl radicals produced by the scission of the propane chain, ethyl radicals in quantities equivalent to those of methyl should be capable of detection among the reaction products. Experiments with mercury similar to those devised by Rice, Johnston and Evering[8] and Rice and Rodowskas[11] for the identification of alkyl radicals were therefore performed. As a result of ternary collisions between methylene, atomic hydrogen and mercury, it was expected that mercury dimethyl, at any rate, would be obtained in appreciable amounts.

In these experiments a filament temperature of 1800° was employed. The products of decomposition were allowed to react with mercury continuously condensing on a water cooled bulb, and the mercury alkyls frozen out in a liquid-air trap from which they were extracted with ether. On filtering this solution into an alcoholic solution of mercuric bromide, a copious precipitate of mercurous bromide (in some cases a mixture of mercury and mercurous bromide) was obtained. This was filtered off, the filtrate evaporated to dryness *in vacuo*, and the residue steam distilled. The white solid so separated after being washed with a little alcohol and dried *in vacuo*, melted at 160° (m. p. of CH_3HgBr, 160°).

In other experiments, the mercury alkyls were diffused into a liquid-air cooled side tube where they condensed as a white solid. After the liquid propane had evaporated, part of the mercury compound was observed to decompose to mercury, leaving a clear colorless liquid which boiled at 95° (b. p. $Hg(CH_3)_2$, 95°).

The product obtained in these experiments behaved as if it were a compound of the formula $HgCH_3$, decomposing at room temperatures in contact with, and in the absence of, air as follows

$$2HgCH_3 \longrightarrow Hg + Hg(CH_3)_2$$

It was, however, stable in a cold ether solution, reacting with mercuric bromide in the following manner

$$2HgCH_3 + HgBr_2 \longrightarrow Hg + 2CH_3HgBr$$

No evidence was thus obtained for the formation of ethyl radicals.

The Decomposition of Normal Butane on Carbon Filaments.—These experiments were performed in exactly the same manner as those for propane. At 1650°, about two-thirds of the olefin product proved to be propylene, 1,2- and 2,3-butylene constituting the remaining third. It is significant that radical formation at this temperature was appreciable.

The products at 1750° contained butadiene, identified as the solid tetrabromide, propylene also being present in relatively increased proportions. No ethylene could be isolated.

The radicals produced here also appeared to be methylene, while experiments with mercury again failed to reveal the presence of ethyl radicals.

The Decomposition of Propylene on Carbon Filaments.—Since these experiments suggest that methylene radicals are produced in the secondary decomposition of the olefin products, probably before they are desorbed from the filament, the reactions of propylene were investigated from the point of view of free radicals. Here also hot tellurium was employed as the radical acceptor. The products obtained were essentially those reported for the decomposition of propane and butane at high temperatures, telluroformaldehyde and dimethyl ditelluride being produced. The presence of hydrogen telluride indicated that dehydrogenation of propylene also occurred. As propadiene and methylacetylene do not appear as products of the decomposition of propane, it is probable that their formation cannot take place when hydrogen is present in appreciable quantities.

In this connection, it is significant that Schneider and Frolich[4] obtained principally ethylene and butylene as decomposition products of propylene. This reaction clearly proceeds in the following stages:

$$CH_3CH{=}CH_2 \longrightarrow CH_2{=}CH_2 + CH_2$$
$$CH_2 + CH_3CH{=}CH_2 \longrightarrow CH_3CH_2CH{=}CH_2$$

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[11] Rice and Rodowskas, THIS JOURNAL, **57**, 350 (1935).

Certain discrepancies in the experimental work of Rice and his co-workers give rise to some doubt as to whether ethyl radicals are formed at all in the reactions of propane and butane. Thus when the decomposition products of butane were allowed to react with mercury and the mercury alkyls converted to mercury alkyl bromides and fractionally sublimed, Rice, Johnston and Evering[8] obtained a product corresponding in melting point to a mixture of CH_3HgBr and C_2H_5HgBr in the ratio of 2.3 to 1. The corresponding experiments of Rice and Glasebrook[10] with tellurium as an acceptor, however, resulted in the formation of pure dimethyl ditelluride only. One must conclude, therefore, that the mercury alkyl bromides of Rice, Johnston and Evering were imperfectly separated from mercuric bromide, and that only methyl radicals were produced in these experiments. In view of the experience of Rice and Glasebrook[9] with the decomposition of diazomethane in the presence of butane or ether at temperatures above 650°, when only methyl and no methylene radicals could be detected, it is not unlikely that all the methyl radicals formed in hot tube decompositions of the hydrocarbons, are in reality only secondary products of methylene.

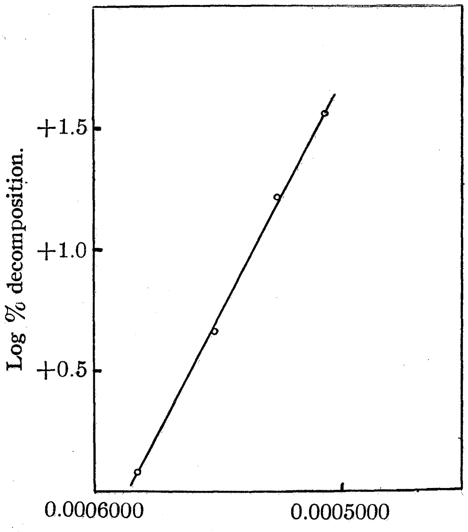

Fig. 1.—Decomposition of *n*-butane on carbon: $E = 93{,}200$ cal.

The Energy of Activation for the Decomposition of Propane and *n*-Butane on Carbon Filaments.—Except for the fact that the products of decomposition were made to pass through a liquid-air trap placed between the Gaede pump and the 2-liter bulb in the forevacuum side of the apparatus instead of being adsorbed on charcoal, the experimental procedure was identical with that employed in the corresponding work with methane and ethane.[2] Here also the rate of reaction was followed with respect to hydrogen, hydrocarbons being frozen out of the sample with liquid nitrogen boiling under reduced pressure. The results for propane are given in Table I, the percentage of the gas decomposing to propylene and hydrogen being calculated on the assumption that this was the only reaction occurring at the temperature of the investigation.

TABLE I

Temp., °K.	H_2 in product, %	Decomposition, %
1723	1.03	1.04
1843	4.75	4.99
1948	17.4	21.4
2023	34.0	51.5

The energy of activation for the decomposition of propane on carbon works out to be 94.2 kcal. (Fig. 1) a value very close to that obtained for methane and ethane.

TABLE II

Temp., °K.	Hydrogen in product, %	Decomposition, %
1713	1.17	1.19
1813	4.31	4.50
1903	14.0	16.3
1973	26.6	36.2

The corresponding data for the decomposition of *n*-butane are shown in Table II, from which an energy of activation of 93.2 kcal. is obtained (Fig. 2).

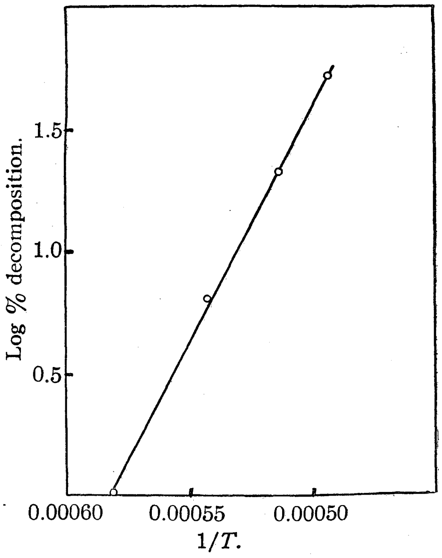

Fig. 2.—Decomposition of propane on carbon: $E = 94{,}200$ cal.

It will be observed that although high percentages of propane and butane passed through the reaction vessel decompose in the region of 1700°, the linearity of the energy of activation curve is very closely preserved. This must mean that secondary processes involving the production of methylene radicals do not appreciably alter the total volume of gaseous products, and that interaction between methylene and the parent hydrocarbon molecules must occur readily. Methane can only have constituted a small percentage of the products (not exceeding 5% at the highest temperatures) as evidenced by the negligible diminution in partial pressure of the residual gas when condensable hydrocarbons were first frozen out with liquid nitrogen boiling under atmospheric pressure, and later with liquid nitrogen boiling under reduced pressure.

Discussion

It would appear from these results that the primary reaction at a carbon surface involves the dissociation of hydrogen from the parent hydrocarbon.

$$CH_3CH_2CH_3 \longrightarrow CH_3CH{=}CH_2 + H_2$$

$$CH_3CH_2CH_2CH_3 \begin{array}{l} \nearrow CH_3CH{=}CHCH_3 + H_2 \\ \searrow CH_3CH_2CH{=}CH_2 + H_2 \end{array}$$

The next stage consists in the further decomposition of the olefin with the production, in the case of propane, of ethylene and methylene.

$$CH_3CH{=}CH_2 \longrightarrow CH_2{=}CH_2 + CH_2$$

Whereas 2,3-butylene dissociates to propylene and methylene

$$CH_3CH{=}CHCH_3 \longrightarrow CH_3CH{=}CH_2 + CH_2$$

1,2-butylene is capable of undergoing further dehydrogenation to butadiene

$$CH_3CH_2CH{=}CH_2 \longrightarrow CH_2{=}CHCH{=}CH_2 + H_2$$

The propylene formed from 2,3-butylene can of course decompose still further to ethylene and methylene, although this step was never realized in our experiments.

It is interesting to note that the energy of activation for the decomposition at a carbon surface is constant, and has the relatively high value of *ca.* 94 kcal. for the four hydrocarbons investigated. Separate experiments indicated that the rate of reaction was approximately proportional to the pressure. We must thus conclude that the reaction velocity is not governed by the desorption of hydrogen but rather by some reaction taking place at collision. The energy of activation may well represent a complex mechanism involving the transformation of a relatively inert carbon surface into a reactive carbon pair similar to that found in dehydrogenation of hydrocarbons. We should thus obtain conditions permitting of a quantum mechanical transfer of two hydrogen atoms from one to another carbon pair at the moment of collision.

In conclusion, one of us (L. B.) would like to express his thanks to the governing bodies of Emmanuel College, Cambridge, and to the University of South Africa, for scholarships, and to the Philgas Co., Bartlesville, Oklahoma, for their gift of C. P. propane and *n*-butane.

Summary

The decomposition of propane and *n*-butane on carbon filaments has been investigated from the point of view of radicals and olefin products.

The experiments indicate that the initial act is the production of hydrogen and the complementary olefin. The latter can then dissociate to methylene and the next lower olefin, except in the case of 1,2-butylene which is capable of further dehydrogenation to butadiene. Methylene subsequently undergoes reaction with the surrounding molecules.

The energies of activation for the two reactions have been determined at 94.2 and 93.2 kcal.

DEPARTMENT OF COLLOID SCIENCE
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[CONTRIBUTION FROM THE INSTITUTE FOR INORGANIC AND ANALYTICAL CHEMISTRY OF THE GERMAN INSTITUTE OF TECHNOLOGY]

The Changes of the Magnetic and Catalytic Properties during the Transformation of a Mixture of Calcium Oxide and Ferric Oxide into Calcium Ferrite[1]

BY GUSTAV F. HÜTTIG, JOSEF FUNKE AND HERBERT KITTEL

1. Purpose of the Investigation

If a stoichiometrical mixture of the oxides of a bivalent metal and of a trivalent metal is brought to higher temperatures, in many cases a crystalline compound will be formed according to the scheme $MeO + R_2O_3 \longrightarrow MeR_2O_4$. In several former communications it was shown[2] by us that *before* the formation of the crystallized addition compound very active intermediate substances are formed, *e. g.*, some with a very high catalytic effect, as high magnetic susceptibility and similar enhanced properties. From the magnetic, optic, x-ray spectroscopic, catalytic, and other properties, it could be concluded without doubt that these active intermediates are by no means mixtures of the starting materials ($MeO + R_2O_3$) with the crystallized end-products (MeR_2O_4) but that the reaction mixture or parts of it are present in specifically characterized compositions. In agreement with the theory of W. Jander,[3] the experimental results pointed to the conclusion that these active intermediates consist of comparatively thin films which envelop the starting material, thus leaving the kernel entirely unaffected. It was possible to obtain about 30% in the system CaO/Fe_2O_3, about 15% in the system SrO/Fe_2O_3, and about 10% in the system BaO/Fe_2O_3 of the total mixture in the form of this film. If the heating is continued further, crystals of the compound MeR_2O_4 begin to form in increasing quantities while the amount of starting material ($CaO + Fe_2O_3$) diminishes. With the onset of this crystallization, the activity of the substance decreases and the film has but little more to do with the building up of the system.

In view of the generality of this phenomenon and of the great significance of oxidic mix-catalyzers in industry, it seemed necessary to find an explanation of the nature of these carriers of the active properties and their changes with time by systematic investigations. For this purpose parts of a stoichiometrical mixture of calcium oxide (as calcium carbonate) and ferric oxide were brought to various temperatures (t_1); each substance thus prepared was tested for its magnetic properties, its catalytic effect at different temperatures (t_2) and other properties which might help to explain its nature. The results of the investigations and the conclusions reached are described in the following sections.

2. Experimental Arrangement and Nomenclature

The substances, after being prepared as described in the following section, were tested for their catalytic activity in the decomposition of nitrous oxide ($2N_2O \longrightarrow 2N_2 + O_2$) at different temperatures (t_2). Further their magnetic susceptibility, their "powder-density" (weight of 1 cc. of the finely ground powder after being shaken to a fairly compact mass), their color, and (in the experimental series II) their carbon dioxide content was determined. The catalytic activity in the formation of carbon dioxide ($2CO + O_2 \longrightarrow 2CO_2$) as well as x-ray data, which had been obtained by us in former similar experiments, were sometimes used for comparison.

The *catalytic activity* in the decomposition of nitrous oxide was measured with the same arrangement as has been described before.[4] In all the experiments mentioned here 577 cc. (*c*, measured at 20°) of nitrous oxide, always purified and dried in the same way, were led past the catalyzer per hour. The cross section of the catalysis tube was 1.54 sq. cm. In experiments with pure, unmixed calcium oxide, the sample weighed 0.208 g. (0.00371 mol calcium oxide) in those with pure, unmixed ferric oxide 0.59 g. (0.00371 mol ferric oxide), and in the mixed catalyzer, consisting of calcium oxide *and* ferric oxide 0.800 g. (0.00371 mol $CaO \cdot Fe_2O_3$). In substances containing the calcium oxide partially or wholly bound to carbon dioxide, 0.800 g. was also weighed out each time; in these cases the number of moles is somewhat smaller (depending on the carbon

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(1) Active oxides, 81st communication.

(2) A summary of 18 treatises has been given by G. F. Hüttig, *Z. Elektrochem.*, **41**, 527 (1935).

(3) W. Jander and W. Scheele, *Z. anorg. allgem. Chem.*, **214**, 56 (1933); W. Jander, *Z. Angew. Chem.*, **47**, 235 (1934).

(4) (a) Hüttig, Zinker and Kittel, *Z. Elektrochem.*, **40**, 307 (1934); (b) Hüttig, Novak-Schreiber and Kittel, *Z. physik. Chem.*, **A171**, 85 (1934); (c) Hüttig, Sieber and Kittel, *Acta physicochimica, U. R. S. S.*, **2**, 129 (1935).

dioxide content) than when carbon dioxide-free samples are used, and the measured catalytic activity is therefore not at once comparable with that of the carbon dioxide-free substances. The percentage of nitrous oxide which was decomposed by the catalyzer is represented by α, while t_2 is the temperature at which the catalysis was observed.

The *magnetic susceptibility* was measured *before* the substance had been used as catalyzer, employing two different field strengths (480 and 950 gauss) and an arrangement which has been applied and described in former investigations.[5] χ represents the "magnetic mass-susceptibility" (susceptibility referred to 1 g. of the substance) and ρ the "powder-density" (defined above).

The *color* of the samples (Ow) is designated according to the color chart (with 24 divisions) of Wilhelm Ostwald (Grosser Farbatlas; editor Unesma G. m. b. H., Leipzig). In our case the following were important:

4	5	6	7	8
reddish	reddish with brown tint	reddish-brown	reddish-purple	purple

The two added letters indicate the content of gray.

In samples where calcium carbonate was used as starting material, the *carbon dioxide content of the catalyzer* is given by the number of moles of carbon dioxide (n) which exist per 1 mole of calcium oxide; *e. g.*, $n = 0.33$ signifies that one-third of the total calcium is present as calcium carbonate.

3. Preparation of the Samples

Series I.—Starting materials: *calcium oxide* (Kahlbaum "pro analysi") was heated for two hours to 1050°; it then showed a $\rho = 0.957$ and $\chi = -0.58.10^{-6}$. The *ferric oxide* (Fe_2O_3) was prepared from an aqueous solution of ferric chloride by precipitation with ammonia[6] and ignition for two hours over the Bunsen burner of the ferric hydroxide formed. *Preparation of the parts of the system CaO/Fe_2O_3:* the calcium oxide and the ferric oxide were mixed in molar proportions ($1CaO:1Fe_2O_3$), pulverized in an agate mortar for one-half hour and pressed through a 10,000-mesh sieve; then they were mixed for two hours in a machine and afterward kept for six hours in a crucible at a temperature t_1 (see Table I). Every sample has been subjected to the complete temperature treatment of the substances prepared at lower temperatures. The samples were cooled from temperature t_1 to room temperature in a vacuum desiccator. After this, they were once more pressed through the same sieve and mixed for one hour; then they were ready for the investigation. Great care was taken to keep moisture and carbon dioxide away from the sample.

Series II.—Calcium carbonate (Schering and Kahlbaum, Berlin, D. A. B. 5; analysis 99.57% $CaCO_3$, 0.43% H_2O) was mixed with the same ferric oxide as in series I in molar proportions ($1CaCO_3:1Fe_2O_3$), then pulverized for one-half hour in an agate mortar and finally mixed for twelve hours with a machine. The further treatment was as in series I, only that instead of pressing it through a sieve, the mixture was pulverized in an agate mortar.

Series III.—These samples were prepared exactly as those of series II with the only difference that after preparing the stoichiometrical mixture ($1CaCO_3:1Fe_2O_3$) a further 3% of crystalline calcium ferrite ($CaFe_2O_4$) was admixed. The latter was identical with the product of series I after the sample had been heated to $t_1 = 1000°$.

Series IV.—In preparing the samples of this series, special care was taken that the heating, and therefore also the changes caused thereby, were the same in all layers of the sample. The preparation was the same as in series II; however, the heating was not done in a crucible but the mixture was made into a paste with purest methanol (puriss. free from acetone) and with that the middle portion of a porcelain tube, which fitted exactly in the center of an Heraeus furnace, was covered evenly with a layer 0.25 mm. thick. Within two hours the furnace was brought to a temperature of 120° while a stream of dry air was passed through it. After leaving it at that temperature for two hours, the passage of air was stopped, the oven heat-insulated and the temperature gradually brought to t_1 in five hours where it was held for $\tau = 6$ hours. Here the various samples do *not* have the same temperature treatment as the substances prepared at lower temperatures.

A number of preliminary experiments have shown that the treatment with methanol is without influence upon the products formed. A crucible was divided into 2 symmetrical parts by an exactly fitting plate of eternite. One-half was filled with the mixture without methanol, while the other half contained the paste prepared with methanol. The whole was then heated as has been described above. By repeating the experiments at different temperatures, t_1, a series of samples were prepared. In all cases the contents of both halves of the crucible showed identical magnetic properties, in particular also the temperature t_1, at which ferromagnetism at first becomes apparent, is the same.

The samples of series V were prepared exactly as those of series IV, with the only difference that the time of heating (τ) to temperature t_1 was not the same in the various samples, as is stated in Table I, column 1.

4. The Results Obtained

The observed catalytic activity in the decomposition of nitrous oxide is given for all samples in Fig. 1. In the lower left corner of each graph the number of the experimental series corresponding to one of the above described modes of preparation is given. The temperature (t_1) of prepara-

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(5) Hüttig and Kittel, *Z. anorg. allgem. Chem.*, **199**, 136 (1931).

(6) Hüttig and Garside, *ibid.*, **179**, 49 (1929).

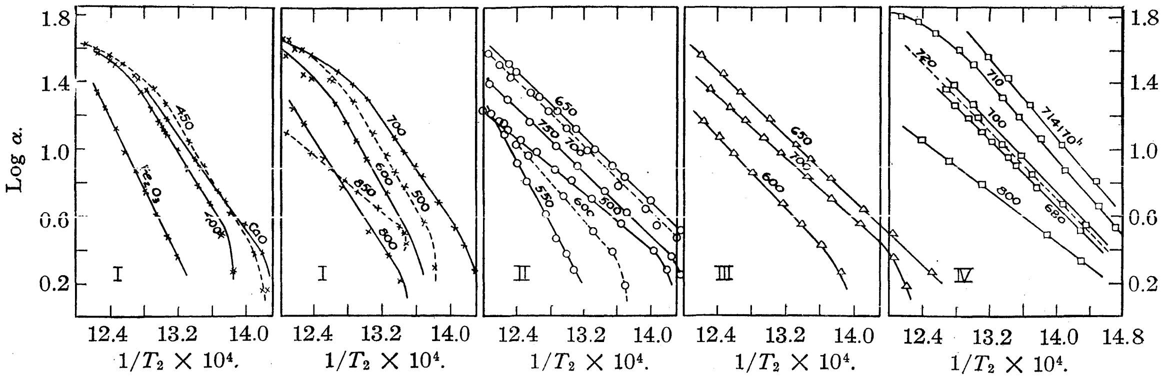

Fig. 1.

tion is given with each curve and identifies the various substances within a given series. The value $1/(t_2 + 273) = 1/T_2$ is plotted as abscissa, while the ordinates represent the corresponding value for $\log_{10} \alpha$. In the interval $\alpha = 2$ to 30%, the experimental results form a straight line on the graph. It is therefore possible to represent these results by the equation $\log_{10} \alpha = -(q'/T_2) + \log n'$, where q' and $\log n'$ are individual constants for each sample. If q (cal.) is set equal to $1.986 \times 2.303\ q'$, then q represents in the usual notation the "heat of activation," *i. e.*, a number which for a given sample must be the smaller, the more catalytically active any single active place, while n' represents a number which is proportional to the number of catalytically active places.

TABLE I

1	2	3	4	5	6	7	8	9
			$\chi \times 10^6$ gauss					
t_1, °C.	q, cal.	Log n'	480	950	Mean value	ρ	Color	γ, %
Series I: CaO, Fe_2O_3, CaO/Fe_2O_3								
	31640	10.233	−0.6	−0.6	−0.6	0.96		
	46280	13.746	37.4	37.5	37.4	2.56	7 pi	
20			30.1	30.0	30.1	1.08	7 le	
200			26.6	26.8	26.7	1.08	7 le	
300			29.7	29.9	29.8	1.36	7 ic	
400	38830	12.197	25.6	25.7	25.6	1.16	7 ic	
450	39198	12.427	28.7	28.7	28.7	1.51	6 ic	
500	39830	12.590	25.2	25.0	25.1	1.54	7 ng	
550			25.3	25.3	25.3	1.32	6–7 ng	
600	41060	12.628	29.5	29.6	29.5	1.14	6 ng	
700	36080	11.596	156.2	131.0		1.31	5 ng	
800	34600	10.230	395.5	300.2	ferro-magnetic	1.71	4 ng	
850	19210	6.172						
900			443.3			2.11	5–6 pi	
1000			766.4			2.18	8 pl	
Series II: $CaCO_3$, Fe_2O_3, $CaCO_3/Fe_2O_3$								
At the 50-degree intervals from 450 to 750°, inclusive, the following fractions of carbon dioxide were evolved: 0.003, 0.019, 0.027, 0.062, 0.279, 0.961, and 1.00.								
20			21.5	21.5	21.5	1.58	7 le	ϕ
200			21.6	21.5	21.6	1.58	7 le	ϕ
300			21.5	21.4	21.5	1.58	7 le	ϕ
400			21.6	21.6	21.6	1.56	7 le	ϕ
450			22.0	21.9	21.9	1.58	6–7 le	1.0
500			22.2	22.2	22.2	1.59	6 le	1.97
550	41480	12.15	22.5	22.5	22.5	1.60	6 le	3.0
600	26390	8.19	23.3	23.5	23.4	1.61	5 ng	6.0
650	22090	7.44	29.9	29.9	29.9	1.46	5 ng	27.68
700	22500	7.52	87.2	80.4	ferro-magnetic	1.65	4 ng	
750	21450	7.06	133.9	116.6		1.65	4 ng	
800	18750	6.16	117.7	103.2		1.93	4–5 ng	

TABLE I (*Concluded*)

Series III: $CaCO_3/Fe_2O_3$

At 700° the carbon dioxide fraction evolved was 1.00.

1	2	3	4	5	6	7	8	9
			$\chi \times 10^6$ gauss					
t_1, °C.	q, cal.	Log n'	480	950	Mean value	ρ	Color	γ, %
20			54.0	46.0		1.55	7 le	
			(21.5)	(21.5)				
600	24100	7.61	56.1	49.1		1.57	5 ng	
			(23.6)	(24.7)				
650	21950	7.43	99.6	94.5		1.51	4–5 ng	
			(68.5)	(71.5)				
700	20350	6.83	110.7	102.5		1.53	4 ng	
			(80.0)	(79.8)				
Series IV: $CaCO_3/Fe_2O_3$								
20			21.6	21.6	21.6	1.68	7 le	ϕ
400			21.6	21.5	21.6	1.61	7 le	ϕ
630			23.7	23.7	23.7	1.52	5 ng	7.0
680	22230	7.48	27.1	27.0	27.1	1.41	4–5 ng	18.0
690			27.8	27.8	27.8	1.44	4–5 ng	20.7
700	23460	7.92	28.2	28.2	28.2	1.41	4–5 ng	21.7
710	25800	8.84	32.2	32.1	32.2	1.39	4–5 ng	34.6
720	22870	7.71	119.1	112.7	ferro-	1.33	5 ng	
800	17290	5.74	132.2	121.4	magnetic	1.71	5 ng	
Series V: $CaCO_3/Fe_2O_3$								
6h at 717			30.9	29.9	ferro-magn.	1.48	5 ng	
12h at 714			33.0	33.2	33.1	1.30		38.0
70h at 714	26340	9.14	38.3	38.2	38.2	1.43	4 ie	54.8
336h at 714			39.8	39.6	39.7	1.38	4 ie	59.5

In Table I, columns 2 and 3, the values q and log n' for the various samples are given; the identity of the samples may be seen in columns 1. As the decomposition products of nitrous oxide have an influence upon the catalytic activity[7] and also other complications are possible, these figures may only be used for qualitative comparisons. In columns 4 to 6 are given the mass susceptibilities (χ) measured with field strengths of 480 and 950 gauss; in column 7 the powder densities (ρ), in column 8 the color. The amount of carbon dioxide given off by the sample during its preparation ($1-n$) is given as a footnote to series II and III. The significance of the figures given in column 9 (γ) is explained in section 5.

Series III (Table I) below the observed χ-values those susceptibilities appear in brackets which are found if the known magnetic effect of the added calcium ferrite is eliminated by calculation from the observed values.

In Figs. 2 and 3 the temperature of preparation (t_1) is always plotted as abscissa and perpendicularly to it some of the properties characterizing the substance. Points referring to samples of series I are always marked with x, those of series II with o, those of series III with Δ and those of series IV with $\Box$. In Fig. 2a the α-values of samples of series I for temperatures of catalysis (t_2) of 500°, 515 and 530° are drawn. For comparison also the catalytic activities, observed previously[8] with a similar set of experiments and measured by the reaction $2CO + O_2 \longrightarrow 2CO_2$ are here drawn as a dotted curve (the divisions of the ordinates are, however, not valid for this curve). Figure 3b gives curves for the α-values of series I (. . . curve), III (--- curve) and IV (-·- curve) for t_2 = 530° and of series II (drawn out curve) for t_2 = 500°, 515 and 530°. In Fig. 2a, the ($1-n$) values are given for series IIa. For the first 4 experimental series, the q-values are given in Figs. 2b and 3c, while the values for log n' of the same series are plotted in Figs. 2c and 3d. Figures 2d and 3e show the magnetic susceptibilities (χ); here in the case of series IV the calculated figures (in brackets in Table I) have been used. Figures 2e and 3f refer to the powder densities (ρ) and Figs. 2f and 3g give a graphical presentation of

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(7) Compare E. W. R. Steacie and J. W. McCubbin, *J. Chem. Phys.*, **2**, 585 (1934); G.-M. Schwab and H. Schultes, *Z. physik. Chem.*, **B25**, 411 (1934); and G.-M. Schwab and R. Staeger, *ibid.*, **B25**, 418 (1934).

(8) See footnote 4a, p. 311; and Kittel and Hüttig, *Z. anorg. allgem. Chem.*, **217**, 193 (1934).

the differences in color, the ordinates representing the number of the color chart. Figure 2g is based on previously obtained x-ray data[4a] (p. 311) curve A representing the estimated intensity of a line of the Debye photograph (characteristic of the oxide mixture) and curve B referring similarly to a line of the crystallized calcium ferrite.

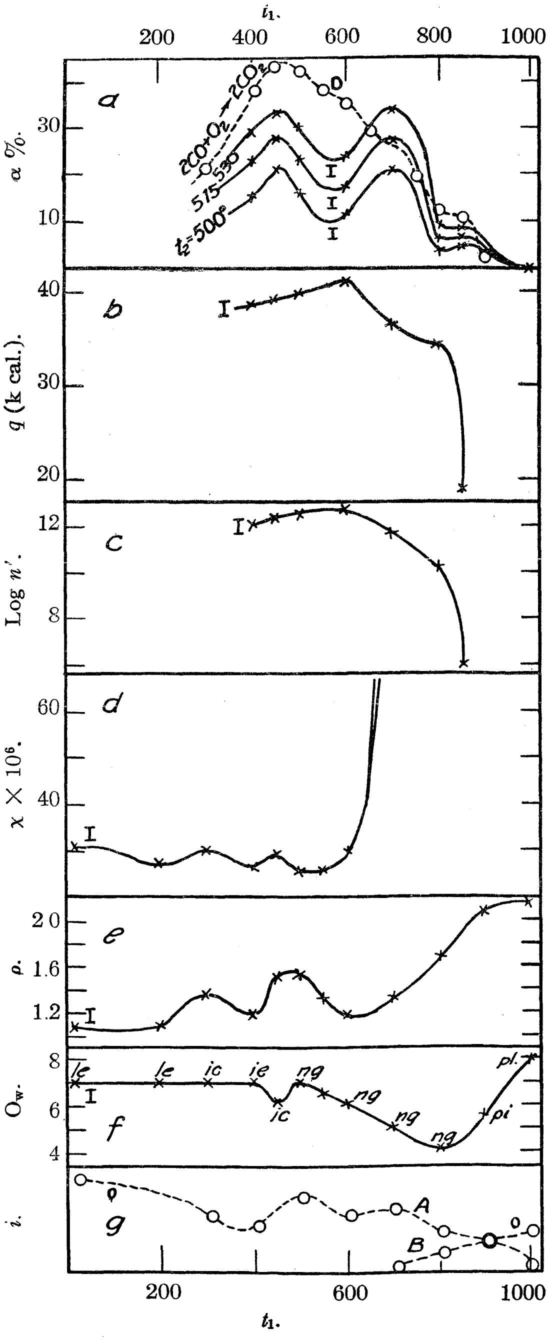

Fig. 2.

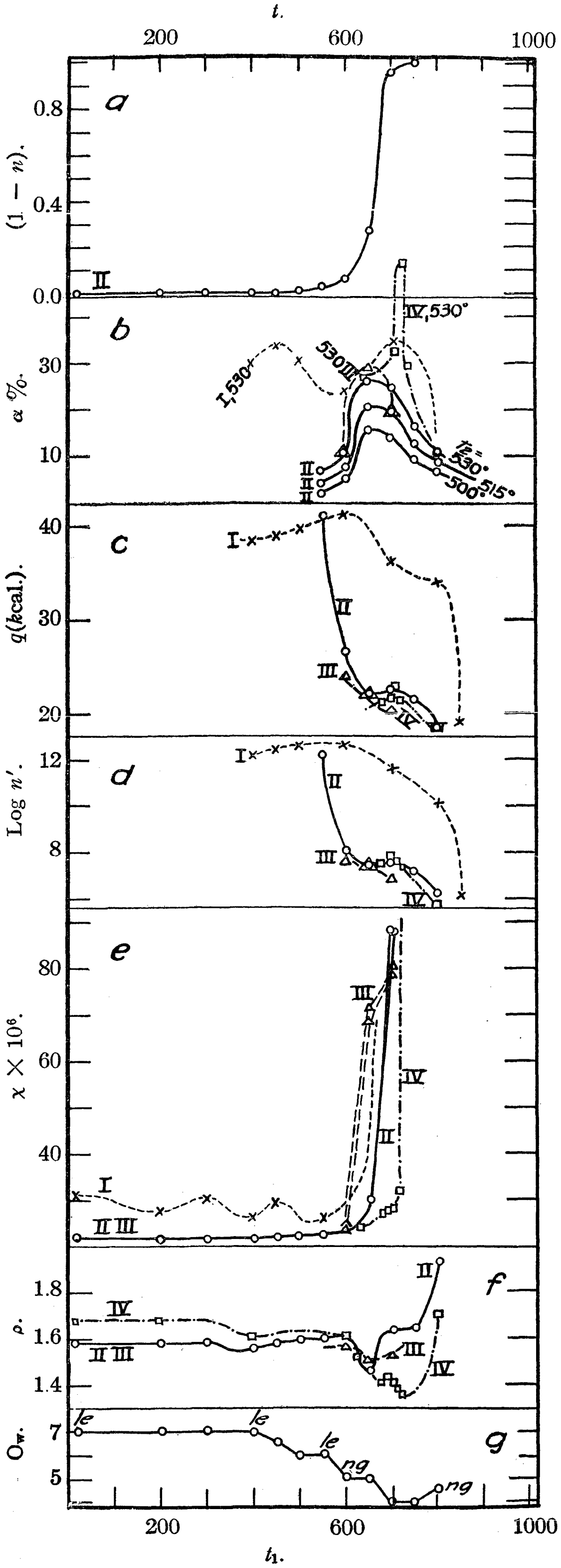

Fig. 3.

For an evaluation of the above catalytic data, the following results from *preliminary experiments* may also be mentioned.

No.	Sample	Amount used for catalysis, g.	Streaming velocity (c) cc./hr.	q, cal.	Log n'
1	CaO	0.800	577	31640	10.67
2	CaO	.208	577	31640	10.23
3	CaO (previously 12h at 1000°)	.800	577	31690	10.56
4	Fe_2O_3	.8000	577	46280	13.81
5	Fe_2O_3	.592	577	46280	13.75
6	Fe_2O_3	.592	200	49780	14.01

The starting substances were the same as described for experimental series I in Section 3.

5. Evaluation of Results

Let us consider first the series II, Table I. The mixture of calcium carbonate and ferric oxide, prepared at room temperature, does not change its properties if it is heated to $t_1 = 400°$. On heating further, a slight loss of carbon dioxide commences in the region from 400 to 450°; the original color 7 le changes toward 6 le and the paramagnetism here shows its first increase.[9]

All these changes take place in the temperature interval from 450 to 650°. At 650° the magnetic susceptibility which is independent of the field strength reaches a maximum with $\chi \times 10^6 = 29.9$; here also the catalytic activity in the decomposition of nitrous oxide reaches maximal values (Fig. 3b). About 28% of the total carbon dioxide content of the sample has been given off by that time and the color has changed to 5 ng. In the region from 650 to 700° ferromagnetism suddenly appears which becomes rapidly larger with increasing temperature of preparation, while simultaneously a decrease of the catalytic activity toward minimum values is observed.[10]

The carrier of the increased activity, as is observed to a greater degree with samples prepared between 400 and 650°, *cannot be the crystallized calcium ferrite,* because even the smallest quantities of calcium ferrite (cryst.) would induce strong ferromagnetic properties in the sample, and no paramagnetism could be observed with substances containing calcium ferrite; besides, no calcium ferrite in this region is determinable even by x-ray spectra (*cf.* Fig. 2g). The carrier of the increased activity must therefore be an intermediate between the original oxide mixture and the crystallized calcium ferrite; it must be a specifically characterized composition which *no longer* possesses the properties of the original mixture *nor yet* the properties of the crystallized calcium ferrite. With regard to the *quantity* of this "*active intermediate*" it could further be determined that it cannot, in general, be limited simply to a covering of the surface in a layer with a thickness of a few molecules. Such a thin covering by the active intermediate, though it would be sufficient to explain the changes of those properties which only depend upon the condition of the surface (*e. g.*, catalysis[11] or color), would never be able to explain the fundamental changes of those observed properties which represent a mean value of the condition of *all* molecules (*e. g.*, the magnetic susceptibility or the pycnometrically determined density).[12]

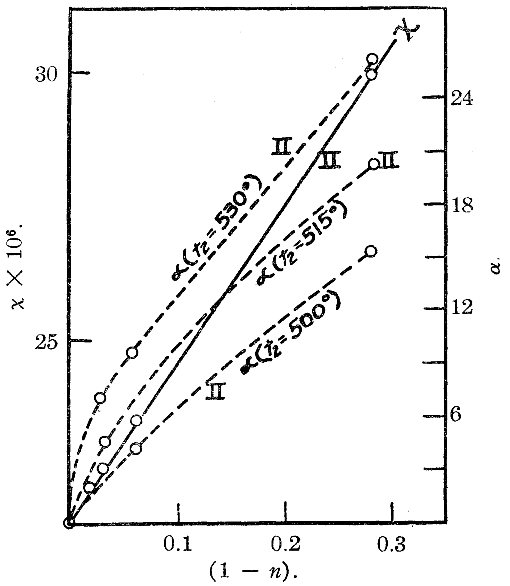

Fig. 4.

In the following way a numerical idea may be obtained from our experiments as to the percentage of the total sample (γ, *cf.* Table I) which is present in the "active intermediate" form. If the number of moles of carbon dioxide $(1 - n)$ which have been given off by the sample per 1 mole of calcium carbonate during its preparation is plotted as abscissa, and the ordinates represent the magnetic susceptibility (χ), the relationships between χ and $(1-n)$ as shown in Fig. 4 (drawn out curve) are obtained. It can be seen that a strict proportionality exists between the increase of susceptibility and the amount of carbon dioxide

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(9) Van Vleck, *Phys. Rev.*, **31**, 587 (1928); Freed and Kasper THIS JOURNAL, **52**, 4671 (1930).

(10) J. H. Chesters and C. W. Parmelee [*J. Am. Ceram. Soc.*, **17**, 50–59 (1934)] have observed the course of ferrite formation by means of dilatometrical measurements.

(11) H. S. Taylor, *Chem. Rev.*, **9**, 1–46 (1931); *Z. Elektrochem.*, **35**, 542 (1929).

(12) The pycnometrically determined densities will be dealt with in a future publication.

given off by the sample.[13] Because calcium oxide as well as calcium carbonate can only be diamagnetic, this probably means only[14] that each mole of calcium oxide, formed by the decomposition of calcium carbonate, at once forms the "active intermediate" with the ferric oxide and remains as such for some time. By extrapolating the straight line (Fig. 4) to the value $(1-n) = 1.0$ a value is obtained for $\chi \times 10^6 = 51.5$; *i. e.*, this susceptibility (*independent* of the field strength) should be observed if 100% of the sample were to exist in the "active intermediate" form; the increase in susceptibility $\chi \times 10^6$ of such a sample compared to that of the original mixture ($\chi \times 10^6 = 21.5$) amounts therefore to $51.5 - 21.5 = 30.0$.[15] By comparison of the actual increase obtained with different samples of this value, which corresponds to a 100% product, the percentage of "active intermediate" present in the different samples is obtained. This is given as γ% in column 9 of Table I. In series II, the sample which was prepared at 650° contains the largest quantity of the "active intermediate" (27.7%).

The "active intermediate," at least in a first approximation, represents a uniform substance. If this substance soon after its formation should undergo slow changes, perhaps by aging, the measurements should show a continuity of states, and such a proportionality as is evident from Fig. 4 would be unthinkable. Aside from the magnetic mass susceptibility $\chi = 51.5 \times 10^{-6}$, this intermediate form may also be characterized by the heat of activation in the nitrous oxide decomposition, which in our experimental arrangement is measured as $q = 20{,}000$ to 25,000 cal. (*cf.* column 4 of the series II, III, and IV). Corresponding to the fact that the magnetic susceptibility of the ferric oxide, which is used as starting material, may have very different values depending upon the preparation, the magnetic susceptibility obtained for the pure active intermediate varies greatly with different starting substances. In the present case, the starting mixture $CaCO_3 + Fe_2O_3$ had $\chi = 21.5 \times 10^{-6}$, the active intermediate $\chi = 51.5 \times 10^{-6}$. In another series[13] the starting mixture had $\chi = 16.3 \times 10^{-6}$ and the active intermediate $\chi = 45.3 \times 10^{-6}$. In both cases, however, the *increase* is practically the same, *viz.*, about 30×10^{-6}.

If, as is demonstrated in Fig. 4 by the interrupted curves, $(1-n)$ is plotted as abscissa and the catalytic activity as ordinate (α), the α becomes larger with increasing $(1-n)$ and accordingly also with increasing χ, however, without having a direct proportionality. Compared to direct proportionality, the α-values slow up in their increase, and that to a greater degree the more "active intermediate" is formed. This means that a smaller portion of the active molecules formed (*cf.* also the log n'-values of column 5, Table I) is available for catalysis, if a more active intermediate is formed. This seems to us a proof that the active intermediates are formed primarily on the surface of the particles, from where further formation proceeds toward the interior of the particles, whereby the molecules are the less accessible for the molecules to be catalyzed the further away they are from the surface.

That in the series II the formation of a 100% "active intermediate" is not reached is due to the fact that the formation of the crystallized calcium ferrite from the active intermediate commences before the whole starting mixture has been transferred into the "active intermediate." If therefore a high content of the "active intermediate" is desired, it is necessary to prevent the premature formation of calcium ferrite, *i. e.*, to let the whole sample in all parts be transformed as uniformly as possible and to interrupt the process at the proper moment. Such conditions are fulfilled in the working method according to which the samples of series IV (see section 3) have been prepared. By this method it was possible to obtain products with a content of active intermediate (γ) as high as 35%. On the basis of experience gained from series IV, samples with even 60% of the active intermediate have been obtained in series V (*cf.* Table I). In the case of these products which contain practically no more carbon dioxide, one has to imagine that the proportionality between the carbon dioxide given off and the increase of susceptibility ceases if the last remaining portions of calcium carbonate have no ferric oxide sufficiently near them to combine to form the active intermediate; in this case the decomposition of calcium carbonate into calcium oxide and carbon dioxide could take place free from complications.

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[13] Kittel and Hüttig, *Z. anorg. allgem. Chem.*, **219**, 256 (1934).

[14] The absolute applicability of this reasoning is probably only then guaranteed, when experiments with mixtures in various proportions $CaCO_3$:Fe_2O_3 have also been made.

[15] See footnote 13, p. 262, where these "increases" for the system CaO/Fe_2O_3, SrO/Fe_2O_3 and BaO/Fe_2O_3 have been calculated, but erroneously have not been stated as increases but as total susceptibilities.

On the other hand, it seemed probable that a little addition of crystalline calcium ferrite (as was the case in series III) would hasten the formation of calcium ferrite. Our respective observations (Fig. 3e, curve III) make it probable that in such a case the "active intermediate" is formed already at a lower temperature, while this statement could not be made for the crystallized calcium ferrite. As the magnetic values which form the basis here are obtained by a complicated correction by calculation, the reliability of these statements is less than in the other observations.

If instead of a mixture of calcium carbonate and ferric oxide a stoichiometric mixture of calcium oxide and ferric oxide is used, as has been done in series I, an excess of calcium oxide is always present, and every calcium oxide molecule necessary for the reaction with ferric oxide does not have to be furnished by the primary decomposition of calcium carbonate. Accordingly portions of the starting material can *at first* proceed toward the formation of a more basic product.[16] Thus the fluctuations of the magnetic susceptibilities (Fig. 2d), as they appear with samples prepared at temperatures up to 600°, can be explained. The double maximum of the catalytic activity (Fig. 2a) could also have the same cause[4a] (pp. 308–309). The q and $\log n'$ values do not show similar double turning points (Figs. 2b and 2c).

Summary

1. Mixtures in stoichiometrical proportions $1CaO{:}1Fe_2O_3$ and $1CaCO_3{:}1Fe_2O_3$ were heated to various high temperatures under varying conditions.

2. Samples thus obtained were tested for their catalytic activity in the decomposition of nitrous oxide at various temperatures; further their magnetic susceptibility, their powder density, color, and carbon dioxide content were determined.

3. A detailed description of the preparation of the samples is given.

4. The results of the experiments are presented in figures and tables. For each sample the heat of activation (q) in cal. and a number n' is given which is proportional to the number of active centers in cases free from complications. Previously obtained results for the catalytic activity in the formation of carbon dioxide and x-ray data are used for comparison.

5. The following conclusions are drawn from the observations. The carrier of the increased activity is a specifically characterized "active intermediate" which no longer possesses the properties of the original mixture nor yet those of the crystallized calcium ferrite. A way to calculate the percentage of the "active intermediate" is given; the most active samples contain up to 60% of it. The "active intermediate" is a uniform substance with a susceptibility which is independent of the field strength and equal to $\chi = 51.5 \times 10^{-6}$, and with a heat of activation (in the decomposition of nitrous oxide from 20,000 to 25,000 cal. Its formation starts on the surface of the particles and proceeds toward their interior.

PRAGUE, CZECHOSLOVAKIA

RECEIVED MAY 28, 1935

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(16) In the literature the compounds $CaO{\cdot}Fe_2O_3$ and $2CaO{\cdot}Fe_2O_3$ are given as definitely known calcium ferrites.

[CONTRIBUTION NO. 26 FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Reduction of Nitroguanidine. II. Preparation and Properties of Nitrosoguanidine[1]

BY V. J. SABETTA, DAVID HIMMELFARB AND G. B. L. SMITH

Introduction

Nitrosoguanidine and aminoguanidine are formed by the reduction of nitroguanidine.[2] Nitrosoguanidine is a mixed ammonocarbonic–aquonitrous acid anammonide or anhydride, or a mixed ammonohydroxylamic carbonic acid and it is related to nitroguanidine as nitrous acid is to nitric acid.[1a] Thiele[2] has prepared nitrosoguanidine by reducing nitroguanidine in a solution of sulfuric acid with zinc. Reduction with zinc employing a solution of ammonium chloride has been used in this Laboratory for the preparation of nitrosoguanidine and has been found to be convenient and to give satisfactory yields. This paper describes the preparation and some of the general properties of this interesting substance.

Preparation

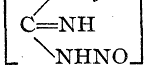
The reduction of nitroguanidine to nitrosoguanidine must be carried out so as to provide the following environmental conditions: (a) the reaction must be controlled so as to prevent the reduction proceeding beyond the nitroso stage; (b) dearrangement and hydrolysis must be minimized by controlling both the temperature and acidity of the solution; (c) nitrosoguanidine formed must be readily isolated without contamination with the reducing agent or with other substances formed by the reaction or present in the reaction system. With these conditions in mind the following method has been developed and has been used repeatedly by many workers.

Nitroguanidine[1b] (60 g.) is dissolved in 1 liter of boiling water and the nitroguanidine is precipitated in a finely divided form by violently agitating the solution while it is being rapidly chilled in an ice bath. Ammonium chloride (15 g. thus giving a concentration of 1.5%) is added to the solution and zinc powder (generally about 60 g.) is introduced at such a rate that the temperature of the reaction mixture is maintained below 50°. Samples of zinc dust vary widely in reducing activity so that the time of reduction and amount of zinc dust required must be established for each new sample of zinc. From twenty to forty minutes is usually sufficient for the reduction and when all the white nitroguanidine has been replaced by the yellow precipitate of nitrosoguanidine (nitroguanidine may be detected also by filtering 10 ml. of the mixture, treating the solid material with 5 ml. of hot ethanol, evaporating to half volume and cooling—white needles indicate the presence of nitroguanidine) ice is added to the reaction mixture and after cooling the solids are separated by filtration. Nitrosoguanidine is extracted from the mixture on the filter with 3–4 liters of water at 70° and recovered from the filtrate by chilling to 5° for half an hour. The product so obtained (98% nitrosoguanidine) is recrystallized from water (60–70°), washed with ethanol, ether and dried *in vacuo;* yield 40 to 60%.

Properties

Nitrosoguanidine is a yellow crystalline solid, individual crystals having a greenish cast by transmitted light and slightly pinkish by reflected light. Aqueous solutions are colored yellow and the intensity of this color is proportional to the concentration at constant temperature and *p*H between 6 and 10. At 10° the color intensity is 70% of that at 40° and at *p*H of 2 and 12 it is 80% of that at *p*H 7.[3] The solid detonates rather sharply at 161° and leaves only a slight amount of solid residue. It may be detonated on the open palm of the hand without any injury resulting. The following are the solubilities of nitrosoguanidine in grams per 100 g. of water at the several temperatures: 5°, 0.093; 15°, 0.118; 20°, 0.154; 25°, 0.185; 30°, 0.246; 40°, 0.365; 50°, 0.527; 72°, 1.22; 73°, 1.31. It is practically insoluble in diethyl ether and sparingly soluble in ethanol. In a slightly acidic solution a large excess of permanganate ion oxidizes nitrosoguanidine to nitroguanidine but in strongly acidic solutions nitric acid and guanidine are formed. In a solution of sodium hydroxide, permanganate ion is reduced to manganate ion and a gas is formed; further reduction yields acid permanganite ion while cyanamide and nitrate ion were identified.

Nitrosoguanidine is an ampholyte. It is dissolved to a greater extent in acidic and basic solution than in neutral solution and the isoelectric point is near *p*H 7.[3] The three forms present in aqueous solutions may be represented as follows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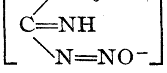
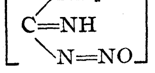

II


III

This amphoteric character of nitrosoguanidine is of importance in connection with hydrolytic and

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(1) First article of series (a) Smith and Sabetta, THIS JOURNAL, **54**, 1034 (1932); see also (b) Smith, Sabetta and Steinbach, *Ind. Eng. Chem.*, **23**, 1124 (1931). This paper is based on the M.S. theses of Mr. Sabetta and Mr. Himmelfarb, the Polytechnic Institute of Brooklyn, 1931 and 1932.

(2) Thiele, (a) *Ann.*, **270**, 1 (1892); (b) **273**, 133 (1893).

(3) Robertson, M.S. Thesis, Polytechnic Institute of Brooklyn, 1935.

dearrangement reactions of the substance in aqueous solutions. Guanidine and nitrous acid are formed in acidic aqueous solutions, nitrous acid having been recovered quantitatively and guanidine nitrate and picrate being isolated from the reaction solution. In neutral solution cyanamide and nitrogen are formed as Thiele[2] observed. In alkaline solutions carbon dioxide, ammonia, cyanamide and nitrogen have been detected.[4]

Measurements of velocity constants of the decomposition in acidic, neutral and basic solutions show that the reactions are all monomolecular or rather pseudo-monomolecular. The constants vary with the hydrogen-ion concentration in acid solution and with the hydroxyl-ion concentration in basic solution. The energy of activation in acidic and basic solutions is about 19,000 calories per mole and is probably somewhat higher in neutral solutions.[5]

Analytical Methods

Five methods for the determination of nitrosoguanidine are indicated from the studies of its properties and have been developed: (1) colorimetric; (2) estimation of nitrous acid formed by hydrolysis of nitrosoguanidine in a dilute solution of nitric acid; (3) titration with a standard solution of potassium permanganate; (4) weighing as silver nitrosoguanidine; (5) weighing silver chloride from the conversion of silver nitrosoguanidine. These methods have all been found to be of moderate precision and (3) which has been used in the routine establishment of the purity of nitrosoguanidine will be described in more detail.

A sample of nitrosoguanidine (approx. 0.2 g.) is dissolved in 100 ml. of 3 *M* sulfuric acid to which has been added about 2 g. of manganous sulfate. A standard solution of potassium permanganate (0.1 *N*) is added only as rapidly as the solution is decolorized and when about three-fourths of the nitrosoguanidine has been decomposed the reaction proceeds slowly. The end-point is taken when the pink color of permanganate ion persists for two minutes during which period the solution is violently agitated.

Analytical Results.—Method 2: Nitrosoguanidine taken: 0.1246, 0.1578, 0.1703, 0.1728 g. Found: 0.1250, 0.1576, 0.1708, 0.1735 g. Method 3: Nitrosoguanidine taken: 0.2000 g. (5 samples). Found: 0.2016, 0.1996, 0.2006, 0.2003, 0.1993 g. Method 4: Nitrosoguanidine taken: 0.1440, 0.2042, 0.1654 g. Found: 0.1447, 0.2046, 0.1653 g. Method 5: Nitrosoguanidine taken: 0.2332, 0.2449, 0.2830 g. Found: 0.2332, 0.2440, 0.2836 g.

Summary

A method for the preparation of nitrosoguanidine by reduction of nitroguanidine with zinc in a solution of ammonium chloride is proposed. Some of the characteristic physical and chemical properties of nitrosoguanidine are described. Five methods for the determination of nitrosoguanidine are suggested.

BROOKLYN, NEW YORK RECEIVED MAY 2, 1935

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[4] For suggestions regarding possible reactions see (a) Pellizzarri, *Atti accad. Lincei*, **30**, I, 171 (1921); (b) Davis and Abrams, *Proc. Am. Acad. Arts Sci.*, **61**, 437 (1926).

[5] These observations are based upon a large number of quantitative measurements under a variety of environmental conditions; see Ref. 3 and also Schmookler, B.S. Thesis, 1932; Weaver, B.S. Thesis, 1934, Polytechnic Institute of Brooklyn.

[CONTRIBUTION NO. 28 FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Reduction of Nitroguanidine. IV. Preparation of Nitrosoguanidine by Catalytic Hydrogenation

BY EUGENE LIEBER AND G. B. L. SMITH

Introduction

In this extended investigation of the reduction of nitroguanidine[1] catalytic hydrogenation to nitrosoguanidine has been accomplished over both the Adams platinum[2] and the Raney nickel catalysts.[3] These reactions may be used for the preparation of nitrosoguanidine, which is obtained in excellent yield and relatively high purity.

Method

Nitroguanidine[1a] (10.4 g.) is suspended in 150 ml. of water and 0.5 g. of Adams or 5 g. of Raney nickel catalyst is added. The reduction is carried out either at four atmospheres pressure using the Burgess–Parr apparatus[2] (p. 452) or at one atmosphere, in which case the hydrogen is introduced from a 100-ml. buret and the Burgess–Parr shaking equipment is employed. The reaction is discontinued when slightly more than one mole of hydrogen (2300 ml.) has been adsorbed. The contents of the reduction bottle are transferred to an Erlenmeyer flask and decolorizing charcoal is added. The solution is diluted to 700–800 ml., heated to 65° and then rapidly filtered. The filtrate is again treated

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[1] See (a) *Ind. Eng. Chem.*, **23**, 1124 (1931); (b) THIS JOURNAL, **54**, 1034 (1932); (c) **57**, 2478 (1935).

[2] Gilman, "Organic Synthesis," Coll. Vol. I, John Wiley and Sons, Inc., New York City, 1st ed., 1932, p. 53.

[3] Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).

with decolorizing charcoal at 65° and refiltered. The filtrate is cooled to 5°, the nitrosoguanidine is separated on a Büchner funnel and dried *in vacuo*. The yield varies from 36 to 62% (3.2–5.5 g.). Typical preparations are summarized in Table I.

TABLE I

TYPICAL DATA REGARDING THE CATALYTIC HYDROGENATION OF NITROGUANIDINE[1c]

H_2 press. atm.	Time of redn.	Rate ml. H_2/min.	Nitroso-guanidine yield, %	Purity of nitroso-guanidine, %
Adams Platinum Oxide Catalyst				
1	108	20.6	55.7	93.5
1	109	20.6	59.2	94.3
4	45	45.2	58.5	98.3
Raney Nickel Catalyst				
1	139	16.6	43.4	96.3
1	137	16.8	39.8	99.5
4	110	18.5	44.3	100.3
4	99	20.5	36.6	100.0

Discussion

Water, methanol, ethanol, dioxane and benzene were used as reaction media and water was found to be the most suitable for the Adams catalyst and satisfactory for the Raney catalyst. Methanol gave somewhat higher adsorption rates with Raney nickel (23 ml. of hydrogen per minute) and yields of 45% were obtained consistently. Higher pressures gave increased adsorption rates for the Adams catalyst but were without much effect for the Raney catalyst. The yields of nitrosoguanidine were not affected markedly. The optimum temperature is 25–35° and a decrease or increase of 10° resulted in a lowering of the rate of hydrogen adsorption of 40–70%. The yields of nitrosoguanidine were not affected with the Adams catalyst but with the Raney nickel the yields were materially decreased.

With the Raney nickel catalyst it was found that the optimum ratio of catalyst mass to nitroguanidine was 0.5 g. of catalyst per gram of nitroguanidine. A smaller ratio decreases the rate of adsorption of hydrogen while a ratio of 1 gives a maximum rate but at the same time the yields of nitrosoguanidine are very greatly lowered.

A more comprehensive study of the catalytic hydrogenation of nitroguanidine, now in progress, will include the further reduction to aminoguanidine, the effect of other catalysts and the reduction of nitroaminoguanidine, alkylnitroguanidines and nitrourea.

Summary

Nitroguanidine can be reduced by catalytic hydrogenation using either the Adams platinum oxide catalyst or the Raney nickel catalyst to give a satisfactory yield of nitrosoguanidine.

BROOKLYN, NEW YORK RECEIVED OCTOBER 4, 1935

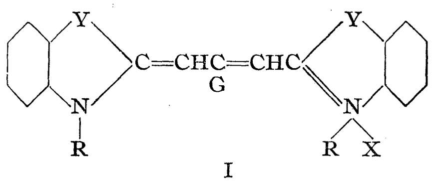
[COMMUNICATION NO. 562 FROM THE KODAK RESEARCH LABORATORIES]

Studies in the Cyanine Dye Series. II.
Carbocyanines with Substituents in the Three-Carbon Chain

BY L. G. S. BROOKER AND FRANK L. WHITE

Ethyl orthoformate was employed for the preparation of dyes of the thiacarbocyanine series by König and Meier[1] and by Hamer.[2] The latter, using ethyl orthoacetate, prepared thiacarbocyanines containing an 8-methyl group.[3]

It is now found that ortho esters of higher aliphatic, of substituted aliphatic and of aromatic acids may be employed for the preparation of new thiacarbocyanines (I, Y = S) where G represents a higher alkyl, a substituted alkyl or an aryl group, according to the ortho ester used.[4]



I

Ortho esters of propionic, *n*-butyric, *n*-valeric, *n*- and isocaproic, phenylacetic, phenoxyacetic and benzoic acids have been made and used in the course of this work, and of these the majority are new. The general method used in the preparation of these ortho esters consists in allowing an alcohol to act upon an imino-ester hydrochloride (preferable to "imino-ether hydrochloride"), prepared in turn from a nitrile. This

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(1) König and Meier, *J. prakt. Chem.*, **109**, 324 (1925).

(2) Hamer, *J. Chem. Soc.*, 2796 (1927).

(3) Hamer, *ibid.*, 3160 (1928).

(4) Brooker, U. S. Patents 1,934,657, 1,934,658, 1,934,659, Kodak Ltd., British Patent 394,692.

method was first applied to the preparation of ethyl orthoformate by Pinner,[5] and to that of ethyl orthoacetate and ethyl orthopropionate by Reitter and Hess.[6] Improved methods for the preparation of these two last ortho esters have since appeared,[7,8] whilst ethyl orthophenylacetate was prepared by Staudinger and Rathsam[9] and later by Sah, Ma and Kao.[10] Ethyl orthobenzoate has been obtained by the interaction of sodium ethylate and benzotrichloride,[11] but in the present work it, too, was prepared by the general method.

In the case of 2,2′,8-triethylthiacarbocyanine iodide (I, G = R = Et), a good yield of dye was obtained when 1-methylbenzothiazole ethiodide (2 mols) and ethyl orthopropionate (3 mols, *i. e.*, 200% excess) were allowed to react together in boiling pyridine solution, but the yield was much poorer if methyl orthopropionate (3 mols) was used, the product, furthermore, being otherwise unsatisfactory for the reason given below. If, however, 1-methylbenzothiazole etho-*p*-toluenesulfonate was employed, the dye being subsequently converted into the iodide, good yields were obtained using both the methyl and ethyl orthopropionates, the former in fact giving the somewhat higher yield. Similar results were obtained in the preparation of 8-ethyl-2,2′-dimethyl- and of 2,2′-diallyl-8-ethylthiacarbocyanine iodide. The yields are given in Table I.

TABLE I

PERCENTAGE YIELDS OF 8-ETHYLTHIACARBOCYANINE DYES

	Quaternary iodide orthopropionate		Quaternary *p*-toluenesulfonate orthopropionate	
Dye	Methyl	Ethyl	Methyl	Ethyl
8-Ethyl-2,2′-dimethylthiacarbocyanine iodide	13 (—)	67 (56)	69 (56)	50 (41)
2,2′,8-Triethylthiacarbocyanine iodide	29 (—)	52 (41)	51 (42)	45 (38)
2,2′-Diallyl-8-ethylthiacarbocyanine iodide	9 (—)	47 (30)		

In each column the yield of crude dye is given, followed in parentheses (except in the first column) by the recrystallized yield. In each of the three cases in the first column the product was found to consist of a mixture of two dyes. In the attempted preparation of 2,2′,8-triethylthiacarbocyanine iodide which resulted in the 29% yield, the product was resolved by fractional crystallization into two fractions, the more soluble of which was proved to be true 2,2′,8-triethylthiacarbocyanine iodide, the less soluble fraction being identical with 2,2′-diethyl-8-methylthiacarbocyanine iodide (I, G = Me, R = Et). This latter fact was established using the means already detailed,[12] when it was shown that 2,2′-diethyl-8-methylthiacarbocyanine iodide is produced when 1-methylbenzothiazole ethiodide is heated alone in pyridine, the =CMe— group at the center of the dye molecule being provided by a breakdown of a portion of the quaternary salt used. There is no doubt that this dye is so produced in the present instance and it is significant that it was not encountered in the three preparations of the 2,2′,8-triethyl dye in which high yields of product were obtained, but only in that in which the yield of crude dye was relatively low. An explanation of these facts is that in the three cases, the reaction between ortho ester and quaternary salt is more rapid than that in which 8-methyl dye is formed from the quaternary salt alone, but in the remaining case, the ortho ester is slow to react with the salt and the latter is available to undergo the reaction which gives the 8-methyl dye.

In the preparation of 8-ethyl-2,2′-dimethylthiacarbocyanine iodide from the quaternary iodide using methyl orthopropionate the dye appeared to be largely that sought for, with some contamination with the related 8-methyl dye, but in the attempted corresponding preparation of 2,2′-diallyl-8-ethylthiacarbocyanine iodide the product, after one recrystallization, appeared to consist almost entirely of the 2,2′-diallyl-8-methyl dye. No attempts were made to isolate the individual components of the mixtures in these two cases.

In the preparation of dyes containing higher alkyl groups (I, G = *n*-Pr, *n*-Bu, *n*- and *i*-Am), 1-methylbenzothiazole alkyl *p*-toluenesulfonates were used in conjunction with the appropriate methyl ortho esters, it being convenient to use these latter, since the methyl imino-ester hydrochlorides from which they are prepared are easier

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(5) Pinner, *Ber.*, **16**, 1644 (1883).

(6) Reitter and Hess, *ibid.*, **40**, 3020 (1907).

(7) Sah, THIS JOURNAL, **50**, 516 (1928).

(8) Sigmund and Herschdörfer, *Monatsh.*, **58**, 280 (1931).

(9) Staudinger and Rathsam, *Helv. Chim. Acta*, **5**, 645 (1922).

(10) Sah, Ma and Kao, *J. Chem. Soc.*, 305 (1931).

(11) Limpricht, *Ann.*, **135**, 87 (1865); see also Sah, THIS JOURNAL, **53**, 1836 (1931).

(12) Brooker and White, *ibid.*, **57**, 547 (1935).

to isolate than the corresponding ethyl compounds.[13]

In the preparation of thiacarbocyanines containing substituted aliphatic groups (I, G = $C_6H_5CH_2$, $C_6H_5OCH_2$), or an aromatic group (I, G = C_6H_5) in the 8-position, the corresponding ethyl ortho esters gave satisfactory results when used with 1-methylbenzothiazole alkyl *p*-toluenesulfonates.

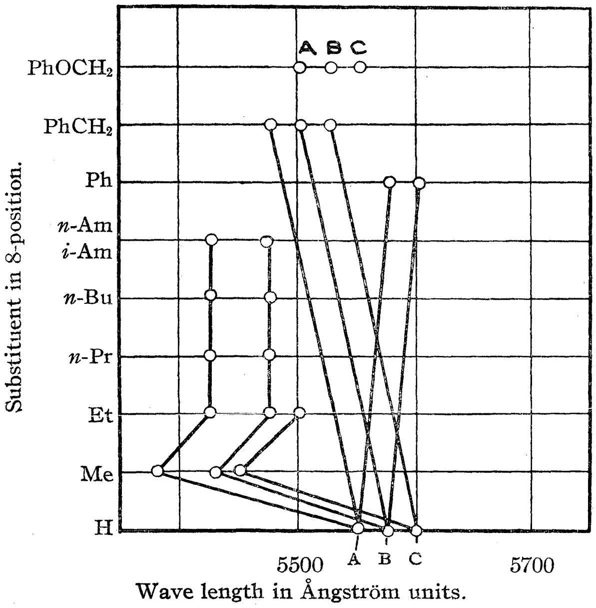

Fig. 1.—Absorption maxima of thiacarbocyanines (I, Y = S): A, 2,2′-dimethyl series; B, 2,2′-diethyl series; C, 2,2′-diallyl series.

The absorption curves of the new dyes showed a well-defined principal band in every case, with, as is often met in cyanine dyes, evidence of a weaker and usually ill-defined secondary band nearer the blue. The positions of the absorption maxima of the main absorption bands are given in Table II, and for comparison there are added the corresponding figures for the related unsubstituted and 8-methyl substituted dyes.

TABLE II

ABSORPTION MAXIMA OF THIACARBOCYANINES IN Å. (I, Y = S)

	R				
G.	Me	Et	*n*-Pr	*n*-Bu	Al
H	5550	5575	5575	5575	5600
Me	5380	5430	5450	5450	5450
Et	5425	5475	5500	5475	5500
n-Pr	5425	5475			
n-Bu	5425	5475			
n-Am	5425	5475			
i-Am	5425	5475			
$PhCH_2$	5475	5500			5525
$PhOCH_2$	5500	5525			5550
Ph	5575	5600			

In Fig. 1 the positions of maximum absorption have been plotted for the 2,2′-dimethyl, 2,2′-diethyl and 2,2′-diallyl series against the groups in the 8-position, these groups being arranged in the order of increasing complexity. There are striking regularities in these curves.

It has already been noted that replacement of 8-hydrogen in 2,2′-dimethylthiacarbocyanine iodide by methyl, results in a shift of 170 Å. of the absorption maximum toward the blue.[12] We now find that replacement of 8-methyl by 8-ethyl shifts the maximum back toward the red by about 45 Å., but replacement of 8-ethyl by higher aliphatic groups brings about no further shift. Introduction of 8-benzyl and 8-phenoxymethyl into 2,2′-dimethylthiacarbocyanine causes shifts toward the blue of 75 and 50 Å., respectively. The 8-phenyl group, on the other hand, causes a shift toward the red of 25 Å. Very similar relationships have been found in the 2,2′-diethyl series, but these dyes invariably have their absorption maxima somewhat nearer the red than those of the corresponding 2,2′-dimethyl dyes, the amount of the difference varying from 25 to 50 Å. In order to ascertain whether members of the 2,2′-di-*n*-propyl and 2,2′-di-*n*-butyl series would have absorption maxima still further toward the red, three members of each series were prepared, these dyes having in the 8-position, hydrogen, methyl and ethyl, respectively. The two dyes with unsubstituted trimethenyl chains, however, had absorption maxima identical in position with that of 2,2′-diethylthiacarbocyanine iodide, but dyes of the 2,2′-di-*n*-propyl and 2,2′-di-*n*-butyl series containing 8-methyl and 8-ethyl groups had their absorption maxima, as a rule, somewhat nearer the red than the corresponding dyes of the 2,2′-diethyl series.

Three dyes of the 2,2′-diallylthiacarbocyanine series were also examined, these being the unsubstituted dye and the 8-methyl and 8-ethyl derivatives. Within this series, the same general relations held as were found to apply in the 2,2′-dimethyl and 2,2′-diethyl series, but the 2,2′-diallyl derivatives had their absorption maxima consistently nearer the red than the corresponding 2,2′-diethyl compounds.

The new dyes described act as photographic sensitizers for the green and yellow portions, and,

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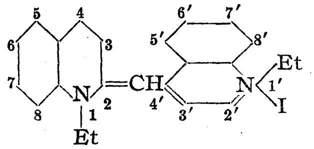
[13] Compare Hill and Rabinowitz, THIS JOURNAL, **48**, 732 (1926).

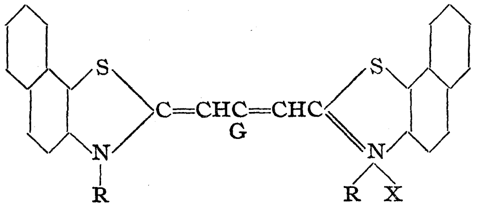
to a varying extent, the red portion of the spectrum.[14]

It was pointed out by Mills and Pope[15] that substitution of a methyl, phenyl or cyano grouping in the 2'-position of 1,1'-diethyl-2,4'-cyanine iodide (II) gave dyes with greatly reduced sensitizing power, the depressant effect of the three groups increasing in the order given. They suggested that this was due to the loading effect of the substituent on the ethylenic chain joining the two nitrogen atoms, the ability of the molecule to interact with light waves being inhibited. From this it might have been expected that loading the ethylenic chain in 2,2'-diethylthiacarbocyanine iodide by the introduction of substituents in the 8-position would materially depress the sensitizing action, but this is not the case.

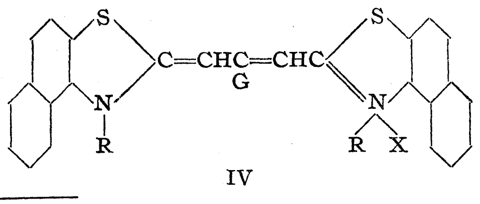
II



8-Methylthiacarbocyanine dyes derived from the methyl-α- and β-naphthothiazoles have previously been described.[12,16] Using ortho esters of propionic and of benzoic acids in conjunction with the alkyl *p*-toluenesulfonates of the two bases, eight more dyes have now been prepared, these being the 8-ethyl and 8-phenyl-5,6,5',6'-dibenzothiacarbocyanines (III) and the 8-ethyl and 8-phenyl-3,4,3',4'-dibenzothiacarbocyanines (IV), the 2,2'-dimethyl and 2,2'-diethyl derivatives being prepared of each of the four types.[17]



III



IV

On account of the insolubility of the iodides of these dyes, the bromides were prepared except in the case of 2,2',8-triethyl-5,6,5',6'-dibenzothiacarbocyanine iodide, which was sufficiently soluble.

In Table III are given the positions of the maximum absorption of these dyes together with similar data on related unsubstituted and 8-methyl substituted dyes.

TABLE III

ABSORPTION MAXIMA OF DIBENZOTHIACARBOCYANINES (III AND IV) IN Å.

(a) 5,6,5',6'-dibenzothiacarbocyanines

G (III)	R (III) Me	R (III) Et
H	5900	5925
Me	5660	5725
Et	5675	5750
Ph	5920	5925

(b) 3,4,3',4'-dibenzothiacarbocyanines

G (IV)	R (IV) Me	R (IV) Et
H	5925	5950
Me	5700	5750
Et	5750	5775
Ph	5950	5925

If these values are plotted against the groups occupying the 8-positions of the dyes, curves are obtained which, in their general characteristics, are very similar to those given in Fig. 1. Figure 2 deals with the 5,6,5',6'-dibenzothiacarbocyanines and Fig. 3 with the 3,4,3',4'-dibenzothiacarbocyanines.

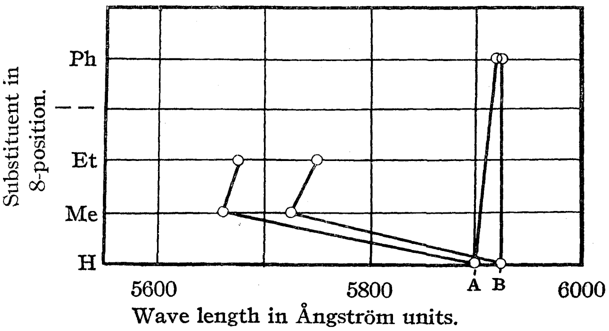


Fig. 2.—Absorption maxima of 5,6,5',6'-dibenzothiacarbocyanines (III): A, 2,2'-dimethyl series; B, 2,2'-diethyl series.

From these curves it is seen that, as in the simple thiacarbocyanines, introduction of an 8-methyl group into a dibenzothiacarbocyanine brings about a marked shift of the absorption maximum toward the blue. This shift is partially canceled if the 8-methyl group is replaced by an 8-ethyl group. The 8-phenyl dyes have

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[14] Brooker, U. S. Patents 1,846,302, 1,846,303, 1,846,304, Kodak Ltd., British Patent 394,691.

[15] Mills and Pope, *Phot. J.*, **60**, 183 (1920).

[16] Hamer, *J. Chem. Soc.*, 2598 (1929).

[17] Brooker, U. S. Patents 1,969,444, 1,969,447; Kodak Ltd., British Patent 378,870.

maxima either identical with or very close to those of the related unsubstituted dyes, but in the 3,4,3′,4′-dibenzo series the usual relative positions of the 2,2′-dimethyl and 2,2′-diethyl dyes are reversed. In every case except this, a 2,2′-dimethyl dye has its absorption maximum nearer the blue than the corresponding 2,2′-diethyl dye. In every case but one, also, a 3,4,3′,4′-dibenzothiacarbocyanine has its absorption maximum somewhat nearer the red than the corresponding 5,6,5′,6′-dibenzothiacarbocyanine.

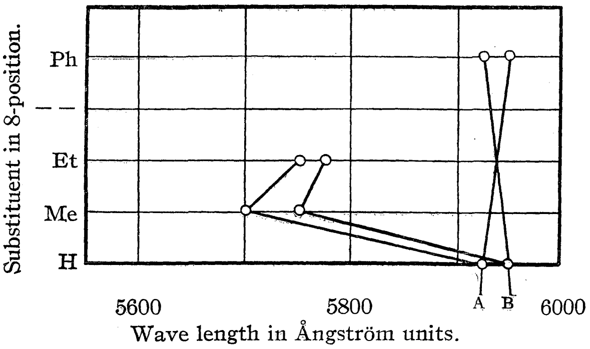

Fig. 3.—Absorption maxima of 3,4,3′,4′-dibenzothiacarbocyanines (IV): A, 2,2′-dimethyl series: B, 2,2′-diethyl series.

All the new dyes derived from the methylnaphthothiazoles act as photographic sensitizers, some of them being exceedingly powerful.[18] They sensitize further in the direction of longer wave length than the corresponding dyes derived from 1-methylbenzothiazole. It is a striking generalization that every one of the eight carbocyanine dyes derived from 2-methyl-β-naphthothiazole is a stronger sensitizer than the related isomeric dye derived from 1-methyl-α-naphthothiazole.

An 8-methylselenacarbocyanine dye (I, R = Et, G = Me, Y = Se, X = I) has recently been described,[12] and the 8-ethyl-2,2′-dimethyl- and 2,2′,8-triethylselenacarbocyanine iodides and the two corresponding 8-phenylselenacarbocyanines have now been prepared.[19] In these syntheses 1-methylbenzoselenazole alkyl *p*-toluenesulfonates were employed. The absorption maxima of these dyes as well as those of the related unsubstituted[20] and 8-methyl substituted dyes are given in Table IV.

Made up into Fig. 4, these values give curves very similar in general appearance to those already obtained. The same sharp recession toward the blue is noticeable upon introducing an 8-methyl group as was found in the previous instances, and on proceeding to the 8-ethyl compounds the absorption maxima advance again toward the red. Introduction of an 8-phenyl group brings about a shift in the absorption maximum toward the red by an amount greater than has been encountered hitherto. It is also worthy of note that in this series the unsubstituted 2,2′-dimethyl- and 2,2′-diethyl dyes both have their maximum absorption at the same wave length.

Table IV

Absorption Maxima of Selenacarbocyanines in Å. (I, Y = Se)

G (I)	R (I) Me	R (I) Et
H	5675	5675
Me	5485	5525
Et	5525	5575
Ph	5725	5740

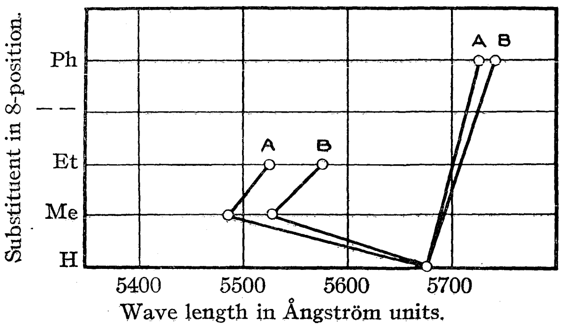

Fig. 4.—Absorption maxima of selenacarbocyanines (I, Y = Se): A, 2,2′-dimethyl series: B, 2,2′-diethyl series.

The new selenacarbocyanines are photographic sensitizers, their sensitizing bands extending somewhat further into the red than those of the corresponding thiacarbocyanines.[21]

In the oxacarbocyanine series an 8-methyl derivative (I, G = Me, R = Et, Y = O, X = I) has been obtained,[12] triethylamine being used in addition to pyridine in its preparation. Using this same device the 8-ethyl-2,2′-dimethyl- and 2,2′,8-triethyloxacarbocyanine iodides have now been prepared. The absorption maxima of these dyes, as well as those of the unsubstituted oxacarbocyanines, are given in Table V and Fig. 5 is based on these values.

The curves in Fig. 5 differ markedly from those preceding it in that introduction of an 8-methyl group into an unsubstituted oxacarbocyanine pro-

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(18) Brooker, U. S. Patent 1,846,301; Kodak Ltd., British Patent 378,885.

(19) White, U. S. Patent 1,990,681.

(20) Clark, *J. Chem. Soc.*, 2313 (1928); 216 (1933).

(21) White, U. S. Patent 1,990,507; Kodak Ltd., British Patent 390,406.

TABLE V

ABSORPTION MAXIMA OF THE OXACARBOCYANINES IN Å. (I, Y = O)

G (I)	R (I) Me	R (I) Et
H	4820	4825
Me	4875	4885
Et	4900	4900

duces a shift toward the red. This advance is continued on introducing an 8-ethyl group. The differences between the positions of the maxima of corresponding members of the 2,2′-dimethyl and 2,2′-diethyl series are very slight and, indeed, the values for the two 8-ethyl dyes are identical.

The new oxacarbocyanines are photographic sensitizers for the blue-green and green.[22]

All the absorption curves used in the present paper were determined for methyl alcoholic solutions using the means already detailed.[12]

TABLE VI

PREPARATION OF IMINO-ESTER HYDROCHLORIDES

Imino-ester hydrochloride	Nitrile	Alcohol	Days A	Days B	Yield, %
Me iminopropionate	C_2H_5CN	MeOH	2	3	88
Me imino-*n*-butyrate	*n*-C_3H_7CN	MeOH	3	3	67
Me imino-*n*-valerate	*n*-C_4H_9CN	MeOH	2	3	63
Me imino-*n*-caproate	*n*-$C_5H_{11}CN$	MeOH	4	2	75
Me iminoisocaproate	*i*-$C_5H_{11}CN$	MeOH	3	3	71
Et iminophenoxyacetate	$C_6H_5OCH_2CN$	EtOH	2	2	82
Et iminobenzoate	C_6H_5CN	EtOH	20	8	90

TABLE VII

PREPARATION OF ORTHO ESTERS

Ortho ester	Stood, days	Yield, %	B. p., °C.	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
OE3 Me *o*-propionate	6	69	126–128	$C_6H_{14}O_3$	53.68	10.52	53.90	10.60
OE5 Me *o*-*n*-butyrate	28	13	145–147	$C_7H_{16}O_3$	56.70	10.88	56.75	10.86
OE6 Me *o*-*n*-valerate	28	12	167–170	$C_8H_{18}O_3$	59.21	11.19	59.45	11.10
OE7 Me *o*-*n*-caproate	5	40	187–190	$C_9H_{20}O_3$	61.31	11.45	61.30	11.36
OE8 Me *o*-isocaproate	35	9	178–181	$C_9H_{20}O_3$	61.31	11.45	61.35	11.34
OE9 Et *o*-phenoxyacetate[a]	28	30	99–100 (1.5 mm.)	$C_{14}H_{22}O_4$	66.10	8.72	66.30	8.34
OE10 Et *o*-benzoate	42	20	239.5–240.5	$C_{13}H_{20}O_3$	69.60	8.99	69.65	8.74

[a] The crude ortho ester fraction, b. p. 130–140° (8.5 mm.), was well washed with water to remove amide. Benzene was added, the solution again washed with water and the benzene layer dried with anhydrous sodium sulfate and fractionated.

Experimental

Ortho Esters.—For the preparation of the imino-ester hydrochlorides, the method of Hill and Rabinowitz[13] and of Sah[7] was used, a mixture of the nitrile (1 mol) and the alcohol (1 mol) in ether being treated at 5–10° with hydrochloric acid gas (1.05–1.1 mols), it being of the utmost importance that the materials should be as free from water as possible. The imino-ester hydrochlorides (listed in Table VI) usually set to a cake of crystals after standing for some days at 0° (Table VI, Days A) and this was well crushed, washed with absolute ether, and the excess of hydrochloric acid removed by standing in a vacuum over powdered potassium hydroxide, a separate dish of phosphorus pentoxide being also included. This treatment was continued until a small quantity of the salt, dissolved in absolute alcohol no longer affected moistened Congo red paper (Table VI, Days B). The hydrochlorides so obtained formed colorless crystals which had no true melting points but decomposed with gas evolution after shrinking.

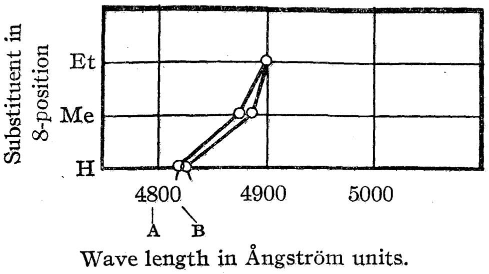

Fig. 5.—Absorption maxima of oxacarbocyanines (I, Y=O): A, 2,2′-dimethyl series; B, 2,2′-diethyl series.

The imino-ester hydrochlorides are unstable compounds and were converted directly into the corresponding ortho esters by treatment at room temperature, with occasional shaking, with the appropriate alcohols for periods which varied from a few days to a few weeks. The solid which separated (largely ammonium chloride) was removed by filtration. The filtrate was distilled from the steam-bath under reduced pressure, a residue of amide usually remaining. The distillate was then repeatedly fractionated, it being necessary in some cases to remove accompanying

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(22) Brooker, U. S. Patent 1,962,124.

normal ester. By this procedure all the ortho esters were obtained analytically pure, and those not previously described are given in Table VII. For convenience they are numbered as shown.

Ortho esters used in addition to the above are ethyl orthoformate, OE1; ethyl orthoacetate, OE2; ethyl orthopropionate,[6,8] OE4; ethyl orthophenylacetate,[9,10] OE11.

Quaternary Salts.—The quaternary salts used are numbered for convenience as follows:

QS1	1-Methylbenzothiazole methiodide
QS2	1-Methylbenzothiazole ethiodide
QS3	1-Methylbenzothiazole *n*-propiodide
QS4	1-Methylbenzothiazole *n*-butiodide
QS5	1-Methylbenzothiazole alliodide
QS6	1-Methylbenzothiazole metho-*p*-toluenesulfonate
QS7	1-Methylbenzothiazole etho-*p*-toluenesulfonate
QS8	1-Methyl-α-naphthothiazole metho-*p*-toluenesulfonate
QS9	1-Methyl-α-naphthothiazole etho-*p*-toluenesulfonate
QS10	2-Methyl-β-naphthothiazole metho-*p*-toluenesulfonate
QS11	2-Methyl-β-naphthothiazole etho-*p*-toluenesulfonate
QS12	1-Methylbenzoselenazole metho-*p*-toluenesulfonate
QS13	1-Methylbenzoselenazole etho-*p*-toluenesulfonate
QS14	1-Methylbenzoxazole metho-*p*-toluenesulfonate
QS15	1-Methylbenzoxazole ethiodide

QS12 and 14 were prepared by heating equimolecular proportions of base and methyl-*p*-toluenesulfonate at 100° for several hours. QS13 was similarly prepared, the mixture being heated for three days. These salts were used without purification. Other new quaternary salts are given in Table VIII, the normal methods of preparation being used.[12] In all cases the crude products were ground with acetone and washed with this solvent and were then sufficiently pure for dye formation. The yields given correspond to this stage. For analysis and melting point determinations those salts which were iodides were recrystallized from methyl alcohol. The *p*-toluenesulfonates were dissolved in hot methyl alcohol and precipitated by adding acetone. The salts were all colorless or almost colorless solids.

Dyes.—The quaternary salts were condensed with the ortho esters in boiling anhydrous pyridine solution, the period of heating varying from ten to ninety minutes. In general, a 200% excess of orthoester was used except that a 100% excess was used of OE5, 6, 7 and 8. When the quaternary salt was an iodide, separation of the dye from

TABLE VIII

PREPARATION OF QUATERNARY SALTS

Salt	Reactants heated, hrs.	Yield, %	M. p., °C.	Formula	Analyses, % Calcd.	
						Found
QS3	72[a]	82	173 –175	$C_{11}H_{14}INS$	I, 39.77	39.88
QS4	72[a]	63	186 –187	$C_{12}H_{16}INS$	I, 38.11	38.10
QS5	20[a]	88	192 –193	$C_{11}H_{12}INS$	I, 40.03	39.95
QS6[a]	3[b]	90	183.5–184.5	$C_{16}H_{17}NO_3S_2$	N, 4.16	4.22
QS8	48[c]	88	232 –233	$C_{20}H_{19}NO_3S_2$	C, 62.29	61.98
					H, 4.97	4.83
QS10	–[d]	94	189 –190	$C_{20}H_{19}NO_3S_2$	C, 62.29	62.10
					H, 4.97	4.90

[a] Heated on steam-bath under reflux. [b] Heated at 100°. [c] Heated at 105–110°. [d] Heated for three hours at 130–140° and for three days at 100°.

TABLE IX

PREPARATION OF THIACARBOCYANINE IODIDES

	Thiacarbocyanine iodide	Quaternary salt, g.		Ortho-ester, g.		C_5H_5N, cc.	Boiled, min.	Method	Yield, %		Soln. MeOH cc./g.	M. p., °C. dec.	Formula	Halogen, % Calcd.	Found
D1	2,2′-di-Al[a]	QS5	6.34	OE1	4.44	25	45	A	96	77	170	264–266	$C_{23}H_{21}IN_2S_2$	24.59	24.46
D2	2,2′-di-*n*-Pr	QS3	6.38	OE1	4.44	25	45	A	95	87	150	296–297	$C_{23}H_{25}IN_2S_2$	24.40	24.46
D3	2,2′-di-*n*-Bu	QS4	6.66	OE1	4.44	25	45	A	95	77	48	275–277	$C_{25}H_{29}IN_2S_2$	23.15	23.20
D4	2,2′-di-Al-8-Me	QS5	6.34	OE2	4.86	25	45	A	75	64	190	267–268	$C_{24}H_{23}IN_2S_2$	23.93	23.86
D5	8-Me-2,2′-di-*n*-Pr	QS3	6.38	OE2	4.86	25	45	A	70	64	1560	295–296	$C_{24}H_{27}IN_2S_2$	23.75	23.77
D6	2,2′-di-*n*-Bu-8-Me	QS4	6.66	OE2	4.86	25	45	A	59	53	63	236–237	$C_{26}H_{31}IN_2S_2$	22.57	22.64
D7	8-Et-2,2′-di-Me[b]	QS1	5.28	OE4	5.28	25	45	A	67	56	440	286–287	$C_{21}H_{21}IN_2S_2$	25.78	25.63
D8	2,2′,8-tri-Et[c]	QS2	6.10	OE4	5.28	25	45	A	52	41	75	236–237[d]	$C_{23}H_{25}IN_2S_2$	24.40	24.32
D9	2,2′-di-Al-8-Et[e]	QS5	6.34	OE4	5.28	25	45	A	47	30	55	214–216	$C_{25}H_{25}IN_2S_2$	23.32	23.37
D10	8-Et-2,2′-di-*n*-Pr	QS3	6.38	OE4	5.28	25	45	A	38	28	110	248–250	$C_{25}H_{29}IN_2S_2$	23.15	23.17
D11	2,2′-di-*n*-Bu-8-Et	QS4	6.66	OE4	5.28	25	45	A	35	28	65	241–243	$C_{27}H_{33}IN_2S_2$	22.03	21.95
D12	2,2′-di-Me-8-*n*-Pr	QS6	6.70	OE5	2.96	25	45	C	59	50	110	268–269	$C_{22}H_{23}IN_2S_2$	25.07	24.97
D13	2,2′-di-Et-8-*n*-Pr	QS7	6.98	OE5	2.96	25	45	B	65	55	58	246–248	$C_{24}H_{27}IN_2S_2$	23.75	23.72
D14	8-*n*-Bu-2,2′-di-Me	QS6	6.70	OE6	3.24	25	45	C	55	42	68	168–169	$C_{23}H_{25}IN_2S_2$	24.40	24.41
D15	8-*n*-Bu-2,2′-di-Et	QS7	6.98	OE6	3.24	25	45	B	64	58	50	233–234	$C_{25}H_{29}IN_2S_2$	23.15	23.03
D16	8-*n*-Am-2,2′-di-Me	QS6	6.70	OE7	3.52	25	45	B	66	55	34	217–219	$C_{24}H_{27}IN_2S_2$	23.75	23.51
D17	8-*n*-Am-2,2′-di-Et	QS7	6.98	OE7	3.52	25	45	B	62	53	39	237–238	$C_{26}H_{31}IN_2S_2$	22.57	22.42
D18	8-iso-Am-2,2′-di-Me	QS6	6.70	OE8	3.52	25	45	C	61	47	80	241–242	$C_{24}H_{27}IN_2S_2$	23.75	23.65
D19	8-iso-Am-2,2′-di-Et	QS7	6.98	OE8	3.52	25	45	B	61	51	35	219–220	$C_{26}H_{31}IN_2S_2$	22.57	22.55
D20	8-PhCH₂-2,2′-di-Me	QS6	6.70	OE11	7.14	25	45	C	27	15	500	288–289	$C_{26}H_{23}IN_2S_2$	22.90	22.87
D21	8-PhCH₂-2,2′-di-Et	QS7	6.98	OE11	7.14	25	45	C	16	11	155	242–243	$C_{28}H_{27}IN_2S_2$	21.80	21.80
D22	2,2′-di-Al-8-PhCH₂	QS5	6.34	OE11	7.14	25	45	A	38	33	180	225–227	$C_{30}H_{27}IN_2S_2$	20.94	20.91
D23	2,2′-di-Me-8-PhOCH₂[f]	QS6	6.70	OE9	7.62	25	30	B	71	48	110	255–257	$C_{26}H_{23}BrN_2OS_2$	15.27	15.37
D24	2,2′-di-Et-8-PhOCH₂	QS7	3.49	OE9	3.80	10	30	B	71	39[g]	52	202–204	$C_{28}H_{27}IN_2OS_2$	21.21	21.05
D25	2,2′-di-Al-8-PhOCH₂	QS5	6.34	OE9	7.62	25	10	A	57	41[g]	80	211–213	$C_{30}H_{27}IN_2OS_2$	20.39	20.38
D26	2,2′-di-Me-8-Ph	QS6	6.70	OE10	6.72	25	45	C	75	56	210	275–277	$C_{25}H_{21}IN_2S_2$	23.49	23.51
D27	2,2′-di-Et-8-Ph	QS7	6.98	OE10	6.72	25	45	C	73	56	210	300–301	$C_{27}H_{25}IN_2S_2$	22.34	22.02

TABLE IX (*Concluded*)

PREPARATION OF 5,6,5′,6′-DIBENZOTHIACARBOCYANINE BROMIDES

5,6,5′,6′-Dibenzothia-carbocyanine bromide	Quaternary salt, g.		Ortho-ester, g.		C_5H_5N, cc.	Boiled, min.	Meth-od	Yield,	%	Soln. MeOH cc./g.	M. p., °C. dec.	Formula	Halogen, % Calcd.	Halogen, % Found
D28 2,2′-di-Me[h]	QS8	3.85	OE1	2.22	30	60	B	99	83	1350	285	$C_{27}H_{21}BrN_2S_2$	15.45	15.45
D29 2,2′-di-Et[i]	QS9	8.00	OE1	4.45	50	60	C	86	68	70	280	$C_{29}H_{27}BrN_2S_2$	14.66	14.66
D30 2,2′-8-tri-Me[h]	QS8	3.85	OE2	2.43	20	60	B	66	42	680	278–281	$C_{28}H_{23}BrN_2S_2$	15.05	14.84
D31 2,2′-di-Et-8-Me[h]	QS9	8.00	OE2	4.85	50	60	B	58	43	215	261	$C_{30}H_{27}BrN_2S_2$	14.29	14.11
D32 8-Et-2,2′-di-Me	QS8	7.70	OE3	4.02	30	60	C	70	54	265	299	$C_{29}H_{25}BrN_2S_2$	14.66	14.53
D33 2,2′,8-tri-Et[j]	QS9	8.00	OE3	4.02	20	60	C	47	37	520	296	$C_{31}H_{29}IN_2S_2$	20.46	20.56
D34 2,2′-di-Me-8-Ph	QS8	7.70	OE10	6.70	30	90	C	70	47	1120	308–310	$C_{33}H_{25}BrN_2S_2$	13.47	13.31
D35 2,2′-di-Et-8-Ph	QS9	8.00	OE10	6.70	20	90	C	50	38	355	296	$C_{35}H_{29}BrN_2S_2$	12.86	12.81
PREPARATION OF 3,4,3′,4′-DIBENZOTHIACARBOCYANINE BROMIDES														
3,4,3′,4′-Dibenzothia-carbocyanine bromide														
D36 2,2′-di-Me[h]	QS10	3.85	OE1	2.22	30	60	C	96	73	2150	237	$C_{27}H_{21}BrN_2S_2$	15.45	15.15
D37 2,2′,8-tri-Me	QS10	7.70	OE2	4.85	20	30	C	31	19[g]	150	240–241	$C_{28}H_{23}BrN_2S_2$	15.05	15.10
D38 8-Et-2,2′-di-Me	QS10	7.70	OE4	5.30	30	30	C	39	24	285	230	$C_{29}H_{25}BrN_2S_2$	14.66	14.79
D39 2,2′,8-tri-Et	QS11	8.00	OE4	5.30	15	30	C	37	29	130	247	$C_{31}H_{29}BrN_2S_2$	13.94	13.81
D40 2,2′-di-Me-8-Ph	QS10	7.70	OE10	6.70	20	15	C	8	3[k]		242–244	$C_{33}H_{25}BrN_2S_2$	13.47	13.34
D41 2,2′-di-Et-8-Ph	QS11	8.00	OE10	6.70	20	30	B	6	4.5	150	252	$C_{35}H_{29}BrN_2S_2$	12.86	12.81
PREPARATION OF SELENACARBOCYANINE IODIDES														
Selenacarbocyanine iodide														
D42 2,2′,8-tri-Me[f]	QS12	7.64	OE2	4.85	25	25	C	51	36	280	290–291	$C_{20}H_{19}BrN_2Se_2$	15.21	15.05
D43 8-Et-2,2′-di-Me	QS12	7.64	OE4	5.28	25	15	C	51	32	1300	271–272	$C_{21}H_{21}IN_2Se_2$	21.64	21.47
D44 2,2′,8-tri-Et	QS13	7.92	OE4	5.28	25	15	C	20	16	35	146–148	$C_{23}H_{25}IN_2Se_2$	20.65	20.53
D45 2,2′-di-Me-8-Ph	QS12	7.64	OE10	6.72	25	15	C	27	18	130	271–272	$C_{25}H_{21}IN_2Se_2$	20.00	19.86
D46 2,2′-di-Et-8-Ph	QS13	7.92	OE10	6.72	25	15	C	19	13	230	280–281	$C_{27}H_{25}IN_2Se_2$	19.15	18.85
PREPARATION OF OXACARBOCYANINE IODIDES														
Oxacarbocyanine iodide														
D47 2,2′,8-tri-Me	QS14	6.4	OE2	6.5	20[l]	7	C	8	6	105	290–292	$C_{20}H_{19}IN_2O_2$	28.45	28.21
D48 8-Et-2,2′-di-Me	QS14	6.4	OE4	7.05	20[l]	7	C	16	11	28	280–282	$C_{21}H_{21}IN_2O_2$	27.58	27.40
D49 2,2′,8-tri-Et	QS15	2.89	OE4	2.64	15[m]	60	A	13	8	45	269–270	$C_{23}H_{25}IN_2O_2$	25.99	25.91

[a] The bromide of this dye was described by Hamer.[2] [b] When methyl orthopropionate (4.02 g.) was used in place of the ethyl ortho ester, the yield of dye was 0.65 g. (13% calculated as 8-ethyl dye). The iodine content was somewhat high (found: I, 25.91) which would correspond to a certain degree of contamination with the 2,2′,8-trimethyl dye. [c] When methyl orthopropionate (4.02 g.) was used instead of the ethyl ortho ester, the method otherwise being the same, the yield of crude dye was 1.52 g. (29% calculated as 2,2′,8-triethyl dye). When a solution of the product in methyl alcohol was allowed to evaporate slowly, large greenish crystals separated together with smaller coppery crystals. These were separated mechanically, and the two fractions were purified by repeated fractional crystallization. The more soluble fraction was identical in properties with the analyzed 2,2′,8-triethyl compound (appearance, melting point and mixed melting point, absorption and sensitizing action) (found: I, 24.47). The less soluble fraction was similarly found to be identical with the 2,2′-diethyl-8-methyl dye (found: I, 25.11. $C_{22}H_{23}IN_2S_2$ required I, 25.07). [d] When the specimen was heated from room temperature. [e] Use of methyl orthopropionate gave a yield of only 9% (calculated as 8-ethyl dye). After one recrystallization (about 200 cc. per gram), the dye was identical with the 8-methyl dye. (Found: I, 23.89. 8-Methyl dye requires I, 23.93.) [f] Bromide. [g] After a further recrystallization. [h] Iodide of this dye was prepared by Hamer.[16] [i] Described by Hamer,[16] who gives melting point 274° (dec.). [j] Iodide. [k] After two recrystallizations from 95% EtOH and two from glacial acetic acid. [l] Plus 2.2 g. NEt_3. [m] Plus 0.5 g. NEt_3.

APPEARANCE OF THE DYES

D1	Bright, bronze needles.
D2	Prism reflecting green and purple.
D3	Dark purplish felt.
D4	Dark crystals with purplish reflex.
D5	Minute purplish-bronze crystals.
D6	Dark crystals reflecting blue and purple.
D7	Minute crystals with green reflex.
D8	Beautiful prisms with double blue and green reflex.
D9	Clusters of greenish crystals.
D10	Granular green crystals.
D11	Dark prisms, some faces reflecting purple, others brilliant bronze.
D12	Minute purplish crystals.
D13	Brilliant greenish-bronze prisms.
D14	Purplish needles with blue reflex.
D15	Pale bronze granular crystals.
D16	Brownish needles (transmitted light) with very brilliant blue reflex
D17	Granular greenish-bronze crystals.
D18	Purplish-brown granular crystals with green reflex.
D19	Prisms with double blue and green reflex.
D20	Small reddish - brown needles.
D21	Magnificent emerald-green prisms.
D22	Beautiful greenish - blue prisms.
D23	Felted mat of minute purplish-brown needles.
D24	Reddish-coppery crystals.
D25	Beautiful green prisms.
D26	Bronze needles.
D27	Greenish-bronze crystals.
D28	Dark purplish felted mat.
D29	Dark greenish needles.
D30	Minute emerald - green crystals.
D31	Dark greenish - bronze needles.
D32	Small purplish crystals with blue reflex.
D33	Minute greenish - bronze crystals.
D34	Dull purplish felted crystals.
D35	Minute dull purplish crystals.
D36	Greenish-bronze felt.
D37	Minute lustrous green needles.
D38	Minute greenish crystals.
D39	Minute glittering crystals with greenish-bronze reflex.
D40	Minute greenish - bronze crystals.
D41	Minute greenish crystals.
D42	Bluish-purple felt.
D43	Minute greenish crystals.

D44 Prisms with double blue and brassy-green reflex.
D45 Greenish-bronze needles.
D46 Metallic greenish prisms.
D47 Beautiful garnet - red prisms.
D48 Orange-red powder.
D49 Orange-red prisms.

the reaction mixture was facilitated by the addition of ether, the crude product being treated with hot acetone and the suspension chilled and filtered. This procedure removed tarry impurities. Any unchanged quaternary salt was removed by washing with water and the dye was finally recrystallized from methyl alcohol. This procedure is referred to as Method A. When the quaternary salt was a *p*-toluenesulfonate, one of two procedures was used. In Method B, the hot reaction mixture was treated directly with excess of hot aqueous potassium bromide or iodide, the precipitated dye washed with water, treated with acetone and then recrystallized as in Method A. In Method C, the dye was precipitated from the cooled reaction mixture as the *p*-toluenesulfonate by the addition of ether. The residue was redissolved in the minimum quantity of hot methyl alcohol and converted into the bromide or iodide by treatment with excess of an aqueous solution of the appropriate potassium salt, the further treatment being the same as in Method B.

The dye condensations are summarized in Table IX. The yield of crude product is given in each case, followed by the yield of recrystallized dye. Methyl alcohol was used as a solvent for recrystallization in all cases except one and the amount required is indicated. The melting points were determined as described in Part I.[12]

Summary

1. Thiacarbocyanines containing various groups attached to the central carbon atom of the three-carbon chain have been prepared utilizing the appropriate ortho esters for the purpose. The following are the groups so introduced: Et, *n*-Pr, *n*-Bu, *n*- and *i*-Am, $PhCH_2$-, $PhOCH_2$- and Ph. Selena- and oxacarbocyanines containing certain of these groups have also been prepared.

2. The following ortho esters are described for the first time: methyl orthopropionate, methyl ortho-*n*-butyrate, methyl ortho-*n*-valerate, methyl ortho-*n*-caproate, methyl orthoisocaproate, ethyl orthophenoxyacetate.

3. Substitution of hydrogen in the molecule of a thiacarbocyanine dye derived from 1-methylbenzothiazole by an 8-methyl group causes the absorption maximum in methyl alcohol to shift about 150 Å. toward the blue, but replacement of 8-methyl by 8-ethyl shifts the maximum about 50 Å. back toward the red. Replacement of 8-ethyl by higher aliphatic groupings up to *n*- and isoamyl causes no further shift. Replacement of hydrogen by 8-benzyl causes a shift (75 Å.) toward the blue, but replacement by 8-phenyl causes a slight shift (25 Å.) toward the red.

4. Somewhat similar relationships to those summarized above can be traced in the 3,4,3′,4′- and 5,6,5′,6′-dibenzothiacarbocyanine series and in the selenacarbocyanines. The oxacarbocyanines are exceptional.

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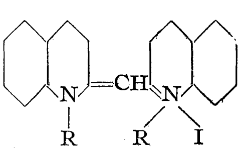
[CONTRIBUTION NO. 563 FROM THE KODAK RESEARCH LABORATORIES]

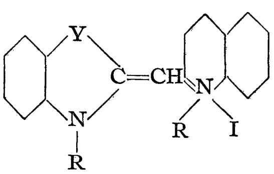
Studies in the Cyanine Dye Series. III. Improvements in the 2′-Cyanine Condensation

BY L. G. S. BROOKER AND G. H. KEYES

Kaufmann and Vonderwahl[1] were the first to observe the formation of a dye of the 2,2′(or ψ)-cyanine class (I) and Fischer and Scheibe[2] succeeded in isolating the 1,1′-dimethyl compound by the action of potassium hydroxide on a mixture of 2-iodoquinoline methiodide and quinaldine methiodide. Higher yields of dyes of this type were obtained by Hamer,[3] who showed further that the reaction was a general one in that the quinaldine alkiodide could be replaced by quaternary salts of other bases containing a reactive methyl group. Alkyl iodides of 1-methylbenzothiazole were found to yield thia-2′-cyanines (II, Y = S) and 2,3,3-trimethylindolenine alkyl iodides yielded indo-2′-cyanines (II, Y = C-$(Me)_2$).



I



II

We have now found that if the method of Hamer is employed for the preparation of the hitherto unknown 1′,2-diethyloxa-2′-cyanine iodide (II, Y = O), using 1-methylbenzoxazole ethiodide and 2-iodoquinoline ethiodide, the yield of purified

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[1] Kaufmann and Vonderwahl, *Ber.*, **45**, 1417 (1912).

[2] Fischer and Scheibe, *J. prakt. Chem.*, ii, **100**, 86 (1919).

[3] Hamer, *J. Chem. Soc.*, 206 (1928).

product is only 3% and is not improved by substituting sodium ethylate for potassium hydroxide. If, however, the quaternary salts are heated together in dimethylaniline or especially diethylaniline, the yield of dye is enormously increased, being 89% with the latter.[4]

If used for effecting other 2′-cyanine condensations, however, the dialkylanilines are not so satisfactory, but triethylamine has been found to be a good general condensing agent, being markedly superior to potassium hydroxide and giving better yields in every case studied.[5] The following yields of purified dyes are those obtained using triethylamine, the figures in parentheses being the corresponding yields using potassium hydroxide: 1,1′-diethyl-2,2′-cyanine iodide, 87% (72%); 1′,2-diethylthia-2′-cyanine iodide, 88% (72%); 1′,2-diethyloxa-2′-cyanine iodide, 43% (3%); 1′,2-diethylselena-2′-cyanine iodide (II, Y = Se), 72% (55%); 1,1′-diethyl-2,4′-cyanine iodide, 92.5% (73.5%). In the experiments which gave these yields, the crude dyes were recrystallized and the purity of the first crops established by analysis. The mother liquors were then concentrated and second, in some cases third, crops obtained, the purity of which was established by melting point determinations, carried out side by side with specimens of the analyzed materials. In no case did a second or third crop melt lower than four degrees below the corresponding first crop.

The preparation of 1′,2-diethylselena-2′-cyanine iodide has been described by the I. G. Farbenindustrie A.-G.[6] and the preparation of the 2,4′ (or iso)-cyanine using 2-iodoquinoline ethiodide has been described by Hamer.[3]

The absorption of 1′,2-diethyloxa-2′-cyanine iodide has been determined as well as the absorptions of the 1′,2-diethylthia- and 1′,2-diethylselena-2′-cyanine iodides, dyes containing ethyl groups being chosen for comparison here as well as in the rest of this paper for the sake of uniformity, and the three curves are shown in Fig. 1.

It is now well known that replacement of sulfur in a cyanine dye by selenium produces but a slight shift in the position of the absorption maximum,[7,8] and this is further illustrated in the present instance, the maximum for the thia-2′-cyanine being at 4850 Å.,[9] while that for the selena-2′-cyanine is at 4875 Å. In each case there is indication of a less well-defined secondary band nearer the blue. The absorption curve of the oxa-2′-cyanine likewise reveals the presence of two overlapping bands, but in this case it is the band nearer the blue end of the spectrum which is the more pronounced, and this has its maximum at 4350 Å. The positions of the maxima are indicated by the arrows in Fig. 1. It will be noted that the difference between the maximum of the oxa-2′-cyanine and that of the thia-2′-cyanine, amounting to 500 Å., is enormously greater than that between the latter and that of the selena-2′-cyanine.

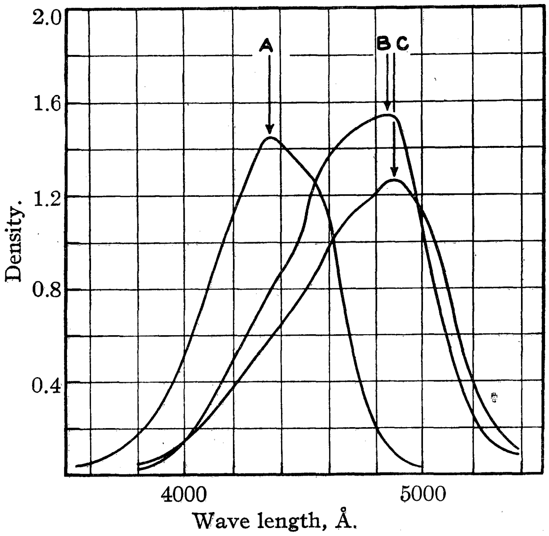

Fig. 1.—Absorption curves of 1:60,000 solutions of 2′-cyanines: A, 1′,2-diethyloxa-2′-cyanine iodide; B, 1′,2-diethylthia-2′-cyanine iodide; C, 1′,2-diethylselena-2′-cyanine iodide.

1′,2-Diethyloxa-2′-cyanine iodide is a photographic sensitizer. In a chloride emulsion its effect extends to about 5100 Å. for moderate exposures with a maximum at 4750 Å. It must be remembered, however, that sensitizing dyes behave very differently with different photographic emulsions, and that general statements as to sensitizing power must be considered in the light of this qualification.

Dyes related to the 2′-cyanines but containing pyridine and β-naphthoquinoline nuclei have been described by Hamer and Kelly,[10] who employed

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[4] Brooker, U. S. Patent 1,969,448.

[5] Kodak Ltd., British Patent 408,571.

[6] I. G. Farbenindustrie A.-G., British Patent 386,791; see also ref. 5.

[7] Fisher and Hamer, *J. Chem. Soc.*, 189 (1933); *ibid.*, 1905 (1934).

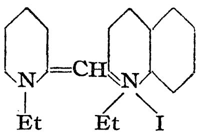
[8] Brooker and White, Part II of this series.

[9] Two absorption curves of 1′,2-diethylthia-2′-cyanine iodide have previously been published [Bloch and Hamer, *Phot. J.*, **68**, 21 (1928); *ibid.*, **70**, 374 (1930)] but differ from one another.

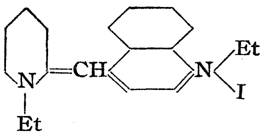
[10] Hamer and Kelly, *J. Chem. Soc.*, 777 (1931).

2-iodopyridine alkyl iodides and 2-iodo-β-naphthoquinoline alkyl iodides, respectively, in their preparation. The general name of 2′-pyridocyanine is now suggested for dyes derived from 2-iodopyridine alkyl iodides.

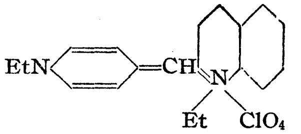
The use of triethylamine results in higher yields of the dye III, for which the name 1,1′-diethyl-2-pyrido-2′-cyanine iodide is proposed. As was pointed out by Hamer and Kelly, this dye is theoretically obtainable by two methods, that which consists in condensing α-picoline ethiodide with 2-iodoquinoline ethiodide being found by them to be fruitless when potassium hydroxide was used. Using triethylamine, however, this method gives a 35% yield of pure dye. The second method, in which 2-iodopyridine ethiodide and quinaldine ethiodide are condensed together, was found by Hamer and Kelly to give a yield of 10% after recrystallization, but optical and photographic tests revealed the presence of impurity. Using triethylamine we have obtained a 41% yield of the pure dye by this method. The specimens obtained by both methods were identical in their appearance, solubility, melting point, absorption and sensitizing effects, thus affording additional evidence of the virtual tautomerism of the cyanine dyes.[3,11]



III



IV



V

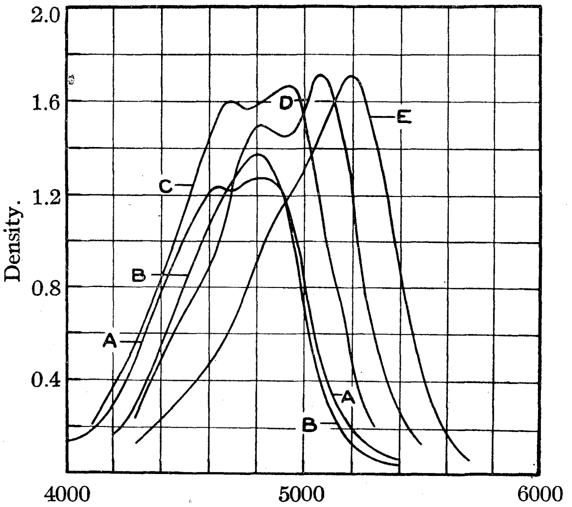
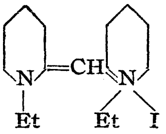


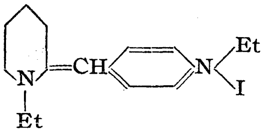
Fig. 2.—Absorption curves: A, 1,1′-diethyl-2,2′-pyridocyanine iodide (1:70,000); B, 1,1′-diethyl-2,4′-pyridocyanine iodide (1:100,000); C, 1,1′-diethyl-2-pyrido-2′-cyanine iodide (1:60,000); D, 1,1′-diethyl-4-pyrido-2′-cyanine perchlorate (1:100,000); E, 1,1′-diethyl-2-pyrido-4′-cyanine iodide (1:75,000).

By condensing 2-iodopyridine ethiodide with lepidine ethiodide, 1,1′-diethyl-2-pyrido-4′-cyanine iodide (IV) was similarly obtained, while an isomeric dye was prepared by condensing γ-picoline etho-*p*-toluenesulfonate with 2-iodoquinoline ethiodide. The dye was, however, easier to purify as the perchlorate (V) and was isolated as such.

Hamer and Kelly were unable to prepare the dye VI by the condensation of α-picoline ethiodide and 2-iodopyridine ethiodide using potassium hydroxide, but it is readily obtainable using triethylamine, it being advantageous to use *n*-propyl alcohol as a solvent here and in a number of the other condensations. This dye, for which the name 1,1′-diethyl-2,2′-pyridocyanine iodide is proposed, may be regarded as the simplest cyanine. The corresponding 1,1′-dimethyl compound was similarly prepared.[12]



VI



VII

Condensation was also effected between 2-iodopyridine ethiodide and γ-picoline etho-*p*-toluenesulfonate giving 1,1′-diethyl-2,4′-pyridocyanine iodide (VII).

The absorption curve of VI (Fig. 2, A) consists of two overlapping bands, that nearer the red with its head at 4825 Å. being only slightly stronger than the second band with its head at 4650 Å. The absorption curve of the corresponding 1,1′-dimethyl compound is very similar in general shape, there being two bands of almost equal strength but situated nearer the blue, the maxima being at 4775 and 4550 Å. The curve of VII differs in shape from that of VI and apparently consists of but a single band with its head at 4800 Å. (Fig. 2, B). It is remarkable that the maximum absorption of VII should be nearer the blue

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[11] Mills and Braunholtz, *J. Chem. Soc.*, **121**, 1489 (1922).

[12] *Cf.* Moir, *ibid.*, **127**, 2338 (1925).

than that of VI, since in the related dyes of the quinoline series the maximum absorption of 1,1′-diethyl-2,4′-cyanine iodide is 350 Å. nearer the red than that of 1,1′-diethyl-2,2′-cyanine iodide.

The absorption curve of III (Fig. 2, C) is very similar in shape to that of VI, there being two overlapping bands of almost equal strength, that nearer the red being the stronger; the maxima are at 4925 and 4700 Å. The absorption curve of V (Fig. 2, D) shows well-marked heads at 4825 and 5075 Å., the latter being the stronger. The maximum of IV (Fig. 2, E) is at 5200 Å., but there is evidence of a less well defined secondary band nearer the blue. Both IV and V may be considered as derived from VII by attachment of a benzene residue to one or the other of the pyridine nuclei of VII. The curves show that the deepening of color brought about by attaching the benzene residue to that pyridine nucleus of VII which is linked through its 4-position, giving IV, is greater than that produced by attaching a benzene residue to the other pyridine nucleus of VII, giving V. All of dyes III to VII show photographic sensitizing action.

Experimental

The condensations are summarized in Table I. In every case a mixture of one mol of each of the quaternary salts, suspended in absolute ethyl or *n*-propyl alcohol, was treated with 2.1 mols (5% excess) of triethylamine and the whole refluxed with constant shaking where ethyl alcohol was used or heated at 100° where *n*-propyl alcohol was used, the time of reaction varying from ten to forty minutes. Dye (D1–9), usually separated during the reaction or on cooling. The yield of crude washed (acetone, water) dye is given in each case followed by the yield after recrystallization, the volume of solvent required for this being indicated. In every case the dye melted with decomposition. The absorptions were measured in methyl alcoholic solutions.

TABLE I

	Dye	Quaternary Salt	g.	NEt_3	Solvent, cc.	Heated, min.	Yield, %	Solvent, cc./g.	M. p., °C., dec.	Formula	Analyses, % Calcd.	Found
D1	1′,2-DiEt-oxa-2′-cyanine iodide[a]	QS4 QS1	2.9 4.1	2.1	EtOH 20	10	56; 43	MeOH 30	290– 292	$C_{21}H_{21}IN_2O$	I, 28.58	28.45
D2	1′,2-DiEt-selena-2′-cyanine iodide[b]	QS5 QS1	3.5 4.1	2.1	EtOH 25	20	87; 72[c]	MeOH 80	280– 282	$C_{21}H_{21}IN_2Se$	I, 25.01	24.81
D3	1,1′-DiEt-2-pyrido-2′-cyanine iodide[d]	QS9 QS1	2.5 4.1	2.1	*n*-PrOH 20	40	45; 35	H_2O 40	237– 239	$C_{19}H_{21}IN_2$	I, 31.41	31.37
		QS6 QS3	3 3.6	2.1	*n*-PrOH 20	40	74; 41[e]					31.35
D4	1,1′-DiEt-2-pyrido-4′-cyanine iodide[f]	QS7 QS3	3 3.6	2.1	*n*-PrOH 15	40	30; 22	MeOH 9	194– 196	$C_{19}H_{21}IN_2$	I, 31.41	31.64
D5	1,1′-DiEt-4-pyrido-2′-cyanine perchlorate[g]	QS11 QS1	5.8 8.2	4.2	EtOH 13	30	25;[h] 12[e]	H_2O 220	211– 214	$C_{19}H_{21}ClN_2O_4$	C, 60.53 H, 5.62	60.35 5.59
D6	1,1′-DiMe-2,2′-pyridocyanine iodide[i]	QS8 QS2	4.8 7	4.2	*n*-PrOH 20	40	20;[j] 14	H_2O 80	315– 317	$C_{13}H_{15}IN_2$	C, 47.85 H, 4.64 I, 38.93	47.98 4.51 38.93
D7	1,1′-DiEt-2,2′-pyridocyanine iodide[k]	QS9 QS3	5 7.2	4.2	*n*-PrOH 10	40	28; 12[l]	H_2O 12	237– 239	$C_{15}H_{19}IN_2$	I, 35.84	35.88
D8	1,1′-DiMe-2,4′-pyridocyanine iodide[m]	QS10 QS2	6.9 8.7	5.5	*n*-PrOH 10	40	15; 10	H_2O 7	214– 217	$C_{13}H_{15}IN_2$	I, 38.93	38.95
D9	1,1′-DiEt-2,4′-pyridocyanine iodide[n]	QS11 QS3	7.3 9	5.5	*n*-PrOH 10	40	19; 13	H_2O 12	163– 166	$C_{15}H_{19}IN_2$	I, 35.84	35.97

[a] This dye was also obtained when the finely pulverized salts were heated with freshly distilled diethylaniline at 100° with frequent shaking for two and one-half hours; the yield after washing was 89% (71% after purification). With dimethylaniline the corresponding yields were 75% (51%), with quinoline 63% (47%). The dye formed orange-yellow needles. [b] Red needles with a blue reflex; the dye acts as a green sensitizer. [c] Two crops. [d] Reddish-brown crystals with green reflex. [e] After two recrystallizations. [f] Reddish-brown tablets, some faces with a green reflex. [g] Beautiful dark red crystals with a double blue and green reflex. [h] The dye iodide was precipitated from the reaction mixture by adding ether and the residue was dissolved in hot water and precipitated as the perchlorate by adding excess of hot aqueous potassium perchlorate (3 g.). [i] Light orange-brown crystals with pale-green reflex. Moir[12] stated that the compound he obtained corresponding to this dye gave absorption maxima at 4280 and 4050 Å. (in, presumably, aqueous solution). We find that in a 1:80,000 aqueous solution the absorption of our dye is similar to that in methyl alcohol except that the two maxima are less widely separated, the crests in water being at 4600 and 4725 Å., the former being now somewhat the stronger. [j] A colorless solid was removed by washing with water. [k] Crystals similar to D6. [l] After three recrystallizations. [m] Reddish-brown needles with a bluish luster. [n] Dull reddish flakes.

The quaternary salts (QS1 to 11) used in the condensations are numbered as follows.

QS1	2-Iodoquinoline ethiodide
QS2	2-Iodopyridine methiodide
QS3	2-Iodopyridine ethiodide
QS4	1-Methylbenzoxazole ethiodide
QS5	1-Methylbenzoselenazole ethiodide
QS6	Quinaldine ethiodide
QS7	Lepidine ethiodide
QS8	α-Picoline methiodide
QS9	α-Picoline ethiodide
QS10	γ-Picoline metho-*p*-toluenesulfonate
QS11	γ-Picoline etho-*p*-toluenesulfonate

QS10 was prepared by heating equimolecular proportions of γ-picoline and methyl-*p*-toluenesulfonate at 100° for fifteen minutes. QS11 was similarly prepared from ethyl-*p*-toluenesulfonate, heating at 100° for ninety minutes. Both salts were used without purification.

Summary

1. Triethylamine is superior to potassium hydroxide as a condensing agent for the preparation of 2′-cyanines. Thus, 1′,2-diethyloxa-2′-cyanine iodide is obtainable in a yield of 43% using triethylamine, whereas with potassium hydroxide the yield is only 3%. A selena-2′-cyanine has also been prepared.

2. The use of triethylamine also greatly facilitates the preparation of 1,1′-diethyl-2-pyrido-2′-cyanine iodide; a 2-pyrido-4′-cyanine and a 4-pyrido-2′-cyanine have likewise been prepared by its aid.

3. The failure of potassium hydroxide in the preparation of dyes of the 2,2′-pyridocyanine series has been recorded previously, but using triethylamine these dyes are readily available. Two 2,4′-pyridocyanines have also been prepared.

4. The absorption characteristics of the new dyes are given.

ROCHESTER, NEW YORK RECEIVED SEPTEMBER 5, 1935

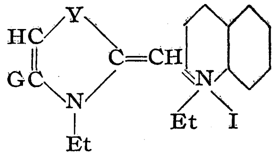
[COMMUNICATION NO. 564 FROM THE KODAK RESEARCH LABORATORIES]

Studies in the Cyanine Dye Series. IV

BY L. G. S. BROOKER, G. H. KEYES AND F. L. WHITE

Up to the present no 2′-cyanine has been described in which the nucleus linked to quinoline consists of a simple 5-membered ring. In a number of instances it has been found that cyanine dyes containing single ring nuclei are difficult to prepare. For example, the thiazolocarbocyanines derived from 2,4-dimethylthiazole were obtained in very much smaller yields than the thiacarbocyanines derived from 1-methylbenzothiazole, and furthermore, whereas the latter base readily gave rise to thiacyanines, the simple thiazolocyanines could not be prepared by the same method.[1]

We have now found, however, that when an equimolecular mixture of 2-methylthiazole ethiodide and 2-iodoquinoline ethiodide is treated with triethylamine, the simplest member of a new group of cyanine dyes, the thiazolo-2′-cyanines, is produced.[2] This dye, 1′,3-diethylthiazolo-2′-cyanine iodide (I, Y = S, G = H) is formed in excellent yield, and 2,4-dimethylthiazole ethiodide and 2-methyl-4-phenylthiazole ethiodide likewise give good yields of the corresponding dyes.



I

These new thiazolo-2′-cyanines give yellowish-orange solutions. The absorption maximum of the 1′,3-diethyl compound is at 4650 Å., and there is a secondary band nearer the red (Fig. 2, B). Introduction of a 4-methyl group shifts the maximum to 4725 Å. (Fig. 1, B) and there is still a secondary band nearer to the red, but in this case it is less pronounced. Replacement of 4-methyl by 4-phenyl produces no further shift, a fact which is worthy of notice, considering that the methyl and phenyl groups have very different effects as 8-substituents in dyes of the thia- and selenacarbocyanine series.[3]

Dyes of the 2′-cyanine series containing the benzoxazole and benzoselenazole nuclei have been described[4] and we have now prepared certain related dyes containing the simple oxazole and selenazole nuclei. 2-Methyloxazole has not itself been prepared, but certain of its substituted derivatives have been known for a long time. Of

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(1) Fisher and Hamer, *J. Chem. Soc.*, 2502 (1930).

(2) Brooker, U. S. Patent 1,969,446.

(3) Brooker and White, THIS JOURNAL, **57**, 2480 (1935).

(4) Brooker and Keyes, *ibid.*, **57**, 2488 (1935).

these, 2,4-dimethyloxazole was prepared by Schuftan[5] and 2-methyl-4-phenyloxazole by Blümlein.[6] Quaternary salts of these bases also react with 2-iodoquinoline alkyl iodides, giving oxazolo-2′-cyanines.[2] Thus, 2,4-dimethyloxazole etho-*p*-toluenesulfonate gives 1′,3-diethyl-4-methyloxazolo-2′-cyanine iodide (I, Y = O, G = Me) while 2-methyl-4-phenyloxazole etho-*p*-toluenesulfonate similarly yields 1′,3-diethyl-4-phenyloxazolo-2′-cyanine iodide (I, Y = O, G = Ph). These dyes give yellow solutions and their absorption curves are almost identical; the maxima are at 4350 Å. and in each case there is evidence of a secondary band nearer the red (Fig. 1, A).

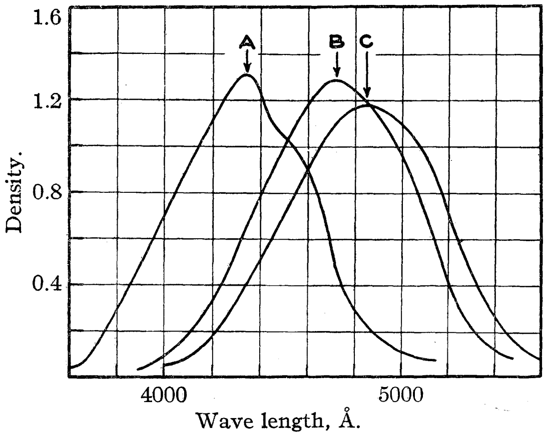
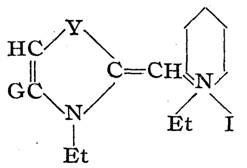


Fig. 1.—Absorption curves of 1:60,000 solutions of 2′-cyanines: A, 1′,3-diethyl-4-methyloxazolo-2′-cyanine iodide; B, 1′,3-diethyl-4-methylthiazolo-2′-cyanine iodide; C, 1′,3-diethyl-4-methylselenazolo-2′-cyanine iodide.

Bases of the 2-methylselenazole series have not hitherto been described but we have prepared 2,4-dimethylselenazole[7] by the action of chloroacetone on selenoacetamide.[8] The new base has an odor very like that of 2,4-dimethylthiazole and its ethiodide underwent condensation with 2-iodoquinoline ethiodide to give 1′,3-diethyl-4-methylselenazolo-2′-cyanine iodide[2] (I, Y = Se, G = Me). The absorption curve of this dye shows a principal maximum at 4850 Å. and has a secondary band nearer the red (Fig. 1, C). The effect of replacing the sulfur atom in 1′,3-diethyl-4-methylthiazolo-2′-cyanine iodide by selenium is therefore to shift the absorption maximum 125 Å. toward the red, this being a greater difference than that between the absorption maxima of the related thia- and selena-2′-cyanines.[4] The difference between the positions of maximum absorption of the oxygen and sulfur containing dyes of the series shown in Fig. 1 is again considerably greater than that between the sulfur and selenium containing dyes.

Triethylamine has also been applied to the condensation of quaternary salts of the 2-methylthiazoles with 2-iodopyridine alkyl iodides. Thus, from 2-methylthiazole ethiodide there was obtained 1′,3-diethylthiazolo-2′-pyridocyanine iodide (II, Y = S, G = H), the absorption maximum of which is at 4425 Å. (Fig. 2, A). The related 4-methyl and 4-phenyl dyes were similarly prepared, and these two dyes have similar absorption curves but with maxima at 4475 Å. From 2,4-dimethylselenazole ethiodide there was similarly prepared 1′,3-diethyl-4-methylselenazolo-2′-pyridocyanine iodide (II, Y = Se, G = Me), the absorption maximum of which is at 4550 Å.



II

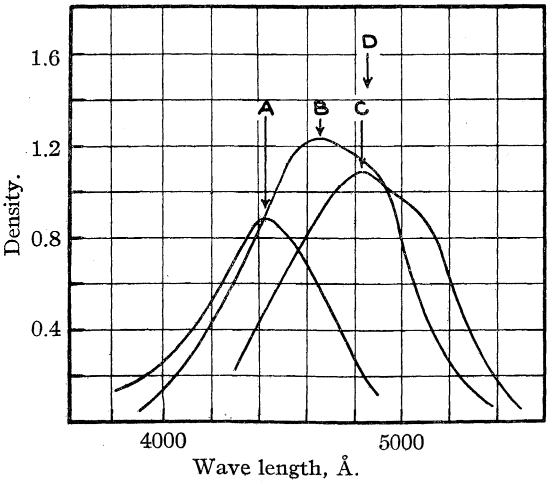


Fig. 2.—Absorption curves of dyes derived from 2-methylthiazole ethiodide: A, 1′,3-diethylthiazolo-2′-pyridocyanine iodide (1:75,000); B, 1′,3-diethylthiazolo-2′-cyanine iodide (1:60,000); C, 1′,3-diethyl-5′,6′-benzo-thiazolo-2′-cyanine iodide (1:75,000).

Triethylamine also proved satisfactory for the condensation of quaternary salts of the 2-methylthiazoles with 2-iodo-β-naphthoquinoline alkyl

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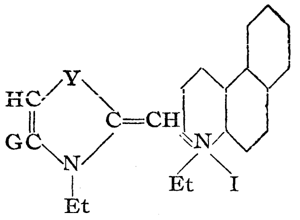
[5] Schuftan, *Ber.*, **28**, 3070 (1895); see also Oesterreich, *ibid.* **30**, 2254 (1897).

[6] Blümlein, *ibid.*, **17**, 2578 (1884); see also Lewy, *ibid.*, **20**, 2576 (1887); **21**, 924 (1888).

[7] Brooker and White, U. S. Patent 2,005,411.

[8] Kindler, *Ann.*, **431**, 187 (1923).

iodides. Thus, 2-methylthiazole ethiodide yielded 1′,3-diethyl-5′,6′-benzo-thiazolo-2′-cyanine iodide (III, Y = S, G = H); maximum absorption 4830 Å. (Fig. 2, C).



III

It will be seen from Fig. 2 that if a benzene residue is attached to 1′,3-diethylthiazolo-2′-pyridocyanine iodide (A) so as to give the thiazolo-2′-cyanine (B) the absorption maximum undergoes a shift toward the red of 225 Å. If a benzene residue is attached in turn to 1′,3-diethylthiazolo-2′-cyanine iodide (B) so as to give the 5′,6′-benzo-thiazolo-2′-cyanine iodide (C) the absorption maximum is shifted 180 Å. nearer the red. It is interesting to note that this is very near the position of maximum absorption of the isomeric 1′,2-diethylthia-2′-cyanine iodide (Fig. 2, arrow D) (Fig. 1, B in Part III of this series[4]).

From the appropriate quaternary salts there were also obtained 1′,3-diethyl-4-methyl- and 1′,3-diethyl-4-phenyl-5′,6′-benzo-thiazolo-2′-cyanine iodides and both of these have absorption maxima at 4875 Å. All three of the 5′,6′-benzo-thiazolo-2′-cyanines have secondary bands nearer the red.

By a similar reaction 2-methyl-4-phenyloxazole gave rise to 1′,3-diethyl-4-phenyl-5′,6′-benzo-oxazolo-2′-cyanine iodide (III, Y = O, G = Ph), which has its maximum absorption at 4475 Å. and 1′,3-diethyl-4-methyl-5′,6′-benzo-selenazolo-2′-cyanine iodide (III, Y = Se, G = Me) was prepared from 2,4-dimethylselenazole ethiodide. The broad absorption band of this dye has its maximum at 5000 Å. Both of these last named dyes have secondary absorption bands nearer the red.

The new dyes act as photographic sensitizers for the blue and green portions of the spectrum and details are given in the Experimental Section.

The absorption curves were determined for methyl alcoholic solutions, the methods used being those already detailed.[9] We wish to acknowledge our indebtedness to Mr. E. E. Richardson and Dr. L. A. Jones, who furnished the curves shown in this paper and in Parts II and III. We are also very grateful to Dr. L. T. Hallett, who carried out the analyses for all three papers, and to several other colleagues for sensitizing data.

Experimental

Selenoacetamide was prepared by a modification of Kindler's method,[8] and we are much indebted to Dr. R. H. Bullard for advice and help with this preparation. The hydrogen selenide, generated by heating a mixture of ferrous selenide and 12 *N* sulfuric acid, was first passed through a series of traps standing in a freezing mixture to remove excess moisture and then through a calcium chloride tower. About 90 g. of the gas (roughly three-quarters of the calculated amount) was dissolved in the chilled (−10°) mixture of acetonitrile (61.5 g.) and absolute ethyl alcohol (1 liter) in which sodium (4.5 g.) had previously been dissolved, all air having already been swept out of the apparatus with a current of nitrogen. After allowing to stand in the freezing mixture overnight, the flask was connected to a mercury manometer and gradually heated to 60°, being maintained at this temperature until the absorption of hydrogen selenide was practically complete. At no time did the excess pressure exceed 720 mm. of mercury. This process required, on an average, a total of about nine hours' heating. The reaction mixture was filtered after allowing it to cool slowly overnight, the filtrate evaporated to dryness under reduced pressure and the residue extracted with boiling benzene. The selenoacetamide crystallized out on chilling the solution and was removed and freed from adhering solvent by standing in a vacuum desiccator. The average yield of several experiments, based on the amount of hydrogen selenide added, was 60%, the highest being 77%. The unstable selenoacetamide was used as soon as possible.

2,4-Dimethylselenazole.—A mixture of chloroacetone (22.7 g., 1 mol) and absolute ethyl alcohol (10 cc.) was warmed on the steam-bath and selenoacetamide (30 g., 1 mol) added in small portions with shaking. A vigorous reaction occurred after each addition. After a further ten minutes' heating, the mixture was allowed to cool and water (100 cc.) was added followed by excess of 45% sodium hydroxide solution. The base was extracted with ether, the ethereal layer dried over anhydrous potassium carbonate, filtered, and the solvent removed by evaporation. The base was purified by fractionation; yield 41%, b. p. 55–58° (13 mm.). After a further fractionation the main portion of the base passed over at 54–55° (12 mm.).

Anal. Calcd. for C_5H_7NSe: C, 37.45; H, 4.40. Found: C, 38.10; H, 4.48.

Quaternary Salts.—The quaternary salts used in the condensations are numbered as follows

QS1 2-Iodoquinoline ethiodide
QS2 2-Iodopyridine ethiodide
QS3 2-Iodo-β-naphthoquinoline ethiodide
QS4 2-Methylthiazole ethiodide
QS5 2,4-Dimethylthiazole ethiodide[1]
QS6 2-Methyl-4-phenylthiazole ethiodide
QS7 2,4-Dimethyloxazole etho-*p*-toluenesulfonate
QS8 2-Methyl-4-phenyloxazole etho-*p*-toluenesulfonate
QS9 2,4-Dimethylselenazole ethiodide

In the preparation of QS7, equimolecular proportions of the base and ethyl *p*-toluenesulfonate were heated at 100° for one day. QS8 was similarly prepared, but the components were heated for two days. In both cases

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[9] Brooker and White, This Journal, 57, 547 (1935).

viscous melts were formed and were used without purification. Three new ethiodides are listed in Table I. These were obtained by the usual method of heating the base on the steam-bath under reflux with excess of ethyl iodide (10% excess for QS4, 100% excess for QS6 and QS9) with exclusion of light and moisture. The products were ground with and well washed with solvent (ether for QS4, acetone for QS6 and QS9) and the nearly colorless powders were sufficiently pure for further use. The yields given correspond to this stage.

TABLE I

PREPARATION OF QUATERNARY SALTS

Quaternary salts	Heating, days	Yield, %	M. p., °C.	Formula	Analyses, % Calcd.	Found
QS4	1	83	195–197[a]	$C_6H_{10}INS$	I, 49.77	49.79[a]
QS6	6	44	175.5–176.5[b]	$C_{12}H_{14}INS$	I, 38.33	38.34[b]
QS9	2	87	157–158[c]	$C_7H_{12}INSe$	I, 40.14	40.53[c]

[a] After a second treatment with ether. [b] After recrystallization from acetone; colorless crystals. [c] After recrystallization from very little methyl alcohol; colorless crystals.

TABLE II

PREPARATION OF DYES

		Quaternary Salt	G.	NEt₃, g.	EtOH, cc.	Heated min.	Yield, %	Solvent, cc./g.	M. p., °C. dec.	Formula	Analyses, % Calcd.	Found
	2′-Cyanine iodides											
D1	1′,3-DiEt-thiazolo-	QS4 QS1	2.5 4.1	2.1	20	20	80; 61	MeOH 15	267– 269	$C_{17}H_{19}IN_2S$	I, 30.94	31.20
D2	1′,3-DiEt-4-Me-thiazolo-	QS5 QS1	2.7 4.1	2.1	23	20	80; 66	MeOH 15	255– 257	$C_{18}H_{21}IN_2S$	I, 29.92	29.91
D3	1′,3-DiEt-4-Ph-thiazolo-	QS6 QS1	3.3 4.1	2.1	23	20	86; 76	MeOH 50	256– 258	$C_{23}H_{23}IN_2S$	I, 26.10	26.18
D4	1′,3-DiEt-4-Me-oxazolo-[a]	QS7 QS1	6.0 8.2	4.2	25	10	53; 49	MeOH 20	255– 258	$C_{18}H_{21}IN_2O$	I, 31.10	30.90
D5	1′,3-DiEt-4-Ph-oxazolo-[a]	QS8 QS1	13.5 15.5	8.0	25	20	25; 19	MeOH 75	262– 264	$C_{23}H_{23}IN_2O$	I, 27.00	26.89
D6	1′,3-DiEt-4-Me-selenazolo-	QS9 QS1	3.16 4.1	2.1	20	15	73; 62	MeOH 17	259– 260	$C_{18}H_{21}IN_2Se$	I, 26.93	26.97
	2′-Pyridocyanine iodides											
D7	1′,3-DiEt-thiazolo-	QS4 QS2	2.5 3.6	2.1	10	20	44; 31[b]	MeOH 15	260– 262	$C_{13}H_{17}IN_2S$	I, 35.25	35.37
D8	1′,3-DiEt-4-Me-thiazolo-	QS5 QS2	2.7 3.6	2.1	13	20	53; 35	MeOH 10	255- 257	$C_{14}H_{19}IN_2S$	I, 33.92	34.12
D9	1′,3-DiEt-4-Ph-thiazolo-	QS6 QS2	3.3 3.6	2.1	18	20	57; 30[b]	MeOH 30	247– 249	$C_{19}H_{21}IN_2S$	I, 29.10	29.18
D10	1′,3-DiEt-4-Me-selenazolo-	QS9 QS2	1.58 1.8	1.1	[c]	20	33;[d] 24	H_2O[e] 50	232– 233	$C_{14}H_{19}IN_2Se$	I, 30.12	30.28
	2′-Cyanine iodides											
D11	1′,3-DiEt-5′,6′-benzo-thiazolo-	QS4 QS3	1.3 2.3	1.1	15	20	56;[f] 24	EtOH 340	268– 270	$C_{21}H_{21}IN_2S$	I, 27.58	27.58
D12	1′,3-DiEt-4-Me-5′,6′-benzo-thiazolo-	QS5 QS3	0.7 1.1	0.6	18	20	50; 33	MeOH 165	278– 280	$C_{22}H_{23}IN_2S$	I, 26.76	26.85
D13	1′,3-DiEt-4-Ph-5′,6′-benzo-thiazolo-	QS6 QS3	0.8 1.1	0.6	13	20	54; 42	MeOH 100	274– 276	$C_{27}H_{25}IN_2S$	I, 23.67	23.67
D14	1′,3-DiEt-4-Ph-5′,6′-benzo-oxazolo-	QS8 QS3	3.6 4.6	2.1	10	40	2.5;[g] 1.5	MeOH 115	279– 282	$C_{27}H_{25}IN_2O$	I, 24.40	24.26
D15	1′,3-DiEt-4-Me-5′,6′-benzo-selenazolo-	QS9 QS3	1.05 1.53	0.75	20	20	60; 49	MeOH 105	275– 277	$C_{22}H_{23}IN_2Se$	I, 24.36	24.46

[a] A small amount of unused QS1 was removed from the hot reaction mixture by filtration and the filtrate deposited the dye on cooling. [b] After two recrystallizations. [c] 10 cc. of *n*-PrOH used as solvent, reaction mixture being heated at 100°. [d] The dye was precipitated from the reaction mixture with ether and impurities removed with acetone. [e] The solution of the dye in hot water was twice refluxed for five minutes with norite, taking of this, on each occasion, one-twentieth of the weight of the dye. [f] The crude dye required treating with hot water and a little piperidine to remove unchanged QS3; it was then recrystallized three times from EtOH. [g] The dye was precipitated by adding ether (100 cc.) with chilling and was washed with water.

Dyes.—The dye condensations are listed in Table II. They were carried out as already detailed.[4] The yields of crude and of purified dyes are given and the volume of solvent required for recrystallization.

D1 formed red needles with a blue reflex, 2 and 3 being similar; 4 and 5 consisted of yellow-brown prisms, 6 reddish-brown needles, 7 yellow-orange tablets, 8 brownish-yellow crystals, 9 light-brown prisms; 10 consisted of amber needles; 11 formed minute orange-brown crystals with a green reflex, and 12, 13 and 15 all consisted of reddish-brown needles with a green reflex; 14 formed reddish-brown crystals.

The dyes were tested photographically by incorporation in a chloride emulsion. The maximum effect of D1 is at about 5175 Å., the effect extending to about 5500 Å. for the moderate exposure given. D2 and 3 both have maxima at 5250 Å., and D6 at 5350 Å. D4 and 5 both have maxima at 4775 Å. The order in which these dyes fall is the same, therefore, whether absorption or sensitizing maxima are considered with respect to increasing wave length, and the difference between corresponding absorption and sensitizing maxima varies from 425 to 525 Å.

In the 2′-pyridocyanine series the sensitizing maxima of D7 to 10 lie at 4700, 4750, 4750, and 4825 Å., respectively, and in the series D11 to 15 the corresponding figures are 5250, 5300, 5300, 4900 and 5400 Å., respectively.

Summary

1. Triethylamine has proved to be an excellent condensing agent for the preparation of the hitherto unknown thiazolo-2′-cyanines from quaternary salts of the 2-methylthiazoles and 2-iodoquinoline ethiodide. Three dyes of this series are described.

2. By using 2-iodopyridine ethiodide and 2-iodo-β-naphthoquinoline ethiodide there have likewise been prepared the corresponding thiazolo-2′-pyridocyanines and 5′,6′-benzo-thiazolo-2′-cyanines, respectively.

3. Bases of the 2-methyloxazole series have been used for the preparation of certain oxygen-containing dyes related to the above, and 2,4-dimethylselenazole has been synthesized and similarly applied to the formation of corresponding cyanine dyes.

4. Four dyes have been prepared in which there is a methyl substituent in the 4-position of the thiazole (or oxazole) nucleus. In every case the absorption maximum occurs at the same wave length as that of the related dye containing a 4-phenyl group. Further absorption relationships are discussed.

5. The new dyes are all photographic sensitizers and details of their action are given.

ROCHESTER, NEW YORK RECEIVED SEPTEMBER 5, 1935

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

A Study of Some Urea Derivatives in the Terpene Series

BY ROBERT L. BATEMAN AND ALLAN R. DAY

In connection with certain studies of urea and its derivatives, it was thought that the preparation and examination of some terpenyl ureas might be of interest. While certain of the terpenes and their derivatives are employed medicinally, little experimental work has been carried out with the purpose of modifying their properties by structural changes and little effort has been made to introduce terpene radicals into compounds of known physiological properties.

Menthyl and bornyl ureas and certain of their derivatives were chosen because of the known physiological properties of substituted ureas and because of the medicinal importance of menthol and camphor which were the starting materials. Menthol is known to possess mild antiseptic and anesthetic properties, while camphor acts as a depressant on the central nervous system and as a stimulant on the circulatory system. If these properties, in greater part, are inherent in the functional groups (hydroxyl and carbonyl, respectively) the introduction of the menthyl and bornyl radicals into urea would not be expected to produce marked effects, as the functional groups are absent. However, if their physiological properties depend in part on their cyclic structure, a definite modifying influence should be observed.

It will be noted that all but one of the derivatives prepared contain the simple menthyl or bornyl group. In order to determine the influence of the functional group, 2-keto-3-carbamidocamphane was prepared. This urea contains in its substituent not only the cyclic structure common to borneol and camphor, but also the functional group of camphor.

The terpenylureas were obtained in satisfactory

TABLE I

MENTHYL AND BORNYLUREA AND DERIVATIVES

Substance	Form	M. p., °C., corr.	$[\alpha]^{25}_D$ in 95% alcohol	Nitrogen, %[a] Calcd.	Found
Menthylurea	Prisms	140.2–140.6	−80.0	14.14	13.96
sym-Acetylmenthylurea	Needles	118 –119	−83.3	11.66	11.63
Chloral addn. product (RNHCONHCHOHCCl$_3$)	Needles	146.2–147.2	−49.1	8.10	8.08
sym-Bromoacetylmenthylurea	Plates	111.8–112.3	−66.9	8.78	8.80
sym-Cinnamoylmenthylurea	Leaflets	144.3–145.1	−67.9	8.54	8.51
sym-*p*-Nitrobenzoylmenthylurea	Needles	158.7–159.2	insol.	12.09	11.75
sym-*p*-Aminobenzoylmenthylurea	Needles	208–210 (dec.)	−72.3	13.25	13.11
Bornylurea	Needles	165.7–166.3	+ 5.83	14.28	14.21
sym-Acetylbornylurea	Needles	129 –129.5	+23.5	11.76	11.70
Chloral addn. product	Cryst. powder	180 (dec.)	+ 7.3	8.15	8.07
sym-Bromoacetylbornylurea	Tabular prisms	136.1–136.5	+16.3	8.83	8.75
sym-Cinnamoyl bornylurea	Needles	220.2–220.8	insol.	8.59	8.54
sym-*p*-Nitrobenzoylbornylurea	Needles	230 (dec.)	insol.	12.17	11.93
sym-*p*-Aminobenzoylbornylurea	Needles	233 (dec.)	+15.6	13.83	12.90
2-Keto-3-carbamidocamphane ($C_{11}H_{18}N_2O_2\cdot{}^1/_2H_2O$)	Cryst. powder	177.8–178.4	+18.3	12.78	12.68

[a] Average values.

yields by the interaction of nitrourea and terpenylamine

$$RNH_2 + H_2NCONHNO_2 = RNHCONH_2 + N_2O + H_2O$$

A number of acyl derivatives as well as the chloral addition products of the above ureas were also prepared for the purpose of modifying the physiological properties of the terpenylureas.

Experimental

***l*-Menthylurea.**[1]—To 20 g. of *l*-menthylamine hydrochloride[2] and 20 g. of nitrourea[3] in 600 cc. of water was slowly added with stirring a slight excess of sodium bicarbonate and after twelve hours the colorless reaction product was recrystallized from dilute alcohol; yield 78%.

A similar procedure was followed in the preparation of *d*-bornylurea[4,5,6] and a yield of 90% was obtained.

The menthyl as well as the bornylurea was acylated directly with acetic anhydride and in benzene solution with bromoacetyl bromide, cinnamoyl chloride and *p*-nitrobenzoyl chloride. The yields were almost the theoretical except in the case of bromoacetylmenthylurea. In the latter case it dropped to 20%. In general the crude products were readily purified by recrystallization from alcohol. *d*-Cinnamoylbornylurea was recrystallized from acetone and *d*-*p*-nitrobenzoylurea from a mixture of glacial acetic acid (2 parts) and acetone (8 parts).

Chloral Addition Products of *l*-Menthyl and *d*-Bornylurea.—Five grams of chloral was slowly added to 5 g. of the urea with stirring and the mixture allowed to stand for one hour in the absence of moisture. The excess chloral was removed with a little ligroin and the crude product recrystallized from alcohol. The compounds were quite stable and did not hydrolyze readily in the presence of water; yields, 80–86%.

1-*p*-Aminobenzoylmenthylurea and *d*-*p*-Aminobenzoylbornylurea.—Seven grams of the corresponding nitro compound was partially dissolved in 60 cc. of hot alcohol and 60 cc. of 6 *M* ammonium sulfide added. After two hours' refluxing on a water-bath, the solution was diluted with water and the crude product recrystallized from alcohol; yield, about 90%. The corresponding hydrochlorides were prepared by saturating an ether solution of the free base with dry hydrogen chloride. They were obtained as colorless powders and were quite insoluble in the common solvents.

***d*-2-Keto-3-carbamidocamphane.**—This compound was prepared by the reduction of the stable (*syn*) form of isonitrosocamphor[7] with zinc dust and acetic acid to the corresponding amine[8] and the latter then converted to the corresponding urea by the nitrourea method. The crude product was recrystallized from hot water; yield, 75–80%, based on the hydrochloride used. Its analysis indicated the probable presence of water of hydration which could not be removed by drying in vacuum or by heating below its decomposition point. Its *p*-nitrobenzoyl derivative analyzed correctly for $C_{18}H_{21}N_3O_5$. Calcd.: N, 11.70. Found: N, 11.63.[9]

The physical constants and analytical data for the various compounds prepared are given in Table I.

Pharmacological Tests

Some preliminary tests on six of these derivatives have been carried out by Dr. Carl F. Schmidt of The Pharmacology Department of the Uni-

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[1] O. Wallach, *Ann.*, **300**, 279 (1898). Wallach obtained a 30% yield by the action of potassium cyanate on menthylamine hydrochloride, m. p. 134–136°.

[2] E. Beckmann, *ibid.*, **250**, 325 (1889).

[3] T. L. Davis and K. C. Blanchard, THIS JOURNAL, **51**, 1794 (1929).

[4] M. O. Forster, *J. Chem. Soc.*, **73**, 390 (1898).

[5] R. Leuchart and Bach, *Ber.*, **20**, 104 (1887).

[6] M. O. Forster and H. M. Atwell, *J. Chem. Soc.*, **85**, 1188 (1904). Leuchart and Bach first obtained this urea by the action of potassium cyanate on *d*-bornylamine hydrochloride, m. p. 164°. Later Forster and Atwell prepared it by the same method and reported a melting point of 175°.

[7] M. O. Forster, *J. Chem. Soc.*, **83**, 514 (1903); **85**, 905 (1904).

[8] Claisen and Manasse, *Ann.*, **274**, 79 (1893).

[9] Rupe [*Ber.*, **27**, 584 (1894); **28**, 778 (1895)] obtained this urea by the action of potassium cyanate on *d*-3-aminocamphor hydrochloride and reported its melting point as 169°.

versity of Pennsylvania School of Medicine. The compounds were dissolved in ethylene glycol and injected intraperitoneally in white rats.

Menthyl urea in dosage of 220 mg. per kg. caused profound unconsciousness with the abolition of all reflexes. The narcosis appeared at the end of fifteen minutes and was undiminished seven hours after injection. At the end of twenty-two hours the animal had recovered completely and appeared normal. In dosage of 63 mg. per kg. there was definite drowsiness without visible muscular incoördination. The animal was easily aroused at all times and seemed normal when aroused. At twenty hours it was quite normal.

The low solubility of bromoacetylbornylurea and *p*-aminobenzoylmenthylurea made adequate testing impracticable. They had no demonstrable narcotic effects in the dosage used. Larger amounts of the solutions caused ethylene glycol poisoning.

Chloral menthylurea was clearly the most potent. It was the most toxic, slowest acting and most persistent of those tested.

Bornylurea and 2-keto-3-carbamidocamphane acted slowly and weakly with considerable muscular incoördination and the latter seemed to be intensely irritant locally.

Summary

1. *l*-Menthylurea, *d*-bornylurea and 2-keto-3-carbamidocamphane have been prepared by the nitrourea method.

2. The following new derivatives of *l*-menthylurea and *d*-bornylurea have been prepared: acetyl, bromoacetyl, chloral addition product, *p*-nitrobenzoyl and *p*-aminobenzoyl.

3. Preliminary tests on the narcotic effects of some of these ureas indicated that menthylurea was the most promising and may have some value. It acted rapidly without evident after-effects.

PHILADELPHIA, PENNA. RECEIVED AUGUST 19, 1935

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

Esters of the Aldehydrol Form of Sugars

BY M. L. WOLFROM

Diacetates of aliphatic aldehydes, $RCH(OAc)_2$, have long been known but have been little studied. Some of the earliest work was carried out by Geuther,[1] who prepared these derivatives by heating aliphatic aldehydes with acetic anhydride at relatively high temperatures (180°). Later work[2] showed that the reaction was greatly accelerated by zinc chloride or sodium acetate. Aceto-halogen compounds of aliphatic aldehydes, $RCHOAc \cdot X$, have also been prepared.[3] From the standpoint of organic structural theory, compounds of this type may be considered as esters of the aldehydrol, $RCH(OH)_2$, irrespective of whether the aldehydrol is an intermediate in their formation.

In the sugar series, the first representative of this type of compound was the crystalline triacetate of gycolaldehyde prepared by H. O. L. Fischer and Dangschat[4] by treating vinyl acetate dibromide with potassium acetate and also directly from the sugar by heating with acetic anhydride. Micheel and co-workers[5] have reported the synthesis of the *d*- and *d,l*- forms of *aldehydo*-galactose heptaacetate as incidental to their important synthetic experiments in the transformation of hexoses into inositols.

Aldehydo-galactose pentaacetate readily forms crystalline carbonyl addition compounds with alcohols and water, the reaction product with the latter being a true aldehydrol.[6] This addition takes place readily at room temperature. We have now found that acetyl halide addition compounds of *aldehydo*-galactose pentaacetate can be readily formed. The resulting compounds are the open chain analogs of the cyclic sugar acetohalogen derivatives and may be named, for example, *aldehydo*-1-chloro-*d*-galactose hexaacetate. In the work herein reported the chloride, bromide and iodide are described. Their rota-

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(1) A. Geuther, *Ann.*, **106**, 249 (1858).

(2) G. Kauffmann, *Ber.*, **16**, 683 (1883); M. Descudé, *Compt. rend.*, **133**, 371 (1901).

(3) A. Wurtz, *Ann. chim. phys.*, [3] **49**, 58 (1857); V. Meyer and L. Dulk, *Ann.*, **171**, 65 (1874).

(4) H. O. L. Fischer and Gerda Dangschat, *Ber.*, **62**, 862 (1929).

(5) F. Micheel, H. Ruhkopf and F. Suckfüll, *ibid.*, **68**, 1523 (1935).

(6) M. L. Wolfrom, THIS JOURNAL, **52**, 2464 (1930); *ibid.*, **53**, 2275 (1931); M. L. Wolfrom and W. M. Morgan, *ibid.*, **54**, 3390 (1932).

tions increase in the above order, as could be predicted from the careful work of Brauns[7] on the cyclic acetohalogen sugars. Although these open chain acetohalogen compounds are quite stable, they tend to lose the acyl halide when subjected to metathetical reactions. The ease of carbonyl addition shown by *aldehydo*-galactose pentaacetates, is a property not shared by the other known aldehydo-acetates, but probably such derivatives could be prepared by the use of catalysts and work in this direction is in progress.

We have found that when the *aldehydo*-sugar acetates are subjected to further acetylation, the carbonyl diacetate compounds are obtained. We wish to report herein the glucose and arabinose derivatives, which may be named *aldehydo-d*-glucose heptaacetate and *aldehydo-l*-arabinose hexaacetate. These compounds are very much more stable than the corresponding free carbonyl compounds and are more easily isolated. They may be expected to be formed occasionally in reactions involving cyclic sugar derivatives. On the other hand, Montgomery and Hudson[8] isolated the free carbonyl form of *aldehydo-d-α*-mannoheptose hexaacetate by a relatively mild acetylation of the free sugar with acetic anhydride and sodium acetate. The acetylation methods we have used involve the use of acetic anhydride with pyridine or zinc chloride, the reactions being carried out at room temperature.

Experimental

Aldehydo-1-chloro-*d*-galactose Hexaacetate.[9]—*Aldehydo*-galactose pentaacetate ethyl hemiacetal[6a] (5 g.) was dissolved in 50 cc. of hot acetyl chloride and the cooled solution poured with stirring into about a liter of ice and water. The product separated at once as colorless crystals which were filtered and washed with ice water; yield, 3.4 g. Pure material was obtained after several recrystallizations from ethanol; m. p. 174–175°; $[\alpha]^{27}_{D}$ −44° (*c*, 4.0; CHCl$_3$). The substance crystallized in individual diamond-shaped plates and showed no tendency to decompose on standing. It was soluble in chloroform and acetone, sparingly so in hot ethanol, and was practically insoluble in ether and petroleum ether.

Anal. Calcd. for $C_6H_7O_6(COCH_3)_6Cl$: Cl, 7.57; saponification value (7 equivalents), 14.9 cc. 0.1 *N* NaOH per 100 mg.; mol. wt., 469. Found: Cl, 7.33; 14.7 cc. 0.1 *N* NaOH; OEt, negative; mol. wt. (Rast), 476.

The same substance was obtained by starting either with the free carbonyl or aldehydrol forms of *aldehydo*-galactose pentaacetate.

Aldehydo-1-bromo-*d*-galactose Hexaacetate.[10]—This substance was prepared as described for the corresponding chloride, except that less acetyl bromide (one-third of the amount used for the corresponding chloride) was employed. The substance showed a tendency to react with ethanol but could be recrystallized from benzene–petroleum ether, acetone–ice water, or chloroform (alcohol free)–petroleum ether. The purified substance crystallized in clusters of needles; m. p. 179–181°; $[\alpha]^{27}_{D}$ −79° (*c*, 4.0; CHCl$_3$, alcohol-free).

Anal. Calcd. for $C_6H_7O_6(COCH_3)_6Br$: Br, 15.58; saponification value (7 equivalents), 13.6 cc. 0.1 *N* NaOH per 100 mg. Found: Br, 15.62; 13.7 cc. 0.1 *N* NaOH.

That the acetyl halide in this compound was attached on carbon one was determined by shaking the substance (dissolved in 1:1 chloroform–ethanol) with silver carbonate, filtering from silver salts and crystallizing the reaction product (after solvent removal) from ethanol. The reaction product was identified as *aldehydo*-galactose pentaacetate ethyl hemiacetal.

Aldehydo-1-iodo-*d*-galactose Hexaacetate.[10]—*Aldehydo*-galactose pentaacetate (4 g.) was added with stirring to 17 g. of acetyl iodide and the resultant thin paste was poured into ice and water. The yellow crystals that separated were purified by repeated recrystallization from chloroform (alcohol-free) by the addition of petroleum ether; m. p. 152–153°; $[\alpha]^{25}_{D}$ −111° (*c*, 2; CHCl$_3$, alcohol-free). These constants are provisional as the substance was unstable and difficult to purify.

Anal. Calcd. for $C_6H_7O_6(COCH_3)_6I$: I, 22.66. Found: I, 22.10.

Aldehydo-*d*-glucose Heptaacetate.[11]—*Aldehydo*-glucose pentaacetate[12] (10 g.) was dissolved in 250 cc. of dry pyridine, the solution allowed to stand for two hours and then 125 cc. of acetic anhydride added and the whole allowed to stand overnight (fifteen hours). The dark solution was then poured into one liter of ice and water and the clear aqueous solution extracted with chloroform. The extract was washed with 5% sulfuric acid until free from pyridine, followed by washing with a solution of sodium bicarbonate and finally with water. The extract was dried and after removal of the chloroform the resultant sirup was dissolved in hot ethanol (carboraffin) and on cooling this solution a mass of fine white crystals separated. Further crops could be obtained by concentration of the mother liquor; yield (3 crops), 2.8 g. The substance was readily recrystallized from warm ethanol, the pure material showing the constants: m. p. 118.5–119.5°; $[\alpha]^{25}_{D}$ +8° (*c*, 4; CHCl$_3$).

The substance crystallized in prisms and rather large crystals (3 mm. long) could be formed on slow evaporation of an alcoholic solution. The substance was very soluble in chloroform, acetone, glacial acetic acid; was soluble, when heated, in water, ethanol, ether, and heptane; and was practically insoluble in petroleum ether.

Anal. Calcd. for $C_6H_7O_7(CH_3CO)_7$: C, 48.76; H, 5.74; acetyl, 14.2 cc. 0.1 *N* NaOH per 100 mg. Found: C, 48.79; H, 5.65; acetyl, 14.2 cc.

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[7] D. H. Brauns, *Bur. Standards J. Research*, **7**, 573 (1931).

[8] Edna Montgomery and C. S. Hudson, This Journal, **56**, 2463 (1934).

[9] W. M. Morgan, Ph.D. Dissertation, The Ohio State University, June, 1932.

[10] J. L. Quinn, Ph.D. Dissertation, The Ohio State University, Dec., 1934.

[11] R. L. Whistler, M. Sc. Thesis, The Ohio State University, Aug., 1935.

[12] M. L. Wolfrom, This Journal, **51**, 2188 (1929).

That the substance was not an acetylated enolic or alkali-interconverted sugar was determined by the fact that it did not decolorize a solution of bromine in carbon tetrachloride and on deacetylation with sodium ethylate followed by reacetylation with warm acetic anhydride and sodium acetate, β-glucose pentaacetate (m. p. 131°; $[\alpha]_D$ +4°, $CHCl_3$) was produced.

The substance was also formed, although in lower yield, by the room temperature acetylation of *aldehydo*-glucose pentaacetate with acetic anhydride and zinc chloride. *Aldehydo*-glucose pentaacetate (2 g.) was added to a solution of 1 g. of freshly fused zinc chloride in 40 cc. of acetic anhydride and the solution allowed to stand overnight (fifteen hours). The solution was then poured on cracked ice and neutralized with sodium bicarbonate, extracted with chloroform and the extract washed with water and dried. The sirup obtained after solvent removal was crystallized from hot ethanol (carboraffin); yield, 0.2 g.; m. p. 117.5–118.5°; $[\alpha]_D$ +8° (*c*, 3; $CHCl_3$).

Aldehydo-*l*-arabinose Hexaacetate.[11]—*Aldehydo-l*-arabinose tetraacetate[13] (20 g.) was acetylated with a solution of 20 g. of zinc chloride (freshly fused) in one liter of acetic anhydride as described above for the preparation of glucose heptaacetate. The resultant sirup was crystallized from hot ethanol; yield, 9 g.; m. p. 85°. Pure material was obtained by solution in just sufficient hot ethanol so that no crystallization occurred on cooling and repeatedly adding water in small quantities to the above solution at ice box temperature; m. p. 89.5°; $[\alpha]^{27}_D$ −27° (*c*, 4; $CHCl_3$). The solubilities of this substance were similar to those of the corresponding glucose compound.

Anal. Calcd. for $C_5H_6O_6(CH_3CO)_6$: C, 48.57; H, 5.76; acetyl, 14.3 cc. 0.1 *N* NaOH per 100 mg. Found: C, 48.57; H, 5.68; acetyl, 14.3 cc.

The experimental work herein reported was carried on in this Laboratory rather incidentally over a considerable period of time and I wish to make due acknowledgment to the assistance rendered by Messrs. W. M. Morgan, J. L. Quinn, R. L. Whistler and M. Konigsberg.

Summary

1. The chloride, bromide and iodide forms of *aldehydo-d*-galactose hexaacetate 1-halide have been synthesized in crystalline form. It is pointed out that these substances are the open chain analogs of the cyclic acetohalogen sugars.

2. *Aldehydo-d*-glucose heptaacetate and *aldehydo-l*-arabinose hexaacetate have been synthesized in pure crystalline form. It is pointed out that these compounds may be expected to be formed in reactions involving the cyclic forms of the sugars, rather than the free carbonyl or *aldehydo*-structures.

COLUMBUS, OHIO RECEIVED OCTOBER 4, 1935

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[13] M. L. Wolfrom and Mildred R. Newlin, THIS JOURNAL, **52**, 3619 (1930).

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

Iodine Substitution Products of Vanillin and Some of their Derivatives

BY L. CHAS. RAIFORD AND EUGENE H. WELLS

In work published from this Laboratory[1] the chlorine and bromine substitution products of vanillin demanded by theory were prepared and characterized by a study of their interactions with typical amino compounds. Steric hindrance[2] was noted only when both ortho positions in the aldehyde were substituted, and was then less pronounced than expected. In the present work the iodine derivatives have been examined. The high yields of products indicated little, if any, hindrance.

The Action of Iodine on Vanillin.—Carles[3] treated vanillin with warm alcoholic solutions of iodine of different concentrations and obtained products that analyzed for mono- and diiodovanillin, respectively. He did not determine the structures of these compounds or study them further, and they are recorded as having the halogen in unknown positions.[4] The monoiodo derivative was reported to melt at 174° and was probably an impure sample of that, m. p. 180°, obtained by Hann[5] and reported as 5-iodovanillin, but without proof of structure. No melting point was given for the diiodo compound. Carles' work has been repeated and, while the monoiodo

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[1] Raiford and Lichty, THIS JOURNAL, **52**, 4576 (1930). Other references to these studies are given there.

[2] Hantzsch [*Ber.*, **23**, 2776 (1890)] could not condense *sym*-tribromo- and trinitroaniline with benzaldehyde, but Lowy and co-workers [THIS JOURNAL, **43**, 1961 (1921)] found that when the nitro radical was in the aldehyde, condensation with aniline did take place, though they studied no aldehyde containing a substituent other than the nitro radical. Their results may not be typical for Meyer [*Z. physik. Chem.*, **24**, 219 (1897)] found that while hindrance in esterification of *o*-substituted benzoic acids was often proportional to the weight of the o-substituent, that produced by the nitro group was much greater than expected. On the other hand, Fischer and Giebe [*Ber.*, **31**, 546 (1898)] found that the *o*-nitro radical in benzaldehyde favors acetal formation.

[3] Carles, *Bull. soc. chim.*, [2] **17**, 14 (1872).

[4] Beilstein, "Handbuch org. Chem.," Vierte Auflage, 1925, VIII, p. 251.

[5] Hann, THIS JOURNAL, **47**, 2000 (1925).

compound only was obtained by his method, both were prepared in other ways and their structures established.

To determine the position of iodine in the first product here studied the start was made with the nitrovanillin, m. p. 137°, first obtained by Pschorr and Sumuleanu.[6] In later work, the hydroxyl group of this compound was methylated, and the resulting product was oxidized into a nitroveratric acid. The latter was reduced, the resulting amine diazotized and converted by the Sandmeyer method into a cyanide that on hydrolysis gave hemipinic acid.[7] The starting material must therefore have been 2-nitrovanillin (CHO = 1). In the present work this nitro compound was reduced and the resulting amino radical replaced by iodine in the usual way.

The position of iodine in the monoiodo compound reported by Carles was oriented as follows. That nitro compound, m. p. 175–176°, obtained by direct nitration of vanillin[8] and proved by Vogl[9] to have the nitro radical in position 5, was in our work reduced by stannous chloride and hydrochloric acid. Though the free amine was not obtained, the hydrochloride and the stannic chloride double salt were isolated, and from the former several derivatives were prepared. The salt was diazotized and separate portions were subjected to the Sandmeyer reaction with cuprous chloride, cuprous bromide and potassium iodide, respectively. In the first two cases 5-chloro- and 5-bromovanillin, in which the position of halogen had previously been determined by a different method, were obtained. In the third case Carles' monoiodovanillin was isolated, which proves that it is 5-iodovanillin.

By methods described below, 5-iodovanillin was converted into acetyl-5-iodovanillin, and into 3-methoxy-4-acetoxy-5-iodobenzal diacetate. Nitration of these products gave the same compound, acetyl-2-nitro-5-iodovanillin. The acetyl group was removed by hydrolysis, the nitro compound was reduced, the resulting amine was diazotized and the diazonium salt treated with potassium iodide. The diiodovanillin formed melted at 199–200°,[10] and was identical with that obtained by direct iodination of 2-iodovanillin.

With the hope of obtaining 6-iodovanillin, acetylvanillin was treated with iodine[11] and with iodine monochloride,[12] respectively. Only 5-iodovanillin and starting material were obtained. Similarly, treatment of 3-methoxy-4-acetoxybenzal diacetate[13] failed to give the desired product.

Experimental Part

2-Iodovanillin.—Twenty grams of 2-aminovanillin[14] was dissolved in 350 cc. of 15% hydrochloric acid, cooled to 0° and diazotized. A cold solution of 30 g. of potassium iodide was added, and the mixture kept at about 0° for two hours, and some tar that had separated was removed and examined. The remainder was heated on the steam-bath for an hour, then boiled over a free flame to remove free iodine; yield 54%. After boiling the alcoholic solution with norite and filtering, addition of hot water to the filtrate and cooling gave nearly colorless needles; m. p. 155–156°.

Anal. Calcd. for $C_8H_7O_3I$: I, 45.68. Found: I, 45.53.

2-Iodo-3,4-dimethoxybenzaldehyde.—To a potassium hydroxide solution of 2-iodovanillin held between 50 and 60°, excess of dimethyl sulfate was slowly added with shaking; yield 84%. Crystallization from dilute alcohol gave pale yellow needles; m. p. 82°.

Anal. Calcd. for $C_9H_9O_3I$: I, 43.49. Found: I, 43.65.

Analytical data for other derivatives are given in Table I.

Stannic Chloride Double Salt of 5-Aminovanillin.—To a boiling suspension of 160 g. of 5-nitrovanillin[15] in 750 cc. of alcohol there was added in small portions a solution of 800 g. of stannous chloride in 800 cc. of concentrated hydrochloric acid. After addition of a few portions the heat of reaction kept the mixture boiling. When all the reducing agent was in, 1500 cc. of concentrated acid was added and the mixture allowed to cool. When the resulting solid was dissolved in hot 2.5 *N* hydrochloric acid, and one volume of concentrated acid was added, orange crystals were obtained; yield 88%.

Anal. Calcd. for $C_{16}H_{20}O_6N_2SnCl_6$: N, 4.19; Cl, 31.88. Found: N, 4.24; Cl, 31.61.

5-Aminovanillin Hydrochloride.—A hot dilute hydrochloric acid solution of the tin salt indicated above was treated with hydrogen sulfide as long as change took place, the mixture filtered, the filtrate mixed with two volumes of concentrated hydrochloric acid, and cooled in ice; yield 70%. Recrystallization as indicated above gave yellowish-brown prisms.

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(6) Pschorr and Sumuleanu, *Ber.*, **32**, 3408 (1899).

(7) Sumuleanu, *Ann. Sci. Univ. Jassy*, **2**, 131 (1902–1903).

(8) Bentley, *Am. Chem. J.*, **24**, 171 (1900); Hayduck, *Ber.*, **36**, 2933 (1903).

(9) Vogl, *Monatsh.*, **20**, 385 (1899).

(10) Carles (Ref. 3) recorded no melting point for his diiodo compound.

(11) Raiford and Stoesser [THIS JOURNAL, **49**, 1078 (1927)] found that treatment of acetylvanillin with bromine in the presence of sodium acetate gave a high yield of 6-bromovanillin, and no other derivative could be isolated.

(12) Prepared as directed by Cornog and Karges, *ibid.*, **54**, 1882 (1932).

(13) Raiford and Lichty (Ref. 1) showed that treatment of this compound with chlorine gave a 90% yield of 6-chlorovanillin.

(14) Prepared as directed by Pschorr and Sumuleanu [*Ber.*, **32**, 3408 (1899)].

(15) This was obtained in 70% yield by Bentley's method [*Am. Chem. J.*, **24**, 171 (1900)], modified to the extent of cooling the vanillin solution and adding the nitric acid slowly.

TABLE I

DERIVATIVES OF 2-IODOVANILLIN

Compound	Yield, %	Solvent	Crystal form	M. p., °C.	Formula	Halogen, %	
						Calcd.	Found
Acetyl	85	Dil. alcohol	Plates	70–72	$C_{10}H_9O_4I$	39.68	39.73
Oxime	98	Dil. alcohol	Diamond plates	Softened[a] about 122	$C_8H_8O_3NI \cdot {}^1/_2H_2O$	42.05	42.01
Semicarbazone	93	Dil. alcohol	Plates	199–200	$C_9H_{10}O_3N_3I$	37.91	38.01
p-Nitrophenylhydrazone	98	Dil. alcohol[b]	Red needles	211–212	$C_{14}H_{12}O_4N_3I$	30.75	30.60
Bis-benzidine	Nearly quant.	Dil. pyridine	Brown plates	228–230 (dec.)	$C_{28}H_{22}O_4N_2I_2 \cdot$[c] $2C_5H_5N$	29.46	29.54

[a] Heating for 24 hours at 107° gave a product that melted at 142.5–143.5°. *Anal.* Calcd. for $C_8H_8O_3NI$: I, 44.34. Found: I, 43.42. [b] Hot water was added to the hot alcoholic solution until turbid. [c] Extraction of the crude material with alcohol to remove foreign matter gave a product that decomposed at about 232–233°. *Anal.* Calcd. for $C_{28}H_{22}O_4N_2I_2$: I, 36.07. Found: I, 36.20.

TABLE II

DERIVATIVES OF 5-IODOVANILLIN

Compound	Yield, %	Solvent	Crystal form	M. p., °C.	Formula	Halogen, %	
						Calcd.	Found
Acetyl	66	50% alcohol	Colorless plates	105–106	$C_{10}H_9O_4I$	39.68	39.78
Benzoyl	82[a]	Dil. alcohol	Fibrous masses	135.5–136.5	$C_{15}H_{11}O_4I$	33.24	33.26
Acetyl diacetate	95	Ligroin	Colorless cubes	132–133	$C_{14}H_{15}O_7I$	30.09	30.16
Oxime	88	Dil. alcohol	Nearly colorless needles	178–179[b]	$C_8H_8O_3NI$	43.34	43.18
Semicarbazone	98	Dil. alcohol	Yellow needles	205–205.5	$C_9H_{10}O_3N_3I$	37.91	37.92
p-Nitrophenylhydrazone	85	80% Alcohol	Red needles	242–243 (dec.)	$C_{14}H_{12}O_4N_3I$	30.75	30.55
Bis-benzidine	88	Pyridine and water	Brown plates	232 (dec.)	$C_{28}H_{22}O_4N_2I_2$	36.08	36.08
Methyl	70	Dil. alcohol	Fibrous masses	69–70	$C_9H_9O_3I$	43.49	43.39

[a] Obtained in presence of pyridine as directed by Einhorn and Hollandt. The Schotten–Baumann method gave only 7%. [b] A mixture of this and 5-iodovanillin, m. p. 179–180°, melted at 150–160°.

TABLE III

DERIVATIVES OF 2-NITRO-5-IODOVANILLIN

Compound	Yield, %	Solvent	Crystal form	M. p., °C.	Formula	Halogen, %	
						Calcd.	Found
Oxime	97	Benzene	Yellow rods	128–129	$C_8H_7O_5N_2I$	37.57	37.76
Semicarbazone	51	Alcohol	Yellow needles	187–188 (dec.)	$C_9H_9O_5N_4I$	33.33	33.31
p-Nitrophenylhydrazone	70	Alcohol	Red plates	228–230 (dec.)	$C_{14}H_{11}O_6N_4I \cdot {}^1/_2C_2H_5OH$	26.40	26.42
Bis-benzidine	82	[a]	Yellow powder	[b]	$C_{28}H_{20}O_8N_4I_2$	31.98	31.43

[a] Purification was accomplished by extraction of foreign material by alcohol. [b] It was heated to about 335° but gave no melting point.

Anal. Calcd. for $C_8H_{10}O_3NCl$: N, 6.87; Cl, 17.44. Found: N, 6.68; Cl, 16.55.

3 - Methoxy - 4 - acetoxy - 5 - acetylaminobenzaldehyde.—A portion of the amino hydrochloride was dissolved in 10% solution of potassium hydroxide by gentle warming, cooled to room temperature and shaken with an ether solution of acetic anhydride; yield 66%. Crystallization from water gave colorless needles; m. p. 174–176°.

Anal. Calcd. for $C_{12}H_{13}O_5N$: N, 5.57. Found: N, 5.36.

3 - Methoxy - 4 - benzoxy - 5 - benzoylaminobenzaldehyde.—This was obtained in 75% yield by treatment of an alkaline solution of the base with benzoyl chloride. Crystallization from alcohol gave colorless needles; m. p. 161–162°.

Anal. Calcd. for $C_{22}H_{17}O_5N$: N, 3.73. Found: N, 3.83.

5-Iodovanillin.—Five grams of the amino hydrochloride was suspended in 20 cc. of dilute hydrochloric acid, cooled below 0° and diazotized. To the clear liquid a cold solution of potassium iodide was added, the mixture warmed slowly and finally boiled to remove free iodine; yield 79% of brown solid. Repeated crystallization from dilute alcohol gave light brown needles, m. p. 179–180°, and identical with Carles' product.[16] Data for derivatives are given in Table II.

Acetyl-2-nitro-5-iodovanillin.—Eighty grams of acetyl-5-iodovanillin was dissolved in 175 cc. of fuming nitric acid at 6° or below with stirring, the solution held at this temperature for half an hour, and the dark red liquid poured into a liter of ice and water. The oil that separated solidified on standing, was washed free from acid and boiled with water to remove a little free iodine; yield 83%. Crystallization from acetic acid, using norite, gave nearly colorless plates, m. p. 124–125°. The same product was obtained by nitration of 3-methoxy-4-acetoxy-5-iodobenzal diacetate.

Anal. Calcd. for $C_{10}H_8O_6NI$: I, 34.79. Found: I, 34.97.

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[16] This compound was also obtained by the action of iodine monochloride an vanillin.

TABLE IV

DERIVATIVES OF 2,5-IODOVANILLIN

Compound	Yield, %	Solvent	Crystal form	M. p., °C.	Formula	Halogen, % Calcd.	Halogen, % Found
Acetyl	97	Dil. alcohol	Square prisms	127–128	$C_{10}H_8O_4I_2$	56.95	57.22
Oxime	95	Dil. alcohol	Needles	174.5–175.5	$C_8H_7O_3NI_2$	60.62	60.47
Semicarbazone	96	Alcohol	Needles	235 (dec.)	$C_9H_9O_3N_3I_2$	55.09	55.36
p-Nitrophenylhydrazone	95	Acetic acid	Orange	252–253 (dec.)	$C_{14}H_{11}O_4N_3I_2$	47.12	46.97
Bis-benzidine	83	[a]	Powder	[b]	$C_{28}H_{20}O_4N_2I_4$	53.13	52.17

[a] Could not be crystallized. [b] Gave no melting point.

Hydrolysis of this product with caustic potash solution gave 2-nitro-5-iodovanillin. Crystallization from 30% acetic acid gave colorless rods; m. p. 146–147°.

Anal. Calcd. for $C_8H_6O_5NI$: I, 39.30. Found: I, 39.57.

Data for derivatives are given in Table III.

2-Amino-5-iodovanillin.—Thirty-four grams of the nitro compound was reduced by ferrous hydroxide in the presence of ammonia water; yield 69%. Repeated crystallization from dilute alcohol, using norite, gave light brown needles, m. p. 155°.

Anal. Calcd. for $C_8H_8O_3NI$: I, 43.34. Found: I, 43.56.

Treatment of the diazonium salt from the above amine with potassium iodide gave 2,5-diiodovanillin, which was also obtained in another way and characterized as indicated below.

2,5-Diiodovanillin.—A mixture of 15 g. of 2-iodovanillin, 8 g. of anhydrous sodium acetate, 80 g. of acetic acid and 14 g. of iodine was kept at about 60° with continual stirring for twenty-four hours, one liter of water was then added and the mixture boiled to remove free iodine; yield 69%. Repeated crystallization from alcohol gave colorless rods; m. p. 200°.

Anal. Calcd. for $C_8H_6O_3I_2$: I, 62.87. Found: I, 62.87.

Treatment of this product with dimethyl sulfate under the conditions described for the monoiodo compound gave a 33% yield of 2,5-diiodo-3,4-dimethoxybenzaldehyde, while 60% of starting material was recovered. The new product was obtained as colorless needles by addition of hot water to the hot alcoholic solution, and cooling; m. p. 94°. Data for derivatives are given in Table IV.

Anal. Calcd. for $C_9H_8O_3I_2$: I, 60.76. Found: I, 60.56.

Summary

Several iodine substitution products of vanillin, including Carles' compounds, have been prepared and their structures determined. The behavior of these products toward typical amino compounds has been tested. No pronounced steric hindrance was noted in the latter reactions.

The relation between the numerical values of the melting points and the positions of the halogen atoms in the iodine derivatives, so far as they have been obtained, is in good agreement with that observed in the cases of the chlorine and bromine compounds, *viz.*, that the lowest value is found for position 2, the next higher for 5 and the highest for 6. Likewise, for a given position the lowest is found for the chloride, the next higher for the bromide and the highest for the iodide.

Further work is in progress.

IOWA CITY, IOWA RECEIVED OCTOBER 2, 1935

[CONTRIBUTION FROM THE GOESSMANN CHEMISTRY LABORATORY, MASSACHUSETTS STATE COLLEGE]

Investigations of the Effects of Some Factors on Rhythmic Crystallization[1]

BY MAJEL M. MACMASTERS, JULIA E. ABBOTT AND CHARLES A. PETERS

In 1853, Sir David Brewster[2] reported the first recorded cases of rhythmic crystallization from aqueous solution. Since that time, numerous investigators have reported similar instances of periodic banding, although but little has been done to explain the cause of the phenomenon or the influence of factors affecting it.

The rhythmic crystallization of potassium dichromate from aqueous solution, first reported by Miers[3] in 1908, is typical of the phenomenon and is easily reproduced. This is described in detail by Hedges.[4]

Experimental

Ordinary non-corrosive white glass microscope slides were used as surfaces on which crystallization took place. Preliminary tests showed that the method of cleaning did not effect crystallization on the slide. Slides prepared at 23 or 25° were placed in a constant temperature room; slides prepared at 50°, or above, were kept at constant temperature in a Freas electric oven. All salts used were C. P. Baker's Analyzed.

Coarse Rhythm, Fine Rhythm and X-Rhythm.—Miers' method gives rows of dendritic crystals alternating with areas more or less devoid of crystalline material. This we shall call *coarse rhythm.* Occasionally there appear small areas of very narrow alternating bands of thickly crystalline area (crests) and thinly crystalline areas (troughs). A crest and a trough comprise a period. This we shall call *fine rhythm.* In fine rhythm the periods are very small, usually 0.005 to 0.01 mm. Fine rhythm is often overlooked unless polarized light is used for the examination of the slides. Coarse rhythm is often irregular, and in many instances occurs over only comparatively small areas, while fine rhythm is extremely regular and usually occurs over large areas. Forms simulating coarse rhythm are often caused by shocks affecting the slide during crystallization, but fine rhythm is never counterfeited by shocks. Areas of fine rhythm crossed by a second system of fine rhythm approximately at right angles to the first have been observed. We shall call this *x-rhythm.*

Influence of Temperature and of Concentration.—The influence of change of temperature and of concentration upon the rhythmic crystallization of potassium dichromate was first investigated by a modification of Miers' method. For this purpose 0.0017, 0.017 and 0.136 M solutions of potassium dichromate were used. Each solution was allowed to crystallize at constant temperatures of 25, 50 and 100°. Slide and solution were kept at constant temperature for some time before the solution was placed on the slide; this temperature was maintained until crystallization was complete. The solution was transferred to the slide by means of a pipet, also at the required temperature.

In the slides made with 0.0017 M potassium dichromate dendrites became less common as the temperature rose, and massive circular crests at the edge of the drop became more common. The amount of simple fine rhythm present was greatest in slides run at 100°, and did not much vary in those run at 50° from those run at 25°. All slides, at all three temperatures, showed good fine rhythm and well defined areas of x-rhythm. Temperature did not affect the period of fine rhythm; periods of 0.005 and 0.01 mm. were most common.

The slides made with 0.0170 M potassium dichromate solution showed an increasing tendency to form heavy crests with increase of temperature. Dendrites were more common at lower temperatures than at 100°. Coarse rhythm decreased in amount with increase of temperature. Fine rhythm was present at all temperatures and did not appear to vary in amount with change of temperature. Only one case of x-rhythm was noted, on a slide made at 23°.

All slides made with 0.136 M potassium dichromate solution were dendritic. At 50 and at 100° numerous small circular crystals were formed. Rhythm decreased with increase of temperature; at 100° there was no evidence of rhythm.

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(1) This paper includes portions of the work offered in partial fulfilment of the requirements for the degree of Master of Science by Julia E. Abbott, 1933, and for the degree of Doctor of Philosophy by Majel M. MacMasters, 1934, at the Massachusetts State College.

(2) Brewster, *Trans. Roy. Soc. Edin.*, **20**, 607–24 (1853).

(3) Miers, *Mineral. Mag.*, **15**, 39–41 (1908); *C. A.*, **2**, 1919 (1908).

(4) Hedges, "Liesegang Rings and Other Periodic Structures," Chapman and Hall, London, 1932.

The influence of concentration was obvious. Slides made with 0.0017 *M* potassium dichromate solution showed much fine rhythm and x-rhythm; those made with 0.017 *M* potassium dichromate solution showed much fine rhythm, but practically no x-rhythm; while slides made with 0.136 *M* potassium dichromate solution showed very little rhythm of any type. Within the limits studied, fine rhythm and x-rhythm occur most frequently in dilute solutions and at low temperatures; the heavy crests formed by concentrated solutions are too thick for observation of rhythm; similar crests are formed by dilute solutions allowed to crystallize at high temperatures.

If all the data are considered, it appears at once that coarse rhythm is often irregular and never constant enough to serve as the criterion of periodicity. It becomes plain, on the other hand, that temperature and concentration differences, within the wide limits studied, have no influence upon the production of fine rhythm, providing only that the solution is not too strong and the temperature not too high for the production of a film of crystals. With a concentrated solution run at a high temperature crystallization proceeds rapidly with the formation of heavy crests which, by their massiveness, prohibit the detection of rhythm which might be present. The periods most commonly observed were those of 0.005 and 0.01 mm.; these were constant over wide areas on slides made at varying temperatures, with different concentrations of the solution. The crest and trough were, in general, of equal width; where this was not the case, the crest was that of one period, while the trough was that of another period either one-half or double the width of the first. All commonly observed periods were either 0.005 mm. in width or some common multiple of this width. x-Rhythm appears to be a special case of fine rhythm, in which periods of fine rhythm have developed in two directions.

New Method.—The method of Miers seemed open to criticism, because it involves motion, strong convection currents and exposures to contaminated atmosphere; the following method, therefore, was developed.

The 0.5 *M* solution of potassium dichromate to be examined was brought to boiling temperature; the cleaned slide was drained from distilled water and dipped, without wiping, into the boiling solution. Of each set of five slides, two were allowed to crystallize while held above the hot solution, while the other three were placed, on edge, on a glass plate to crystallize. A temperature difference in the surrounding atmosphere was thus introduced. In no case did there appear to be any difference between the two slides and the three, and in most cases these films showed periodic banding. This method gives, consistently, large areas of fine rhythm.

Influence of Specific Impurities.—Preliminary tests showed that typical rhythm was formed in the presence of 12% ethyl alcohol, 4% sodium hydroxide or small quantities of various acids.

Sodium dichromate and ammonium dichromate were introduced, in turn, in order to study the effect of a single foreign ion upon rhythmic crystallization. Further investigation showed, however, that each of these salts exhibited rhythmic crystallization from aqueous solution. The banding shown by ammonium dichromate was very similar to that exhibited by potassium dichromate. Sodium dichromate gave finer but less continuous rhythm. The rhythmic crystallization of these salts has not hitherto been reported.

Specific Effect of Anions.—This part of the work was undertaken assuming that the cation was the most important factor in rhythmic crystallization. This assumption arose from the observation that potassium dichromate and ammonium dichromate, with similar cations, showed very similar rhythmic crystallization, while sodium dichromate, with a smaller cation, showed finer spacing of the periods, and finally, introduction of sufficient hydrogen ion, a very small cation, completely inhibited fine rhythm. The results obtained were surprising; apparently the foreign cation has little or no effect on the rhythm, while anion has a specific inhibitory effect.

A 0.5 *M* potassium chloride solution was mixed with the 0.5 *M* potassium dichromate solution to give molar ratios of chloride ion to dichromate ion varying from 10/2 to 10/7, increasing always by whole numbers. The tests showed that a 10/5 molar ratio of chloride ion to dichromate ion had a slight effect upon the rhythmic crystallization of potassium dichromate, while a 10/3 molar ratio completely inhibited the rhythmic crystallization of potassium dichromate. When the large amounts of the chloride ion were present, potassium dichromate built dendritically upon cubic crystals of potassium chloride, and no fine rhythm found when all of the dichromate was used in building such dendrites. Under the influence of the potassium chloride coarser dendrites of the potassium dichromate appeared coincident with the disappearance of fine rhythm. It seems probable, therefore, that potassium chloride inhibited fine rhythm by modifying the surface attractions of the potassium dichromate crystals. The period of fine rhythm when present was always that normally shown by pure potassium dichromate solutions.

The effect of the presence of 0.5 *M* sodium chloride upon the rhythmic crystallization of 0.5 *M* potassium dichromate was investigated in a similar way. Inspection of the various sets of slides in this series showed that the period of fine rhythm did not decrease, but remained constant at the normal value for potassium dichromate; it may be concluded from this that sodium dichromate did not form to any large extent, as preliminary tests had shown that sodium dichromate crystallizes rhythmically with a period smaller than that of the potassium salt. Fine rhythm persisted only slightly longer in this series than in that in which potassium chloride was used as impurity. A molar ratio of chloride ion (or sodium ion) to dichromate ion of 10/4 caused appreciable decrease in the amount of fine rhythm present, while a ratio of 10/2 caused complete absence of fine rhythm.

It appeared desirable to try the effect of the presence of a divalent cation; for this purpose a series of slides was made and examined, using a 0.25 *M* solution of calcium chloride as the specific impurity. When the molar ratio of chloride ion to dichromate ion was 10/4 fine rhythm was still present, but when the ratio was 10/3 fine rhythm was not typical, although a transitional type of rhythmic branching of dendrites was observed.

The transition from parallel branching of dendrites to typical fine rhythm is of especial interest, as it indicates more clearly the ultimate cause of fine rhythm. Fine rhythm is due to very regular branching of dendrites. The present writers have observed the crystals in crest and trough to be lying at right angles to each other; the branch lies at right angles to the parent stem.

The molar ratio of chloride ion to dichromate ion at disappearance of fine rhythm was 10/2, 10/3, 10/3, in the presence of sodium chloride, potassium chloride and calcium chloride, respectively. The charge on the cation cannot be an important factor, since the effect of the chloride ion is constant, no matter whether it is introduced with monovalent cation as sodium or potassium or with a divalent cation as calcium. There is also further substantiation of the view that the anion alone affects the inhibition of fine rhythm, in this case at least, since the ratio of chloride ion to dichromate ion is constant in the presence of sodium ion, calcium ion or excess potassium ion. These results were unexpected in view of the preliminary work.

Potassium nitrate, 0.5 *M*, was used with the 0.5 *M* potassium dichromate solution to introduce a monovalent anion other than the chloride ion. All fine rhythm of the series showed the usual period for potassium dichromate. Definite curtailment of fine rhythm did not appear until the molar ratio of nitrate ion to dichromate ion was 6/15; with a ratio of 7/15 fine rhythm was entirely suppressed. The corresponding ratio of chloride ion to dichromate ion was 10/3; the nitrate ion is, therefore, far more effective than the chloride ion in the inhibition of rhythmic crystallization of potassium dichromate from aqueous solution.

Potassium sulfate, 0.5 *M*, was used with 0.5 *M* potassium dichromate to determine the effect of the sulfate ion, a divalent anion, upon the periodic crystallization of potassium dichromate. The period of the fine rhythm was not affected. When the molar ratio of sulfate ion to dichromate ion was 1/1 the amount of fine rhythm formed began to decrease. When the ratio was 4/3 rhythm was almost completely inhibited. The sulfate ion is, therefore, more effective in inhibiting the formation of fine rhythm by potassium dichromate than is the chloride ion, but is less effective than the nitrate ion. From this evidence it would further appear that the charge on the anion is not a prime factor in the effect of the anion on rhythmic crystallization.

Spacing of Periods from the Center of Crystallization.—No data concerning the spacing of rings from the center of crystallization in cases of rhythmic crystallization from solution have been found in the literature. Such measurements are often difficult, as in some cases the center is surrounded by a large, irregular area of undifferentiated or dendritic precipitate; in other cases the arc of crystallization is so great

TABLE I

DATA ON SPACING OF PERIODS FROM CENTER OF CRYSTALLIZATION

No.	Soln. used	Dist. of period from center, mm.	Values of A $\frac{h_3 - h_2}{h_2 - h_1} = A$	Agreement with Jablczynski	Agreement with Hughes (see Fig. 1)
1	150 cc. 0.5 M $K_2Cr_2O_7$ with 100 cc. 0.5 M K_2SO_4	0.045 0.070 0.095 .125 .155	1.00 1.20 1.00	Partial	Fair
2	0.5 M $K_2Cr_2O_7$	.060 .075 .090 .105 .120 .135 .150	1.00 1.00 1.00 1.00 1.00	Perfect	Fair
3	50 cc. 0.5 M $K_2Cr_2O_7$ with 10 cc. 0.166 M $FeCl_3$	.010 .015 .020 .025 .030 .035 .040 .045	1.00 1.00 1.00 1.00 1.00 1.00	Perfect	Almost perfect
4	50 cc. 0.5 M $K_2Cr_2O_7$ with 20 cc. 0.25 M $CaCl_2$	.020 .040 .060 .100 .120 .140 .160	1.00 2.00 0.50 1.00 1.00	Partial	Good
5	50 cc. 0.5 M $K_2Cr_2O_7$ with 40 cc. 0.25 M $CaCl_2$	.015 .030 .045 .060 .075 .090	1.00 1.00 1.00 1.00	Perfect	Excellent
6	40 cc. 0.5 M $K_2Cr_2O_7$ with 100 cc. 0.25 M $CaCl_2$	.060 .095 .150 .160 .200 .235	1.85 0.15 4.00 .88	Negative	Fair

that the center would lie at a considerable distance off the slide. Measurements were undertaken, however, in an attempt to determine whether potassium dichromate, in the solutions under investigation, gave rhythmic bands similar in arrangement to those found by Jablczynski[5] in Liesegang rings, or by Hughes[6] and Dippy[7] in melts which crystallized rhythmically.

Jablczynski found the ratio between rings formed by metathesis of silver nitrate and potassium dichromate in gelatin gel to be constant, expressed by $(h_3 - h_2)/(h_2 - h_1) = A$, when h_n is the distance of the nth ring from the point of entrance of the diffusing silver nitrate solution.

Hughes and Dippy investigated cases of rhythmic crystallization from the melt, found that by plotting the logarithm of N, the number of rings counted from the center against the logarithm of r, the distance of the ring from the center, a straight line was obtained with the general equation

$$\log N = a \log r + \log K$$

when N and r are defined as above, a is the slope of the line to the axis of log r, and log K is the intercept on the axis of log N.

Slides were chosen at random, but only areas where the center of crystallization was clearly defined, and in which fine rhythm progressed evenly in all directions from the center of crystallization were used. Data and comparison with Jablczynski and with Hughes are given in Table I. The graph, Fig. 1, developed from Table I shows agreement with the work of Hughes.

Slides 2, 3 and 5, Table I, showed perfect agreement with the Liesegang ring relationship found by Jablczynski, while slides 1 and 4 showed partial agreement. Slide 6, however, showed negative agreement. The relationship apparently holds for many cases of rhythmic crystallization from solution, but may not be universally true.

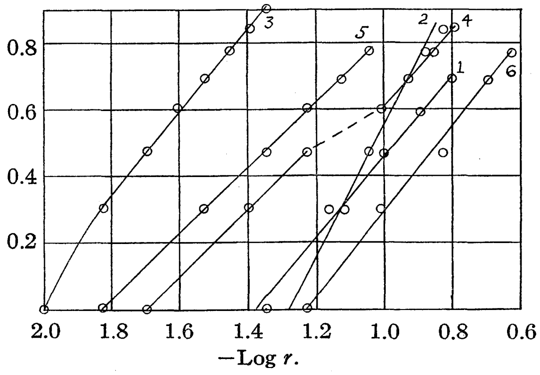

Fig. 1.—Log of number of period plotted against log of distance from center.

When the data from slides 1, 2 and 3, Fig. 1, are plotted as suggested by Hughes, they show a tendency to give a curve when the data are taken from near the centers of crystallization (curve 3), but the data as a whole give a statistically straight line. Only the statistically straight lines given by the data as a whole have been drawn in for slides 1 and 2. Many more cases would have to be investigated to prove that the tendency to give a curve from data near the center of crystallization is significant. Slide 4 shows two lines, both excellently straight, one from data near the center of crystallization, the other from data more re-

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[5] Jablczynski, *Kolloid-Z.*, **40**, 22–28 (1926).

[6] Hughes, *Nature*, **123**, 603–604 (1929).

[7] Dippy, *J. Phys. Chem.*, **36**, 2354–2361 (1932).

moved from the center. Slides 5 and 6 show statistically straight lines, in good agreement with the work of Hughes.

If slides had been taken exhibiting the usual fine rhythm of extremely constant spacing over wide areas in large arcs such that the theoretical center of crystallization would be situated off the slide, no distances from the center could have been measured. If the first period formed had been used as a center of crystallization, and measurements made from it, however, a regular series like those in slides 2, 3 and 5 would have been found in those numerous cases in which the periods are of equal width over large areas. These cases would give perfect agreement with the work of Jablczynski and good agreement with the work of Hughes and of Dippy.

For suggestion of the subject of research, acknowledgment and thanks are due to Professor Cecil H. Desch, George Fisher Baker lecturer in Chemistry at Cornell University, October, 1931, to January, 1932.

Summary

Distinction has been made between *coarse rhythm* and *fine rhythm* produced by crystallization of potassium dichromate from aqueous solutions. Fine rhythm has been shown to be the true criterion of periodicity. A method has been described by which very regular fine rhythm can be obtained over large areas.

It has been shown that differences in temperature and in concentration do not, within wide limits, materially affect the rhythmic crystallization of potassium dichromate from aqueous solution.

The rhythmic crystallization of ammonium dichromate and of sodium dichromate from their aqueous solutions has been reported.

The specific influence of a foreign anion in inhibiting the formation of fine rhythm of potassium dichromate has been shown. It has been determined that the nitrate ion is more effective than the sulfate ion, while the sulfate ion is more effective than the chloride ion. The molar ratio of each of these ions to dichromate ion necessary completely to inhibit formation of rhythm has been reported.

It has been shown that the spacing of periods from the center of crystallization, in rhythmic crystallization of potassium dichromate from aqueous solution, agrees, roughly, with the spacing of Liesegang rings reported by Jablczynski, and with the spacing of rhythmic banding resulting from crystallization from the melt, as reported by Hughes and substantiated by Dippy. This would indicate that there may be a common cause underlying the formation of Liesegang rings, rhythmic banding from the melt and rhythmic crystallization from solution.

AMHERST, MASS. RECEIVED JUNE 27, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DEPAUW UNIVERSITY]

Additions to Conjugated Systems in the Anthracene Series. III. Factors Influencing the Mode and Extent of Reaction of the Grignard Reagent with Ketones

BY PERCY L. JULIAN, WAYNE COLE AND THOMAS F. WOOD[1]

When benzalanthrone (I) is treated with methylmagnesium iodide, the main product (II) isolated is the one formed by 1,2-addition. The reaction was puzzling for a long time, first of all because it is difficult to duplicate results unless the proper concentration of reactants is consistently maintained. Secondly, the behavior of our product (II) toward bromine, as well as behavior on attempted rearrangement into the isomer with the anthracene structure,[2] were not what we had expected. All these results appear, however, to find satisfactory explanation in the ease with which (II) loses water, possessing as it does a very reactive hydroxyl group.

The product secured on treatment of (II) with one mole of bromine in the cold indicates addition of two atoms of bromine and elimination of a molecule of water. It is highly fluorescent in solution, and both bromine atoms are very reactive, as is shown by the ease with which the dibromide is converted into a diacetate. We are suggesting structure (V) for it, and (III) and (IV) as logical intermediates. The diacetate would then have the structure (VI). On further treat-

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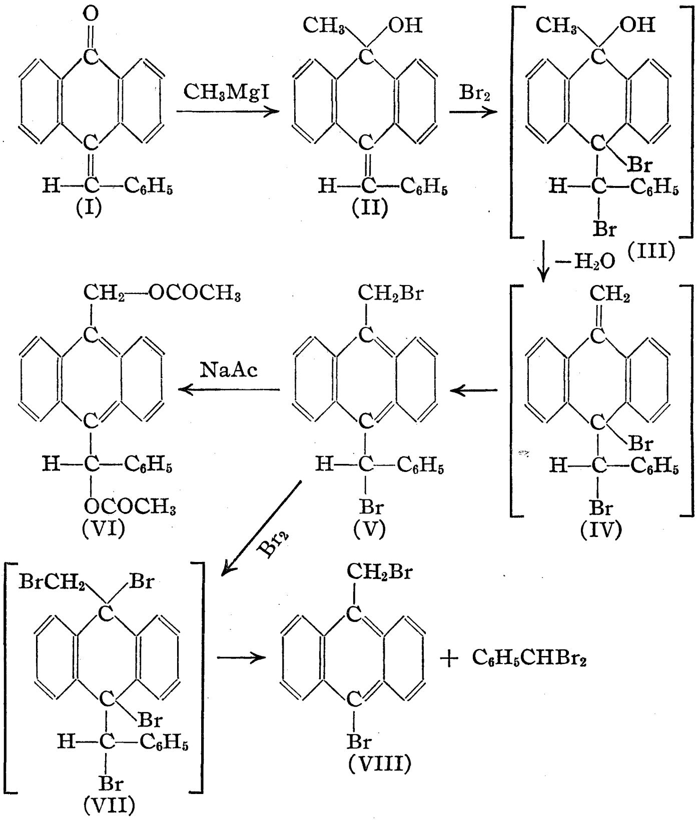
[1] Abstracted from the senior researches of Messrs. Cole and Wood at DePauw University, 1934–1935.

[2] *Cf.* Julian and Cole, THIS JOURNAL, **57**, 1607 (1935).

ment with bromine in the cold (V) absorbs, somewhat more slowly than (II), a second molecule of bromine, the compound (VIII) being deposited, a substance identical with one of the products secured by Barnett and Matthews[3] on brominating 9-methylanthracene and assigned this structure. The residue on evaporation of the mother liquor is hydrolyzed on warming with water into benzaldehyde and hydrogen bromide. Compound (VII) is suggested as the intermediate in the formation of (VIII) from (V).



With the behavior of (II) satisfactorily explained, our attention was directed to the original object of these investigations, namely, a study of the factors influencing different types of addition of the Grignard reagent to ketones of the anthracene series. It was conceivable that, in view of the fact that a small quantity of anthraquinone is always secured on working up the product from the reaction between phenylmagnesium bromide and benzalanthrone (indicating in all probability formation of a small amount of 1,6-addition product), the action of methylmagnesium iodide might result in a larger percentage of 1,6-addition.[4]

Actually on working up the reaction products on treatment of benzalanthrone with methylmagnesium iodide, an appreciable quantity of anthraquinone was always obtained. Accordingly we employed the usual procedure[2,5] for isolation of peroxides and obtained a very small quantity of a highly insoluble crystalline substance, which decomposed violently at 74° without melting, and yielded anthraquinone. Since its isolation in workable quantities was difficult and no criterion of its purity was available, we decided to undertake the preparation of this same compound by the action of phenylmagnesium bromide on ethylidene anthrone (IX).

The only reference to ethylidene anthrone in the literature is that of Liebermann.[6] Employment of his procedure as well as several other methods which should lead to a compound of this structure yielded invariably anthraquinone. The conclusion was inevitable that ethylidene anthrone (IX) is easily oxidized by atmospheric oxygen to anthraquinone. That atmospheric oxygen should cleave a carbon–carbon double linkage of this type is hardly conceivable in view of the stability of methylene anthrone and benzalanthrone. Since it has been shown[2,5b] that atmospheric oxygen readily converts anthranols into peroxides, it seemed reasonable, proceeding from the principle of vinylogy,[7] to expect that the fundamental difference in behavior between ethylidene anthrone (IX) and methylene and benzalanthrone resides in the ability of the former to exist in the anthranol modification (X), which would be expected to undergo oxidation by atmospheric oxygen to anthraquinone and vinyl alcohol *via* the peroxide (XI).

To test out this hypothesis we undertook the identification of vinyl alcohol as acetaldehyde. A sample of ethyloxanthrone (XII) was dissolved in glacial acetic acid, a few drops of sulfuric acid added and the solution allowed to stand under

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[3] Barnett and Matthews, *Ber.*, **59**, 1434 (1926).

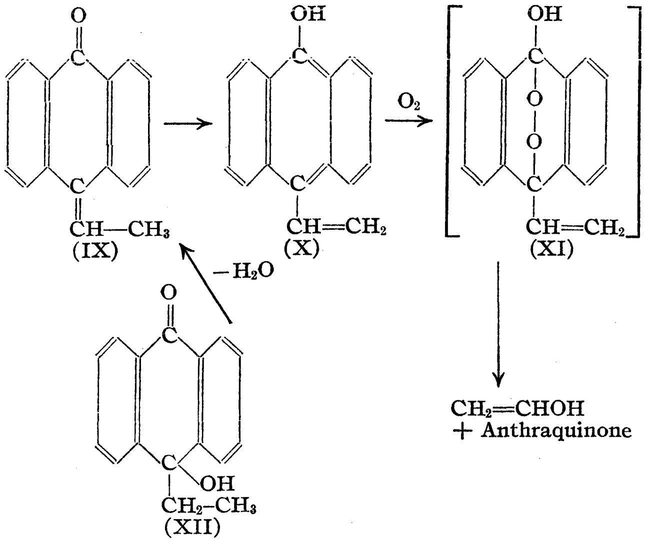
[4] *Cf.* Julian and Gist, THIS JOURNAL, **57**, 2030 (1935); Kohler and Nygaard, *ibid.*, **52**, 4132 (1930).

[5] (a) Kohler, *Am. Chem. J.*, **36**, 189, 192; (b) Julian and Magnani, THIS JOURNAL, **56**, 2174 (1934).

[6] Liebermann, *Ber.*, **13**, 1598 (1880).

[7] Fuson, *Chem. Rev.*, **16**, 1 (1935).

oxygen in a closed system. Acetaldehyde was distilled from the reaction mixture and identified by its odor, by means of Tollens' reagent, and by conversion into ethylidene-β-dinaphthyl oxide.[8]



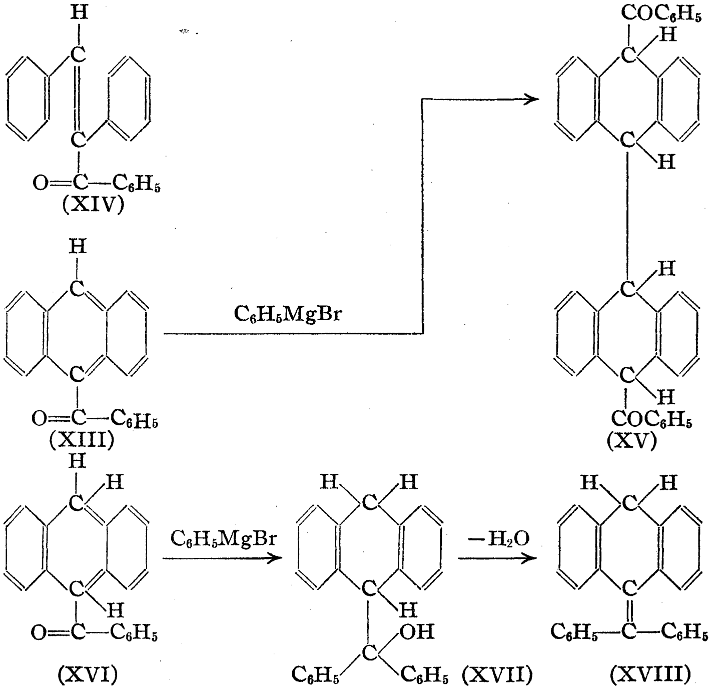
(IX) (X) (XI) (XII)

Ethylidene anthrone was obtained as a red oil by destructive distillation of ethyloxanthrone in an atmosphere of nitrogen at ordinary pressure. On redistillation in vacuum this oil boiled constantly at 245–247° at 20 mm.; on attempting to distil this material under atmospheric conditions, however, considerable decomposition took place, yielding anthraquinone and a combustible gas which was collected over water and identified as acetylene. The formation of acetylene is further proof of the proposed oxidation mechanism, since vinyl alcohol formed in this manner at high temperature would be expected to lose water rather than rearrange to acetaldehyde.

The properties of ethylidene anthrone and related anthrones are being further investigated in these laboratories, and our studies of the influence on the mode of reaction with the Grignard reagent, occasioned by substitution of the hydrogen atoms in the methylene group of methylene anthrone, must await the results of these investigations.

We, therefore, turned our attention to the other side of the problem, namely, the influence of the anthracene nucleus on the mode of reaction, selecting as starting material anthraphenone (XIII). Viewed from the standpoint of meso-unsaturation this substance resembles benzaldesoxybenzoin (XIV) and phenylbenzaldesoxybenzoin. Since 1,2-addition of phenylmagnesium bromide seemed highly improbable in view of the sluggish character of the carbonyl group (anthraphenone gives none of the typical ketone reactions),[9] it was expected that either 1,4-addition into the phenyl ring might occur, or what was less probable 1,6-addition to the conjugated system extending to the 9-carbon atom of the anthracene nucleus, yielding a dihydroanthracene derivative. In fact neither of these reactions occurred, instead dimolecular 1,6-reduction took place yielding 10,10′-dibenzoyl-9,9′,10,10′-tetrahydro-9,9′-dianthranyl (XV), a compound already described by Cook and secured by reducing anthraphenone with zinc and acetic acid.[10]

In the case of dihydroanthraphenone (XVI) in which the meso-unsaturation is removed, all hindrance to 1,2-addition disappears and phenylmagnesium bromide gives the expected carbinol (XVII) in practically quantitative yield. The in-



(XIV) (XIII) (XV) (XVI) (XVII) (XVIII)

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[8] Mulliken, "Identification of Pure Organic Compounds." 1st edition, 1904, Vol. I, p. 23.

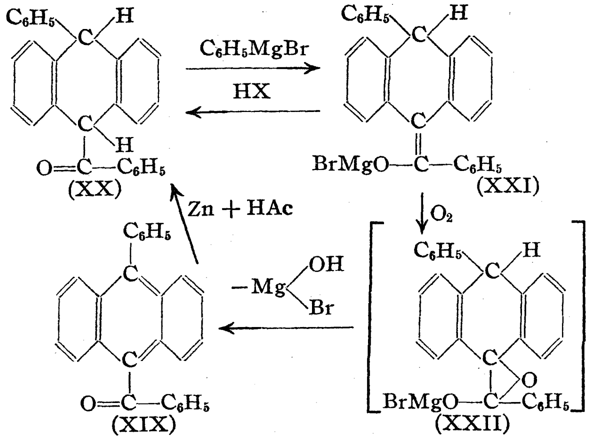
[9] Cook, *J. Chem. Soc.*, **129**, 1282, 1677, 2170 (1926).

[10] Cook, *ibid.*, 1680 (1926).

fluence of this meso-unsaturation upon the additive powers of the carbonyl group is in striking analogy to the difference in behavior, reported by Kohler, between phenylbenzaldesoxybenzoin and its saturated derivative, α,β,β-triphenylpropiophenone.[11] The structure of the carbinol (XVII) was proved by elimination of water to form the hydrocarbon (XVIII), the latter oxidized with chromic acid to one mole of anthraquinone and one mole of benzophenone.

Following up the analogy between these meso-unsaturated anthracene ketones and α,β-unsaturated ketones, we next investigated 9-phenylanthraphenone (XIX). Despite numerous attempts we have been unable to isolate any pure products from the reaction between this substance and phenylmagnesium bromide. Most of the material is recovered unchanged. A quantity of gum was always obtained and this is still under investigation. We are therefore not prepared to state with certainty that no reaction takes place in view of the difficulty often experienced in the isolation of pure products from Grignard reactions involving highly phenylated unsaturated compounds.

Here again the situation is quite different when the meso-unsaturation is removed by hydrogen. The dihydro derivative (XX) reacts readily with phenylmagnesium bromide in ether solution, but on working up in the usual manner the products consisted of unchanged material (XX) and phenylanthraphenone (XIX). The reaction was carefully checked, perfectly pure dihydro compound (XX) containing no phenylanthraphenone being employed. The results were consistent, (XX) and (XIX) representing the products. To explain this peculiar oxidation of (XX) during the course of the Grignard reaction, we again call attention to Kohler's experience with an analog of (XX), namely, α,β,β-triphenylpropiophenone.[12] The reactions are entirely analogous, especially in view of the fact that Cook[9,10] has called attention to the similarity in enolizing power between (XX) and diphenylacetophenone. This enolizing power of our compound (XX) constitutes the main difference between our substance (XX) and α,β,β-triphenylpropiophenone of Kohler, enabling the substance (XX) to form a magnesium derivative (XXI) directly on treatment with phenylmagnesium bromide.



It is understood in the abbreviated flow sheet that the oxide (XXII) has been formed from the action of a peroxide of (XXI) on (XXI) itself, something as Kohler has indicated for his highly phenylated ketones. We are at present engaged in attempts to isolate compounds of the type represented by (XXII), a feat involving difficulty because of the ease with which dihydroanthracene derivatives lose constituents across the ring, passing over into anthracene derivatives with the true aromatic structure.

Our present inadequate understanding of "steric" influences does not allow an explanation of the influence of unsaturation upon the additive power of a carbonyl group; such as is revealed in these results. Taken together with those recorded by Kohler and Nygaard[11] they show this influence to be a definitely indisputable factor in determining both extent and mode of reaction with the Grignard reagent.

The authors acknowledge gratefully a generous grant to one of them from the Rosenwald Fund, and likewise their indebtedness to their first teacher of Chemistry, Dean W. M. Blanchard, Head of the Department, whose untiring efforts have made possible this research program.

Experimental Part

Action of Methylmagnesium Iodide on Benzalanthrone.—The procedure described herewith is that found satisfactory for isolation of the maximum quantity of the carbinol (II). Fourteen grams of powdered benzalanthrone was added gradually to a Grignard reagent prepared from 3.6 g. of magnesium and 22 g. of methyl iodide in 700 cc. of ether. The ketone dissolved to yield a clear, green-yellow fluorescent solution. The solution was stirred cold for three hours, decomposed with ammonium chloride and oxygen passed into the washed ethereal solution; 0.3 gram of colorless, compact crystals separated and was filtered. They decomposed at 74° with separation

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[11] Kohler and Nygaard, THIS JOURNAL, **52**, 4129 (1930).

[12] Kohler and Mydans, *ibid.*, **54**, 4667 (1932).

of anthraquinone, and were insoluble in any solvents boiling lower than this temperature. Analysis of the crude material giving results which could not be interpreted, further investigation of this substance was postponed, pending our results with ethylidene anthrone. From the ethereal solution on concentration and addition of petroleum ether, 13 g. of crude carbinol (II) was obtained. Recrystallized from ether–petroleum ether, 12 g. of material melting at 148° was secured.

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.59; H, 6.09. Found: C, 88.75; H, 6.25.

In the Grignard machine it gave 1 mole of gas and consumed one mole of reagent. On oxidation with chromic acid it gave anthraquinone and benzoic acid.

Behavior of Carbinol (II) toward Bromine.—To a well-cooled solution of 3 g. of carbinol (II) in 20 cc. of chloroform, a solution of 1.6 g. of bromine in 10 cc. of chloroform was added dropwise. The bromine was momentarily absorbed without evolution of hydrogen bromide. Allowed to stand in the cold for one hour, the solvent was removed under diminished pressure, ether added to the residue, which on stirring crystallized. Recrystallized from chloroform–ether, the substance (V) weighed 4 g. and melted at 168° with decomposition.

Anal. Calcd. for $C_{22}H_{16}Br_2$: C, 60.00; H, 3.64. Found: C, 59.57; H, 3.75.

Bromination of 1 g. of (V) in exactly the same manner with 0.5 g. of bromine yielded 0.6 g. of hard yellow crystals, m. p. 200° (VIII).

Anal. Calcd. for $C_{15}H_{10}Br_2$: C, 51.43; H, 2.86. Found: C, 51.11; H, 3.00.

A mixture of 2.5 g. of the dibromide (V), 2.5 g. of fused sodium acetate and 25 cc. of glacial acetic acid was refluxed for forty minutes. The warm acetic solution was filtered and 2 cc. of water was added (no turbidity). On cooling and scratching 1.6 g. of light yellow crystalline material separated, m. p. 188°, recrystallized from chloroform–methyl alcohol, which solutions displayed strong blue fluorescence. It gave no test for halogen.

Anal. Calcd. for $C_{26}H_{22}O_4$: C, 78.39; H, 5.60. Found: C, 77.90; H, 5.60.

Attempts to Prepare Ethylidene Anthrone

(a) Adapted from Procedure for Preparation of Methylene Anthrone.[13]—Twenty cc. of a 40% solution of acetaldehyde in water was added portionwise to a warm mixture of 10 g. of anthrone, 50 cc. of methyl alcohol and 5 drops of piperidine. After a small quantity of the acetaldehyde had been added the anthrone dissolved to yield a clear yellow solution. Obtaining no crystalline material on cooling the solution, 10 cc. of water was added, precipitating a yellow oil which solidified on standing. Attempts to recrystallize it gave only anthraquinone in large quantity.

(b) From Ethyl Oxanthrone.—The preparation of ethyl oxanthrone in workable quantities is best achieved as follows. To a stirred suspension of 140 g. of anthraquinone in 800 cc. of dry benzene, a Grignard reagent prepared from 13 g. of magnesium and 65 g. of ethyl bromide in 300 cc. of ether was added from a dropping funnel in the course of two and one-half hours. After addition was complete the mixture was stirred at room temperature for one hour, poured onto ice and hydrochloric acid and filtered through glass wool to remove anthraquinone. The filtrate was separated, and the washed and dried benzene layer was concentrated to about 200 cc. Petroleum ether was added and 65 g. of crude ethyl oxanthrone precipitated. Recrystallized from ether–petroleum ether it gave colorless prisms, m. p. 107°.

Attempt was first made to eliminate water by passing dry hydrogen chloride into a benzene solution of ethyl oxanthrone. On concentrating and adding petroleum ether, the tertiary chloride crystallized out, 1.6 g. out of 2 g. of the oxanthrone, m. p. 85°. On heating to about 120–130° this chloride lost hydrogen chloride and left behind a yellow oil which could not be crystallized and on standing deposited crystals of anthraquinone.

Two grams of ethyl oxanthrone was dissolved in 6 cc. of glacial acetic acid and 6 drops of sulfuric acid added. On standing for fifteen hours at room temperature, approximately 1 g. of anthraquinone was deposited, and on attempting to work up the mother liquors only more anthraquinone could be obtained.

Eight grams of ethyloxanthrone was dissolved in 15 cc. of glacial acetic acid, 1 cc. of concentrated sulfuric acid added, the flask filled with oxygen under pressure and carefully stoppered. After standing overnight, it was warmed gently and volatile material collected in a receiver cooled in a freezing mixture. Various tests already referred to were made on the distillate to demonstrate the presence of acetaldehyde, the most convincing one being its conversion into ethylidene-β-dinaphthyl oxide, m. p. 173°, which compound gave no depression with a sample prepared from an authentic specimen of acetaldehyde.

The formation of acetylene by distillation of ethylidene anthrone in the presence of atmospheric oxygen has been described in foregoing paragraphs. The acetylene was identified by its odor and by conversion into cuprous acetylide.

Action of Phenylmagnesium Bromide on Anthraphenone.—When the ketone was added to 4 moles of reagent in ether solution, allowed to stand overnight and worked up in the usual way, the solid material from 5 g. of ketone consisted of 1.1 g. of reduction product (XV) and 3.5 g. of unchanged anthraphenone. The latter was removed from the mixture by continued extraction with warm ether. The reduction product was recrystallized from benzene, m. p. 265°. With a specimen prepared by the method of Cook[9,10] it gave no depression. When benzene was substituted for the ether and the substance heated with the Grignard reagent in this solvent, the proportions of the products were unaltered. Phenylmagnesium iodide gave the same results. With methylmagnesium iodide, the original ketone was recovered quantitatively, no reaction taking place.

Action of Phenylmagnesium Bromide on Dihydroanthraphenone.—Five grams of the dihydro product (XVI) —prepared according to the method of Cook[10]—dissolved in ether was added to the Grignard reagent prepared from 1.4 g. of magnesium and 9.5 g. of bromobenzene in 200 cc. of ether. A noticeable warming of the reaction mixture accompanied the addition. Worked up in the usual way,

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(13) Barnett and Matthews, *Ber.*, **59**, 767 (1926).

the ethereal solution on concentration and addition of petroleum ether gave 4 g. of pure material (XVII), m. p. 173°, recrystallized from ether–petroleum ether or from methyl alcohol.

Anal. Calcd. for $C_{27}H_{22}O$: C, 89.50; H, 6.08. Found: C, 89.30; H, 6.19.

The product (XVII) examined in the Grignard machine gave one mole of gas and consumed one mole of reagent.

Elimination of Water from (XVII) to Give (XVIII).—Eight drops of concentrated sulfuric acid was added to a solution of 2 g. of carbinol (XVII) in 35 cc. of glacial acetic acid. On allowing to stand for three days 1.5 g. of material (XVIII) was deposited. Recrystallized from chloroform–methyl alcohol it gave colorless, glistening flakes, m. p. 258°.

Anal. Calcd. for $C_{27}H_{20}$: C, 94.13; H, 5.87. Found: C, 94.10; H, 5.79.

Half a gram of the hydrocarbon on oxidation with 0.5 g. of chromic acid in glacial acetic acid solution yielded 0.3 g. of anthraquinone and 0.2 g. of benzophenone.

Action of Phenylmagnesium Bromide on Dihydrophenylanthraphenone (XX).—Three and one-half grams of (XX) dissolved in ether was added to a Grignard solution from 0.72 g. of magnesium and 5.7 g. of bromobenzene. On first addition the solution was deep violet in color, gradually changing to red and on continued stirring to pale yellow. Worked up in the usual manner 2.0 g. of crystalline product was obtained, which was separated by fractional crystallization from ether into 1.2 g. of starting material and 0.7 g. of phenylanthraphenone.

Summary

1. Benzalanthrone gives mainly 1,2-addition with methylmagnesium iodide.
2. Ethylidene anthrone exists in an enolic modification involving a 1,7-shift of hydrogen, the anthranol suffering oxidation to a peroxide, which cleaves spontaneously to anthraquinone and vinyl alcohol.
3. Anthraphenone undergoes 1,6-dimolecular reduction on treatment with phenylmagnesium bromide or iodide, and no reaction with methylmagnesium iodide. Dihydroanthraphenone gives normal 1,2-addition.
4. No clean products could be isolated from the reaction between phenylanthraphenone and phenylmagnesium bromide. Dihydrophenylanthraphenone yielded with phenylmagnesium bromide phenylanthraphenone and unchanged material.
5. Striking analogies have been brought forward between meso-unsaturated anthracene ketones and α,β-unsaturated ketones. The analogies are likewise maintained when the unsaturation is removed in both types of ketones.

GREENCASTLE, INDIANA RECEIVED AUGUST 19, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

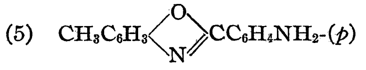
The Preparation and Tinctorial Properties of Certain Benzoxazole Dyes[1]

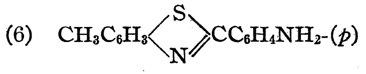
BY VLADIMIR J. MIKESKA AND MARSTON TAYLOR BOGERT

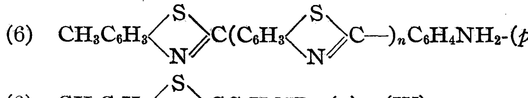
In a previous article,[2] we have pointed out certain of the similarities and dissimilarities which appear on comparing the chemical properties of the structurally related series of oxazoles, thiazoles and imidazoles.

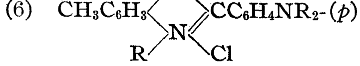
Having been interested for several years in the connection between chemical constitution and tinctorial properties in the thiazole series,[3] we have conducted some experiments also in the oxazole field and the present communication records the results. Our prior paper[2] described the syntheses of the necessary intermediates.

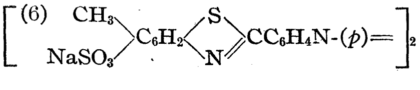
From the standpoint of the dye chemist, the thiazole derivatives of most interest are the intermediates dehydrothio-*p*-toluidine (II) and primuline (III), from which are manufactured dyes of the Thioflavine (IV) (Colour Index No. 815) or Chloramine Yellow (V) (Colour Index No. 814) types; or azo derivatives like the so-called "Ingrain colors" (Colour Index No. 812), prepared by diazotizing (II) or (III), or their sulfonates, and combining with suitable couplers.


$(5)\ \mathrm{CH_3C_6H_3}\left\langle{}^{\mathrm{O}}_{\mathrm{N}}\right\rangle\mathrm{CC_6H_4NH_2}\text{-}(p)$ (I)


$(6)\ \mathrm{CH_3C_6H_3}\left\langle{}^{\mathrm{S}}_{\mathrm{N}}\right\rangle\mathrm{CC_6H_4NH_2}\text{-}(p)$ (II)


$(6)\ \mathrm{CH_3C_6H_3}\left\langle{}^{\mathrm{S}}_{\mathrm{N}}\right\rangle\mathrm{C(C_6H_3}\left\langle{}^{\mathrm{S}}_{\mathrm{N}}\right\rangle\mathrm{C}\text{—})_n\mathrm{C_6H_4NH_2}\text{-}(p)$ (III)


$(6)\ \mathrm{CH_3C_6H_3}\left\langle{}^{\mathrm{S}}_{\mathrm{N(R)(Cl)}}\right\rangle\mathrm{CC_6H_4NR_2}\text{-}(p)$ (IV)


$\left[(6)\ {}^{\mathrm{CH_3}}_{\mathrm{NaSO_3}}\!\!>\mathrm{C_6H_2}\left\langle{}^{\mathrm{S}}_{\mathrm{N}}\right\rangle\mathrm{CC_6H_4N}\text{-}(p)\text{=}\right]_2$ (V)

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(1) Based upon the dissertation submitted by V. J. Mikeska, June, 1934, for the Ph.D. degree under the Faculty of Pure Science, Columbia University, New York, N. Y., to which dissertation the reader is referred for further experimental details and literature citations.—M. T. B.

(2) Mikeska and Bogert, THIS JOURNAL, **57**, 2121 (1935).

(3) Bogert and Allen, *ibid.*, **49**, 1315 (1927).

Our own experiments in the benzoxazole series have been mainly with the azo derivatives and dyes of the Chloramine Yellow class.

In so far as azo dyes of the oxazole, thiazole and imidazole series are concerned, all three yield substantive cotton dyes, which show generally about the same fastness to light, acids or alkalies.[4]

The azo derivatives of benzoxazole described beyond carry the azo grouping either in the *p*-position on the 2-phenyl nucleus, or in position 5 on the benzoxazole portion. One object in preparing these two series was to learn what effect this difference in the location of the azo group would have upon the tinctorial properties of the resulting dyes.

In this part of our research, the investigations of Lellmann and his associates were of especial interest, for Lellmann and Haller[5] prepared an imidazole analog of dehydrothio-*p*-toluidine (II) which, when diazotized and coupled, gave azo dyes as fast to cotton as the corresponding thiazole dyes. This was followed in 1895 by the work of Lellmann and Ebel,[6] who synthesized an oxazole analog (I) from *m*-nitro-*p*-cresol, then diazotized and coupled it. The azo compounds resulting closely resembled the analogous thiazole and imidazole derivatives in the color and fastness of their dyeings.

Our azo dyes, therefore, differed from those of Lellmann and Ebel[6] in carrying a phenyl in place of a methyl group on the benzene portion of the benzoxazole molecule, and from dehydrothio-*p*-toluidine in having this substituent in position 5 instead of 6. It was believed that the phenyl would have certain advantages over the methyl group in increasing the stability of the derivatives and in giving deeper shades on dyeing. The researches of Bogert and Allen,[3,7] in the benzothiazole series, have shown that such a change in the location of the hydrocarbon radical has but little influence upon the color or fastness of the dyeings obtained, and the results reported by Lellmann and his co-workers, in the benzoxazole series, lend support to this view. The replacement of sulfur by oxygen is ordinarily hypsochromic, so far as tinctorial effects are concerned, whereas the substitution of a methyl by a phenyl group, as just mentioned, generally exerts a bathochromic influence. In the case of the dyes synthesized by us, it was interesting to find that the former factor was the more potent one, for all of them gave paler shades than the corresponding dehydrothio-*p*-toluidine derivatives; and a repetition of the work of Lellmann and Ebel[6] showed that neither the depth of shade, nor the fastness of the dyeing, was greatly affected by whether the hydrocarbon radical in position 5 was a methyl or a phenyl.

Of the two amines (or their sulfo acids) used as initial materials for the production of our dyes, *viz.*, 2-*p*-aminophenyl-5-phenylbenzoxazole (A) and 2,7-diphenyl-5-aminobenzoxazole (B), both yielded azo dyes which were substantive for cotton and could be applied either direct or developed in the fabric. Of the two sets of dyes, those prepared from (B) were much the weaker. In other words, the azo grouping in the *p*-position on the 2-phenyl nucleus gives much better dyes than when this same grouping is in position 5 on the benzoxazole nucleus. On silk or wool, however, the (B) dyes also gave good deep shades by either method.

This influence of the position of the azo grouping upon the affinity of these dyes for cotton, coincides with the experience of Kym,[8] who investigated a few azo dyes of these types and found that the dyeings on cotton were much weaker when the azo grouping was moved from the *p*-2-phenyl position to the benzoxazole nucleus.

The same was true in the case of the Chloramine Yellow types obtained from (A) and from (B), those from the former being far superior as direct cotton dyes. Both could be developed in the fabric to deep shades. There was but little difference in depth of color, whether the dyeings were made on cotton, wool or silk, in the case of the (A) dyes; but the dyeings obtained with the (B) dyes on cotton were much paler than those on wool or silk.

In so far as the method of dyeing was concerned, examination of the dyed samples after the lapse of five years, showed in every case that the direct dyed fabric held its color much better than those samples dyed by the "ingrain" process.

Experimental

To economize space in what follows, the two dye intermediates used, *i. e.*, 2-*p*-aminophenyl-5-

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[4] (a) Bayer & Co., German Patent 165,102; *Friedländer*, **8**, 693 (1905); (b) Meister, Lucius and Brüning, German Patent 284,181; *Friedländer*, **12**, 458 (1915); (c) Fischer, *J. prakt. Chem.*, [2] **73**, 436 (1906); (d) Kym, *Ber.*, **44**, 2919 (1911).

[5] Lellmann and Haller, *ibid.*, **26**, 2759 (1893).

[6] Lellmann and Ebel, *ibid.*, **28**, 1128 (1895).

[7] Bogert and Allen, *Ind. Eng. Chem.*, **18**, 532 (1926).

[8] Kym, *Ber.*, **33**, 2847 (1900).

phenylbenzoxazole and 2,7-diphenyl-5-aminobenzoxazole, will be referred to respectively as (A) and (B), and their sulfo acids similarly as (A^1) and (B^1).

I. Azo Dyes from (A) or (A^1)

These dyes are akin to the so-called "Ingrain Colors" of Green,[9] and were prepared in the customary way, by diazotizing the intermediate and combining the diazo product with suitable couplers, the basic dyes being coupled in acid and the acid ones in alkaline solution. All of these products gave good deep shades on cotton, either as direct or as developed dyes.

The direct dyeing was carried out with 1 g. of unbleached cotton, 20 cc. of 0.1% dye solution, 4 drops of 10% sodium carbonate solution, 15 cc. of 1% sodium chloride solution and 25 cc. of water, the bath being heated for thirty minutes. Silk was dyed in a weakly acid bath.

For the developed dyeings, with the sulfo acids for example, the cotton was boiled for thirty minutes in a 5% solution of (A^1) or (B^1), after neutralization with sodium carbonate, and to the boiling solution there was added 5% (by weight) of sodium chloride. After this impregnation, the cloth was washed thoroughly in cold water, to avoid surface colors and subsequent bleeding, and was passed through a bath containing 1 g. of sodium nitrite in 400 cc. of water and faintly acid with sulfuric acid. Diazotization was completed in about twenty minutes and, after washing in cold water, the cotton was immersed in a bath of the coupler selected. If a red color (Oxazole Red) was desired, a 1% solution of beta-naphthol was used dissolved in the calculated amount of caustic alkali and containing an excess of sodium carbonate. The color developed rapidly and after five minutes the cloth was removed and freed from surface dye by thorough washing with cold water and soap. Amines were coupled in acid solution.

The results with the developed dyes can be tabulated as follows.

TABLE I

DEVELOPED AZO DYEINGS FROM (A) OR (A^1)

	Base	Coupler	Shade on cotton	Type
(1)	(A)	α-Naphthol	Bluish-red	Mono-azo
(2)	(A^1)	Phenol	Yellow	Mono-azo
(3)	(A^1)	β-Naphthol	Orange-red	Mono-azo
(4)	(A^1)	Resorcinol	Orange	Mono-azo
(5)	(A^1)	α-Naphthylamine	Purple	Mono-azo
(6)	(5)	α-Naphthylamine	Black	Bis-azo

Through the courtesy of Professor Hal T. Beans and Dr. A. Dingwall, of the Columbia University Department of Chemistry, the two beta-naphthol azo dyes were examined spectrographically and their absorption curves plotted, as shown on Fig. 1. Of these two dyes, the one designated "Ingrain Red" was prepared by diazotizing dehydrothio-*p*-toluidine and coupling with beta-naphthol. The analogous "Oxazole Red" was prepared similarly from (A^1). An examination of the graph will show the similarity of the two curves. Both show maximum absorption at about 4980 Å. Practically all of the blue and none of the red is absorbed in each case. Both transmit a portion of the yellow, so that the dyes have an orange shade, but the oxazole transmits more and is therefore a lighter orange-red than the thiazole dye. Further, the thiazole dye has a wider absorption range and this accounts for its greater intensity. These results are in harmony with previous observations made on the tinctorial properties and the colors of solutions of such dyes. It is quite clear, therefore, that the bathochromic effect of the benzothiazole is slightly but definitely greater than that of the benzoxazole nucleus in dyes of analogous structure.

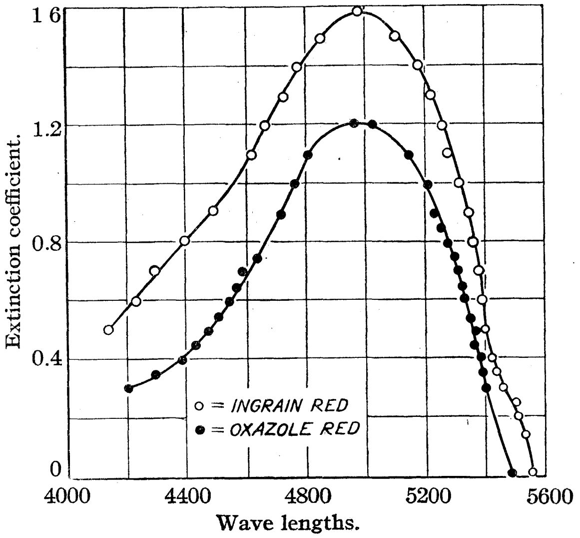

Fig. 1.—Absorption spectra curves.

The solvent for both dyes was 95% ethanol. The concentration of the oxazole was 1:37,500; of the thiazole, 1:50,000.

The fastness of these developed dyes on cotton was tested with the results exhibited in Table II. The dyes are represented by the Arabic numerals used in Table I.

For purposes of comparison, a similar set of developed azo dyes was prepared from 2-*p*-aminophenyl-5-methylbenzoxazole (I), as described by Lellmann and Ebel,[6] and subjected to similar tests for fastness. The results are given in Table III, the Arabic numerals used for the column headings representing the same type of dye as in Table II.

In general, these azo dyes were much the same as the original "Ingrain Colors" of Green,[9] in the thiazole series, prepared from Primuline. Although Green's results showed that there was but little difference between the corresponding dyes prepared from Primuline and from dehydrothio-*p*-toluidine sulfo acid, nevertheless we prepared the same series of dyes as listed above from the latter and our results were in entire accord with his.

Identical dyeings were carried out with the corresponding azo dyes from dehydrothio-*p*-toluidine sulfo acid and from the oxazole analog (A^1). In general, the shade of the thiazole was deeper than that of the corresponding oxazole dye; the red dyes were fastest in both series; in both, the purples were turned brown by alkali, but the original color was restored by acid; the orange dyeings were less fast, and the yellow ones lost most of their color when boiled with 10% sodium hydroxide.

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[9] (a) Green, *J. Soc. Chem. Ind.*, **7**, 179 (1888); (b) *J. Chem. Soc.*, **55**, 229 (1889).

TABLE II

FASTNESS OF DEVELOPED AZO DYEINGS FROM (A) OR (A^1)

Reagent	(1)	(2)	(3)	(4)	(5)	(6)
Boil + 5% HCl	Fair	Fair	Fast	Fast	Fast	Fast
Boil + 10% NaOH	Bleeds	Bleeds	Fair	Bleeds	Browns	Brownish-black
Boil + soap soln.	Bleeds	Bleeds	Fair	Bleeds	Browns	Fair
Bleaching	Bleached	Bleached	Fair	Fair	Browns	Fast
Light	Fugitive	Fugitive	Fair	Fugitive	Fair	Fair

TABLE III

FASTNESS OF DEVELOPED AZO DYEINGS FROM 2-*p*-AMINOPHENYL-5-METHYLBENZOXAZOLE (I)

Reagent	(1)	(2)	(3)	(4)	(5)	(6)
Boil + 5% HCl	Fair	Fair	Fast	Fast	Fast	Fast
Boil + 10% NaOH	Bleeds	Bleeds	Fair	Bleeds	Browns	Browns
Boil + soap soln.	Bleeds	Bleeds	Fair	Bleeds	Browns	Fair
Bleaching	Bleached	Bleached	Fair	Fair	Browns	Fast
Light	Fugitive	Fugitive	Fair	Fugitive	Fair	Fair

II. Azo Dyes from (B) or (B^1)

These were prepared and used in essentially the same manner as already recorded for the azo dyes from (A) or (A^1), *i. e.*, either as direct or as developed dyes ("ingrain colors"), and gave good deep shades on wool or silk by either process. As substantive cotton dyes, however, they were far inferior to those obtained from (A) or (A^1), the shades produced being weak and poor.

The results secured with these as developed dyes, are given in Table IV.

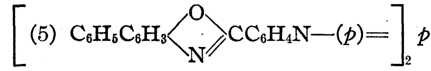
TABLE IV

DEVELOPED AZO DYEINGS FROM (B) OR (B^1)

	Base	Coupler	Shade on cotton	Type
(7)	(B)	α-Naphthol	Saffron	Mono-azo
(8)	(B^1)	Phenol	Yellow	Mono-azo
(9)	(B^1)	β-Naphthol	Orange-red	Mono-azo
(10)	(B^1)	Resorcinol	Orange	Mono-azo
(11)	(B^1)	α-Naphthylamine	Purple	Mono-azo
(12)	(11)	α-Naphthylamine	Black	Bis-azo

Subjected to the same fastness tests as shown in Tables II and III, the results given in Table V were obtained, in which table the Arabic numerals stand for the same dyes as in Table IV.

III. Chloramine Yellow Dyes



$$\left[(5)\ C_6H_5C_6H_3\genfrac{<}{>}{0pt}{}{O}{N}CC_6H_4N\text{—}(p)=\right]_2$$

***p,p'*-(5-Phenyl-benzoxazole-2)-azobenzene.**—A solution of 2 g. of 2-*p*-aminophenyl-5-benzoxazole in 500 cc. of alcohol was treated, at 0–10°, for twenty-four hours with a freshly prepared solution of sodium hypochlorite, the precipitated azo compound collected, washed thoroughly with water, dried and extracted with small portions of hot glacial acetic acid and of toluene, to remove impurities. The insoluble material crystallized from nitrobenzene gave an amorphous brownish-red powder, which did not melt but decomposed above 300°; yield, 1.2 g., or 65.5%.

Anal. Calcd. for $C_{38}H_{24}O_2N_4$: C, 80.21; H, 4.23. Found: C, 79.26; H, 4.22. This low figure for carbon was due to difficulties in eliminating final traces of impurities and in completely burning the compound, because of its azo character and high molecular weight.

The compound was difficultly soluble or insoluble in most of the usual neutral organic solvents. In concentrated sulfuric acid it dissolved to a deep blood-red solution, which color reaction appeared to be a very sensitive one.

A Chloramine Yellow from *p,p'*-(5-Phenyl-benzoxazole-2)-azobenzene.—To a solution of 2 g. of the above azo compound in 4 cc. of concentrated sulfuric acid at 20°, there was added 10 cc. of fuming (50% free sulfur trioxide) sulfuric acid. After standing for twenty-four hours, the mixture was poured upon ice, the orange-red precipitate collected, washed with a cold 15% salt solution, dissolved in dilute sodium hydroxide and the sodium salt precipitated by the addition of alcohol. The dry product was nearly black, but was a deep orange when pulverized. In water, it dissolved freely to an orange-red solution. Its analysis showed it to be a disulfonate.

Anal. Calcd. for $C_{38}H_{22}O_8N_4S_2Na_2$: N, 6.62; S, 8.16. Found: N, 7.25; S, 8.94.

The impossibility of obtaining accurate analytical figures for such dyes is recognized by all dye chemists. The purpose of the analysis was to determine whether our product was a di- or a tetra-sulfo acid, and this it does.

A minute amount was sufficient to impart to concentrated sulfuric acid a deep blood-red color. It dyed cotton, wool or silk, a direct yellow, corresponding closely to com-

TABLE V

FASTNESS OF DEVELOPED AZO DYEINGS FROM (B) OR (B^1)

Reagent	(7)	(8)	(9)	(10)	(11)	(12)
Boil + 5% HCl	Fair	Fair	Fast	Fast	Fast	Fast
Boil + 10% NaOH	Bleeds	Bleeds	Fair	Bleeds	Browns	Browns
Boil + soap soln.	Bleeds	Bleeds	Fair	Bleeds	Browns	Fair
Bleaching	Bleached	Bleached	Fair	Fair	Browns	Fast
Light	Fugitive	Fugitive	Fair	Fugitive	Fair	Fair

mercial Chloramine Yellow in fastness, although somewhat lighter in shade.

The direct dyeing on cotton was carried out as already described for the direct azo dyes.

A Chloramine Yellow from 2-*p*-Aminophenyl-5-phenylbenzoxazole Disulfonic Acid.—A solution of 5 g. of the disulfonic acid in 500 cc. of an aqueous solution of excess of sodium carbonate was boiled for thirty minutes, cooled and filtered. The filtrate was subjected to the action of a freshly prepared sodium hypochlorite solution, at 0–10°, for twelve hours, maintaining a slight excess of hypochlorite (as indicated by potassium iodide paper), or until the solution became yellowish-orange, after passing through an intermediate red stage. The dye was then salted out, washed with a 15% salt solution, dissolved in dilute sodium hydroxide and the sodium salt precipitated by the addition of alcohol. The final product resembled closely the dye described in the immediately preceding paragraph, except that the shade produced on cotton was a very pale greenish-yellow. Chemically it differed from the latter in being a tetra- instead of a di-sulfonic acid.

A Chloramine Yellow from 2-*p*-aminophenyl-5-methylbenzoxazole was also prepared by the customary procedure of sulfonation and hypochlorite oxidation and was found to resemble closely the above dye, in its direct dyeings on cotton, both as to shade and fastness.

A Chloramine Yellow from 2,7-diphenyl-5-aminobenzoxazole sulfonic acid, prepared similarly, dyed both wool and silk good deep shades. Its direct dyeings on cotton, however, were much paler and weaker than those obtained with the Chloramine Yellows from the 2-*p*-aminophenyl-5-phenyl- or 5-methylbenzoxazole sulfo acids.

Summary

1. From 2-*p*-aminophenyl-5-phenylbenzoxazole, 2,7-diphenyl-5-aminobenzoxazole, and their sulfo acids, azo dyes have been prepared, of mono- or bis-azo type, as well as some of Chloramine Yellow structure.

2. The tinctorial properties of these new dyes have been studied and it has been shown that those in which the azo grouping is in the *p*-position on the 2-phenyl nucleus are far better substantive cotton dyes than those having this grouping in position 5 on the benzoxazole portion of the molecule.

3. Azo dyes of Ingrain Red type, in the thiazole and oxazole series, were examined spectroanalytically. The curves plotted from these observations paralleled each other closely.

4. In general, these benzoxazole dyes resemble the analogously constituted benzothiazoles but, as expected, give lighter shades.

NEW YORK, N. Y. RECEIVED AUGUST 21, 1935

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Structure of the Metallic Derivatives Which Are Formed by Adding Grignard Reagents to Unsaturated Ketones

BY E. P. KOHLER, M. TISHLER AND H. POTTER

It is known that when a Grignard reagent is added to an α,β-unsaturated ketone which has a hydrocarbon residue in the α position, the product is an enolate in which a magnesium halide group is joined to oxygen. In all other addition products obtained in this manner the location of the halide residue is uncertain. Magnesium compounds of the type of these addition products can now be obtained in other ways. Thus the magnesium bromide derivative of β,β-diphenylpropionylmesitylene may be prepared by any of the three reactions which are represented by the equations

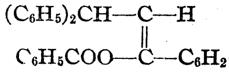
(1) $C_6H_5CH{=}CHCOC_6H_2(CH_3)_3 + C_6H_5MgBr \longrightarrow [(C_6H_5)_2CHCHCOC_6H_2(CH_3)_3]MgBr$

(2) $(C_6H_5)_2CHCH_2COC_6H_2(CH_3)_3 + C_2H_5MgBr \longrightarrow [(C_6H_5)_2CHCHCOC_6H_2(CH_3)_3]MgBr + C_2H_6$

3) $(C_6H_5)_2CHCHBrCOC_6H_2(CH_3)_3 + C_2H_5MgBr \longrightarrow [(C_6H_5)_2CHCHCOC_6H_2(CH_3)_3]MgBr + C_2H_5Br$

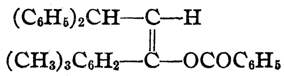
In appearance, in solubility and in many of their chemical properties the magnesium derivatives which are obtained in these various ways seem to be identical but their reactions with benzoyl chloride show that they are not. When the derivative that is formed in the first reaction is treated with benzoyl chloride at least 96% of the product is a benzoyl derivative which melts at 161°, while similar treatment of the magnesium derivative obtained by either of the other two methods leads to an equally high yield of an isomeric benzoyl derivative melting at 148°. These results are not affected by the solvents used or the temperature at which the successive operations are conducted. And in the case of the second and third reactions the nature of the Grignard reagent is likewise of no moment. These reactions—the one addition and the other substitution—therefore give rise to two isomeric magnesium compounds.

The two benzoyl derivatives that are formed from these magnesium derivatives must both be benzoates because both are much more easily hydrolyzed than the isomeric diketone which can be synthesized by a different method. These benzoates are evidently the geometrical isomers represented by formulas I and II and the magnesium halides from which they are formed must be the corresponding enolates. In the case of benzal acetomesitylene, therefore, addition of a Grignard reagent to the conjugated system C═C—C═O gives rise to an –OMgX compound even though there is no hydrocarbon residue in the α position.



$$\begin{array}{c}(C_6H_5)_2CH—C—H \\ \| \\ C_6H_5COO—C—C_6H_2(CH_3)_3\end{array}$$

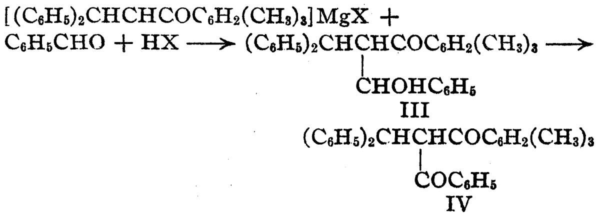
I



$$\begin{array}{c}(C_6H_5)_2CH—C—H \\ \| \\ (CH_3)_3C_6H_2—C—OCOC_6H_5\end{array}$$

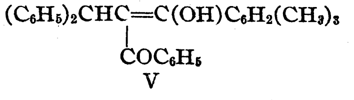
II

The isolation of these stereomeric magnesium derivatives supports the views of Michael and Ross[1] who obtained stereomeric O-carbmethoxy keto esters by treating the sodium compounds of benzoyl acetone with chlorocarbonic ester and concluded that solutions of the sodium derivatives contain the corresponding stereomeric enolates. The magnesium enolates, even though they give almost exclusively O-benzoyl derivatives, can nevertheless be added to benzaldehyde in the same manner as simple Grignard reagents. Ability to combine with aldehydes, therefore, is no criterion for the structure of a magnesium halide derivative. This reaction with aldehydes provides an excellent method for securing the β-diketone corresponding to the benzoates



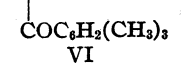
$$[(C_6H_5)_2CHCHCOC_6H_2(CH_3)_3]MgX + C_6H_5CHO + HX \longrightarrow \underset{\underset{\text{III}}{CHOHC_6H_5}}{(C_6H_5)_2CHCHCOC_6H_2(CH_3)_3} \longrightarrow \underset{\underset{\text{IV}}{COC_6H_5}}{(C_6H_5)_2CHCHCOC_6H_2(CH_3)_3}$$

This diketone, like most other alkylated di-aryl β-diketones does not enolize to a detectable extent in solution but as it is not easily cleaved it can be converted without difficulty into one of two possible enolic modifications



$$\underset{COC_6H_5}{(C_6H_5)_2CHC}{=}C(OH)C_6H_2(CH_3)_3$$

V

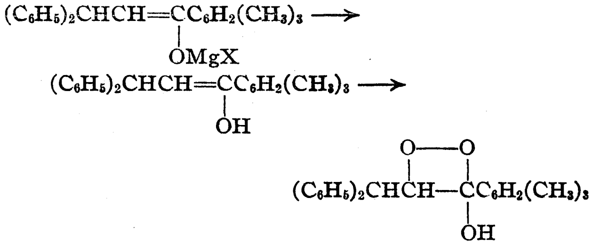


$$\underset{COC_6H_2(CH_3)_3}{(C_6H_5)_2CHC}{=}C(OH)C_6H_5$$

VI

The enol has remarkable vitality; in solid form it appears to be completely permanent and it can be crystallized from all common solvents without recognizable change. Even in glacial acetic acid it retains for weeks its power of giving a color reaction with ferric chloride. It however reverts rapidly to the diketone in solutions containing traces of alkalies or piperidine. The unusual lack of mobility in this enol, doubtless, is due largely to the mesityl group, because one of the phenyls of the benzhydryl groups can be replaced with methyl without materially affecting the mobility but when the mesityl group is replaced with phenyl the mobility becomes normal, the enol of benzhydryl dibenzoylmethane ketonizing as rapidly as the corresponding methyl and ethyl compounds.

If the relative stability of the enolic form of the diketone is really due to the influence of the mesityl group, then this group should exercise a similar influence upon the enol of the mono ketone. It does. Its effect is sufficiently great to permit the formation of the type of peroxides which, heretofore, could be obtained only from the enols of mono ketones that have hydrocarbon residues in the α-position.



$$(C_6H_5)_2CHCH{=}\underset{OMgX}{C}C_6H_2(CH_3)_3 \longrightarrow (C_6H_5)_2CHCH{=}\underset{OH}{C}C_6H_2(CH_3)_3 \longrightarrow (C_6H_5)_2CH\overset{O—O}{CH—\underset{OH}{C}}C_6H_2(CH_3)_3$$

VII

As will be evident from the foregoing account, a considerable variety of mono ketones can be acylated by means of their magnesium halide derivatives. For various reasons it is possible to follow these acylations much more accurately than those with sodium or potassium compounds. A series of selected ketones, turned into magnesium bromide derivatives and benzoylated under similar conditions, gave the following percentages of diketones, the remainder of the product being composed mainly of benzoates representing O-acylation.

$(C_6H_5)_2CHCH_2COC_6H_5$	100
$(C_6H_5)_2CHCH(C_6H_5)COC_6H_5$	0
$CH_3COC_6H_2(CH_3)_3$	100
$C_6H_5CH_2CH_2COC_6H_2(CH_3)_3$	12
$C_6H_5CH(CH_3)CH_2COC_6H_2(CH_3)_3$	8
$(C_6H_5)_2CHCH_2COC_6H_2(CH_3)_3$	1.5

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[1] Michael and Ross, THIS JOURNAL, 53, 2394 (1931).

To judge from this limited number of cases there is a certain degree of correlation between the complexity of the hydrocarbon residues surrounding the carbonyl group, the stability of the enol and the mode of acylation. The results therefore lend some support to the view that C-acylation is preceded by ketonization of the metallic derivative or its ion.

Experimental Part

The general methods employed for preparing the isomeric magnesium derivatives have been described in earlier papers.[2] In order to ensure comparable conditions, all reactions were conducted in an atmosphere of nitrogen and the resulting solutions or suspensions were boiled until most of the magnesium compound had separated in solid form. After the addition of the acid chloride the mixture was boiled again until the benzoylation was manifestly complete. The magnesium derivatives were then treated with iced acid in the usual manner.

In the quantitative experiments the entire product was dissolved in cold dilute methyl alcoholic sodium hydroxide, separate experiments with the pure substances having shown that in these conditions the diketones are not affected while the benzoates are hydrolyzed with great rapidity. The separation of the resulting mixtures presented no great difficulty. After acidification all the organic components were collected in ether, and from this ethereal solution the benzoic acid was removed with bicarbonate and the diketone or its enol by successive extractions with methyl alcoholic sodium hydroxide or sodium methylate—leaving only the mono ketone and other indifferent materials to be separated by physical methods.

The Isomeric Benzoates of Benzhydryl Benzoyl Acetomesitylene.—The higher melting benzoate crystallizes from acetone in large transparent prisms melting at 162°, the lower melting isomer, which is much more soluble, in needles melting at 142°.

Anal. Calcd. for $C_{31}H_{28}O_2$: C, 86.3; H, 6.5. Found (162°): C, 86.2; H, 6.5. (142°): C, 86.0; H, 6.7.

Alcoholic solutions of sodium hydroxide rapidly hydrolyzed both benzoates to diphenylpropionyl mesitylene and sodium benzoate. Toward acid they are much more stable but they can be hydrolyzed by prolonged heating in sealed tubes with methyl alcoholic hydrochloric acid, the lower melting being destroyed much more rapidly than its isomer. They are not interconvertible by protracted heating above the melting point or by exposure to sunlight. It has not been possible thus far to devise any method for determining the configuration of these benzoates.

The Magnesium Halide Derivatives.—The stereometric magnesium compounds are of special interest because they show that both addition to the conjugated system and the enolization of the mono ketone are controlled by mechanisms that lead to products which have definite configurations. Benzoylation of the derivative which is obtained by addition (equation 1) usually gave along with the lower melting benzoate and from one to two per cent. of diketone, a very small quantity of the higher melting benzoate. Neither the amount of diketone nor that of the isomeric benzoate were increased by prolonged boiling in ether–benzene before benzoylation. By treatment with bromine both magnesium derivatives were converted into α-bromo-β,β-diphenylpropionyl mesitylene.

Acetylation with Trimethylbenzoyl Chloride, $(C_6H_5)_2CH—CH{=}C(C_6H_5)OCOC_6H_2(CH_3)_3$.—When the magnesium compound of diphenylpropiophenone obtained by the third reaction was acylated in the usual manner with trimethylbenzoyl chloride it gave a mixture which was separated by crystallization from methyl alcohol and petroleum ether. One of the products was the same β-diketone (IV) which had been obtained by benzoylating the mesitylenic ketone. The second product was an isomer which was readily hydrolyzed by bases to diphenylpropiophenone and mesitylene carbonic acid—therefore a trimethyl benzoate due to O-acylation. It crystallizes in flattened needles and melts at 93°. As nearly as can be estimated from the results of a separation that was not very accurate 40% of the product was diketone and at least 95% of the remainder was the trimethylbenzoate.

α-Benzhydryl-β-phenyl-β-hydroxy Propionyl Mesitylene, III.—To a magnesium compound obtained by boiling 20 g. of α-bromo-β,β-diphenyl propionyl mesitylene with a solution of ethylmagnesium bromide containing 1.5 g. of magnesium was added 5.5 g. of benzaldehyde. The mixture was boiled for two hours, then decomposed in the usual manner. After the removal of excess of benzaldehyde there remained a yellow solution which yielded 18 g. of condensation product—the balance being a yellow oil and a small quantity of diphenyl propionyl mesitylene. The hydroxyl compound crystallizes well from ether–petroleum ether in colorless plates and it melts at 132°.

Anal. Calcd. for $C_{32}H_{30}O_2$: C, 85.7; H, 6.9. Found: C, 85.7; H, 7.1.

Benzhydryl Benzoylacetomesitylene, IV.—The oxidation of the hydroxyl compound to the diketone presents considerable difficulty. The best results were obtained by the following procedure. To a solution of 5 g. of the hydroxyl compound in 40 cc. of glacial acetic acid was added 1 cc. of a solution of 2.5 g. of chromic acid in 2.5 g. of water and 7.5 g. of glacial acetic acid. The mixture was warmed until oxidation was rapid, then the remainder of the oxidizer was added and the mixture was kept at the oxidizing temperature for five minutes before it was poured on ice. The result was a mixture of diketone and some complex yellow polymer from which the diketone was most easily isolated by repeated extraction with cold petroleum ether.

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[2] Kohler and Tishler, THIS JOURNAL, **54**, 1594 (1931); Kohler and Baltzly, *ibid.*, **54**, 4015 (1931).

Anal. Calcd. for $C_{31}H_{28}O_2$: C, 86.3; H, 6.5. Found: C, 86.3; H, 6.5.

The diketone crystallizes well from petroleum ether in small colorless prisms or tables and it melts at 107°. It was subsequently obtained in small quantities in the benzoylation of the magnesium derivatives of diphenyl propionyl mesitylene and in much larger quantities by treating the magnesium derivative of diphenyl propiophenone with trimethylbenzoyl chloride. The diketone is unusually insensitive to alkalies; practically all of it was recovered after it had been boiled for six hours with 40% methyl alcoholic potassium hydroxide but by boiling it for ten hours with 50% aqueous sodium hydroxide most of it was hydrolyzed to diphenyl propiophenone and sodium trimethyl benzoate.

Enolization, V or VI.—The diketone dissolves freely in methyl alcoholic sodium hydroxide but unlike the corresponding dibenzoylmethane derivative it is not reprecipitated by diluting the solution with water. When the cold aqueous alcoholic solution is acidified with a mineral acid it precipitates an isomeric compound which crystallizes in minute colorless prisms and which melts at 137°.

Anal. Calcd. for $C_{31}H_{28}O_2$: C, 86.3; H, 6.5. Found: C, 86.3; H, 6.6.

This isomer is evidently one of the enolic forms of the diketone; it reacts instantaneously with bromine, gives with ferric chloride the blue-purple color reaction which is characteristic of mono-alkylated β-diketones, and forms a green copper compound when its ethereal solution is shaken with aqueous copper acetate. In small quantities the enol is most easily recrystallized from ether–petroleum ether, in larger quantities from methyl alcohol. It can also be recrystallized from glacial acetic acid–water but in the presence of piperidine or other organic bases it reverts quantitatively to the diketone. As it could neither be reduced catalytically nor ozonized in such a manner as to secure significant products it could not be definitely related to either of the possible formulas.

α-Benzoyl-β-phenylbutyro Mesitylene, $CH_3CH(C_6H_5)CH(COC_6H_5)COC_6H_2(CH_3)_3$.—An ethereal solution of benzalacetomesitylene was added to excess of methylmagnesium iodide and the resulting magnesium compound was benzoylated in the usual manner. The product was an oil which could not be induced to crystallize. It was therefore treated with cold methyl alcoholic methyl hydroxide and thus converted into benzoic acid and one of the enolic modifications of the diketone. The yield of enol was only 8%, all the rest of the product being benzoate.

Anal. Calcd. for $C_{26}H_{26}O_2$: C, 84.4; H, 7.0. Found: C, 84.5; H, 6.9.

The enol is readily soluble in all common organic solvents including petroleum ether from which it crystallizes in small prisms melting at 128°. Its chemical properties are the same as those of the corresponding benzhydryl compound.

The Diketone.—When the foregoing enol is recrystallized from methyl alcohol containing piperidine it is converted into the diketone which crystallizes in thin needles and melts at 130°. Solutions of the diketone do not contain enough enol, if any, to give a color reaction with ferric chloride.

Anal. Calcd. for $C_{26}H_{26}O_2$: C, 84.4; H, 7.0. Found: C, 84.5; H, 7.2.

Benzyl Acetomesitylene, $C_6H_5CH_2CH_2COC_6H_2(CH_3)_3$.—The saturated ketone was prepared by shaking benzal acetomesitylene with hydrogen and Adams catalyst until the calculated quantity of hydrogen was absorbed. It was obtained as a very pale yellow, viscous oil which boiled at 191–2° under a pressure of about 5 mm.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 85.6; H, 7.9. Found: C, 85.5; H, 7.8.

Benzyl Benzoylaceto Mesitylene $C_6H_5CH_2CH(COC_6H_5)COC_6H_2(CH_3)_3$.—Benzyl aceto mesitylene was converted into the magnesium bromide derivative with ethylmagnesium bromide and the solid magnesium compound was boiled with excess of benzoyl chloride. The product—a colorless viscous oil—was hydrolyzed in the usual manner with methyl alcoholic sodium hydroxide. It was thus converted into sodium benzoate and a solid which crystallized from petroleum ether in flat colorless needles and which melted at 118°.

Anal. Calcd. for $C_{25}H_{24}O_2$: C, 8.43; H, 6.8. Found: C, 84.2; H, 7.2.

The product has the composition of an enol and it both gave the characteristic color reaction of these enols with ferric chloride and formed a copper derivative but it could not be converted into an isomeric diketone by the usual treatment with piperidine. A titration with bromine by the method of Kurt Meyer showed that fresh solutions in methyl alcohol contain relatively small quantities of enol (4–6%), that the proportion of enol increases gradually with time and that 4% solutions in methyl alcohol which have been equilibrated with piperidine contain nearly equal quantities of enol (49.3%) and diketone.

As the mobility of this keto–enol system was quite unexpected we prepared the benzyl compound by benzylating the sodium derivative of benzoyl acetomesitylene with benzyl chloride. The product was identical in every respect with the substance obtained by acylation. Finally we decided to prepare the benzyl derivative by a third method which was devised to give as pure a product as it is possible to make. To this end we first prepared benzal benzoylaceto mesitylene by condensing benzaldehyde with benzoylacetomesitylene by the general method of Knoevenagel.[3]

Benzal Benzoylaceto Mesitylene, $C_6H_5CH{=}C(COC_6H_5)COC_6H_2(CH_3)_3$.—The unsaturated diketone crystallized well from methyl alcohol in large yellow crystals. The yield was poor.

Anal. Calcd. for $C_{25}H_{22}O_2$: C, 84.6; H, 6.2. Found: C, 84.6; H, 6.3.

The unsaturated ketone was easily reduced, catalytically, and the benzyl compound which was prepared in this manner was likewise identical with the substance that was obtained by acylation.

Benzoylation of Mesityl Phenyl Propiophenone, $(CH_3)_3C_6H_2CH(C_6H_5)CH = C(C_6H_5)OCOC_6H_5$. — Trimethylbenzal acetophenone was added to phenylmagnesium bromide and the resulting magnesium compound was benzoylated in the usual manner. The product was separated into a solid and an oil which has not been identified. The

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(3) Knoevenagel, *Ber.*, **36**, 2131 (1903).

solid crystallized from methyl alcohol in small prisms and melted at 110°.

Anal. Calcd. for $C_{31}H_{28}O_2$: C, 86.3; H, 6.5. Found: C, 86.3; H, 6.6.

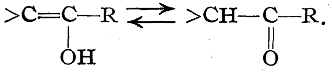
This solid is evidently a benzoate because cold methyl alcoholic sodium hydroxide hydrolyzes it rapidly to mesityl phenyl propiophenone. The yield was about 50%.

α-Mesityl-γ,γ-diphenyl Propenol Peroxide, VII.—To a solution of phenylmagnesium bromide containing 1.9 g. of magnesium was added 10 g. of benzalaceto mesitylene. The mixture was boiled for fifteen minutes, then decomposed with iced hydrochloric acid. The ethereal layer was diluted with about five times its volume of petroleum ether and washed thrice with ice water. A rapid stream of oxygen was then passed through the moist solution. It gradually caused the precipitation of a solid which separated in microscopic needles. The solid was purified by solution in ether and reprecipitation with petroleum ether. The yield was 9 g.

Anal. Calcd. for $C_{24}H_{24}O_3$: C, 80.1; H, 6.7. Found: C, 80.6; H, 6.5.

In a capillary tube the peroxide melts quietly with decomposition at 116–117°. Heated in larger quantity on a spatula it decomposes with a flash, one of the decomposition products being mesitylene carbonic acid. Like other peroxides of this type it liberates iodine from alcoholic solutions of iodides.

Summary

A study of the magnesium halide derivatives of a series of related mesitylenic ketones showed that the mesityl group in some manner decreases the speed of the processes represented by  $\mathrm{>C{=}\underset{\substack{|\\ OH}}{C}{-}R \rightleftarrows >CH{-}\underset{\substack{\|\\ O}}{C}{-}R}$. It also showed that there is a certain degree of correlation between the complexity of the hydrocarbon residues surrounding a carbonyl group, the stability of the enolic form and the mode of acylation.

CAMBRIDGE, MASS.

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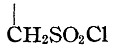
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

Some Derivatives of Beta-Sulfopropionic Acid[1]

BY LUCIUS A. BIGELOW, HUGH W. SIGMON AND DAVID H. WILCOX, JR.

The original point of interest which led to the choice of β-sulfopropionic acid as a subject for study, was the fact that it is the aliphatic analog of *o*-sulfobenzoic acid, the imide of which is the well-known sugar substitute, saccharin. While the latter acid has been the subject of intensive and detailed research, our knowledge concerning the former is very meager and incomplete. The purpose of this paper is to present the results of a study of a number of the simpler derivatives of this interesting aliphatic sulfonic acid.

β-Sulfopropionic acid was originally described by Rosenthal[2] in 1886. He also prepared a large number of the salts, the ethyl ester, and an impure acid chloride, to which he assigned the formula  $\begin{array}{l}\mathrm{CHCl{-}COCl}\\ |\\ \mathrm{CH_2SO_2Cl}\end{array}$ on the basis of rather unsatisfactory evidence. His work includes practically all that is known about the compound or its derivatives, although certain of them have been mentioned indirectly by Kohler[3] and others.

In the present work, barium β-sulfopropionate was prepared from β-iodopropionic acid, and subsequently converted into the silver salt, which, in turn, was treated with the appropriate alkyl halides to form the corresponding neutral methyl-, ethyl-, *n*-propyl- and *n*-butyl esters. These were colorless liquids at room temperature, crystallized from ether at low temperatures and melted at 17, 4, −7 and −25° (all ± 1°), respectively. The methyl ester boiled with slight decomposition at 132–3° at 1 mm., and the others could not be distilled.

In the hope of obtaining a solid ester, the silver salt was treated with benzyl bromide, benzyl iodide and phenacyl bromide, but without results. Phenylethyl iodide, however, reacted normally, yielding the neutral phenylethyl ester in white needles, melting at 59°. This ester, on saponification with barium hydroxide, yielded the barium salt of the acid, in 73% yield, apparently identical, under the microscope, with the corresponding salt obtained from β-iodopropionic acid.

When the dry potassium salt of the acid, in benzene suspension, was treated with phosphorus pentachloride, it yielded, ultimately, a light colored oil, thermally unstable even at 0°, which, when crystallized from ether at low temperatures

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(1) This paper has been abstracted from the Doctorate Thesis of Hugh W. Sigmon, and the Master's Thesis of David H. Wilcox, Jr., presented to the Graduate School of Arts and Sciences of Duke University in 1935 and 1932, respectively.

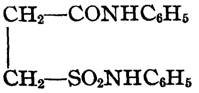
(2) Rosenthal, *Ann.*, **233**, 15 (1886).

(3) Kohler, *Am. Chem. J.*, **19**, 732 (1897).

deposited as a white solid, melting at −9° (±1°). It was undoubtedly the acid chloride, since on hydrolysis with barium hydroxide solution it regenerated the original barium salt in 77% yield, and on treatment with phenylethyl alcohol it formed the phenylethyl ester, melting at 58° although in small yield.

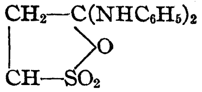
This chloride, when treated in benzene solution with aniline, gave rise to the corresponding dianilide, melting at 161°. This compound presumably had the structure I rather than II

I



$$\begin{array}{l} CH_2\text{—}CONHC_6H_5 \\ | \\ CH_2\text{—}SO_2NHC_6H_5 \end{array}$$

II

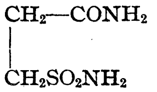


$$\begin{array}{l} CH_2\text{—}C(NHC_6H_5)_2 \\ |\qquad\quad \rangle O \\ CH\text{—}SO_2 \end{array}$$

because it was similar in properties to the well-known symmetrical dianilide of *o*-sulfobenzoic acid, and not to the corresponding unsymmetrical isomer. On hydrolysis with sulfuric acid, it formed the free sulfonic acid, recovered in 69% yield as the barium salt. The fact that the anilide contained no chlorine indicated that the acid chloride from which it was derived was not substituted in the carbon chain, contrary to Rosenthal.[2]

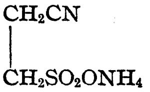
When anhydrous ammonia gas was passed through a solution of the chloride in benzene, a white solid was precipitated quantitatively. After removing the inorganic salts, the product was crystallized from alcohol in white prisms melting at 164–168° with some decomposition.

On theoretical considerations this product could have three reasonably possible configurations, representing it as β-sulfopropiondiamide III, ammonium β-cyanoethyl sulfonate IV or ammonium β-sulfopropionimide V.



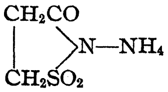
$$\begin{array}{l} CH_2\text{—}CONH_2 \\ | \\ CH_2SO_2NH_2 \end{array}$$

III



$$\begin{array}{l} CH_2CN \\ | \\ CH_2SO_2ONH_4 \end{array}$$

IV



$$\begin{array}{l} CH_2CO \\ |\qquad \rangle N\text{—}NH_4 \\ CH_2SO_2 \end{array}$$

V

Formula III was eliminated readily since the compound had definite salt-like properties, being insoluble in organic solvents, highly soluble in water and having a fairly high melting point. In addition, on analysis by the Van Slyke method for amide and amino nitrogen, it evolved less than one-fourth of its total nitrogen content. The structure IV, derived from the possible unsymmetrical acid chloride, seemed improbable, especially since the compound could be converted readily into a corresponding barium salt in almost quantitative yield, while Remsen and Karslake[4] have found that ammonium *o*-cyanobenzene sulfonate tended to undergo hydrolysis under these conditions. Consequently, the product has been assigned provisionally the structure V, making its formation strictly analogous to that of the ammonium salt of saccharin under comparable conditions.

The salt V, dissolved in water, yielded no precipitate with acids, and was not sweet. When the corresponding barium salt, mentioned above, was treated in aqueous solution with one equivalent of sulfuric acid, the free imide was not produced. Instead, hydrolysis occurred, with the formation in part of the diammonium salt of β-sulfopropionic acid.

An effort was made, also, to obtain the free imide by the pyrolysis of pure ammonium β-sulfopropionate. When this salt was heated for forty to ninety hours at 111° and 3–4 mm. it lost 0.8–1.0 mole of ammonia per mole of sample, yielding a solid product having the composition of the corresponding acid ammonium salt, which on treatment with barium hydroxide regenerated the ordinary barium salt. However, when the temperature of the pyrolysis was increased to 184°, a slow but complete disruption of the molecule took place, and the desired imide was not formed.

Experimental Part

Barium β-Sulfopropionate.—This salt was prepared according to the method of Rosenthal,[2] using a 20% excess of fresh ammonium sulfite and separated from water as colorless plates, in 60–70% yield after dehydration at 150–170°.

Silver Salt.—A sample of 15.5 g. of the anhydrous barium salt was dissolved in 500 cc. of water and one equivalent of sulfuric acid added. After filtration, 13.7 g. of silver oxide (10% excess) was added, and the mixture again filtered. On cooling and subsequent concentration the silver salt separated in gray crystals, weighing 15.7 g., which is 78%. A sample dried over calcium chloride did not lose weight when further dried over phosphorus pentoxide for forty hours at 2 mm., and was therefore anhydrous, contrary to Rosenthal.[2]

Anal. Calcd. for $C_3H_4O_5SAg_2$: Ag, 58.7. Found: Ag, 58.7, 58.6.

Methyl Ester.—Exactly 15.0 g. of the silver salt was heated with 15 cc. of methyl iodide in a sealed tube for six and one-half hours at 100°. The product was diluted with ether, filtered, extracted with 1% sodium sulfite solution, dried over anhydrous sodium sulfate and the solvent removed under reduced pressure at room temperature, leaving 5.77 g. of a yellow oil, which is 77%. The crude ester was crystallized twice from 15-cc. portions of

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(4) Remsen and Karslake, *Am. Chem. J.*, **18**, 819 (1896).

dry ether at about −65° (solid carbon dioxide–ether bath). The mother liquor in each case was withdrawn by means of a small suction tube with a cloth filter. The product separated in white crystals, which were freed from ether by allowing them to melt, and aspirating the colorless liquid with dry air for one hour at 50° and 1 mm. The pure ester boiled at 132–133° at 1 mm., with slight decomposition, and melted at 17°.

Other Esters.—The ethyl ester was synthesized by refluxing the silver salt with ethyl iodide. It was analyzed by Rosenthal[2] but he did not report the melting point. The *n*-propyl ester formed readily on refluxing the silver salt with *n*-propyl iodide, but in the case of the *n*-butyl ester the salt was heated with the corresponding halide for seven hours at 100°. The phenylethyl ester was made by heating the salt with phenylethyl iodide for ten hours at 100°. The halide in this case was prepared by refluxing 20 g. of phenylethyl bromide with an equal weight of sodium iodide in 100 cc. of acetone for four hours. After filtration and rectification the iodide was obtained in 71% yield, b. p. 117–121°. The phenylethyl ester, being solid at room temperature, was crystallized from ethanol.

When 0.20 g. of the phenylethyl ester was refluxed with a mixture of 2 cc. of sulfuric acid and 25 cc. of water for three and one-half hours it was hydrolyzed readily, and the free acid recovered as the barium salt, in 73% yield, identical with that obtained from β-iodopropionic acid.

TABLE I

ANALYTICAL AND OTHER DATA FOR THE ESTERS OF β-SULFOPROPIONIC ACID

Ester	Crude yield, %	M.p., °C.	Calculated		Found			
			S, %	Mol. wt.	S, %		Mol. wt. (K, 5.12)	
Methyl	78	17	17.6	182	17.6	17.7	188	194
Ethyl	78	4	..	...	..	..	...	...
n-Propyl	86	− 7	13.4	238	13.4	13.4	236	235
n-Butyl	96	−25	12.0	266	11.9	12.1	266	262
Phenylethyl	64	59	8.9	362	9.0	9.0	366	366

The Acid Chloride.—Pure potassium β-sulfopropionate was prepared, in quantitative yield, by treating the barium salt in aqueous solution, with an equivalent of potassium sulfate. It was dried for several hours at 150–170°. Then 47 g. of the potassium salt was suspended in 250 cc. of dry benzene, in a 1-liter 3-necked flask equipped with a mechanical stirrer, and 85 g. of phosphorus pentachloride (2 moles) added all at once. Reaction set in immediately, and the mixture was stirred and refluxed for two hours after which it was filtered by suction through asbestos. The light straw colored solution was then extracted at room temperature with 2-liters of water in 200-cc. portions, which freed it completely from phosphorus compounds (molybdate test). After drying the mixture with anhydrous sodium sulfate, the solvent was removed, first by aspirating with dry carbon dioxide at 15 mm., finally for one-half hour at 1–2 mm., at room temperature. There remained a light pink oil, together with a small quantity of white solid, weighing in all 15.5 g., which is 39%. The solid was removed by filtration through a cotton plug, using a suction tube, and the liquid product kept frozen at −65°, or in solution, as it decomposed thermally on standing at room temperature evolving hydrogen chloride. The chloride was then dissolved in 50 cc. of dry ether, in an atmosphere of dry carbon dioxide, cooled to −65°, and seeded, when a small crop of crystals separated, which were removed and discarded, this process being repeated five times. Then the solvent was evaporated under reduced pressure at 0°, and the remaining oil crystallized twice from 20-cc. portions of dry ether, in a carbon dioxide atmosphere at −65°. Finally the white solid was allowed to melt, and the solvent removed completely by keeping the mixture at 2 mm. and −5° for three and one-half hours. A U-tube filled with sulfuric acid, and placed in the train, did not increase in weight after the first two hours. The final product was a light colored oil, which on cooling froze to a white solid, melting at −9° (±1°).

In spite of this extremely careful purification, the chloride still retained a little of the free acid, presumably, as chlorine and sulfur analyses showed it to be only about 92% pure. However, when a sample was hydrolyzed by boiling for ten minutes with 7% $Ba(OH)_2 \cdot 8H_2O$ solution, the original barium salt was recovered readily in 77% yield. Also, when the chloride was treated with an excess of phenylethyl alcohol, which was later distilled off at 101–104° at 2 mm., the residue solidified on cooling. The solid was crystallized from ethanol and separated as white needles melting at 58°. When these were mixed with an authentic sample of the phenylethyl ester, the melting point was not depressed. The yield was 17% of the theoretical.

The Dianilide.—A sample of crude acid chloride, weighing 5.8 g., was dissolved in 100 cc. of dry benzene, and cooled in an ice-bath. Then a solution of 12 cc. of aniline in 25 cc. of benzene was added, drop by drop, with shaking, which caused the separation of a pasty solid. The liquid was decanted and evaporated, but contained no residue. The solid product was extracted with 1% hydrochloric acid solution, until the extract failed to give a test for aniline. Then it was dissolved in 25 cc. of boiling 50% ethanol, and separated on cooling as white crystals which contained no chlorine, weighing 2.1 g., which is 22% of the theoretical. After recrystallization twice from 10-cc. portions of 50% ethanol, it deposited as white leaflets, which melted sharply at 161°.

Anal. Calcd. for $C_{15}H_{16}O_3N_2S$: S, 10.5; N, 9.2; mol. wt., 304. Found: S, 10.4, 10.6; N, 9.2, 9.1; mol. wt., 316.

On refluxing the anilide with a mixture of 2 cc. of sulfuric acid and 25 cc. of water for five hours it was hydrolyzed, and the acid was recovered as the original barium salt in 69% yield.

Ammonium β-Sulfopropionimide.—A sample of the phosphorus-free acid chloride weighing 15.5 g. was dissolved in 200 cc. of dry benzene, cooled in an ice-bath and saturated with dry ammonia gas. A white solid separated, which dissolved completely when the mixture was subsequently extracted with 150 cc. of water. The benzene layer, on evaporation, left no appreciable residue. Then the aqueous solution was triturated, in portions, with solid silver carbonate, until it was entirely free from Cl^-. After the excess silver carbonate and the silver chloride had been removed, the filtrate was saturated with hydrogen sulfide and filtered again. The final filtrate was evaporated to dryness on a water-bath under reduced pressure, and left a yellow viscous oil, which solidified completely on cooling. The solid, which contained neither silver nor chlorine, was crystallized from 50 cc. of ethanol, and separated in white prisms, melting at about 162°, and weighing 6.64 g., which is 53%. After many crystallizations, the melting point varied irregularly from 164–168°, due to decomposition, as the compound evolved some ammonia even at 110°.

Anal. Calcd. for $C_3H_8O_3N_2S$: S, 21.0; N, 18.4. Found: S, 21.0, 21.0; N, 18.4, 18.3.

It should be mentioned that repeated crystallization of the original precipitate from dry *n*-propyl alcohol until the product was free from chlorine yielded the same compound, although in much less yield.

Barium Salt of the Imide.—A sample of the ammonium salt weighing 3.47 g. was dissolved in 100 cc. of water and treated with barium hydroxide solution, equivalent to half the nitrogen contained in the sample. No precipitate was formed, so the mixture was evaporated to dryness under reduced pressure. The white residue was crystallized from 20 cc. of dilute ethanol, and separated as white needles, in practically quantitative yield. After one more crystallization it was quite pure.

Anal. Calcd. for $C_6H_8O_6S_2N_2Ba$: Ba, 33.7; N, 6.9. Found: Ba, 33.8, 33.5; N, 6.9, 6.9.

When this barium salt in aqueous solution was treated with one equivalent of ammonium sulfate, ammonium β-sulfopropionimide was regenerated in 63% yield, melting at 167–168°. On admixture with the original ammonium salt, the melting point was not depressed.

Attempt to Prepare the Free Imide.—A solution of 4.5 g. of barium β-sulfopropionimide in 25 cc. of water was treated with the calculated quantity of dilute sulfuric acid. The filtrate was evaporated to dryness under reduced pressure, and left a solid residue, which on crystallization three times from methanol separated as white crystals which contracted at 170°, and melted at 175–176°. The compound contained neither barium nor chlorine, and seemed to be the diammonium salt of β-sulfopropionic acid.

Anal. Calcd. for $C_3H_{12}O_5N_2S$: N, 14.9. Found: N, 14.7.

Pyrolysis of Diammonium β-Sulfopropionate.—This compound was prepared by treating an aqueous solution of the barium salt with one equivalent of ammonium sulfate. After filtration, the solution was evaporated to a small volume, during which time it gave off ammonia. Finally the mixture was saturated with ammonia gas, and the crystals which deposited on standing in the cold, filtered off, washed with ethanol and dried to constant weight over sulfuric acid, at 2 mm. The yield was 68–70%, and, under these conditions, was anhydrous and not very hygroscopic.

Anal. Calcd. for $C_3H_{12}O_5N_2S$: S, 17.0; N, 14.9. Found: S, 16.9, 17.2; N, 15.0, 14.6.

For the pyrolysis, a weighed sample of the salt was placed in a boat contained in an oven tube so arranged that it could be entirely surrounded by the vapors of boiling toluene (111°). It was connected to a train consisting of a U-tube filled with solid potassium hydroxide, and two U-tubes containing glass beads and sulfuric acid. The pressure in the system was reduced to 3–4 mm., the sample heated to 111°, and its loss in weight observed, as well as the corresponding gain in the absorption tubes. Blank runs were made each time, and adequate corrections applied. The potassium hydroxide gained very little weight under these conditions. The results are expressed in the table below.

TABLE II

PYROLYSIS OF DIAMMONIUM β-SULFOPROPIONATE AT 111°

No.		1	2
Time, hours		40	90
Moles NH_3 per mole sample	Evolved	0.83	0.97
	Absorbed	.82	1.0
Analysis of product	S, %	18.7	...
	N, %	8.6	8.7

Calcd. for $C_3H_9O_5NS$: S, 18.7; N, 8.2.

The writers take pleasure in expressing their thanks to Mr. John G. Womack, for his contribution to this work.

Summary

A study has been made of a number of derivatives of β-sulfopropionic acid, including a series of esters, the chloride, the anilide and the ammonium salt of the imide, which is the aliphatic analog of the corresponding salt of saccharin. This last substance was not sweet.

The free imide underwent complete hydrolysis when formed in aqueous solutions, and it was not produced by the pyrolysis of diammonium β-sulfopropionate at 111° and 3–4 mm., which yielded the acid ammonium salt almost quantitatively.

Seven new compounds have been characterized.

DURHAM, NORTH CAROLINA RECEIVED AUGUST 22, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SMITH COLLEGE]

The Potential of the Ag(s), Ag_2CrO_4(s), $CrO_4^=$ Electrode[1]

BY JESSIE Y. CANN AND GRETCHEN B. MUELLER

The purpose of this investigation was to determine, by means of electromotive force measurements, the potential of the Ag(s), Ag_2CrO_4(s), $CrO_4^=$ electrode.

A search of the literature revealed that very little work had been done on this electrode.[2] No description of an electrolytic deposition of silver chromate could be found.

Method and Apparatus

In this investigation the cell Ag(s), Ag_2CrO_4(s), K_2CrO_4(aq), KCl(aq), AgCl(s), Ag(s) was measured. The apparatus used was suggested by the work of Randall and Cann.[3] The electrodes were placed in the outer arms of the electrode vessels so as to prevent the flow of liquid over the electrodes.[4]

The cell was placed in the usual oil thermostat, regulated at 25°, and measurements were made with a shielded Leeds and Northrup Type K potentiometer.

Materials

All solutions were made up by weight, moles per 1000 g. of water in vacuum, from high grade "analyzed" salts and conductivity water. Either pure hydrogen or nitrogen was bubbled through the solutions to remove traces of oxygen.

The Ag(s), AgCl(s) spiral electrodes were made according to the method of Randall and Young.[5]

The Ag(s), Ag_2CrO_4(s) spiral electrodes were also made electrolytically. Many trials showed that the best results were obtained with a 0.02 molal chromic acid solution using an e. m. f. of 1.5 volts for about two hours. A solution of chromic acid instead of potassium chromate was used to prevent contamination by the potassium ion. The electrodes were then washed in distilled water and short-circuited together for some hours. When not in use they were kept in a dilute solution of potassium chromate, for according to Margosches[6] the solubility of silver chromate is less in potassium chromate than in water. Immediately before being introduced into the cell the electrodes were placed in the particular potassium chromate solution to be used and evacuated for about thirty minutes, with gentle heating, to make sure of the complete removal of all oxygen.

Experimental Results

The molality of the potassium chloride was twice that of the potassium chromate in order to have the same concentrations of potassium ions in the two solutions. This is necessary for the Lewis and Sargent[7] formula for liquid junction potentials. Table I gives the average values of at least ten cell readings for each concentration used. The readings in general did not vary from the average by more than ±0.5 millivolt, except in the most dilute solutions, where the maximum variation was ±1.0 millivolt.

TABLE I

Molality of K_2CrO_4	Molality of KCl	E. m. f. at 25°C. v.	Liquid junction π, v.	E. m. f. $-\pi$, v.	E. m. f. Ag, AgCl, v.	E. m. f. Ag, Ag_2,CrO_4, v.
0.100	0.200	−0.2223	0.0036	−0.2259	0.2709	−0.4968
.050	.100	− .2152	.0026	− .2178	.2872	− .5050
.025	.050	− .2078	.0019	− .2097	.3035	− .5132
.010	.020	− .1876	.0010	− .1886	.3255	− .5141
.005	.010	− .1784	.0005	− .1789	.3425	− .5214
.00375	.0075	− .1726	.0003	− .1729	.3494	− .5223
.0025	.0050	− .1659	.0001	− .1660	.3596	− .5256

The liquid junction potential was calculated for each concentration by using the Lewis and Sargent[7] formula for common cations, *i. e.*

$$E = -\frac{RT}{F} \ln \Lambda_{\mathrm{KCl}}/\Lambda_{1/2\mathrm{K_2CrO_4}}$$

The values for the individual ion conductances were taken from the "International Critical Tables."[8]

In order to determine the potential of the silver–silver chromate electrode from the cell readings, it is necessary to know the potential of the silver–silver chloride electrode for each dilution used. Since both silver and silver chloride

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[1] The experimental part of this paper is a portion of a thesis submitted by G. B. Mueller in partial fulfilment of the requirements for the degree of Master of Arts at Smith College.

[2] Abegg and Cox, *Z. physik. Chem.*, **46**, 1 (1904); Bolam and MacKenzie, *Trans. Faraday Soc.*, **22**, 162 (1904); *C. A.*, **20**, 2772 (1926); *Trans. Faraday Soc.*, Advance Proof; Hass and Jellinek, *Z. physik. Chem.*, **162**, 153 (1932).

[3] Randall and Cann, THIS JOURNAL, **52**, 589 (1930).

[4] Carmody, *ibid.*, **54**, 210 (1932); Cann and LaRue, *ibid.*, **54**, 3456 (1932).

[5] Randall and Young, *ibid.*, **50**, 989 (1928).

[6] Margosches, *Z. anorg. Chem.*, **51**, 231 (1906).

[7] Lewis and Sargent, THIS JOURNAL, **31**, 363 (1909).

[8] "International Critical Tables," McGraw-Hill Book Co., Inc., New York City, 1930, Vol. VI, pp. 234, 253.

are solids, this value is calculated for each concentration by means of the equation

$$E = E^0 - (RT/F) \ln (m\gamma)_{Cl^-}$$

and since it is generally assumed that the activity coefficients of the potassium and chloride ions are equal, the activity coefficients of potassium chloride may be used for those of the chloride ion. These values were taken from Lewis and Randall.[9]

The value of E^0 for the silver–silver chromate electrode was calculated from the values listed in Table I. Since the electrode reaction is

$$2Ag(s) + CrO_4^= \longrightarrow Ag_2CrO_4(s) + 2e$$

we may write

$$E = E^0 - \frac{RT}{2F} \ln \frac{1}{a_{CrO_4^=}} = E^0 - \frac{RT}{2F} \ln \frac{1}{(m\gamma)_{CrO_4^=}}$$

By subtraction of $(RT/2F) \ln m$ from both sides of the equation

$$E - \frac{RT}{2F} \ln m = E^0 - \frac{RT}{2F} \ln \frac{1}{\gamma_{CrO_4^=}}$$

At infinite dilution the activity coefficient is equal to one, and the last term drops out; thus

$$E - (RT/2F) \ln m = E^0$$

We therefore determine E^0 by plotting $(E - (RT/2F) \ln m)$, *i. e.*, $E - 0.02958 \log m$ against the molality and extrapolating the curve to infinite dilution. The values so determined are given in Table II. From the plot of these values E^0 was taken as -0.4463 v. This gives $\Delta F^0 = 20{,}596$ cal.

TABLE II

Molality of K_2CrO_4	E. m. f., v.	0.02958 log *m*, v.	E. m. f. −0.02958 log *m*, v.	C. & M. $\gamma_{CrO_4^=}$	H. & J. $\gamma_{CrO_4^=}$
0.50					0.14
.10	−0.4968	−0.0296	−0.4672	0.19	.24
.05	− .5050	− .0394	− .4656	.21	.28
.025	− .5132	− .0474	− .4658	.32	
.010	− .5141	− .0592	− .4549	.51	.465
.005	− .5214	− .0681	− .4533	.64	.54
.00375	− .5223	− .0718	− .4505	.72	
.0025	− .5256	− .0770	− .4476	.83	

Combining

$$2Ag(s) + CrO_4^= \longrightarrow Ag_2CrO_4(s) + 2e; \quad \Delta F^0 = 20{,}596$$

and

$$2Ag(s) \longrightarrow 2Ag^+ + 2e; \quad \Delta F^0 = 36{,}896$$

we have

$$2Ag^+ + CrO_4^= \longrightarrow Ag_2CrO_4(s); \quad \Delta F^0 = -16{,}300 \text{ cal.}$$

The activity coefficients of the chromate ion were calculated by the equation

$$E = E^0 - \frac{RT}{2F} \ln \frac{1}{(m\gamma)_{CrO_4^=}}$$

The temperature coefficient was determined for the cell containing 0.05 *M* KCl and 0.025 *M* K_2CrO_4. The values listed in Table III are the averages of at least five readings at each temperature. From the plot of these values $dE/dT = -0.000228$.

Hence, since

$$E + \frac{\Delta H}{n\,F} = T \frac{dE}{dT}$$

$\Delta H_{298.1}$ for the reaction was found to be 6225 cal.

TABLE III

°C	E. m. f., v.
14.8	−0.2102
25.0	− .2078
30.0	− .2069
35.0	− .2060
40.0	− .2044
45.0	− .2023

To obtain the heat of formation of silver chromate, we make the combinations

$2AgCl(s) + CrO_4^= \longrightarrow Ag_2CrO_4 + 2Cl^-; \quad \Delta H^0 = 6225$ cal.

$2Ag^0 + Cl_2 \longrightarrow 2AgCl; \quad \Delta H^0 = -60{,}540$ cal.[10]

$2Ag^0 + Cl_2 + CrO_4^= \longrightarrow Ag_2CrO_4 + 2Cl^-; \quad \Delta H^0 = -54{,}315$ cal.

$Cl_2 \longrightarrow 2Cl^-; \quad \Delta H^0 = -79{,}166$ cal.[11]

$2Ag^0 + CrO_4^= \longrightarrow Ag_2CrO_4; \quad \Delta H^0 = 24{,}851$ cal.

$Cr^0 + 2O_2 \longrightarrow CrO_4^=; \quad \Delta H^0 = -203{,}952$ cal.[12]

$2Ag^0 + Cr^0 + 2O_2^0 \longrightarrow Ag_2CrO_4; \quad \Delta H^0 = -179{,}101$ cal.

Thus the heat of formation of silver chromate from its elements is

$$\Delta H^0_{298.1} = -179{,}101 \text{ cal.}$$

It is also interesting to calculate the heat of formation of silver chromate from its ions. We combine

$2Ag^0 + CrO_4^= \longrightarrow Ag_2CrO_4; \quad \Delta H^0 = 24{,}851$ cal.

$2Ag^0 \longrightarrow 2Ag^+; \quad \Delta H^0 = 49{,}724$ cal.[13]

$2Ag^+ + CrO_4^= \longrightarrow Ag_2CrO_4; \quad \Delta H^0 = -24{,}873$ cal.

The entropy change for this reaction is obtained from

$$\Delta F^0 = \Delta H^0 - T\Delta S^0$$

$$-16{,}300 = -24{,}873 - 298.1\ \Delta S^0$$

$$\Delta S^0_{298.1} = -28.75$$

Discussion of Results

Abegg and Cox[2] measured the cell

$$Ag(s),\ Ag_2CrO_4(s),\ K_2CrO_4\ (0.1\ N),\ KCl(N),\ Hg_2Cl_2,\ Hg$$

and found it to give an e. m. f. of −0.227 v. at

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[9] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York City, 1923, pp. 360, 362.

[10] Wolff, *Z. Elektrochem.*, **20**, 19 (1914); Jellinek and Uloth, *Z. physik. Chem.*, **119**, 161 (1926); Ref. 8, Vol. V, p. 188.

[11] Trautz and Geissler, *Z. anorg. allgem. Chem.*, **140**, 116 (1924); Ref. 8, Vol. V, p. 176.

[12] Ref. 8, Vol. V, p. 193.

[13] Ref. 8, Vol. V, p. 188.

25°. Using the value −0.2800 v.[5,14] for the normal calomel electrode, we obtain for Ag(s), Ag_2CrO_4(s), 0.1 N $CrO_4^=$ the value E = −0.507 v. This is in good agreement with our value of −0.5050 v. Next, calculating the value of E^0 from Abegg and Cox's results, we obtain −0.448 which again agrees with our value of −0.4463.

Bolam and MacKenzie[2] measured the cell Ag, $AgNO_3$(0.1 N), NH_4OH(10 N), K_2CrO_4(0.1 N), Ag_2CrO_4, Ag and obtained the value 0.2247 v. Lewis[15] found E = −0.399 v. for the cell Ag, $AgNO_3$(0.1 M), KNO_3(0.1 M), KCl(0.1 M) Hg_2Cl_2, Hg. Noyes and Brann[16] found for this same cell E = −0.3992 v. Lewis and Randall,[9] (p. 414) on the basis of these results, corrected for the liquid junction and obtained E = −0.3985 v. Since the value of the decinormal calomel electrode is −0.3351 v., we thus obtain for Ag(s), Ag_2CrO_4(s), CrO_4 = (0.1 N) the value E = −0.5089 v. This gives E^0 = −0.4504 v.

The standard electrode potential calculated from the data of Hass and Jellinek[2] is E^0 = −0.462 v.

The change in free energy for the reaction

$$Ag_2CrO_4(s) \longrightarrow 2Ag^+ + CrO_4^=$$

may be calculated from the solubility product as well as from the standard electrode potentials. Values calculated from various data are summarized in Table IV. Hass and Jellinek[2] measured the potential of the silver–silver chromate electrode in order to calculate the activity coefficients of the chromate ion. Their values, compared with ours, are listed in Table IV.

TABLE IV

Investigator	E^0, v.	K s. p.	ΔF^0 $Ag_2CrO_4 \rightarrow 2Ag^+ + CrO_4^=$ cal.
Hass and Jellinek[2]	−0.462		15,576
Bolam and MacKenzie[2]	− .4504		16,111
Abegg and Cox[2]	− .448		16,222
Cann and Mueller	− .4463		16,300
Abegg and Shäfer[a]		2.64 × 10^{-12}	15,803
Kohlrausch[b]		4.05 × 10^{-12}	15,550
Sherrill[c]		9.0 × 10^{-12}	15,077

[a] *Z. anorg. Chem.*, **45**, 293 (1905).

[b] *Z. physik. Chem.*, **64**, 149 (1908).

[c] THIS JOURNAL, **29**, 1641 (1907).

The variation in these values may be due to the fact that electrolytic silver chromate was used in the present work, whereas Hass and Jellinek used the precipitated salt. The thermodynamic properties of substances prepared by dissimilar methods may be very different.

Summary

The cell Ag(s), Ag_2CrO_4(s), K_2CrO_4(aq), KCl(aq), AgCl(s), Ag(s) was investigated.

The normal electrode potential of Ag(s), Ag_2CrO_4(s), $CrO_4^=$ was found to be E^0 = −0.4463 v.; ΔF^0 = 20,596 cal.

NORTHAMPTON, MASSACHUSETTS RECEIVED JUNE 26, 1935

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(14) Spencer, THIS JOURNAL, **54**, 3649 (1932).

(15) Lewis, *ibid.*, **28**, 158 (1906).

(16) Noyes and Brann, *ibid.*, **34**, 1016 (1912); Bray and Hershey, *ibid.*, **56**, 1891 (1934).

[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE]

The Adsorption of Hydrogen and Deuterium on Copper at Low Pressures[1]

BY RALPH A. BEEBE, GEORGE W. LOW, JR., EDWIN LINCOLN WILDNER AND SEYMORE GOLDWASSER

Attention has been called by Pace and Taylor[2] to the fundamental importance which is attached to experimental studies of the relative velocities of the activated adsorption of hydrogen and deuterium on catalytically active surfaces. These authors have found no difference in the rates of adsorption for the two isotopes on the hydrogenating catalysts chromium oxide, zinc oxide–chromium oxide and nickel at one atmosphere pressure and over the temperature range 110–184°. This observation was unexpected because, on account of the difference in zero point energies, the activation energy should be greater for deuterium than for hydrogen, and the rate of adsorption correspondingly less for deuterium.

More recently direct experimental evidence has been presented by Klar,[3] and indirect evidence based upon the interpretation of the rates of catalytic reactions has been presented independently by Klar,[4] and by Fajans[5] to show very definite differences in the adsorption of the two hydrogen isotopes on active nickel.

Because of the apparent discordance among the

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[1] Presented before the Division of Physical and Inorganic Chemistry at the ninety-first meeting of the American Chemical Society held in New York City on April 22–26, 1935.

[2] Pace and Taylor, *J. Chem. Phys.*, **2**, 578 (1934).

[3] R. Klar, *Naturwiss.*, **22**, 822 (1934).

[4] R. Klar, *Z. physik. Chem.*, **27B**, 319 (1935).

[5] E. Fajans, *ibid.*, **28B**, 239 (1935).

results which have been described above, it seems advisable at this time to present our data on the adsorption of the two gases by copper, although we feel that more detailed experimental work will be needed before a satisfactory explanation of all our results will be possible. Our measurements have extended over the temperature range −78 to 125° and the pressure interval, 0 to 2 mm. In agreement with Klar's work we have found great differences in the behavior of the two gases, both in the rates of adsorption and in the amounts adsorbed. In the course of this work we have also determined, by direct measurement, the heats of adsorption of the two gases at 0°. An interesting by-product of the work has arisen from a detailed study of the rates of adsorption at −78° on a comparatively bare copper surface. Under these conditions it has been found that the adsorption process is autocatalytic.

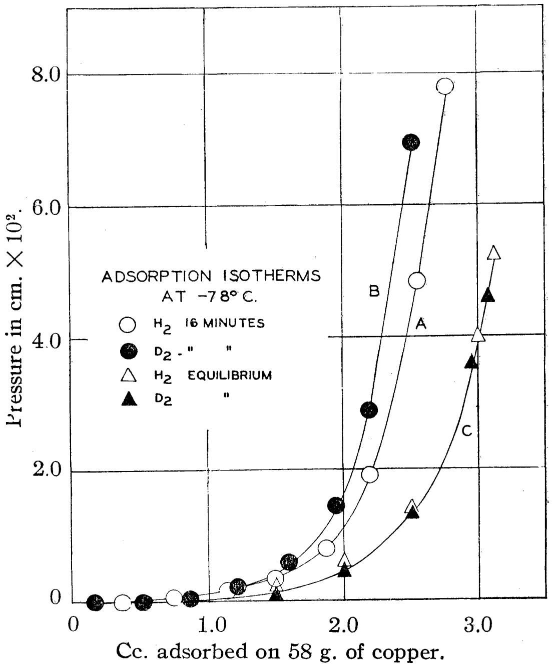

Fig. 1.

Experimental Details

Apparatus.—The general apparatus assembly and experimental procedure were in most details identical with those previously used by Beebe.[6] In the heat measurements smoother time–temperature curves were obtained by protecting strained portions of the constantan thermocouple wire from chance changes in room temperature. Moreover the sensitivity of the thermometric system was approximately tripled by use of a more sensitive galvanometer and a longer optical arm. The velocity of adsorption was measured on a McLeod gage by observing the rate of decrease of pressure in the system after admission of gas.

Materials.—Copper No. 1, used in most of the experiments, was prepared by reduction of high grade copper oxide granules in a stream of pure, dry hydrogen first at 120 and finally at 170°. After each series of adsorption measurements, the catalyst was degassed at 170° by use of a mercury diffusion pump over a period of five to fifteen hours. The copper, protected from mercury vapor by a trap containing cadmium turnings and gold foil, maintained a constant adsorptive capacity after several months of use. Copper No. 2 was prepared in exactly the same manner as No. 1, but a different sample of copper oxide was used. Copper samples No. 1 and 2 had approximately equal adsorptive capacity.

Copper No. 3, a much less active sample than the others, was prepared from copper powder made by rapid deposition from a solution of copper sulfate at high current density. This powder, supplied through the courtesy of Dr. F. H. Willard, was reduced in the same manner as were the others to remove surface oxide.

Electrolytic tank hydrogen was purified by passing it over copper at 450°, solid potassium hydroxide, and anhydrous magnesium perchlorate in sequence.

The deuterium gas, kindly supplied by Professor H. S. Taylor, was made by electrolysis of 99% heavy water produced in the Princeton Laboratory of Chemistry. A part of the work reported in this paper was done with a sample of deuterium received in February, 1934. Because of the unexpected differences between the results obtained and those of Pace and Taylor on other adsorbents another sample was requested from Professor Taylor. This deuterium, received in September, 1934, yielded results entirely consistent with those from the earlier sample.

The source of helium, used to measure the dead space in the apparatus, has been described previously.[7]

Experimental Results

Comparison of Hydrogen and Deuterium.—That our experiments very definitely demonstrate differences in the adsorption of the two hydrogen isotopes will be seen from the data which follow. In Fig. 1 are shown the isotherms for hydrogen and deuterium at −78° on copper No. 1. Increments of gas were admitted at thirty-minute intervals. Curves A and B are plotted from data taken sixteen minutes after admission of each increment of gas. That the difference in the isotherms A and B is due entirely to a difference in the rates of adsorption is shown by curve C. Each point on this curve represents data taken after the pressure had remained constant for twelve hours or more indicating that equilibrium had been reached. The coincidence of the data for hydrogen and deuterium on curve C indicates that, at equilibrium, the two gases are adsorbed in equal amounts at −78° although their rates of

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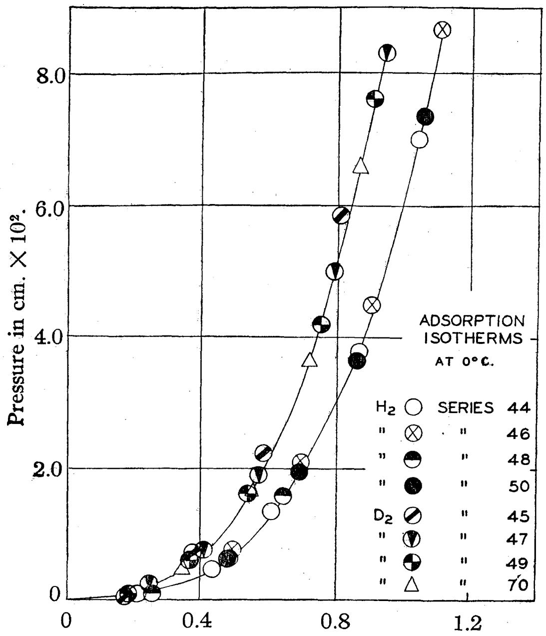
(6) Beebe, *Trans. Faraday Soc.*, **28**, 761 (1932).

(7) Beebe and Wildner, This Journal, **56**, 642 (1934).

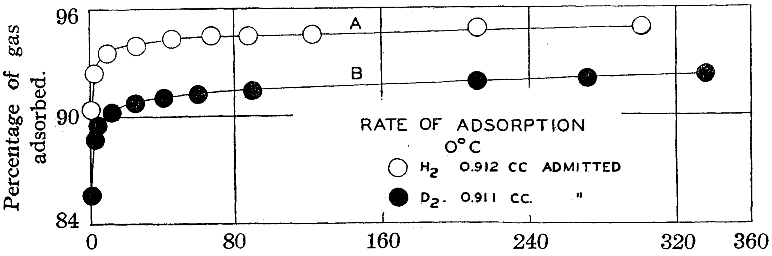
adsorption differ, the rate for deuterium being slower. These conclusions were confirmed by direct rate measurements.



Cc. of gas adsorbed on 58 g. of copper.

Fig. 2.

At 0° and higher temperatures the nature of the adsorption phenomena appears to be more complex than at −78°. It seems probable that a single type of sorption occurs at −78°, but that two types occur at the higher temperatures.[8] In obtaining the data at 0° for the isotherms shown in Fig. 2, increments were admitted to the catalyst at fifteen-minute intervals and readings were taken five minutes after each admission. That the isotherms do not represent equilibrium conditions is shown in Fig. 3, curve A. Ninety-two per cent. of the hydrogen admitted was adsorbed after five minutes, yet adsorption proceeded at a slow rate so that 2% more of the gas initially admitted had disappeared after six hours. Curve B shows similar results for deuterium. At first it seemed probable that the difference in the isotherms at 0° was due only to a difference in the rates of adsorption of hydrogen and deuterium, as was true at −78°. However, comparison of curves A and B in Fig. 3 reveals that there was still a definite difference in the amount of gas adsorbed under identical conditions even after six hours. In fact the two rate curves remained parallel at the end of five days although both hydrogen and deuterium were being adsorbed very slowly even then. As a further check of this apparent greater adsorption of hydrogen than of deuterium, rate measurements were repeated on copper No. 3. The results, which are entirely consistent with those of copper No. 1 at 0°, are shown in Fig. 4, (two curves at top).



Time in minutes.

Fig. 3.

Investigation of the adsorption process in the temperature range 0 to 125° revealed a rather surprising temperature inversion in the ratio of the amounts of the two isotopes adsorbed under identical conditions. The data measured on copper No. 3 are shown in Fig. 4. In all experiments 0.74 cc. of gas was admitted to a previously degassed sample weighing 45 g. which had been brought to the desired temperature. Experiments not shown were also performed at 19 and 125°. These yielded results which were entirely consistent with those which are shown for 0, 56 and 100°. The order of experiments was H_2 at 0°, D_2 at 0°, H_2 at 0°, H_2 at 19°, D_2 at 19°, H_2 at 56° D_2 at 56°, D_2 at 100°, H_2 at 100°, H_2 at 125°, D_2 at 125°, D_2 at 0°, H_2 at 0°.

It is important to observe that the points at 0° indicated by triangles were obtained at the end of the series of experiments, whereas those represented by circles were obtained at the beginning of the series. It is therefore demonstrated that no change had occurred in the copper surface during the whole series. Moreover, it seems improbable that any effects due to exchange reaction could have been present. Otherwise one would not expect identical results for the initial experiment for deuterium at 0° (Fig. 4) conducted after a hydrogen experiment at 0°, and the final experiment for deuterium at 0° conducted after a deuterium experiment at 125°. The tempera-

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[8] Ward, *Proc. Roy. Soc.* (London), **A133**, 506 (1931).

ture inversion was also observed on copper No. 2 in experiments at 0 and 100°.

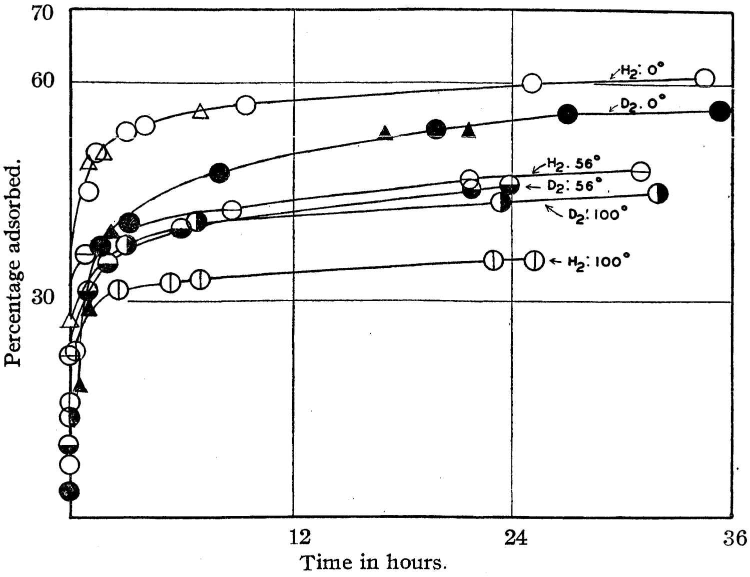

Fig. 4.—○ and ●: initial experiments; △ and ▲: final experiments.

Rates of Adsorption for Initial Stages.—A detailed study at −78° of the rates of adsorption of the two gases in the initial stages upon a comparatively bare copper surface revealed the surprising fact that the rate *increased* with increasing amounts of adsorbed gas on the surface. In other words, the process was autocatalytic. This point is best understood from Table I. A typical experiment (expt. 3 for H_2) will be described. To a newly degassed surface of copper No. 1, was admitted 0.387 cc. (increment 1); after four minutes 0.298 cc., or 77%, had been adsorbed, and after thirty minutes the whole 0.387 cc. was adsorbed. At this point increment 2, approximately equal in volume to 1, was admitted; after four minutes 97% was adsorbed, and after thirty minutes 100%. Increment 3 now followed and was 97.6% adsorbed after four minutes and 100% adsorbed after thirty minutes.

TABLE I

RATES OF ADSORPTION OF H_2 AND D_2 ON COPPER (58 G.) AT −78°

Expt.	Gas adsorbed	Cc. added	% adsorbed at 4 min.
3	H_2	0.387	77.0
		.369	97.0
		.383	97.6
7	H_2	.376	77.1
		.375	98.1
		.399	98.5
5	H_2	.170	94.2
		.170	99.4
		.174	100.0
4	D_2	.392	57.2
		.378	95.2
		.371	96.2
8	D_2	.387	53.5
		.394	95.0
		.366	96.0
9[a]	D_2	.381	46.5
		.393	95.2
		.387	96.2
6	D_2	.166	66.2
		.179	92.2
		.164	98.2

[a] Experiment 9 was made after another D_2 experiment, Expts. 4, 8 and 6 were made after H_2 experiments.

Examination of the data in Table I shows that deuterium exhibits the same unexpected rate phenomenon. The difference in rate between the first and second increments is even more marked than in the case of hydrogen. More details are to be seen in Fig. 5 showing the percentages adsorbed at two, four, six and eight minutes for experiments 3 and 4. It is also obvious from Fig. 5 that the velocity of adsorption on the comparatively bare surface at −78° is definitely less for the heavier isotope.

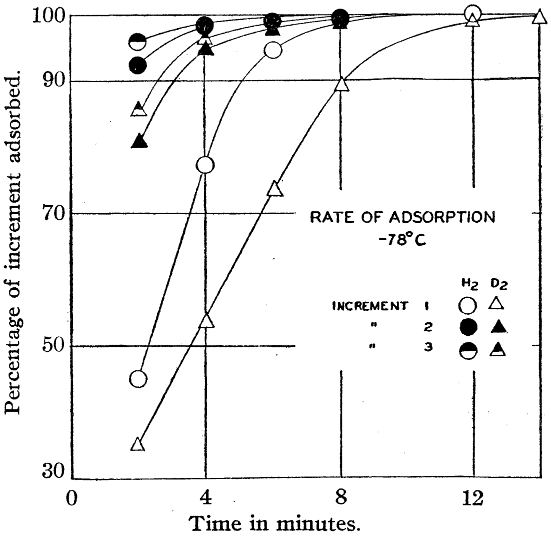

Fig. 5.

Owing to the rather striking results shown in Fig. 5 and in Table I, the authors have made a critical examination of the experimental procedure to see if the data could in any way be traced to experimental error. No such source of error was found. The obvious objection that the abnormal results could arise because the copper might not have cooled to −78° at the beginning of each experiment is eliminated because the catalyst tube was always left immersed in the bath at −78° overnight before each experiment. That this was sufficient time for thermal equilibrium was shown by the thermo-element which was used in the heat measurements.

Heats of Adsorption.—Altogether six series of measurements of differential heats of adsorption were made for hydrogen and five series for deuterium on two different samples of copper No. 1 weighing 67 and 58 g., respectively. Typical data are shown in Table II. The heats of adsorption are approximately 11,000 calories per mole of gas. No measurable difference was detected for the two gases. This observation is consistent with a calculated difference of 200 calories per mole, based on the values of the zero point energies of the H_2 and D_2 molecules and of the Cu–H and Cu–D bindings given by Eyring and Sherman.[9] The differential heats of adsorption for both isotopes decreased slightly with increasing amounts of gas already adsorbed. This decrease was not so marked, however, as was the case previously reported[10] for carbon monoxide on copper.

TABLE II

SERIES 23, ADSORPTION OF H_2 ON COPPER AT 0°

Increment	Volume of gas, cc. admitted	Volume of gas, cc. adsorbed	Residual pressure, mm. × 10^3	Differential heat of adsorption kcal. per mole
1	0.144	0.144	1.9	11.4
2	.138	.137	5.9	11.7
3	.186	.183	20.5	11.2
4	.163	.158	42	11.3
5	.161	.154	75	10.4
6	.162	.152	121	10.7
7	.207	.192	163	10.5
8	.322	.279	374	10.4
Total	1.483	1.399		

Series 25, adsorption of D_2 on copper at 0°

Increment	Volume of gas, cc. admitted	Volume of gas, cc. adsorbed	Residual pressure, mm. × 10^3	Differential heat of adsorption kcal. per mole
1	0.230	0.230	16.6	12.4
2	.196	.191	41	11.8
3	.205	.194	88	11.3
4	.278	.252	202	11.1
5	.248	.208	375	11.5
6	.364	.293	778	10.5
Total	1.521	1.368		

Discussion of Results

Difference in Behavior of Hydrogen and Deuterium.—Our results like those of Klar and of Fajans previously cited appear to be in disagreement with the work of Pace and Taylor.[2] However, it should be mentioned that all of our measurements were carried out at low pressures (0 to 2 mm.), whereas those of Pace and Taylor were at 760 mm. It therefore seems possible that measurements on Pace and Taylor's active adsorbents at low pressure may very well uncover differences between hydrogen and deuterium which have been masked at 760 mm. On the basis of their observations Pace and Taylor have drawn certain conclusions concerning the probable rate determining factors in the adsorption process. Because of the apparent disagreement mentioned above, these conclusions should be reserved pending further experimental work.

Special attention is called to the similarity between our results and the data of Klar[4] on the relative rates of hydrogenation of ethylene over iron catalyst by the two hydrogen isotopes. The latter author reports that although the hydrogenation rate is greater for hydrogen than for deuterium at 0°, the reverse is true at temperatures above 100°; and suggests as a tentative explanation the possibility of a temperature inversion in the ratio H_2/D_2 adsorbed entirely analogous to that directly observed by us in the case of copper. Pease and Wheeler[11] recently have reported preliminary data on the rates of hydrogenation of ethylene over copper catalyst. They have found for the ratio of rates H_2/D_2 a value of 1.59 at 0°, 1.34 at 184° and 1.04 at 306°. They suggest the possibility that their results may be accountable to an exchange reaction absent at 0°, but increasingly present at higher temperatures. It seems possible to us that an explanation similar to that offered by Klar in the case of iron catalyst may be applied to Pease and Wheeler's results. Our data show that deuterium is relatively more strongly adsorbed with increasing temperature as compared to hydrogen. It may be that the higher energy of activation for the deuterium reaction causing a slower rate of hydrogenation of ethylene at 0°, is increasingly compensated with rising temperature by the relatively greater adsorption of deuterium as compared to hydrogen.

It is difficult at this time to attain a satisfactory theoretical explanation of the complex

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(9) Eyring and Sherman, *J. Chem. Phys.*, **1**, 348 (1933).

(10) Beebe and Wildner, THIS JOURNAL, **56**, 642 (1934).

(11) Pease and Wheeler, *ibid.*, **57**, 1144 (1935).

differences in the adsorption data for the two gases. All of our data on rates of reaction were obtained by measuring change of pressure with time. Because changes in pressure effect changes in the activation energies of adsorption processes,[12] no attempt has been made to calculate activation energies from the velocity curves. It is highly desirable to procure velocity data at constant pressure using a method for pressure control during the adsorption in the low pressure region (0 to 2 mm.).

Autocatalytic Adsorption at −78°.—One other example of autocatalytic adsorption has been observed previously by Benton and White[13] for hydrogen on iron at 0°. In these cases of autocatalytic adsorption the gas is apparently more readily adsorbed on those portions of the surface which are adjacent to atoms or molecules already adsorbed. There is little doubt that the adsorption of either hydrogen isotope on copper at −78°, which we have found to be autocatalytic, is of the activated type.[14] This possibility of an autocatalytic activated adsorption process presents a complicating factor which must be considered in connection with any adsorption theory of catalysis.

Summary

1. Very definite and complex differences have been found between the adsorptions of light and heavy hydrogen on active copper at low pressures (0 to 2 mm.).

2. At −78° the rate of adsorption is less for deuterium than for hydrogen, but equal amounts of the two isotopes are adsorbed at equilibrium.

3. In the temperature interval 0 to 125° the ratio H_2/D_2 adsorbed undergoes an inversion, hydrogen being more strongly adsorbed at the lower temperatures and less strongly at the higher temperatures.

4. The differential heats of adsorption have been measured by a direct calorimetric method, and are identical for the two isotopes within the limits of experimental error.

5. The early rate of adsorption of hydrogen at −78° is autocatalytic. The same is true for deuterium.

AMHERST, MASS. RECEIVED JUNE 28, 1935

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[12] Taylor and Strother, THIS JOURNAL, **56**, 586 (1934).

[13] Benton and White, *ibid.*, **54**, 1820 (1932).

[14] At −78° the adsorption proceeded at a measurably slow rate and the residual pressure, even after the third increment of gas, was less than 10^{-3} cm. Both these observations together with evidence not detailed here, indicate activated adsorption. See also Benton and White, *ibid.*, **53**, 3304 (1931).

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Coefficient of Expansion of Silver Iodide and of the Halides of Thallium

BY GRINNELL JONES AND FREDERIC C. JELEN

Introduction

Silver iodide has been reported to have a negative cubical coefficient of expansion. Since this property is almost unique it seemed desirable to test the reliability of the reports by a new experimental method and to measure the expansion of several analogous salts in the hope that another similar case might be found. In this paper data on silver iodide and the halide salts of thallium are reported.

The coefficient of expansion of silver iodide was determined many years ago by Fizeau,[1] and by Rodwell[2] with very discordant results, although both agree as to the negative sign.[3] Fizeau, using an optical interference method, obtained agreeing results on a cylinder which had been previously fused and therefore consisted of closely packed crystals and on precipitated silver iodide which was compressed into a cylinder. He found the cubical coefficient to be -4.1×10^{-6} at a mean temperature of 40°. A single large crystal gave -2.7×10^{-6}. Rodwell who measured the cubical coefficient by a dilatometer method obtained a much larger value, namely -55.7×10^{-6} between 21 and 67°. Klemm, Tilk and v. Müllenheim,[4] using a dilatometer method have found the cubic coefficient of expansion from 20 to 120° of thallous chloride to be 1.68×10^{-4}, and of thallous bromide to be 1.72×10^{-4}.

Outline of the Principle of the New Method.—Our method was suggested by the Richards[5]

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[1] H. Fizeau, *Pogg. Ann.*, **132**, 292 (1867).

[2] G. F. Rodwell, *Chem. News*, **31**, 5 (1875).

[3] Grinnell Jones, THIS JOURNAL, **31**, 191 (1909).

[4] W. Klemm, W. Tilk and S. v. Müllenheim, *Z. anorg. allgem. Chem.*, **176**, 1 (1928).

[5] T. W. Richards and W. N. Stull, *Publ. Carnegie Inst. Wash.*, No. 7 and No. 76; T. W. Richards and Grinnell Jones, THIS JOURNAL, **31**, 158 (1909).

method for the determination of the compressibility of solids and liquids, which it resembles in principle. The glass dilatometer is first weighed and then filled with mercury and the exact temperature needed to bring the mercury meniscus to a reference mark in a capillary tube is determined. Then a weighed drop of mercury is added and a new lower temperature determined which will bring the greater quantity of mercury to the same reference mark. This step may be repeated as often as is desired until the range of temperature to be studied has been covered. The total weight of mercury present is then found by weighing the dilatometer and its contents. It is evident that these data permit a computation of the difference between the coefficient of expansion of mercury and of glass per gram of mercury and per degree centigrade averaged over each temperature interval used in the experiments. Then a large part of the mercury in the dilatometer is replaced by a known weight of some other solid or liquid substance and the measurements repeated. By taking the difference between these series of measurements the effect of the variation in volume of the glass dilatometer is eliminated and the result is the difference between the cubical coefficient of expansion of the solid or liquid under investigation and that of an equal volume of mercury. The cubical coefficient of expansion of mercury,[6] which is known more precisely than that of any other substance (with the possible exception of water) may then be added to this experimental result to give the coefficient of expansion of the solid or liquid.

The principle of the method is simple and direct, but mercury does not wet most solids so it is necessary to have present a small amount of some wetting liquid. The necessity of determining the amount of wetting liquid present complicates the procedure and diminishes the precision of the result. Toluene was chosen for the wetting liquid because it does not dissolve any of the salts to be investigated and its boiling point and volatility are suitable for the purpose. Its coefficient of expansion was of course determined separately in our dilatometer.

Another novel feature of our method is that the dilatometer serves also as a thermo-regulator and automatically adjusts its own temperature so that the dilatometer is completely filled to the reference mark. This feature contributes greatly to the convenience of the experimentation and the precision of the final result.

Experimental

The dilatometer, which is shown in Fig. 1(D), was made of Pyrex glass and had an internal diameter of 2 cm. and a volume up to the point, P, of about 60 cc. It had two pieces of platinum, P and Q, extending into side tubes as shown in the figure. A little mercury in the side tubes served to make electrical contact and to make the platinum seals gas-tight. The stiff platinum rod P has a sharp point which is located in the center of the capillary at the height where it commences to flare. It will be sufficiently obvious from the figure that when the dilatometer is filled with mercury in whole or part it will also serve as a regulator and automatically adjust the temperature of a thermostat in which it is immersed so that it will be completely filled up to the tip of the pointed platinum rod, P.

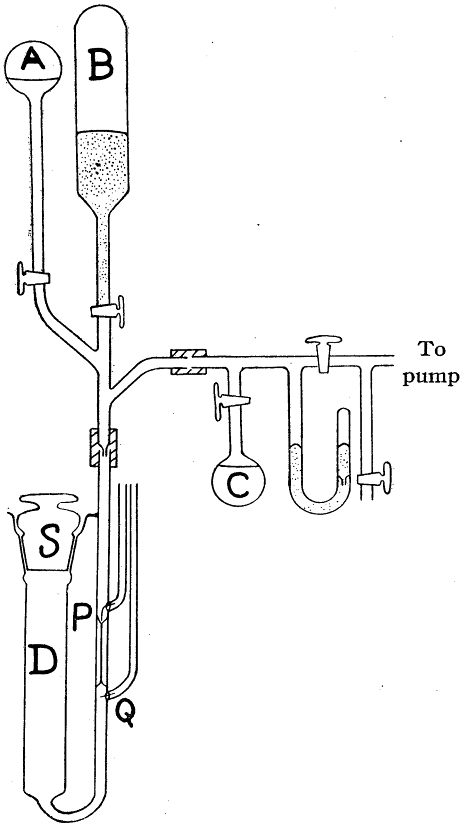

Fig. 1.—Dilatometer and filling device.

In order that the location of the stopper, S, should be as definite and reproducible as possible it was made with somewhat greater taper than the standard grindings and was rotated to a standard position by the aid of suitable guide marks. Our experience showed that determinations of the total volume were reproducible within 0.02 cc., which is sufficiently precise. It is of much greater importance that the stopper should not move vertically with reference to the jacket during a series of measurements. It was found impossible to get the desired precision without

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(6) "Smithsonian Physical Tables," 1923, 7th ed., p. 121.

the use of a sealing compound which is solid at the highest temperature used in the measurements (about 60°).

When toluene is used as a wetting liquid, organic waxes or resins are excluded on account of their solubility. Having found that anhydrous metaphosphoric acid may be used, a suitable quantity of molten metaphosphoric acid was placed on the upper part of the grinding of the stopper where it immediately froze. The stopper was then inserted into the dilatometer (either empty or containing a weighed amount of salt) and the upper part of the instrument heated in a free flame until the acid melted, whereupon the stopper was pressed into place and then on cooling the metaphosphoric acid froze and held the stopper completely immobile during the experiment. To prevent solution of the metaphosphoric acid in the water of the thermostat melted "arochlor" (Swann Chemical Company) was poured into the annular channel above the ground glass joint. Arochlor is sufficiently stiff at 60° and insoluble in water and adheres to glass so it served its purpose well.

A good grade of thallous nitrate was twice recrystallized. Iodine was purified by distillation from a solution of an iodide, washed and converted into hydriodic acid by reaction with yellow phosphorus and water, and the resulting hydriodic acid distilled twice. Dilute solutions of thallous nitrate and of hydriodic acid (in excess) were mixed and the precipitated thallous iodide washed repeatedly. The salt was then fused in a Pyrex test-tube and allowed to solidify from the bottom upward. There were a few minute cracks in the material which toluene could penetrate but mercury could not. The other salts were prepared by a similar procedure. Thallous bromide and thallous iodide were prepared by the addition of ammonium bromide and hydrochloric acid solutions, respectively, to thallous nitrate solutions. Silver iodide was precipitated from a nitrate solution by the addition of a potassium iodide solution.

Since the coefficient of expansion of gases is very great in comparison with liquids and solids it is necessary to fill all of the space in the dilatometer not occupied by salt with mercury or with toluene and without any air bubbles. This was accomplished by the device shown in Fig. 1. After the salt had been placed in the dilatometer, the stopper frozen in place and the contents weighed, it was connected to the filling device by a stout rubber connection as shown. All air had been removed completely from the bulbs A, B, C in advance. The air in the dilatometer was replaced by toluene vapor by alternately exhausting and opening the cock of bulb C. This was repeated about a dozen times, thus removing the air completely. Then about a gram of liquid toluene was run into the dilatometer by opening the cock of bulb A, followed by opening the cock of bulb B to admit sufficient mercury to seal the lower bend in the dilatometer. The liquid toluene in the narrow arm of the dilatometer was then evaporated. More mercury was added, thus completely filling the dilatometer. During this process the layer of toluene on top of the mercury rises and wets every particle of salt. The filling was not considered a success unless there was a slight surplus of liquid toluene visible under the stopper and no air bubbles were present. The dilatometer was then separated from the filling device. The capillary in the dilatometer was cleaned by treatment in succession with nitric acid, water, and acetone, followed by evaporation of the acetone. The amount of mercury was adjusted until it would fill the instrument at approximately 60°, and the total weight of the instrument and contents was determined. The dilatometer was then placed in the thermostat where it functioned as a thermostat regulator and adjusted its own temperature until the mercury meniscus came exactly to the platinum tip, P. A thyratron tube was used instead of the usual electromagnetic relay.

The proper amount of mercury to require a lowering of about 10° in the temperature was then weighed out and added to the dilatometer, which again functioned as a regulator and established a new lower temperature of about 50°, which was read as before. In a similar manner readings were taken at about 40, 30 and 20°.

Then without disturbing the stopper the bulk of the mercury and toluene were removed into a weighed Pyrex dish. The toluene remaining inside the dilatometer was removed by evaporation at room temperature by repeatedly exhausting and admitting air. The dish was placed in a vacuum desiccator and the toluene removed in a similar manner. The loss in weight gives the weight of toluene.

TABLE I

DATA OF TYPICAL EXPERIMENT ON CHANGE IN VOLUME OF PYREX DILATOMETER

T, °C.	Mercury added, g.	Round T, °C.	Mercury required for 10° depression, g.	Spec. vol. mercury cc./g.	ΔV_D, cc.	$(\Delta V_D/V_D) \times 10^6$
59.80_7	1.4102	60	1.443_0	0.0743592	0.0246_2	$392._3$
50.03_4	1.4670	50	1.446_9	.0742250	$.0184_2$	$293._5$
39.89_5	1.4359	40	1.451_6	.0740910	$.0123_0$	$195._9$
30.00_3	1.4575	30	1.453_9	.0739571	$.0062_1$	$99._0$
19.97_8		20		.0738233	0	0

Weight of mercury filling dilatometer at 59.807° = 844.32 g.

Results on Pyrex Glass.—The data of one typical experiment with mercury alone in the dilatometer are given in sufficient detail in Table I to permit a judgment in regard to the factors which control the precision of the results and to make clear how the data are interpreted. The results of other similar experiments are given only in a summarized form in Table II.

In this experiment it was found that when the dilatometer contained 844.32 g. of mercury (corrected to vacuum) it was completely full up to the point P at 59.80_7°. Then 1.4102 g. of mercury was added which required a drop in temperature to 50.03_4°, to permit the extra mercury to enter the instrument. Then in succession the several amounts of mercury shown in column 2 were added and the equilibrium temperature after each addition of mercury is shown on the line below in the first column. The weights of mercury which would have been required for successive drops of exactly 10°, assuming that the initial temperature had been exactly 60°, are shown in column 4. The weight of mercury required to fill the dilatometer at each ten-degree interval is easily computed from these data. By using the known values for specific volume of mercury given in column 5, the volume at each temperature may be computed. The increase in volume of the dilatometer from 20°, ΔV_D, is shown in column 6. The total expansion per cubic centimeter of dilatometer at 20° is given in column 7. This is of course a measure of the expansion of Pyrex glass.

TABLE II

SUMMARY OF CHANGES IN VOLUME OF PYREX DILATOMETER FROM 20° TO t° PER CC. OF VOLUME AT 20°. $\Delta V/V_{20} \times 10^6$

	Temp., °C.				
	20	30	40	50	60
	0	99.0	195.9	293.5	392.3
	0	100.5	198.7	296.2	393.8
	0	98.5	197.7	294.4	393.9
	0	99.4	196.2	291.5	389.9
	0	98.3	198.9	297.7	396.3
Average	0	99	197	295	393

The equation $V_t = V_{20}[1 + 9.85 \times 10^{-6}(t - 20)]$ agrees with these results within the experimental error. These experiments therefore give $9.8_5 \times 10^{-6}$ as the cubical coefficient of expansion of Pyrex glass over the range from 20 to 60°. The linear coefficient of expansion of Pyrex glass is given in the "International Critical Tables" on the authority of the Corning Glass Company as 3.2×10^{-6} over the range 19 to 350°. This corresponds to a cubical coefficient of 9.6×10^{-6}.

TABLE III

SUMMARY OF EXPERIMENTS ON EXPANSION OF TOLUENE

The volume of toluene at the temp., t, divided by its volume at 20°: $V_{T,t}/V_{T,20}$.

	Temp., °C.				
	20	30	40	50	60
	1.00000	1.01089	1.02208	1.03362	1.04552
	1.00000	1.01086	1.02206	1.03358	1.04547
	1.00000	1.01086	1.02204	1.03356	1.04545
	1.00000	1.01087	1.02205	1.03358	1.04545
Av.	1.00000	1.01087	1.02206	1.03359	1.04547
Comp.	1.00000	1.01086	1.02206	1.03359	1.04546

Results on Toluene.—Four complete experiments were carried out in which the dilatometer contained toluene for about three-fourths of its volume. The results are summarized in Table III.

The figures given in Table III are the volumes which 1 cc. of toluene measured at 20° would occupy at the temperatures specified at the top of the columns. These results may be expressed within the limit of error of the experiments by the equation $V_t = V_{20}[1 + 0.001069(t - 20) + 0.00000169(t - 20)^2]$ as shown in the last line of Table III. The true coefficient of expansion dV/Vdt, at any temperature is readily found by differentiation of the above equation. The values are as follows: 20°, 0.001069; 30°, 0.001091; 40°, 0.001112; 50°, 0.001133; 60°, 0.001151.

Results on Salts.—The data for one typical experiment on a salt are given in sufficient detail in Table IV to permit a judgment of the factors which control the precision of the results, and the results of the other experiments are given only in summarized form in Table V. In our first experiment with thallous bromide, the dilatometer contained 229.51 g. of thallous bromide, 1.09 g. of toluene and, when completely filled at 20°, it contained 391.68 g. of mercury. The volume of the dilatometer at 20° was 60.994 cc., of which 1.09/0.866 = 1.259 cc. was occupied by toluene; and 391.68 × 0.0738233 = 28.915 cc. was occupied by mercury. The volume of the thallous bromide was therefore 60.994 − 1.259 − 28.915 = 30.820 cc. The significance of the first four columns will be sufficiently obvious by analogy with Table I. The change in volume of the dilatometer is computed from our special experiments with mercury alone in the instrument. Column 6 gives the change in volume of the mercury present. The seventh column gives the change in volume of the toluene which is computed from the weight of toluene and its coefficient of

TABLE IV

DATA ON TYPICAL EXPERIMENT WITH THALLOUS BROMIDE

T, °C	Mercury added, g.	Round T, °C	Mercury added for 10° dep., g.	ΔV_D	ΔV_{Hg}	ΔV_T	ΔV_S	$V_{S,t}/V_{S,20}$
59.79_2	1.4256	60	1.464_9	+0.02404	−0.22284	+0.05724	+0.18964	1.00615_3
50.06_0	1.4886	50	1.455_8	.01805	− .16589	.04227	.14167	1.00459_7
39.83_5	1.4280	40	1.452_1	.01214	− .10993	.02777	.09430	1.00306_0
30.00_1	1.4475	30	1.446_8	.00608	− .05459	.01369	.04698	1.00152_4
19.99_6		20						1.00000_0

Weight of thallous bromide used, 229.51 g. Weight of toluene, 1.09 g. Weight of mercury at 20°, 391.68 g.

TABLE V

SUMMARY OF EXPERIMENTAL DATA ON THE EXPANSION OF SOME SALTS

Salt		Comparative volumes at °C. 20	30	40	50	60
AgI		1.000000	1.00000_0	0.99999_8	0.99998_5	0.99997_2
AgI		1.000000	0.99999_4	$.99997_9$	$.99996_6$	$.99993_7$
AgI		1.000000	$.99999_2$	$.99997_9$	$.99995_4$	$.99993_2$
AgI		1.000000	$.99998_8$	$.99996_7$	$.99993_9$	$.99990_3$
AgI	Av.	1.000000	0.99999_3	0.99998_1	0.99996_1	0.99993_6
TlI		1.000000	1.00135_0	1.00271_0	1.00407_0	1.00544_7
TlI		1.000000	1.00135_0	1.00268_0	1.00403_6	1.00540_4
TlI		1.000000	1.00135_4	1.00269_9	1.00405_1	1.00541_8
TlI		1.000000	1.00135_2	1.00270_2	1.00405_6	1.00542_4
TlI	Av.	1.000000	1.00135_2	1.00269_9	1.00405_3	1.00542_3
TlBr		1.000000	1.00152_4	1.00306_0	1.00459_7	1.00615_3
TlBr		1.000000	1.00152_5	1.00304_9	1.00460_2	1.00615_1
TlBr	Av.	1.000000	1.00152_5	1.00305_5	1.00460_0	1.00615_2
TlCl		1.000000	1.00157_9	1.00316_8	1.00477_0	1.00638_2
TlCl		1.000000	1.00158_7	1.00318_0	1.00478_7	1.00640_9
TlCl	Av.	1.000000	1.00158_3	1.00317_4	1.00477_9	1.00639_6

expansion already determined. It is obvious that the change in volume of the salt $\Delta V_S = \Delta V_D - \Delta V_T - \Delta V_{Hg} = +0.04698$. Column 9 gives the volume of the salt at temperature, t, relative to the volume at 20°; $(V_S + \Delta V_S)/V_S = V_{S,t}/V_{S,20} = (30.820 + 0.04698)/30.820 = 1.00152_4$.

The experimental error in the determination of the weight of mercury required to be added for each ten-degree interval may be as much as 0.1% since the error in measuring this interval may be as much as 0.01°. Errors in temperature, however, are not cumulative. In this experiment an error of 0.1% in the weight of mercury for a change of 10°, will cause an error of 0.00011 cc. in the ΔV_{Hg} and hence in ΔV_S. On the other hand, an error of as much as 0.8 g. in the total weight of mercury present would be required to cause an equally great error (0.00011 cc.) in ΔV_{Hg} but since the weight of mercury can be determined within about a centigram the error from this cause is negligible. Further, an error of 0.01 g. in weight of toluene used would make an error of 0.00013 cc. in ΔV_T and therefore in ΔV_S. It is evident that great care must be taken in the determination of the weight of toluene and the unavoidable error in finding the weight of toluene used is probably the greatest single source of error in the final result. Table V summarizes the results for the four salts studied.

These results may be expressed in the form

$$V_t = V_{20}\,[1 + a(t - 20) + b(t - 20)^2]$$

for AgI; $V_t = V_{20}\,[1 - 0.0000016\,(t - 20)]$

for TlI; $V_t = V_{20}\,[1 + 0.00013419\,(t - 20) + 0.0000000321\,(t - 20)^2]$

for TlBr; $V_t = V_{20}\,[1 + 0.00015182\,(t - 20) + 0.0000000493\,(t - 20)^2]$

for TlCl; $V_t = V_{20}\,[1 + 0.00015754\,(t - 20) + 0.0000000586\,(t - 20)^2]$

These equations agree with our experimental data over the range from 20 to 60° with an average deviation of less than three parts in a million for thallous iodide, and within one part in a million for the other three salts. The true coefficient of expansion at any temperature, t, would be

$$\frac{dV}{Vdt} = \frac{a + 2b\,(t - 20)}{1 + a\,(t - 20) + b\,(t - 20)^2}$$

The coefficients of expansion of these salts are as follows:

TABLE VI

COEFFICIENTS OF EXPANSION

	Temp., °C. 20	30	40	50	60
TlCl	$1.57_6 \times 10^{-4}$	$1.58_5 \times 10^{-4}$	$1.59_4 \times 10^{-4}$	$1.60_3 \times 10^{-4}$	$1.61_3 \times 10^{-4}$
TlBr	$1.51_8 \times 10^{-4}$	$1.52_6 \times 10^{-4}$	$1.53_4 \times 10^{-4}$	$1.54_0 \times 10^{-4}$	$1.54_8 \times 10^{-4}$
TlI	$1.34_2 \times 10^{-4}$	$1.34_6 \times 10^{-4}$	$1.35_1 \times 10^{-4}$	$1.35_6 \times 10^{-4}$	$1.36_0 \times 10^{-4}$
AgI	$-0.01_6 \times 10^{-4}$	$-0.01_6 \times 10^{-4}$	$-0.01_6 \times 10^{-4}$	$-0.01_6 \times 10^{-4}$	$-0.01_6 \times 10^{-4}$

A discussion of the correlation of the coefficient of expansion with the compressibility and other properties will be postponed until data on more salts are available.

Summary

1. A new form of differential weight dilatometer for the determination of the cubical coefficient of expansion of solids and liquids is described. The instrument functions simultaneously as a thermostat regulator and controls its own temperature so that it is exactly filled.

2. Measurements have been made on six substances between 20 and 60°, giving the following mean cubical coefficients of expansion: Pyrex glass, $9.8_5 \times 10^{-6}$; toluene, 1.111×10^{-3}; silver iodide, $-1._6 \times 10^{-6}$; thallous chloride, 1.59×10^{-4}; thallous bromide, 1.53×10^{-4}; thallous iodide, 1.35×10^{-4}.

CAMBRIDGE, MASS.

RECEIVED SEPTEMBER 10, 1935

An Unknown Property of the Calomel Half-Cell and the Estimation of Bromide–Chloride Mixtures

By F. L. Hahn

It is a well-known fact that calomel reference electrodes, although prepared in the same manner and with carefully purified salts, do not always show exactly the same potential and they sometimes change as to their potential some months after their formation. The reasons for this change are not known. The author has found that rather small amounts of bromide contained in the potassium chloride vary the potential of the electrodes to such a degree that no one could anticipate it.

Furthermore, it was found that commercial potassium chloride always contained bromide, up to a degree of 0.1 and 0.01% or occasionally somewhat more even in the purest grades.[1] Potassium chloride free from bromide may be prepared by precipitating a saturated solution several times with alcohol. The calomel used will also contain varying quantities of bromides. In all cases where for this reason the solid phase is not in equilibrium with the solution the electrodes will not be stable.

Experiments

I. Eight tubes like A and B in Fig. 1 were filled with equal quantities of mercury, calomel and 1 *N* potassium chloride. They were connected with each other by a siphon filled with potassium chloride and agar. The e. m. f. of these cells was measured by a compensation apparatus; the measurements could be made with no more error than 0.2 mv. No difference of potential was found between two of these half-cells during a period of five days. Then 1 *N* potassium bromide solution was added to the tubes and the following differences of potential were measured with tube 1 as a reference electrode (Table I).

Table I

Tube	1	2	3	4	5	6	7	8
Mole % KBr	0	0.02	0.05	0.1	0.2	0.5	1	0
E. m. f. (mv.)	..	− .7	−0.9	−3.0	−3.7	−6.2	−12.8	0
Two days later	..	− .5	−0.9	−1.8	−2.7	−5.3	− 6.2	0

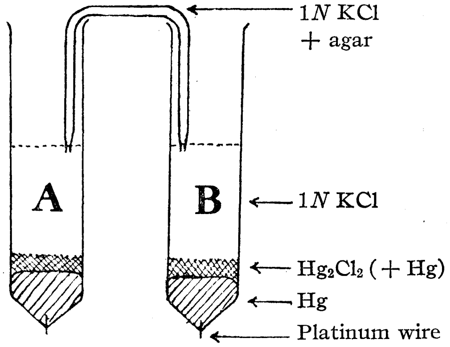

Fig. 1.

II. A calomel half-cell was used as a reference electrode. The siphon of the cell was finely drawn out on the exterior end and stopped by addition of agar. One cc. of mixtures of 1 *N* potassium chloride and bromide was poured into tubes like those in Fig. 1 but smaller, and one drop of a phosphate buffer solution ($p_H \sim 6$) and one drop of 0.01 *N* mercurous perchlorate were added thereto. The e. m. f. of the cell formed in this way was measured by compensation. By standardizing this combination, using mixtures of known percentages of bromide, it was possible to estimate the composition of unknown mixtures within a few minutes.

Summary

1. The potential of a calomel half-cell is strongly influenced by even the smallest contents of bromide in the potassium chloride used.

2. It is possible to use this effect in order to obtain a rapid estimation of bromide in chloride.

Escuela Politecnica
Quito, Ecuador

Received March 28, 1935

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(1) It was rather difficult to estimate such small contents of bromide before the colorimetric reaction published by the author was known (*Compt. rend.*, **197**, 245 (1933)).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Reaction of Organic Anions with Basic Thorium Chloride Hydrosols. Reversal of Charge with Salts of the Hydroxy Acids and with Nitric Acid

BY ARTHUR W. THOMAS AND CHESTER B. KREMER

A previous investigation[1] dealing with the effect of neutral salt solutions upon thorium oxychloride hydrosols has established an order of reactivity for twelve anions in respect to their ability to displace hydroxo groups from the micellar complex, the increase in *p*H of the hydrosol upon addition of the salt solutions serving as a measure of this displacement. It was found that, as in the case of other "oxide" hydrosols, this action of different anions varied widely; citrate and oxalate being very potent, while chloride and nitrate had but slight effect. Since displacement of hydroxo groups from the complex may be considered to constitute chemical combination of the displacer with the central metallic atom, the reactivity of these anions should be determined by the number and position of combining groups present in each. For the purpose of investigating the influence of chain length and number of carboxyl groups, the potassium salts of the aliphatic monocarboxylic series from formate to valerate, inclusive, and the potassium salts of the aliphatic dicarboxylic series from oxalate to pimelate, inclusive, were studied.

Preparation of the Hydrosols.—The hydrosols used in this investigation were prepared either by the peptization of hydrous thorium dioxide with dilute hydrochloric acid (Sols D, E, F) or by the addition of ammonia to thorium chloride solutions until a permanent turbidity was produced (Sols A and B). All sols were dialyzed against distilled water for varying lengths of time. The micelles of the sols thus prepared were charged positively. These five hydrosols, of which A, B and F were turbid and D and E cloudy in appearance, are described in Table I.

TABLE I

COMPOSITION OF HYDROSOLS

Sol	Thorium, milliequiv. per liter	Chloride, milliequiv. per liter	Eq. Th/Eq. Cl	*p*H[a]
A	51.8	7.3	7	4.02
B	62.8	11.6	5	4.06
D	37.3	3.9	10	3.89
E	63.9	5.7	11	3.97
F	100.9	13.1	8	4.16

[a] *p*H values are those obtained immediately at the completion of dialysis.

Reactions with Salt Solutions.—By means of a technique previously described[1] the *p*H increasing effect of various salts was measured. The results with the potassium monocarboxylates for Sols A and D (typical of all) are given in Table II. It is seen that the difference in reactivity between these homologous anions is slight. This is as expected, since their combination in the complex is controlled by the same factor, *i. e.*, the single carboxyl group.

TABLE II

*p*H INCREASING EFFECT OF POTASSIUM MONOCARBOXYLATES UPON BASIC THORIUM CHLORIDE HYDROSOLS

Final concn. of salt (N)	Formate	Acetate	Propionate	Butyrate	Valerate
		Sol A			
0.0000	3.3	3.3	3.3	3.3	
.0025	3.9	4.4	4.5	4.4	
.0050	4.6	5.2	5.3	5.2	
.0100	5.3	5.6	5.6	5.6	
.0150	5.6	5.8	5.8	5.9	
.0250	5.9	5.9	6.0	6.0	
.0500	6.2	6.2	6.2	6.1	
		Sol D			
0.0000	3.9	3.9	3.9	3.9	3.9
.0025	5.2	5.6	5.6	5.5	5.6
.0050	5.7	6.0	6.1	6.0	6.1
.0075	5.9	6.2	6.2	6.1	6.3
.0150	6.3	6.5	6.4	6.3	6.5
.0250	6.4	6.6	6.5	6.4	6.5
.0500	6.6	6.8	6.6	6.4	6.5

The results with the potassium dicarboxylates are shown for Sol A (typical of all) in Fig. 1. Oxalate is the most reactive of the dicarboxylic anions tried. Malonate is easily seen to be somewhat more reactive than succinate; glutarate, adipate and pimelate are practically the same in reactivity and only slightly less active than succinate. It seems apparent that from glutarate upward in the homologous series the carboxyl groups are too far away to have any effect upon each other and these higher members act more like the monocarboxylates. It also follows from these results that the closer the carboxyl groups are to each other, in the lower members of this series, the more reactive they are as complex formers.

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[1] A. W. Thomas and C. B. Kremer, THIS JOURNAL, 57, 1821 (1935).

Comparative Action of Isomeric Salts.—It follows from the experiments cited that anions containing the same number of combining groups in the same relative position (or separated sufficiently so as to be without effect upon one another) should exhibit essentially the same reactivity with basic thorium chloride hydrosols; but if the relative positions of the combining groups differ, then the reactivity differs and the one with the combining groups in closest proximity should be the more reactive. A study of the following isomeric salts offered an opportunity to test the above statement: (1) isomers in the monocarboxylic series—potassium butyrate and isobutyrate, potassium valerate and isovalerate; (2) optical isomers—the potassium salts of the inactive tartaric and malic acids and the salts of *d*-tartaric and *l*-malic acids; (3) *cis–trans* isomers—potassium maleinate and potassium fumarate.

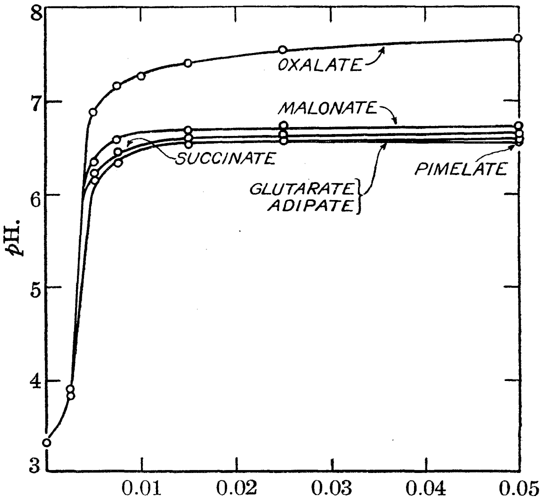

Fig. 1.—Effect of potassium salts of dicarboxylic acids upon the *p*H value of a basic thorium chloride hydrosol.

The ability of the monocarboxylic isomeric salts to raise the *p*H value of the sols was found to be identical throughout the concentrations used. The same was true for optical isomers. The fact that no measurable difference in effects between butyrate–isobutyrate and valerate–isovalerate existed, was not unexpected since the variation between each pair is restricted to that end of the molecule which does not enter into combination with the metal atoms of the micellar complex.

With the *cis–trans* isomers, however, potassium maleinate proved to be more effective than potassium fumarate. The results obtained with these two isomers upon two of the hydrosols (typical of all) are depicted in Fig. 2. It is interesting to note in this connection that in the crystalloidal chemistry of certain metals, the *cis* acid, citraconic, is a more active complex former than the *trans* acid, mesaconic.[2] Likewise, when the combining groups are hydroxylic rather than carboxylic, the *cis* diols are more active than the *trans* diols.[3]

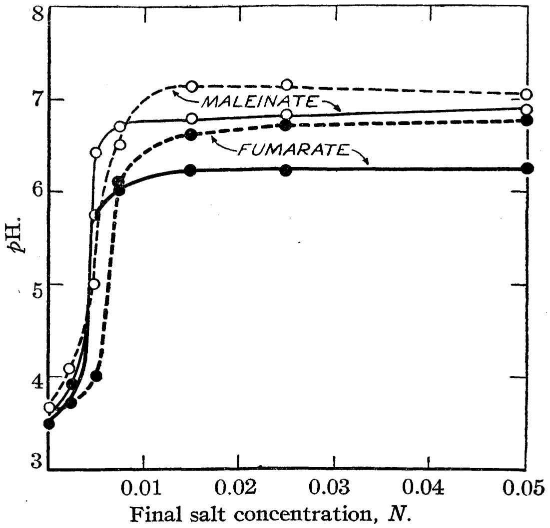

Fig. 2.—Effect of potassium maleinate and fumarate upon *p*H values of basic thorium chloride hydrosols: – – – –, Sol F; ————, Sol E.

Action of Hydroxy Organic Anions.—When certain salts, such as potassium citrate, tartrate, malate, glycolate, lactate and mucate were added to basic thorium chloride hydrosols, small amounts produced precipitation followed by redispersion upon further addition of the electrolyte. Electrophoresis experiments upon the redispersed solution showed that the charge on the micelles (originally positive) had become negative. Other organic anions, not containing hydroxy groups, did not cause charge reversal with the exception of malonate which showed a slight tendency at higher concentrations which may be explained by the existence of the enol form.

Since the potassium salts of hydroxy acids produced negatively charged micelles when added to basic thorium chloride sols, it was thought probable that negatively charged hydrosols could be produced by action upon hydrous thoria. Hy-

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(2) E. Ferrell, J. M. Ridgion and H. L. Riley, *J. Chem. Soc.*, 1440 (1934).

(3) J. Böeseken, *Bull. soc. chim.*, **53**, 1332 (1933).

drous thoria was prepared by precipitation from thorium chloride with ammonia and was washed free of chloride by distilled water with the aid of a centrifuge. Portions of the purified hydrate were then placed in 250-cc. "Non-Sol" bottles, 200 cc. of 0.1 N salt solution added and the mixture rotated at 7 r. p. m. at 25 ± 0.2° for forty-eight hours. At the end of that period the mixture was centrifuged (1200 r. p. m., 42 cm. radius) for one hour and the charge on the dispersed material determined in an electrophoresis "U" tube. The salts used, potassium, citrate, tartrate, glycolate, mucate and malate, all produced turbid dispersions containing negatively charged micelles.

Action of Concentrated Acids.—It was noted, upon the addition of 12 molar nitric acid to a thorium oxychloride sol, that the latter was first precipitated; then on further addition of the acid, the precipitate redispersed forming a solution as turbid as the original sol. When water was then added to this turbid solution, reprecipitation occurred and on adding a small excess of water, a solution resembling the original sol in turbidity, was produced. Addition of concentrated nitric acid again first produced a precipitate, then a turbid liquid; and water again reversed the procedure as described above.

The sol produced on addition of excess concentrated nitric acid existed at room temperature for only ten or fifteen minutes, when it changed to a clear crystalloidal solution. The sol produced by adding excess water to the acid sol was much more stable, dispersing to a clear solution after standing a few hours at room temperature. Electrophoresis experiments showed that the acid sol micelles were negatively charged; while the micelles of the sol obtained upon addition of excess water to the acid sol, were positively charged.

The following explanation is advanced for what has been described. Nitrate ion has but slight tendency to be coördinatively bound to the central atom. Increasing the concentration, however, will cause such a weak "penetrator" to enter the micelle, but it will only remain in the complex if a high concentration of nitrate ion be maintained. Thus when concentrated nitric acid is added to the sol, the increasing concentration of nitrate ion forces some of this anion into the micelle, replacing aquo groups mainly, while the hydrogen ion converts hydroxo groups in the complex to aquo groups. Replacement of water molecules by nitrate ions results in a diminution of charge on the cation, leading eventually to precipitation. Upon further addition of acid, continued penetration of the nitrate ion takes place and the charge on the micelle becomes negative. After this has happened, addition of water decreases the concentration of nitrate ion present. Nitrate ion therefore moves out of the complex and is replaced by water molecules. This continues upon further dilution and is accompanied by a decrease in negative charge on the micelle until once again the vicinity of zero charge is reached and precipitation occurs. Excess water causes further replacement of nitrate by water molecules and now the charge on the particles becomes positive and the precipitate redisperses.

While the above is happening, deolation is also occurring owing to the high hydrogen-ion activity of the solution. Continued deolation leads to the crystalloidal state. Stiasny[4] working with the crystalloidal chromium complexes, has pointed out that order of tenacity with which certain anions are held to the metal atom and the resulting deolating effect is $SO_4 > Cl > NO_3$. In the case of hydrous alumina[5] and with basic zirconium chloride hydrosols[6] it has also been shown that deolation occurs more readily when the aluminum oxide is treated with acids or the zirconium sol with salts containing strongly coördinative binding anions. The increased attraction of the metal atom for these anions apparently lessens the strength with which it holds the ol groups and deolation by acid is thereby facilitated. The metal atom in this case has little attraction for nitrate and therefore the ol bonds are considerably stronger than if chloride or sulfate were in the complex. It should therefore be expected, with acids of comparable strength as to hydrogen ion, that the order for deolation and subsequent formation of the crystalloidal state should be $H_2SO_4 > HCl > HNO_3$. That this is true for basic thorium sols has been demonstrated qualitatively. The deolating reaction described above with 12 M nitric acid, required from ten to fifteen minutes for completion.[7] When 12 molar hydrochloric acid was used, precipitation occurred and further addition of this acid caused redispersion as in the case of nitric acid but deolation to the crystalloidal state was much

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(4) E. Stiasny, "Gerbereichemie," Verlag Theodor Steinkopff, Dresden-Blasewitz, Germany, 1931, p. 351.

(5) A. W. Thomas and R. D. Vartanian, THIS JOURNAL, **57**, 4 (1935).

(6) A. W. Thomas and H. S. Owens, *ibid.*, **57**, 2131 (1935).

(7) There are individual differences in sols.

apid. Dilution with water tended to effect al reversal, but this procedure could not be ed as in the case of nitric acid. When the sed was 6 molar sulfuric, precipitation re- followed by rapid conversion to a clear lloidal solution on addition of more acid and ersibility with water could be effected.

Summary

reactivity of an organic anion with basic m chloride hydrosols depends not only on mber of combining groups present, but on elative positions, and the closer the com- groups are to each other, the more active anion.

Hydroxy organic anions reverse the charge of basic thorium chloride (cationic) micelles producing aniono thoreate micelles. Peptization of hydrous thorium dioxide by the potassium salts of these anions also results in the production of hydrosols containing negatively charged micelles.

Concentrated nitric acid reverses the charge of basic thorium chloride micelles producing short-lived nitrato thoreate micelles.

The order of deolation of basic thorium chloride sols and subsequent formation of the crystalloidal state with concentrated inorganic acids has been found to be sulfuric > hydrochloric > nitric.

NEW YORK, N. Y. RECEIVED OCTOBER 2, 1935

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

A New Organic Reagent for Cadmium

BY ALFRED W. SCOTT AND ELEANOR G. ADAMS

Introduction

lack of a specific easily recognizable test for um ion in the presence of cupric ion has rise to many difficulties, especially in ele- ry classes in qualitative analysis. Copper ally converted into the cyanide complex or itated as the sulfide. The cyanide separa- s dangerous for inexperienced students, and dmium sulfide precipitated by the second d is often masked by traces of impurities. nvestigation was undertaken in an attempt pare a new organic reagent which would be c for cadmium ion, characterized by a d precipitate, sensitive to fairly low concen- ns of the metallic ion and not too easily ed by interfering ions.

eral new organic compounds containing were prepared by combining organic radi- hich are present in reagents that have been useful in detecting cadmium ions. These tested as analytical reagents with nitrate ons of the cations met in qualitative analy- The most effective precipitant prepared was uinolyl)-4-allyl thiosemicarbazide. A satu- solution of this reagent in 50% alcohol, in resence of potassium iodide, gave a yellow itate with cadmium ion as dilute as one part nillion. Cadmium was detected in the pres- of copper (in the absence of ammonia and sulfate) by the addition of potassium iodide solution, thiosemicarbazide solution, and ammonium hydroxide; cadmium gave a yellow precipitate, while copper gave a blue solution.

Experimental

Materials.—Allyl isothiocyanate, 2-aminoresorcinol hydrochloride (practical), 2-amino-4-nitrophenol, and 2-quinolylhydrazine, all were from Eastman Kodak Company.

$C_3H_5NHCSNHC_6H_3(OH)_2$, **N-Allyl-N′-2,6-dihydroxyphenyl thiourea,** was prepared from equimolar solutions of allyl isothiocyanate and 2-aminoresorcinol hydrochloride in 95% alcohol. The brown needles from alcohol–ether decomposed at 230°. This compound is too insoluble in water for use as a precipitant.

$C_3H_5NHCSNHC_6H_3(OH)(NO_2)$, **N-Allyl-N′-2-hydroxy-5-nitrophenyl thiourea,** was prepared from equimolar solutions of allyl isothiocyanate and 2-amino-4-nitrophenol in ether. The orange-red needles, melting at 122°, are soluble in alcohol, and somewhat soluble in water and in chloroform. The saturated water solution of this reagent added to nitrate solutions of the cations gave precipitates only with cadmium, copper, iron and nickel, the first three being yellow and the last white. The use of a 1% solution of the reagent in alcohol makes the precipitation of cadmium more complete and more sensitive, but care must be taken that excess reagent itself does not precipitate because of its slight solubility in water.

$C_3H_5NHCSNHNHC_9H_6N$, **1-(2-Quinolyl)-4-allyl-thiosemicarbazide,** was prepared from 10 cc. of allyl isothiocyanate and 16 g. of crystalline 2-quinolylhydrazine in ether; yield 20 g. Slow recrystallization from ether gave colorless crystals, melting at 158°, fairly soluble in ether alcohol, and benzene, slightly soluble in cold water. The molecular weight of the thiosemicarbazide was estimated by the Rast camphor method to be approximately 258. Element analyses proved the presence of C, H, N and S.

Anal. Calcd. for $C_{13}H_{14}N_4S$: C, 60.47; H, 5.43; N, 21.72. Found: C, 59.69; H, 5.41; N, 21.77.

The saturated solution of this reagent in 50% ethyl alcohol (0.05 g. per 100 cc.) added to normal nitrate solutions of the cations gave yellow precipitates with cadmium, zinc, and mercurous mercury, and brown precipitates with copper, nickel, cobalt, and silver. The presence of various anions (chloride, bromide, iodide, sulfate, cyanate, and thiocyanate) was found to affect the completeness of precipitation and the appearance of the precipitate to some extent. The most satisfactory test was secured in the presence of iodide ions, when a bright greenish-yellow precipitate was formed even with traces of cadmium ions. This precipitate contained cadmium, nitrogen, sulfur, potassium and iodine.

The sensitivity of the cadmium thiosemicarbazide iodide precipitation was tested by adding 1 cc. of 50% aqueous alcohol (saturated with the thiosemicarbazide and with potassium iodide) to 10 cc. each of solutions con respectively, 1, 0.05 and 0.01 mg. of cadmium ion.

$Cd(NO_3)_2 \cdot 4H_2O$, g./l.	Cd^{++}	Effect
0.278	1/10,000	Filterable precipitate
.0139	1/200,000	Filterable precipitate
.00278	1/1,000,000	Opalescence; precipitate after two minutes

The detection of cadmium ions in the presence o ions was accomplished by a modification of th procedure, in the absence of the ions of zinc, nic cobalt. Interfering ammonia and sulfate, if prese removed by boiling off ammonia and precipitat sulfate with barium chloride. To this solution wa saturated potassium iodide solution and brown iodide precipitated. Without filtering, the add saturated thiosemicarbazide solution (50% alcoh cipitated the yellow cadmium thiosemicarbazide complex. Upon addition of ammonium hydrox copper salt dissolved but not the cadmium c Thus a blue solution indicated copper, while a yell cipitate indicated cadimum.

Summary

1. N-Allyl-N′-2,6-dihydroxyphenyl tl and N-allyl-N-2-hydroxy-5-nitrophenyl were prepared and tested as analytical re

2. 1-(2-Quinolyl)-4-allyl thiosemicarb prepared. It is a sensitive precipitant cadmium ion, and a good qualitative re cadmium in the presence of copper.

ATHENS, GA. RECEIVED JUNE

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE

Activity Coefficients of Sulfuric Acid in Anhydrous Ethyl Alcohol from Electrom Force Data

BY A. W. SCHOLL,[1] A. WITT HUTCHISON AND G. C. CHANDLEE

In continuation of the work in this Laboratory on the properties of non-aqueous solutions it was thought that a study of the activity coefficients of sulfuric acid in ethyl alcohol solutions would be of interest. Data were obtained by the electromotive force method using the cell H_2, H_2SO_4, Hg_2SO_4s, Hg. Activity coefficients were calculated from these data by the use of the Debye–Hückel first approximation and also by the use of the extended equation of Gronwall, La Mer and Sandved.

Experimental

All electromotive force measurements were made with a Leeds and Northrup type K potentiometer by the null method. A Weston standard cell was used as a reference. It was checked from time to time during the course of the experiments against several other cells of the same type recently calibrated at the Bureau of Standards. A type R galvanometer was used as an indicating inst All lead wires and the standard cell were shielded.

The thermostat was maintained at a tempera 25 ± 0.01°. The cells were placed in a copper tan with oil, suspended in the thermostat water.

The cells were of the H type and were made by c ing two Pyrex test-tubes by means of a short p Pyrex tubing. A piece of 7-mm. tubing was seale bottom of each test-tube and bent so that it becam lel to the tube. One tube then became the m mercurous sulfate half-cell, and connection was m it by means of a platinum wire dipping into the m The test-tubes were fitted with well ground, gas tigh stoppers. Through the one stopper two tubes were into the ends of which platinum wires were sealed t as the platinum electrodes. Hydrogen was bubl through the bottom of the hydrogen half cell and e from the top through an alcohol trap. It was sa with alcohol by bubbling it through a wash bott mersed in the thermostat, containing the solutio measured.

The more concentrated solutions were prepared addition of sulfuric acid from a weight pipet to a w

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[1] From a thesis presented by A. W. Scholl in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1934.

amount of the alcohol. The others were prepared by dilution of the stronger solutions. The electrodes were freshly platinized before each run. It was found that the cells reached a constant electromotive force (±0.2 mv.) after hydrogen had bubbled through them for about one hour. In the several cases studied the cells maintained this value for at least five or six hours. In general when the value had been constant for ninety minutes it was assumed that equilibrium had been reached.

Materials.—Ninety-five per cent. ethyl alcohol was purified by distilling from concentrated sulfuric acid (15 cc. of acid per liter of alcohol) to remove amines and most of the water. The distillate was next distilled from alkaline silver nitrate (5 g. per liter) to remove the aldehydes and similar oxidizing bodies. Finally, the last trace of water was removed by refluxing with fresh calcium oxide and then fractionated from aluminum ethoxide. The alcohol thus obtained had a specific conductivity of 1.5×10^{-7} mhos.

Anhydrous sulfuric acid was made by mixing concentrated acid with fuming acid of Baker's Analyzed Grade, as described by Kendall and Carpenter.[2] It had a freezing point of 10.46°.

Mercurous sulfate[3] was made electrolytically from redistilled mercury and dilute sulfuric acid. It gave results in good agreement with those obtained by using Baker's C. P. grade.

Mercury of C. P. grade was further purified by washing with dilute nitric acid, dilute alkali and water and then by vacuum distillation.

Electrolytic hydrogen was passed over finely divided platinum in a furnace at approximately 600° to remove the oxygen. The hydrogen was then dried with phosphorus pentoxide and passed into the cell through a saturating trap kept at the thermostat temperature.

Results and Discussion

The experimental values of the electromotive forces corrected to a partial pressure of hydrogen of one atmosphere together with the corresponding molalities are listed in Table I. In the third column are listed values of the square root of the ionic strength calculated from the volume concentration on the assumption that the sulfuric acid is completely dissociated. The concentrations were obtained from the molalities by use of the expression $C = M/(V_0 + K\text{M})$, where V_0 is the specific volume of pure alcohol and where K was given the value of 0.034 corresponding to its value in aqueous solutions of sulfuric acid.

In order to calculate the activity coefficient by the use of the well-known equation $E = E_0 - (3RT/2F) \ln \gamma M4^{1/3}$, it is necessary to evaluate E_0. This is ordinarily done by extrapolating to zero concentration a plot of E_0' against some function of the concentration where $E_0' = E + (3RT/2F) \ln M4^{1/3}$. Examination of the lower curve of Fig. 1 where the open circles represent experimental values of E_0' plotted against the square root of the ionic strength show that a simple extrapolation would yield an uncertain value

TABLE I

EXPERIMENTAL DATA AND THE COMPUTATION BY THE DEBYE–HÜCKEL THEORY AS A 1,2-TYPE ELECTROLYTE. $N = 2$, AND "A" = 2.5 Å.

Soln. no.	Molality	$\mu^{1/2}$	E	Calcd. $-\log \gamma$	E_0
1	0.003562	0.0916	0.6478	0.4777	0.406
2	.007748	.1345	.6468	.6641	.419
3	.01143	.1641	.6457	.7815	.422
4	.01303	.1752	.6433	.8231	.421
5	.01820	.2071	.6426	.9381	.423
6	.02912	.2619	.6416	1.117	.426
7	.04154	.3128	.6344	1.266	.417
8	.04622	.3250	.6337	1.270	.420
9	.05462	.3670	.6327	1.405	.414
10	.07738	.4269	.6254	1.549	.407
11	.1170	.5241	.6192	1.747	.399
12	.1649	.6217	.6170	1.916	.396
13	.2245	.7248	.6104	2.070	.387
14	.2801	.8090	.6064	2.179	.382
15	.5854	1.165	.5900	2.531	.363
16	.6667	1.242	.5895	2.589	.357

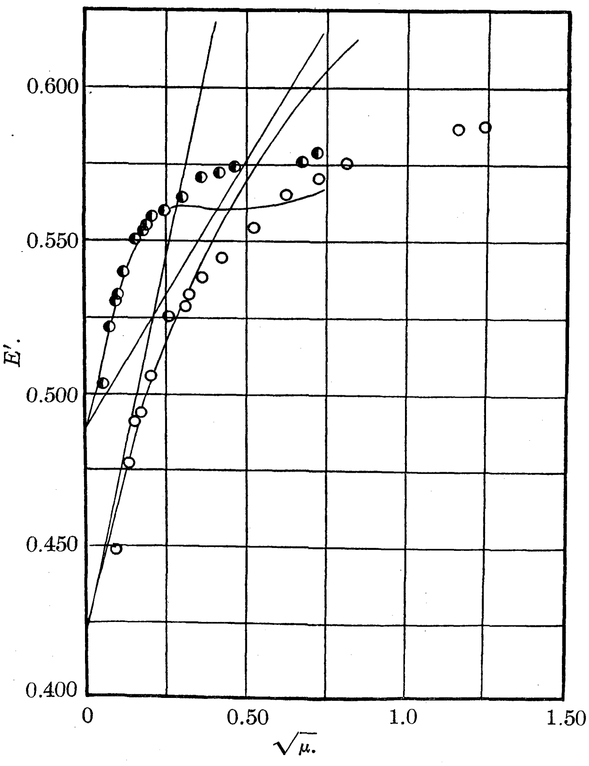

Fig. 1.—Open circles represent experimental data as a 1,-2 type electrolyte. Shaded circles represent experimental data as a 1,-1 type electrolyte. Straight lines are the limiting law in each case.

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[2] Kendall and Carpenter, THIS JOURNAL, **36**, 2498 (1914).

[3] Carhart and Hulett, *Chem. News*, **90**, 226 (1904).

of E_0 in this case. If it is assumed that the Debye–Hückel equation[4]

$$-\log \gamma = \frac{2.96\ Z_1Z_2\ \sqrt{\mu}}{1 + .592 \times 10^8\ a\ \sqrt{\mu}}$$

with a reasonable value of the ion diameter is applicable to these solutions a value of E_0 may be calculated from each experimental measurement. The constancy of these values indicates the validity of the assumptions made. In columns five and six of Table I values of $-\log \gamma$ and of the corresponding E_0 are listed. These calculations were made with a value of 2.5×10^{-8} cm. for the ion diameter. In the figure the solid curve represents a plot of E_0' calculated from the values of $-\log \gamma$ and the value of 0.420 for E_0. The slope of the limiting law is also indicated on the figure. As may be seen from the figure and also from Table I the calculated and experimental values are in reasonably good agreement in the dilute solutions except for the first point.

Since the dissociation of the second hydrogen ion from sulfuric acid is not complete even in water solutions it might reasonably be assumed to be even less so in the solutions of alcohol. The limiting case would of course be one in which only the primary dissociation would be considered. The equation for the electromotive force, from this point of view, becomes $E = E_0 - (2RT/2F) \ln \gamma M$ and the ionic strength is equal to the concentration. Calculations from this point of view were made using the extended equation of Gronwall, La Mer and Sandved,[5] and an assumed ion diameter of 1.7×10^{-8} cm. The shaded circles of the figure represent the experimental points, the full curve the calculated values and the straight line the limiting law on this basis. Results of these calculations showed that the equation is not convergent for this small ion diameter in alcohol. However, a larger value for the ion diameter would not be in agreement with the experimental values.

Since the experimental curve lies above the limiting law in dilute solutions it is obvious that the application of the first approximation of Debye and Hückel will not account for the experimental curve. Although the extended equation does give constant values for E_0 on this basis the significance of this is perhaps questionable in view of the non-convergence of the series.

Summary

Activity coefficients of sulfuric acid solutions in ethyl alcohol have been determined by measurement of the cell H_2, H_2SO_4, $Hg_2SO_4(s)$, Hg. The data have been treated by the Debye–Hückel equation and by the extended equation of Gronwall, La Mer and Sandved.

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[4] The constants in this equation were evaluated using for the dielectric constant of ethyl alcohol the value of 24.20 as given by Åkerlöf [THIS JOURNAL, **54**, 4126 (1932)].

[5] Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928). For alcohol solutions at 25° the constants become, +5.00, −5.30 and −28.11.

STATE COLLEGE, PENNSYLVANIA RECEIVED AUGUST 5, 1935

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY, BROWN UNIVERSITY]

The Nature of the Surface of Copper Catalysts

BY W. WALKER RUSSELL AND LEONARD G. GHERING[1]

Experimental evidence concerning the nature of catalytic surfaces is conflicting. Kinetic measurements are in general consistent with the concept of a uniformly active catalytic surface, while adsorption phenomena for the most part require a surface of non-uniform nature. This apparent conflict would largely disappear were it found that the reaction catalyzed proceeded predominantly on a relatively few surface types out of many existing on a surface. It is well recognized that a knowledge of the different qualities of catalytic surface present and their distribution is vital to any theory of the catalytic surface or mechanism of catalysis.

By studying the changes in catalytic activity produced by controlled, selective poisoning, much can be learned about the nature of a catalyst surface. Studies have been made of synthetic ammonia catalysts[2] using oxygen and water as poisons; of thoria as a catalyst using water and acetaldehyde to poison the decomposition of

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[1] Metcalf Fellow in Chemistry at Brown University.

[2] J. A. Almquist and C. A. Black, THIS JOURNAL, **48**, 2814 (1926); J. A. Almquist, *ibid.*, **48**, 2820 (1926); P. H. Emmett and S. Brunauer, *ibid.*, **52**, 2682 (1930).

ethyl alcohol;[3] and of platinum[4] employing mercury ions as poison for hydrogen peroxide decomposition and for hydrogenation of several unsaturated organic compounds in the liquid phase. In this last work the activity of the catalyst was found to decrease in a linear manner as the extent of poisoning increased, and this has been interpreted to mean that the catalytic surface of platinum is predominantly uniform in character.

Previous work[5] had shown oxygen to be strongly sorbed by active copper catalysts, and since the heats of sorption decreased with increasing sorption, at least some selectivity in the sorption process was to be anticipated. Furthermore, sorbed oxygen was known[5] to be capable of completely suppressing the hydrogenating activity of copper at 0° and yet to be easily removed by subsequent reduction at higher temperatures. Because of these facts, it was decided to use oxygen as a poison in the study of the nature of the catalyst surface which the well-known ethylene–hydrogen reaction finds active at 0°. Although ease of manipulation has caused this reaction to be employed frequently in a static system, a flow method has been used throughout the present work in order that the results should be free from errors due to adsorption, induction periods,[6] transitory fluctuations in catalytic activity,[7,8] and the like. The principal significance of the work which follows lies in its elucidation of the nature of the surface of catalytically active copper in the light of three different methods of oxygen poisoning as well as measurements of heats of oxygen sorption.

Apparatus and Experimental Method

Apparatus.—The apparatus used in the controlled poisoning of the catalysts was similar to that used earlier[9] except that provision was now made for admitting gases to either one or both ends of the catalyst bulb. The reaction velocity measurements necessitated ethylene and hydrogen flow-meters which were cut in ahead of the catalyst bulb and trap. These flow-meters were filled with dibutyl phthalate. To the exit tube of the catalyst bulb there was attached a constant-head gas collecting buret[10] so designed that measured volumes of the exit gases could be collected without producing any disturbance of gas flow in the system.

The Bunsen ice calorimeter used for the thermal measurements was essentially of the type already used by others[11] except that the capillary was permanently sealed in place and the stopcock and mercury reservoir for adjusting the position of the mercury thread were omitted. Also, because the calorimeter construction prevented direct observation of the ice mantle, an indicator manometer was temporarily attached to the outer end of the capillary during the formation of the mantle. After a quick movement of the manometer mercury signaled the formation of a mass of ice crystals, heat was introduced until the original manometer reading was nearly reached thus leaving but a few ice nuclei. Upon cooling a second time the mantle formed slowly and the amount of mercury in the calorimeter was such that a suitable mantle thickness was obtained when the mercury thread was well out on the scale. Otherwise the method of using and calibrating the calorimeter was the same as before.[5]

Preparation and Purification of Gases.—The treatment of the helium, hydrogen and oxygen was the same as already described[9] except that in the reaction velocity measurements the hydrogen was further purified by passage over a thoria promoted nickel scrubbing catalyst heated to 250°. Cylinder ethylene was passed at room temperature over a similar scrubbing catalyst after first going through activated charcoal at about 25°. After metering, both gases were further dried and mixed in a tube containing anhydrone and then passed through a trap cooled with solid ammonia before admission to the catalyst. Cylinder nitrous oxide was purified by passing through caustic potash solution, calcium chloride, phosphorus pentoxide and then into a liquid air trap from which only the middle raction was used.

Preparation of Catalysts.—Granular copper catalysts were prepared by sifting Kahlbaum granular cupric oxide "for analysis" so as to retain only particles of about 2–4 mm. diameter, and then reducing slowly with hydrogen at 250°. Cu XXI weighed 36.28 g. Cu XXII was produced by again reducing Cu XXI after accidental admission of air to the latter at 180°. Cu XXII proved more active yet sorbed somewhat less oxygen than Cu XXI. Cu XXIII and Cu XXV were approximately half portions of Cu XXII and weighed 19.83 g. and 16.45 g., respectively. Cu XXIV was produced from Cu XXIII by sintering the latter at 400°.

Procedure for Reaction Velocity Runs.—The reaction velocity runs were made, on either poisoned or unpoisoned surfaces, by admitting hydrogen to the evacuated catalyst at 0° and immediately displacing it with the metered, one-to-one ethylene–hydrogen reaction mixture at a constant rate of flow, *e. g.*, 10 to 20 cc. per minute. Zero time was taken as the instant of admitting the reaction mixture, and after five minutes the conversion was computed from the flow meter readings and the time required to collect 10 or 20 cc. of exit gases. Similar data were taken at ten-minute intervals for from one and one-half to two hours, the period of the run. At the end of the run the catalyst was flushed with hydrogen at 0° for half an hour, and then

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[3] E. K. Rideal and G. I. Hoover, THIS JOURNAL, **49**, 104 (1927).

[4] E. B. Maxted and G. J. Lewis, *J. Chem. Soc.*, 502 (1933); E. B. Maxted and V. Stone, *ibid.*, 672 (1934).

[5] W. W. Russell and O. C. Bacon, THIS JOURNAL, **54**, 54 (1932).

[6] E. K. Rideal, *J. Chem. Soc.*, **121**, 309 (1922).

[7] G. Harker, *J. Soc. Chem. Ind.*, **51**, 323T (1932).

[8] E. G. Insley, *J. Phys. Chem.*, **39**, 623 (1935).

[9] W. W. Russell and L. G. Ghering, THIS JOURNAL, **55**, 4468 (1933).

[10] L. G. Ghering, Thesis, Brown University, 1935.

[11] M. J. Marshall and H. E. Bramston-Cook, THIS JOURNAL, **51**, 2019 (1929).

heated slowly to the temperature of reduction at which the hydrogen flow was continued for the necessary time. The catalyst was then evacuated.

Direct Oxygen Poisoning.—In order to obtain reliable and reproducible catalyst activities with this and the other methods of poisoning, it was necessary to employ a strictly standardized method of procedure. The well-evacuated catalyst was cooled to 0°, a small amount of helium added, and then an accurately measured amount of oxygen was admitted slowly in small increments to both ends of the catalyst bulb. As previously found[5] the oxygen was instantaneously, completely and irreversibly sorbed until saturation of the surface was closely approached. Then sorption became less instantaneous. Because some slow sorption occurred near saturation, the oxygen sorptive capacity of the copper could not be very accurately determined, but was taken arbitrarily as the total amount sorbed when an increment equal to about 2% of the previous sorption required as long as five minutes to drop to a pressure of 0.05 mm. After a reaction velocity run on the oxygen poisoned surface, reduction with hydrogen was carried out at 275° for one hour followed by evacuation at 225° for two hours. Following a run on an unpoisoned surface the temperature of reduction was 225.°

Indirect Poisoning with Oxygen.—Indirect poisoning was accomplished by three methods of selective reduction. Selective reduction (1), used for Cu XXI, comprised flushing the catalyst for one hour at 275° followed by evacuation for two hours at 225°; cooling to 0° in helium and sorbing an accurately measured amount of oxygen (15 cc. equal to about 85% saturation) from both ends of the catalyst bulb; adding a known increment of hydrogen (5 to 6 cc.); raising the temperature to 50° in the first half hour, to 75° in the second half hour, to 100° in the next hour (about 95% of the hydrogen had now disappeared), and finally to 125° for two hours in order to make the hydrogen disappear completely; closing off the catalyst and removing water from the trap (solid ammonia removed) then evacuating the catalyst for one half hour at 150°; then repeating the procedure with successive increments of hydrogen until a surface poisoned with the desired amount of oxygen remained; and finally evacuating for three hours at 160° prior to a reaction velocity run. The amount of oxygen poisoning was considered to be the difference between the amount of oxygen initially sorbed and the oxygen equivalent of the hydrogen admitted to the catalyst. A very small correction was necessitated for any traces of hydrogen not reacting. The most completely unpoisoned surfaces were prepared by flow reduction of sorbed oxygen for ten hours at 160° followed by evacuation for three hours at the same temperature.

Selective reduction (2), used for Cu XXII, differed from selective reduction (1) in that only 10 cc. of oxygen (67% saturation) were initially sorbed; in that the successive increments of hydrogen were somewhat smaller (3 to 4 cc.); and in that the time intervals were an half hour each at 25, 50, 75 and 100°. Probably due to the lower maximum temperature, about 5% of the hydrogen did not react under this treatment so that the oxygen remaining on the surface could not be as confidently calculated as before. Therefore, the amount of oxygen poisoning was determined also at the end of a velocity run by weighing the amount of water retained by a phosphorus pentoxide tube during the subsequent reduction at 275°. This "gravimetric" determination of oxygen poisoning has an advantage over the "buret" method in that it is direct, and it constitutes a valuable check on the latter method.

Selective reduction (3), used for Cu XXIII, differed from selective reduction (2) in that the reduction was prolonged for an additional hour at 100° and followed by an hour at 125°. The amount of oxygen poisoning was determined by the gravimetric method and also by the buret method since the hydrogen again reacted practically completely. The agreement of the two methods is apparent from experimental points shown on Curve 6, Fig. 2.

Nitrous Oxide Poisoning.—Direct poisoning by nitrous oxide was accomplished by two methods. Nitrous oxide poisoning (1), used for Cu XXIV, comprised flushing the surface with hydrogen for five hours at 300° and evacuating for two hours at 375°; cooling to liquid ammonia temperature; admitting a measured amount of nitrous oxide; raising the temperature to 300° for one hour; and then cooling to 0°. The amount of oxygen poisoning was determined after the velocity run by the gravimetric method.

Nitrous oxide poisoning (2), used for Cu XXV, differed from nitrous oxide poisoning (1) in that the copper was flushed with hydrogen first at 275° for two hours, then at 225° for three hours and finally was evacuated for two hours at 225°. Furthermore, the nitrous oxide was heated only to 160°, which was the highest temperature to which sorbed oxygen was exposed in any of the selective reductions.

Experimental Results

A. Preliminary Work.—Although a number of copper catalysts both promoted and unpromoted, and in pulverulent and supported form were investigated, the granular copper[12] produced by the reduction of Kahlbaum cupric oxide proved to be the most active for the hydrogenation of ethylene at 0°. The reaction velocity–time curves obtained with all catalysts had a characteristic form when hydrogen was the gas to be displaced by the reaction mixture. During the first half hour the percentage conversion decreased at a diminishing rate and then remained constant, or at most showed a very gradual decrease with time (indicating that the scrubbing catalysts required regeneration). If ethylene were the gas displaced by the reaction mixture, the curve rose from a low initial conversion during the first half hour and then followed the course of the normal curve. It may be noted that the same type of curve was obtained for this reaction with a nickel catalyst down to −50°. Even with this metal when a steady state of conversion had been reached at 0° it was only necessary to displace temporarily the reacting gases with

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(12) Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, THIS JOURNAL, **57**, 65 (1935).

hydrogen in order to cause a marked increase in conversion which, however, soon dropped back to the lower value. The initial period of diminishing catalytic activity in the velocity runs appears to be due to a rather slow removal of adsorbed hydrogen by interaction and displacement with ethylene in the establishment of a steady state. This same phenomenon has been found for this reaction using copper in static systems by others.[7,8]

Preliminary studies using copper poisoned with oxygen sorbed at 0° showed that while there was an extremely slow removal of sorbed oxygen at 20°, in the reaction velocity runs, no sorbed oxygen disappeared at 0°. This was particularly important to establish because former work[5] with thoria promoted, pulverulent copper indicated that some of the oxygen sorbed at 0° could, if not subsequently heated, react with hydrogen at this temperature. In the present work even a slow loss of sorbed oxygen, in the steady state, would have been indicated in the velocity runs by an ascending section in the velocity–time curve, and this never occurred at 0°. Furthermore, the amounts of oxygen found present at the end of the velocity runs agreed, within the experimental error, with the amounts of oxygen present before the runs.

It became apparent early in the present work that the catalyst surfaces were extremely sensitive to slight variations in their mode of production. For example when oxygen was sorbed at 0° and then removed by hydrogen at a lower temperature than that used in the production of the surface, marked activation occurred. However, subsequent evacuation of this surface at this lower temperature caused a considerable loss (sintering) in this activation. In order to ensure reliable and reproducible catalyst activity, therefore, all details of procedure were strictly standardized.

B. Direct Oxygen Poisoning.—The effects of different amounts of oxygen poisoning upon the activity of Cu XXI are shown graphically in Curve 5, Fig. 2. The oxygen was admitted to both ends of the catalyst bulb at 0°. Catalytic activity was determined here, and in all of the remainder of this work, by use of the ethylene–hydrogen reaction at 0° employing a one to one reaction mixture. The recorded catalyst activity refers always to the steady state. Oxygen appears to be a uniformly effective poison and a slight extrapolation of Curve 5 shows catalytic activity to disappear completely at 40% (6.3 cc. of oxygen sorbed) saturation of the surface with oxygen. The linear relation shown by Curve 5 would not be expected in view of the fact that the heats of oxygen sorption on copper decrease with increasing sorption,[5] unless the reaction were proceeding on uniform catalytic surface, or the oxygen poisoning were non-preferential. The latter possibility seemed the more probable.

C. Heats of Oxygen Sorption.—In order to gain information about the distribution of oxygen throughout the catalyst mass in the direct poisoning experiments, oxygen was now admitted to only the top or the bottom of the catalyst bulb. Such a procedure should make no difference in the successive values of the heat of sorption if the oxygen were uniformly distributed. The experimental results obtained on Cu XXI are shown graphically in Fig. 1. Curve 4 is taken from earlier work on copper (Cu 11)[5] for purposes of comparison and represents a case where the oxygen has been admitted to the catalyst bulb entirely from one end. Also, in the case of Curve 2 oxygen was admitted to Cu XXI entirely at the top of the bulb. The somewhat lower initial heats of sorption shown by Curve 2 may be attributed to the slightly lower temperature of outgassing used, while the still lower values shown on Curve 4 may be explained, in part perhaps, by the fact that Cu 11 was in pulverulent rather than in granular form. It is at once apparent from a comparison of the smooth Curves 2 and 4 with Curves 1 and 3, that the different method of

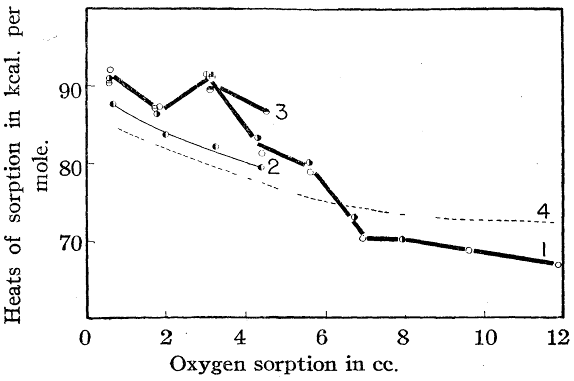

Fig. 1.—Heats of oxygen sorption on copper. Symbols indicate to which end of catalyst oxygen was admitted. Curve 1: ◑ bottom, ⦶ top, Run 138, Cu XXI; ○ top, ◡ bottom, Run 139, Cu XXI. Curve 2: ◐ top, Run 143, Cu XXI. Curve 3: ⊖ top, ◓ bottom, Run 144, Cu XXI. Curve 4: top, earlier work on Cu 11.

admitting oxygen employed for the latter curves has been responsible for the introduction of maxima and minima. In the case of the composite Curve 1 all of the oxygen except the third increment was admitted to the same end of the catalyst bulb. Curve 3 differs in that both the third and fourth (last) increments were admitted to the same end.

The interpretation of these curves seems fairly clear if, when an increment of oxygen is admitted to one end of a cylindrical copper catalyst, it is assumed that although the gas is pretty largely sorbed upon the first portions of the catalyst encountered, yet some preferential sorption occurs and a sorption gradient is set up in which the concentration is greatest on those parts of the catalyst surface first contacting the oncoming oxygen molecules. A larger and larger part of each successive increment of oxygen admitted to the given end will be sorbed upon previously, partially saturated surface with the observed decrease in the heats of sorption, which can be neither strictly integral nor differential values. A comparison of the fourth points on Curves 1 and 3 indicates the additional decrease in heat of sorption which an increment of oxygen suffered when it had to encounter surface which had been partially saturated by two, rather than one earlier increment of oxygen. When in addition to traversing surface partially saturated by earlier increments from the same end, an increment of oxygen meets surface saturated in part by oxygen admitted to the other catalyst end, an abnormally large decrease in heat of sorption would be anticipated. With Curve 1 it is clear that the third increments of oxygen were sorbed upon surface entirely unreached by the first and second increments admitted from the other end. It was not until five increments were admitted from one end, that the drop in this curve indicates that oxygen had penetrated to surface which sorbed the single increment admitted to the other end. When increments of oxygen were added alternately to the two ends of the granular copper catalyst, a curve (not shown) was obtained which showed a sharp drop at roughly 70 k. cal. and about 5 cc. of oxygen sorbed. From a slight extrapolation of Curve 5, Fig. 2, it is clear that when oxygen was admitted to both ends simultaneously, no more than 6.3 cc. was necessary for complete penetration of the catalyst. From the foregoing it appears that from 5 to 6 cc. of oxygen was required in the direct oxygen poisoning experiments before all parts of the catalytically active surface of the granular catalyst came into contact with any oxygen. Thus as far as surface capable of catalyzing the ethylene–hydrogen reaction is concerned, the direct sorption of oxygen proves to be largely, if not entirely, non-preferential. Therefore, no significant correlation can be expected between catalytic activity and either extent of direct oxygen poisoning, or heats of sorption, and the linear relation shown in Curve 5, Fig. 2, need give no true picture of the catalyst surface.

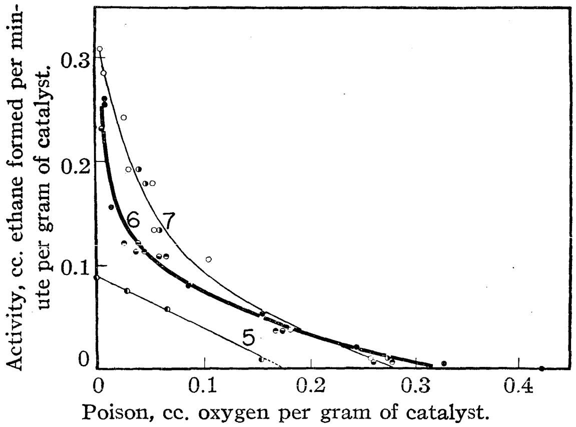

Fig. 2.—Direct and indirect oxygen poisoning. Direct poisoning: Curve 5, Runs 131–137 on Cu XXI at gas flow (cc. per min.) of H_2 = 5.9 and C_2H_4 = 5.6.

Indirect poisoning by means of selective reductions (S.R.): Curve 6, S. R. (1), ● "buret" method, Runs 153–161 on Cu XXI at gas flow of H_2 = 11.6 and C_2H_4 = 11.2; S. R. (3), ◓ "buret" method, ◒ "gravimetric" method, Runs 180–185 on Cu XXIII at gas flow of H_2 = 5.9 and C_2H_4 = 5.6. Curve 7, S.R. (2), ◑ "buret" method, O "gravimetric" method, Runs 166–174 on Cu XXII at a gas flow of H_2 = 11.6 and C_2H_4 = 11.2.

D. Indirect Oxygen Poisoning.—Inasmuch as it was clear from the work already done that a preferential poisoning of copper had not been achieved, it was decided to investigate the possibility of a selective removal of oxygen from a previously poisoned surface. Curves 6 and 7, Fig. 2, relate catalytic activity and various amounts of oxygen poisoning produced by the successive removal of larger and larger portions of previously sorbed oxygen by means of the careful, low-temperature reductions with measured amounts of hydrogen, described in detail under Experimental Method. Curve 7 was obtained with Cu XXII, which was Cu XXI after it had been accidentally activated, and thus its major portion lies above Curve 6. Because of the experimental arrangements, the hydrogenation of ethylene on the nearly unpoisoned surface of Cu XXII was now close to 100%. The two uppermost points on Curve 7 are, therefore, somewhat too low and thus displace the curve too far to the left. The various symbols employed on Curves 6 and 7 indicate the experimental method used in determining the amount of oxygen poisoning. The "buret" and "gravimetric" methods agree within their experimental errors. The lowest points on Curves 6 and 7, which were obtained after heating the sorbed oxygen to 160° for three hours and prior to any reduction, indicate that 15 cc. of oxygen poisoned Cu XXI completely while Cu XXII and XXIII showed a slight activity for 10 and 5.5 cc. of oxygen, respectively. Comparison of Curves 5 and 6 indicates that about twice as much oxygen was required completely to poison Cu XXI in the latter case. This decrease in the poisoning efficiency of oxygen may be attributed to a partial "regeneration" of the poisoned copper by the heating at 160°, a phenomenon encountered in earlier work.[5]

Inasmuch as not quite all of the oxygen poisoning could be removed even by very prolonged flow reduction at 160°, no experimental values could be obtained for completely unpoisoned surfaces. Complete removal of sorbed oxygen could be effected at 275° but this caused the loss in activity apparent from a comparison of the ordinates of the highest portions of Curves 5 and 6. The phenomenon of activating copper by alternate oxidation and reduction at successively lower temperatures is well known, and it now appears that oxygen sorption at 0° followed by reduction at 160° produced a more active surface than when reduction occurred at 275°, and when reduction was carried out at 90° about twice the activation noted above in Fig. 2 occurred. Furthermore, the activities of these surfaces were strictly reproducible. It is suggested that the activations in the present work are associated with a displacement of surface copper atoms during the highly exothermic oxygen sorption. It appears, therefore, that the surface uncovered in the selective reductions was not exactly the same surface which was previously poisoned, and it is not known whether the former would be more or less active than that produced by a similar reduction of normal copper oxide. Although the Cu XXI of Curve 6 is not quite the Cu XXI of Curve 5, it is believed that the two surfaces are not unrelated. The general form of Curves 6 and 7 shows that the removal of sorbed oxygen was accompanied by an exponential increase in the catalyst activity. It appears, therefore, that various portions of the sorbed oxygen differed in ease of reducibility. It is believed that this is to be attributed to the presence of different surface types on the copper upon which sorption occurred. It is felt that in the successive selective reductions the factor for regeneration was kept constant, and also that appreciable penetration of sorbed oxygen below the available surface of the catalyst was unlikely because the copper was only partially saturated with strongly held oxygen at 0° and became much less saturated at higher temperatures, and furthermore were the oxygen last removed, in the successive reductions, from the interior of the catalyst, it would seem necessary to associate the greatest catalyst activity with this location. It seems reasonable to conclude, therefore, that the successive reductions were selective in that surface less active in the ethylene–hydrogen reaction was released first and increasingly more active surface thereafter.

E. Nitrous Oxide Poisoning.—Because of the desirability of finding a direct method for poisoning copper it was decided to investigate the possibilities of decomposing nitrous oxide at the catalyst surface. Preliminary studies with a catalyst similar to Cu XXI at temperatures up to 75° indicated that decomposition occurred with no increase in pressure and that, therefore, most probably one atom of oxygen was sorbed for each molecule of nitrogen liberated. This mechanism, which also occurs in the case of silver,[13] was supported by later work with Cu XXIV and XXV. The preliminary studies also indicated that a portion of the nitrous oxide was decomposed probably instantaneously at −78°, and after sintering the copper at 400° some still decomposed similarly at −45°. In an endeavor to make the poisoning as selective as possible, Cu XXIII was now sintered at 400° thereby producing Cu XXIV, and the nitrous oxide was in all cases admitted at about −40°. To ensure more complete decomposition and a strong sorption of oxygen the temperature was then raised to 300° for Cu XXIV and to 160° for Cu XXV.

The effects of various amounts of poisoning

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[13] A. F. Benton and C. M. Thacker, THIS JOURNAL, **56**, 1300 (1934).

from nitrous oxide upon the catalytic activity of Cu XXIV are shown in Curve 8, Fig. 3. The considerable horizontal portion of this curve indicates that some 3.5 cc. of oxygen was taken up by the catalyst before its capacity for hydrogenating ethylene under the experimental conditions was diminished. Curve 8 falls fairly rapidly once poisoning starts but its form is obviously uncertain in the vicinity of the last point. Even though relatively large excesses of nitrous oxide were employed more complete poisoning was not achieved.

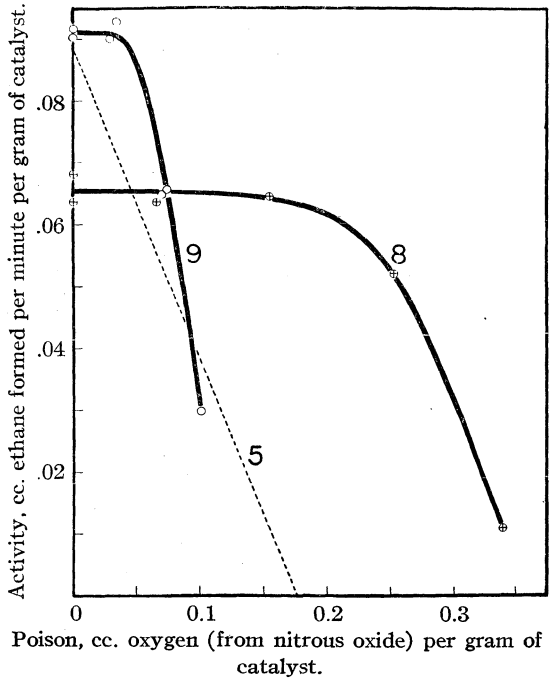

Fig. 3.—Nitrous oxide poisoning. Gas flow (cc. per min.): $H_2 = 4.6$; $C_2H_4 = 4.5$; Curve 8: nitrous oxide poisoning (1); Runs 190–195, Cu XXIV. Curve 9: nitrous oxide poisoning (2); Runs 204–211, Cu XXV. (Curve 5: direct oxygen poisoning (Fig. 2).)

Curve 9, Fig. 3, shows the effects of poisoning Cu XXV with nitrous oxide at the lower maximum temperature of 160°. In a comparison of unpoisoned surfaces the relative position of Curve 5 in Figs. 3 and 2 clearly shows the absence on Cu XXV of the activation characteristic of the indirect poisoning (Curve 6). While the displacement of Curve 9, Fig. 3, above Curve 8 is to be attributed to the greater activity of Cu XXV, the considerable lateral displacement of the former curve toward the left must be due, for the most part, to the increased efficiency of the nitrous oxide when decomposed at the lower temperature of 160°. Although the horizontal portion of Curve 9 is much shorter, it should be noted that it still proves to be roughly the same fraction of the total abscissa of its curve, so that its relative length is little changed. At all points except the last on Curve 9 decomposition was considered complete, in that the amount of oxygen poisoning found by the "gravimetric" method after a velocity run agreed with the oxygen present in the charge of nitrous oxide admitted. Since at the last point on Curve 9 nitrous oxide decomposition was incomplete at 160°, this curve was not extended farther and no extrapolation appears justified on the basis of the present experimental evidence. Since an excess of nitrous oxide was present at the last points on both Curve 8 and 9, it appears that the surfaces were completely poisoned for further nitrous oxide decomposition at the temperatures employed. It seems important to note, however, that the remaining unpoisoned surface was still active enough to catalyze the hydrogenation of ethylene at 0°. From this it appears that more active surface is required for nitrous oxide decomposition than is required for the ethylene–hydrogen reaction, although there must be some overlapping as is evident from the fact that nitrous oxide acts as a poison at all for the latter reaction. Further evidence for the selective nature of the nitrous oxide poisoning rests upon the interpretation of the horizontal portions of Curves 8 and 9. While regeneration must be a considerable factor at 300°, it becomes smaller at 160°, and one experiment gave qualitative evidence that the horizontal portion is present when the maximum temperature of nitrous oxide decomposition was 25°. Inasmuch as the decomposition of nitrous oxide is a surface reaction, it appears hardly probable that the horizontal portions of the curves resulted from the diffusion of all the oxygen into the catalyst interior leaving the surface bare. It seems reasonable, therefore, to assume that the nitrous oxide poisoning was selective in nature.

Discussion

Evaluation of the curve obtained in the direct oxygen poisoning experiments, in the light of the work on heats of oxygen sorption, clearly shows that this curve need not constitute a true picture of the catalytic surface of copper. Thus caution must be employed in the interpretation of experiments involving strongly sorbed poisons. Only if the poison is capable of being preferentially or selectively sorbed (portions of a non-uniform surface are progressively poisoned in the order of their relative activities) will a linear relation between activity and extent of poisoning constitute proof for a uniform surface.

All of the evidence in the present work may be considered support for a non-uniform copper surface. Thus (a) the direct oxygen poisoning experiments reveal that a large fraction of the surface was catalytically inactive, (b) the heats of oxygen sorption diminished as sorption increased, (c) the indirect oxygen poisoning experiments released a surface having portions of widely different hydrogenating capacities, and (d) the nitrous oxide poisoning experiments also appear to require the existence of a surface which is non-uniform in catalytic activity.

The experimental work furnishes evidence that the ethylene–hydrogen reaction at 0° proceeded on a portion of the catalyst surface having intermediate activity. Thus a slight extrapolation of the linear curve obtained in the direct oxygen poisoning experiments indicates that about 60% of the surface, which sorbed oxygen strongly, possessed no catalytic activity for the reaction studied. This does not mean, however, that all of the remaining 40% of the surface was catalytically active. In fact the non-selective nature of the direct oxygen sorption makes this unnecessary and, furthermore, the initial horizontal portions of the curves for nitrous oxide poisoning (Curves 8 and 9, Fig. 3) appear to constitute direct evidence that some of the copper surface was too active to contribute to the catalysis of the hydrogenation of ethylene. This too active surface, which preferentially decomposed nitrous oxide, may well be wholly or in part that which is inhibited by the known strong sorption of ethylene during the hydrogenation reaction at 0°.[14] At higher temperatures, due to desorption of ethylene, this "too active" surface may actively participate in the catalysis.

Taken together, Curves 6 to 9 (Figs. 2 and 3) constitute evidence as to the nature of the catalyst surface upon which the low-temperature hydrogenation of ethylene proceeded. It is highly improbable that the removal of sorbed oxygen by the selective reductions was entirely preferential. Also regeneration appears to have decreased the poisoning efficiency of the oxygen. A correction for both of these factors should have the effect of diminishing the horizontal length of Curve 6, while causing the curve to rise even more slowly in the region of large amounts of poisoning, and still more rapidly for the smaller amounts. The possibility that such a curve might bend sharply from the rapidly rising portion to a nearly horizontal portion, similar to that found experimentally in Curve 9, is not excluded. In fact, this might be expected if in the selective reductions none but the most active surface were released at the end. In the present work the general form of Curve 6 appears to constitute the best experimental evidence for the nature of the surface capable of catalyzing the hydrogenation of ethylene under the experimental conditions, and is consistent with an exponential distribution of reaction centers such as has been postulated by Constable on copper,[15] the bulk of the reaction occurring on relatively few centers of low activation energy. However, as has been noted above, these most active centers for the hydrogenation of ethylene appear not to be those centers most active in the decomposition of nitrous oxide.

Because of the different schools of thought concerning the structure and behavior of catalyst surfaces, the experimental details of this work have been rather fully presented in order to afford adequate basis for independent interpretation. While the foregoing interpretation appears to us simple and in accord with the present evidence, it is realized that more evidence is highly desirable and, therefore, further work is being undertaken with this end in view.

Summary

1. Active, granular, copper catalysts have been poisoned to various degrees with oxygen both directly and indirectly, and with nitrous oxide. The catalytic activity of both poisoned and unpoisoned surfaces has been measured by means of the ethylene–hydrogen reaction at 0° using a flow method.

2. As the amount of oxygen directly sorbed by the copper at 0° was increased, both the heats of oxygen sorption and the catalytic activity of the surface decreased, the latter in a linear manner.

3. By means of suitable heat of oxygen sorption measurements it was shown that active copper sorbed oxygen at 0° in an almost non-

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[14] R. N. Pease, THIS JOURNAL, **45**, 1196 (1923).

[15] F. H. Constable, *Proc. Roy. Soc.* (London), **108**, 355 (1925).

selective manner and, therefore, that the linear relation in 2 need give no true concept of the catalyst surface.

4. An indirect method of poisoning active copper with oxygen appears to be selective in character.

5. Direct poisoning of active copper with nitrous oxide also appears to be selective.

6. All of the experimental evidence is considered to indicate (a) that the copper surface is non-uniform and (b) that at 0° the hydrogenation of ethylene proceeds almost exclusively on a relatively few surface types, probably of intermediate character.

7. The interpretation of the experimental evidence is consistent with an exponential distribution of centers active at 0° in catalyzing the ethylene–hydrogen reaction.

PROVIDENCE, RHODE ISLAND
RECEIVED SEPTEMBER 12, 1935

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

A Study of the Dehydration of Hydrated Cobaltic Oxide

BY H. ARMIN PAGEL, WILLIAM K. NOYCE AND MYRON T. KELLEY

The literature[1,2,3,4] gives various temperatures, ranging from about 150 to 385°, at which hydrated cobaltic oxide begins to decompose into Co_3O_4, oxygen and water. The observations made in this Laboratory indicate the reason for the apparent disagreement of the investigators.

Experimental

Various lots of hydrated cobaltic oxide were prepared by alkaline decomposition of chloropentammino-cobalti chloride, as recommended by Hüttig and Kassler[1] except that the colloidal oxide was isolated by centrifuging instead of using a membrane filter. The oxide was then dried two days over concentrated sulfuric acid in a vacuum desiccator and ground in an agate mortar. Analyses of the partially dehydrated oxides showed the practical absence of divalent cobalt, and a water content corresponding to about $Co_2O_3 \cdot 1.6H_2O$, or a calculated value of about 15% water and 85% of the hypothetical anhydrous Co_2O_3. The oxide thus prepared was then dehydrated at various temperatures. This was done by passing highly purified air over the oxide samples while the latter were constantly agitated with a mechanical shaker to provide uniform conditions. The approximate progress of the dehydration was determined at twelve or twenty-four-hour intervals by weighing the amount of water collected in dehydrite absorption tubes connected to the air exhaust. Each run was continued until the loss of water decreased to about 0.5 mg. in twenty-four hours. This usually required from two to four days. The oxide was then analyzed for trivalent cobalt by the oxalate–permanganate method as recommended by LeBlanc and Möbius[5] and for water by heating the oxide to red heat in a combustion furnace, using a dehydrite absorption tube to collect the water.

TABLE I

RESULTS OF EXPERIMENTS

Temp., °C., ±3°	% Co_2O_3[a] remaining	% H_2O remaining	% H_2O, calcd. for $Co_2O_3 \cdot 1H_2O$
155	35.3	4.6	3.83
168	19.0	3.8	2.06
177	17.3	2.7	1.88
195	13.3	3.1	1.44
205	19.3	2.3	2.09
220	9.7	1.5	1.05
235	10.3	1.4	1.12
260	15.7	2.2	1.70

[a] Hypothetical anhydrous oxide.

It was noticed in all cases that the rate of dehydration is very slow up to 90°, but in the range from 100 to 180° rapid dehydration takes place. For example, a 1.5-g. sample heated for twenty-four hours at 105° lost 0.006 g.; during the next forty-eight hours at 180° it lost an additional 0.163 g.; then during the next eighty-four hours at 250°, only 0.003 g. additional. In some cases, however, the dehydration at the end of 200° treatment was not nearly as complete as shown above for 180°, and a considerable amount of water continued to be evolved at still higher temperatures.

Further information was obtained in attempts to prepare anhydrous Co_2O_3 by oxidation with

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(1) G. Hüttig and R. Kassler, *Z. anorg. Chem.*, **184**, 283 (1929).

(2) G. Natta and M. Strada, *Gazz. chim. ital.*, **58**, 428 (1928).

(3) F. Merck and E. Wedekind, *Z. anorg. allgem. Chem.*, **186**, 68 (1930).

(4) T. Carnelley and J. Walker, *J. Chem. Soc.*, **53**, 90 (1888).

(5) M. LeBlanc and E. Möbius, *Z. physik. Chem.*, **142**, 170 (1929).

dry oxygen at relatively high pressures. Large samples of dry Co_3O_4, prepared by igniting cobaltous carbonate in air, were placed in an electrically heated high pressure bomb. These were subjected to about 100 atm. of oxygen pressure at various temperatures ranging from 200 to 400°, followed by rapid cooling to room temperature at full pressure. The results were negative throughout. Further experiments were then carried out as follows. A large porcelain boat containing about 5 g. of very pure, partially hydrated, cobaltous carbonate was placed in the hot end of the bomb, and another boat containing freshly ignited calcium oxide was placed in the cooler end to absorb carbon dioxide and water. One experiment (A) of this type was carried out at 330° for sixty-eight hours at 107 atm.; another (B) at 275° for forty-four hours at 72 atm. A different type of experiment (C) was then tried in which partially dehydrated cobaltic oxide was heated for twenty hours with calcium oxide as dehydrating agent at 315° and 127 atm.; followed by twenty hours with phosphorus pentoxide as dehydrating agent at the same temperature and pressure. The following results were found:

TABLE II

	% Co_2O_3* remaining	% H_2O remaining	% H_2O calcd. for $Co_2O_3 \cdot H_2O$	% CO_2
(A)	9.5	1.15	1.03	0.5
(B)	15.3	2.03	1.66	.6
(C)	7.9	1.05	0.86	

Conclusions

Table I shows that decomposition takes place slowly in the 150° temperature region as claimed by Hüttig and Kassler.[1] Both Tables I and II furnish evidence in support of their observations that cobaltic oxide is stable only with a minimum water content corresponding to the monohydrate. The irregularities in "% Co_2O_3 remaining" at increasing temperatures (Table I) are believed to be due to the differences of speed with which water vapor could be physically removed from the various samples having different physical properties. Since no attempt was made to centrifuge the various hydrated oxide preparations the same length of time, their porosity and particle size, no doubt, varied enormously. It should be noted that Hüttig and Kassler in their study of the water vapor equilibrium pressures also found decided variations with different samples.

Since the hydrated oxide sample used in (C) contained about 85% hypothetical Co_2O_3 and about 15% water before dehydration at 315°, it appears that the oxygen dissociation pressure of anhydrous Co_2O_3, formed by the dehydration, is greater than 127 atm. at 315°. Experiments (A) and (B) show, however, that the reaction is reversible in presence of water, and that the amount of divalent cobalt which can be oxidized to cobaltic oxide is, in general, proportional to the amount of water still available to form the monohydrate.

The observations throughout seem to indicate that the prolonged existence of rather large amounts of residual hydrated cobaltic oxide, at temperatures much higher than the 150° region, can be explained on the basis of a retarded rate of dehydration in the inner regions of the oxide particles, due to a very slow rate of outward diffusion of the liberated water. It would therefore seem plausible that wet hydrated cobaltic oxide might be dried for short periods of time, at the higher temperatures mentioned by some investigators, without appreciable decomposition into Co_3O_4, provided the physical conditions are unfavorable for the rapid and complete escape of the liberated water.

LINCOLN, NEBRASKA

RECEIVED AUGUST 29, 1935

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, CITY COLLEGE, COLLEGE OF CITY OF NEW YORK]

Reduction of Organic Compounds by Ethanolamines

BY M. MELTSNER, C. WOHLBERG AND M. J. KLEINER

During an investigation of the properties of triethanolamine the senior author noticed that the ethanolamines reduced aqueous solutions of silver, lead, mercury and other metallic salts. The literature records do not mention this reaction. The present paper reports the results of some experiments on the reduction of organic compounds of different types by the ethanolamines.

The reactions are very easily carried out, requiring the heating of the organic compound with one of the ethanolamines, preferably the diethanolamine. While all the end-products have not as yet been isolated, the reaction depends on the decomposition of the amino alcohol into ammonia and an aldehyde.

Table I records the compounds reduced and the reduction products isolated and identified.

TABLE I

Name of compound	Reduction products
Anthraquinone	Anthranol
Acetone	Isopropyl alcohol
Azobenzene	Aniline
Chrysoidine	1,2,4-Triaminobenzene
Nitrobenzene	Azobenzene, azoxybenzene, aniline
o-Nitrotoluene	*o*-Azotoluene, *o*-azoxytoluidine, *o*-toluidine

TABLE II

Nitro compound	Weight, g.	Amino alcohol	Weight, g.	NaOH	Time, hours	Yield, g.		
						Azo	Azoxy	Amino
Nitrobenzene	25	Monoethanolamine	48	None	4	1.9		2
Nitrobenzene	25	Diethanolamine	84	None	2	5.1		1.7
Nitrobenzene	25	Diethanolamine	64	None	2	3.5		1
Nitrobenzene	10	Diethanolamine	25	15 g.	2	6	1	Trace
Nitrobenzene	25	Diethanolamine	84	5 g.	2	9.3		0.7
Nitrobenzene	25	Triethanolamine	84	None	4	1.7		1
Nitrobenzene	10	Triethanolamine	25	20 g.	2	4	3	Trace
o-Nitrotoluene	27	Diethanolamine	84	None	2	1.9		2.6
o-Nitrotoluene	13	Diethanolamine	21	5 g.	2	0.2	6	0.3
o-Nitrotoluene	13	Diethanolamine	21	10 g.	2	.2	8.4	Trace
o-Nitrotoluene	13	Diethanolamine	21	15 g.	2	8.2		Trace

Table II shows the results of a more extended investigation of the reduction of the nitro group. It will be noticed that the nitro group on reduction yields azo, azoxy and amino compounds, the yields of each being dependent on the presence or absence of alkali, the amino alcohol and the time of reaction.

Experimental Part

Reduction of Anthraquinone.—Ten grams of anthraquinone and 32 g. of triethanolamine are heated in an oil-bath at 185° for six hours. The mixture is extracted with water and filtered. The insoluble portion is extracted with benzene and the benzene evaporated. The residue of anthranol is recrystallized and identified by its melting point and oxidation to anthraquinone.

Reduction of Azobenzene.—Thirty-two grams of triethanolamine and 10 g. of azobenzene are heated in an oil-bath at 185–190° for four hours. The resulting mixture was steam distilled. The excess azobenzene is filtered off from the distillate which after acidification with hydrochloric acid is evaporated to dryness. The residue was identified as aniline hydrochloride.

Reduction of Acetone.—Thirty-two grams of triethanolamine and 10 g. of acetone were refluxed for six hours. The solution was distilled and a fraction between 75–85° was collected. Isopropyl alcohol was identified by conversion into the 3,5-dinitrobenzoic ester.

Reduction of Nitrobenzene with Amino Alcohol and Alkali.—Ten grams of nitrobenzene and 25 g. of diethanolamine are mixed with a solution of 15 g. of sodium hydroxide in 10 cc. of water and heated with a small flame for two hours. After cooling, water is added and the mixture filtered. The solid residue is fractionally crystallized from alcohol and yields azobenzene (6 g.) and azoxybenzene (1 g.). The aqueous filtrate is steam distilled, the distillate acidified with hydrochloric acid and evaporated to dryness to yield aniline hydrochloride.

Conclusions

1. Ethanolamines have been found to act as reducing agents for inorganic salts and for some classes of organic compounds.
2. Nitro compounds when reduced with ethanolamines yield azo, azoxy and amino compounds.

NEW YORK, N. Y.

RECEIVED OCTOBER 21, 1935

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

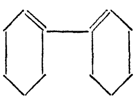
Synthesis of Certain Hydrogenated Phenanthrenes

BY E. E. GRUBER[1] AND ROGER ADAMS

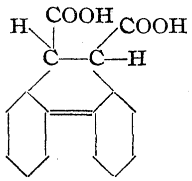
A recent communication by Barnett and Lawrence[2] describes the condensation of maleic anhydride and benzoquinone with the dienes obtained from the pinacols of cyclopentanone and cyclohexanone. A similar study has been under way for some time in the University of Illinois laboratories and occasion, therefore, is taken now to present some of these results which are closely related to the work of Barnett and Lawrence.

The British authors have neglected to mention that di-$\Delta^{1,1}$-cyclohexene (I) had previously been prepared by Wallach and Pauly[3] through dehydration of the corresponding pinacol with diluted sulfuric acid and indeed the yield by the latter procedure was found by us to be fully as satisfactory as that reported by Barnett and Lawrence using dehydrated alum as a catalyst.

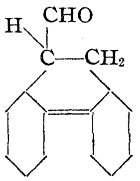
Condensation between maleic anhydride and the diene (I) mentioned, takes place readily with formation of the $\Delta^{4a,5a}$-dodecahydrophenanthrene-9,10-dicarboxylic acid anhydride (II).



I



II



III

The anhydride may be converted into the free acid, and the imide.

The diene (I) also readily condenses with acrolein with the formation of $\Delta^{4a,5a}$-dodecahydrophenanthrene-9-al (III), a product now being used by us in another investigation.

Experimental

1,1′-Dihydroxy-1,1′-dicyclohexyl.—In place of the aluminum used by Barnett and Lawrence in the synthesis of this compound, magnesium was employed.

To 94.6 g. of magnesium turnings and one liter of dry benzene in a 5-liter, two-necked flask (equipped with a reflux condenser and separatory funnel) was added 170 g. of mercuric chloride dissolved in 603 g. of dry cyclohexanone. Heat was applied to initiate the reaction, which then continued with increasing vigor until it was necessary to cool with an ice-bath. After the first vigorous reaction had subsided, the reaction mixture was heated on a steam cone for two hours, was broken up and 450 cc. of water was slowly added. Heating with occasional shaking was continued for about three hours longer. After filtering off the liquid, the residue in the flask was extracted with two 400-cc. portions of hot benzene. The combined filtrates were fractionally distilled *in vacuo*. About 308 g. of cyclohexanone was recovered. The fraction 140–175° (6.5 mm.) was chiefly the desired diol and was purified by recrystallization from high-boiling petroleum ether as white needles, m. p. 128.5–129.5°. Zelinsky[4] reports m. p. 128–129° and Barnett and Lawrence[2] report m. p. 130°. The yield was 35% based on cyclohexanone actually used.

It was found that by allowing the reaction to proceed as rapidly as possible and by avoiding a large excess of cyclohexanone, the major by-product cyclohexenylcyclohexanone was reduced in amount.

Di-$\Delta^{1,1}$-cyclohexene (I).—By heating under reflux for four hours a mixture of 132 g. of the dihydroxycyclohexyl in 600 cc. of 10% sulfuric acid,[2] then subjecting it to steam distillation, a colorless oil was obtained which was extracted with low boiling petroleum ether; b. p. 101–102° (5.5 mm.); d_{20} 0.9581; $n^{20}\text{D}$ 1.5322; yield 88 g. (82%).

$\Delta^{4a,5a}$-Dodecahydrophenanthrene-9,10-dicarboxylic Acid Anhydride (II).—A solution of 10 g. of dicyclohexene and 6 g. of powdered maleic anhydride in 12 cc. of benzene was warmed gently for a few minutes until the anhydride dissolved. After four hours of standing the solvent was evaporated and the oily crystalline mass thus obtained was washed with high-boiling petroleum ether and finally with 2 cc. of benzene. The anhydride was recrystallized from high-boiling petroleum ether and thereby obtained as colorless prismatic needles, m. p. 122.5–123.5°. Barnett and Lawrence[2] report the same m. p.; yield 5.5 g.

Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.8; H, 7.74. Found: C, 73.5; H, 7.96.

$\Delta^{4a,5a}$-Dodecahydrophenanthrene-9,10-dicarboxylic Acid.—A solution of 20 g. of the powdered dodecahydrophenanthrene-9,10-dicarboxylic anhydride in 250 cc. of 5% sodium hydroxide was refluxed until the anhydride dissolved, filtered and cooled to about 5°, and then diluted with about 200 cc. of cold water. Dilute acetic acid was added slowly with stirring and the gummy precipitate was transferred to 250 cc. of hot glacial acetic acid, in which it solidified and then dissolved. Upon cooling it crystallized out as colorless prisms; m. p. 242° (bloc Maquenne); yield 12 g.

The aqueous solution from the neutralization was still milky and upon standing and diluting yielded more of the above acid in a white powdery form; yield 5 g.

Anal. Calcd. for $C_{16}H_{22}O_4$: C, 69.02; H, 7.97. Found: (I) C, 68.96; H, 8.37; (II) C, 69.41; H, 8.09.

$\Delta^{4a,5a}$-Dodecahydrophenanthrene-9,10-dicarboxylic Acid Imide.—A mixture of 0.5 g. of anhydride and 5 cc. of

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

[2] Barnett and Lawrence, *J. Chem. Soc.*, 1104 (1935).

[3] Wallach and Pauly, *Ann.*, **381**, 112 (1911).

[4] Zelinsky, *Ber.*, **34**, 2801 (1901).

concentrated aqueous ammonia was heated slowly under reflux to about 250–300°. At this temperature the reaction reached a homogeneous melt. Anhydride, which sublimed into the condenser, was pushed back with a glass rod. After cooling, 95% alcohol was added and the solution filtered. Addition of water to the alcoholic solution precipitated a light tan solid, m. p. 145–150° (yield 0.3 g.). For purification it was dissolved in ethyl alcohol and water added to the hot solution until almost cloudy. Upon cooling prismatic needles separated. After recrystallizing three times from benzene and low boiling petroleum ether, the product formed colorless needles, m. p. 182–183°.

Anal. Calcd. for $C_{16}H_{21}O_2N$: N, 5.40. Found: N, 5.36.

$\Delta^{4a,5a}$-Dodecahydrophenanthrene-9-al (III).—A mixture of 17 g. of the dicyclohexene in 15 cc. of dry benzene and 6 g. of pure acrolein was heated under reflux for twenty-two hours at 50–60°. The benzene and the unreacted acrolein were removed and the residue fractionally distilled in vacuo. After distilling off all of the unreacted dicyclohexene (up to 126° (6.5 mm.)), the residue was dissolved in a small amount of ether and shaken with a 10% solution of sodium bisulfite. The solid which formed was filtered, washed with a little alcohol and decomposed with warm dilute aqueous sodium carbonate. The oil which separated was extracted with ether. The aldehyde was a colorless oil and was distilled in an atmosphere of nitrogen, b. p. 136–137° (4 mm.); yield, 4.2 g. (20%).

Anal. Calcd. for $C_{15}H_{22}O$: C, 82.50; H, 10.65. Found: C, 82.87; H, 10.49.

The semicarbazone, purified from dilute alcohol, melted at 179–180°.

Anal. Calcd. for $C_{16}H_{25}ON_3$: N, 15.21. Found: N 14.99.

Summary

Addition of maleic anhydride and acrolein to di-$\Delta^{1,1}$-cyclohexene gives the hydrogenated phenanthrene derivatives, $\Delta^{4a,5a}$-dodecahydrophenanthrene-9,10-dicarboxylic acid anhydride and $\Delta^{4a,5a}$-dodecahydrophenanthrene-9-al.

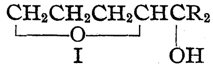
URBANA, ILLINOIS RECEIVED OCTOBER 10, 1935

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

The Preparation and Reactions of Tertiary Tetrahydrofurylcarbinols

BY A. L. DOUNCE, RALPH H. WARDLOW[1] AND RALPH CONNOR[2]

Two methods are available for the synthesis of tertiary tetrahydrofurylcarbinols (I): (1) the action of the appropriate Grignard reagent upon ethyl tetrahydrofuroate, obtained by the hydrogenation of ethyl furoate over nickel, or (2) the reaction of the Grignard reagent with ethyl furoate, followed by the hydrogenation over nickel of the furyldialkylcarbinols thus obtained. Both of these methods have been used for the preparation of tetrahydrofuryldiethylcarbinol (II) and tetrahydrofuryldi-*n*-butylcarbinol (III). The former method gave

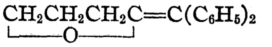


$CH_2CH_2CH_2CHCR_2$ (ring O; OH) I

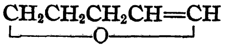
II, R = $—C_2H_5$
III, R = n-C_4H_9
IV, R = $—C_6H_5$

in over-all yields of 71% (II), 50% (III) and 77% (IV) and is to be preferred to the latter, which gave 52% (II) and 45% (III). Because of the well-known tendency[3] for hydrogenolysis of the carbon–oxygen bond in the α-position to aromatic nuclei, the latter method is not applicable to such compounds as IV.

Dehydration of these carbinols was readily accomplished by heating with magnesium sulfate until the theoretical amount of water had distilled. The product obtained by the dehydration of tetrahydrofuryldi-*n*-butylcarbinol (III) was a mixture of isomers which could not be separated by fractional distillation. With tetrahydrofuryldiphenylcarbinol (IV), however, the sole product isolated was 1,1-diphenyl-2,5-epoxy-1-pentene (V). The structure of the latter was established by the isolation of benzophenone and γ-butyrolactone from the hydrolysis of the ozonide; examination of the ozonolysis products failed to show any evidence of the formation of a dihydropyran during the dehydration.



$CH_2CH_2CH_2C{=}C(C_6H_5)_2$ V



$CH_2CH_2CH_2CH{=}CH$ VI

$CH_2CH_2CH_2C{=}CH_2$ VII

The fact that no ring enlargement occurred under the conditions used in the dehydration of IV is in contrast to the results of Paul,[4] who obtained a dihydropyran (VI) by the catalytic dehydration of tetrahydrofurfuryl alcohol at 370–380°. Fur-

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(1) A portion of this communication is abstracted from the thesis submitted by Ralph H. Wardlow in partial fulfilment of the requirements for the degree of Master of Science at Cornell University in June, 1933.

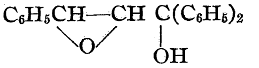
(2) Present address, Harrison Laboratory, University of Pennsylvania, Philadelphia, Pa.

(3) *Cf.* Covert, Connor and Adkins, THIS JOURNAL, **54**, 1660 (1932).

(4) Paul, *Bull. soc. chim.*, [4] **53**, 417 (1933); *ibid.*, **1489** (1933); *Compt. rend.*, **196**, 1409 (1933); *Bull. soc. chim.*, [5] **2**, 311 (1935); *ibid.*, 745 (1935).

thermore, a comparison of the properties of V with the properties of 2,5-epoxy-1-pentene (VII), obtained by Paul by the action of alkaline reagents upon tetrahydrofurfuryl bromide, shows that they are markedly different. The former (V) was very stable; it was distilled without decomposition (b. p. 195° at 10 mm.), was stored for several months without decomposition or polymerization, and was recovered unchanged from contact with dilute sulfuric acid. The product (VII) isolated by Paul was a very unstable and reactive substance; it was hydrolyzed almost instantly by dilute acid, was attacked by oxygen of the air, and was not obtained in an analytically pure state. The conjugation of the olefinic double bond of V with the aromatic nuclei may be responsible for its greater stability.

The formation in excellent yields of tetrahydrofuryldiphenylcarbinol (IV) by the reaction of phenylmagnesium bromide with ethyl tetrahydrofuroate in ether solution indicated that cleavage of the tetrahydrofuran ring did not occur to any appreciable extent during the reaction. It therefore seemed of interest to test the stability of the ring under "forced" conditions. It was found, however, that when IV was refluxed for fifty-two hours in boiling xylene with three equivalents of phenylmagnesium bromide there were no indications of cleavage. Instead, an 87% yield of the dehydration product (VII) was obtained. That the dehydration product was formed after hydrolysis of the reaction mixture was indicated by the facts (a) that water appeared in the distillate *after* most of the xylene had been distilled (at atmospheric pressure), (b) that α,β-unsaturated ethers react with the Grignard reagent,[5] and (c) that in another experiment in which the time of refluxing was nine hours and in which the xylene was removed under diminished pressure, 76% of IV was recovered unchanged along with a small amount of impure dehydration product. The stability of V toward phenylmagnesium bromide is interesting in comparison with the reactivity of the α-oxido carbinol (VIII) which suffers cleavage both of the oxide ring and the carbon chain.[6] The two carbon atoms between which cleavage occurs in VIII bear substituents similar to those on the corresponding carbon atoms in IV; the well-known difference in the stability of three-and five-membered rings undoubtedly is responsible for the difference in the reactions of these compounds.


VIII

Experimental

Ethyl Tetrahydrofuroate.—Ethyl furoate was hydrogenated[7] in the presence of the Raney catalyst[8] at 150°, using pressures of 100–130 atmospheres. With 15 g. of catalyst and 200 g. of ethyl furoate, hydrogenation was complete in four hours; average yield from five hydrogenations, 93.3%, b. p. 188–190° (740 mm.).

Furyldiethylcarbinol.[10]—An ethereal solution of 0.5 mole of ethylmagnesium bromide was prepared in the usual manner and a solution of 35 g. (0.25 mole) of ethyl furoate in anhydrous ether was added to the solution, the rate of addition being determined by the vigor of the reaction. The reaction mixture was refluxed on a water-bath for three hours, cooled, poured into a mixture of 200 g. of cracked ice with 200 ml. of a saturated aqueous solution of ammonium chloride, stirred vigorously, allowed to stand for three hours, the ethereal layer separated, and the aqueous layer extracted twice with ether. The combined ether extracts were then washed with 100 ml. of saturated ammonium chloride solution, dried with magnesium sulfate and distilled. There was obtained 28.5 g. (77%) of furyldiethylcarbinol, b. p. 92–95° (14 mm.). The distillation residue was tarry and was larger in quantity when heating during distillation was prolonged.

Furyldi-*n*-butylcarbinol.—The procedure was exactly like that described above for furyldiethylcarbinol. The yield was 40.9 g. (78%), b. p. 128–131° (14 mm.), n^{25}_D 1.4703, d^{25}_{25} 0.9251, MR'_D found 63.30, MR'_D calcd. 62.29.

Anal. Calcd. for $C_{12}H_{22}O_2$: C, 74.28; H, 10.47. Found: C, 74.47; H, 10.60.

Tetrahydrofuryldiphenylcarbinol (IV).—To a solution of phenylmagnesium bromide prepared from 8.2 g. (0.34 gram atom) of magnesium in 500 ml. of dry ether was added with stirring 24.5 g. (0.17 mole) of ethyl tetrahydrofuroate at such a rate as to maintain gentle refluxing. The reaction mixture was refluxed with stirring on the water-bath for one hour, cooled, and added to a mixture of 200 g. of cracked ice and 20 ml. of 1:1 sulfuric acid. The ether layer was washed with a cold 5% solution of sulfuric acid, dried with anhydrous magnesium sulfate, concentrated on the steam-bath and the solid residue recrystallized from petroleum ether (b. p. 60–70°). The product weighed 41 g. (83%), m. p. 79–80° (uncorr.).

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.31; H, 7.08. Found: C, 80.38; H, 7.20.

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[5] Hill and Tallman, unpublished results.

[6] Kohler, Richtmyer and Hester, THIS JOURNAL, **53**, 205 (1931); Bachman and Wiselogle, *ibid.*, **56**, 1559 (1934); Kohler and Bickel, *ibid.*, **57**, 1099 (1935).

[7] The bomb used for the hydrogenations had a capacity of 275 ml. and did not differ in any important respects from those previously described.[9] The authors are very grateful to Professor Homer Adkins of the University of Wisconsin for his advice and aid in planning the hydrogenation equipment.

[8] Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).

[9] Adkins, *Ind. Eng. Chem., Anal. Ed.*, **4**, 342 (1932); THIS JOURNAL, **55**, 4272 (1933).

[10] Hale, McNally and Peter, *Am. Chem. J.*, **35**, 68 (1906).

Tetrahydrofuryldiethylcarbinol (II).—This preparation was carried out like that of IV, except that 1.0 mole of ethyl tetrahydrofuroate (with correspondingly larger amounts of the other materials) was used. The yield was 120 g. (76%), b. p. 200–203° (740 mm.). The product was a colorless liquid with an agreeable ethereal odor, d^{25}_{25} 0.9744, n^{25}_D 1.4552, MR'D found 44.01, MR'D calcd. 44.75.

Anal. Calcd. for $C_9H_{18}O_2$: C, 68.35; H, 11.39. Found: C, 68.20; H, 11.41.

Hydrogenation of 18.0 g. of furyldiethylcarbinol in the presence of 5.0 g. of Raney nickel catalyst and 25 ml. of absolute ethanol at an initial hydrogen pressure of 115 atmospheres was complete in three hours at 150°. Some tarry material was formed but there was also obtained 12.0 g. (67%) of II, b. p. 203° (740 mm.).

Tetrahydrofuryldi-*n*-butylcarbinol (III).—This preparation was carried out like that of II. The yield was 114.5 g. (53.4%), b. p. 151–152° (24 mm.), 251–252° (740 mm.), d^{25}_{25} 0.9219, n^{25}_D 1.4543, MR'D found 62.90, MR'D calcd. 63.18.

Anal. Calcd. for $C_{13}H_{26}O_2$: C, 72.89; H, 12.14. Found: C, 72.84; H, 12.20.

Hydrogenation of 11.8 g. of furyldi-*n*-butylcarbinol in the presence of 1.5 g. of Raney nickel catalyst and 25 ml. of absolute ethanol at an initial hydrogen pressure of 120 atmospheres was complete in one and one-half hours at 175°. A small amount of low-boiling material was formed, presumably hydrogenolysis products, along with 7.0 g. (58%) of III, b. p. 254° (740 mm.), n^{25}_D 1.4545.

1,1-Diphenyl-2,5-epoxy-1-pentene (V).[11]—Tetrahydrofuryldiphenylcarbinol (IV) was dehydrated under a variety of conditions and the following procedure was found to be the most satisfactory. To 101.6 g. (0.4 mole) of IV was added 5.0 g. of anhydrous magnesium sulfate and the mixture heated in a 100-cc. round-bottomed flask until the theoretical amount of water had distilled through a Vigreux column 8 cm. long and 1.5 cm. in diameter. The dark residue which solidified on cooling was crystallized once from alcohol with decolorizing charcoal, once from alcohol alone and once from petroleum ether, b. p. 60–70°. After these recrystallizations the product was slightly yellow and melted at 107.5–108.5° (uncorr.). Further recrystallizations rendered it white but did not change the melting point. The yield was 52.6 g. (56%). The compound reduced alkaline potassium permanganate solution, decolorized a 5% solution of bromine in carbon tetrachloride and could be distilled without decomposition, b. p. 195° (10 mm.).

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.44; H, 6.77. Found: C, 86.10; H, 6.87.

Ozonolysis of 1,1-Diphenyl-2,5-epoxy-1-pentene.—The ozonide prepared from 1.5 g. of V dissolved in 35 ml. of a 50–50 mixture of petroleum ether, b. p. 30° and b. p. 60–70° was hydrolyzed, after removal of the solvent under diminished pressure, by gentle boiling with 2 to 3 ml. of superoxol. The insoluble material was then extracted with ether and an insoluble compound,[12] m. p. 210–214° (dec.) removed by filtration. Distillation of the ether solution gave 0.5 g. (50%) of benzophenone, b. p. 156° (10 mm.), m. p. 46–48°, m. p. of oxime 139–140°. A sample of authentic benzophenone, m. p. 47–48.5°, boiled at 153–154° (10 mm.) in the same apparatus and the melting point of benzophenone oxime (140–141°) was not altered by mixture with the oxime of the ozonolysis product.

The ozonide prepared by passing ozone through a solution of 23.6 g. (0.1 mole) of V in 175 ml. of dry carbon tetrachloride was hydrolyzed with zinc and water, using hydroquinone and silver nitrate as catalysts by the recently described method.[13] The water-insoluble portion of the product was removed by extraction with ether, the zinc removed from the water layer by filtration, the ether distilled from the water-insoluble layer and the residue added to the aqueous filtrate to remove water-soluble materials. The water insoluble layer was separated and distilled. The sole product was benzophenone (b. p. 140–150° (10 mm.), m. p. 46.5–48.5°, m. p. of oxime, 141.5–142°) the identity of which was confirmed by its mixed melting point with an authentic sample of benzophenone and by the mixed melting point of its oxime with benzophenone oxime. The melting points of the mixtures were 46.5–48.5° and 141–142°, respectively. The aqueous layer from which the benzophenone had been separated was distilled through a small indented column until a sirupy residue remained. This residue contained zinc chloride (because of the incomplete removal of carbon tetrachloride before decomposition of the ozonide) and was extracted repeatedly with ether and the ether extracts dried and distilled. The ether extracts contained enough zinc chloride to cause considerable decomposition during distillation but there was obtained 0.5 g. of pure γ-butyrolactone, b. p. 95° (15 mm.).

γ-Butyrolactone.—Two hundred grams of ethyl succinate was heated at 250° with 18 g. of copper–chromium–barium oxide catalyst[14] (37KAF) for ten hours at a pressure of 90 to 130 atmospheres. Fractional distillation of the product through a very efficient fractionating column gave 10 g. (10%) of γ-butyrolactone, b. p. 92–94° (18–19 mm.).

Hydrazide of γ-Hydroxybutyric Acid.—The procedure was exactly like that previously used[15] with ε-caprolactone. The solid product obtained from the reaction of hydrazine hydrate with the γ-butyrolactone prepared from the hydrogenation of ethyl succinate gave, upon recrystallization from ethanol, a small amount of the dihydrazide of succinic acid,[16] m. p. 165–166° (uncorr.), and a much larger amount of the hydrazide of γ-hydroxybutyric acid, m. p. 89–90° (uncorr.).

Anal.[18] Calcd. for $C_4H_{10}O_2N_2$: N, 23.7. Found: N, 24.03, 24.05.

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[11] The authors wish to express their gratitude to Professor J. R. Johnson for his interest and advice during this portion of the work.

[12] The same compound was formed from the ozonolysis of unsymmetrical diphenylethylene under these conditions.

[13] Whitmore and Church, THIS JOURNAL, **54**, 3711 (1932); Church, Whitmore and McGrew, *ibid.*, **56**, 178 (1934).

[14] Connor, Folkers and Adkins, *ibid.*, **54**, 1138 (1932).

[15] Van Natta, Hill and Carothers, *ibid.*, **56**, 456 (1934).

[16] This melting point was unchanged when the product was mixed with an authentic sample of the hydrazide of succinic acid.[17] This shows that γ-butyrolactone was not completely separated from ethyl succinate by the fractional distillation. This dihydrazide is quite insoluble in alcohol, while the hydrazide of the hydroxy acid is very soluble.

[17] Schöfer and Schwan, *J. prakt. Chem.*, **51**, 190 (1895).

[18] The micro-Dumas analyses were made by Dr. M. T. Bush.

The reaction of hydrazine hydrate with the ozonolysis product believed to be γ-butyrolactone gave a solid hydrazide, m. p. 90.5–92° (uncorr.). The mixture of this product with the hydrazide of the γ-butyrolactone prepared from ethyl succinate melted at 90.5–91.5° (uncorr.).

Dehydration of Tetrahydrofuryldi-*n*-butylcarbinol.—A mixture of 10 g. of the carbinol (III) with 0.5 g. of magnesium sulfate and 0.5 g. of potassium hydroxide was heated under a small Vigreux column. Water and an oil with an ethereal odor distilled and the residue in the flask became tarry. The experiment was repeated with similar results using lime in place of the magnesium sulfate. The combined dried products from both experiments distilled between 40 and 150° (740 mm.) with a uniform temperature rise.

Tetrahydrofuryldiphenylcarbinol with Phenylmagnesium Bromide.—To a solution of 0.6 mole of phenylmagnesium bromide in 400 ml. of ether was slowly added in small portions 48.5 g. (0.2 mole) of tetrahydrofuryldiphenylcarbinol (IV). To the reaction mixture was then added 500 ml. of dry xylene, the reflux condenser replaced by a short fractionating column with a condenser set downward for distillation and the mixture heated on an oil-bath until the vapors reached a temperature of 131°. The reflux condenser was then replaced and the xylene refluxed for fifty hours. After the reaction mixture was cooled it was poured into a mixture of cracked ice with 40 ml. of 1:1 sulfuric acid and the xylene layer separated and distilled at atmospheric pressure. Water appeared in the distillate near the end of the distillation. The residue (50 g.) solidified upon cooling and after recrystallization from petroleum ether (b. p. 60–70°) and from alcohol gave 41 g. (87%) of pure material, m. p. 107.5–108.5° (uncorr.). This melting point was unchanged when the material was mixed with a sample of V prepared by the dehydration of IV. In another experiment in which the time of refluxing was nine hours and in which the xylene was removed under reduced pressure, 76% of IV was recovered unchanged (m. p. 77–79°) along with 4 g. of an oil (b. p. 250°) which decolorized bromine in carbon tetrachloride and was apparently impure dehydration product.

Summary

Tetrahydrofuryldialkylcarbinols have been synthesized by the reaction of alkylmagnesium halides with ethyl tetrahydrofuroate and by the catalytic hydrogenation of furyldialkylcarbinols. Tetrahydrofuryldiphenylcarbinol was readily dehydrated to give 1,1-diphenyl-2,5-epoxy-1-pentene; in contrast to the dehydration of furfuryl alcohol, there was no indication of ring enlargement. The dehydration product was much more stable than 2,5-epoxy-1-pentene. Tetrahydrofuryldiphenylcarbinol was not cleaved by phenylmagnesium bromide under "forced" conditions.

ITHACA, NEW YORK RECEIVED OCTOBER 5, 1935

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF JOHNS HOPKINS UNIVERSITY]

The Preparation of Some of the Lower Alkyl Sulfonic Acids

BY D. L. VIVIAN AND E. EMMET REID

Much work has been done by earlier investigators on the preparation of alkyl sulfonic acids by various procedures, but very little effort has been made to isolate and characterize the anhydrous acids. Two exceptions occur in the work of Noller and Gordon[1] on the acids containing from nine to fourteen carbon atoms, and in that of Berthoud[2] on methyl sulfonic and ethyl sulfonic acids. The present paper gives data on the four straight-chain primary sulfonic acids containing from three to six carbon atoms.

The propyl, amyl and hexyl sulfonic acids were prepared from barium salts remaining from a previous investigation[3] by precipitating the barium with sulfuric acid. The butyl sulfonic acid was prepared by oxidation of *n*-butyl mercaptan[4] by dropping 48 g. of it into 180 cc. of concentrated nitric acid with mechanical stirring and evaporating on the steam-bath until the oxides of nitrogen were completely removed. The crude acid was diluted with ten volumes of water, neutralized with lead carbonate, filtered and the filtrate evaporated to dryness. The crude lead salt obtained in 72–96% yields was recrystallized from 80% alcohol and then decomposed in aqueous solution with hydrogen sulfide. After removing the lead sulfide the aqueous solution was concentrated on the steam-bath.

The pure anhydrous sulfonic acids were obtained from the concentrated aqueous solutions as colorless liquids after four or five distillations at 1 mm. Their hot vapors attack rubber but a coating of sodium silicate on the stoppers prevents this. The pure acids soon darken even in a vacuum.

The average purity of these acids as determined by two concordant titrations with methyl orange

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(1) Noller and Gordon, THIS JOURNAL, **55**, 1090 (1933).

(2) Berthoud, *Helv. Chim. Acta*, **12**, 859 (1929).

(3) Wagner and Reid, THIS JOURNAL, **53**, 3407 (1931).

(4) This acid was also prepared by converting butyl mercaptan into disulfide (b. p. 107–109° at 12 mm.) and oxidizing this with nitric acid, but the yield was not quite as good.

TABLE I

PROPERTIES OF THE ALKYL SULFONIC ACIDS

Acid	B. p. Temp., °C.	B. p. Pressure, mm.	M. p., °C.	Density$^{25}{}_4$
Methyl sulfonic[2]	167	10	+20	1.4844
Ethyl sulfonic[2]	...	..	−17	1.3341
n-Propyl sulfonic	136	1	+ 7.5	1.2516
n-Butyl sulfonic	147	0.5	−15.2	1.1906[a]
n-Amyl sulfonic	163	1	+15.9	1.1226
n-Hexyl sulfonic	174	1	+16.1	1.1047

[a] $d^0{}_4$ 1.2117.

as indicator was as follows: propyl, 99.2; butyl, 100; amyl, 100; hexyl, 99.8%. Presumably the propyl acid still retained a trace of moisture.

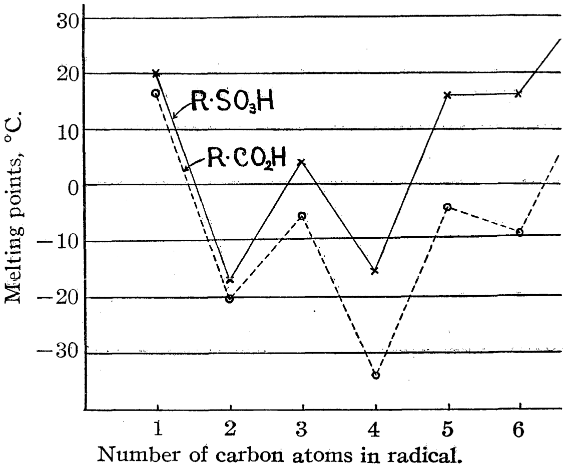

Fig. 1.—Melting points of sulfonic and carbonic acids.

The physical data obtained with these acids, together with the corresponding data for methyl and ethyl acids, are given in Table I.

These melting points are plotted along with those of the carboxy acids containing the same radicals in Fig. 1. The alternation is remarkably alike in the two series.

The acid chloride of the butyl sulfonic acid was prepared by the action of phosphorus pentachloride on the potassium salt. It boiled at 90° at 11 mm.,[5] and had $d^{25}{}_4$ 1.2140, and $d^0{}_4$ 1.2404.

It was thought that butyl sulfonic acid might resemble sulfuric acid in substitution reactions, but it did not react with benzene at 80°. Aniline sulfate rearranges to sulfanilic acid, but the aniline salt of butyl sulfonic acid did not undergo any change when heated several hours at 130°. This salt is readily made by adding aniline to the acid and warming slightly. After one recrystallization it melted at 162°. Gilman and Morris[6] give m. p. 159° for this salt obtained by the reaction of thionylaniline with butylmagnesium bromide.

Summary

n-Propyl, *n*-butyl, *n*-amyl and *n*-hexyl sulfonic acids have been prepared and characterized.

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(5) Von Braun and Weissbach, *Ber.*, **63**, 2836 (1930).

(6) Gilman and Morris, THIS JOURNAL, **48**, 2399 (1926).

BALTIMORE, MARYLAND RECEIVED OCTOBER 3, 1935

[CONTRIBUTION FROM THE DEPARTMENTS OF ANIMAL HUSBANDRY AND HOME ECONOMICS RESEARCH, FLORIDA AGRICULTURAL EXPERIMENT STATION]

The Isolation and Some Properties of an Alkaloid from *Crotalaria spectabilis* Roth[1]

BY W. M. NEAL, L. L. RUSOFF AND C. F. AHMANN

The literature relative to the toxic species of the *Crotalariae* was reviewed in another paper,[2] in which the toxicity of *C. spectabilis* Roth was established. Previously known toxic species included *C. sagittalis* L., *C. juncea* L., *C. burkeana* Benth., *C. dura* Wood and Evans, and *C. globifera* E. Mey. Still other species have been suspected. Bessey and Stalker[3] suspected the toxic principle of *C. sagittalis* to be an alkaloid. Timson[4] found the seeds of *C. juncea* to give reactions suggesting the presence of an unidentified alkaloid. In no case had a specific alkaloid been isolated from any member of the genus.

This is a report of the isolation and some of the properties of an alkaloid isolated from *C. spectabilis*. Because of the large number of species (over 600) of *Crotalaria*, several of which have proven toxic, the name *monocrotaline* is suggested for this alkaloid. Succeeding alkaloids from this genus can then be named *dicrotoline*, *tricrotaline*, etc., following Couch's[5] recommendation for the lupine alkaloids.

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(1) Presented in part before the Division of Medicinal Chemistry of the American Chemical Society at the 87th Meeting of the Society, St. Petersburg, Fla., March 25 to 30, 1934.

(2) Becker, Neal, Arnold and Shealy, *J. Agr. Research*, **50**, 911 (1935).

(3) Bessey and Stalker, *Iowa Agr. Coll. Dept. Bot. Bull.*, 111 (1884).

(4) Timson, *Rhodesia Agr. J.*, **26**, 668 (1929).

(5) Couch, THIS JOURNAL, **56**, 155 (1934).

Experimental

The first extracts of the seeds of *C. spectabilis* were made by soaking them in 1.25% sulfuric acid. The filtrate was shaken with Lloyd's alkaloid reagent. The basic material was liberated from the reagent with 0.1 *N* sodium hydroxide. This solution was extracted with successive portions of chloroform. Opaque crystals remained upon evaporation of the solvent.

Later extracts were made by soaking the seeds in 5% ammonium hydroxide for forty-eight hours, and extracting the filtrate with successive portions of chloroform. The crystals obtained upon evaporation of the solvent were dissolved in 1:1 hydrochloric acid, the solution thus formed was made alkaline with ammonium hydroxide, and extracted as above. Further purification was by repeated recrystallization from chloroform or absolute alcohol. Crystals from the alcohol were transparent. Crude extracts equivalent to 0.4, 0.07 and 0.015% of the dry weights of the seeds, leaves and stems, respectively, of *C. spectabilis* were prepared.

The extracted substance is soluble in chloroform and alcohol, slightly soluble in ether and very slightly soluble in water.

The compound slowly decolorizes potassium permanganate, and gives a yellowish color with Fröhde's (sulfomolybdic acid) reagent. It yields a yellowish precipitate with picric acid, a reddish-brown precipitate with Wagner's iodide reagent, a white precipitate with Mayer's reagent and a yellowish-white precipitate with Sonnenschein's phosphomolybdic acid reagent. It forms precipitates with salts of the heavy metals. All the tests were characteristic of alkaloids.

Melting point determinations of the purified compound were between 196 and 197° (uncorr.).

Anal. Calcd. for $C_{16}H_{26}O_6N$: C, 58.51; H, 7.98; N, 4.27. Found: C, 57.97; H, 7.85; N, 4.15.[6] The molecular weight, by the above formula, is 328.3. The determination of the neutral equivalent indicated a molecular weight of 324.

Pharmacologically, it lowers the blood pressure in dogs, and decreases the rate and amplitude of terrapin heart *in situ*. This decrease was observed even when the vagus nerve was severed. The rate of contraction of isolated heart muscle strips from terrapin is stimulated immediately, followed by a decrease in rate and amplitude.

The same lesions were observed in experimental animals administered lethal doses when either the whole seeds or alkaloid *per se* was used. This would indicate that the alkaloid isolated is the toxic principle of this plant. The twenty-four-hour lethal dose for chickens is 65 mg./kg. live weight.

Summary

The initial isolation of a specific alkaloid from the genus *Crotalaria* is reported. This compound has been named *monocrotaline* and was isolated from *C. spectabilis* Roth.

The compound melts at 196–197°, and has been given the empirical formula $C_{16}H_{26}O_6N$, tentatively.

The identity of the compound as the toxic principle of *C. spectabilis* has been established.

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[6] The authors are indebted to Dr. H. G. Shaw for the combustion analysis.

GAINESVILLE, FLA. RECEIVED OCTOBER 25, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Energy Levels in Electrochemistry

BY WILDER D. BANCROFT AND JAMES E. MAGOFFIN

When measured against any standard electrode the changes $Cu \rightleftharpoons Cu^{++}$ and $Fe^{++} \rightleftharpoons Fe^{+++}$ are practically reversible. The change $H_2 \rightleftharpoons 2H^+$ is practically reversible at platinum black; but may show a large difference at zinc or mercury because the rate of change of atomic hydrogen to molecular hydrogen is rapid at platinum and relatively slow at zinc or mercury. To pass from hydrogen ion to molecular hydrogen, the system may have to pass through a higher energy level than molecular hydrogen. Given a substance which can be reduced at a lower energy level than that of molecular hydrogen, and it will be reduced at a platinum cathode. If the required energy level is above the molecular hydrogen level and below the atomic hydrogen level which we get with a zinc or mercury cathode, the substance cannot be reduced at a platinum cathode but can be at a zinc or mercury cathode. If the required energy level is above that to be reached with a zinc or mercury cathode, the substance cannot be reduced electrolytically in aqueous solution. Nobody is surprised at not being able to reduce methyl alcohol to paraffin; but no explanation has ever been given why it is impossible to reduce aqueous sodium sulfate or dilute sulfuric acid to sodium sulfite or sulfurous acid. The facts were known to Faraday. We have sealed up a sodium sulfate solution with platinum and hydrogen for six months without anything being formed in that time that would decolorize potassium permanganate.

This is the more remarkable because sodium sulfate and sulfurous acid can easily be oxidized electrolytically and can also be reduced electrolytically under suitable conditions. The answer is that in trying to go electrolytically from sodium sulfate to sodium sulfite, the system must pass through an energy level which is higher than any one can get with nascent hydrogen at a mercury cathode. The same thing holds true for sulfuric acid with this exception that the energy hump disappears experimentally if the sulfuric acid solution is made concentrated enough or hot enough.

We electrolyzed a 25 *N* solution of sulfuric acid with a smooth platinum foil anode and a platinized wire cathode at 50, 80 and 130°. At 50° no reduction of the sulfuric acid took place and the reaction products were hydrogen and oxygen. At 80° hydrogen and hydrogen sulfide were formed at the cathode because the rate of reduction was so slow compared with that of sulfurous acid that the latter was reduced as fast as formed. At 130° hydrogen and sulfur were formed, showing that the rate of reduction of sulfuric acid is fast enough to build up an appreciable concentration of sulfurous acid which then reacted with hydrogen sulfide to form sulfur. With a plain platinum foil cathode reduction of the sulfuric acid was not accomplished until a temperature of 130° was reached, at which temperature the products were hydrogen and hydrogen sulfide when a zinc cathode was used, reduction was obtained at 100°, sulfur and hydrogen being the products. The fact that platinized platinum accomplishes the reduction at a lower temperature than plain platinum indicates that absorption and activation of the sulfuric acid are important factors in the lowering of the energy hump of sulfuric acid.

One may ask why the reverse reaction is not identical with the forward reaction except in sign. The answer is that electrolysis sets free or tends to set free ions. There is no direct decomposition of an ion, such as $SO_4^{=} = SO_3^{=} + O$ or $NO_3^- = NO_2^- + O$. The forward reaction in the oxidation of a sulfite may be written: $SO_3^{=} + O = SO_4^{=}$ and the reverse reaction may be written $SO_4^{=} + 2H = SO_3^{=} + H_2O$; but the two reactions are not the same and are possibly never the same when there is a change in the composition of the ion. This concept of an intermediate energy level which may be higher than that of nascent hydrogen is quite different from the assumptions made by Conant and Lutz[1] of a reversible electrolytic process and a practically irreversible nonelectrolytic one.

It is well known that among metallic oxides the higher ones are stronger oxidizing agents and are more acidic than the lower oxides. With oxygen in the complex anion, this is not always true. Sulfuric acid is an oxidizing agent only at high concentrations or high temperatures, as in the oxidation of naphthalene and even there a catalyst is a great help. Potassium chlorate and perchlorate are weaker oxidizing agents at moderate temperatures than potassium hypochlorite, because of the high intermediate energy levels that must be passed through.

By changing the catalytic surface it is possible to do almost anything with sodium nitrate and nitrite.[2] Nitrate and nitrite are reduced about equally readily at a smooth platinum or copper cathode. Nitrite is reduced more readily than nitrate at a platinized cathode, and nitrate than nitrite at a pulverulent copper or silver cathode. With boiling solutions sodium nitrate can be reduced very effectively to nitrite either at a mercury cathode or with sodium amalgam. Measurements of the cathode potentials showed that overvoltages were a minor factor and that the phenomenon was a function of the nature and structure of the cathode.

At 25° there is practically no reduction of sodium chlorate at a smooth platinum cathode. On the other hand, Gladstone and Tribe[3] found, nearly sixty years ago, that pulverulent platinum or copper, saturated with hydrogen, reduced sodium chlorate to chloride. This could not be a question of electromotive force and experiment showed that there was a specific catalytic effect due to the form of the metal. Decomposition voltage curves were determined for 25 and 80°. Even at 25° there is a marked break in the curve for platinized platinum at a voltage at which no break can be detected in the corresponding curve for smooth platinum. At 80° with the platinized cathode there is first a curve representing reduction of the chlorate. Suddenly the cathode goes apparently passive and the curve changes to that for the evolution of hydrogen. This is due to impoverishment of sodium chlorate in the pores of

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(1) Conant and Lutz, THIS JOURNAL, **45**, 1047 (1923).

(2) Müller, *Z. anorg. Chem.*, **26**, 1 (1901); *Z. Elektrochem.*, **9**, 955 (1903); **11**, 509 (1905); Boehringer and Sons, *ibid.*, **12**, 745 (1906); Bancroft and George, *Trans. Am. Electrochem. Soc.*, **57**, 400 (1930).

(3) Gladstone and Tribe, *J. Chem. Soc.*, **33**, 139 (1878).

the platinized cathode. The effect comes on later and is more marked at the higher temperature owing to the higher rate of diffusion. The cathode can also be made to stay active longer by rotating it, thus increasing the rate of diffusion. The effect of rotation was not so striking as we had hoped that it would be.

Chlorate is evidently adsorbed and activated more strongly by pulverulent platinum or copper than by the smooth metals. This adsorption and activation of sodium chlorate by copper accounts for the puzzling reduction of chlorate by hydrazine in presence of pulverulent copper. Hodgkinson[4] reports that hydrazine can be boiled with a solution of sodium or potassium chlorate without any reduction of the chlorate taking place. In the presence of tarnished copper, quantitative reduction is obtained, apparently at room temperature. Only traces of copper are corroded, so the action must be catalytic. This is in accord with the electrolytic results. The tarnished copper is reduced to pulverulent copper which adsorbs and activates the chlorate so that it is reduced by the hydrazine. It is not the dissolved cuprous salt which acts catalytically, because we have shown that ammoniacal cuprous sulfate will not reduce chlorate. It is essential to oxidize all the cuprous salt with air before testing for chloride, because it was found that some chlorate is reduced if the solution is acidified before all of the cuprous salt has been removed.

With perchlorates the energy level to which the system must be raised is evidently much higher than with chlorates because nobody has yet succeeded in reducing perchlorates electrolytically in neutral or alkaline solutions. Williams[5] has shown that sodium perchlorate can be reduced by boiling with titanous sulfate and sulfuric acid. Since boiling sulfuric acid, if sufficiently concentrated, will decompose perchlorates,[6] there should be no difficulty in reducing perchlorates electrolytically near the boiling point if the right concentration of sulfuric acid is taken.

Chilesotti[7] found that molybdic acid, MoO_3, is reduced more rapidly to Mo_2O_3 at a platinized cathode than at a smooth platinum cathode; but that the reduction goes farther at a smooth platinum cathode. The first stage must be due to adsorption and activation; but it should be shown that the second stage calls for a higher voltage. Tafel[8] showed that in a sulfuric acid solution caffeine is reduced more readily at a mercury cathode than at a lead cathode, while the reverse is true for succinimide. This reversal must be due to selective adsorption in one or the other case, perhaps in both cases.

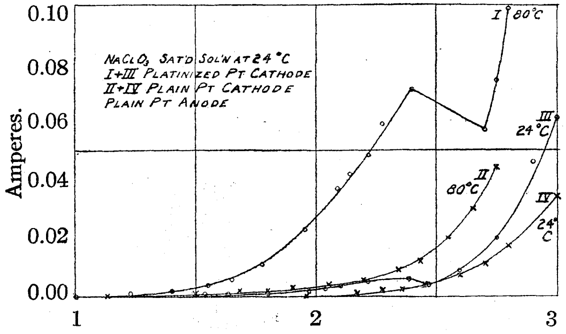

Fig. 1.

Conant and Cutter[9] have observed what appears to be a striking case of adsorption and activation. Dimethylacrylic acid is reduced by platinum and hydrogen but not by a chromous chloride solution, even though the latter is a stronger reducing agent than hydrogen by about 0.3 volt. Evidently the platinum activates the dimethylacrylic acid. If platinum is kept in a suitable chromous chloride or acetate solution until all the hydrogen is given off, that solution will undoubtedly reduce dimethylacrylic acid in presence of platinum. It is not yet necessary to differentiate in principle between hydrogenation and reduction.

People have become so used to speaking of electromotive forces of reversible reactions that most physical chemists believe that an irreversible reaction—assuming one to exist—cannot give a definite electromotive force. This is wrong. A given solution of sodium sulfite is at a definite energy level and changes to another energy level when it is oxidized to sodium sulfate. Since this reaction can be made to take place electrolytically under practically constant conditions, it must and does give a definite electromotive force.

If the sulfite–sulfate electrode were reversible, the limiting, ideal potential difference at a sulfite–sulfate electrode at constant *p*H would be given by the equation

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(4) Hodgkinson, *J. Soc. Chem. Ind.*, **33**, 815 (1914).

(5) Williams, *Chem. News*, **119**, 8 (1919).

(6) Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II, 1922, p. 381.

(7) Chilesotti, *Z. Elektrochem.*, **12**, 146, 173, 197 (1906).

(8) Tafel, *Z. physik. Chem.*, **50**, 713 (1905).

(9) Conant and Cutter, THIS JOURNAL, **44**, 2651 (1922).

$$nFE = RT \ln \frac{P \cdot p_{SO_3}}{p_{SO_4}}$$

where p_{SO_3} and p_{SO_4} are the osmotic pressures of the sulfite and sulfate ions, respectively, and ln P is the Nernst integration constant. If the reaction is not reversible, the concentration of the sulfate ions has theoretically no effect, and the equation becomes

$$nFE = RT \ln P' \times p_{SO_3}$$

The same formula is obtained if the concentration of sulfuric acid is kept constant and this equation has been verified by Lewis, Randall and Bichowsky,[10] who did not know that the reaction was irreversible. They say that "equilibrium conditions apparently were not reached with great rapidity; but, upon standing, steady values were obtained reproducible to within about a millivolt."

"An iridized platinum electrode over which bubbled sulfur dioxide (diluted with air) was used in a solution of sulfuric acid. The other electrode was of mercury covered with mercurous sulfate in the same acid."

Their data are given in Table I.

TABLE I

ELECTROMOTIVE FORCE OF THE CELL $Pt_{SO_2}H_2SO_4$, $HgSO_4$-Hg AT 25°

Mol. % H_2SO_4	Pressure of SO_2 in atmospheres	E. m. f. volt	E. m. f. calcd. SO_2 1 atm. volt
0.09555	0.01328	0.301	0.356
.09555	.00689	.295	.358
.8946	.1091	.274	.302
.8946	.05080	.266	.305
.8946	.02479	.253	.306
.8946	.01328	.251	.306
.8946	.00689	.238	.302
.915	.969	.324	.324
.915	.969	.324	.324
4.618	.02489	.200	.247
4.618	.01333	.192	.247
10.303	.9814	.189	.189

In the cells in which the sulfuric acid concentration was kept constant at 0.8946 M, the equation describes with surprising accuracy the effect of changing the pressure of sulfur dioxide from 0.007 atm. to 0.109 atm., a ratio of more than fifteen to one. Increasing the concentration of the sulfuric acid decreases the electromotive force. We believe that this is not due to the change in the concentration of the sulfate ion, but to a change in the concentration of the hydrogen ion for which no term occurs in the equation. The experiment confirms the part of the theory which is right and disproves the parts that are wrong. Conant and Lutz[11] apparently obtained similar results for their irreversible reduction, though their wording is unnecessarily obscure.

We have confirmed the general results obtained by Lewis in our experiments on sodium sulfite, which of course gives a larger electromotive force against a calomel electrode than an equimolecular solution of sulfurous acid does. Some of our data are given in Table II. The calomel electrode is always cathode and no correction has been made for the liquid junction.

TABLE II

	Cell	E_c
1	Pt | $M/10$ Na_2SO_3 | Calomel	0.1308
2	Pt | M Na_2SO_3 | Calomel	.1455
3	Pt | M Na_2SO_3 + $M/10 Na_2SO_4$ | Calomel	.1533
4	Pt | M Na_2SO_3 + M Na_2SO_4 | Calomel	.1488
5	Pt | M Na_2SO_3 + M NaCl | Calomel	.1816
6	Pt | M Na_2SO_3 + M NaBr | Calomel	.1878
7	Pt | M Na_2SO_3 + M NaCNS | Calomel	.2280
8	Pt | M Na_2SO_3 + M NaOH | Calomel	.2713
9	Pt | M Na_2SO_3 + M NaI | Calomel	.3015

Changing from tenth molar to molar sodium sulfite increases the observed electromotive force from 0.131 to 0.146, which is in the right direction. Adding sodium sulfate increases the electromotive force instead of decreasing it, as would be the case if the reaction were reversible. The fact that tenth molar sodium sulfate increases the electromotive force more, to 0.153, than does molar sodium sulfate, to 0.149, shows that at least two factors are at work. We have not yet tried to determine what the second one is. It was sufficient for the present to show that addition of the reaction product in considerable amounts did not lower the voltage. Addition of molar caustic soda raised the electromotive force from 0.156 to 0.271, which was in the direction to be expected.

Experiments with other salts were very interesting, as there is apparently a marked Hofmeister series, the electromotive force decreasing in the order: $I > OH > CNS > Br > Cl > SO_4$, with iodide coming above thiocyanate as it should do when adsorption is eliminated. The difference is very marked, $E_c = 0.149$ volt for sulfate and 0.302 volt for iodide. It is a question to what extent caustic soda owes its position to the pH or to displacing the water equilibrium. There are no facts which would have enabled us to predict that the electromotive force would be larger in iodide solutions rather than smaller.

One thing that must be done as soon as possible

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[10] Lewis, Randall and Bichowsky, THIS JOURNAL, **40**, 356 (1918).

[11] Conant and Lutz, *ibid.*, **46**, 1256 (1924).

is to devise methods for determining, at least approximately, the intermediate energy levels for sulfates, chlorates, perchlorates, etc. It should be clear that the difficulties that we have with these electrolytes are similar in principle to the difficulties that we have with organic compounds. Most of the passive resistances to change will prove to be energy humps.

Summary

The general results of this paper are:

1. The oxidation of dilute aqueous sulfurous acid or sodium sulfite is an irreversible reaction because, for reduction to take place, the system must pass through an energy level or energy hump which is higher than the energy level for nascent hydrogen as obtained by electrolysis.

2. With sulfuric acid solutions, and presumably with all other solutions, the energy hump decreases with increasing concentration, rising temperature and activating adsorption.

3. The stabilities of sodium chlorate and sodium perchlorate relatively to sodium hypochlorite are due to the intermediate energy levels which must be surmounted if reduction is to take place.

4. Sodium chlorate is adsorbed and activated so much by pulverulent copper that it can then be reduced by hydrazine.

5. An irreversible reaction may give a definite electromotive force. The limiting, ideal equation for the irreversible sulfite-sulfate electrode at constant pH is $nFE = RT \ln P' \times p_{\mathrm{SO_3}}$.

6. All of Conant's work on irreversible reduction falls into line if one rejects the two assumptions of a reversible electrolytic step and a practically irreversible, non-electrolytic step. There is no experimental evidence for either, and both are superfluous. There is no reason at present for making any fundamental distinction between hydrogenation and reduction.

ITHACA, N. Y. RECEIVED AUGUST 27, 1935

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE]

A Procedure for the Separation of the Six Platinum Metals from One Another and for their Gravimetric Determination[1,2]

BY RALEIGH GILCHRIST AND EDWARD WICHERS

In a paper[3] from this Laboratory, presented at the Ninth International Congress of Pure and Applied Chemistry in Madrid, April, 1934, a group of reactions was described which can be used for the quantitative separation of the six platinum metals from one another, and for their determination. The paper likewise contained a discussion of the analytical methods most generally used, and of certain others of special interest.

In this new system of analysis, the detailed procedure of which is given in the present paper, precipitation with ammonium chloride, fusion with pyrosulfate and extraction of metallic residues with acids are avoided entirely. The separation of platinum from palladium, rhodium and iridium is accomplished by controlled hydrolytic precipitation. When a boiling solution containing these four metals as chlorides, and in addition sodium bromate, is neutralized to approximately pH 7, the hydrated dioxides of palladium, rhodium and iridium precipitate quantitatively, leaving platinum in solution. A second precipitation of the dioxides suffices to effect complete removal of platinum. This method is applicable not only to the joint separation of palladium, rhodium and iridium from platinum, but also to the individual separation of these metals from platinum. It has a very great advantage over the older method by which platinum is separated from palladium, rhodium and iridium by precipitation with ammonium chloride. The hydrolytic method effects a clean separation of the platinum, whereas that in which the platinum is precipitated as ammonium chloroplatinate involves at least two inherent types of error. One type of error results from the persistent contamination of the platinum salt by rhodium and iridium (even though tervalent) and, to a less extent, by palladium. The other error occurs be-

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[1] Publication approved by the Director of the National Bureau of Standards of the U. S. Department of Commerce.

[2] Presented at the Meeting of the American Chemical Society in New York, April 25, 1935.

[3] R. Gilchrist and E. Wichers, "A New System of Analytical Chemistry for the Platinum Metals." Paper No. 178 of the Scientific Program of the Ninth International Congress of Pure and Applied Chemistry. As the proceedings of the Congress have not been published, reprints of this paper are not yet available.

cause ammonium chloroplatinate is appreciably soluble. It is true that the solubility of the platinum salt can be reduced to an amount which may be negligible in some analytical procedures by adding a large excess of ammonium chloride and digesting the solution. These conditions, however, greatly increase the contamination of the salt by other platinum metals. The same criticism applies to the separation of quadrivalent iridium from rhodium and palladium, by means of ammonium chloride. A full discussion of the shortcomings of the traditional methods of separating the platinum metals from one another cannot be given in this paper, but will be found in detail in the paper presented at the International Congress.

Palladium is readily and completely separated from rhodium and iridium, in chloride solution, by precipitation with dimethylglyoxime, a single precipitation being sufficient.

Rhodium is separated from iridium by reducing it to metal with titanous chloride in a boiling solution of the sulfates in diluted sulfuric acid. The metallic rhodium is dissolved in hot sulfuric acid and precipitated a second time, to remove iridium completely.

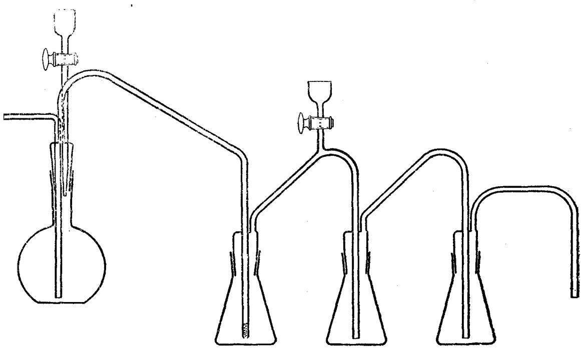

Fig. 1.—Distilling flask with train.

When this new procedure is applied to the separation of all six of the platinum metals from one another, osmium is the first metal which is isolated. This is accomplished by distilling its volatile tetroxide from a nitric acid solution. Ruthenium is next isolated by distilling its tetroxide from a solution of the sulfates in diluted sulfuric acid to which sodium bromate is added. A very suitable reagent for the absorption of osmium tetroxide, and also of ruthenium tetroxide, is 6 *N* hydrochloric acid saturated with sulfur dioxide.

In the recovery and determination of each of the six metals, the new features of the procedure consist in the precipitation of osmium, of ruthenium and of iridium, as hydrated oxides, with final ignition to metal. Rhodium, and also platinum, are recovered as sulfides, and ignited to metal. Palladium is recovered as the glyoxime compound, in which form it may be weighed, or it may be determined as metal, after ignition of the glyoxime precipitate.

The accuracy of this new method is comparable to that of the best analytical procedures for the common metals. The reagents used are generally available, and no special equipment is required. While the operations must be performed carefully, they do not involve technique unfamiliar to a trained analyst.

The individual procedures upon which the general scheme for the group as a whole is based are to be found in the papers to which the references in this paper are given. These papers also contain a detailed account of the experimental work upon which the individual procedures were developed. They should be consulted for details which obviously cannot be included in the present paper. The general procedure, as given in this paper, was tested by analyzing solutions containing, simultaneously, known quantities of the six pure metals. The procedure is designed for the analysis of the platinum group, in the absence of other metals.

Consideration of the elements occurring in crude platiniferous materials will be taken into account in the extension of this scheme to their analysis.

Procedure Recommended for the Analysis of the Platinum Group

I. Separation and Determination of Osmium[4]

1. Distilling Apparatus.—The distilling apparatus, which is shown in Fig. 1, consists of three main parts, namely, a 700-ml. distilling flask, a set of three 300-ml. absorbing flasks and a train of inlet and delivery tubes which are sealed into one piece. The thistle tube, closed by a stopcock and placed between the first and second absorbing flasks, serves to replenish the absorbing solution with sulfurous acid if an unusual amount of nitric acid is distilled and also, at the end of the operation, to rinse the tube connecting the two flasks. The entire apparatus is constructed of Pyrex glass. The joints must be very carefully ground, and it is advantageous if they are made so that the flasks are interchangeable. It is important to note that these joints are sealed with a film of water only and not with lubricating grease, because the latter would cause reduction of some osmium tetroxide to dioxide

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[4] R. Gilchrist, *Bur. Standards J. Research*, **6**, 421 (1931); RP 286.

which cannot be readily recovered. It was found necessary to grease the stopcock in the tube used for the introduction of nitric acid into the distilling flask, but this constitutes the only exception. During distillation, this delivery tube is frequently flushed with water in order to remove any osmium tetroxide which may have diffused into the column of water held in it. Three absorbing flasks are used, but the absorption of osmium tetroxide is practically complete in the first flask, and no osmium has been found to escape the second flask.

2. **Separation of Osmium by Distillation as Osmium Tetroxide.**—Place 150 ml. of diluted hydrochloric acid (1 + 1),[5] which has been freshly saturated with sulfur dioxide, in the first absorbing flask and 50 ml. of the same reagent in each of the other two flasks. Place the solution containing the platinum metals in the distilling flask and make sure that the separate parts of the entire apparatus are properly connected. If necessary, dilute the solution in the distilling flask to about 100 ml. with water, and add through the inlet tube 40 ml. of diluted nitric acid (1 + 1). Flush the thistle tube and stopcock with 10 ml. of water. Pass a slow current of air through the apparatus and heat the solution in the distilling flask to boiling. Continue the distillation for one hour. This length of time should be sufficient to ensure complete elimination of osmium from solutions in which it was originally present as an alkaline osmate or bromoosmate. If, however, the osmium is present as chloroosmate, the time required will be from seven to eight hours. In this case, it is preferable to distil from concentrated sulfuric acid, thereby greatly reducing the time required, or, if ruthenium is known to be absent, from concentrated sulfuric acid to which a few milliliters of nitric acid is added.

3. **Recovery of Osmium by Precipitation as the Hydrated Dioxide.**—Unite the portions of the absorbing solution and evaporate as far as possible on the steam-bath in a clean, unetched beaker. It is important, in precipitating the platinum metals hydrolytically, that the beakers used do not have an etched surface. An etched beaker often becomes stained with the precipitate, and this stain cannot always be removed readily. Digest the residue with 10 ml. of hydrochloric acid for fifteen minutes, and evaporate a second time. Repeat the digestion with hydrochloric acid and the evaporation three times more. This is done to ensure complete decomposition of any sulfite compounds of osmium. Dissolve the residue from the last evaporation in 150 ml. of water. Heat the resulting solution to boiling, and add to it a filtered 10% solution of sodium bicarbonate until a precipitate appears and suddenly coagulates. Add a few drops of brom phenol blue indicator solution (0.04%) to the hot solution. This indicator changes from yellow to blue at *p*H 4. Add the bicarbonate solution dropwise until the indicator assumes a faint bluish color. Finally, boil the solution for five to six minutes to ensure complete precipitation of the hydrated osmium dioxide.

4. **Determination of Osmium as Metal.**—Filter the solution through a Munroe platinum crucible,[6] carefully pouring the supernatant liquid through first. Transfer the precipitate, and wipe the inner walls of the beaker and also the glass rod with a rubber policeman which has been thoroughly wetted so that the precipitate will not cling to it. It should be borne in mind that filter paper must not be used to wipe the beaker, although it is used when handling precipitates of any of the other five platinum metals. Wash the precipitate thoroughly with a hot 1% solution of ammonium chloride, and then cover it with solid ammonium chloride. Moisten the ammonium chloride with a few drops of the wash solution and saturate the precipitate by applying suction. If desired, a saturated solution of ammonium chloride may be used to impregnate the precipitate. Continue the suction until the bottom of the crucible is coated with solidified ammonium chloride. Wipe off this coating of salt and place the platinum cap on the bottom of the crucible.

Cover the crucible with a Rose lid, preferably of quartz. Ignite a stream of hydrogen from a Rose delivery tube, likewise of quartz, and regulate the stream so that a very small flame is produced. Then insert the tube through the opening in the lid. The hydrogen flame will probably become extinguished by this operation and must be reignited. This is done by momentarily placing a burner flame under the crucible. The hydrogen will now burn as it emerges from under the lid at the edge of the crucible. The ignited hydrogen generates the requisite amount of heat to dehydrate the osmium compound without causing deflagration. After five minutes, gradually heat the crucible with the burner flame until all of the ammonium chloride is expelled. Ignite the osmium residue strongly in hydrogen for ten minutes. Remove the burner and allow the crucible to cool somewhat. Extinguish the hydrogen flame by momentarily breaking the current of hydrogen, and allow the crucible to cool to room temperature. Finally, displace the hydrogen with a current of carbon dioxide without even momentary access of air. If the hydrogen is not displaced by an inert gas, such as carbon dioxide, the reduced metal will be rapidly attacked when first exposed to the air, with significant loss of osmium. Weigh the residue as metallic osmium.

II. Separation and Determination of Ruthenium[7,8]

1. **Preparation of the Solution.**—Evaporate to dryness on the steam-bath the solution which remains in the distilling flask after the elimination of osmium. Add 5 to 10 ml. of hydrochloric acid and again evaporate. Repeat the evaporation with hydrochloric acid until oxides of nitrogen are no longer evolved. Dissolve the residue from the last evaporation in about 20 to 30 ml. of water. Add 10 ml. of sulfuric acid and evaporate the resulting solution carefully until vapors of sulfuric acid are evolved. Trans-

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[5] Throughout this paper, whenever acids are mentioned, hydrochloric acid will mean the concentrated acid of specific gravity 1.18; nitric acid, the concentrated acid of specific gravity 1.42; sulfuric acid, the concentrated acid of specific gravity 1.84. Diluted acids will be designated as follows: for example, diluted hydrochloric acid (1 + 1) will mean one volume of the concentrated acid of specific gravity 1.18 diluted with one volume of water.

[6] The chief disadvantage in the use of a Gooch crucible with an asbestos pad is the difficulty encountered during the ignition of the dioxide to metal. Even when the Gooch crucible is protected from the burner flame by setting it in a circle of asbestos board in a larger porcelain crucible, one is not always able to extinguish the hydrogen flame readily. Another disadvantage is the inadequate protection of the reduced metal from attack by air diffusing through the holes in the bottom of the crucible.

[7] Gilchrist, *Bur. Standards J. Research*, **3**, 993 (1929); RP 125.

[8] Gilchrist, *ibid.*, **12**, 283 (1934); RP 654.

fer the solution, and any residue of platinum which may have separated, to the distilling flask that was used for the distillation of osmium tetroxide. Dilute the solution in the distilling flask to 100 ml. with water.

2. **Separation of Ruthenium by Distillation as Ruthenium Tetroxide.**—Place 150 ml. of diluted hydrochloric acid (1 + 1), freshly saturated with sulfur dioxide, in the first receiving flask and 50 ml. of the same reagent in each of the other two flasks. Add 100 ml. of a filtered 10% solution of sodium bromate through the thistle tube to the distilling flask. This tube should be flushed with water occasionally in order to remove any ruthenium tetroxide which dissolves in the column of liquid held in the tube. In order to maintain an excess of sulfur dioxide in the absorbing solution, a saturated solution of sulfur dioxide in water should be added from time to time through the thistle tube situated between the first and second receiving flasks. Pass a gentle current of air through the apparatus, and heat the solution in the distilling flask to boiling. Distil[9] in this fashion for one and one-half hours. Add 25 ml. of the bromate solution, and continue to distil for an additional hour.

3. **Recovery of Ruthenium by Precipitation as a Hydrated Oxide.**—Combine the portions of the absorbing solution and evaporate to a moist residue on the steam-bath. Add 10 ml. of hydrochloric acid and digest the solution, in a covered beaker, on the steam-bath for one-half hour. Add 50 ml. of water and heat the solution to boiling in order to dissolve completely the somewhat difficultly soluble ruthenium compound formed on evaporation. When the ruthenium compound is completely dissolved, filter the solution and wash the filter with diluted hydrochloric acid (1 + 99). Filtering ensures the elimination of a small amount of silica which may be present. Dilute the ruthenium solution to 200 ml., heat it to boiling and add a filtered 10% solution of sodium bicarbonate until a precipitate begins to form. Add 3 or 4 drops of brom cresol purple indicator solution (0.04%). Continue neutralization of excess acid by adding the bicarbonate solution dropwise until the indicator changes from yellow to blue. Boil the solution for five to six minutes to coagulate the precipitate.

The precipitate which is formed is a hydrated oxide of ruthenium, probably of tervalent ruthenium. In general appearance, it resembles other hydrated oxides of tervalent platinum metals. It does not settle as quickly nor appear as compact as the precipitate formed on the hydrolysis of compounds of quadrivalent ruthenium. However, it is quantitatively precipitated, and no difficulty is encountered in handling it.

4. **Determination of Ruthenium as Metal.**—Filter the solution and wipe the inner walls of the beaker and also the glass rod with a small piece of ashless filter paper. Wash the filter and the precipitate thoroughly with a hot 1% solution of ammonium sulfate. Finally, wash three or four times with a cold (room temperature) 2.5% solution of ammonium sulfate.

Place the filter and precipitate in a porcelain crucible, dry them and char the filter slowly. The dried filter will usually char completely when once it begins to smoke. This operation should be done carefully in order to prevent loss of ruthenium by deflagration. Ignite the residue strongly in air and then in hydrogen. The ignition in hydrogen is made in a manner similar to that described for the determination of osmium. Cool the resulting metal in hydrogen and leach it well with hot water. This is done to ensure the removal of traces of soluble salts. It is well to leach the residue in the crucible first and then to transfer it to a filter. Ignite the filter and metal sponge in air and in hydrogen. Cool the residue in hydrogen and weigh it as metallic ruthenium.

III. Separation and Determination of Platinum[10]

The solution which remains in the distilling flask after the elimination of ruthenium contains the four metals, platinum, palladium, rhodium and iridium, together with sulfuric acid, sodium sulfate or acid sulfate, bromine and undecomposed bromate. Experience shows that the platinum, rendered partly insoluble in the preparation of the solution for the distillation of ruthenium, is entirely dissolved during the distilling operation. A trace of iridium sometimes separates as the dioxide toward the end of the distilling period.

1. Preparation of the Solution

a. **Treatment of the Solution from the Distilling Flask.**—In order to prepare the solution for subsequent operations, transfer the contents of the distilling flask to a liter beaker. Cautiously decompose the remaining bromate with hydrochloric acid. Unless precaution is taken in this treatment, mechanical loss may occur owing to the vigorous evolution of gas. Evaporate the solution when it has become quiescent. Make certain that any bromate remaining is decomposed, by evaporating with hydrochloric acid. Occasionally, the distilling flask is found to be slightly stained with iridium dioxide near where the level of the solution has stood. It is well, therefore, always to clean the flask with 5 to 10 ml. of aqua regia, which then must be evaporated with hydrochloric acid to decompose nitroso compounds before it is added to the main solution. Finally, evaporate the solution as far as possible on the steam-bath, and then dilute it to 200 ml. with water.

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(9) See original paper for a discussion of various solutions from which to distil ruthenium. The usual way is to distil from an alkaline solution which is saturated with chlorine. If this procedure is used, one can never be sure that the elimination of ruthenium is complete, even though additional alkali is added and the distilling process repeated, owing to the precipitation, near the neutral point, of iridium hydroxide which carries with it some ruthenium. It is necessary, therefore, in order to prevent the precipitation of iridium, to distil from an acid solution. The distillation of ruthenium tetroxide may be made immediately after the elimination of osmium, without removing the contents of the distilling flask, by adding a solution of sodium bromate. From 5 to 10 ml. of nitric acid should be added to increase the acid concentration of the solution. The minimum time required for complete removal of ruthenium from a boiling solution is about three and one-half hours. Although the solution requires some preparation, distillation from a solution of ruthenium sulfate in diluted sulfuric acid, as given in the procedure, is preferable. The elimination of ruthenium tetroxide from such a solution is much more rapid than from a solution containing the ruthenium as chlororuthenate. A further advantage is gained by being able to conduct the entire distillation at the boiling temperature without danger of depositing ruthenium dioxide on the walls of the flask and delivery tube, since the cause of such deposition, namely, hydrochloric or hydrobromic acid, is removed during the preparation of the solution for distillation.,

(10) Gilchrist, *Bur. Standards J. Research*, **12**, 291 (1934); RP 655.

b. Treatment of a Solution which has not Contained Osmium or Ruthenium.—If the solution being analyzed is known not to contain either osmium or ruthenium and the parts of the general procedure referring to these metals have not been followed, evaporate it to a moist residue on the steam-bath. If the solution has contained nitric acid, add 5 ml. of hydrochloric acid and again evaporate, repeating this operation to ensure the decomposition of nitroso compounds. Add 2 g. of sodium chloride and 5 ml. of hydrochloric acid and evaporate this time to dryness on the steam-bath. Add 2 ml. of hydrochloric acid and dilute the solution to 300 ml. with water.

2. Separation of Platinum by Joint Precipitation of Palladium, Rhodium and Iridium as Hydrated Dioxides.—Heat the solution containing platinum, palladium, rhodium, and iridium to boiling, and add to it 20 ml. of a filtered 10% solution of sodium bromate. Carefully add a filtered 10% solution of sodium bicarbonate until the dark green solution shows evidence of the formation of a permanent precipitate. Test the acidity of the hot solution from time to time by allowing a drop of brom cresol purple indicator solution (0.01%) to run down the stirring rod into the drop which clings to it as it is lifted from the solution. Enough bicarbonate has been added when the color of the indicator changes from yellow to blue. At this stage, add 10 ml. more of the bromate reagent and boil the solution for five minutes. Increase[11] the *p*H of the solution slightly by carefully adding dropwise bicarbonate solution until a faint pink color is produced in the test drop by a drop of cresol red indicator solution (0.01%). Again add 10 ml. of the bromate reagent and boil for fifteen minutes.

On removing the beaker from the source of the heat, the mixed precipitate will settle quickly, leaving a mother liquor containing the platinum. Filter the solution by suction, using a porcelain filtering crucible[12] having solid walls and a porous base.

It is highly desirable to avoid the use of filter paper when repeated precipitations are to be made. The material of which the paper is composed undoubtedly reacts with acids and probably forms small quantities of organic compounds with the platinum metals which are not easily hydrolyzed. Iridium dioxide, which dissolves much less readily than either palladium or rhodium dioxide, tends to stain paper pulp. The stain cannot always be removed by washing. These difficulties are avoided if the porcelain filtering crucible is used. Furthermore, such crucibles have the advantage that concentrated hydrochloric acid can be used to dissolve the hydrated dioxides, and considerable time is saved in preparing the solution for subsequent treatment.

Pour the supernatant liquid through first, then transfer the precipitate. Rinse the beaker and wash the precipitate with a hot 1% solution of sodium chloride, the acidity of which has been adjusted to between *p*H 6 and 7. Place the crucible with the precipitate, and also the stirring rod, in the beaker used for the precipitation. It may be necessary to remove a small amount of the precipitate which has crept over the lip of the beaker during filtration. It is preferable to do this with moistened crystals of sodium chloride, on the finger, rather than to use paper or a rubber policeman. Replace the watch glass and add from 10 to 20 ml. of hydrochloric acid, pouring most of it into the crucible. Place the covered beaker on the steam-bath. The rhodium and palladium compounds will dissolve quickly, the iridium dioxide much more slowly. Carefully lift the crucible with the stirring rod, wash it with water and place it in a 250-ml. beaker. Pour 5 ml. of hydrochloric acid into the crucible. Cover the beaker with a watch glass and set it on the steam-bath. This treatment will usually leach out the small quantity of metal chlorides in the porous bottom. This operation should be repeated with fresh acid to ensure complete removal. Combine the leachings with the main portion of the dissolved precipitate, add 2 g. of sodium chloride, and evaporate to dryness on the steam-bath. Add 2 ml. of hydrochloric acid, dilute the solution to 300 ml. with water, and repeat the precipitation of the hydrated dioxides. Two such precipitations are sufficient ordinarily to effect the complete separation of platinum from palladium, rhodium and iridium.

3. Recovery of Platinum by Precipitation with Hydrogen Sulfide.—Add 20 ml. of hydrochloric acid to each of the filtrates obtained from the hydrolytic precipitation of the dioxides of palladium, rhodium and iridium. Carefully warm the solutions until they become quiescent. Partially concentrate the filtrates, combine them and then evaporate to dryness. Make certain that all of the bromate is destroyed, by evaporation with hydrochloric acid. Dilute the yellow platinum solution somewhat and filter it. Wash the filter with diluted hydrochloric acid (1 + 99). Dilute the filtered solution to about 400 ml. with water and have it contain 5 ml. of hydrochloric acid in each 100 ml. volume.

Precipitate the platinum, in a hot solution, with hydrogen sulfide, using a rapid stream. Continue the passage of hydrogen sulfide as the solution cools somewhat, to ensure complete precipitation.

4. Determination of Platinum as Metal.—Filter the solution and wash the precipitate with diluted hydro-

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[11] Since previous publication on this subject [*Bur. Standards J. Research*, **12**, 291 (1934); RP 655], it has been found that, whereas a *p*H of 6 ensures complete precipitation of rhodium and of iridium, this acidity is on the borderline with respect to the precipitation of palladium. In the procedure as finally recommended, hydrolytic precipitation is made, during the first boiling period, at a *p*H value (approximately *p*H 6) corresponding to the change in color of brom cresol purple (0.01%) when a drop of the indicator solution is allowed to react with a drop of the boiling solution. A second boiling period, at a *p*H value (approximately *p*H 8) corresponding to the change in color of cresol red (0.01%), ensures quantitative precipitation of palladium. It is preferable to perform the precipitation in two stages in order to be able to observe the faint pink color of cresol red in the test drop. It was determined experimentally, with solutions made to contain the same quantity of acid and salts as do those which result from the removal of osmium and ruthenium by distillation, that no interference is encountered in the precipitation of palladium, rhodium and iridium. It was further observed that rhodium and iridium are quantitatively precipitated under the conditions specified for precipitating palladium, and that platinum does not contaminate the precipitated dioxides to any greater extent than when the hydrolytic operation is conducted at *p*H 6 alone. In the absence of palladium, it is recommended that the hydrolytic precipitation be made at the color change of brom cresol purple (*p*H 6).

[12] This type of crucible is manufactured by the State Porcelain Works, Berlin, Germany. A crucible of convenient size is one having a height of 45 mm., a diameter at the top of 40 mm. and a capacity of 30 ml. The crucible designated by the mark "A1" filters rapidly and allows no trace of the precipitate to escape. Crucibles marked "A2," but somewhat smaller in size, were found to be perfectly satisfactory. No doubt glass crucibles of suitable porosity could also be used.

chloric acid (1 + 99). Ignite the dried filter and precipitate in a porcelain crucible. Leach the metal residue with diluted hydrochloric acid, transfer it to a filter and wash it thoroughly with hot water. Ignite the filter and metal again strongly in air. Weigh the residue as metallic platinum. The metal so obtained will usually contain a small but significant amount of sulfur[13] which cannot be eliminated by ignition in either air or hydrogen.

If the highest accuracy is desired, dissolve the metallic platinum, obtained by ignition of the sulfide, in aqua regia. Destroy nitroso compounds by evaporation with hydrochloric acid. Filter the solution into a clean, unetched beaker. Wash the filter with diluted hydrochloric acid (1 + 99). Dilute the solution to 100 ml., heat it to boiling and add to it a solution containing 3 g. of sodium acetate and 1 ml. of formic acid for each 0.25 g. of platinum. Boil the resulting solution gently until the precipitated metallic platinum is well coagulated and the supernatant liquid is colorless. Filter the solution and wash the metallic deposit with a hot 1% solution of ammonium chloride. Place the filter and the spongy metal in a porcelain crucible and ignite them strongly in the air. Leach and wash the ignited metal as previously directed. This precaution is taken to ensure the removal of soluble salts. Finally ignite the platinum in air again. Weigh the residue as metallic platinum, which will now be free from sulfur.

It is far better to precipitate the platinum first by hydrogen sulfide, and then to reprecipitate it by formic acid in a buffered solution, than it is to attempt to precipitate the platinum directly by formic acid. The precipitation with hydrogen sulfide eliminates the relatively large amount of sodium salts which cause trouble in the formic acid reduction.

IV. Separation and Determination of Palladium[10]

1. Separation of Palladium by Precipitation with Dimethylglyoxime.—Dissolve the precipitate of the hydrated dioxides of palladium, rhodium and iridium in hydrochloric acid as previously directed. Filter the solution and dilute it to a volume of about 400 ml. Add a sufficient volume of a 1% solution of dimethylglyoxime in 95% ethyl alcohol to precipitate all of the palladium (2.2 g. of the solid reagent is required for 1 g. of palladium). An excess of the reagent amounting to 10% should be added to ensure complete precipitation. Let the solution stand for one hour and then filter it. The manner of filtration will depend upon the form in which the palladium is to be determined. Wash the precipitate with diluted hydrochloric acid (1 + 99), and finally with hot water. The precipitate can be washed with a considerable volume of water without a trace of it dissolving. A single precipitation of the palladium is sufficient to separate it completely from rhodium and iridium.[14]

2. Determination of Palladium

a. As Palladium Dimethylglyoxime.—Palladium dimethylglyoxime is sufficiently stable and constant in composition to be dried and weighed. If the determination is to be made in this manner, catch the precipitate in a porcelain or glass filtering crucible, using suction. Wash the precipitate as previously directed and dry it at 110° for one hour. Calculate the quantity of palladium, using the theoretical factor, 0.3167.

b. As Metal.—If the palladium is to be determined as metal, which in certain cases may be more convenient, catch the precipitate on an ashless filter. Wipe the inner walls of the beaker and also the glass rod with a small piece of ashless paper. Wrap the filter and precipitate in a second filter and place them in a porcelain crucible. Dry them, and ignite them carefully in the air. Only sufficient heat should be supplied to keep the papers smoking gently. Ignite the charred residue strongly in air, and then in hydrogen. Ignite the metallic palladium in carbon dioxide[15] for two minutes and cool it in carbon dioxide. Weigh the residue as metallic palladium.

V. Separation and Determination of Rhodium[10,16]

1. Preparation of the Solution.—Place the solution containing the rhodium and iridium as chlorides, together with the excess of dimethylglyoxime remaining from the precipitation of palladium, in a 500-ml. Erlenmeyer flask. Place a short-stemmed funnel in the mouth of the flask. Add 10 ml. of sulfuric acid and 2 to 3 ml. of nitric acid, and evaporate until heavy vapors of sulfuric acid are evolved. To ensure complete destruction of organic matter, add a small quantity of nitric acid from time to time and continue to heat over a free flame, keeping the solution in constant motion. Dilute the cooled solution with 20 ml. of water and again evaporate it until vapors of sulfuric acid appear. This is done to destroy nitroso compounds which may interfere in the precipitation of rhodium by titanous chloride.

2. Separation of Rhodium by Precipitation with Titanous Chloride.—Transfer the sulfate solution to a clean, unetched beaker, dilute it to 200 ml. and heat it to boiling. Add dropwise a solution of titanous chloride (a 20% solution of this reagent may be purchased) until the supernatant liquid appears slightly purple. If the solution is placed over a 100-watt light and stirred, observation of the end-point is greatly facilitated. The metallic rhodium which is precipitated quickly coagulates into a spongy mass. If much iridium is present, the end-point can be determined by the lack of formation of any further precipitate and the appearance of an orange color in the solution. Boil the solution for two minutes and filter it.

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(13) In 17 experiments, the weights of platinum (0.25-g. portions) recovered by ignition of the sulfide in air exceeded those taken by amounts which ranged from 0.0 to 1.0 mg., and averaged 0.5 mg. The retention of sulfur by palladium is very marked, and the sulfide may even fuse into globules which cannot be completely decomposed by ignition. Therefore, palladium must not be determined by ignition of its sulfide. No significant amount of sulfur is retained when rhodium sulfide is ignited.

(14) If, for any reason, it is desired to reprecipitate the palladium, catch the precipitate on paper. Transfer the washed filter and precipitate to an Erlenmeyer flask, closed with a short-stemmed funnel and decompose them in a mixture of sulfuric and nitric acids. Heat the solution until vapors of sulfuric acid are evolved, dilute it somewhat and filter it. Precipitate the palladium from the diluted solution of its sulfate with dimethylglyoxime.

(15) Palladium possesses the property of absorbing a considerable quantity of hydrogen, so that it is difficult to obtain constant weight. If the absorbed hydrogen is eliminated by igniting the metal so obtained in an inert gas, no difficulty is encountered. Strong ignition in air is sufficient to decompose all oxides of palladium, without resort to hydrogen, but the gray metal tarnishes as it cools unless an inert gas protects it. The error involved, however, amounts to only 0.1 mg. with quantities of palladium weighing 100 mg.

(16) Gilchrist, *Bur. Standards J. Research*, **9**, 547 (1932); RP 489.

Wipe the walls of the beaker and also the stirring rod with a piece of ashless filter paper. Wash the filter and precipitated metal thoroughly with cold (room temperature) diluted sulfuric acid (2.5 + 97.5).

Place the filter with its contents in a 500-ml. Erlenmeyer flask, add 10 ml. of sulfuric acid, char gently, add 5 ml. of nitric acid and digest the solution on a hot plate. Usually, the rhodium dissolves fairly readily. Complete the solution of the rhodium by heating the flask over a free flame, keeping the contents of the flask in constant motion. Ensure the destruction of organic matter and the elimination of nitroso compounds. If some black specks remain, dilute the solution, filter it and return the filter to the flask. Wipe down the walls of the flask with a piece of ashless filter paper. Add 5 ml. of sulfuric acid, char the paper, and destroy all organic matter with nitric acid. Heat the solution until heavy vapors of sulfuric acid are evolved. This treatment will dissolve any remaining metal and will leave only a slight deposit of colorless silica.

Precipitate the rhodium a second time in the manner described above. Redissolve the rhodium as before, dilute the sulfuric acid solution with 20 ml. of water and 10 ml. of hydrochloric acid and boil the resulting solution for fifteen minutes. This treatment is necessary to convert the rhodium into a form which will allow complete precipitation by hydrogen sulfide. During this treatment, the color of the solution will change from yellow to rose. Filter the solution and wash the filter with diluted hydrochloric acid (1 + 99). Finally, dilute the solution to a volume of from 400 to 500 ml.

3. Recovery of Rhodium by Precipitation with Hydrogen Sulfide.—Precipitate the rhodium as sulfide from a solution, kept just at the boiling point, by passing a rapid stream of hydrogen sulfide through it. Allow the solution to cool somewhat, with the hydrogen sulfide still passing through it.

4. Determination of Rhodium as Metal.—Filter the solution and wash the precipitate with diluted sulfuric acid (2.5 + 97.5), and finally with diluted hydrochloric acid (1 + 99). Place the filter with the sulfide precipitate in a porcelain crucible. Ignite the dried precipitate carefully in air. Finally, ignite the oxidized residue in hydrogen, cool the resulting metal in hydrogen and weigh it as metallic rhodium.

VI. Recovery and Determination of Iridium[10,16]

Iridium may be determined in either of two ways. If the solution containing both rhodium and iridium can be divided conveniently into aliquot parts, the determination of iridium is greatly simplified and the precipitations of titanium by cupferron avoided. The rhodium and iridium in one portion of the solution can be recovered by hydrolytic precipitation as described in the procedure for the separation of platinum. If this is done, the mixed precipitate of rhodium and iridium dioxides is washed with a hot 1% solution of ammonium chloride, neutral to brom thymol blue (pH 7), instead of with a solution of sodium chloride. The dried filter and precipitate are impregnated with a few drops of a saturated solution of ammonium chloride, in order to prevent deflagration, and carefully ignited to a mixture of the anhydrous oxides. The oxidized residue is ignited and cooled in hydrogen, and weighed as a mixture of metallic rhodium and metallic iridium. In order to calculate the quantity of iridium, it is necessary, in addition, to determine rhodium as previously described in a separate portion of the solution.

If the iridium cannot be determined in this way, it is necessary to recover it from the filtrates resulting from the precipitation of rhodium by titanous chloride.

1. Elimination of Titanium by Precipitation with Cupferron.—Dilute the combined filtrates from the precipitation of rhodium by titanous chloride to 800 ml. Cool the solution by placing the beaker in crushed ice. Add a chilled, filtered, freshly prepared 6% solution of cupferron (ammonium salt of nitrosophenylhydroxylamine, $C_6H_5N{\cdot}NO{\cdot}ONH_4$) in slight excess. Filter the solution and wash the titanium precipitate with chilled diluted sulfuric acid (2.5 + 97.5) containing some cupferron. The cupferron precipitate is usually slightly contaminated by iridium, but the amount does not exceed 1 mg. when about 0.2 g. of iridium is being handled. Return the filter and precipitate to the beaker, add 20 ml. of nitric acid, and heat until the precipitate is mostly decomposed. Add 20 ml. of sulfuric acid and heat the solution until vapors of sulfuric acid appear. Destroy the remaining organic matter by adding nitric acid, and heating. Dilute the resulting solution to 800 ml. and repeat the precipitation of the titanium. Unite the filtrates from the cupferron precipitations and evaporate until approximately 10 ml. of sulfuric acid remains. Ensure the destruction of all organic matter. Dilute the solution somewhat and filter it.

2. Recovery of Iridium by Precipitation as the Hydrated Dioxide.—Dilute the solution to 200 ml. with water and neutralize most of the acid contained in it with a filtered solution of sodium bicarbonate. Heat the solution to boiling and complete its neutralization with bicarbonate to the end-point of brom cresol purple, as described in the procedure for the separation of platinum. Add 20 ml. of a filtered 10% solution of sodium bromate, and boil the solution for twenty to twenty-five minutes. Be sure that sufficient bromate is present to oxidize all of the iridium to the quadrivalent state. Filter the solution and wash the precipitate thoroughly with a hot 1% solution of ammonium chloride.

3. Determination of Iridium as Metal.—Place the filter and precipitate in a porcelain crucible. Dry them somewhat and then moisten them with a few drops of a saturated solution of ammonium chloride. Ignite the filter and precipitate carefully in the air and then in hydrogen. Leach the metallic residue with diluted hydrochloric acid, then transfer it to a filter, and wash it with hot water. Ignite the filter and metallic residue in air. Finally, ignite the resulting oxidized metal in hydrogen, cool it in hydrogen and weigh it as metallic iridium.

The procedure as herein written is designed for the highest degree of accuracy. If, however, one is not interested in such accuracy, the procedure may be shortened in a number of places. For instance, some of the reprecipitations which are recommended may be omitted. Time can be saved by making only one hydrolytic precipitation of palladium, rhodium and iridium, in separating them from platinum, and by determining platinum by simply igniting its sulfide. The second reduction with titanous chloride might be dispensed with, and also the precipitations with cupferron can be avoided by determining rhodium and iridium together in aliquot portions of the solution at this stage. It must be remembered, however, that in so doing errors of varying magnitude will be introduced, depending upon the relative proportions of the metals present.

Accuracy of the Proposed Method

The accuracy which can be attained with the procedure described in this paper is best illustrated by means of data which have been taken from the publications cited and compiled in the accompanying table. In addition, the results of the complete analysis of three solutions, to which all six of the metals were added, are included.

In the development of the various parts of the general procedure, given in detail in the original papers cited, it was found by chemical means that no ruthenium, platinum, palladium, rhodium or iridium appeared in the absorbing solutions under the conditions established for distilling osmium tetroxide. In the separation of platinum from rhodium, no platinum was detected by means of ammonium chloride in the solutions of the second hydrolytic precipitate of rhodium, whereas, in solutions of known platinum content, 0.1 mg. of platinum was readily detected, and a precipitate was formed with 0.05 mg. of platinum. Rhodium was detected in only one of the five residues of platinum, obtained in the same experiments, by a test which is capable of detecting an extremely small amount of rhodium, namely, the greenish discoloration of the small amount of ammonium chloroplatinate which remains in solution when the bulk of the redissolved platinum is precipitated by ammonium chloride. In the separation of platinum from palladium, no palladium was detected with dimethylglyoxime in the dissolved platinum residues, nor was any platinum found, by means of ammonium chloride, in the filtrates from the precipitation of the palladium with dimethylglyoxime. In the separation of plati-

TABLE I

RESULTS WHICH ILLUSTRATE THE ACCURACY OF THE PROCEDURE

No.	Osmium, g. Taken	Osmium, g. Recovered	Ruthenium, g. Taken	Ruthenium, g. Recovered	Platinum, g. Taken	Platinum, g. Recovered	Palladium, g. Taken	Palladium, g. Recovered	Rhodium, g. Taken	Rhodium, g. Recovered	Iridium, g. Taken	Iridium, g. Recovered
1	0.1608	0.1606	0.075	....	0.100	....	0.020	....	0.016	....	0.200	....
2	.1390	.1388	.075	....	.100	....	.020	....	.016	....	.200	....
3	.1548	.1546	.075	....	.100	....	.020	....	.016	....	.200	....
4	....	....	.1090	0.1091	....	....	....	....	....	....	.093	....
5	....	....	.1564	.1565	....	....	....	....	....	....	.1426	0.1427
6	....	....	.1556	.1556	....	....	....	....	....	....	.1605	.1603
7	....	....	.1243	.1244	....	....	....	....	....	....	.2125	....
8	....	....	.1153	.1152	.2739	....	.1084	....	.0076	....	.1955	....
9	....	....	....	....	....	....	....	....	.0451	0.0451	.0735	....
10	....	....	....	....	....	....	....	....	.1355	.1354	.1103	....
11	....	....	....	....	....	....	....	....	.1442	.1442	.1413	.1412
12	....	....	....	....	....	....	....	....	.1216	.1215	.1624	.1622
13	....	....	....	....	....	....	....	....	.0840	.0838	.1320	.1320
14	....	....	....	....	.2848	0.2849	.1044	0.1043	....	....	....	....
15	....	....	....	....	.2793	.2794	.1243	.1243	....	....	....	....
16	....	....	....	....	.2469	.2469	....	....	.0291	.0291	....	....
17	....	....	....	....	.2479	.2479	....	....	.0244	.0243	....	....
18	....	....	....	....	.2617	.2618	....	....	.0295	.0296	....	....
19	....	....	....	....	.2359	.2358	....	....	....	....	.1944	.1945
20	....	....	....	....	.2692	.2694	....	....	....	....	.2039	.2040
21	....	....	....	....	.2501	.2501	....	....	....	....	.2455	.2456
22	....	....	....	....	.2642	....	....	....	.0465	.0464	.1385	....
23	....	....	....	....	....	....	.0342	.0342	.0177	....	.2300	....
24	....	....	....	....	....	....	.0333	.0333	.0112	....	.2154	....
25	.1155	.1153	.1117	....	.1141	....	.1013	....	.1145	....	.1194	....
26	.1507	.1505	.1195	....	.1008	....	.1109	....	.1109	....	.1159	....
27	.1623	.1622	.1323	.1321	.1341	.1342	.1301	.1299	.0905	.0904	.1042	.1042
28	.1882	.1880	.1399	.1397	.1104	.1102	.1278	.1277	.0922	.0922	.1416	.1414
29	.1602	.1600	.0999	.0994	.1123	.1124	.1184	.1183	.0967	.0968	.1145	.1145
30	....	....	....	....	.1234	.1234	.1194	.1195	.1008	....	.1083	.2090[a]
31	....	....	....	....	.1340	.1339	.0875	.0875	.1263	....	.1092	.2355[a]

[a] This figure is that of the combined determination of rhodium and iridium.

iridium, a quantity of iridium less than was detected, in one experiment, in the s obtained from the precipitation of plati- first by hydrogen sulfide and then by formic , whereas no iridium was detected in the two er experiments.

In order to ascertain, in the separation of thenium by the recommended procedure, hether any of the other platinum metals reached the absorbing solutions, the ruthenium recovered from each of the three complete analyses was examined spectrochemically by Bourdon F. Scribner for osmium, platinum, palladium, rhodium and iridium, but no trace of these metals was detected.

The results of 31 experiments are given in Table I. Those reported in Nos. 1 to 24, inclusive, are taken from previous publications cited in this paper. Experiments Nos. 25 to 29, inclusive, were conducted according to the recommended procedure, except that brom cresol purple was used to determine the end-point for the hydrolytic precipitation. In these experiments some palladium escaped precipitation and was subsequently separated from the platinum by means of dimethylglyoxime. The results in Nos. 30 and 31 were obtained by following the procedure as herein written. Although osmium and ruthenium were not included, the solutions were, nevertheless, subjected to the same treatment as if they had been present, except that the distilling operations were omitted, in order to duplicate conditions which normally obtain at the end of the ruthenium distillation. In these two experiments, rhodium and iridium were not separated from each other but were recovered together by hydrolytic precipitation. The mixed precipitate was washed with a hot 1% solution of ammonium chloride, neutral to brom thymol blue (*p*H 7), and ignited to a mixture of metallic rhodium and iridium. The final filtrates obtained in these two experiments were found to be free from the four metals concerned.

The quantities of metal listed in the table can be conveniently handled, analytically. In the case of platinum, 2 g. of this metal is easily handled, and 5 g. should introduce no difficulties.

Summary

1. A new and reliable procedure is described for the separation, recovery and determination of each of the six platinum metals.

2. The accuracy of this new method is comparable to that of the best analytical procedures for the common metals. No special equipment or reagents are necessary and the operations do not involve technique unfamiliar to a trained analyst.

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

Structural Changes Taking Place upon Aging of Freshly Prepared Crystalline Precipitates. V. The Thermal Aging of Freshly Prepared Lead Sulfate

BY I. M. KOLTHOFF AND CHARLES ROSENBLUM

In papers III and IV of this series[1] it has been shown that the rapid internal perfection of the crystalline particles of freshly precipitated lead sulfate on aging in the supernatant mother liquor at room temperature is to be attributed to a rapid recrystallization process by way of the solution[2] and not to a free mobility of the lead ions in the amicronic particles within the microcrystals as originally concluded from the results reported in papers I and II.[3] Aside from the aging in liquid media it appears reasonable to expect that aging will occur in the dry state as well, provided that the fresh precipitate is heated to temperatures high enough to increase the thermal energy of the ions at the active surface. The results of this study are reported in this paper.

We may distinguish between two principal types of thermal aging.

1. **Microscopic Aging.**—At the higher temperatures a *sintering* of the microscopic particles may occur, resulting in a decrease of the external surface. The magnitude of this surface can be determined from the dimensions of the particles as seen with a microscope. Since the precipitates used in these studies were highly heterodisperse,

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[1] THIS JOURNAL, **57**, 597, 607 (1935).

[2] This matter will be dealt with in detail in a subsequent paper of this series.

[3] THIS JOURNAL, **56**, 1264, 1658 (1934).

more accurate results were obtained by calculating the external surface from the amount of wool violet adsorbed on shaking the crystals with a solution of the dye of a concentration sufficient to assure a saturated surface layer.[4]

2. **Internal Aging.**—At temperatures much lower than where the sintering takes place, an internal aging may occur, resulting in an internal perfection of the microscopic crystals. An indication of the extent of this kind of aging was obtained from the speed with which thorium B distributes itself through the precipitate.[1,3]

Experimental

Preparation of Lead Sulfate Samples.—A main supply of 70 g. of fresh lead sulfate was prepared by fairly slow precipitation at a speed which approximated the rate of formation of earlier samples.[1] To avoid excessive aging when in contact with the supernatant liquid, the precipitate was prepared in 3-g. batches by adding 98.6 ml. of 0.1 M potassium sulfate to 103.5 ml. of 0.1 M lead nitrate solution, while stirring with an electrically driven stirrer. Immediately after precipitation each portion of precipitate was filtered on a Gooch crucible, washed rapidly (suction) with water and absolute ethanol, and then air-dried.[1a] The precipitates thus obtained from the different batches were mixed and kept in a desiccator over sulfuric acid at room temperature. From previous investigations[3] it was known that under such conditions a fresh precipitate remains practically unaged. However, to eliminate any uncertainty, blanks were run on the dye adsorption and the Th B exchange at frequent intervals throughout the investigation. For the sake of brevity these results will not be reported since it appeared that within the given periods of time no distinct aging could be detected in the product stored at room temperature. Various other batches of lead sulfate prepared in a similar way were used to ascertain the validity of all effects encountered.

Adsorption of Wool Violet.—Eight-tenths to one-gram portions of lead sulfate were shaken for thirty minutes with 25 ml. of a wool violet solution containing 250 mg. of the dye and 40 mg. of lead sulfate per liter. It was shown that at this dye concentration the surface of the lead sulfate was saturated with wool violet, since the same amount of dye was adsorbed when the concentration in solution was increased to 350 and 500 mg. per liter, respectively. The quantity of wool violet left in the solution after shaking and centrifuging was determined colorimetrically in an aliquot part of the supernatant liquid. All determinations were run in duplicate at least and the average result is reported.

Exchange with Thorium B.—Exactly the same technique was followed as described in previous papers.[1,3] Approximately 0.3-g. portions of lead sulfate were shaken with 23.53 ml. of a solution of thorium B containing 0.00162 mole of lead nitrate and 0.065 mole of potassium nitrate per liter, corresponding to the composition of the solution in previous work.[1,3] Samples were shaken in paraffined containers for fifteen minutes and three hours and portions of supernatant liquid were withdrawn with a pipet after centrifuging. All determinations wer duplicate at least and the average value is reporte

It should be realized that the reproducibility w aged or slightly aged precipitates, especially after f minutes of shaking, is not very good. Great accura hardly to be expected under these conditions, since thorium B distributes itself very quickly, and a sli change in the experimental conditions may have a mark effect. For the reasons mentioned, slight changes foun in the amounts of lead exchanged do not indicate a definit aging. Such experimental errors are insignificant in comparison with the magnitude of the effects reported.

Losses in Weight of the Samples During Heating.—Weighed samples (varying between 5 and 10 g.) of the air-dried lead sulfate were placed in wide weighing bottles and heated at different temperatures in an electric oven, the temperature of which could be kept constant within 5°. At noted intervals of time the bottles were removed, cooled in a sulfuric acid desiccator and weighed with ground glass covers in place. The losses in weight were found to be very small: at 105° after two hours of heating 0.02%, after twenty-seven hours 0.03%; at 200° after two and one-half hours 0.08%, after twenty-eight hours 0.095%; at 250° after one hour 0.12%, after four hours 0.14%, after twenty-seven hours 0.15%; at 305° after one-half hour 0.14%, after three hours 0.18%, after twenty hours 0.25%; at 400° after one hour 0.24%, after four hours 0.29%; after twenty-seven hours 0.46%. Since the losses in weight were very small, a more elaborate and accurate study is desirable with regard to their proper interpretation.

The results obtained in the study of the microscopic and internal aging on heating of the fresh precipitate are summarized in Table I.

TABLE I

THERMAL AGING OF LEAD SULFATE

Temp. of heating, °C.	Time of heating, hours	Wool violet adsorbed in mg./1 g. of PbSO$_4$	Lead exchanged in mg./1 g. PbSO$_4$ after shaking with Th B for 15 minutes	3 hours
Unheated	..	1.45	38–45	600–800
105	2	..	33	790
105	27	1.57	25	800
200	2.5	..	39	780
200	27	1.60	*4.3*	*39*
250	1.2	..	*15*	*40–60*
250	4	..	*5.5*	20
250	27	1.40	*2.4*	7.2
305	0.5	..	17	110
305	1.2	1.56	13	92
305	3	..	17	70
305	20	1.19	10–15	61
400	1	1.10	16	76
400	4	..	7	18
400	27	0.39	8	17

Discussion

1. The results show clearly the difference between the external and the internal aging. On heating the fresh lead sulfate to temperatures

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(4) THIS JOURNAL, **56**, 832 (1934).

between 100 and 200° and even for short periods to 305°, a slight but definite increase of the external surface was found as indicated by the increase of the adsorption of wool violet. This might be attributed to a slight decrepitation of the precipitate which in the fresh form is highly porous. From the figures given in the third column of the table it follows definitely that no sintering occurs at temperatures below 250°, and even after heating for twenty-seven hours at 250° there was only a very slight decrease of the external surface. The sintering becomes more pronounced but is still very slow upon heating at 300°. After heating for one hour at this temperature no indication of sintering was found, but it was very definite after twenty hours of heating at this temperature. At 400° the sintering became very pronounced, even after one hour of heating. After twenty-seven hours at this temperature the total external surface as measured by the wool violet adsorption had decreased about four times.

2. The internal aging occurs at much lower temperatures than the microscopic sintering. Thus it is evident from the data that after heating for twenty-seven hours at 200° a marked aging had occurred. On the other hand, after heating for two and one-half hours at this temperature there was no indication of an internal aging. From this behavior one would infer that there is a certain incubation period before the perfection starts. A drastic aging was found on heating to 250°, the fresh samples appearing quite "old" after having been kept for twenty-seven hours at this temperature. Apparently it is possible to perfect crystals of lead sulfate by heating to temperatures far below the sintering temperature. This conclusion will be substantiated by x-ray studies.

3. The internal aging of fresh lead sulfate at temperatures far below the sintering temperature may be compared with that of the various active catalysts, which show a marked decrease of catalytic activity when heated to considerably below sintering temperatures.[5] It has been shown[1,3] that our fresh precipitates are porous and have a large internal surface development. The mobility of the ions at the active surface will be greater than that of the ions in the inside of the normal lattice, where they are completely surrounded by lattice ions of opposite electrical charge. In the terminology of I. Langmuir and of Taylor,[6] the heat of evaporation of the ions will decrease as they become less saturated with neighboring ions. Langmuir and Taylor concluded that the rate of evaporation will fall off exponentially as the number of atom linkages increases. The thermal aging is thus attributed to a high mobility of lattice ions on the active surface, these ions moving to less active surface spots, resulting in a perfection of the crystals.

According to the above it is to be expected that after a certain time of heating at a given temperature a final state of perfection corresponding to that particular temperature will be found. In order to obtain a further aging the temperature has to be raised. From the results in Table I it is seen that virtually a final state of perfection is reached after heating for three hours at 305°. At 400° a much more drastic aging is found, a final state being reached after about four hours of heating. The experiments have been repeated with four different batches of lead sulfate, yielding qualitatively the same results. Incidentally it may be mentioned that during the thermal aging the crystals become more compact and less porous as indicated by their decreasing capacity of absorbing water when kept at room temperature at a relative humidity of 0.85 after the heating.

4. *The most striking and unexpected result of this study is that, upon heating at 250°, a much more pronounced aging was obtained than when heated at 300° and even at 400° for the same length of time.* A precipitate heated for twenty-seven hours at 400° behaved as though it were less aged internally than when heated for the same period at 250°, in spite of the fact that in the former case a pronounced sintering had occurred. Moreover it is of great interest to notice that the extent of aging at 250° depends upon the duration of heating, and that no final state was reached even after twenty-seven hours. At 300 and at 400°, on the other hand, maximum aging is attained after several hours.

From experiments reported in Table II it is seen that no further aging occurs at 305°, once the fresh lead sulfate has been heated for twenty-four hours at 250°. On the other hand, a 305° sample can be further aged at 250°. A new batch of lead sulfate different from that used in the experiments of Table I was used. Clearly, aging at 250° is more effective than at 305°.

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[5] For a review see H. S. Taylor, *J. Phys. Chem.*, **28**, 897 (1924).

[6] See H. S. Taylor, *ibid.*, **30**, 145 (esp. p. 162) (1926).

TABLE II

Treatment of sample	Lead exchanged in mg./1 g. $PbSO_4$ 15 min.	3 hours
24 hours at 250°	3.1	14.1
30 minutes at 305°	6.3	26.7
20 hours at 305°	9.0	23.5
24 hours at 250°, then 0.5 hour at 305°	3.3	12.6
24 hours at 250°, then 20 hours at 305°	4.7	14.7

It was thought at first that lead nitrate coprecipitated with lead sulfate during precipitation might be responsible for the peculiar results. It was thought possible that coprecipitated lead nitrate might decompose at temperatures of 300° and above. The lead oxide formed might then be able to protect the crystals from further aging. In order to test this point the nitrate content in the fresh product and after heating for twenty-four hours at 105, 200, 250, 305 and 400° was determined. The samples were decomposed with sodium carbonate solution and the nitrate in the filtrate measured colorimetrically according to the procedure developed by Kolthoff and Noponen.[7] It was shown that no decomposition of the coprecipitated nitrate occurred at temperatures of 300° and below, whereas the greatest part of the nitrate was removed after heating for twenty-four hours at 400°. In addition it was shown that no nitrite was formed after heating to temperatures of 300° and below. Hence the coprecipitated lead nitrate is not responsible for the fact that less aging is found when samples are heated for long periods of time at 300 to 400° than at 250° and even at 200°.

The only other impurity present in the lead sulfate is water in the adsorbed and occluded state. (See losses in weight upon heating, reported earlier in this paper.) Water present in the adsorbed state may promote the thermal aging of lead sulfate. There are indications that the adsorbed water is not removed at 250°, but is removed at temperatures of 300° and above. The presence of such a film of adsorbed water could be responsible for certain of the observations being reported, *i. e.*, that a continuous aging is found at a temperature of 250°, and that the aging is much more pronounced after longer times of heating at 250 than at 300° and even at 400°. From the results recorded in Table III it is quite evident that the coprecipitated water is responsible for the continuous and drastic aging at 250°. A new batch of fresh lead sulfate was prepared for these experiments. Duplicate samples were heated for varying times at 305°. One of the samples was removed from the oven, while the other was left in the oven and the temperature quickly readjusted to 250°. The heating was then continued at this temperature. After cooling, the exchange with Th B solutions was determined in the usual way. In addition the adsorption of wool violet was measured.

TABLE III

AGING OF LEAD SULFATE WHEN FIRST HEATED TO 305° AND THEN AT 250°

Treatment of sample	Lead exchanged in mg./1 g. $PbSO_4$ after shaking with Th B for 15 min.	3 hours	Wool violet adsorbed in mg./1 g. $PbSO_4$
2 hours at 305°	8.7	59	1.75
2 hours at 305°, then 24 hrs. at 250°	7.7	30	1.7
45 hours at 250°	2.9	8.2	1.75
21 hours at 305°	7.3	23	1.45
21 hours at 305°, then 21 hrs. at 250°	6.7	23	1.4

The last two results given in Table III are especially conclusive. Once the lead sulfate had been heated for twenty-one hours at 305°, no further aging occurred if the sample was maintained for twenty-one hours at 250°, and provided the solid had not been removed from the furnace. The final product remained fresher than when heated for twenty-one hours at 250° only. Apparently long periods of heating at 305° cause the removal of adsorbed and occluded water.

That the water actually is responsible for the continuous aging at 250° was shown conclusively by the following experiment. A sample of the fresh lead sulfate was heated for twenty-one hours at 305°, then for twenty-one hours at 250°, and finally cooled and placed in a desiccator over a deliquescent sodium sulfate decahydrate for a week. A similar sample was kept for the same time over concentrated sulfuric acid. Both samples were heated again at 250° for twenty-one hours. The amounts of lead exchanged after the final heating after fifteen minutes and three hours of shaking at room temperature were 1.0 and 7.3 mg., respectively, for the sample which had been stored over deliquescent sodium sulfate and 5.0 and 26 mg., respectively, for the sample kept over sulfuric acid.

The experiments reported in Table III have been repeated with a number of different batches

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[7] I. M. Kolthoff and G. Noponen, THIS JOURNAL, **55**, 1448 (1933).

of lead sulfate. All conclusions drawn from these abbreviated data have been substantiated by experiments with each independently prepared batch.

Summary

Fresh lead sulfate appears to undergo three distinct types of thermal aging.

1. *Microscopic aging by a sintering of the particles.* A pronounced sintering has been found at temperatures of 400°, and a very slow sintering at 300°.

2. *Internal thermal aging* at temperatures far below that of sintering. This aging is attributed to the high speed of evaporation of lattice ions on the active surface (Taylor and Langmuir). After a sufficiently long heating period the "age" approaches a final state which is characteristic for each temperature.

3. *Thermal aging promoted by adsorbed and occluded water.* This aging occurs at temperatures below the point where internal aging begins. It proceeds continuously with the time of heating. It accounts for the much more pronounced perfection after heating for twenty hours at 250° than after the same time of heating at 305 and 400°.

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

Structural Changes Taking Place During the Aging of Freshly Formed Precipitates. VI. The Perfection and Aging of Lead Sulfate Precipitated under Various Conditions

BY I. M. KOLTHOFF AND CHARLES ROSENBLUM

In previous studies the aging of fresh lead sulfate obtained by mixing 0.1 *M* solutions of lead nitrate and potassium sulfate has been reported. In the present study, the effect of varying conditions of precipitation upon the perfection and the speed of aging of lead sulfate has been investigated.

Designation of the Various Precipitates of Lead Sulfate

1. **Lead Sulfate from 0.025 M Solutions.**—To 103.6 cc. of 0.025 *M* lead nitrate, 98.6 cc. of 0.025 *M* potassium sulfate was added in about five or six minutes. Four such precipitations were performed and the four portions of solid combined. The precipitate formed slowly, about half a minute being required before it appeared. One minute after the addition of the sulfate, the precipitate was filtered on a Büchner funnel, and treated further as sample 2. The "fresh" precipitate was thirteen to fourteen minutes old after washing with alcohol. Another sample was prepared by gently rotating the precipitate in the supernatant liquid for an hour before filtration.

2. **Lead sulfate from 0.1 M solutions** was prepared as described in a previous paper.[1]

3. **Lead Sulfate from 0.4 M Solution.**—To 53 cc. of 0.4 *M* lead nitrate was added 50 cc. of 0.4 *M* potassium sulfate while stirring. After the precipitation was complete, half of the suspension was decanted and placed in a rotatory shaker for one hour. The remainder was filtered immediately, washed with four 20-cc. portions of water, then with alcohol and finally air-dried. The fraction of the precipitate which had been shaken for one hour was treated in a similar way. Both the filtration and the washing process were rather slow, because the fine precipitate tended to cake on the filter and clog it. The "fresh" precipitate after the washing with water was twenty-four to twenty-five minutes old.

4. **Lead Sulfate from Extremely Dilute Solutions.**[2]—To 25 cc. of conductivity water were added simultaneously and dropwise from two dropping pipets 50 cc. of 0.1 *M* lead nitrate and 50 cc. of 0.1 *M* potassium sulfate, the suspension being stirred continuously during the precipitation. The precipitate which settled readily was filtered, washed and air-dried. The "fresh" precipitate was twelve minutes old.

5. **Lead Sulfate from 0.1 M Solutions at Boiling Temperature.**—To 103.6 cc. of 0.1 *M* lead nitrate heated to boiling was added in about five to six minutes 98.6 cc. of 0.1 *M* potassium sulfate solution at a temperature of about 95–100°. After precipitation, half of the suspension was decanted and placed on a rotatory shaker for

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[1] THIS JOURNAL, **56**, 1264 (1934) [Procedure A 1].

[2] F. Hahn, *Z. anorg. allgem. Chem.*, **126**, 257 (1923).

TABLE I

DISTRIBUTION OF THORIUM B THROUGH, AND ADSORPTION OF WOOL VIOLET BY LEAD SULFATE PRECIPITATED UNDER VARIOUS CONDITIONS

Sample of lead sulfate	Age of lead sulfate	Amount of PbSO shaken with Th B, g.	Mg. of Pb exchanged per 1 g. $PbSO_4$ after shaking in Th B for 5 min.	15 min.	1 hr.	3 hrs.	Wool Violet adsorbed in mg. per 1 g. $PbSO_4$
I 0.025 *M* Sol; R. T.	Fresh (14 min.)	0.300		0.75		5.3	0.43
	74 min.	.300		.57		4.2	.43
II 0.1 *M* Sol; R. T.	Fresh (9 min.)	.300	50		500	700	1.8
	50 min.	.300	20	30	80	350	
III 0.4 *M* Sol; R. T.	Fresh (24 min.)	.300		95		460	2.8
	84 min.	.300		31		180	2.6
IV Hahn; R. T.	Fresh (12 min.)	.300		4.0	7.8	11.4	.6
V 0.1 *M* Sol; hot	Fresh (14 min.)	.300	10	16		85	1.2
	74 min.	.300	2.4	2.5		3.4	.95

one hour, the suspension slowly cooling in the air. The remainder was filtered two minutes after addition of lead nitrate, washed and made air-dry. After washing with the water, the "fresh" precipitate was fourteen to fifteen minutes old.

Experimental Procedures

Adsorption of Wool Violet.—The relation between the magnitudes of the external surfaces of the various precipitates was found from the amounts of wool violet adsorbed in the saturated state.[3] Weighed portions of the air-dried precipitates were shaken for thirty to forty minutes with 20 cc. of a wool violet solution containing 0.25 g. of dye per liter. After shaking, the suspension was centrifuged and the dye concentration determined colorimetrically. The sample of dye used was different from that in previous experiments.[1,3]

Distribution of Thorium B.—Weighed portions of the air-dried precipitates were shaken violently (400 phases p. m.) at room temperature for various periods of time with 23.53 cc. of a radioactive lead nitrate solution which was 0.00162 molar in lead nitrate and 0.065 molar in potassium nitrate. The amounts of thorium B taken up by the precipitates were measured as usual.[1] The results obtained are reported in a condensed form in Table I.

Discussion

From the results it appears that the concentrations of the reacting lead nitrate and potassium sulfate solutions are important factors in determining the size and the perfection of the precipitated lead sulfate crystals. The surface of a precipitate obtained from 0.025 molar solutions is about four times smaller than that from 0.1 *M* solutions, whereas that of the latter is about half as great as the surface of the lead sulfate from 0.4 *M* solutions. These conclusions follow from the amounts of wool violet adsorbed by the various precipitates.

The degree of perfection of a fresh precipitate obtained from 0.025 *M* solutions is relatively great; consequently the speed of its further perfection is relatively small. By carrying out the thorium B distribution experiments at a smaller lead-ion concentration in the solution, the progress of the perfection on aging of this precipitate could be shown more conclusively than by the data reported in Table I. To 10.30 cc. of 0.025 *M* lead nitrate in paraffined containers was added 9.82 cc. of 0.025 *M* potassium sulfate. After aging for one minute and one hour, respectively, after precipitation, 9.94 cc. of a stock thorium B solution in 2.5 $\times$ 10^{-5} molar lead sulfate was added and the whole shaken for various periods of time. The results obtained are given in Table II.

TABLE II

PROGRESS OF AGING OF LEAD SULFATE PRECIPITATED FROM 0.025 *M* SOLUTIONS AT ROOM TEMPERATURE

Amount of lead sulfate 0.0745 g.; lead concentration in solution 5.5 $\times$ 10^{-4} *M*.

Age of precipitate	Mg. of Pb exchanged per 1 g. of $PbSO_4$ after shaking with Th B for 5 min.	15 min.	1 hour	3 hours
1 minute	34	70	175	320
1 hour	7	10	26	60

The results of the experiments reported in Table I regarding the perfection and the speed of aging of precipitates obtained from 0.4 *M* solutions are not entirely conclusive. It is to be expected that the crystals obtained from 0.4 *M* solutions would be much less perfect than those formed on mixing of 0.1 *M* solutions. The results in the table seem to indicate just the opposite. It is possible that the speed of distribution of the thorium B, which is a direct function of the speed

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(3) I. M. Kolthoff, W. von Fischer and C. Rosenblum, THIS JOURNAL, **56**, 832 (1934).

of recrystallization, is greater with a precipitate obtained from 0.1 *M* solutions than from 0.4 *M* solutions. Thus, it has been shown by Roller[4] that the dissolution factor of calcium sulfate crystals reaches a maximum at a size of 2.8 microns, and decreases with increasing and decreasing size of the particles. However, it should be realized that the results are but qualitative in nature since the precipitate obtained from 0.4 *M* solutions is hard to filter and wash and has a tendency to cake together in the air-dried state after washing with alcohol. Therefore, during the filtration and washing, it might have been subjected to a drastic aging process, and the specific surface might have been greater in the unfiltered than in the filtered and air-dried state. Moreover, it should be mentioned that the "fresh" precipitate was twenty-four minutes old and was compared with a nine-minute old precipitate obtained from 0.1 *M* solutions. If the latter had been twenty-four minutes old the speed of distribution of thorium B would have been found of the same order as that found with precipitate III.

It has been ascertained that the unexpected results are not due to an excessive coprecipitation of lead nitrate by precipitate III. Such a contamination would increase $Pb_{soln.}$ so that the true $Pb_{exch'ged}$ value might actually exceed values obtained with precipitate II. "Fresh" precipitates obtained from 0.1 and 0.4 *M* solutions were filtered, washed and air-dried in the usual manner. Three-tenth-gram portions were shaken with the "standard" solution, which is 0.00162 molar in lead nitrate and 0.065 molar in potassium nitrate, and the supernatant liquids analyzed for lead. In all cases the total lead concentration was found to be $1.72\ (\pm\ 0.02) \times 10^{-3}$ *M*. Subsequent work, designed to study in greater detail the degree of perfection of a precipitate obtained from 0.4 *M* solutions, is planned.

A precipitate obtained by F. Hahn's extreme dilution method is fairly coarse but still highly imperfect. As a matter of fact, it appears that the precipitate obtained at room temperature from 0.025 *M* solutions is more perfect than a precipitate formed according to Hahn from 0.1 *M* solutions.

It is of great interest to notice that the effect of concentration of the reacting solutions exerts a greater influence upon the degree of perfection of the separated lead sulfate than does the temperature. A precipitate rapidly formed at higher temperatures from 0.1 molar solutions is much less coarse and much less perfect than when obtained from 0.025 *M* solutions at room temperature. The former, when aged in the slowly cooling liquid, is subjected to a rapid perfection process. This is to be expected since the speed of recrystallization rapidly increases with the temperature.

Summary

A preliminary study was made of the degree of perfection and the speed of aging of lead sulfate as a function of the concentrations of lead nitrate and potassium sulfate and of the temperature during the precipitation. A precipitate obtained from 0.025 *M* solutions is much more perfect and coarser than a precipitate obtained from 0.1 *M* solutions. A precipitate obtained from 0.1 *M* solutions at boiling temperature in the fresh state is much less perfect and has a smaller size than a precipitate obtained from 0.025 *M* solutions at room temperature.

MINNEAPOLIS, MINNESOTA RECEIVED AUGUST 19, 1935

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[4] P. S. Roller, *J. Phys. Chem.*, **35**, 1133 (1931).

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

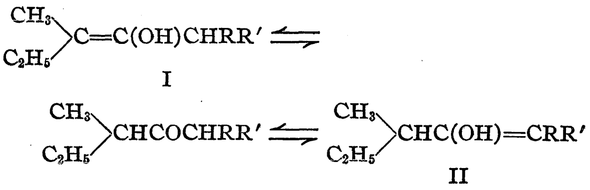
Enolization as Directed by Acid and Basic Catalysts. III. The Acid-Catalyzed Enolization of Some Secondary Butyl Ketones

BY PAUL D. BARTLETT AND CHARLES H. STAUFFER

Qualitative facts in the literature indicate that the activity of hydrogen in the alpha position to a carbonyl group varies in a manner that is not understood according as the alpha carbon atom is primary, secondary or tertiary. For example, the product of monochlorination of methyl ethyl ketone in a slightly acid medium, either at room temperature or at 70°, contains about 80% of 3-chloro-2-butanone and only 20% of 1-chloro-2-butanone;[1] the chlorination and bromination of menthone and carvomenthone have led to tertiary halogen compounds[2] as the only identified products. Such facts convey an impression that hydrogen in the alpha position to a carbonyl group is most active toward substitution when tertiary and least active when primary. Results from a study of the base-catalyzed Michael condensation,[3] which also depends upon the activity of hydrogen, lead to the opposite view. In the condensation of methyl ethyl ketone with benzaldehyde, it is reported[4] that the use of an acid catalyst leads to condensation at the methylene group, while a basic catalyst brings about condensation at the methyl group.

It is not surprising that no simple parallelism among these results should appear. In a two-step reaction, the yield alone affords no clue as to the equilibria and rates of the two steps involved, and the dependence of the rates on different catalysts. In the halogenation of an unsymmetrical ketone, the yields of the two products may well be affected, not only by the relative rates of formation of the two possible intermediate enols,[5] but by the possibility of establishment of an equilibrium between the products, altering the original ratio in which they were formed.[6] If, as is commonly postulated, enols and enolates are involved in the aldol, Claisen, Claisen–Schmidt, Michael and Perkin condensations, then the yields in these reactions may be functions of the rate and equilibrium of enolization, and also the rate and equilibrium of the further reaction of the enol. No one of these variables can be singled out and alone correlated with the final yield.

The reactions dependent upon active hydrogen are of wide enough importance to render a quantitative study of the first of these factors—the competitive rates of enolization—of interest, even though it is but a partial attack upon the problem of "reactivity" of such hydrogen atoms. We have applied the method of the first paper of this series[5] to the determination of the relative rates of formation of the enols I and II in a series of optically active secondary butyl ketones.



$$\begin{matrix}CH_3\\ C_2H_5\end{matrix}\!\!>C{=}C(OH)CHRR' \rightleftharpoons \quad \text{I}$$

$$\begin{matrix}CH_3\\ C_2H_5\end{matrix}\!\!>CHCOCHRR' \rightleftharpoons \begin{matrix}CH_3\\ C_2H_5\end{matrix}\!\!>CHC(OH){=}CRR' \quad \text{II}$$

Conditions of acid catalysis similar to those of the first paper were used; glacial acetic acid was the solvent, and nitric acid (1.19 *N*) served the double purpose of a catalyst for enolization and an oxidizing agent to ensure irreversible iodination. The rate of racemization divided by the rate of iodination, measured under identical conditions, is then a measure of the relative rates of formation of the enols I and II.

These experiments were carried out with phenyl secondary butyl ketone as a check upon the method, for this ketone has only one hydrogen available for enolization and the rates of iodination and of racemization should be identical. This question was tested by Ingold and Wilson[7] for the racemization and bromination of 2-*o*-carboxybenzylindanone-1; in our case, as in theirs, the rates are identical within the experimental error. At 36.75°, the velocity constant for iodination of phenyl *s*-butyl ketone is 0.0298, that for racemization, 0.0296.

The rates of iodination and racemization for $RCOCH(CH_3)C_2H_5$, where R is methyl, ethyl,

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[1] Kling, *Bull. soc. chim.*, [3] **33**, 325 (1905).

[2] Kötz and Steinhorst, *Ann.*, **379**, 13 (1911).

[3] Andrews and Connor, THIS JOURNAL, **57**, 895 (1935).

[4] Harries and Müller, *Ber.*, **35**, 966 (1902).

[5] Part I of this series, THIS JOURNAL, **55**, 4992 (1933); other references there.

[6] For an example of this, see L. I. Smith, *ibid.*, **44**, 216 (1922).

[7] Ingold and Wilson, *J. Chem. Soc.*, 773 (1934).

and benzyl, were measured at different temperatures from 15 to 40°, with the intention of resolving the rates into action and activation constants. The low optical rotations of the ketones prevented sufficiently accurate racemization runs for this purpose. As far as can be judged from the data, the relative rates of the two modes of enolization of a ketone do not vary with temperature.

Table I shows the results of the reaction rate measurements, together with an estimate of their precision, obtained by taking the mean deviation of the results of individual runs from the weighted mean, at each temperature. In Fig. 1 the logarithm of the rate constant is plotted against the reciprocal of the absolute temperature, to show the similar slopes of all lines and the agreement of the data for the methyl and ethyl ketones with the Arrhenius equation.

TABLE I

RATES OF IODINATION AND RACEMIZATION OF RCOCH-$(CH_3)C_2H_5$

R	Temp., °C.	$k_{\text{Iod.}}$	No. of runs	% deviation	$k_{\text{Rac.}}$	No. of runs	% deviation
CH_3	15	0.578	2	7.8			
	25	1.41	2	3	0.248	4	29
	38.75	4.54	2	6			
	38.95	4.61	2	5.4			
	38.7				1.3	1	3.5
C_2H_5	15	0.33	2	9			
	25	.852	3	4.2	0.103	4	10
	38.75	2.74	2	3	.339	2	21
$C_6H_5CH_2$	24.45	.309	4	10			
	25				.0118	1	14
	38.75	1.325	1	3			
	44.6				.0708	1	28
Cyclohexyl	25	.026	1	50	.0183	2	20

For the purpose of interpreting the results, the standard temperature of 25° was taken, since the competitive enolizability of different active hydrogens seems but little affected by temperature. To get an expression of the mobility of a single hydrogen atom in the position in question, a statistical correction needs to be made by dividing the fractional velocity by the number of equivalently situated hydrogen atoms, as has been done in Table II.

TABLE II

COMPETITIVE ENOLIZATION VELOCITY OF HYDROGEN IN SECONDARY BUTYL KETONES, $RCOCH(CH_3)C_2H_5$, 25°

R	$k_{\text{Iod.}}$	$k_{\text{Rac.}}$	v_R	v_H
CH_3	1.41	0.248	4.68	1.56
C_2H_5	0.852	.103	7.27	3.63
Benzyl	.324	.0118	26.4	13.2
Cyclohexyl	.026	.0183	0.42	0.42

In this table v_R is the enolization velocity of all the active hydrogen in the group R, relative to that of the secondary butyl hydrogen taken as unity; v_H is the enolization velocity of a single active hydrogen atom in the group R, relative to that of the secondary butyl hydrogen as unity.

The competitive velocities per hydrogen in the four ketones measured vary over a 31-fold range. It is not surprising that benzyl hydrogen should be the most active competitively; but the result is unexpected that under these acid catalytic conditions the tertiary hydrogen atoms are less active, as regards rate of enolization, than either primary or secondary hydrogen. This is directly contrary to the indications of Part I of this series, wherein it was found that, using our present notation, v_H for one of the secondary hydrogen atoms of position 2 of menthone is only 0.13 relative to the tertiary hydrogen of position 4.

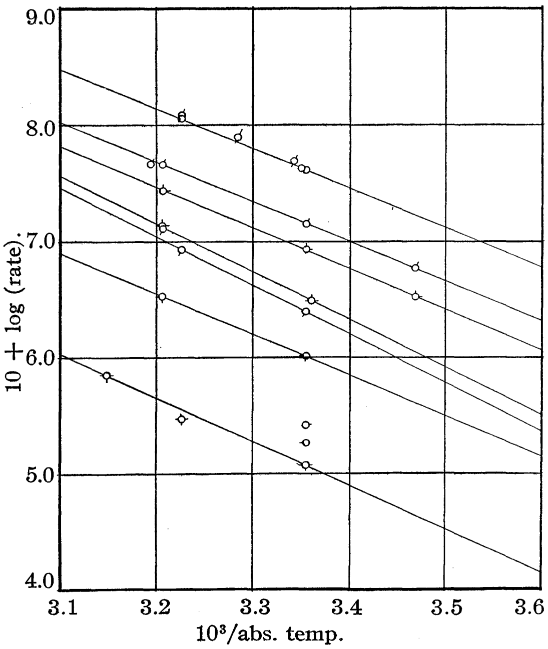

Fig. 1.—The common logarithms of the rate constant plotted against the reciprocal of the absolute temperature: Ọ́ iodination of *l*-menthone; O racemization of *l*-menthone; Ó iodination of methyl *s*-butyl ketone; Ọ racemization of methyl *s*-butyl ketone; Ȯ- iodination of ethyl *s*-butyl ketone; -Ọ racemization of ethyl *s*-butyl ketone; -Ȯ- iodination of benzyl *s*-butyl ketone; -Ọ- racemization of benzyl *s*-butyl ketone; O- iodination of cyclohexyl *s*-butyl ketone; -O racemization of cyclohexyl *s*-butyl ketone; -ϕ- iodination and racemization of phenyl *s*-butyl ketone.

This striking contrast between acyclic and cyclic ketones led us to repeat the earlier work on menthone, with a resulting revision of the figures, which, however, widens the difference between menthone and the secondary butyl ketones. For the iodination of menthone at 25° we now get a unimolecular rate constant of 4.08, and for the racemization we get 4.27. Allowing for experimental uncertainties we may say that v_H for the methylene hydrogen is not greater than 0.04 relative to the tertiary hydrogen. We cannot account for the difference between this result and the earlier one; the only known differences of conditions in the present experiments were the use of 1.19 *N* instead of 0.955 *N* nitric acid, closer temperature control on both kinds of run, and the use of a spectrophotometer instead of a colorimeter, which resulted in these new iodination runs being very intensely illuminated with white light. The runs did not show the departure from first order kinetics observed in Part I,[5] (p. 4994, 4995) which bears out the suggestion there made that the iodination of the enol may be photochemically promoted. The necessity of revising the figures for menthone is also a warning that these results may have only qualitative significance.

Discussion.—The isolated cases of the acid-catalyzed enolization of menthone and the base-catalyzed enolization of chloracetone[8] supported a mechanism undertaking to account for the direction of enolization in terms of the nature of the catalyst and the alpha-substituted groups and two electronic mechanisms of enolization. The results of the present work show that such a formulation is entirely too simple and is incapable of affording reliable predictions concerning rates of reaction or energies of activation in the enolization process. The ethyl and isopropyl groups are both feebly electron-repelling, relative to hydrogen. One of these, introduced into a cyclohexanone, strongly enhances the competitive enolization rate of the neighboring hydrogen atom; the other, introduced in the alpha position into diethyl ketone, markedly *diminishes* the competitive enolization rate of the neighboring hydrogen atom. In both cases the conditions of study are so strongly acid that there can scarcely be any question of the basic mechanism of enolization coming into play. This work affords a possible further example of the unique character of cyclohexanones, which it might be profitable to investigate in connection with the other abnormalities of these ring compounds.

It is noteworthy also, as Table II shows, that the rates of enolization of the *s*-butyl ketones do not in any sense run parallel to the competitive enolization rates of the groups introduced. Although the benzyl group, for instance, has a v_R five times as great as that of the methyl group, benzyl *s*-butyl ketone enolizes only one-fourth as fast as methyl *s*-butyl ketone.

Experimental

The acetic acid used as solvent was prepared by fractional distillation of acid obtained from the Baker and Adamson Co. The nitric acid was purified by distillation from an equal volume of concentrated sulfuric acid, followed by removal of oxides of nitrogen by passage of dried air through the distilled acid. The iodine used had been resublimed.

Methylethylacetic acid was prepared by the method of "Organic Syntheses,"[9] with the time-saving modification that the *s*-butylmagnesium chloride was carbonated by dropping onto excess solid carbon dioxide. This reduced the yields from 86 to 72%, but was very much more rapid.

Methylethylacetic acid was resolved with brucine as described by Schütz and Marckwald.[10] No attempt was made to carry the resolution to a maximum, acid of a specific rotation as high as +7.2° being obtainable from the mother liquors from which several fractions of the brucine salt had been crystallized. The maximum rotation at 20° for the D line of sodium is reported as −16.67° by Schütz and Marckwald.

The ketones were prepared by the same procedure as was followed by Conant and Carlson[11] in preparing a series of optically active ketones. The active acid was converted into the acid chloride by refluxing with thionyl chloride, this reagent having been purified by distillation first from quinoline, and then from linseed oil.[12] The acid chloride boiled at 118° at 760 mm. pressure. Grignard reagents prepared respectively from methyl iodide, ethyl bromide, benzyl chloride, cyclohexyl chloride and bromobenzene, were treated with equivalent amounts of freshly fused zinc chloride dissolved in dry ether. Magnesium chloride was precipitated and the resulting solutions of organozinc compounds were treated, with warming, with the methylethylacetyl chloride, the solution hydrolyzed after a few minutes with dilute sulfuric acid, the ether layer washed with sodium carbonate solution and water, and dried with sodium sulfate. There was evidently always some racemization in the formation of the ketones, for successive samples of the same ketone showed varying ratios between their optical rotations and the rotations of the acid from which they were prepared. Hydrolyzing the product of the coupling reaction with ammonium chloride instead of dilute sulfuric acid did not eliminate this racemization. In spite of care in removing acids and bases from the ketones, all except menthone were

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[8] Bartlett, THIS JOURNAL, **56**, 967 (1934).

[9] "Organic Syntheses," Collective Volume I, John Wiley and Sons, Inc., New York City, pp. 353–355.

[10] Schütz and Marckwald, *Ber.*, **29**, 52 (1896).

[11] Conant and Carlson, THIS JOURNAL, **54**, 4056 (1932).

[12] Fieser, "Laboratory Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1935, p. 339.

found to undergo racemization in ordinary glass-stoppered bottles over a period of several days. The following are the rotations of the samples of ketone actually used for the racemization measurements, immediately before use.

TABLE III

SPECIFIC ROTATIONS OF SECONDARY BUTYL KETONES, C_4H_9COR

R	$[\alpha]^{25}_D$ of acid	$[\alpha]^{25}_D$ of ketone
CH_3-	+5.4°	+8.15°
C_2H_5-	+5.0	+8.5
C_6H_5-	+5.7	+9.27
$C_6H_5CH_2$-	+4.5	+4.3
Cyclohexyl	+7.2	+4.4

Measurements of racemization were made in all-glass polarimeter tubes. For the slow racemizations the tubes were simply kept in a thermostat between readings; for the rapid ones water from the thermostat was circulated through the tube jackets. Iodination measurements were carried out with a Keuffel and Esser color analyzer, using a wave length of 620 mμ. The same concentrations of ketone and nitric acid were used in the racemizations as in the iodinations; the amount of iodine used in the latter never exceeded 3% of the total amount of ketone, nor 2% of the total nitric acid present. The period of observation for the racemizations extended until the rotations were too small to measure, and included from five to ten readings; readings were made on the iodination runs up to total disappearance of the iodine, and numbered between ten and twenty to a run.

The velocity constants were determined graphically as the slope of the straight line drawn through the points when the logarithm of the molal concentration of ketone (or of the optical rotation) was plotted against time. The constants were corrected to the basis of natural logarithms, and are expressed in minutes as the time unit. In averaging the results of different check runs, the runs were weighted since they varied among themselves in precision. Most of the runs necessarily consist of determinations made at about equal time intervals, and there is no way of pairing the points for calculation of deviations of the constants calculated from different pairs without unduly weighting those which are close together. We therefore adopted a purely graphical method of assigning weights to the different runs: the lines of maximum and minimum slope were taken which could be reasonably drawn through the points, and the runs were given weights inversely proportional to the individual differences between the maximum and minimum slopes. Figure 2 illustrates this procedure.

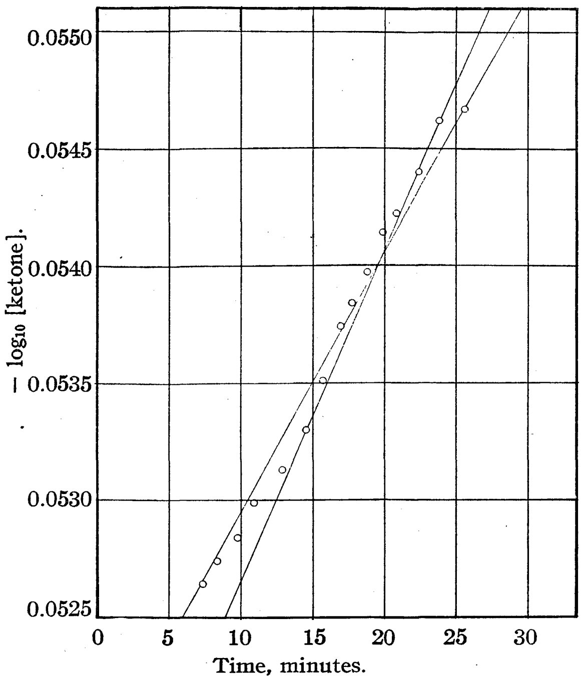

Fig. 2.—An iodination of the benzyl *s*-butyl ketone on which the estimated uncertainty is 20%, showing the two lines of greatest and least slope which might reasonably be drawn through the experimental points.

Summary

1. The competitive rates of enolization in the two possible manners have been measured for the ketones *d*-$C_2H_5(CH_3)CHCOR$, where R is methyl, ethyl, cyclohexyl and benzyl, in glacial acetic acid solution with nitric acid as catalyst.

2. The method has been checked with the observation that under these same conditions the rates of iodination and racemization of *d*-methylethylacetophenone are identical.

3. The relationship between alkyl substitution and competitive enolization rate of an active hydrogen does not bear out any simple hypothesis of enolization mechanism previously advanced.

4. The relationship between alkyl substitution and competitive enolization rate is opposite in menthone to what it is in the acyclic secondary butyl ketones.

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[CONTRIBUTION FROM THE RICHARDSON CHEMICAL LABORATORY OF TULANE UNIVERSITY]

Kinetics of the Friedel–Crafts Reaction, and Activity of Mixed Catalysts in the Reaction of Benzoyl Chloride with Toluene

BY LAWRENCE F. MARTIN, PHILIP PIZZOLATO AND LYNN S. MCWATERS

It has been observed frequently that relatively impure, technical aluminum chloride is a more active catalyst for certain Friedel–Crafts reactions than the C. P. reagent. The activity of a catalyst is here considered as the velocity of a given reaction produced by it as distinguished from the yield of product obtained. The latter point has been investigated by Riddell and Noller,[1] who determined the yields of a number of ketones and hydrocarbons obtained with various mixtures of ferric and aluminum chlorides, and by Boswell and McLaughlin,[2] who determined the total amounts of hydrogen chloride evolved by the reaction of chloroform and benzene using similar mixtures. Studies of the velocity of reaction of benzoyl and benzyl chlorides with toluene, using pure aluminum chloride and pure ferric chloride, have been made by Steele,[3] and of similar reactions with benzene by Olivier.[4] Both concluded that these reactions involve complexes of catalyst and reagent, and that the reactions are unimolecular when less than one mole of catalyst is used, if the toluene is in large excess. The reactions proceeded smoothly to completion, and Riddell and Noller,[1] using mixed catalysts, also obtained good yields in the synthesis of benzophenone.

Steele's method in which the hydrogen chloride was removed by a constant stream of hydrogen and titrated was more rapid and convenient than Olivier's, in which the unreacted benzoyl chloride had to be hydrolyzed and the benzoic acid extracted with ether for titration. Olivier adopted the latter procedure after criticizing the uncertainty of Steele's analytical method, the uncertainty of the simpler method being due obviously to the possibility that the hydrogen chloride is not removed completely by the hydrogen. We found that the removal of the acid from solution is in fact much slower than was supposed by Steele, who plotted a curve for the desaturation of a saturated solution of hydrogen chloride in toluene and corrected his titrations by adding the amounts remaining dissolved at corresponding times as read from this curve. Actually the removal of the hydrogen chloride is approximately a unimolecular process, the rate of removal being proportional to the concentration in solution. If the initial reaction is unimolecular there are two consecutive unimolecular processes, and the amount, x, removed and titrated in time t is given by the equation

$$x = a - ak_2e^{-k_1t}/(k_2 - k_1) + ak_1e^{-k_2t}/(k_2 - k_1) \quad (1)$$

in which k_1 is the velocity constant of the initial reaction, a is the initial concentration of the reacting complex in the Friedel–Crafts reaction, and k_2 is the velocity constant for the desaturation of the solution.[5] Solving for the required velocity constant gives

$$k_1 = -(1/t)\ \ln\{(k_1/k_2)(e^{-k_2t} + (x - a)/a) - (x - a)/a\} \quad (2)$$

for which values of k_1 must be found by approximation. The value of the constant obtained from the simple unimolecular law for the later stages of the reaction is a useful first approximation, as it differs only slightly from k_1 when t is large; two successive applications of Newton's method usually yield a value of k_1 which is within the limits of accuracy of the experimental data.

The desaturation of the solution by hydrogen is only approximately unimolecular under suitable conditions and k_2 depends upon the volume of solution used. If c is the variable concentration of hydrogen chloride in solution, its partial pressure in the gas in equilibrium is $p_{HCl} = Kc$, from Henry's law. The respective volumes of gases and vapor in unit volume of saturated gas are

$$V_{HCl} = p_{HCl}/760$$
$$V_T = p_T/760$$
$$V_{H_2} = (760 - p_T - p_{HCl})/760$$

The volume of toluene vapor, V_T, is practically constant as the toluene is in large excess and its concentration does not change appreciably. Unit volume of dry hydrogen leaves the solution as saturated gas of volume $760/(760 - p_T - p_{HCl})$, in which the volume of hydrogen chloride is $p_{HCl}/(760 - p_T - p_{HCl})$. Substituting for the partial pressure of hydrogen chloride in terms of

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[1] W. A. Riddell and C. R. Noller, THIS JOURNAL, **52**, 4365 (1930); **54**, 290 (1932).

[2] M. C. Boswell and R. R. McLaughlin, *Can. J. Res.*, **1**, 400 (1929).

[3] D. B. Steele, *J. Chem. Soc.*, **83**, 1470 (1903).

[4] S. C. J. Olivier, *Rec. trav. chim.*, **37**, 205 (1918).

[5] K. Jablczynski, *Z. anorg. Chem.*, **60**, 38, (1908); see also J. B. Cohen, "Organic Chemistry," 1924, Vol. I, 365.

its concentration gives $Kc/(760 - p_T - Kc)$, and since p_T is practically constant it is possible to put $b = (760 - p_T)/K$, obtaining for the rate of removal of hydrogen chloride

$$dx/dt = kc/(b - c)$$

If the constant term b is large compared to c, as is the case in the experiments under consideration, the denominator may be combined with the velocity constant k to give

$$dx/dt = k_2c$$

In these equations x is the amount of hydrogen chloride removed and titrated, while c is its concentration in solution, and in order to integrate either it is necessary to express c and the initial concentration of reacting complex, in terms of x and the initial amount, a, of reacting complex, and the volume of solution, v. This leads in the simpler case to a unimolecular equation

$$k_2/v = (1/t) \ln a/(a - x)$$

except that the volume of solution must be taken into account in the manner indicated if it is not the same in all experiments, as was the case in Steele's investigation.

The experiments to be described in this report were concerned with three objectives: first, to determine the relative activities of several samples of aluminum chloride in two distinct types of the Friedel–Crafts reaction; second, to determine the activity as measured by the reaction velocity of benzoyl chloride with toluene of a series of mixtures of aluminum and ferric chloride covering a wide range of composition; and third, to investigate the significance of the data obtained by Steele's method when the constants are calculated by equation (2). Since commercial aluminum chloride containing iron was most active in the benzoyl chloride reaction, it seemed likely that ferric chloride might be responsible for the higher activity. This is further indicated by the variations in the yield curves of the reactions studied by Riddell and Noller[1] when ferric chloride was added, showing that it affects the course of the reactions in a specific manner. It has also been claimed that aluminum chloride is activated for use in the Gattermann–Koch synthesis by small additions of titanium chloride or mixtures of titanium and ferric chlorides.[6]

Experimental

Apparatus and Procedure.—The apparatus was the same as that used by Steele[3] except for the supply of hydrogen which was drawn from a commercial cylinder through a suitable system of reducing valves, dried by sulfuric acid, and measured by a calibrated flowmeter. In order to obtain a constant reading the gas passed through the meter under a static pressure of 50 to 75 mm., for which the necessary correction was made in each experiment. Variations in the rate from one experiment to another were corrected on the basis that the desaturation velocity constant varies in direct proportion to the hydrogen rate, other conditions being constant.

We found it preferable to weigh the catalysts used in thin glass bulbs which were broken by a plunger at the instant the watch was started, which minimized the absorption of moisture and permitted more accurate determination of the zero time. The benzoyl or benzyl chloride was dissolved in the toluene, the first increment of 2.5 or 5.0 cc. of standard sodium hydroxide was run into the absorber, and phenolphthalein added. The hydrogen was next turned on and adjusted and finally the catalyst bulb was broken. Benzoyl or benzoyl chloride was not carried over into the absorber in amounts sufficient to give an appreciable titer either while adjusting the hydrogen rate or after the reaction was complete.

Materials.—The toluene was C. P., sulfur-free grade, dried by standing over sodium.

The benzoyl and benzyl chlorides were C. P. grade, and were freshly distilled in quantities sufficient for each series of experiments, a constant boiling middle third fraction being collected in each case in glass-stoppered bottles which were kept in a desiccator. Samples were weighed rapidly into a weighing bottle.

Aluminum chloride samples of several grades were used: (1) Mallinckrodt C. P. grade specified to contain 0.1% Fe; (2) Mallinckrodt C. P. containing 0.005% Fe; (3) a purer sample prepared by action of dry hydrogen chloride on the purest aluminum powder available and resublimed, which contained less Fe than the sample marked 0.005%; and (4) Gulf technical grade specified to contain 92.6% $AlCl_3$, 3.6% $FeCl_3$, 1.04% $TiCl_4$ and 0.28% $SiCl_4$.[7]

Ferric chloride was prepared by the action of chlorine on C. P. iron powder and resublimed.

Mixed catalysts were prepared by weighing the required quantities of Mallinckrodt aluminum chloride containing 0.005% Fe and ferric chloride into small narrow necked tubes. A rod passed through a rubber tube fitted to the neck was used to grind and mix the chlorides until they were sufficiently homogeneous. Samples were transferred directly from the tubes into bulbs exactly as in weighing

TABLE I

MIXED CATALYSTS

No.	Sample, g.	Al_2O_3 + Fe_2O_3, g.	$K_2Cr_2O_7$ (1 cc. = 0.00889 g. Fe) cc.	$FeCl_3$, %	$AlCl_3$, %	$FeCl_3$ mole % (aver.)
1	0.5744	...	2.3	10.5	..	..
	.4286	0.1776	1.8	10.8	94.3	9.1
2	.6383	...	13.4	54.3	..	..
	.3668	.1649	7.6	53.2	49.1	48.8
3	.2756	.1276	7.9	74.2	25.6	..
	.5161	.2349	14.7	73.5	24.4	69.9
4	.3745	.1548	2.8	19.3	83.2	16.4

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(6) I. G. Farbenind. A. G., British Patent 334,009 (1929); *C. A.*, **25**, 710 (1931).

(7) A quantity of this grade was supplied by the Gulf Refining Co.

material for the experiments, and analyzed for aluminum and iron. The mixtures used are given in Table I.

The excess over 100% in the total percentages is a measure of the extent of hydrolysis which unavoidably occurred in weighing and mixing the preparations. The mole percentages were calculated on the basis of the ferric chloride, which was determined directly by electrometric titration. More elaborate precautions to obtain greater accuracy of composition did not seem to be justified at present by the accuracy with which the velocity constants can be determined.

Determination of Desaturation Velocity.—Results of two experiments to determine the constant k_2 are given in Table II.

TABLE II

DESATURATION VELOCITY CONSTANTS

NaOH (0.193 N) (Both experiments), cc.	Toluene = 50 cc., 30° H_2(corr.) = 282 cc./min. Time, min.	k_2	Toluene = 45 cc., 30° H_2(corr.) = 250 cc./min. Time, min.	k_2
20.0	0.70	0.575	0.53	0.641
30.0	1.17	.586	.90	.630
40.0	1.93	.563	1.42	.609
45.0	2.55	.535	1.80	.580
50.0	3.33	.527	..	..
55.0	4.55	.530	2.67	.590
60.0	8.58	.560	3.42	.585
60.5	∞	..	..	..
65.0	..	..	4.78	.573
69.0	..	..	9.50	.522
70.0	..	..	∞	..
Average		0.554		0.587

Using 20.0 cc. of toluene saturated with hydrogen chloride at 25°, Steele[3] obtained the value 1.46 for a hydrogen velocity of 250 cc./min. On calculating this value and the two values given above to the uniform basis of 50.0 cc. of toluene and 250 cc./min. of hydrogen, the values of k_2 are: Steele, 0.584; 1st experiment, 0.491; and 2d experiment, 0.528. These results are in fair agreement, and we used the average of our values, $k_2 = 0.510$, in computing our velocity constants, while the higher value given by Steele was used in recalculating his results.

Determination of Reaction Velocities.—Table III gives the data of experiment 16 on benzoyl chloride with Gulf technical aluminum chloride as catalyst, which are typical of the results obtained by Steele's method. The values of k obtained by means of the simple unimolecular equation are to be compared with those of k_1 calculated from equation (2). In this particular experiment the initial reaction is fairly rapid, k_1 being almost as large as k_2, and both the trend in the k values and the difference in the magnitude of the two constants are emphasized. In experiments in which k_1 is much smaller than k_2 the discrepancy is less, but is always significant. The values of k_1 are sufficiently constant to permit of averaging with reasonable accuracy for the purposes of the present investigation.

TABLE III

DETAIL OF TYPICAL EXPERIMENT—No. 16

Toluene = 50.0 cc. (0.47 mole), temp. 30°. Catalyst = 0.6741 g. (0.00505 mole). C_6H_5COCl = 1.4926 g. (0.0106 mole). Hydrogen = 256 cc./min. $k_2 = 0.525$.

NaOH (0.170 N), cc.	Time, min.	k Unimol.	k_1 Eq. (2)
3.0	1.12	0.082	0.365
5.0	1.57	.097	.340
7.5	1.93	.128	.388
10.0	2.33	.148	.394
15.0	3.17	.181	.413
20.0	4.23	.205	.409
25.0	5.97	.217	.360
30.0	9.70	.211	.285
34.5	∞ = 0.00587 moles HCl		

Average (excluding last point) 0.381
Mole ratio $HCl/AlCl_3$ = 1.16

The results of all experiments are summarized in Table IV. The first group of eight experiments shows the velocity of reaction of benzyl and of benzoyl chloride with each of the three commercial grades of aluminum chloride and the resublimed sample. The next nine experiments are those made with the mixed catalysts of Table I, while the last three were made to determine the effect of concentration in increasing the reaction velocity.[4]

Recalculation of Steele's Results.—Velocity constants for several representative experiments were recalculated using equation (2) with the results shown in Table V. As Steele gave corrected titrations, the "corrections" were deducted to obtain the original values, but in experiment 17 this was impossible as the "correction" was larger than most of the recorded titers. The average k values reported by Steele do not differ greatly from k_1 in experiments 1 and 5, in which k_2 is large. In the experiments with benzyl chloride 30 cc. of toluene was used, making k_2 smaller, and the discrepancy is greater. In addition most of Steele's benzyl chloride experiments do not yield constants for k_1, but show a steady drift between the extreme values given below. We cannot account for this in view of the very satisfactory constants obtained in our experiments with this reagent, even in cases when k_2 was smaller than k_1.

Discussion

Comparison of the Reactions of Benzoyl Chloride and Benzyl Chloride.—The first eight experiments in Table IV show that the behavior of the three technical samples and the resublimed aluminum chloride is quite different with each of these reagents. With benzoyl chloride the reaction velocity increases as the percentage of ferric chloride present is increased. On the other hand, experiments with benzyl chloride and the same four catalysts show that, while the velocity constant is greatly increased by very small percentages of ferric chloride, it decreases again when substantial amounts are present as in the Gulf technical sample. Steele's observation is confirmed that approximately one mole of catalyst is required per mole of ketone formed, while fifteen to twenty moles of hydrocarbon are produced per mole of catalyst.

TABLE IV

SUMMARY OF EXPERIMENTAL RESULTS

Toluene = 50 cc.;[a] Expts. 13–16, 24–26, temp. 30°; Expts. 17–19, temp. 25°

Expt.	Reagent $C_6H_5CH_2Cl$, g.	Catalyst, g.	$FeCl_3$ mole, %	$AlCl_3$ moles × 10^5	$FeCl_3$ moles × 10^5	$HCl/MeCl_3$ moles	k_1 (Eq. 2) aver.
13	0.7911	0.0298	0.002	22.3	...	18.3	0.293
14	.5142	.0203	.012	15.2	...	19.0	0.974
9	.7743	.0268	.239	20.1	...	14.4	1.388
6	.7659	.0282	2.98	20.3	0.6	19.4	0.771
	C_6H_5COCl						
12	1.5173	0.7365	0.002	552	...	1.385	0.050
15	1.4636	.5965	.012	447	...	1.388	.106
2	1.5343	.6570	.239	493	...	1.155	.145
16	1.4926	.6741	2.98	486	1.5	1.205	.381
17	1.5386	.6090	0.012	456	...	1.015	.115
18	1.5922	.6356	9.1	424	43	0.723	.280
28	1.5085	.6366	16.4	385	76	.830	.143
27	1.5742	.6957	48.8	241	231	.610	.203
20	1.5773	.9259	9.1	620	61	.769	.304
23	1.4897	.7874	16.4	476	94	.821	.275
21	2.0220	.9154	48.8	318	304	.640	.625
22	1.5734	.7095	69.9	139	323	0.502	.527
19	1.5115	.5935	100.0	...	365	1.020	.077
24	0.7182	.3312	0.012	248	...	1.000	.088
25[a]	1.7791	.8600	.012	645	...	1.072	.189
26[a]	3.4662	1.6993	.012	1271	...	1.003	.354

[a] Toluene, 25 cc.

TABLE V

RECALCULATION OF STEELE'S DATA

Expt.	Reagent	Catalyst	k_2	k (Unimol.)	k_1 (Eq. 2)
1	C_6H_5COCl	$AlCl_3$	1.46	0.129	0.138
5	C_6H_5COCl	$AlCl_3$	1.46	.080	.084
18	$C_6H_5CH_2Cl$	$AlCl_3$	0.974	.533	.757
17	$C_6H_5CH_2Cl$	$AlCl_3$	.974	.258	.580–.315
21	$C_6H_5CH_2Cl$	$FeCl_3$	.974	.104–.260	.140–.301
22	$C_6H_5CH_2Cl$	$FeCl_3$	.974	.037–.112	.044–.114

Activity of Mixed Catalysts.—In the ketone synthesis studied all of the mixed catalysts are much mole active than either of the samples from which the mixtures were prepared. A significant result of the experiments in this group is the decrease in the ratio of moles of hydrogen chloride produced to the total moles of metal chlorides used, as the percentage of ferric chloride is increased. Pure ferric chloride produces almost exactly one mole of hydrogen chloride per mole of catalyst, as does the aluminum chloride. This indicates that, with mixed catalysts, the ketone formed removes both aluminum and ferric chlorides in the form of a stable complex, and that the reacting substance also probably consists of a complex such as $C_6H_5COCl \cdot AlCl_3 \cdot FeCl_3$, at least in part. In the case of the catalyst containing 16.4 mole per cent. ferric chloride (experiments 28 and 23) the ratio $HCl/AlCl_3$ is very nearly unity, which agrees with a mechanism in which all of the ferric chloride is combined as $C_6H_5COC_6H_4CH_3 \cdot AlCl_3 \cdot FeCl_3$, while the remaining aluminum chloride is removed as $C_6H_5COC_6H_4CH_3 \cdot AlCl_3$. The other mixtures do not give results agreeing with such a simple mechanism, but all of them definitely indicate the formation of larger complexes involving both chlorides in the molecule.

This explanation is not contradictory to the observation of Riddell and Noller[1] that good yields of benzophenone are obtained with similar mixed catalysts, as their experiments were made with excess of catalyst and at higher temperatures at which the complexes postulated may be unstable. Further evidence in favor of the removal of ferric chloride as part of the final complex is found in Steele's results with benzyl chloride in conjunction with our own. Steele showed that ferric chloride acts practically as a true catalyst in the hydrocarbon synthesis, forming 2500 moles of product per mole of catalyst. If even the small percentage of ferric chloride in the Gulf chloride used for experiment 6 were free to catalyze the reaction independently, it would be sufficient to convert all of the benzyl chloride present. Actually the ratio of product to catalyst is about the same as that obtained with the purest sample of aluminum chloride, and the reaction stops when considerable excess benzyl chloride still is unconverted.

As Olivier has shown,[4] and we have confirmed, the reaction velocity increases markedly with increase of the concentration of the reacting substance. If the reacting molecules are composed in part of the larger complex involving both chlorides, the effective concentration is less than the total concentration of metal chlorides present. The average velocity constants for the mixed catalysts are plotted against mole per cent. ferric chloride in Fig. 1; curve I is that obtained for experiments in which the total concentration of the metal chlorides was constant, while curve II represents experiments in which the effective concentration of reacting complex was approximately the same, as measured by the hydrogen chloride evolved. The latter curve indicates the large increase in activity of mixed catalysts at comparable concentrations as ferric chloride is added. The scale is enlarged for the first 0.25% to include constants for the purer technical samples. The Gulf aluminum chloride is much more active than can be accounted for by its ferric chloride content alone, and its greater activity is probably due in part to the titanium tetrachloride which it contains, the latter being claimed as an activator of aluminum chloride catalysts.[6]

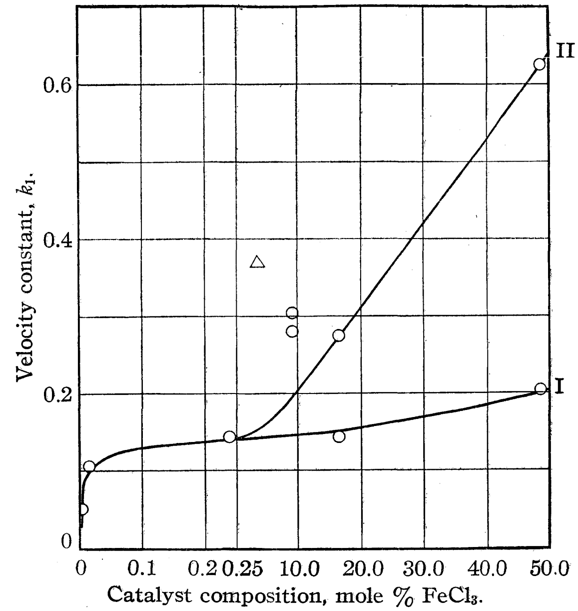

Fig. 1.—(Table IV) Variation of reaction velocity with catalyst composition: △, Gulf tech. $AlCl_3$; I, concn. of metal chloride constant; II, concn. of active complex constant.

Effect of Concentration and Order of Reaction.—The last three experiments in Table IV together with experiments 15 and 17, all of which were made with the same grade of catalyst, show the effect of concentration in increasing the reaction velocity. In Fig. 2 the average velocity constants are plotted against the mole fraction of catalyst used. The increase in k_1 is almost the same in magnitude as that found by Olivier[4] in his work on benzoyl chloride and benzene, and can be represented over the ten-fold range of concentration by $k_1 = 0.075 + 2.395c + 60.5c^2$, in which c is the mole fraction of the reacting substance. The complete reaction is, of course, bimolecular and the constants are understood to represent the pseudounimolecular mechanism obtained by using a large excess of toluene. For this reason the constant would be expected to vary with concentration, but the variation given by $k_{\text{bimol.}} = k_1/b$, in which b is the approximately constant concentration of toluene for each experiment, would be much smaller and in the opposite direction, k_1 decreasing with an increased concentration of catalyst.[8] If it is possible, as postulated above, for the aluminum chloride complex to form a larger complex with ferric chloride which has a higher

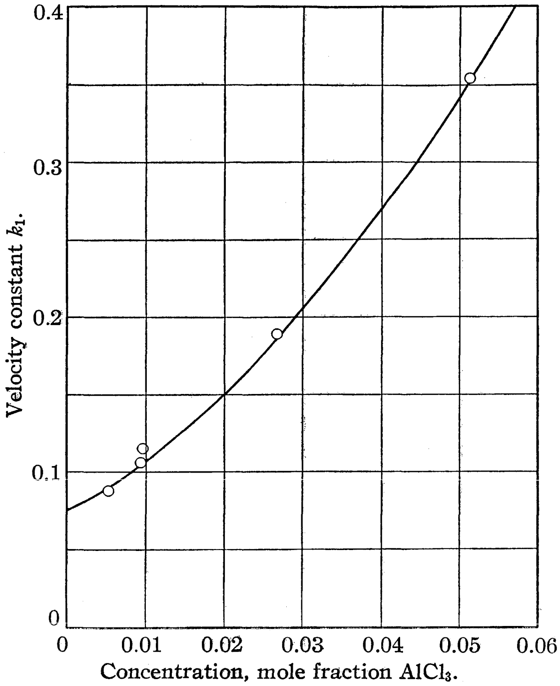

Fig. 2.—(Table IV) Variation of reaction velocity with concentration for $AlCl_3$ containing 0.005% Fe.

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[8] F. O. Rice in Taylor, "Treatise on Physical Chemistry," 1925, Vol. II, 874.

activity, Olivier's explanation[4] of association of the aluminum chloride complex itself would seem tenable in accounting for the higher reaction velocity at higher concentrations. Except for this variation, in regard to which independent evidence would be desirable, our method of calculation leads to results in good agreement with a unimolecular reaction order, and may be taken as supporting the mechanism of this Friedel–Crafts reaction previously advanced by Steele.

Summary

1. A correct method of calculating velocity constants from data obtained by Steele's method has been applied to experiments on the Friedel–Crafts reactions of benzoyl and benzyl chlorides with toluene.

2. The relative order of activity of various catalysts depends upon the type of reaction, and in the case of benzoyl chloride the activity increases with increasing percentage of ferric chloride.

3. Mixed catalysts covering a wide range of composition of aluminum and ferric chlorides have been investigated in respect to the reaction of benzoyl chloride with toluene. At comparable concentrations the activity increases with increasing mole percentage of ferric chloride and reaches a maximum at percentages in excess of 50 mole per cent.

4. The mixed catalysts have been shown to produce less than one mole of product for each mole of total metal chlorides present. Evidence is given in support of the explanation that this is due to the removal of the catalyst in the form of a bimetal complex with the reaction product, such as $C_6H_5COC_6H_4CH_3 \cdot AlCl_3 \cdot FeCl_3$.

5. Variation of the reaction velocity over a ten-fold range of concentration, the toluene being always in large excess, has been determined, and is of the same order of magnitude as that reported in a similar reaction by Olivier. The present work furnishes evidence in support of the explanation of this effect as being due to association of the reacting complex.

6. The new experimental data and method of calculation lead to results in satisfactory agreement with a unimolecular order for the reaction, and thus lend support to the mechanism proposed by Steele.

NEW ORLEANS, LOUISIANA RECEIVED JULY 29, 1935

[CONTRIBUTION FROM THE DEPARTMENTS OF AGRICULTURAL CHEMISTRY AND AGRICULTURAL BACTERIOLOGY, UNIVERSITY OF WISCONSIN]

The Chemistry of Mold Tissue. X. The Phospholipides of Aspergillus Sydowi[1]

BY D. W. WOOLLEY, F. M. STRONG, W. H. PETERSON AND E. A. PRILL

While several papers have been published dealing with the simple lipides of molds, no report has been found regarding the characterization of the compound lipides. A few workers have reported preliminary analyses of the phospholipides,[2] but no detailed study of these compounds has been reported. In a previous paper[3] the simple lipides of *A. sydowi* have been described; the examination of the phospholipides of this same organism is herein described.

Experimental Part

Extraction and Purification.—The mold was grown for ten days on glucose–inorganic salt medium in large sterilized incubators.[4] While still growing it was removed from the medium, washed with cold water, squeezed out by hand and dried rapidly at 30–60° in air. Two batches of mycelium were grown at intervals of eight months and the phospholipides of each batch examined separately. The phospholipides from the first batch will be designated as A, and those from the second batch as B. A was extracted from 7.27 kg., and B from 3 kg. of dry mold.

The mold was extracted continuously for about a week in a Lloyd type extractor. A was obtained by extraction with alcohol, and B by extraction with alcohol–ether (1:1). The solution from the extractor was evaporated, and the residue redissolved by adding water and ether. (In this and subsequent operations air was excluded by a stream of carbon dioxide.) The two layers were separated, filtered and the water layer discarded. A very small amount of matter remained undissolved in both preparations. The water layer contained only traces of nitrogen and phosphorus, and contained mannitol.

The ether layer was concentrated, and poured into a

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[1] This work was supported in part by a grant from the Wisconsin Alumni Research Foundation.

[2] (a) Aso, *J. Tokyo Chem. Soc.*, **20**, 921 (1900); (b) Takata, *J. Soc. Chem. Ind.*, Japan, **32**, 171B (1929); (c) Thomas, *Am. J. Botany*, **17**, 779 (1930).

[3] Strong and Peterson, THIS JOURNAL, **56**, 952 (1934).

[4] Peterson, Pruess, Gorcica and Green, *Ind. Eng. Chem.*, **25**, 213 (1933).

large volume of acetone. In the preparation of A, alcoholic magnesium chloride was added, but by concentrating the ether solution sufficiently precipitation was effected in the case of preparation B without the use of any inorganic salt. After standing for a few days in the cold the precipitate was filtered, washed with acetone and redissolved in ether. After centrifuging,[5] the clear solution was precipitated by pouring into cold acetone. A was precipitated six times and B five times. The purified phospholipides were stored in ether solution under carbon dioxide. 54.26 g. of A (0.73% of the mold, and 9.2% of the crude lipides) was obtained and 12.74 g. of B (0.43% of the mold and 6.15% of the crude lipides). The remaining simple lipides contained only a trace of phosphorus.

Anal. Preparation A: N, 1.71; P, 3.65; N/P, 1.03. Preparation B: N, 1.68; P, 3.78; N/P, 0.99; ash, 2.8.

Hydrolysis.—The phospholipides were hydrolyzed in 5 to 6 g. lots by refluxing for about six hours with 5% sulfuric acid. Ether was added, and the layers separated and filtered. The ether layer contained only traces of nitrogen and phosphorus.

For the separation of the water-soluble constituents the scheme of Newman and Anderson[6] was employed, with a few slight modifications. The crude barium glycerophosphate was purified by precipitating it as the lead salt, decomposing the latter with hydrogen sulfide in the presence of excess barium hydroxide, passing in carbon dioxide to remove excess barium, and reprecipitating the barium glycerophosphate with alcohol. A pure white product was obtained.

Anal.:[7] Calcd. for $C_3H_7O_6PBa \cdot {}^1/_2H_2O$: Ba, 43.4; P, 9.8. Found: Preparation A, Ba, 43.7; P, 9.8. Preparation B, Ba, 43.3; P, 9.8.

The presence of glycerol was shown by the specific test proposed by Eegruive.[8] The intensity of the test as compared to that given by an equal quantity of barium α-glycerophosphate indicated that a mixture of α- and β-glycerophosphates was present.

Choline was separated as the chloroplatinate, after removing barium glycerophosphate.[6] Choline chloroplatinate from A melted at 241–243° with decomposition, and from B at 242–243° with decomposition. *Anal.* Calcd. for $(C_5H_{14}ON)_2PtCl_6$: Pt, 31.42. Found: Pt, 31.64.

Cholamine was precipitated by picrolonic acid after removing barium glycerophosphate and choline chloroplatinate.[6] Cholamine picrolonate from A melted at 223–225° with decomposition, and from B at 222–226° with decomposition.[6]

Anal.: Calcd. for $C_{12}H_{15}O_6N_5$: NH_2-N, 4.31. Found: NH_2-N, 4.3.

By continued steam distillation of another portion of the aqueous hydrolysate made alkaline with sodium hydroxide, a small amount of cholamine was separated and was identified as the picrolonate. This afforded additiona evidence for the presence of cholamine in the hydrolysate

NITROGEN DISTRIBUTION IN THE AQUEOUS HYDROLYSATE

	Total water soluble N, % In A	In B
Ammonia N[9]	13.8	7.86
Amino N (Van Slyke)	50	57.8

By the method of Lintzel[10] all the N other than ammonia-N and primary amino N was approximately accounted for as choline.

The Ether Solution.—This made up 62% of the phospholipides in A, and 56.2% in B. Of this material, 14.4% in A was insoluble in petroleum ether. This insoluble material was acidic, and black in color, and was perhaps a decomposition product, since with rapidly prepared phospholipides (preparation B) it amounted to only 0.44%. Also, the amount of petroleum ether insoluble material seemed to increase with the age of the phospholipides.

The ether-soluble fatty acids of B were separated by the lead soap–ether method[11] into 13.8% saturated acids having an iodine number of 6[12] and 86.2% unsaturated acids having an iodine number of 95.7.

The saturated acids melted at 55.5–56.5° and had a neut. eq. of 276. Hence, they were probably a mixture of about equal parts of palmitic and stearic acids.[13]

On hydrogenation of the unsaturated acids in ethanol with a Raney nickel catalyst under about 100 atmospheres at 25–125°,[14] followed by one recrystallization from acetone of the hydrogenated acids, an acid melting at 69.5°, showing no depression of the melting point with pure stearic acid, and with a neut. eq. of 284.2 (calcd. for stearic acid, 284.3) was obtained.

On oxidation[15] of the unsaturated acids with cold permanganate only a trace of acids insoluble in chloroform was obtained. The chloroform soluble product melted at 130°[16] and showed no depression of the melting point with pure 9,10-dihydroxystearic acid.

On bromination of the unsaturated acids from A only traces of petroleum ether-insoluble acids were produced. The main product was a dark oil, presumably dibromostearic acid.

On fractionation of the ethyl esters of the unsaturated acids from 17.6 g. of A, a main fraction boiling at 175–177° (3 mm.) having an iodine number of 83.5, and a smaller fraction boiling at 175–180° (3 mm.) having an

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[5] The solid matter was a light-colored solid, insoluble in ether. It contained nitrogen and phosphorus, and preliminary work indicated that it consisted of two compounds of very peculiar composition. The study of these compounds is being continued.

[6] Newman and Anderson, *J. Biol. Chem.*, **102**, 229 (1933).

[7] Barium was determined according to King, *Biochem. J.*, **26**, 586 (1932).

[8] Eegruive, *Z. anal. Chem.*, **100**, 31 (1935).

[9] Characterized as ammonia by the formation of hexamethylenetetramine tetraiodide according to Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York City, 1916, Vol. II, pp. 20–21.

[10] Lintzel, *Biochem. Z.*, **238**, 438, 452; **241**, 273 (1931). The accuracy of this method in our hands was about ±10%.

[11] Assoc. Official Agr. Chem., "Methods of Analysis," Washington, D. C., 1930, 3 ed., p. 324.

[12] All iodine numbers were determined according to Rosenmund and Kuhnhenn, *Z. Nahr. Genussm.*, **46**, 154 (1923).

[13] "International Critical Tables," McGraw-Hill Book Co., Inc., New York City, 1928, Vol. IV, p. 165.

[14] The authors wish to express their thanks to Homer Adkins of the Department of Chemistry for hydrogenating the unsaturated acids.

[15] Lapworth and Mottram, *J. Chem. Soc.*, **127**, 1628 (1925).

[16] Crowther and Hynd, *Biochem. J.*, **11**, 139 (1917); Bosworth and Brown, *J. Biol. Chem.*, **103**, 115 (1933).

iodine number of 97 were obtained. Ethyl oleate has an iodine number of 82.

Hence, oleic acid was the chief unsaturated acid; traces of a more unsaturated acid were also present. No palmitoleic acid was found.

Summary

The ether-soluble phospholipides of *A. sydowi* were found to be a mixture of lecithin and cephalin. From the mycelium 0.4–0.7% of phospholipides was isolated. Glycerophosphoric acid, choline, cholamine and oleic acid were identified as the chief hydrolysis products. Stearic, palmitic, and a more unsaturated acid were also probably present in small amounts.

MADISON, WISCONSIN RECEIVED OCTOBER 17, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

An x-Ray Investigation of the Solid Solution Nature of Some Nitrate Contaminated Barium Sulfate Precipitates[1]

BY GEORGE H. WALDEN, JR., AND M. U. COHEN

Almost from the inception of quantitative analysis the contamination of precipitates by foreign substances has been a universal difficulty encountered by analytical chemists. The cause of the phenomenon has been assigned[2] in general to (1) inclusion of the mother liquor in the precipitate mass, (2) adsorption on the crystal faces, both "inner" and "outer," (3) compound formation and (4) solid solution. That such theories have been purely speculative in character is demonstrated by the fact that their application has varied with different workers from the assumption of one such theory to explain all cases of contamination, almost to the assumption of all such theories to explain any particular case.

The resulting confusion in a field as complex as this is easily understood when the experimental evidence is examined. This has been almost entirely confined to analytical studies of precipitate contamination as a function of the medium in which the precipitates have been formed, or even to the purely pragmatic study of the weight relations of contaminated precipitates. It is clear from a survey of the literature that such methods by themselves cannot furnish conclusive evidence for the mechanism of contamination, and that a truly critical evaluation of the various possibilities awaits the development of experimental methods of an entirely different character. It is further desirable that such experimental methods be applicable almost universally, and not limited either to certain precipitates or to certain contaminants. In these respects the method of radioactive indicators, for example, is severely limited. However, a very positive and direct experimental test is available, at least for theories (3) and (4), in the combination of chemical analysis with x-ray diffraction studies.

In the application of this method to precipitate contamination, that which is due to inclusion and adsorption will lead to no observable changes in the diffraction pattern. Compound formation will lead to the formation of a new solid phase which if present in sufficient amount will manifest itself by the appearance of new lines in the diffraction pattern. Finally, the entrance of a contaminant by the process of solid solution will cause a change in the lattice dimensions dependent on the proportion of contaminant present in the precipitate without affecting the lattice symmetry of the latter.

The great power of this method has been recognized in the case of crystals prepared from melts particularly in metallic systems,[3] and the very numerous studies in that field prove beyond question its validity and utility. There has been, however, but very meager application to crystals formed by precipitation from solution. As part of a systematic investigation by Grimm[4] and his students of solid solutions in ionic crystals, Wagner[5] studied the system $BaSO_4$–$KMnO_4$ with the help of the x-ray technique and established its solid solution nature.

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[1] This article is based upon part of a dissertation submitted by M. U. Cohen in partial fulfilment of the requirements for the degree of Doctor of Philosophy under the Faculty of Pure Science of Columbia University, May, 1935. The material was presented at the New York Meeting of the American Chemical Society, April, 1935.

[2] I. M. Kolthoff, *J. Phys. Chem.*, **36**, 860 (1932); *Chem. Weekblad*, **31**, 102 (1934), and following papers.

[3] Westgren, *Trans. Am. Inst. Min. Met. Eng.*, Inst. Metals, p. 13 (1931); Jette, *ibid.*, **111**, 75 (1934).

[4] (a) Grimm, "Handbuch der Physik," **24**, 1096 ff. (1933); (b) Dahlmann, Diss., Wurzburg, 1930; (c) Peters, Diss., Wurzburg, 1930.

[5] Wagner, *Z. physik. Chem.*, **2B**, 27 (1929).

In order to form "mixed crystals," *i. e.*, solid solutions, in such systems, their constituents, Grimm asserts, must possess: (1) identical types of chemical structure, *e. g.*, $BaSO_4$–$KMnO_4$; (2) identical types of crystal structure, *e. g.*, $BaSO_4$ and $KMnO_4$ are both orthorhombic and in the same space group, V_h^{16}; (3) nearly identical lattice parameters.

Such requirements may perhaps be valid for the occurrence of complete miscibility, but their force is certainly weak in the case of limited solubility. Thus in metallic systems a necessary condition for complete miscibility is that the components be of identical lattice type. On the other hand, for a limited range of solid solution no such condition is necessary, and as a matter of fact systems which fail to meet this requirement are fully as numerous as those which do comply.[3] While the very different nature of the metallic and the ionic types of bond makes any wide-spread analogy between ionic and metallic systems a very dangerous one, the fact is that in ionic systems also the available evidence[4a] points to the absence of such conditions of isomorphism for limited solid solubility. It is precisely this case, rather than that of complete miscibility, which is of most interest in the problem of precipitate contamination.

It is our aim to study, without regard to the limitations imposed by such rules as those of Grimm, the possible incidence of solid solution of foreign ions in analytical precipitates. As an initial study, the analytically important example has been chosen of barium sulfate precipitated in the presence of nitric acid.

While it has been known for a long time that such precipitates may contain quite large amounts of nitrate, the mode of entrance of this contaminant has been quite unknown, and indeed even the actual amount of nitrate in such precipitates has hardly been investigated.[6] To these facts may be added the additional one that, while the chemical nature and crystal structure of the contaminant are unknown, it is certainly not of the same chemical type as barium sulfate (MXY_4), and therefore according to Grimm should not form a solid solution. Further, Wagner reported[5] that barium nitrate did not form solid solutions with barium sulfate, stating that the contaminated crystals showed diffraction patterns identical with those from barium sulfate prepared in other ways.

All of these points total to the sum that the contamination of barium sulfate in the presence of nitric acid is a very interesting case for study, and one likely to prove most illuminating for the interpretation of precipitate contamination in general.

Since the proof or disproof of the existence of solid solution in any system depends entirely on the precision of the x-ray work, it should be emphasized that methods of the highest precision are essential. The greatest variation in the lattice parameters of the precipitates here investigated is about 0.3%, and this would have been overlooked entirely as being within the experimental error, if the usual type of powder camera and method of calculation had been used. The apparatus to be described, when used in conjunction with the method of interpretation developed by one of us,[7] permits the measurement of lattice parameters with a precision of at least 0.01%. This greatly extends the application of the x-ray method into the dilute solid solution range, the region of interest in connection with precipitate contamination.

Experimental

x-Ray Apparatus.—The self-rectifying gas x-ray tube used in this investigation was designed to provide for high asymmetry of the anode–cathode parts to give good rectifying and focusing properties; for efficient cooling of all parts of the tube to give high power dissipation; and for simplicity in construction and assembly.

Fig. 1 shows a longitudinal section through the corners of the tube and a top view with the plate B removed. Cooling water flows through tube b into the annular chamber A and then through the four longitudinal holes t drilled in the corners of the anode block to connect A with the water jacket D. The body of the tube and the 0.01-mm. aluminum windows are thus cooled very effectively. These aluminum foil windows are placed on three of the tube faces, the fourth face being occupied by 1.9-cm. flexible metal tubing (American Flexible Metal Hose Co.) which serves to connect the tube with the vacuum pumps. The tube is mounted vertically when used with the focusing cameras described below.

A simple regulator (Fig. 2) holds the tube current very constant. The solenoid is shunted across a tapped resistance placed in series with the primary of the high voltage transformer. An increase in the tube current increases the current in the transformer primary and therefore changes the current in the solenoid, causing the iron armature to rise. The resulting increase in the effective pumping speed of the diffusion pump reduces the gas pressure in the tube, bringing the current back to its original value. On the other hand, a decrease in the

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(6) Weiser and Sherrick, *J. Phys. Chem.*, **23**, 234 (1919).

(7) For the theory of these cameras see M. U. Cohen, *Rev. Sci. Instr.*, **6**, 68 (1935).

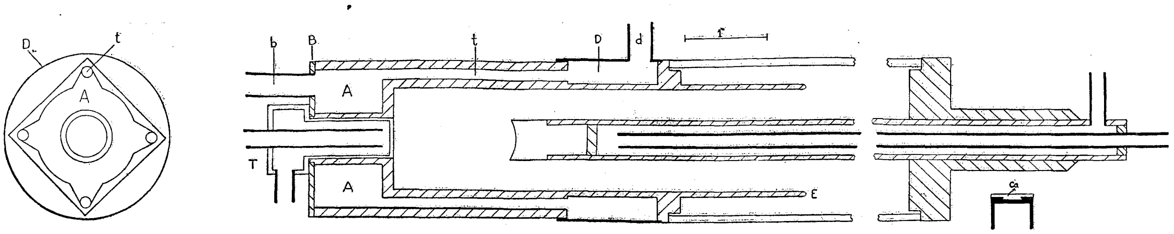

Fig. 1.

tube current lowers the armature, increasing the gas pressure and again restoring the original current. Changes in the equilibrium current are made by varying the proportion of the tapped resistance shunted across the solenoid.

Other supplementary equipment which may be of interest in view of its utility and the inexpensiveness includes a synchronous AC time clock and switch (New Haven), a solenoid-controlled water valve (General Electric No. CR9507-C1B), and a pressure-controlled switch (Detroit Lubricator No. 250) which opens the electrical circuits if the water pressure drops below a safe value. The inclusion of such auxiliary apparatus is invaluable because the operating time of the x-ray equipment may thereby be safely extended to periods when no personal attention is available.

The Precision Camera.—The design of the symmetrical focusing powder camera[7] for high angle reflections used in this investigation was conditioned by the difficulties encountered in securing x-ray photograms of barium sulfate powders which could be measured with sufficient precision. These crystals are orthorhombic and have relatively large lattice parameters. The use of long wave length x-rays is therefore indicated; short x-rays will be reflected only from planes so complicated that the intensity of the reflected beam will be very low and not very much greater than that of the general background. As a matter of fact copper radiation ($\lambda \sim 1.5$ Å.) gives very poor films; those taken with chromium are somewhat better; but really satisfactory photograms are secured only when resort is had to the use of calcium metal targets. This is the first extensive use reported of such radiation for powder work.[8]

Since the wave length of the calcium K lines is about 3.3 Å. they are very strongly absorbed and scattered by air. This makes it necessary to use an evacuated camera. The large size of the crystal grains leads to very spotty reflections if the sample is kept stationary during the exposure, and it is desirable therefore to arrange for continuous motion *in vacuo* of the powder under investigation. Constructional details of the camera designed with these points in mind will be evident from the photograph, Fig. 3.

The inner camera rings 6 and 6′ are machined to a diameter equal to that of the case 1 minus twice the film thickness, the latter being held to very close tolerances in the process of manufacture. Only the upper ring 6′ need be removed in loading the film 4. To facilitate this operation the diaphragm system 5, into which is inserted the replaceable lead slit 5′, is also removed. By means of the sector 3′ the sample 2 is pressed against the sample holder 3, the radius of the arc on which it is held being equal to that of the inner rings. The mechanism 9 for oscillating the sample holder operates through a stuffing box 10 and has the advantages that the sample holder is easily removable and that the need for a vacuum-tight central bearing is eliminated. The opening in the case through which the x-rays enter the slit system is covered by a cellophane window. The cover 8 carries a rubber gasket which forms a vacuum-tight seal when the camera is evacuated by a Hyvac pump connected to the outlet 7. The powder is mounted for exposure by dusting it on a sheet of mica on which a thin film of rubber cement has been allowed to set. The photograms obtained are excellent, the lines being very sharp and giving good contrast with the background.

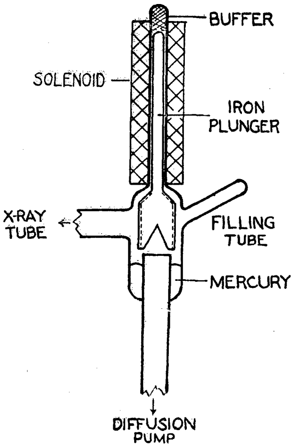

Fig. 2.

A millimeter scale for measuring purposes is printed on the single-coated x-ray film directly under the exposed portion. The original scale which serves as a negative was ruled on a Société Génévoise dividing engine by cutting through the blackened emulsion of a photographic plate. A vernier scale (10 divisions = 9.00 mm.) prepared in a similar way was printed on a photographic plate. Line distances on the photograms are measured by setting the zero of this vernier scale on the center of the line, tenths of a millimeter being given by coincidence of a vernier division with the millimeter scale printed on the film. The precision of such a setting is ±0.1 mm. and the distance between two lines is therefore precise to ±0.2 mm. The precision of the lattice constant determinations is discussed below for the case of the contaminated precipitates.

Preparation of the Precipitates.—The contaminated barium sulfate precipitates used in the present research have been prepared by the slow addition of sulfuric–nitric acid solutions to boiling barium nitrate–nitric acid

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(8) By the pressure exerted in a vise a calcium metal disk may be squeezed into good contact with the brass target body, if this is machined as indicated in Fig. 1. Such a target will carry 15 ma. at 40 kv. [*cf.* Haag, *Z. Krist.*, **A86**, 246 (1933), and Kersten and Maas, *Rev. Sci. Instr.*, **4**, 381 (1933)], but for continuous service it is better to use somewhat less power. At 5 ma. and 35 kv. good photograms of the cubic metals are obtainable in thirty minutes. Under these conditions the exposure time for the barium sulfate precipitates is about eight hours. The authors are indebted to Prof. H. T. Beans for pointing out that metallic calcium is sufficiently inert to be used in this way. Single targets have given several hundred hours of service over a period of months.

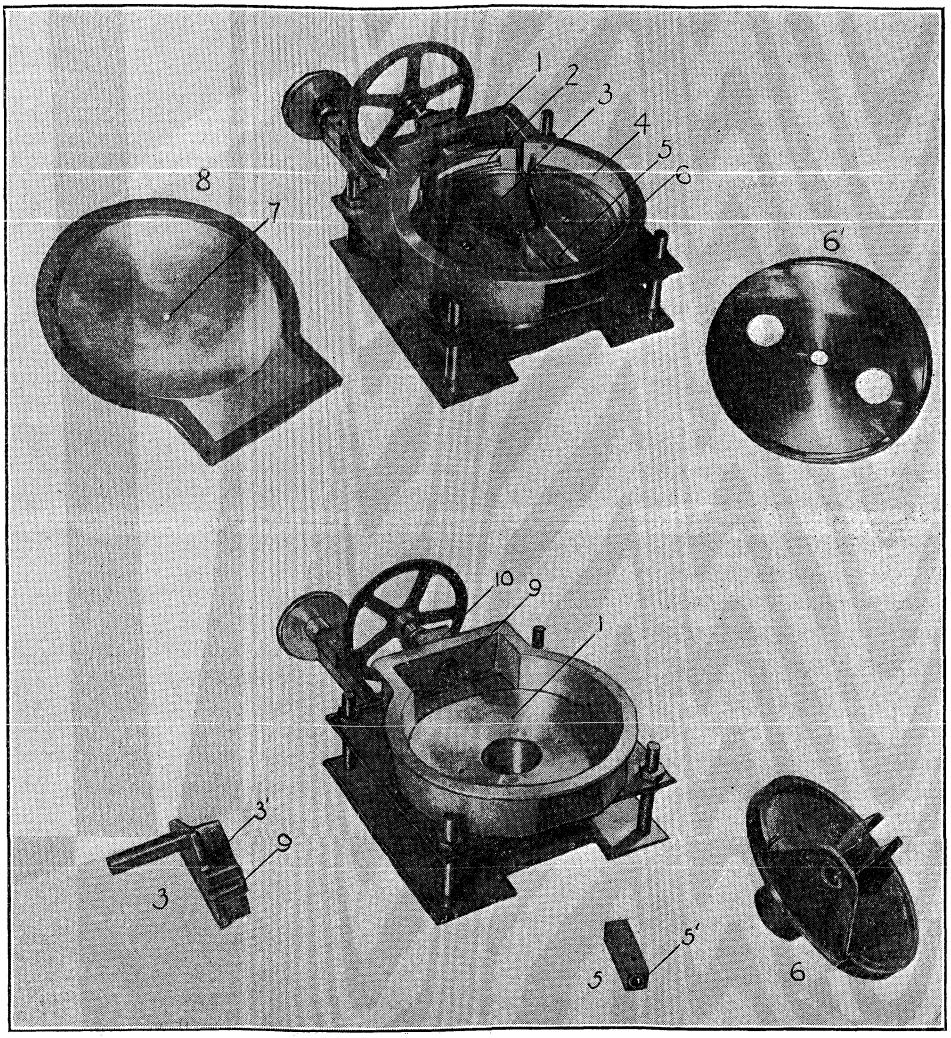

Fig. 3.

solutions with vigorous mechanical stirring. The ratio of sulfuric acid to barium nitrate was so chosen that only one-half of the initial barium ion was precipitated. The concentration of nitric acid in the sulfuric acid solution was adjusted to give the same concentration of nitrate ion as existed in the barium nitrate–nitric acid solution. This arrangement allowed the precipitates to form in the presence of a constant concentration of nitrate ion and a not too greatly varying concentration of barium ion. The precipitates were thoroughly washed by decantation with boiling water until the washings were neutral. They were then collected on a Büchner funnel and after air-drying preserved in glass-stoppered bottles.

Experience with a number of preliminary preparations led us to make the final precipitates in fairly large quantities; these are indicated in Table I. Five-liter flasks were used in the preparations, the sulfuric–nitric acid solutions being added from a separatory funnel drawn down to give a thirty-minute rate of addition. Digestion of the precipitates at the boiling point extended for thirty minutes, after which they were washed six times by decantation with boiling water and several times after transfer to the filter. The total volume of wash water was about four liters.

TABLE I

COMPOSITION OF PRECIPITATING SOLUTIONS

Ppt.	Solution A Concn., *M* Ba^{++}	NO_3^-	Solution B Concn., *M* NO_3^-	$SO_4^=$	Moles $BaSO_4$ precipitated
11	0.2	3.2	3.2	0.5	0.4
12	.2	1.6	1.6	.5	.4
13	.2	0.8	0.8	.5	.4
14	.2	.4	.4	.5	.4
15	.02	.32	.32	.05	.04
18	.02	.04	.04	.05	.04

Total volume A = 4 l. B = 0.8 l.

The precipitates prepared with nitric acid present in solution A were extraordinarily coarse and their crystalline character obvious. On the other hand, precipitates formed with only barium nitrate present in solution A (14 and 18) were much finer and about twice as bulky in the air-dried state as the others. As a matter of fact they took much longer to dry than any of the others, and for analytical purposes No. 14 had to be dried at 110° for a short time. Professor P. F. Kerr of the Department of Mineralogy, Columbia University, reports that microscopic examination shows No. 14 to consist of crystals which are smaller and not as well formed as No. 11, whose crystal grains are quite uniform and perfect. In neither case is there any evidence of the presence of more than one phase.

The standard barium sulfate No. 1, later referred to as "pure" barium sulfate, was prepared by the slow addition of barium chloride to an excess of boiling dilute sulfuric acid. The washed precipitate was treated with 18 *M* sulfuric acid, the excess being fumed off in a platinum crucible. The word "pure" is here used for convenience rather than as a claim.

Nitrate Analysis.—The complete analysis of the precipitates offers various difficulties, and the nitrate content alone is here reported. Even this determination is not simple, because of the lack of a completely satisfactory method for small quantities of nitrate, coupled with the insolubility of the substances in question. The method evolved after extensive trials of other schemes depends on the release of the nitrate from the precipitates by metathesis of the barium sulfate with concentrated sodium carbonate–sodium hydroxide solution, followed by determination of the nitrate in the alkaline solution by the Devarda method.[9]

That digestion with boiling sodium carbonate solution is effective in metathesizing barium sulfate to the carbonate has been shown previously.[10] It is evidenced further by the fact that the residue after digestion dissolves practically completely in dilute acid, a faint opalescence being the only sign of incomplete conversion. The solution of the residue also gives a negative ring test for nitrate with diphenylamine.

A sample of about 1 g. was digested in a 300-ml. Kjeldahl flask for one-half to one hour with 150 ml. of a boiling solution containing 12 g. of sodium hydroxide and 30 g. of sodium carbonate. When the contents of the flask were sufficiently cool, 3 g. of Devarda's alloy was introduced, and the mixture warmed gently until the reduction was complete. Distillation of the ammonia was then started and continued until 75–100 ml. of the solution had passed over into a cylindrical separatory funnel in which there was held 25.00 ml. of standard 0.1 *N* hydrochloric acid. At the conclusion of the distillation, the stopcock of the funnel was opened and the distillate run into a 500-ml. flask. The funnel was then washed down, and the contents of the flask titrated with standard 0.1 *N* sodium hydroxide solution. In these titrations brom cresol purple (2 drops of a 0.1% solution in 20% ethanol per 100 ml.) was used. It does not appear to be generally recognized that brom cresol purple is an excellent indicator for this titration; the color change, while fleeting, is so sharp as to be unmistakable.

All apparatus used in the analytical work was calibrated. The hydrochloric acid was standardized against a Bureau of Standards sample of potassium acid phthalate.

The nitrate determinations were made on the air-dried precipitates in all cases but No. 14, as indicated above. This sample, dried for one hour at 110° is numbered 14.2. The results of the determinations are expressed in weight per cent. of nitrate ion, Table II.

TABLE II

NITRATE CONTENT OF THE PRECIPITATES, WT. %

Ppt.	Determination 1	2	Mean, %
11	4.43	4.41	4.42
12	4.51	4.56	4.53
13	4.21	4.30	4.25
14.2	3.53	3.68	3.61
15	1.42	1.44	1.43
18	1.29	1.26	1.28

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. An eight-fold variation in the nitrate concentration of the solutions produces in precipitates 11 and 14 (Table I) a change only from 4.42 to 3.61% in nitrate content. Nos. 15 and 18 exhibit a similar phenomenon. To be noted however is the fact that the nitrate content of the precipitates varies with the barium ion concentration; in Nos. 11–14 the solutions were ten times as concentrated as in Nos. 15 and 18 (Table I).

Attempts to extend the range of concentrations for further study will lead in the more dilute region to the use of very large volumes or microanalytical methods; in the more concentrated range the precipitates settle as muds which are difficult to wash and filter, and which give poor x-ray photograms.

Lattice Constants.—The lattice constants of the contaminated barium sulfate precipitates have been measured using the precision focusing camera. All the x-ray photograms were taken with calcium K radiation. In most cases every measurable line was used in the computations, but the overlapping of two sets of doublets with varying composition caused these to be neglected in some of the films. At any rate, no fewer than fourteen pairs of lines have been used in any film, and as many as nineteen pairs have been utilized in the case of the pure barium sulfate preparation. A typical set of data is shown in Table III.

One of the authors has derived[7] a very general method for the calculation of lattice constants from x-ray powder photograms whereby account is taken of the inevitable presence of various systematic errors which have hitherto severely

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(9) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929.

(10) Wolesensky, *Ind. Eng. Chem., Anal. Ed.*, **1**, 29 (1929).

TABLE III

$BaSO_4$ No. 1 (T = 26°) Calcium $K\alpha_1 = 3.35169$ Å., $K\alpha_2 = 3.35495$ Å., $K\beta_1 = 3.08343$ Å.

$\sin^2 \Theta \longrightarrow K\alpha_1$[a]

Plane	Exptl.	Calcd.	$\Delta \times 10^5$
$321\alpha_1\alpha_2$	0.75478	0.75477	− 1
$303\alpha_1$	.81630	.81639	+ 9
$303\alpha_2$	.81640	.81639	− 1
230β	.99550	.99551	+ 1
421β	1.00552	1.00545	− 7
114β	1.01086	1.01090	+ 4
$004\alpha_1$	.88060	.88060	0
$004\alpha_2$	.88073	.88060	−13
231β	1.05089	1.05086	− 3
$031\alpha_1$	.90824	.90819	− 5
$313\alpha_1$	.91186	.91186	0
$313\alpha_2$	.91196	.91186	−10
$104\alpha_1$	.91654	.91661	+ 7
$104\alpha_2$	.91662	.91661	− 1
132β	1.10914	1.10936	+22
$131\alpha_1$	.94425	.94419	− 6
$131\alpha_2$	.94434	.94419	−15
$501\alpha_1$	.94859	.94864	+ 5
$501\alpha_2$	.94866	.94864	− 2
		Av. dev.	± 6

$a_0 = 8.8625 \pm 0.0002$ Å.

$b_0 = 5.4412 \pm 0.0001$ Å.

$c_0 = 7.1401 \pm 0.0002$ Å.

[a] $\sin^2 \Theta \longrightarrow K\alpha_1 = (\lambda\, K\alpha_1/\lambda_i)^2 \sin^2 \Theta_i$.

limited the precision obtainable, particularly in non-cubic systems. The complete elimination of systematic errors by this method is very well shown by the random distribution of the difference of experimental and calculated $\sin^2 \Theta$ values given as Δ in Table III, 10 units in Δ representing approximately 0.1 mm. With the complete elimination of systematic error the data may be combined by the method of least squares, thus reducing to a minimum the effect on the lattice parameters of accidental errors of measurement. A very great advantage of this method is the fact that the probable errors as defined in the theory of least squares[11] may also be determined and thus a purely objective statement can be made of the precisions of the derived lattice parameters.

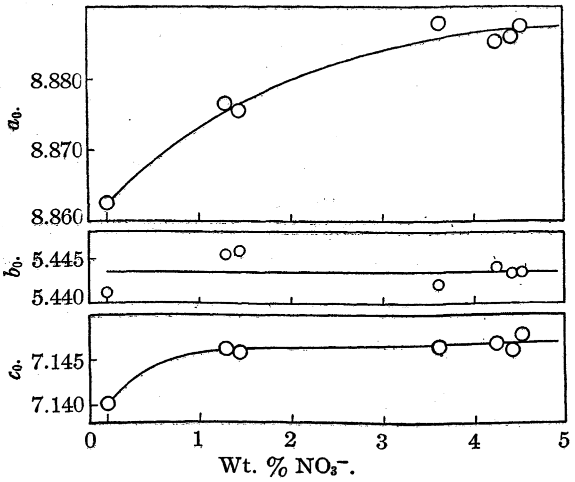

Fig. 4.

The approximate range of the probable errors on the various films is $a_0 = \pm 0.002$–0.01%, $b_0 = \pm 0.002$–0.004%, $c_0 = \pm 0.002$–0.004%. In practically every case values of the lattice parameters obtained from different films of the same precipitate check within the probable errors calculated from the individual films. The parameters reported here are values from the best photograms of the various preparations. However, because of differences in the temperature and perhaps other influencing factors under which the various exposures were made, comparison of the results is probably valid only within 0.01–0.02%.

In Fig. 4, which shows the relation between the lattice parameters and the nitrate content of the crystals, the radius of the circles is equivalent to 0.01%. Table IV gives the numerical values of the parameters.

TABLE IV

LATTICE PARAMETERS OF THE PRECIPITATES (Å.) (23–26°)

Ppt.	a_0	b_0	c_0
1	8.8625	5.4412	7.1401
18	8.8763	5.4455	7.1462
15	8.8753	5.4459	7.1458
14	8.8876	5.4422	7.1465
13	8.8849	5.4441	7.1469
11	8.8856	5.4434	7.1461
12	8.8871	5.4435	7.1478

Visual comparison of the x-ray photograms has been shown by the experience gained in this work to have semi-quantitative significance. In this way two interesting observations have been made. In the first place, drying the precipitates at 110° produces no visible change in the diffraction pattern. In the second place, when the nitrate content of the precipitates is eliminated by fuming with sulfuric acid, the residues show a pattern and relative spacing identical with that of pure barium sulfate.

Discussion

In the contaminated barium sulfate precipitates prepared as described in this work, there is no doubt but that the phenomenon of solid solution

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(11) Wright and Hayford, "Adjustment of Observations," D. Van Nostrand Co., New York.

appears. The orderly variation of the lattice spacing with the nitrate content shown in Fig. 4, and the regular change in the volume of the unit cell shown in Fig. 5, are conclusive evidence for the expansion of the fundamental barium sulfate lattice. Such an expansion, it has been pointed out in the introduction, is due to the entrance of foreign ions into the lattice. It cannot conceivably be due to any adsorption or occlusion process known at present. That such mechanisms may account for 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.

It is abundantly clear from the extensive literature of the subject that such essentially *ad hoc* theories as adsorption or occlusion have been of relatively slight value in the problem of precipitate contamination. That this failure is due to the absence of critical and positive experimental evidence for them has already been pointed out.

On the other hand, theories of a more or less *a priori* character, such as the Grimm rules for solid solution formation, have had a tendency to control the direction in which, it was thought, the existence of solid solution might profitably be investigated. As a result, its possible importance in precipitate contamination has been largely neglected. In the precipitates examined in this investigation the entrance of the contaminant as a solid solution emphasizes the fact that such considerations of isomorphism have little bearing for small ranges of solubility, and that therefore solid solution phenomena may play a very large part. The extent and importance of such a mechanism in other cases of precipitate contamination are impossible to predict. The function of the present research has been to show that this question may be decided in certain cases with a high degree of certainty, and by the use of a physical method whose evidence can scarcely be misinterpreted.

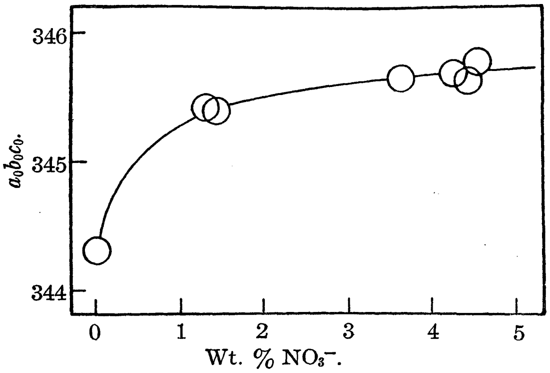

Fig. 5.

Summary

1. Apparatus is described which when used with a method of calculation previously developed makes it possible to determine the lattice parameters of powdered crystals with a precision of better than 0.01%. A feature of this apparatus is the use of a vacuum focusing camera in conjunction with long wave length x-rays from a calcium metal target.

2. A series of nitrate-contaminated barium sulfate precipitates has been prepared in the absence of all foreign cations except hydrogen ion, and in such a manner as to avoid large changes in the composition of the precipitating media.

3. The nitrate content of these precipitates has been determined by an adaptation of Devarda's method. Their compositions depend primarily on the barium ion concentration of the precipitating solutions, and only to a slight extent on the nitrate ion concentration.

4. The lattice parameters of the precipitates have been determined and correlated with their nitrate content.

5. The evidence indicates that the contaminant enters the barium sulfate lattice with the formation of a solid solution.

6. The role of such solid solution formation in the general problem of precipitate contamination has been discussed.

NEW YORK, N. Y. RECEIVED JUNE 13, 1935

[Contribution from the Pittsburgh Experiment Station, U. S. Bureau of Mines]

Kinetics of Ethylene Polymerization. II[1]

By H. H. Storch[2]

Effect of Oxygen

In a preliminary paper[3] the author showed that the rate of ethylene polymerization was increased markedly by minute amounts of oxygen. Subsequent experiments, which are described below, were designed to eliminate this impurity and to redetermine the rate, temperature coefficient, and character of primary products in oxygen-free ethylene.

Several procedures were tried in an effort to obtain oxygen-free ethylene, namely: (1) passage over a large surface of metallic sodium. This is the method used in preliminary experiments.[3] (2) Removal of oxygen from redistilled "anaesthesia" grade ethylene by slow passage over reduced metal oxide and thoria mixtures, such as Ni–ThO_2 (used at 25–150°) and Cu–ThO_2 (used at 300–350°). These mixtures contained about 5% ThO_2 and were prepared by precipitation with ammonia from a solution of the nitrates and subsequent heating of the washed hydrated oxides at 100 to 200° and finally at 500° before use.

(3) Preparation of ethylene by the reaction of ethylene bromide and zinc, both reactants being outgassed carefully by heating and evacuation before the reaction was started. The reaction rate was controlled by the rate of distillation of the ethylene bromide onto the zinc. It was found desirable to add about 0.1% of copper to the 40-mesh zinc by washing with a cupric chloride solution. The ethylene was fractionated by distillation before use.

(4) Preparation of ethylene by the dehydration of ethyl alcohol by passage over a thoria catalyst at 350°, the alcohol and catalyst being outgassed by heating and evacuation. The ethylene was fractionated by distillation before use.

All the experiments of Table I were made using the same apparatus[4] and procedure as described in the preliminary paper.[3] In the experiments with ethylene made by procedure 2 the Ni (or Cu) + ThO_2 tube was sealed directly onto an 8-liter storage vessel, so that the ethylene always was passed through the bed of reduced metal oxide plus thoria at a slow rate upon withdrawal from or admission to the reservoir.

Table I

Polymerization Rates of Ethylene Prepared by Different Methods

Temperature, 377° Pressure 142 cm.
Reaction volume 1700 cc.

C_2H_4 prepn. procedure no.	1	2 (Cu)	2 (Ni)	3	4
ΔP in 2 hours, mm.	15.0	10.1	10.8	15.7	2.0
Cc. of product (760 mm. and 27°)	16.4	11.0	11.1	17.3	1.8

Because the polymerization rate of ethylene prepared by procedure 4 was so much lower than that of ethylene obtained by any other method, a large number of experiments were made with this ethylene preparation. The rate increased slowly upon prolonged storage of the ethylene, and it was found that detectable amounts of hydrogen sulfide were present in the gas. This compound was probably formed by the reduction of traces of sulfur compounds present in the thoria catalyst. Upon introducing a tube containing sodium hydroxide sticks in the apparatus for procedure 4 to remove hydrogen sulfide from the gas as it left the catalyst tube, the resulting sulfur-free ethylene yielded a polymerization rate about equal to that prepared by procedure 3. It was therefore suspected that hydrogen sulfide was acting as an antioxidant and destroying the accelerating influence of the minute amounts of oxygen present. The origin of this oxygen is somewhat uncertain, especially in procedures such as nos. 3 and 4 (plus sodium hydroxide sticks) of Table I. The preparation and storage apparatus was tested repeatedly after prolonged evacuation, and it was found to be as vacuum-tight as one can reasonably expect without baking at a red heat which is necessary to secure and retain very high vacua. It is probable that very small amounts of oxygen were being desorbed continuously from the glass walls. It is also conceivable that the many necessary operations of the mercury valves "dragged" thin films of gas into the system. Tank nitrogen containing 0.5% oxygen was used to raise the mercury.

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(1) Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.) This work is part of a research program concerning the utilization of waste natural gas.

(2) Principal physical chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

(3) Storch, This Journal, **56**, 374 (1934).

(4) Except that all stopcocks were replaced by mercury valves.

After considerable experimentation it was apparent that even if oxygen-free ethylene could be prepared it could not be kept free of contamination by traces of oxygen in the apparatus used. Hence it was decided to add small amounts of ethyl mercaptan to the ethylene used in each experiment and to assume that the reaction kinetics of this mixture is quantitatively identical with that of oxygen-free ethylene.

The plausibility of this assumption was indicated by the following experiments.

Tank ethylene of anaesthesia grade was passed through alkaline pyrogallol, 60% aqueous sulfuric acid solution, and solid potash fragments, and then condensed at liquid nitrogen temperatures. The ethylene was subsequently distilled at about 2 cm. pressure, the first and last thirds of the distillate being discarded. Experiments at 142 cm. C_2H_4 plus 1.4 mm. C_2H_5SH pressure and 393° were made which yielded rate data reproducible to within about 5% of the mean value. The same batch of ethylene was used in all such experiments, the portion used to fill the reaction vessel (about 75% of the total ethylene in the reservoir) being recovered by fractional distillation which separated the ethylene from the polymerization products and from the ethyl mercaptan. After about fifteen experiments with the same batch of ethylene another rate determination was made omitting the mercaptan. The polymerization rate obtained in this experiment was practically identical with that of the last experiment using 1.4 mm. of mercaptan.

It was also found that additions of more than about 0.1 per cent. of mercaptan to the ethylene did not decrease the rate of polymerization any further, hence this concentration of mercaptan was used in all subsequent experiments.

Induction Period

The apparent autocatalytic nature of ethylene polymerization has been indicated elsewhere.[3] Similar results were obtained with ethylene to which 0.1% of ethyl mercaptan had been added. This is shown in Table II. The yields were measured as described in the first paper.[3] The data given for item (a) are the average results of eight experiments for the one- and two-hour intervals and of six experiments for the three-hour periods. The average and maximum deviations from the mean are 6 and 10%, respectively, for both the one-hour and two-hour intervals and 3 and 8%, respectively, for the three-hour intervals. The data for the other items in Table II represent single experiments.

The pressure decreases for the second hour are, with the exception of item (c), identical for the various gas mixtures used. This indicates that the same steady state has, in cases (a), (b), (d) and (e), been reached before the end of the first hour.

TABLE II

DATA ON AUTOCATALYSIS IN ETHYLENE POLYMERIZATION

Temperature, 393°. Initial pressure, 142 cm. Volume of reaction bulb, 4400 cm.

Time intervals	a C_2H_4 + 0.1% C_2H_5SH	b a + 1.3 mm. C_3H_6	c a + 1.7 mm. C_3H_6	d a + 1.4 mm. C_4H_8[a]	e a + 4.5 mm. C_4H_8[a]
	Pressure drop in mm.				
First hour	1.6	1.2	2.4	2.4	2.6
Second hour	4.4	4.4	3.6	4.4	4.4
Third hour	3.8	...	...	...	...
	Volume of product, cc. at 760 mm. and 27°				
Two hours	12.1	7.5[b]	11.3[b]	9.8[b]	18.8[b]
Three hours	21.7	...	...	...	...
Time interval ratios	Ratios of pressure drop for different time intervals				
Second/First (hour)	2.8	3.7	1.5	1.8	1.7
Third/Second (hour)	0.87	...	...	...	...

[a] 1-Butene was used in these tests. Similar tests with the low-boiling isomer of 2-butene gave identical results.

[b] Includes any unreacted propylene or butylene. Correction for C_2H_5SH is made in all cases (a) to (e).

The introduction of small amounts of propylene or butylene does not eliminate the increased pressure drop in the second hour compared with that of the first hour. The apparent reduction in the ratio of pressure drop for the second to the first hour in (c), (d), and (e) probably is due to a somewhat more rapid rate of reaction of propylene and butylene with ethylene. In fact, this must be true, for otherwise it would not be possible to explain the smaller volume of the products in items (b), (c), and (d). Item (e) apparently has a larger volume of products than item (a), but unquestionably this is due to the fact that the butylene added initially was almost equal to the amount of polymer obtained in item (a).

The data for the second and third hours of item (a) in Table II, when compared with the similar data in Table I of the preliminary paper,[3] show that the addition of mercaptan apparently has eliminated the autocatalysis after the first hour. The results with varying amounts of mercaptan from 0.05 to 0.15% show that after 0.1% has been added, further additions do not change the pressure decreases in any of the time intervals. Hence it seems that the polymerization reaction may have an induction period of its own, independent of any of the catalytic effects of small amounts of oxygen. The intermediary compounds whose rates of formation result in the induction period are stable enough to survive the condensation of the reaction mixture[5] after about ninety minutes reaction time and subsequent revaporization into the reaction chamber. In such an experiment, using C_2H_4 + 0.1% C_2H_5SH, the reaction rate a few minutes after revaporization was identical with that during the sixty- to ninety-minute interval. This evidence shows that the building up of any chain involving only free radicals or only energy-rich molecules as chain carriers is not responsible for the induction period. It is therefore certain that the rate of formation of a moderately stable intermediate compound must be the source of the induction period. Energy chains or free radical chains may of course be involved also in the reaction mechanism, but they cannot be of any importance in explaining the origin of the induction period.

Temperature Coefficient

The time necessary to obtain the same volume of reaction product at 377° as is obtained in 2 hours at 393° was found to be 4.5 hours. The pressure was the same (142 cm.) in both cases. The activation energy calculated in the usual way from these two data is 43,500 cal. The value previously reported by the author[3] for ethylene prepared by procedure 1 was 42,000 cal., and that reported by Pease[6] for tank ethylene of "anaesthesia" grade was 35,000 cal. It seems reasonable to conclude that the presence of oxygen lowers the apparent heat of activation and that 43,500 cal. is closer to the true value than any of the other values.

A calculation, using 43,500 + $RT/2$ as the activation energy (rate in pressure units = Const. $T^{-1/2}e^{-E/RT}$) and the average pressure drop 6.0 mm. of Table II for the two-hour experiments at 393° and 142 cm. initial pressure, shows that about 4.0% of all collisions with the requisite energy are efficient in polymerization. A similar calculation made for the data presented by Pease[7] on the hydrogen-ethylene reaction shows that about 14% of all collisions are efficient.[8] The calculations for ethylene polymerization are, however, of doubtful significance in view of the fact that the reaction is not a simple bimolecular process.

Order of the Reaction

Pease[5] showed that for tank ethylene of "anaesthesia" grade the reaction is second order in the range from 2.5 to 10 atmospheres. He also makes the statement that "at one atmosphere there is some evidence of a fall in rate more rapid than would be expected of a second-order reaction."

Two experiments were made; one at 71 cm. C_2H_4 pressure plus 0.1% C_2H_5SH, and the other with 71 cm. C_2H_4 + 71 cm. CH_4 + 0.1% C_2H_5SH. The temperature was 393°, and the time necessary to obtain the same pressure drop as is obtained at this temperature in two hours at 142 cm. C_2H_4 pressure was found to be exactly eight hours; this would indicate precisely a second-order reaction. However, the yields obtained in these two experiments were 6.5 cc. and 7.5 cc. for the 71-cm. C_2H_4 and the 71-cm. C_2H_4 + 71-cm. CH_4 experiments, respectively. These yields are considerably smaller than the 12.1 cc. obtained in two hours at 142 cm. C_2H_4 pressure. Since the pressure drops were identical, these lower yields indicate that the molecular weight of the products of the 71-cm. C_2H_4 pressure experiments was much higher than for the 142-cm. rate measurement; hence, the percentage of ethylene polymerized must have been much greater in the latter experiments. This conclusion supports Pease's statement that the order at about atmospheric pressure drops faster than would be predicted for a second-order reaction. The somewhat higher yield obtained with 71 cm. C_2H_4 + 71 cm. CH_4 would seem to indicate that although methane helps a little in keeping the rate up it is not very efficient in stabilizing the "hot" molecules of butylene. This fact also shows that if energy chains are present CH_4 is not very efficient in stopping them, for the yield when CH_4 is present is somewhat larger than when CH_4 is absent, whereas one would expect the reverse, namely, a considerably lower yield in the presence of this diluent if gas-phase breaking of energy chains occurred.

Analysis

Reaction Products.—Owing to the relatively small amounts (100 to 150 cc. of gas at normal temperature and pressure) of product available for analysis, no attempt at fractional distillation with controlled reflux was made. Four separations of the Shepherd–Porter type by fractional distillation without reflux were made for each

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(5) A small bulb attached to the mercury valve which closed off the reaction vessel from the rest of the system served as a receiver for the liquefied gases. The mercury valve was lowered until the connection to this bulb was open, and the bulb immersed in a bath of liquid nitrogen.

(6) Pease, THIS JOURNAL, **53**, 613 (1931).

(7) Pease, *ibid.*, **54**, 1876 (1932).

(8) A calculation made by Vaughan, *ibid.*, **55**, 4115 (1933), is erroneous due to the use of 40,300 cal. as the activation energy instead of 44,000 cal.

olefin. Measurements of gas density made by a magnetic gas-density balance showed that three separations were not sufficient, as 1 to 5% of the olefin one carbon atom lower in the series was present.

Owing to the presence of relatively large amounts of ethyl mercaptan in the C_6 fraction, it was necessary to find a satisfactory method for separating C_2H_5SH and C_6H_{12}. Condensation on a bright surface of metallic sodium was found fairly satisfactory. Experiments made with pure C_2H_5SH showed that at temperatures between 0° and −10° hydrogen and sodium mercaptate were the main products, only a few per cent. of diethyl sulfide being obtained. The analytical data are given in Table III.

TABLE III

ANALYSIS OF REACTION PRODUCTS, PER CENT.

Compound	2-hour experiments	3-hour experiments
Propylene	34.4	39.2
Butylenes	31.4	29.1
Pentenes	29.0	14.4
Hexenes	2.8	14.4
Higher olefins	2.4	2.9
Ratio of propylene to butylene	1.1	1.35

The increase in the C_3H_6/C_4H_8 ratio in the third hour seem to confirm the evidence presented in the first paper[3] concerning the primary product of the reaction. The question is, however, not answered, for even in the two-hour sample corresponding to polymerization of only about 1% of the total ethylene present the fractions of C_3H_6 and C_5H_{10} are of the same order as that of C_4H_8.

Summary

Several methods of preparation of "pure" ethylene were tried in an unsuccessful effort to obtain reproducible rates of polymerization. It was found that the addition of small amounts (about 0.1 per cent.) of ethyl mercaptan to ethylene prepared by fractionation of "anaesthesia grade" tank ethylene, decreased the rate of polymerization about tenfold; and the C_2H_4 + C_2H_5SH mixture polymerized at rates which were reproducible to within about 5%. These rates were in good agreement with the lowest rates obtained in the absence of the mercaptan. The addition of mercaptan did not eliminate the induction period observed in ethylene to which no mercaptan had been added; but did cut down markedly the duration of this induction period. The latter appears to be due to the rate of formation of some intermediate compound which survives freezing to −180° and subsequent revaporization into the reaction chamber at 393°. The polymerization of ethylene is probably not a simple bimolecular reaction. The evidence as to the nature of the primary product is not conclusive but indicates that butylene precedes propylene. The activation energy is 43,500 cal.

PITTSBURGH, PA. RECEIVED JULY 19, 1935

[CONTRIBUTION FROM FERTILIZER INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

The Partial Molal Volumes of Ammonia and Hydrogen in Liquid Ammonia–Hydrogen Mixtures under Pressure at 100°

BY R. WIEBE AND T. H. TREMEARNE

Ångström[1] measured the change of volume of water and various other organic liquids when hydrogen and other gases were dissolved in them. From his measurements he calculated

$$\Delta V/\Delta V_g = \delta \qquad (1)$$

wherein ΔV_g denotes the volume of gas at standard temperature and pressure dissolved, and ΔV the attending increase in the volume of solvent at constant temperature and pressure. He found that under atmospheric pressure, δ remained constant with varying V_g, Horiuti[2] extended the work of Ångström and confirmed the constancy of δ with concentration in the low pressure region, with sulfur dioxide in various organic liquids an exception.

Upon multiplying both sides of Eq. (1) by V_0, the volume of a mole of the dissolved gas at standard temperature and pressure we obtain $\Delta V/(\Delta V_g/V_0) = \Delta V/\Delta n_2 = V_0\delta$, which leads at once to the relation

$$(\mathrm{d}V/\mathrm{d}n_2)_{P,T} \equiv \bar{v}_2 = V_0 \qquad (2)$$

first stated explicitly by Horiuti[2] (p. 136).

Ångström and Horiuti both worked at low concentrations. At the relatively high concentra-

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[1] Ångström, *Wied. Ann.*, **15**, 297 (1882); *ibid.*, **33**, 223 (1888).

[2] Horiuti, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), No. 341, **17**, 125–256 (1931).

tions used in the present work it is found that for hydrogen in liquid ammonia, $\bar{v}_2$, and hence δ also, is positive and increases with the concentration of hydrogen except at the lowest pressure. Then because[3] $N_1(\mathrm{d}\bar{v}_1/\mathrm{d}N_1)_{P,T} = -N_2(\mathrm{d}\bar{v}_2/\mathrm{d}N_2)_{P,T}$, it follows that the partial molal volume $\bar{v}_1$ of ammonia decreases as the concentration of hydrogen increases.

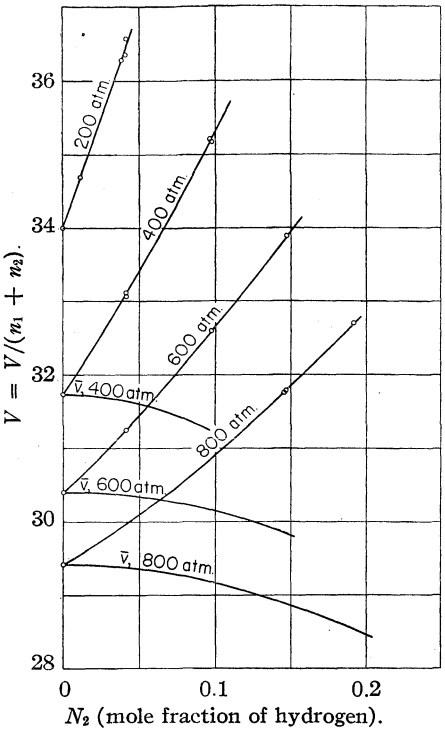

Fig. 1.—Molal volume of liquid ammonia hydrogen mixtures and partial molal volumes of liquid ammonia.

Apparatus and Procedure

The apparatus was identical with one used previously[4] except for a section of tubing fitted with a valve at each end and connected with the lower part of the high pressure bomb. At frequent intervals the volume of this section of tubing was measured by filling it with hydrogen at 100 and 200 atmospheres. In each experiment a sample of the equilibrium mixture from the bomb was turned into this calibrated section, and cut off. The amount of each constituent contained therein could then be determined, following methods previously outlined.

This device permits samples to be made up at concentrations intermediate between pure solvent (liquid ammonia) and saturation. The mixture in the calibrated tube—taken, for example, from a 400 atmosphere equilibrium mixture—can be raised quickly to a higher pressure, say 600 atmospheres, by increasing the pressure of the gas above the solution in the bomb to this figure. This new pressure is transmitted instantly to the contents of the tube, which then unsaturated can be cut off and analyzed as before.

The mixture in the bomb is itself unsaturated when it is suddenly subjected to a new pressure, whereupon diffusion begins at once, attended by a downward creep in pressure. The pressure reading is taken at the moment of cut-off. Diffusion to the bottom of the bomb is slow and there is sufficient opportunity to make one or two analyses before the composition of the samples is affected.

Results

The data are given in Table I and the figure. The molal volumes for pure liquid ammonia were calculated from the results of Keyes.[5] The first

Table I

Average Values Calculated from Number of Runs Given

Number of runs	Mole fraction of ammonia N_1	$v = V/(n_1 + n_2)$
	100 atm.	
	1.0000	35.456
6	0.9888	37.189
	200 atm.	
	1.0000	34.017
2	0.9888	34.695
7	.9612	36.276
2	.9589	36.343
4	.9584	36.577
	400 atm.	
	1.0000	31.739
1	0.9588	33.118
1	.9582	33.071
5	.9094	34.963
3	.9036	35.211
1	.9026	35.244
3	.9024	35.172
	600 atm.	
	1.0000	30.399
1	0.9591	31.147
1	.9025	32.597
3	.8527	33.891
	800 atm.	
	1.0000	29.419
1	0.8529	31.779
3	.8083	32.701

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[3] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York City, 1923, p. 43.

[4] R. Wiebe and T. H. Tremearne, This Journal, **55**, 975 (1933).

[5] Frederick G. Keyes, *ibid.*, **53**, 965 (1931).

column of Table I gives the number of individual runs from which the data were computed. The partial molal volumes were calculated from the relations[3] (p. 38)

$$\bar{v}_1 = v - N_2\,(\mathrm{d}v/\mathrm{d}N_2)$$
$$\bar{v}_2 = v + N_1\,(\mathrm{d}v/\mathrm{d}N_2)$$

$v = V/(n_1 + n_2)$ being the molal volume of the mixture and N_1 the mole fraction of ammonia, both of which are given in Table I. The derivative $\mathrm{d}v/\mathrm{d}N_2$ was obtained from suitable equations representing the molal volume *vs.* N_2 curves in the figure. Table II and the figure show the partial molal volumes.

TABLE II

N_1	$\bar{v}_1$	$\bar{v}_2$
	100 atm.	
1.0000	35.46	190.2
0.99	35.46	190.2
.9888	35.46	190.2
	200 atm.	
1.0000	34.02	95.16
0.99	34.02	94.20
.9888	34.03	93.88
.96	34.10	90.92
.9586	34.11	90.77
	400 atm.	
1.0000	31.74	62.13
0.99	31.73	63.23
.96	31.65	66.45
.9585	31.64	66.65
.91	31.29	71.60
.9029	31.22	72.62
	600 atm.	
1.0000	30.40	50.66
0.99	30.40	51.13
.96	30.36	52.50
.9591	30.36	52.54
.91	30.21	54.68
.9025	30.18	55.00
.86	29.94	56.75
.8527	29.89	57.04
	800 atm.	
1.0000	29.42	41.91
0.99	29.42	42.39
.96	29.38	43.80
.91	29.22	46.06
.86	28.95	48.20
.8529	28.42	48.49
.8083	28.53	50.28

We wish to point out briefly the thermodynamic significance of the work. At equilibrium where

$$\mathrm{d}\bar{F}_1 = \mathrm{d}\bar{F}_1' \qquad (3)$$

$\bar{F}_1$ and $\bar{F}_1'$ being the partial molal free energies of constituent 1 in the liquid and gas phases respectively, we have at constant temperature[3] (p. 216)

$$(\mathrm{d}\bar{F}/\mathrm{d}P)_{N_1}\,\mathrm{d}P + (\mathrm{d}\bar{F}_1/\mathrm{d}N_1)_P\,\mathrm{d}N_1 = (\mathrm{d}\bar{F}_1'/\mathrm{d}P)_{N_1'}\,\mathrm{d}P + (\mathrm{d}\bar{F}_1'/\mathrm{d}N_1')_P\,\mathrm{d}N_1'$$

Transposing and noting that

$$(\mathrm{d}\bar{F}_1/\mathrm{d}P)_{N_1} = \bar{v} \text{ and } (\mathrm{d}\bar{F}_1'/\mathrm{d}P)_{N_1'} = \bar{v}_1'$$

we obtain at constant temperature

$$(\mathrm{d}N_1/\mathrm{d}P)_{\mathrm{sat.}} = (\bar{v}' - \bar{v}_1 + (\mathrm{d}\bar{F}'/\mathrm{d}N')_P\,(\mathrm{d}N'/\mathrm{d}P)_{\mathrm{sat.}})/(\mathrm{d}\bar{F}_1/\mathrm{d}N_1)_P$$

The values of $(\mathrm{d}N_1/\mathrm{d}P)_{\mathrm{sat.}}$ are readily calculated from previous work[6] and are given in Table III. The value of $\bar{v}_1$ is known from the present work. Further work on the gas phase at this Laboratory will supply directly $\bar{v}_1'(\mathrm{d}\bar{F}_1'/\mathrm{d}N_1')_P$ and $(\mathrm{d}N_1'/\mathrm{d}P)_{\mathrm{sat.}}$. The solubility $(\mathrm{d}N_1/\mathrm{d}P)_{\mathrm{sat.}}$ could be calculated indirectly provided we knew the value of $(\mathrm{d}\bar{F}_1/\mathrm{d}N_1)_P$ at one isobar.

TABLE III

Total pressure, in atm.	Mole fraction of ammonia N_1	$\mathrm{d}N_1/\mathrm{d}P$
75	0.9956	0.00031
100	.9882	30
150	.9731	30
200	.9585	29
300	.9302	28
400	.9035	27
500	.8783	25
600	.8546	23
700	.8329	22
800	.8118	21
900	.7917	20
1000	.7723	19

This scheme has already been used for liquid–solid system under pressure by Adams and Gibson.[7]

Summary

The volumes of ammonia–hydrogen mixtures in the liquid phase have been measured.

The partial molal volumes of both constituents were calculated.

The thermodynamic significance of the data has been discussed and the desirability of further measurements pointed out.

WASHINGTON, D. C. RECEIVED SEPTEMBER 30, 1935

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[6] R. Wiebe and T. H. Tremearne, THIS JOURNAL, **56**, 2357 (1934).

[7] L. H. Adams, *ibid.*, **53**, 3769 (1931); *ibid.*, **54**, 2229 (1932); L. H. Adams and R. E. Gibson, *ibid.*, **54**, 4520 (1932).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Transition Cases in the Distribution of Ions

BY RAYMOND M. FUOSS

Introduction

In a recent paper,[1] it was stated that "the conductance of incompletely dissociated binary electrolytes as a function of concentration obeys the equation

$$\Lambda = \gamma(\Lambda_0 - \alpha\sqrt{c\gamma}) \qquad (1)$$

exactly up to concentrations at which specific ionic interactions of higher order than pairwise become appreciable." Equation (1) is derived on the assumption that free ions and ion pairs are the only molecular species present. Using a distribution function for ion pairs, derived by the author,[2] it is possible to show that a critical concentration

$$c_0 = \frac{1000}{4\pi N}\left(\frac{DkT}{\epsilon^2}\right)^3 e^{-x}\, x^3(2 - x) \qquad (2)$$

where

$$x = 3 - \sqrt{3} \qquad (3)$$

exists, above which interactions of higher order than pairwise become significant. This concentration agrees with the concentration found experimentally above which deviations between observed conductances and values calculated from (1) exceed the experimental error.

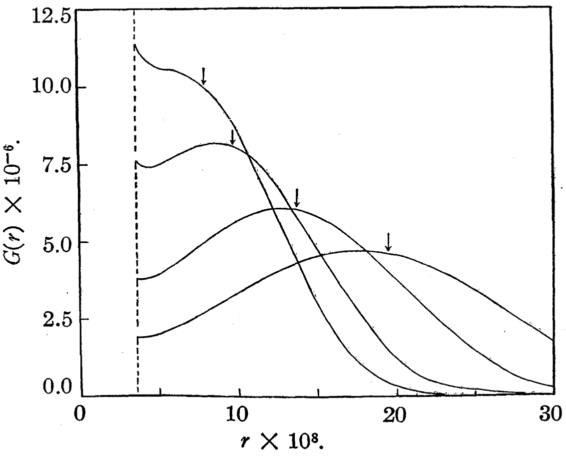

Fig. 1.—Distribution curve for $D = 78.6$; $a = 3.67 \times 10^{-8}$; $c = 0.025, 0.05, 0.10, 0.15$; arrow marks $1/\kappa$.

Derivation and Discussion

The distribution function mentioned above gives the probability that a given positive ion will have a negative ion in dr at r such that the negative ion is the nearest otherwise unpaired ion to the central positive ion. The mathematical form of the function is

$$G(r) = \frac{4\pi N}{V} r^2 \exp.\left(\frac{\beta}{r} - \frac{4\pi N}{V}\int_a^r e^{\beta/x}\, x^2\, \mathrm{d}x\right) \qquad (4)$$

where N = total number of positive ions of charge ϵ in a total volume V, r = center to center distance between ions, $\beta = \epsilon^2/DkT$, D = dielectric constant, k = Boltzmann constant, T = absolute temperature and a = ion size.

Examples of the distribution function are given in Figs. 1 and 2. For Fig. 1, $D = 78.57$, $t = 25°$ and $a = 3.67 \times 10^{-8}$ cm.; the example thus refers to aqueous solutions. The lowest curve corresponds to $c = 0.025$. Here $G(r)$ has a maximum at 18×10^{-8} cm. and the distribution to both sides of the maximum is fairly symmetrical. Pairs for which $r = 18 \times 10^{-8}$ are better than twice as probable as pairs in contact, so that association is negligible. The next two higher curves correspond to $c = 0.05$ and $c = 0.10$, respectively; with increasing concentration the maximum moves to smaller pairwise distances and at $c = 0.15$ the maximum has practically vanished. At higher concentrations, the shorter the pairwise distances, the greater the probability for the configuration. This effect is not to be con-

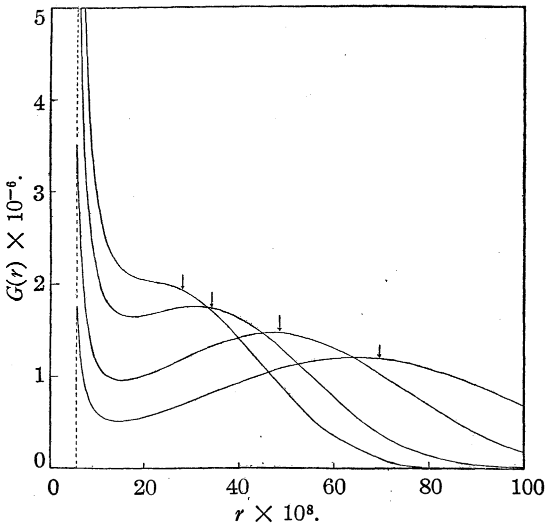

Fig. 2.—Distribution curve for $D = 20$; $a = 5.57 \times 10^{-8}$; $c = 0.5, 1, 2, 3 \times 10^{-3}$.

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(1) Fuoss, This Journal, **57**, 488 (1935).

(2) Fuoss, *Trans. Faraday Soc.*, **30**, 967 (1934); *Chem. Rev.*, **17**, 27 (1935).

sidered an association due to Coulomb forces; it is simply a space crowding. In Fig. 2, we have an example of true association. Here $D = 20$, $t = 25°$, $\beta = 27.8 \times 10^{-8}$, $a = 5.57 \times 10^{-8}$ cm. The lowest curve is for $c = 5 \times 10^{-4}$; it has a long range maximum corresponding to high probability for free ions and also an exponential peak at $r = a$ corresponding to a high probability for associated short range pairs. As concentration is increased, the long range maximum moves to shorter distances, and the peak at $r = a$ climbs rapidly, so that the long range maximum eventually vanishes. Above $c = 3 \times 10^{-3}$, the pair probability is greater, the shorter the distance. Here we have both Coulomb attraction and space crowding responsible for the disappearance of the free ion maximum.

The general behavior of these curves reminds one somewhat of the isotherms for a van der Waals gas near the critical point. At low concentrations there are, in general, two well-defined peaks, one corresponding to free ions and one to associated. As concentration is increased, a concentration is finally reached at which the maximum, the minimum and the included inflection point coincide. Above this concentration, free and associated ions, as defined on the basis of $G(r)$, become indistinguishable, and we should expect that equations based on the classification of ions by means of $G(r)$ relating properties and concentration would fail at concentrations of this critical order of magnitude, no matter how closely they reproduced experimental data at lower concentrations.

The critical concentration can be found very easily. We have, on differentiating (4)

$$\frac{\mathrm{d}G}{\mathrm{d}r} = G(r)\left(\frac{2}{r} - \frac{\beta}{r^2} - \alpha r^2 e^{\beta/r}\right) \tag{5}$$

$$\frac{\mathrm{d}^2G}{\mathrm{d}r^2} = G(r)\left(\frac{2}{r^2} - \frac{2\beta}{r^3} + \frac{\beta^2}{r^4} - 6\alpha r e^{\beta/r} + 3\alpha\beta e^{\beta/r} + \alpha^2 r^4 e^{2\beta/r}\right) \tag{6}$$

where

$$\alpha = 4\pi N/V \tag{7}$$

Setting $\mathrm{d}G/\mathrm{d}r = 0$, we obtain

$$\alpha e^{\beta/r} = 2/r^3 - \beta/r^4 \tag{8}$$

and setting $\mathrm{d}^2G/\mathrm{d}r^2 = 0$ and substituting (8) to eliminate the transcendental, we obtain the equation

$$x^2 - 6x + 6 = 0 \tag{9}$$

where

$$x = \beta/r \tag{10}$$

as the condition which must be fulfilled at the critical point. The root of (9) which has physical meaning is

$$x = 3 - \sqrt{3} \tag{11}$$

Substituting in (8) we finally obtain, after rearrangement

$$c_0 = \frac{1000}{4\pi N}\left(\frac{DkT}{\epsilon^2}\right)^3 e^{-x}\, x^3(2 - x) \tag{2}$$

which is the result announced in the introduction. At 25°

$$c_0 = 3.2 \times 10^{-7}\, D^3 \tag{12}$$

for 1-1 electrolytes.

Another derivation of (2) can be obtained by requiring that the two roots of (5) coincide; by writing (5) in the form

$$r = \beta/2 + \alpha r^4 e^{\beta/r}/2 = f(r) \tag{13}$$

it is obvious that this condition will be fulfilled when $\mathrm{d}f/\mathrm{d}r = 1$. Combining this requirement with the vanishing of (6), a fourth degree equation is obtained, which, of course, has $(3 - \sqrt{3})$ as one of its roots.

The value, r_0, of r at $c = c_0$ is given by

$$r_0 = 0.789\beta = (440/D) \times 10^{-8}\ \text{cm. at } 25°$$

In water, this corresponds to 5.6×10^{-8} cm. and the critical concentration is 0.155 N, with $1/\kappa = 7.7 \times 10^{-8}$ cm. Here $1/\kappa$ is the characteristic distance of the Debye–Hückel theory

$$\kappa^2 = 8\pi N\epsilon^2/VDkT$$

If we assume that ordinary ions have diameters about equal to 3×10^{-8} cm. in water, then at 0.155 N, the maximum charge in the ionic atmosphere would be roughly two diameters away from a given ion. It seems dangerous, therefore, to extrapolate the concept of ionic atmosphere or equations based on it into concentrations greater than the critical; the ions are too close together to permit a time average treatment of their interaction.

Incidentally, $1/\kappa$ agrees in order of magnitude with ρ, the distance at which $G(r)$ has its long range maximum. At $r = r_0$

$$\kappa r_0 = 2/\sqrt{e^x(4/x - 1)} = 0.7228$$

which, as a numerical constant, is the same for all 1-1 electrolytes in all solvents. With decreasing concentration, both $1/\kappa$ and ρ increase; the ratio of these distances, $\kappa\rho$, is approximately 18.7 $c^{1/6}D^{-1/2}$ for $\rho > 2\, r_0$. Since $c^{1/6}$ changes only very slowly with concentration, we see that over quite a wide range of concentration, $\kappa\rho$ remains in order of magnitude unity. At very low concentrations, $1/\kappa >> \rho$, but when such concentrations are reached, the interionic effects become negligible practically in that they become unobservable experimentally. The ionic atmosphere thus appears as an approximation device for the average effects of free ions on free ions, where the average distances are of the order of $(V/2\pi N)^{1/3}$.

Let us now consider a typical example of the application of our result. The conductance of potassium chloride in liquid ammonia ($D = 22.38$ at $-33.35°$)[3] obeys equation (1) at low concentrations[4] but deviations larger than experimental error begin to appear at several thousandths normal. For liquid ammonia at $-34°$

$$c_0 = 1.8 \times 10^{-3} \qquad (14)$$

In Table I are given the conductance data, together with the deviation between Λ observed and Λ calculated from (1) using $\Lambda_0 = 347.85$ and $K = 8.73 \times 10^{-4}$. At 1.8×10^{-3} N, the deviation is well beyond the experimental error, but as concentration decreases, exact agreement is found.

TABLE I

$c \times 10^5$	Λ (obsd.)	% deviation
2.471	334.27	−0.12
3.957	328.27	− .04
5.766	322.00	+ .02
9.320	311.77	+ .02
12.030	305.08	+ .03
15.619	297.48	− .04
24.021	282.42	+ .01
33.413	268.63	+ .03
50.79	250.93	+ .02
80.52	229.28	− .03
104.20	216.62	+ .05
137.60	202.81	+ .30
209.91	182.23	+ .69
313.94	163.74	+1.16
453.25	147.42	+1.99
702.29	130.21	+2.86
973.98	118.45	+4.14

In ethylene chloride ($D = 10.2$), the deviations between calculated and observed values become significant at several ten thousandths normal;[5,6] in anisole ($D = 4.29$) at several hundred thousandths;[5,7] and in benzene ($D = 2.27$), divergence from simple binary properties appears at several millionths normal.[8] In every case, equation (2) predicts the concentration above which conductance data cannot be computed by means of (1).

It is of interest to consider the physical interpretation of the result. Using the distribution function $G(r)$, we have divided the ions into several groups: free ions, which have no unpaired ion in the immediate neighborhood, associated ions, which have a single partner of opposite charge at a distance of molecular dimensions, and transition ions, which are those for which the pair distance is of the order of that corresponding to the probability barrier at $r = \beta/2$, the Bjerrum radius. Assuming that the equilibrium betweeen free and associated ions may be treated by the law of mass action, if allowance is made for the long range interaction of free ions on free ions, a conductance equation (1) is derived which is in exact agreement with data at low concentrations. In other words, as long as free ions have a relative maximum probability in terms of $G(r)$, we find properties which can be ascribed to an association equilibrium of the following type

$$A^+ + B' \rightleftharpoons AB$$

When, according to (3), free ions are no longer definable, a new set of properties appears; in the conductance curves, for example, Λ becomes larger with increasing concentration than (1) allows, and eventually a minimum in the Λ–c curve appears, after which conductance *increases* with increasing concentration. This effect has been explained in terms of higher association to triple ions;[9] the same hypothesis can be arrived at if we consider the approximations made in the derivation of $G(r)$. Long range interaction of short range pairs with free ions was neglected as a $1/r^2$ energy, compared to the $1/r$ energy of free ion-free ion interaction, but when a large fraction of the solute is present as short range pairs, it is clear that this interaction must be taken into account. If we redefine free ions to be those which are relatively far from either another free ion or from an ion pair, then we can again predict properties, but now five (+, −, + −, + − +, − + −) rather than only three molecular species are assumed to be present. Counting part of the solute present as triple ions is in effect removing some area (ions) from the $G(r)$ curve near $r = \beta/2$, and the maximum is thus restored.

Summary

Using the ion pair distribution function previously derived by the author, a critical concentration is shown to exist, above which free and pairwise associated ions become indistinguishable. This concentration, $3.2 \times 10^{-7} D^3$ at 25° for 1-1

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(3) Hooper and Kraus, THIS JOURNAL, **56**, 2265 (1934).

(4) Vincent F. Hnizda, Thesis, Brown University, 1935.

(5) Cox, Kraus and Fuoss, *Trans. Faraday Soc.*, **31**, 750 (1935).

(6) Donald L. Fowler, Thesis, Brown University, 1935.

(7) Bien, Kraus and Fuoss, THIS JOURNAL, **56**, 1860 (1934).

(8) Fuoss and Kraus, *ibid.*, **55**, 3614 (1933).

(9) Fuoss and Kraus, *ibid.*, **55**, 2387 (1933).

electrolytes, is experimentally the concentration above which the simple laws of dilute solutions of electrolytes are no longer obeyed, so that a numerical significance is attached to the phrase "at low concentrations." At higher concentrations, higher types of association must be considered for the case of non-aqueous solutions.

PROVIDENCE, R. I. RECEIVED JUNE 1, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Potentiometric Determination of Quadrivalent Osmium with Chromous Sulfate

BY WILLIAM R. CROWELL AND HARLAN L. BAUMBACH

In previous papers we have presented a direct[1] and an indirect[2] method of determining quadrivalent osmium. The former method is highly inaccurate, and the latter has the disadvantages of having two volatile constituents involved and of being applicable only to dilute acid solutions. The work of Thornton and Sadusk[3] suggested to us the possibility of using chromous sulfate as the reducing agent and the present work deals with the use of solutions of this salt. As in the case of titration with titanous salts the osmium is reduced from the quadrivalent to the trivalent state.

Because of the rapid reaction between chromous sulfate and oxygen we found it most satisfactory to have the apparatus all of glass as far as possible, to have all rubber connections of best quality heavy rubber, and all joints sealed with a suitable material such as lacquer cement. Of lesser importance is the tendency for chromous sulfate to react with hydrogen ion. Asmanoff[4] states that solutions may be as high as 10 N in sulfuric acid or 3 N in hydrochloric acid before any appreciable evolution of hydrogen takes place. Thornton and Sadusk state that they prepared 0.07 N solutions 0.18 N in sulfuric acid which remained unchanged in titer for two months. The solutions used by us were not greater than 0.03 N in sulfuric acid.

Reagents

The chromous sulfate solution was prepared by a method developed by Messrs. Stone and Beeson of the Chemistry Department at the University of California at Los Angeles. A solution of 0.01 M chrome alum 0.01 N in sulfuric acid was reduced by passage over amalgamated zinc. The yield of chromous ion was nearly 100% and the acid concentration was practically unchanged by the process.

The potassium bromoosmate and the potassium chloroosmate were prepared from osmium tetroxide in much the same manner that Gilchrist[5] prepared the ammonium bromo and chloro compounds in his determination of the atomic weight of osmium. A potassium hydroxide solution of osmium tetroxide was prepared as previously described.[6] The solution was acidified with sulfuric acid, the osmium tetroxide distilled into hydrobromic or hydrochloric acid, and the procedure carried out according to the method of Gilchrist except that potassium instead of ammonium salts were used.

The hydrobromic acid was prepared from red phosphorus and bromine. The middle fraction of the distillation of the products of the reaction was redistilled several times until a water-white liquid was obtained.

The constant boiling hydrochloric acid was obtained by twice distilling a mixture of equal volumes of concentrated hydrochloric acid and distilled water and retaining the middle fraction of the second distillation.

The potassium ferricyanide and potassium iodate used in standardizing the chromous sulfate and the sodium thiosulfate were recrystallized from the chemically pure salts.

Apparatus, Experimental Procedure and Results

The titration beaker consisted of a heavy-walled Pyrex beaker of about 125-cc. capacity. The cover consisted of a large rubber stopper which was cemented in place. In this stopper were openings for a mercury-sealed stirrer calomel and platinum electrodes, carbon dioxide inlet and outlet, burets, apparatus for introducing solids, and apparatus for treating and transferring solutions. In the bottom of the beaker was sealed a heavy stopcock to allow solutions to be withdrawn and the beaker to be rinsed without admitting air.

Figure 1 shows a diagram of the apparatus used for storing and handling the chromous sulfate solution. The system was flushed with nitrogen and the standard solution forced into the 5-liter flask A and stored under a total pressure of about 1.5 atm. of nitrogen. The nitrogen was purified by passing it through a strong solution of chromous sulfate. The capacity of the flask was about two liters of solution. E, F and G are heavy stopcocks. The solution was allowed to flow into the buret C and fill the bulb B. I was sealed off and after standing long enough to remove all adsorbed oxygen from the walls of the buret and bulb, the solution was displaced by nitrogen at

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[1] Crowell and Kirschman, THIS JOURNAL, **51**, 1695 (1929).

[2] Crowell, *ibid.*, **54**, 1324 (1932).

[3] Thornton and Sadusk, *Ind. Eng. Chem., Anal. Ed.*, **4**, 240 (1932).

[4] Asmanoff, *Z. anorg. allgem. Chem.*, **160**, 209 (1927).

[5] Gilchrist, *Bur. Standards J. Research*, **9**, 279 (1932).

[6] Crowell and Kirschman, THIS JOURNAL, **51**, 175 (1929).

one atmosphere pressure by passing the gas through D and allowing the solution to flow out through E and F. The solution in A was shaken over the walls of the flask occasionally over a period of a day or two and it was ready for use. Solutions stored in such a manner remained unchanged in titer for a month.

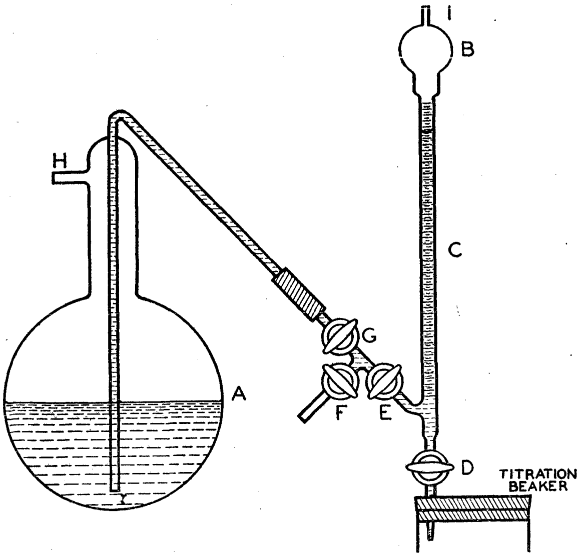

Fig. 1.—Apparatus for storing and titrating chromous sulfate solutions.

The oxygen-free water and acids were stored in bottles provided with heavy rubber stoppers and connected by siphon tubes to the side arms of burets. A slight pressure of carbon dioxide was maintained over the solutions in the bottles, burets and titration beaker at all times. The carbon dioxide was purified by passage through chromous sulfate solution.

The chromous sulfate solution, which was approximately 0.01 *N*, was standardized with solid potassium ferricyanide and with potassium dichromate solution. The high equivalent weight of potassium ferricyanide, the ease with which it can be prepared in the pure state, and the sharp end-point obtainable with it recommended its use as a standard. About 80 mg. of the crystals dried at 130° was introduced into an apparatus similar to that shown in Fig. 2 except that the tube connecting with the titration beaker was larger and attached in such a manner that the sample could be washed directly into the beaker with water. After carbon dioxide had been passed over the crystals for fifteen minutes, they were washed into the beaker with 20–40 cc. of oxygen-free water, 5 cc. of 2 *N* hydrobromic acid added, and the solution titrated potentiometrically with chromous sulfate. About 25 cc. of the reducing agent was required. It was not necessary to add zinc salt because the presence of the zinc ions in the reducing agent had sufficient influence on the potential of the solution to produce an end-point change of 600–800 millivolts per 0.1 cc. of reagent.

The normality of the dichromate solution was determined by means of thiosulfate standardized with potassium iodate. 0.9980 cc. of 0.2297 *N* dichromate was pipetted into the apparatus shown in Fig. 2 and 5 cc. of 6 *N* sulfuric acid added. Carbon dioxide was bubbled through the solution slowly from the titration beaker, escaping by way of the two-way stopcock while the solution was boiled gently for fifteen minutes to remove all oxygen. After cooling, the solution was forced into the beaker by connecting with a higher pressure of carbon dioxide than that in the beaker. Finally the flask was rinsed with 20–40 cc. of water and the contents of the beaker titrated. The end-point potential change was 400–600 millivolts per 0.1 cc.

In the titration of six chromous sulfate solutions with ferricyanide the average deviation of each normality from the mean was 0.05%. In the titration of three solutions with dichromate the average deviation was 0.02%. The difference between the averages of two ferricyanide and three dichromate titrations was 0.03%.

Table I shows the results of determinations of the equivalent weights of potassium bromoosmate and potassium chloroosmate. About 150 mg. of the salt was introduced into the beaker in the same manner as the ferricyanide and sufficient acid added to furnish the concentration stated in column 3. The titration was conducted with the chromous sulfate which had been standardized with ferricyanide. The volume of reagent required was about 19–24 cc. in the case of bromoosmate and 21–33 cc. in the case of chloroosmate.

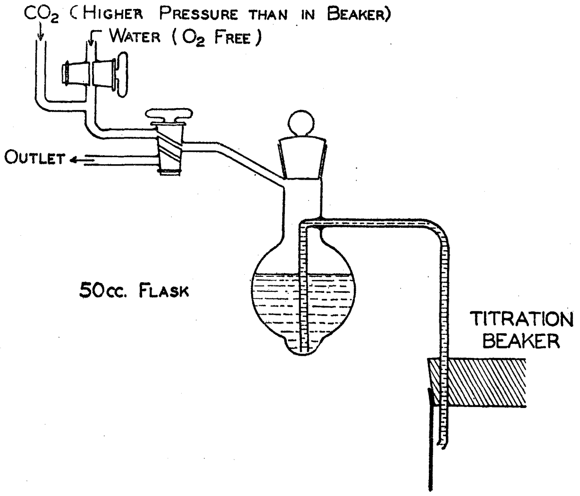

Fig. 2.—Apparatus for treating and transferring solutions.

The potential change per 0.1 cc. at the end-point was about 75 millivolts for the bromoosmate in 1 *N* hydrobromic acid, 130 millivolts in 0.1 *N* hydrobromic acid, and for the chloroosmate 80–100 millivolts in the 0.8 *N* hydrochloric acid. In column 4 are shown the values of the equivalent weights calculated from the titration data, and in the last column the percentage differences between these values and those calculated by use of Gilchrist's atomic weight of osmium. The results indicate that the acid concentration should not be below 0.1 *N* in the case of bromoosmate and 0.5 *N* in the case of chloroosmate.

At the foot of the table are shown the average deviations of the values of the equivalent weights obtained with the two salts. In spite of the fact that the percentage deviation in the values of the corresponding atomic weights of osmium is multiplied by about four in the case of bromoosmate and 2.5 in the case of chloroosmate, it is interesting to note how closely the two averages agree with that reported by Gilchrist.

TABLE I

THE DETERMINATION OF THE EQUIVALENT WEIGHTS OF POTASSIUM BROMOOSMATE AND POTASSIUM CHLOROOSMATE

Salt used	Detns.	Acid used and its concn., *N*	Average equiv. wt. by titrn.	Av. diff. between equiv. wt. found and Gilchrist's value, %
K_2OsBr_6	3	0.02–0.05 HBr	752.7	+0.45
K_2OsBr_6	8	0.13–0.25 HBr	749.1	− .03
K_2OsBr_6	2	0.60–0.95 HBr	749.8	+ .07
K_2OsCl_6	4	0.10–0.40 HCl	484.4	+ .39
K_2OsCl_6	8	0.50–0.80 HCl	482.6	+ .02

Average deviation last 10 results with K_2OsBr_6 = 0.10%
Average deviation last 8 results with K_2OsCl_6 = 0.10%
Average atomic weight of osmium by K_2OsBr_6 = 191.5
Average atomic weight of osmium by K_2OsCl_6 = 191.7
Gilchrist's value of atomic weight of osmium = 191.55

Since considerable difficulty due to hydrolysis was experienced when solutions of the osmium salts were heated to remove the last traces of oxygen, several solutions of the bromoosmate were treated in the apparatus shown in Fig. 2, and titrated in the same manner as the dichromate solutions. It was found that the concentration of the hydrobromic acid in the flask during boiling could be as low as 2 *N* without decomposition of the osmium salt taking place. Six 20.00-cc. portions of bromoosmate ranging in normality from 0.01333 to 0.01335 were titrated with 0.01187 *N* chromous sulfate and the maximum difference between the titrated value of the normality and that based on the amount of salt in the solution was less than 0.2%.

Summary

Apparatus and procedure are described for storing and handling chromous sulfate solutions, for standardizing these solutions with potassium ferricyanide and potassium dichromate, and for determining the osmium in potassium bromoosmate and potassium chloroosmate by potentiometric titration.

Solutions stored as described remained constant in titer for a month. Standardizations of chromous sulfate by the two methods agreed within 0.1% and the error in the osmium determinations was less than 0.2%.

LOS ANGELES, CALIF. RECEIVED SEPTEMBER 27, 1935

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

The Preparation of Potassium Molybdo- and Molybdicyanides[1]

BY HOBART H. WILLARD AND R. C. THIELKE

In attempting to prepare potassium molybdocyanide, $K_4Mo(CN)_8 \cdot 2H_2O$, the methods previously used were found to give very poor yields. This investigation was undertaken to find a more satisfactory method for preparing this compound. The methods of Rosenheim and co-workers,[2] Chilesotti,[3] later used by Bucknall and Wardlaw,[4] were found to be unsatisfactory. The method of Jakob and Turbiewicz[5] was not tried because it seemed to offer difficulties. Sand and Burger[6] reported that ammonium thiocyanate and molybdate when dissolved in dilute hydrochloric acid and reduced electrolytically gave a product which could be extracted by ether and which was precipitated by pyridine from the dry ethereal solution. The oil after separation from ether solidified to a dark solid which melted at 189°. This reaction was modified to prepare potassium molybdocyanide.

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(1) From a dissertation by R. C. Thielke presented to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1935.

(2) Rosenheim and Koss, *Z. anorg. Chem.*, **49**, 148 (1906); Rosenheim, *ibid.*, **54**, 97 (1907).

(3) Chilesotti, *Gazz. chim. ital.*, **34**, ii, 493 (1904).

(4) Bucknall and Wardlaw, *J. Chem. Soc.*, 2981 (1927).

(5) Jakob and Turbiewicz, *Roczniki Chem.*, **11**, 569 (1931).

(6) Sand and Burger, *Ber.*, **38**, 3384 (1905).

Experimental

Preliminary experiments showed that molybdic oxide dissolved in 8 *N* hydrochloric acid was not completely reduced by shaking with mercury for several hours. However, the octocyanide could be obtained with a 50% yield from the reduced molybdenum solution by following a procedure similar to that of Sand and Burger.[6]

Electrolytic reduction was finally adopted as the most convenient and rapid method. The cathode consisted of a hollow lead tube 0.5 cm. in diameter and of 126 ml. capacity. A graphite rod in a porous cup served as the anode. The anolyte was a 15% hydrochloric acid solution. A current of 5–10 amperes was used and the cathode was water cooled. Ten per cent. solutions of molybdic oxide in 8 *N* hydrochloric acid were used for most of the reductions. Carbon dioxide was bubbled through the solution to maintain an inert atmosphere. It was found that when trivalent molybdenum chloride was added to thiocyanate a green solution was produced instead of the characteristic blood-red thiocyanate complex, and that none of the molybdenum complex was extracted by ether. When the reduction was stopped at an apparent valence of four, as found by removing samples from time to time and titrating with permanganate, the blood-red complex was obtained when the molybdenum chloride was added to thiocyanate, and two-thirds of it could be extracted by ether. If a sample was completely reduced to the trivalent form, treated with the theoretical quantity of molybdic oxide to oxidize the molybdenum to the quadrivalent state, then treated with thiocyanate and extracted with ether, it was found that roughly one-tenth of the complex was extracted. These experiments explain the low yields obtained in the preparation of the octocyanide when this procedure was used with trivalent or quadrivalent molybdenum.

Preliminary experiments showed that a pyridine molybdenum thiocyanate complex could be precipitated from the thiocyanate solution by making it slightly alkaline with ammonia after the addition of pyridine. With trivalent molybdenum the aqueous solution contained about two-thirds of the molybdenum. The pyridine complex could not be successfully converted into the octocyanide. Quadrivalent molybdenum, however, was nearly quantitatively precipitated. A representative run contained only 0.03 g. of Mo in the aqueous solution. With this as a basis many experiments were performed to determine the best procedure for converting the complex to the octocyanide, separation of the complex cyanide from the reaction products and the final purification of the compound.

The following procedure has been found to be best and gives a 70–75% yield of potassium molybdocyanide based on the molybdic oxide used. Fifteen grams of pure molybdic oxide or an equivalent amount of the 85% material is dissolved in 150 ml. of warm 8 *N* hydrochloric acid. The solution is electrolytically reduced to trivalent molybdenum in the apparatus described and is then treated with 7.5 g. of molybdic oxide dissolved in 75 ml. of 8 *N* hydrochloric acid. The green solution assumes a reddish color at this stage. The mixture is added to a concentrated solution of 95 g. of ammonium thiocyanate. Sixty grams of pyridine is added and the solution is then made slightly alkaline with ammonia. These operations are best carried out in the absence of oxygen. Saturating the solutions with carbon dioxide has been found to work very well. A black oil is formed during the neutralization. After cooling in ice the black tar is separated from the aqueous solution by decantation and washed. The black tar is added slowly to a hot saturated solution of ten molecular proportions of potassium cyanide. The reaction mixture is concentrated until crystallization starts, is cooled in ice and filtered. The mother liquor is further concentrated and the double cyanide precipitated by adding alcohol with rapid swirling. The impure product is dissolved in a little water, heated with charcoal, filtered, concentrated and again precipitated with alcohol. The golden yellow crystals are then quite pure but still contain traces of thiocyanate. This may be removed by another crystallization. The yield of $K_4Mo(CN)_8 \cdot 2H_2O$ is about 55 g.

It was noticed that in some cases the crystals of the octocyanide were golden yellow and in other cases they were a bright yellow. Analyses of both showed them to be identical. Both were titrated to molybdicyanide with standard permanganate with the following result.

Yellow, % Mo	19.51	
Golden yellow, % Mo	19.56	Calcd. 19.35

A sample of each was decomposed with concentrated sulfuric acid by evaporation to fumes, diluted, reduced to the trivalent sulfate in a Jones reductor and titrated with standard permanganate.

Yellow, % Mo	19.51
Golden yellow, % Mo	19.97

Preparation of Potassium Molybdicyanide

The method given in the literature for the preparation of potassium molybdicyanide, $K_3Mo(CN)_8$, is very troublesome. It consists in oxidizing the molybdocyanide in acid solution with permanganate, precipitating in the dark gelatinous silver molybdicyanide and converting this into the potassium salt by treatment with potassium chloride. It is extremely difficult to obtain a pure solution because of the instability of the silver salt.

A quantitative yield of potassium molybdicyanide in solution is obtained by the following procedure. The molybdocyanide is oxidized in a slightly acid solution with permanganate until the purple tint is faintly perceptible, then two-thirds of an equivalent amount of permanganate is added in excess. Upon making the solution slightly alkaline with potassium hydroxide, the excess permanganate oxidizes the manganous ion and is itself reduced to manganese dioxide which is removed by filtration through asbestos. In order to make the resulting molybdicyanide solution more stable, it should again be slightly acidified. Even then, however, the solution is quite unstable. A solution which was prepared by the above method, stored in a brown bottle and kept from strong light was found to be decomposed to the extent of 20% after ten days. The preparation of the crystalline salt was not attempted.

Summary

1. Quantitative studies showed that the trivalent and quadrivalent molybdenum thiocyanate

complexes were only partially extracted by ether, resulting in a poor yield of molybdocyanide.

2. A quadrivalent molybdenum pyridine thiocyanate is almost completely precipitated in ammoniacal solution. By treatment of this with potassium cyanide a 70–75% yield of $K_4Mo(CN)_8 \cdot 2H_2O$ was obtained.

3. Quantitative yields of potassium molybdicyanide in solution were obtained by oxidizing potassium molybdocyanide with permanganate in acid solution and removing the manganese by oxidation to dioxide with permanganate after making the solution alkaline.

ANN ARBOR, MICHIGAN RECEIVED SEPTEMBER 28, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

Studies on Hydrazine: Heats of Solution of Hydrazonium Salts at 25°. II

BY E. C. GILBERT AND V. C. BUSHNELL

The heat of solution of a number of hydrazonium salts has recently been reported from this Laboratory.[1] To complete the series the heats of solution of hydrazonium dibromide (anhydrous), hydrazonium sulfate, and hydrazonium dibromide (hydrated) have now been determined. That of the sulfate has also been determined by Bach[2] at a lower temperature.

Experimental

Apparatus.—The calorimeter was the same as previously used and the procedure was unchanged. It was again checked by measuring the heat of solution of sodium chloride.

Materials.—The salts were prepared from the free base and acids and purified by repeated crystallization. The anhydrous bromide was prepared from the hydrate by drying over phosphorus pentoxide. The preparation of the hydrate with exactly two molecules of water is somewhat difficult. It is very soluble in water and addition of nonaqueous solvents like alcohol removes one equivalent of acid, precipitating the monobromide. This peculiarity likewise precludes washing the crystals with anything but water. Forced drying practically always results in a slight loss either of water or hydrobromic acid. The samples used were analyzed both for hydrazine and for bromide. The preparation of the hydrated bromide used indicated by such analysis the presence of 0.2% of the monobromide. Samples of different origin were used in different runs and the heat quantities showed good agreement among themselves.

Results and Calculations

The results are shown in Table I. Specific heats for the bromide solutions were taken from the work of Cobb and Gilbert.[3] The specific heat of solutions of the sulfate is not found in the literature, hence it has been determined over a limited concentration range by the same method (3) and is given in Table II. From the values of the total molal heat of solution ΔH in Column 4 of Table I,

TABLE I

HEATS OF SOLUTION AT 25° (IN 15° CAL.)

The molality of the dibromide is expressed in every case as moles of anhydrous salt in 1000 g. of water in the resulting solution.

Molality Initial m_1	Final m_2	Heat absorbed per mole of salt dissolved	Total molal heat of solution m_2
	Hydrazonium Sulfate		
0.00	0.0576	8132	8132
.00	.0579	8134	8134
.00	.0567	8171	8171
	Hydrazonium Dibromide Dihydrate		
0.00	0.1327	11106	11106
.00	.1322	11130	11130
	Hydrazonium Dibromide, Anhydrous		
0.00	0.1314	4862	4862
.00	.1326	4866	4866
.00	.1874	4840	4840
.1314	.2455	4718	4794
.1874	.2768	4686	4790
.1326	.3181	4671	4755
.2455	.4566	4493	4655
.3181	.5111	4336	4600
.4556	.6641	4164	4502
.6641	.8387	3882	4372

TABLE II

SPECIFIC HEAT OF AQUEOUS HYDRAZONIUM SULFATE AT 25°

Molality	Sp. ht. in 15° cal. per g.
0.00	0.9979
.0476	.9930
.0795	.9889
.0856	.9891
.1058	.9852

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[1] Gilbert and Cobb, THIS JOURNAL, **57**, 39 (1935).

[2] R. Bach, *Z. physik. Chem.*, **9**, 241 (1892).

[3] Cobb and Gilbert, THIS JOURNAL, **57**, 35 (1935).

the partial molal heat of solution of the solute and the relative partial molal heat content of the solvent were computed for the bromide solutions by the methods of the previous paper.[1] They are shown in Table III.

TABLE III

PARTIAL MOLAL HEATS OF SOLUTION OF SOLVENT AND SOLUTE AT 25° IN 15° CAL.

Molality	$\overline{H}_2 - H_2(s)$	$\overline{H}_1 - \overline{H}_1^0$
	Hydrazonium Dibromide	
0.1	4849	0.0427
.2	4712	.4268
.3	4571	1.059
.5	4265	3.216
.8	3870	7.739

Discussion

The low solubility of the sulfate limited this study to small concentrations. The most disturbing aspect of the problem, however, was the extreme slowness with which this salt dissolved even at concentrations considerably removed from saturation. The runs on the sulfate took from ninety to one hundred twenty minutes for completion. This resulted in a relatively large correction for heat of stirring, and required the use of small samples (5 g.) with attendant small temperature effects. For this reason the probable error in the heat of solution of the sulfate is larger than for any other salt in the series investigated.

Examination of the results obtained for the two series of chlorides and bromides (from this and the previous paper[1]), in which hydrazine functions, respectively, as a mono- and di-acid base, and comparison with other salts reveals some interesting correlations. In Table IV have been collected the differences in the molal integral heats of solution for a number of chlorides and bromides of the alkali and alkaline earth groups.[4] Inspection of this table of rounded values shows that salts of the monovalent hydrazonium ion $N_2H_5^+$ exhibit a behavior analogous to those of potassium, ammonium, rubidium and cesium, in that the bromide absorbs *more* heat than the chloride. In the hydrazonium salts containing two equivalents of acid, however, the bromide absorbs *less* heat than the chloride, a behavior similar to that of lithium, sodium, barium, strontium, and other hydrated cations. This difference in heat of solution, however, may be almost quantitatively accounted for by the difference in the heats of solution of the additional mole of halogen acid. The further similarity of the hydrated hydrazonium dibromide to the other bromides shown in the table is not so easily explained, but re-emphasizes[5] the similarity of the behavior of hydrazonium and sodium salts.

TABLE IV

COMPARISON OF MOLAL INTEGRAL HEATS OF SOLUTION: BROMIDES AND CHLORIDES OF THE ALKALI AND ALKALINE EARTH GROUPS, AND HYDRAZINE

Data for Li, Rb and Cs are given for 15°; Na, Ba, Sr, K and NH_4, 18°; hydrazine salts, 25°. Concentration in all cases except NH_4 is *ca.* 1 mole of salt to 400 or more moles of water; for NH_4, 1 to 200.

Element	$\Delta H(Br^-) - \Delta H(Cl^-)$	$\Delta H(Br^- \cdot 2H_2O) - \Delta H(Br^-$ Anhyd.)
Li	−2900	(*ca.*) +12000
Na	−1100	+ 4900
Ba	−2900	+ 9160
Sr	−4880	+ 9825
$N_2H_6^{++}$	−1164	+ 6250
K	+ 680	
NH_4^+	+ 550	
Rb	+1500	
Cs	+2000	
$N_2H_5^+$	+1100	

Summary

New data are reported on the heats of solution in water at 25° of hydrazonium dibromide, anhydrous and hydrated, and of hydrazonium sulfate.

The partial molal heat of solution of the solute and the solvent have been computed for the bromide.

The specific heat capacity of hydrazonium sulfate solutions at 25° has been determined.

CORVALLIS, OREGON RECEIVED AUGUST 13, 1935

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(4) "International Critical Tables," Vol. V, p. 169 ff.; Lange, "Handbook of Chemistry," 1934, pp. 1017–1024, Handbook Publishing Co., Sandusky, Ohio.

(5) Christensen and Gilbert, THIS JOURNAL, **56**, 1897 (1934).

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

Photochemical Responses of the Wheat Plant to Spectral Regions

BY E. J. LEASE AND W. E. TOTTINGHAM[1]

An earlier paper[2] reported increased absorption of nitrate by the young wheat plant when exposed to radiation from the carbon arc, as a supplement to winter sunlight. This response was later[3] obtained to the extent of 30%, with plants three weeks of age, by supplementing the mazda lamp with an arc of high amperage. Refinement of characterization for radiation of the later test gives an increase to 15-fold in radiation of the region 3100–4000 Å., by use of the arc, or to essentially 6% of the total between 3100 and 14,000 Å. In the region 4000 to 5000 Å. the increase was 270%, or to essentially 12% of the total. Apparently the value originally attributed[4] to this radiation was too high and should be revised to about 1200 f. c.

In the earlier study nitrate absorption was associated with the appearance of organic forms of nitrogen at the expense of sugar content and yield of dry matter. The present paper deals in greater detail with compositional responses of the plant to increases in proportion of the shorter rays of light.

Experimental

By the use, under water cells, of selective filters supplied by the Corning Glass Works, the spectrum emitted by the mazda lamp was altered to exclude radiation shorter than about either 3900 or 5200 Å. Space beneath was inclosed to exclude daylight. A range comparable with sunlight was obtained by use of the sunlight lamp[5] installed above a water cell of Corex D glass, and with a frosted pane of this glass to reduce the intensity of radiation. Adjustment of lamps was made to give, at the predominant leaf level, essentially equal intensities of about 1200 f. c. Forced ventilation of the plant chambers and surrounding greenhouse maintained a temperature range of essentially 17–18°. Earlier tests[6] placed these values of temperature and radiation as fairly favorable for the young wheat plant, with reference to production of dry matter. The plants were exposed nightly to a 15-hour period of irradiation, with a flow of about 1 cm. depth over the water cell.

A comparison of the forms of radiation transmitted to the plants is shown in Fig. 1, together with a distribution curve for mid-day, summer sunlight.[7] These graphs show marked deficiency of blue-violet and discontinuity of ultraviolet in our substitute for sunlight as compared with the normal. As shown in Fig. 2,[8] the cutoff of filters under the sunlight lamp conformed closely to the lower limit of sunlight. The total effective radiation was measured by a thermopile supplied for the purpose by the Eppley Laboratory. Distribution of the radiation is given in Table I.

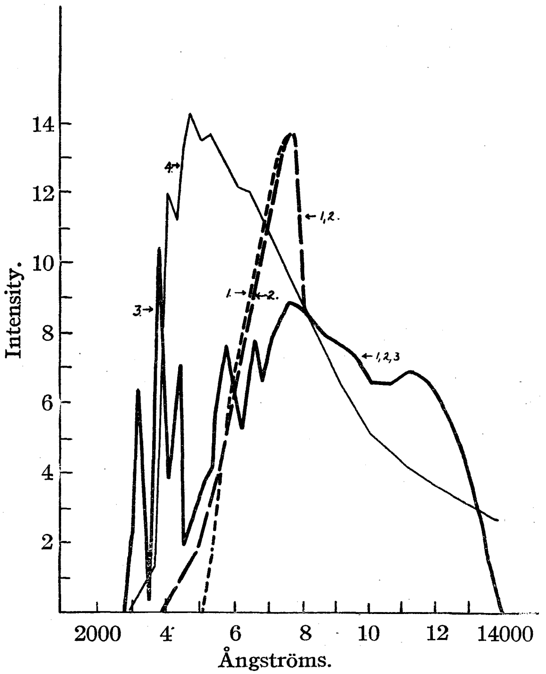

Fig. 1.—Effective radiation: 1 = No. 349 filter - - - - -; 2 = Noviol O filter —— ——; 3 = Sunlight lamp ━━━; 4 = Unfiltered sunlight ——.

Irradiation was continued daily for three weeks

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[1] With collaboration from E. R. Frank, who evaluated the radiation. Published with permission of the director of the Wisconsin Agricultural Experiment Station. Supported by grants from the Division of Biology and Agriculture, National Research Council.

[2] Tottingham and Lowsma, THIS JOURNAL, **50**, 2436 (1928).

[3] Tottingham, Stephens and Lease, *Plant Physiol*, **9**, 127 (1934).

[4] Ref. 3, p. 130.

[5] Luckiesh, "Artificial Sunlight," D. Van Nostrand Co., New York, 1930, p. 216. We are indebted to the General Electric Company for a loan of such lamps. The Corex glass was donated by the Corning Glass Works.

[6] Tottingham, *Plant Physiol.*, **1**, 328 (1926).

[7] Abbot and Fowle, *Ann. Astrophy. Obsv.*, **2**, Pl. XVI, Curve 11 (1908); Ref. 5, Tab. VI.

[8] Prepared by Dr. R. W. Haman with the use of a Hilger Type E37 quartz spectrograph and Kipp microphotometer.

TABLE I

TOTAL ENERGIES INCIDENT ON PLANTS AND PERCENTAGE DISTRIBUTION THEREOF

Source of radiation microw. per sq. cm.	1000 W. mazda lamp over Corning glass No. 349 and plain glass water cell	500 W. mazda lamp over Corning glass noviol 0 and plain glass water cell	Type S1 sunlight lamp over frosted Corex glass and Corex water cell
Spectral regions, Å.	20,540	20,900	20,900
3100- 4000	0	0.2	5.6
4000- 4500	0	.7	3.6
4500- 5000	0	2.3	2.2
5000- 5500	1.0	3.5	3.4
5500- 6000	4.6	5.0	5.4
6000- 6500	6.6	6.0	4.9
6500- 7000	8.1	7.9	5.8
7000- 7600	11.0	10.9	8.1
7600-14000	68.7	63.5	61.0

from the seedling phase. For proximate analysis the harvested tops were killed at 98° and dried at 55° with ventilation. In the determination of constituents likely to be unstable tissue was analyzed from the fresh state.

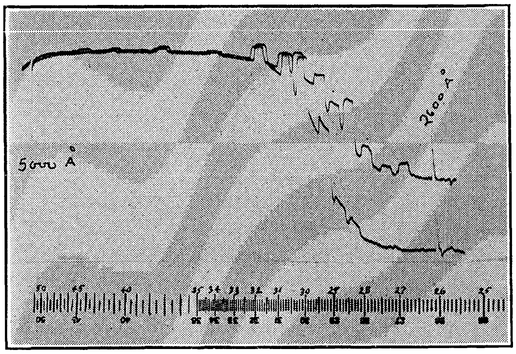

Fig. 2.—Radiation curves of the naked sunlight lamp (upper) and with Corex D water cell and frosted plate interposed (lower).

Tissue Composition.—Proximate analyses of three crops in each case, by standard[9] procedure, gave the average data presented in Tables II and III.

TABLE II

COMPOSITION OF WHEAT TOPS PRODUCED IN WATER CULTURE

Minimal radiation effective, Å.	Dry matter, g.	Ash, %	Crude fiber, %	Crude fat, %	Crude protein, %	Nitrogen-free extract, %
2900	14.4	21.7	16.9	5.9	30.7	24.8
3900	22.9	21.6	19.3	5.3	27.6	26.2
5200	27.2	21.5	19.5	5.3	26.4	27.3

TABLE III

COMPOSITION OF WHEAT TOPS PRODUCED IN SOIL CULTURE

Minimal radiation effective, Å.	Ash, %	Crude fiber, %	Crude fat, %	True protein, %	Nitrogen-free extract, %
2900	20.4	16.7	5.6	24.9	31.9
3900	19.8	19.1	4.2	23.8	33.1
5200	20.0	19.6	4.1	22.0	34.2

The decline of yield with exposure to shorter wave lengths of light was anticipated from differences in stem diameter, and especially from the stunted form, of plants under the sunlight lamp. There was no external evidence of injury in the latter case but the tissue was characterized by a sharp increase of lipide content and a prominent decline in the percentage of crude fiber. Had this response of lipides depended upon the "wax" content of an increased proportion of plant surface it should have been much greater. The more available carbohydrates, as represented by the nitrogen-free extract, decreased relatively uniformly with extension of spectral exposure. Protein shows the opposite response, for evidence in Table II indicates that the sharp maximum of crude protein in Table I was probably affected by non-protein nitrogen. Irradiation was without effect upon the proportion of mineral elements in the tissue.

As suggested by the preceding results, the following determinations were selected. Pentosans were determined by the method of McCance[10] on samples prepared by extraction with acetone, ether and hot 80% alcohol. Uronic anhydrides were determined by the procedure of Dickson, Otterson and Link[11] on the extract obtained by boiling with 2.0% hydrochloric acid for two and one-half hours, after extraction of the tissue by ether and water. The first of these constituents was determined on two crops, the second on one. Nitrate and nitrite were determined on fresh tissue by colorimetric procedure,[12] data for the former representing six crops and the latter three. The results appear in Table IV.

TABLE IV

SELECTED DETERMINATIONS ON WHEAT TOPS OF PERCENTAGES IN DRY MATTER

Minimal radiation effective, Å.	Xylan	Uronic anhydride	NO_3	NO_3 (× 1000)
2900	6.9	5.0	1.9	1.3
3900	8.2	4.4	2.2	1.1
5200	9.3	4.0	2.3	1.0

Correlation appears between exposure to ultraviolet and the reduction of nitrate to nitrite. De-

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(9) Assoc. Offic. Agric. Chem., "Official and Tentative Methods of Analysis," 3d ed., Washington, D. C., 1930.

(10) McCance, *Biochem. J.*, **20**, 1111 (1926).

(11) Dickson, Otterson and Link, THIS JOURNAL, **52**, 775 (1930).

(12) (a) Holtz and Larson, *Plant Physiol.*, **4**, 288 (1929); (b) Ref. 9, p. 405.

creases of pentosans and increases of uronic acids are about proportional to the introduction of blue-violet, as shown in Table I, but this does not exclude possible functioning of ultraviolet. Supplementary to the present evidence, we found in another investigation a 20% increase of uronic acid in the wheat stem at prebloom in association with a heavy application of nitrate to the soil. In the present relation this constituent appears to arise as a product of oxidation associated with the reduction of nitrate. It might be expected that ascorbic acid should increase in parallel with uronic acid, but limited titrimetric data obtained by the method of Birch, Harris and Ray[13] indicated very small amounts of this constituent. This situation can be understood on the basis of the observation of Karrer and Bendas[14] that the former constituent reduces nitrite. The results for xylan indicate that the path by which pentosans are formed, commonly supposed to involve decarboxylation of uronic acids, is partially diverted by extensive absorption of nitrates. Press sap from three crops was examined for content of reducing sugars by the Shaffer–Hartman method and for hydrogen ion concentration by use of the quinhydrone electrode. The data, as shown in Table V, are in agreement with those just discussed as indicating increased oxidation of sugars to acids under the influence of shorter visible and longer ultraviolet radiation.

TABLE V

COMPOSITION OF PRESS SAP FROM WHEAT PLANTS THREE WEEKS OLD

Minimal effective radiation, Å.	2900	3900	5200
Reducing sugars, %	2.0	3.2	3.8
*p*H	4.9	5.2	5.4

A search was made for constituents which might serve as trigger mechanisms in the above effects. Several enzyme forms which function in oxidation–reduction relations were inappreciably affected as to activity by the differences in radiation, but it was not feasible to examine dehydrogenases. Three crops of wheat reared under minimal radiation of 2900, 3900 and 5200 Å. gave by titration with potassium iodate according to the procedure of Okuda and Ogawa[15] relative proportions in glutathione of 100, 91 and 68, respectively. Similar results were obtained for the sulfhydryl group in tomato leaves irradiated for three hours daily by the sunlight lamp as a supplement to July sunlight under glass. Six samples showed an increase of about 100% by this exposure as compared with supplementary use of the mazda lamp as a control. In this case the method of Guthrie[16] was applied, excepting that the alcoholic extract was inactive and the whole tissue was exposed to reaction with colloidal sulfur. In view of the absorptive capacity of cystine for both blue-violet and ultraviolet light, as observed by Ward,[17] it is suggestive to find here a reduction product of that form of sulfur. Szent-Gyorgyi[18] has shown that glutathione reduces hexuronic acids, a relation which might confer upon sulfhydryl compounds in the present instance significance in the utilization of sugars for nitrate assimilation under shorter rays of light.

Some attention was devoted to the leaf pigments. Six samples gave the average data of Table VI, by colorimetric procedure.

TABLE VI

PERCENTAGES OF PIGMENTS IN LEAF DRY MATTER OF WHEAT PLANTS 25 DAYS OLD

Minimal effective radiation, Å.	Chlorophylls	Carotenes	Xanthophylls
2900	0.74	0.10	0.19
5200	.61	.09	.18

The lesser content of chlorophylls where shorter radiations were excluded could be anticipated by color differences of the leaves. It agrees with previous observations[19] of ineffectiveness of red and infra-red rays in synthesis of these pigments. This increase of pigment in plants receiving the more complete spectrum may be highly significant in relation to increased nitrate assimilation. Substantial physiological information indicates that it could function through stimulating respiration,[20] the latter process in turn providing for reduction of nitrate.[21]

Large-scale lipide preparations were recovered by ether from plants exposed to April sunlight under glass, supplemented by the use of either mazda or sunlight lamps. These were found to have the same proportion and character of wax fraction under the differences of radiation. Fatty acids recovered from the non-waxy fraction were

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(13) Birch, Harris and Ray, *Biochem. J.*, **27**, 590 (1933).

(14) Karrer and Bendas, *Helv. Chim. Acta*, **17**, 743 (1934).

(15) Okuda and Ogawa, *J. Biochem.*, **18**, 75 (1933).

(16) Guthrie, *Contrib. Boyce Thomp. Inst.*, **4**, 99 (1932).

(17) Ward, *Biochem. J.*, **17**, 898 (1923).

(18) Szent-Gyorgyi, *ibid.*, **22**, 1399 (1929).

(19) Sayre, *Plant Physiol.*, **3**, 71 (1928); Johnston, Smithson, *Misc. Coll.*, **87**, No. 14 (1932).

(20) Spoehr and McGee, Carnegie Inst. Wash., Pub. 325, 76 (1923).

(21) Warburg and Negelein, *Biochem. Z.*, **110**, 66 (1920).

somewhat less saturated under the sunlight lamp than under the mazda, with iodine numbers of 106.6 and 103.9, respectively. Sterols were recovered as digitonides to the extent of 37 and 34 mg. per 100 mg. of dry tissue in these respective samples. These data supply limited evidence of increased dehydrogenation under the higher proportion of short-wave radiation.

Summary

Elimination of wave lengths shorter than about 3900 or 5200 Å. from radiation resembling sunlight decreased the assimilation of nitrate and conserved carbohydrates in young wheat plants. The primary factors to which increased reducing power under shorter radiation could be attributed were increased tissue contents of chlorophylls and sulfhydryl compounds. Paths are indicated by way of which these factors could function as trigger mechanisms in the reduction of nitrate. Depression of pentosan formation was associated with increased assimilation of nitrate. Most of the compositional effects in the tissue could be attributed to variations in the proportion of blue-violet light, but the reduction of nitrate to nitrite was more distinctly associated with long ultraviolet radiation. Apparently the high proportion in sunlight of radiation from 3900 to 4920 Å. and the low proportion above 8000 Å., in comparison with the light sources here tested, favor the assimilation of nitrate by plants.

MADISON, WISCONSIN RECEIVED JULY 15, 1935

[CONTRIBUTION FROM THE DIVISION OF INSECTICIDE INVESTIGATIONS, BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, U. S. DEPARTMENT OF AGRICULTURE]

The Dimorphism of Rotenone

BY ERNEST L. GOODEN AND CHARLES M. SMITH

The fact that rotenone occurs in two forms characterized by melting points of 163° and about 180° was briefly referred to by Butenandt and Hildebrandt[1] and later considered more fully by Cahn.[2] This phenomenon has also been studied in the Insecticide Division and, since certain characteristics of the two materials not previously recorded have been determined, the results of this study are given here.

No attempt has been made to confirm the statement of Butenandt and Hildebrandt that the higher melting form of rotenone can be prepared from the ordinary form by grinding, but the transition during melting-point determinations and the melting and resolidification of rotenone that was rapidly heated to a temperature between the two melting points have been observed. Neither of these two methods of preparation gives a product suitable for microscopical study, but the higher melting material can be prepared easily in well-crystallized form by the process given in the following section.

Preparation of Materials

The sample of low-melting rotenone was obtained from cubé root, being crystallized once from carbon tetrachloride as the solvate, and then twice from a 1:1 mixture of acetone and water as rotenone itself.

The high-melting rotenone was prepared from this sample by immersing it in a petroleum oil less volatile than kerosene and heating to 140–150°. The mixture was maintained in this temperature range, with frequent stirring, at least until examination with a polarizing microscope showed apparently complete transformation of the original thin six-sided plates to chunky, granular crystals.[3] The petroleum oil was decanted, and the crystals were washed by decantation with petroleum ether and dried at room temperature. Four batches were prepared in this manner, with different periods of heating, lasting from one to five hours. None of the batches was pure white, as it is presumed they should have been, but the one heated least was the best looking preparation and was considered most nearly pure.

That this material was not a solvate was proved by microanalysis[4] and a determination of the opti-

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[1] Butenandt and Hildebrandt, *Ann.*, **477**, 245 (1930).

[2] Cahn, *J. Chem. Soc.*, 1129 (1934).

(3) No method of proving the completeness of the transformation was devised. The writers feel certain that it was nearly enough complete to demonstrate a difference in density if any considerable difference existed. The optical data are, of course, not affected by this uncertainty, for they were determined on individual crystals known to be of the high-melting form.

(4) The writers wish to thank Dr. J. R. Spies for determinations of carbon and hydrogen.

cal rotatory power in acetone at 20° (*i. e.*, below the transition temperature), both of which agreed within experimental limit with the values for the low-melting form.

The failure of Cahn to get crystalline high-melting rotenone by working in tetralin and in xylene at 100° was very likely due to the fact, considered later, that the transition temperature is apparently above 100°. Even if it is below this, his method would probably fail because of the very rapid retransformation which occurs in such good solvents as tetralin and xylene. For example, if a mount of high-melting rotenone is made in amyl acetate, and examined under the microscope, the transformation is seen to begin almost immediately, small crystals of the low-melting form appearing in the liquid surrounding each crystal of the high-melting form. Further, in one experiment ethyl ether was used to wash, by decantation, a lot of high-melting rotenone prepared by the method described in this paper, and the entire mass transformed before the washing could be completed. It is only the very low solubility of rotenone in petroleum fractions that accounts for the success of our method.

General Appearance

Figure 1 shows the most characteristic habit of the ordinary low-melting form, the small faces beveling two opposite edges being commonly present. Thicker crystals have at times been obtained, and these might be difficult to differentiate from those of the high-melting form by casual inspection. The crystals of the high-melting form, shown in Fig. 2, contain the same faces as those of the low-melting form, and others in addition. A comparison of the two compounds with respect to the plane angles of the faces that are parallel to the optic axial planes shows large differences, indicating a distinct difference in crystallographic axial ratios.

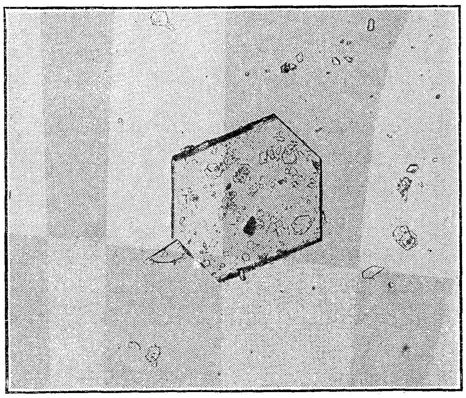

Fig. 1.—Low-melting rotenone (the common form) × 60.

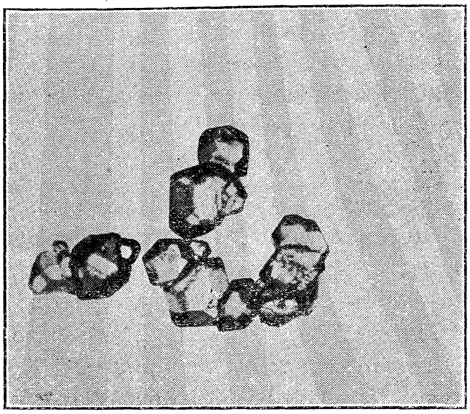

Fig. 2.—High-melting rotenone (the unstable form) × 60.

Optical Characteristics

The crystals of low-melting rotenone have symmetrical extinction and are biaxial with the axial plane parallel to the large face upon which the crystals normally lie.

The crystals thus permit the direct determination of the α- and γ-indices, which were found to be 1.616 and 1.662, respectively, in good agreement with the values given by Clark.[5] The α-index is shown when the beveled edges are parallel to the vibration direction of the polarizer. Pieces suitable for the measurement of β are difficult to obtain, but by working with thick crystals grown especially for the purpose it was possible to determine it as being 1.635. The accuracy of these figures (±0.003) is not great enough for determining the optical character, nor could this character be determined from the interference figures. From the parallelism of the optical directions and the principal crystallographic directions it is inferred that the crystals belong to the orthorhombic system.

High-melting rotenone is also biaxial with symmetrical extinction, and again many crystals lie upon a face which is parallel to the axial plane, so that, except for the greater thickness, the general aspect is similar to that of ordinary rotenone. The indices of refraction are, however, significantly different, having the following values:

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(5) Clark, *Science*, **70**, 478 (1929).

$\alpha = 1.600$, $\beta = 1.650$, $\gamma = 1.685$. The various indices are shown in the same comparative positions as with low-melting rotenone. The interference figures definitely prove the substance to be optically negative, which fact is in accord with the relative values of the indices. The optic axial angle is greater than 65°, the limit of the microscope used. From these data it appears probable that high-melting rotenone also belongs to the orthorhombic system.

Density

Density determinations on both forms of rotenone were first made by the displacement method in a pycnometer, the immersion medium being a 0.3% water solution of gelatin which improved the wetting power of the water and prevented the retention of air bubbles. The two forms were found to be indistinguishable in density within the limits of accuracy of the procedure. the value being 1.33 g. per cc. at 20°.[6]

This result was checked by suspension experiments with solutions of potassium iodide which had densities the same as and slightly different from that of the solids. No difference in behavior could be demonstrated.

Melting Point

Practically all observers agree in assigning a melting point of 163° to ordinary rotenone, and this figure was obtained on the material used in this investigation. Butenandt and Hildebrandt[1] found a melting point of 176° for the high-melting rotenone prepared by them by grinding the ordinary form, and Cahn[2] observed melting points of from 176 to 183° for material prepared by dry heating. At various times in this Laboratory values of 179 to 181° have been observed with samples of ordinary rotenone that evidently were converted during the course of the melting-point determination. Attempts to establish the melting point more definitely on the material used in this investigation failed. A series of observations conducted in a manner similar to that usually employed in this Division gave a range of 5°, with a mean of 175°. Then a series of tests was made in which the melting-point tube was plunged into a bath previously adjusted to some temperature between 170 and 180°, and in one instance prompt melting occurred at 174°. When the tubes were put into a bath previously brought to 170° (approximately) and then slowly heated, melting points of 174, 174 and 175° were obtained on three separate batches. The behavior was such, however, that we feel these values are too low, and are inclined to suspect that the samples may have contained small amounts of impurities either decomposition products formed during the heating of the rotenone or some petroleum oil dissolved or entrained in the crystals at the time of their formation.

Transition Temperature

There seems to be no doubt that the rotenone melting at 163° is the stable form at room temperature; for, as stated before, the transformation of the high-melting form into it can be watched under the microscope in a mount prepared with a good solvent such as amyl acetate. No estimate of the transition temperature has been published except the figure 125° given by Roark,[6] and that figure was based on some work by one of the writers in which portions of low-melting rotenone were immersed in white oil (a petroleum fraction) and maintained at various fixed temperatures, the occurrence of transformation being watched for by periodic microscopic examination. Transformation was plainly evident at 131°, and apparently did not take place at 120°. In the absence of definite knowledge that the white oil does not affect the transition point, it cannot be said that the true transition temperature will have the estimated value of 125°.

Summary

Rotenone exists in two enantiotropic forms, with melting points of 163° and approximately 180°, respectively.

Both forms apparently belong to the orthorhombic system and develop with similar habit except for a greater tendency of the low-melting form to appear in crystals tabular parallel to the optic plane.

The refractive indices are as follows: for low-melting rotenone, $\alpha = 1.616$, $\beta = 1.635$, $\gamma = 1.662$; for high-melting rotenone, $\alpha = 1.600$, $\beta = 1.650$, $\gamma = 1.685$. The high melting form is optically negative, the other practically without sign.

Both forms have a density of 1.33 g. per cc. at 20°.

The transition temperature has not been determined.

WASHINGTON, D. C. RECEIVED JUNE 17, 1935

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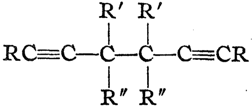
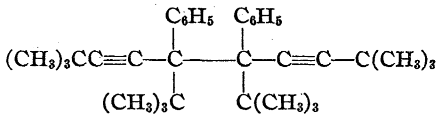
[6] Note that this is appreciably higher than the 1.27 given for low-melting rotenone by R. C. Roark [*Ind. Eng. Chem.*, **25**, 639–642 (1933)]. That figure was merely a rough approximation.

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

Rearrangements of Polyynes. VII.[1] Formation of Allenes

BY J. H. FORD, C. D. THOMPSON AND C. S. MARVEL

Previous work has shown that many hexasubstituted ethanes of the type  $RC{\equiv}C{-}C(R')(R''){-}C(R')(R''){-}C{\equiv}CR$ undergo rearrangement to produce more stable hydrocarbons of unknown structure and that the ease with which this rearrangement occurs in any given case is largely determined by the nature of R′ and R″. The aim of the present work was to obtain diphenyldi-*t*-butyldi-*t*-butylethynylethane (I)

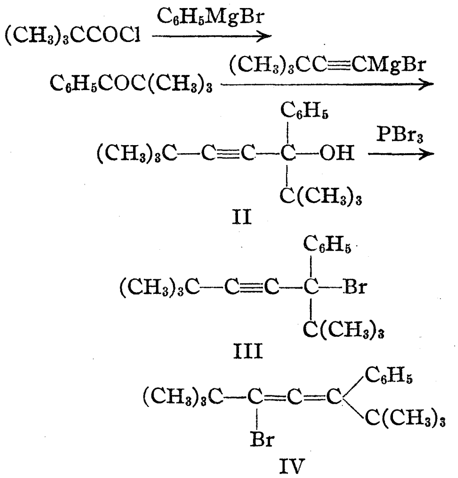


$$(CH_3)_3CC{\equiv}C{-}C(C_6H_5)(C(CH_3)_3){-}C(C_6H_5)(C(CH_3)_3){-}C{\equiv}C{-}C(CH_3)_3$$

I

in which R′ is a phenyl group and R and R″ are *t*-butyl groups. Some interesting rearrangements were observed in the reactions which were used in the synthesis of the desired ethane and these seem to offer some clues as to the nature of the rearrangements of the polyynes themselves.

Phenyl-*t*-butyl-*t*-butylethynylbromomethane (III) was synthesized by the series of reactions



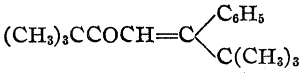
$$(CH_3)_3CCOCl \xrightarrow{C_6H_5MgBr} C_6H_5COC(CH_3)_3 \xrightarrow{(CH_3)_3CC{\equiv}CMgBr} (CH_3)_3C{-}C{\equiv}C{-}C(C_6H_5)(C(CH_3)_3){-}OH\ \text{(II)} \xrightarrow{PBr_3}$$

$$(CH_3)_3C{-}C{\equiv}C{-}C(C_6H_5)(C(CH_3)_3){-}Br\ \text{(III)}$$

$$(CH_3)_3C{-}C(Br){=}C{=}C(C_6H_5)(C(CH_3)_3)\ \text{(IV)}$$

IV

The carbinol (II) did not react readily with phosphorus trichloride to give an organic chloride but the bromide (III) was formed without difficulty. The bromide had an abnormally high molecular refraction and the bromine was not easily removed by silver, which suggested that possibly the compound did not have the acetylenic structure but was a rearranged allenic bromide of structure IV. However, structure III was established for the bromide by hydrolysis with moist silver oxide to give the carbinol (II). The



$$(CH_3)_3CCOCH{=}C(C_6H_5)(C(CH_3)_3)$$

carbinol structure was checked by converting it to the unsaturated ketone by the action of sulfuric acid in acetic acid.[2]

The bromide (III) did not couple to yield a hydrocarbon when it was treated with silver or copper. The carbinol (II) did not reduce to give a coupled hydrocarbon when it was treated with titanous chloride solution. The bromide did react with magnesium in dry ether to give about an 80% yield of the Grignard reagent and 10–15% of a mixture of hydrocarbons which had the molecular formula $C_{34}H_{46}$ corresponding to the desired ethane (I). When this Grignard reagent was treated with water, carbon dioxide or methyl chlorocarbonate the resulting product in each case was an allene derivative. The structures of the products were established by ozonization. The product of the action of water on the Grignard reagent was 2,2,6,6-tetramethyl-3-phenyl-3,4-heptadiene (V) as was shown by the fact that on ozonization and oxidative hydrolysis of the ozonide, it yielded trimethylacetic acid and phenyl *t*-butyl ketone. That the phenyl *t*-butyl ketone was not a secondary oxidation product of phenyl-*t*-butylacetic acid was established by synthesizing this acid and showing that it did not oxidize to phenyl *t*-butyl ketone under the conditions used in oxidizing the allene (V). The structure of the 2,2,6,6-tetramethyl-3-phenyl-5-carbomethoxy-3,4-heptadiene (VII) was established by the fact that it yielded methyl trimethylpyruvate $(CH_3)_3CCOCO_2CH_3$ on ozonization. The structure of the acid (VI) follows from the fact that it has been obtained by hydrolysis of the ester (VII).

The formation of an allenic hydrocarbon (IX) by the action of water on diphenyl-*t*-butylethynylmethyl sodium[3] (VIII) has been observed before. It is of some interest to note that 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene (IX) readily dimerizes

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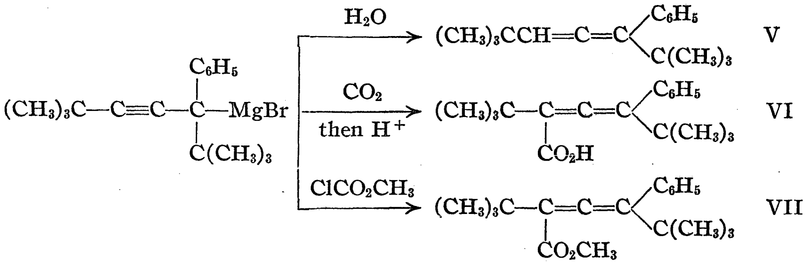
[1] For the sixth paper see Tsao and Marvel, THIS JOURNAL, **55**, 4709 (1933).

[2] Meyer and Schuster, *Ber.*, **55**, 819 (1922).

[3] Stampfli and Marvel, THIS JOURNAL, **53**, 4057 (1931).

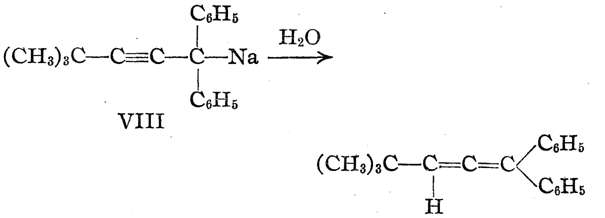


V

VI

VII

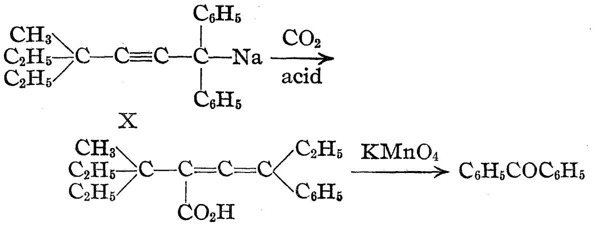
whereas 2,2,6,6-tetramethyl-3-phenyl-3,4-heptadiene (V) does not. Apparently the addition reactions of the allene group are blocked by the two *t*-butyl groups in this latter molecule.



VIII

IX

Many acids and esters[4] have been prepared in this Laboratory by the action of carbon dioxide or methylchlorocarbonate on metallic derivatives of the type $R-C\equiv C-\overset{R'}{\underset{R'}{C}}-\text{metal}$ and these have been assumed to be the acetylenic acids $R-C\equiv C-\overset{R'}{\underset{R'}{C}}-COOH$. The present work leads us to believe that all of these compounds may also be allene derivatives of the type $R-\underset{COOH}{C}=C=\overset{R'}{\underset{R'}{C}}$. In fact Harmon and Marvel[4g] did observe that the acid (XI) obtained by the action of carbon dioxide on diphenyl-(3-methyl-3-ethylpentynyl-1)-methyl sodium (X) yielded benzophenone

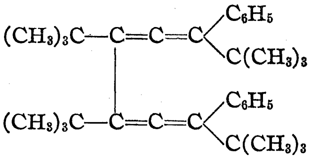


X

XI

on oxidation with neutral permanganate. Benzophenone would be expected from an acid of structure XI, whereas an acid of acetylenic structure would be expected to give diphenylmalonic acid or, by loss of carbon dioxide, diphenylacetic acid.

Since the bromide (III) was inert toward silver and copper, an attempt was made to convert it to the sodium derivative in order to obtain the ethane (I) by the method of Ziegler and Schnell.[5] It was found that 40% sodium amalgam in ether converted the bromide into a mixture of hydrocarbons and that no sodium derivative could be demonstrated to be present. One hydrocarbon which was isolated from the reaction mixture was the allene (V) which had been obtained by the action of water on the Grignard reagent prepared from the bromide. This allene must have been produced by the formation of some of the desired sodium derivative which then reacted with the ether present to give the allene.[6] In addition to the simple allene, the same mixture of coupled hydrocarbons of the formula $C_{34}H_{46}$ which was formed as a side reaction in the formation of the Grignard reagent, was isolated from the reaction of the bromide and sodium amalgam. Apparently there were two isomeric hydrocarbons in this mixture. One, the less soluble, was isolated in a pure condition but the other, more soluble one, was never completely freed from the less soluble isomer. We believe these two hydrocarbons are stereoisomers of each other but whether they represent the meso and racemic forms of the acetylenic ethane (I) or of a rearrangement product which by analogy to the other derivative obtained from the Grignard reagent would be the diallene (XII) cannot as yet be said. The fact



XII

that this mixture of hydrocarbons is formed by the action of sodium amalgam on the bromide and that the hydrocarbons are therefore not cleaved by this reagent seems to be evidence in favor of the diallenic structure.

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[4] (a) Salzberg and Marvel, This Journal, **50**, 1737 (1928); (b) Rossander and Marvel, *ibid.*, **51**, 932 (1929); (c) Gillespie and Marvel, *ibid.*, **52**, 3368 (1930); (d) Davis and Marvel, *ibid.*, **53**, 3840 (1931); (e) Stampfli and Marvel, *ibid.*, **53**, 4057 (1931); (f) Munro and Marvel, *ibid.*, **54**, 4445 (1932); (g) Harmon and Marvel, *ibid.*, **55**, 1716 (1933).

[5] Ziegler and Schnell, *Ann.*, **437**, 227 (1924).

[6] Sodium alkyls have been shown to cleave ethyl ether to give the hydrocarbon which corresponds to the alkyl group. Schorigin, *Ber.*, **43**, 1931 (1910).

Experimental Part

Phenyl *t*-Butyl Ketone.—In a 2-liter three-necked flask fitted with a stirrer, separatory funnel and reflux condenser was placed a solution of 129 g. of trimethylacetyl chloride in 400 cc. of dry ether. The mixture was cooled in an ice-salt bath. A slow stream of dry nitrogen was passed over the surface of the solution to avoid oxidization and 1050 cc. of a 1.6 *N* ether solution of phenylmagnesium bromide was added from the separatory funnel during five hours. The reaction mixture was hydrolyzed with dilute acid and the ether solution was washed with sodium bicarbonate solution to remove trimethylacetic acid. On distillation the ketone boiled at 80–84° at 3 mm. The yield was 116 g. (67%), n^{20}_D 1.5102. The physical properties check those previously reported for the ketone as prepared by other methods.[7]

The 2,4-dinitrophenylhydrazone was prepared by the method of Allen[8] and after two crystallizations from 95% alcohol the yellow needles melted at 194–195°.

Anal. Calcd. for $C_{17}H_{18}O_4N_4$: N, 16.37. Found: N, 16.14.

Phenyl-*t*-butyl-*t*-butylethynylcarbinol.—A solution of 162 g. of phenyl *t*-butyl ketone in 250 cc. of dry ether was added over a period of three hours to the Grignard reagent prepared from 82 g. of *t*-butylacetylene[9] in about 700 cc. of ether. After ten hours the reaction mixture was worked up in the usual manner and the carbinol was very carefully fractionated. The yield was 200 g. (68%) of a viscous liquid, b. p. 125–128° (4 mm.); n^{20}_D 1.5025; d^{20}_4 0.9334. M_D calcd., 76.65; found, 77.27.

Anal. Calcd. for $C_{17}H_{24}O$: C, 83.54; H, 9.91. Found: C, 83.46; H, 10.09.

2,2,6,6-Tetramethyl-3-phenyl-3-heptene-5-one.—The carbinol was converted to the unsaturated ketone by heating a few grams of it in a glacial acetic acid solution containing a few drops of sulfuric acid. The ketone boiled at 96–97° (1 mm.); n^{20}_D 1.5063; d^{20}_4 0.9309; M_D, calcd., 76.67; found, 77.98. On cooling the liquid to about −40° it crystallized to a solid which melted at 30.5°.

Anal. Calcd. for $C_{17}H_{24}O$: C, 83.54; H, 9.91. Found: C, 83.70; H, 10.16.

The 2,4-dinitrophenylhydrazone was a bright orange-red solid melting at 150–151°.

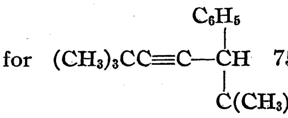
Anal. Calcd. for $C_{23}H_{24}O_4N_4$: N, 13.39. Found: N, 13.40.

Phenyl-*t*-butyl-*t*-butylethynylbromomethane.—To a solution of 30 g. of the carbinol in 150 cc. of low boiling petroleum ether was added 5.4 cc. of phosphorus tribromide. After standing overnight, a layer of phosphorous acid had separated. The upper layer was separated, washed throughly with sodium bicarbonate, dried over magnesium sulfate and distilled. The yield was 34.4 g. (91%) of a slightly yellow liquid, b. p. 115–117° (1 mm.); n^{20}_D 1.5400; d^{20}_4 1.1081; M_D calcd., 82.89; found, 86.93.

Anal. Calcd. for $C_{17}H_{23}Br$: C, 66.43; H, 7.55; Br, 26.02; mol. wt., 307.1. Found: C, 66.54; H, 7.47; Br, 25.75; 25.82; mol. wt. (Rast.), 282.

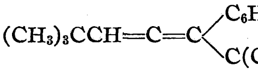
A small amount of the bromide was hydrolyzed by boiling a solution in acetone with a suspension of moist silver oxide.[10] The product was separated by distillation; b. p. 105–110° (1 mm.); n^{20}_D 1.5028; d^{20}_4 0.9332, and was identical with the carbinol from which the bromide had been prepared.

2,2,6,6-Tetramethyl-3-phenyl-3,4-heptadiene.—The Grignard reagent was prepared from 58 g. of the bromide and 5 g. of magnesium turnings in 500 cc. of ether. Iodine was used to start the reaction. The Grignard reagent was then decomposed by adding water and finally a little hydrochloric acid and ice. The ether layer was separated and distilled. After removal of the solvent, the main portion boiled at 78–80° (1 mm.). The yield of the hydrocarbon was 35 g. (82%); n^{20}_D 1.5039; d^{20}_4 0.8808; M_D calcd. for



$(CH_3)_3CC\equiv C-CH(C_6H_5)C(CH_3)_3$

75.13; calcd. for



, 76.19; found, 76.67.

Anal. Calcd. for $C_{17}H_{24}$: C, 89.40; H, 10.60; mol. wt. 228.2. Found: C, 89.26; H, 10.71; mol. wt. (Rast.), 222.

This hydrocarbon was heated to 145° in a sealed tube for about ninety hours and then vacuum distilled.[11] About 85% of the hydrocarbon was recovered unchanged and no definite products could be obtained from the residue.

The original high boiling residue which remained after distilling the allene, slowly solidified. Crystallization gave two products, one melting at 148° and one melting at 115–125°, which were identified as coupled products and will be described in more detail later.

Ozonolysis of the Allene.—A solution of 5 g. of the above allene in 100 cc. of carbon tetrachloride was cooled to −20° and ozonized oxygen was passed through the solution for about ten hours at the rate of 0.5 liter per minute. A white sticky solid separated from solution during this treatment. The reaction mixture was decomposed by adding 75 cc. of water and stirring for several hours at 25°. An excess of sodium bicarbonate solution was then added and the mixture stirred for a short time. The carbon tetrachloride solution was evaporated and the residue treated with 2,4-dinitrophenylhydrazine. The product of this reaction melted at 193–194° and proved to be the 2,4-dinitrophenylhydrazone of phenyl *t*-butyl ketone. The water layer was acidified and distilled with steam. The volatile acid was converted to the *p*-bromophenacyl ester which melted at 75–76° and proved to be identical with the *p*-bromophenacyl ester of trimethylacetic acid.[12]

Phenyl-*t*-butylacetic Acid.—Phenyl *t*-butyl ketone was reduced to the carbinol by the method of Ramart-Lucas[13] in yields of 95%, and this carbinol was converted to the bromide by the method of Lepin[14] in yields of 93%.

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[7] Haller and Bauer, *Compt. rend.*, **148**, 70 (1909): Ramart-Lucas, *Ann. chim.*, [8] **30**, 385 (1913).

[8] Allen, THIS JOURNAL, **52**, 2955 (1930).

[9] Salzberg and Marvel, *ibid.*, **50**, 1737 (1928).

[10] Conant, Small and Sloan, *ibid.*, **48**, 1756 (1926).

[11] Lebedev, *J. Russ. Phys.-Chem. Soc.*, **45**, 1357 (1913); *Chem. Zentr.*, **85**, I, 1402 (1914).

[12] Powell, THIS JOURNAL, **53**, 1172 (1931).

[13] Ramart-Lucas, *Ann. chim.*, **30**, 361 (1913).

[14] Lepin, *J. Russ. Phys.-Chem. Soc.*, **44**, 1178 (1912); *Chem. Zentr.*, **83**, II, 2081 (1912).

The Grignard reagent, prepared from 10 g. of this bromide and 1.2 g. of magnesium in 100 cc. of dry ether, was treated with carbon dioxide and the organic acid isolated in the usual manner. The yield was 1.1 g. (13%) of a product m. p. 105° after two crystallizations from dilute alcohol and one from low-boiling petroleum ether.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.96; H, 8.38; neut. equiv., 192.1. Found: C, 74.74; H, 8.37; neut. equiv., 192.8.

The main portion of the bromide reacted with the magnesium to yield diphenyldi-*t*-butylethane, m. p. 185–186°.[15]

A solution of phenyl-*t*-butylacetic acid in carbon tetrachloride was treated with ozonized oxygen under the conditions used for the ozonolysis of the allene. Only about one-fourth of the acid was recovered from the mixture but no phenyl *t*-butyl ketone could be detected in the mixture.

2,2,6,6-Tetramethyl-3-phenyl-5-carbomethoxy-3,4-heptadiene.—The Grignard reagent prepared from 30.7 g. of phenyl-*t*-butyl-*t*-butylethynylbromomethane and 2.5 g. of magnesium in 250 cc. of ether was added during one hour to a solution of 9.45 g. of methyl chlorocarbonate in 100 cc. of dry ether. The reaction mixture was cooled to 0° and nitrogen was passed through the flask to avoid oxidation. The reaction mixture was worked up in the usual way. The yield was 18.5 g. (64%) of a colorless liquid, b. p. 116–120° (2 mm.); n^{20}_{D} 1.5029; d^{20}_{4} 0.9584; M_D calcd., 87.08; found, 87.84.

Anal. Calcd. for $C_{19}H_{26}O_2$: C, 79.67; H, 9.15. Found: C, 79.62; H, 9.02.

A solution of 2 g. of this ester in 50 cc. of carbon tetrachloride was ozonized in the usual manner. The neutral fraction from the decomposition of the ozonide was treated with 2,4-dinitrophenylhydrazine and a lemon-yellow solid, m. p. 205–206° (after recrystallization from alcohol) was isolated. This product was identical with the 2,4-dinitrophenylhydrazone of the methyl trimethylpyruvate described below. Indications of the presence of the 2,4-dinitrophenylhydrazone of phenyl *t*-butyl ketone were also obtained, but since this hydrazone is more soluble than the one isolated above, it could not be purified sufficiently for positive identification.

2,4-Dinitrophenylhydrazone of Methyl Trimethylpyruvate.—Trimethylpyruvic acid was obtained from pinacolone in 50% yields by the method of Richard.[16] Its 2,4-dinitrophenylhydrazone was prepared and melted at 169–171° with decomposition.

Anal. Calcd. for $C_{12}H_{14}O_6N_4$: N, 18.01. Found: N, 18.17.

Methyl trimethylpyruvate was formed in 70% yields by direct esterification of the acid with methyl alcohol[16] and its 2,4-dinitrophenylhydrazone was prepared in the usual manner. This product melted at 205–206°. It could be crystallized from alcohol but acetone was a better solvent. This product showed no depression in melting point when mixed with the material obtained from the ozonolysis of the methyl ester of the allenic acid.

Anal. Calcd. for $C_{13}H_{16}O_6N_4$: N, 17.29. Found: N, 17.46.

2,2,6,6-Tetramethyl-3-phenyl-5-carboxy-3,4-heptadiene.—The Grignard reagent prepared from 47 g. of phenyl-*t*-butyl-*t*-butylethynylbromomethane and 4 g. of magnesium in 400 cc. of dry ether was carbonated and the reaction mixture was worked up in the usual way. The yield of crude solid acid was 30 g. (72%). Two crystallizations from benzene gave a product melting at 160–161°. The acid was quite weak and only slightly soluble in sodium bicarbonate solution, although readily soluble in either sodium carbonate or sodium hydroxide solution.

Anal. Calcd. for $C_{18}H_{24}O_2$: C, 79.35; H, 8.88; mol. wt., 272.2. Found: C, 79.21; H, 9.02; mol. wt. (titration) 274, (ebullioscopic in acetone) 275, 220.

This same acid was obtained by boiling a solution of 2 g. of the ester obtained from the Grignard reagent and methyl chlorocarbonate and 2 g. of potassium hydroxide in 30 cc. of methyl alcohol for two hours. From this mixture 1.7 g. of the ester was recovered, but a small amount of acid melting at 159–160° was separated by acidification of the alkaline solution. A sample of this material mixed with some of the acid obtained by direct carbonation of the Grignard melted at 160°.

Action of 40% Sodium Amalgam on Phenyl-*t*-butyl-*t*-butylethynylbromomethane.—A solution of 20 g. of the bromide in 200 cc. of dry ether was shaken for about thirty-five hours with 25 cc. of 40% sodium amalgam in an atmosphere of dry nitrogen. The amalgam was frozen, the green colored ether solution was decanted into another nitrogen-filled flask and water was added. On working up the ether solution in the usual manner, a white solid and a yellow oil were obtained. By crystallization from absolute alcohol about 5.12 g. (34%) of solid material was obtained. By fractional crystallization from a mixture of absolute alcohol and petroleum ether, about one-fourth of this solid material was obtained as a pure hydrocarbon, m. p. 148–149°.

Anal. Calcd. for $C_{34}H_{46}$: C, 89.80; H, 10.20; mol. wt., 454.4. Found: C, 89.88; H, 10.38; mol. wt. (Rast.), 435.

The remaining solid was crystalline but melted over a range of ten degrees (115–125°). It contained some of the compound just described and an isomeric hydrocarbon.

Anal. Calcd. for $C_{34}H_{46}$: C, 89.80; H, 10.20; mol. wt. 454.4. Found: C, 89.84; H, 10.44; mol. wt. (Rast.), 436.

The yellow oil which was obtained from the original alcoholic solution was distilled under reduced pressure. The first fraction (2.1 g.) boiled at 83–85° (1 mm.); n^{20}_{D} 1.5090 and proved to be the allene 2,2,6,6-tetramethyl-3-phenyl-3,4-heptadiene.

Anal. Calcd. for $C_{17}H_{24}$: C, 89.40; H, 10.60. Found: C, 89.70; H, 10.44.

The second fraction (4.4 g.) boiled at 190–198° (1 mm.) and on long standing a few crystals separated. Analysis showed it to be a mixture of the two hydrocarbons of the composition $C_{34}H_{46}$ which had been obtained from the solid fraction.

In some preliminary experiments the bromide was treated with 40% sodium amalgam and to this mixture tetramethylethylene bromide was added. The same mixture of hydrocarbons was produced as was obtained in the

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(15) Conant and Blatt, THIS JOURNAL, **50**, 556 (1928).

(16) Richard, *Ann. chim.*, [8] **21**, 360 (1910).

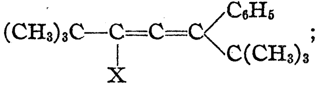
experiment described above. Hence the tetramethylethylene bromide apparently was not concerned in the reaction.

Action of Other Metals on the Bromide.—Silver and copper had no effect on solutions of the bromide. Lithium reacted with an ether solution of the bromide to give the same products that were obtained by the action of sodium amalgam. Reduction of the bromide with zinc dust in alcohol also gave the same mixture of hydrocarbons.

Properties of the Hydrocarbons $C_{34}H_{46}$.—Neither the pure hydrocarbon (m. p. 147–148°) nor the mixture (m. p. 115–125°) showed any sign of cleavage with alkali metals. Neither hydrocarbon could be converted to the other isomer by the action of heat. Neither hydrocarbon showed the property of absorbing oxygen. Both products showed signs of slow oxidation when heated in boiling xylene in the air, but no definite products were isolated. Attempts to ozonize these hydrocarbons gave only tarry products similar to the products previously obtained by the ozonization of other rearranged polyynes.

Summary

1. The Grignard reagent prepared from phenyl-*t*-butyl-*t*-butylethynylbromomethane reacts with water, methyl chlorocarbonate and carbon dioxide to give allene derivatives of the type



$$(CH_3)_3C{-}C(X){=}C{=}C(C_6H_5)C(CH_3)_3$$

; where X represents the group introduced into the organic molecule by the reaction.

2. Phenyl-*t*-butyl-*t*-butylethynylbromo-methane reacts with 40% sodium amalgam but does not give a stable sodium alkyl. Instead some of the bromide is reduced to the allene and some of it is coupled to give two isomeric hydrocarbons of the composition $C_{34}H_{46}$ which are thought to be diallenic hydrocarbons.

URBANA, ILLINOIS RECEIVED AUGUST 26, 1935

[CONTRIBUTION FROM THE UNIVERSITY OF MARYLAND]

The Action of Sulfuric Acid on Butanol-2[1]

BY NATHAN L. DRAKE AND FLETCHER P. VEITCH, JR.

In continuation of our study of the conversion of alcohols to higher olefins by acid catalysts, we have examined the effect of sulfuric acid on butanol-2.

When treated with 75% sulfuric acid under conditions which were found to be most favorable for converting methylisopropylcarbinol into a mixture of decenes,[2] butanol-2 yielded no octene. It was likewise impossible to obtain appreciable yields of octene by use, at atmospheric pressure, of any concentration of acid from 50 to 100%, although time of heating was varied from twenty minutes to forty-eight hours, and reaction temperature from 25 to 100°. Acid of higher than 90% concentration caused the formation of a quantity of high boiling material, probably a mixture of substances of the composition $(C_4H_8)_x$ where x is greater than 2.

The failure to obtain any octene in the experiments cited is unquestionably due to the fact that at the temperatures investigated the formation of butene takes place more readily than does its polymerization, with the consequence that the butene produced escapes before it has had the opportunity to polymerize.

It seemed logical, therefore, to study the effect of operating in a closed system, and preliminary experiments demonstrated that if the butene formed was not allowed to escape, but held in contact with the acid, slow formation of octene took place. Various conditions for effecting the polymerization under pressure were studied, and it was found that with our particular apparatus (see experimental part) the best yield of octene was obtained by the action of 75% sulfuric acid at 80° for forty-eight hours.

The formation of higher polymers from the dimer takes place very readily; distillation of the octene in the presence of a very small quantity of acid results in the formation of substances of higher molecular weight.

A quantity (2.5 kg.) of product having a boiling range which would include any octenes formed, (110–125°) was prepared and subjected to fractional distillation, from which it became apparent that there were at least two chemical individuals present.

Ozonolysis of several fractions of nearly constant refractive index yielded acetaldehyde and methyl *s*-butyl ketone. From these facts it became apparent that the octene present in the fractions ozonized was 3,4-dimethylhexene-2.

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[1] From the Ph.D. dissertation of Fletcher P. Veitch, Jr.

[2] Drake, Kline and Rose, THIS JOURNAL, **56**, 2076 (1934).

When a quantity of a higher boiling fraction was subjected to ozonolysis, it was found that only a very small quantity of unsaturated material was present. This unsaturated material (3,4-dimethylhexene-2) was removed by ozonolysis, and the resulting substance subjected to fractional distillation. The physical properties of the product indicated that it was di-*s*-butyl ether. Further investigation left no doubt as to the identity of the ether.

Exploratory ozonolyses of various other fractions failed to yield any evidence of the presence of any unsaturated substance other than 3,4-dimethylhexene-2.

Experimental

Apparatus and Method.—A lead-lined, steel autoclave of about four liters capacity was used. The desired temperature was maintained by means of an electrically heated water jacket controlled by a thermostat. Because of mechanical difficulties it was impossible to stir the charge. The temperature of the reaction mixture was determined by means of a thermometer located in a well which extended some distance below the surface of the charge.

Sixteen hundred and sixty grams of 75% sulfuric acid and 800 g. of *s*-butyl alcohol were heated at 80° for forty-eight hours. These conditions had been found to give the best yield of product of the desired boiling range. The autoclave was then allowed to cool, opened and the hydrocarbon layer siphoned off. A considerable quantity of butene escaped when the autoclave was opened and during the purification of the product. After treatment to remove the acid and water the product was distilled through a short column and the fraction from 110 to 125° (188 g.) collected for investigation as described below. An additional 100 g. of distillate boiling above 125° was also collected.

Purification and Fractionation of Reaction Products.—Two and a half kilograms of material (boiling range 110–125°), prepared from 6 kg. of *s*-butyl alcohol, was refluxed over sodium for fifty hours; the mixture was distilled from the sodium and 2 kg. of distillate was collected between 116 and 125°. A careful fractionation[3] of this mixture yielded 32 fractions of approximately 50 ml. each and a residue of 300 ml. The total volumes, b. p. (barometer varied from 751 mm. to 762 mm.) and $n^{25}\text{D}$ were as follows: Nos. 1–6, 355 ml., to 114.5°, 1.4065–1.4145; Nos. 7–14, 468 ml., to 116.6°, 1.4152 to 1.4156; Nos. 15–23, 560 ml., to 121.6°, 1.4142 to 1.4017; Nos. 24–32, 496 ml., to 122.5°, 1.3992–1.3931; residue, 300 ml., above 122.5°, 1.4118.

Ozonolysis of Fractions 7–14.—These fractions were ozonized in portions of 56 g. each dissolved in 180 ml. of ethyl acetate. The ozonizer furnished ozone at the rate of 0.03 to 0.04 mole/hr. when oxygen was supplied at the rate of 16.3 liters/hour; the temperature of the olefin was maintained between −15 and −25°. Only the amount of ozone theoretically required was supplied. The ozonide was decomposed[4] without removal of the solvent. The water layer from the decomposed ozonide gave a strong aldehyde reaction with fuchsin reagent, but a negative test for formaldehyde using resorcinol. The presence of acetaldehyde was demonstrated by the formation of a *p*-nitrophenylhydrazone which showed no depression of melting point when mixed with the *p*-nitrophenylhydrazone of acetaldehyde. The ethyl acetate layer was dried over anhydrous sodium sulfate and fractionated through a 50-cm. Widmer column to remove the ethyl acetate. The residue (250 ml.) was then subjected to careful fractionation in a Podbielniak[5] column. A considerable quantity of acetic acid was found in all fractions of the distillate, but after the removal of this acid by treatment with alkali, approximately 100 g. of a substance (A) boiling at 116.2° at 758 mm. was obtained.

Identification of A as Methyl *s*-Butyl Ketone.—(A) gave no color with Schiff's reagent, but gave a positive haloform reaction when tested in dioxane solution.[6] It was apparent, therefore, that (A) was a methyl ketone. The physical properties of (A) correspond very closely with those recorded[7] for methyl *s*-butyl ketone, and differ considerably from those of the other possible six carbon methyl ketones: for (A) b. p. 116.2°, d^{25} 0.812, $n^{18}\text{D}$ 1.4000; for methyl *s*-butyl ketone b. p. 117.8, d^{20} 0.815, $n^{20}\text{D}$ 1.3990.

Product (A) yielded a 2,4-dinitrophenylhydrazone which melted at 71.2°. No depression of melting point was observed when this product was melted mixed with the 2,4-dinitrophenylhydrazone prepared from pure methyl *s*-butyl ketone obtained synthetically via an acetoacetic ester synthesis.

Conversion of (A) to Methylethylacetic Acid.—In order to confirm our belief in the identity of (A) and methyl *s*-butyl ketone, (A) was degraded in the usual way by alkaline hypobromite to an acid whose amide agreed in melting point (110.9°) with that described for the amide of methylethylacetic acid, and whose *p*-phenylphenacyl ester possessed the composition required; 10 g. of (A) yielded 7 g. of acid.

The 2,4-Dinitrophenylhydrazone of (A).—This product which is not described in the literature melts at 71.2°.

Anal. Calcd. for $C_{12}H_{16}N_4O_4$: C, 51.42; H, 5.71. Found: C, 51.31, 51.56; H, 5.60, 5.86.

The *p*-Phenylphenacyl Ester of Methylethylacetic Acid.—The ester, prepared in the usual way, melts at 70.6°.

Anal. Calcd. for $C_{19}H_{20}O_3$: C, 77.03; H, 6.75. Found: C, 76.76, 76.98; H, 6.93, 6.83.

Purification of Fractions 24–31.—Five hundred milliliters of material representing fractions 24–31 inclusive was ozonized until no more ozone was absorbed. After decomposition of the ozonide the water-insoluble layer was dried and distilled; 435 ml. was distilled and 395 ml. of distillate (B) whose $n^{25}\text{D}$ varied from 1.3927 to 1.3930 was

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[3] We wish to express our thanks to S. Schicktanz and the others of the Petroleum Research Section of the Bureau of Standards for their valuable assistance in fractionating this mixture; see Schicktanz [*Bur. Standards J. Research*, **11**, 89 (1933)] for a description of the still used; *cf.* also *ibid.*, **7**, 851 (1931).

[4] Whitmore and Church, THIS JOURNAL, **54**, 3710 (1932).

[5] Podbielniak, *Ind. Eng. Chem.*, *Anal. Ed.*, **5**, 119 (1933).

[6] Fuson, *Chem. Rev.*, **15**, 775 (1934).

[7] "Int. Crit. Tables," Vol. I, pp. 203, 276; Beilstein, 4th Ed. Julius Springer, Berlin, 1918, Vol. I, p. 694.

obtained. The density of the distillate was 0.759 at 25° and its boiling point 121° at 760 mm.

Anal. Calcd. for $C_8H_{18}O$: C, 73.84; H, 13.84; mol. wt. 130. Found: C, 73.86; H, 13.84; mol. wt. 126.

From the analytical data and the fact that (B) did not react with sodium, it seemed likely that (B) was a dibutyl ether.

Conversion of (B) to *s*-Butyl Bromide.—Forty grams of (B) was saturated with hydrogen bromide and heated under reflux for three hours. The product was washed with water and saturated sodium bicarbonate solution, dried and distilled; 68.5 g. of a bromide with the following physical properties was obtained (81.2%): b. p. 90–91° at 757 mm.; $n^{25}\text{D}$ 1.4341; d^{25} 1.250. From these physical constants[8] it is apparent that the bromide formed is probably *s*-butyl bromide.[8]

This conclusion is strengthened by a comparison of densities and boiling points of the three known di-butyl ethers with those of (B).[9]

Preparation of the 3,5-Dinitrobenzoate of *s*-Butyl Alcohol from (B).—One milliliter of (B) was mixed with 0.5 g. of 3,5-dinitrobenzoyl chloride and 0.15 g. of anhydrous zinc chloride and refluxed for one hour. After purification 0.1 g. of ester melting at 75.5° was obtained. This dinitrobenzoate was shown by the method of mixed melting points to be identical with the ester obtained directly from *s*-butyl alcohol and 3,5-dinitrobenzoyl chloride.

Discussion

The theory of the mechanism of the polymerization of olefins by acid catalysts suggested by Whitmore[10] would predict the formation of 3,4-dimethylhexene-2 and 3,4-dimethylhexene-1 from *s*-butyl alcohol under the conditions studied, with the latter olefin present in smaller quantity than the former. We have been unable to detect the presence of formaldehyde after ozonization of any of the fractions of the reaction product, and must conclude that 3,4-dimethylhexene-1 is not formed under the condition studied.

The theory of the mechanism of polymerization of olefins suggested by Kline[11] would likewise lead to the prediction of two products only one of which was found. In this case, however, the product expected in greatest abundance, *viz.*, 4,5-dimethylhexene-2 is not the one actually produced.

Summary

1. The formation of 3,4-dimethylhexene-2 and di-*s*-butyl ether by the action of 75% sulfuric acid on *s*-butyl alcohol at 80° under pressure has been demonstrated.

2. The theory of the mechanism of polymerization by acids suggested by Whitmore explains the observed facts better than that of Kline.

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[8] "Int. Crit. Tables," Vol. I, pp. 188, 276, 277.

[9] "Int. Crit. Tables," Vol. I, p. 204.

[10] Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934).

[11] Kline and Drake, *Bur. Standards J. Research*, **13**, 705 (1934).

COLLEGE PARK, MD. RECEIVED SEPTEMBER 27, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF ST. JOHN'S UNIVERSITY AND WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

Studies in the Synthesis of Certain Alkyl and Aryl Cryptophenols[1]

BY MARTIN E. MCGREAL AND JOSEPH B. NIEDERL

Introduction

Since *p*-*t*-octylphenol (*p*-(2,2,4,4-tetramethyl)-butylphenol)[2] has a rather high phenol coefficient (150), it was one of the objects of this investigation to prepare and study the yet unreported *p*-*t*-hexyl and *p*-*t*-heptylphenols. These phenols were prepared by condensing dimethylisopropylcarbinol (I) (b. p. 116–120°) and dimethyl-*n*-butylcarbinol (II) (b. p. 130–130.5°) with phenol in the presence of zinc chloride, utilizing the method of Liebmann, Fischer and Gruetzner.[3]

The condensation of diisobutyl alcohol (2,2,4-trimethylpentanol-4) (b. p. 145–149°) with phenol under identical reaction conditions, however, did not yield the expected *p*-*t*-octylphenol, but *p*-*t*-butylphenol as the main reaction product.[4]

The second object was to investigate the applicability of these condensations to primary, secondary and tertiary aromatic alcohols, and the following carbinols were therefore studied: phenyl (VI), phenylmethyl (VII), benzyl (VII), phenylmethylethyl (VIII) and phenylmethylisopropyl (IX). The last was prepared by the action of isopropylmagnesium bromide on acetophenone.[5]

The condensation products with phenol (VIII

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[1] Presented before the Division of Organic Chemistry at the New York meeting of the American Chemical Society, April, 1935.

[2] J. B. Niederl, U. S. Patent 2,008,337 (1935); British Patent 431,487 (1935); Niederl, Natelson and Beekman, THIS JOURNAL, **55**, 2571 (1933).

[3] (a) A. Liebmann, *Ber.*, **14**, 1842 (1881); (b) Fischer and Gruetzner, *ibid.*, **26**, 1646 (1893).

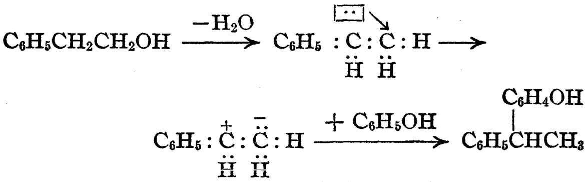
[4] P. W. Hodges, M.Sc. Thesis, New York University, 1935.

[5] B. Gutchin, M.Sc. Thesis, New York University, 1935.

and IX) of the last two compounds were also prepared by the addition of phenol to β-phenyl-β-butylene and phenyl-β-amylene[5,6] using the method of Niederl and co-workers.[7]

In the condensation of β-phenylethyl alcohol (benzylcarbinol) with phenol, apparently simultaneous rearrangement took place as the end-product does not appear to be the expected 4-hydroxydibenzyl but the *p*-(α-phenylethyl) phenol (VII).

Interpretation of this rearrangement phenomenon seems to involve the electronic postulations of Whitmore, Kline and Drake and others[8] and would indicate that dehydration of the β-phenylethyl alcohol precedes the addition of the phenol. The dehydration would activate the alpha carbon of the intermediary styrene as follows.



$$C_6H_5CH_2CH_2OH \xrightarrow{-H_2O} C_6H_5 : \underset{H}{\underset{\cdot\cdot}{C}} : \underset{H}{\underset{\cdot\cdot}{\overset{\boxed{\cdot\cdot}\searrow}{C}}} : H \longrightarrow$$

$$C_6H_5 : \underset{H}{\underset{\cdot\cdot}{\overset{+}{C}}} : \underset{H}{\underset{\cdot\cdot}{\overset{-}{\ddot{C}}}} : H \xrightarrow{+\ C_6H_5OH} C_6H_5\overset{C_6H_4OH}{\overset{|}{C}}HCH_3$$

1-phenyl-1-(4-hydroxy)-phenylethane

Under the influence of the cationoid condensing agent it can be assumed that on account of incipient ionization of the phenol, or the phenol-condensing agent addition compound, the positive *p*-hydrogen ion would have to add on to the negative primary carbon atom, consequently addition of the negatively charged phenol ion would then have to take place at the secondary carbon atom with the incomplete electron octet thus yielding the above 1-phenyl-1-(4-hydroxy)-phenylethane. The repeatedly observed rearrangements in the butyl series to *t*-butyl compounds may be interpreted in an analogous manner.[3a,9]

The third object in these studies was to extend these condensations to the alkylated cyclohexanol series. Here positive condensations were observed in all the cases investigated. The condensation system of the three isomeric methylcyclohexanols, the hydrogenation products of the three cresols (1-methylcyclohexanol-2 (III), 1-methylcyclohexanol-3 (IV), 1-methylcyclohexanol-4 (V)) proved to be positive in all instances and the corresponding (methylcyclohexyl)-phenols (III, IV and V) were obtained, with the para substituted phenol forming the major reaction product.

An exception again was the condensation of the 4-*t*-octylcyclohexanol-1 (prepared by catalytic hydrogenation of *p*-*t*-octylphenol). In this case, not the expected *p*-(4-*t*-octyl)-cyclohexylphenol, but *p*-*t*-butylphenol again appeared to be the main reaction product, an observation which is entirely in harmony with the experimental findings of Gilman and Burtner[9c] who observed the formation of the *t*-butyl group in their alkylation reactions in the furan series not only involving a butyl, but also an amyl, a hexyl and even an octadecyl radical.

Experimental Part

The molar mixture of the alcohol and of phenol was first warmed to about 150° and to this preheated mixture 1.5 moles of finely powdered, anhydrous zinc chloride was added and the whole refluxed for several hours at 180° (two to ten hours depending upon the reactivity of the alcohol). The reaction mixture, while still warm, was then poured into warm water (80°) acidified with hydrochloric acid. Slowly the phenolic condensation products separated and were then dissolved in toluene following the procedure of Behaghel and Freiensehner.[10] This toluene extract was shaken out first with acidified water and then repeatedly with Claisen solution (50% aqueous potassium hydroxide solution mixed with an equal volume of methyl alcohol).[11] The combined Claisen solution extracts, containing the phenolic condensation products, were washed once with toluene and then acidified with dilute hydrochloric acid (10%). The phenolic condensation products thus separated were then dissolved in ether. This ether extract was dried over calcium chloride and allowed to stand until a clear solution resulted. After removal of the ether by distillation, the residue was repeatedly fractionated under diminished pressure. The solid condensation products were recrystallized from diisobutylene; yield 40–80%.

The above phenol coefficients are the average of four to five determinations employing the standard phenol coefficient technique (30% alcoholic

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(6) Ch. Zimmerman, M.Sc. Thesis, New York University, 1935.

(7) Niederl and Riley, THIS JOURNAL, **56**, 2412 (1934).

(8) Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934); Kline and Drake, *Bur. Standards J. Research*, **13**, 705 (1934); Kharasch and Sher, *J. Phys. Chem.*, **29**, 625 (1925); Kharasch and Darkis, *Chem. Rev.*, **5**, 571 (1928); G. N. Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York City, 1923.

(9) (a) Reilly and Hickinbottom, *J. Chem. Soc.*, **117**, 103 (1920); (b) Effront, *Ber.*, **17**, 2324 (1884); (c) Gilman and Burtner, THIS JOURNAL, **57**, 909 (1935); (d) Read and Miller, *ibid.*, **54**, 1195 (1932).

(10) Behaghel and Freiensehner, *Ber.*, **67**, 1368 (1934).

(11) Claisen, *Ann.*, **418**, 96 (1919).

Compound	M. p., °C.	B. p., °C.	Phenol coefficient	Analyses, % Calcd. C	H	Found C	H
t-alkyl phenols							
I *p*-(2,2,3-Trimethyl)propylphenol $(CH_3)_2CHC(CH_3)_2C_6H_4OH$	105		45	80.85	10.16	80.72	10.02
II *p*-*t*-Heptylphenol $(CH_3)_2(C_4H_9)CC_6H_4OH$		280 (760 mm.)		81.18	10.49	81.35	10.70
Cycloalkyl phenols							
III *p*-(2-Methyl)-cyclohexylphenol $CH_3C_6H_{10}C_6H_4OH(2)$	107		50	82.04	9.54	82.37	9.71
IV *p*-(3-Methyl)-cyclohexylphenol $CH_3C_6H_{10}C_6H_4OH(3)$	101		105	82.04	9.54	82.22	9.60
V *p*-(4-Methyl)-cyclohexylphenol[a] $CH_3C_6H_{10}C_6H_4OH(4)$	108		70				
Alkyl-aryl phenols							
VI *p*-Benzylphenol[b] $C_6H_5CH_2C_6H_4OH$	82						
VII *p*-(α-Phenylethyl)phenol $C_6H_5CH(CH_3)C_6H_4OH$	64		40				
VIII 2-Phenyl-2-(4-hydroxy)[c]phenylbutane $C_6H_5C(CH_3)(C_2H_5)C_6H_4OH$[6]		145–148 (2.5 mm.)	33	84.90	8.02	85.00	8.22
IX 2-Methyl-3-phenyl-3-(4-hydroxy)phenylbutane $C_6H_5C(CH_3)(CH(CH_3)_2)C_6H_4OH$[5]		157–160 (3 mm.)		84.94	8.39	85.12	8.51

[a] Meyer and Bernhauser, *Monatsh.*, **54**, 721 (1929). [b] Paternò, *Gazz. chim. ital.*, **2**, 1 (1872); Fileti, *ibid.*, **3**, 121 (1873); *Ber.*, **6**, 757 (1873); Rennie, *J. Chem. Soc.*, **41**, 34 (1882); Zincke and Walter, *Ann.*, **334**, 373 (1904); Perkin and Hodgkinson, *J. Chem. Soc.*, **37**, 725 (1880). [c] Pickard and Littlebury, *ibid.*, **89**, 469 (1906); Stoermer and Kippe, *Ber.*, **36**, 4012 (1903); Koenigs and Carl, *ibid.*, **24**, 3894 (1891).

solutions at 37°) using *Staphylococcus aureus*. The authors desire to thank Dr. Wm. A. Feirer of Sharp and Dohme, Philadelphia, for performing these determinations.

Summary

1. The Liebmann method of condensing alcohols with phenols in the presence of zinc chloride has been extended to include *t*-hexyl, *t*-heptyl and *t*-octyl alcohols, giving in the first two cases the corresponding substituted phenols, while *p*-*t*-butylphenol was obtained from 2,2,4-trimethylpentanol-4.

2. Application of the same method to aromatic alcohols led to positive results in all cases, encountering a rearrangement in the case of β-phenylethyl alcohol.

3. Methylcyclohexanols also could be condensed with phenols by this method, with the *t*-octylcyclohexanol again giving *p*-*t*-butylphenol, instead of the expected *t*-octylcyclohexylphenol.

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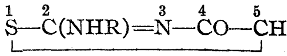
[CONTRIBUTION FROM THE UNIVERSITY OF KANSAS]

Some Alkyl Derivatives of Certain Aryl Substituted Thiazolidones[1]

BY JOHN A. DAVIS AND F. B. DAINS

In a recent paper by Eberly and Dains[2] it was shown that the alkylation of the mono-aryl thiazolidones,  $\overset{1}{S}—\overset{2}{C}(NHR)=\overset{3}{N}—\overset{4}{C}O—\overset{5}{C}H_2$, gave two isomeric products, one of the 2-aryl-2-alkylthiazolidone and the other the 2-aryl-3-alkylthiazolidone; results not in harmony with the structure assigned by Beckurts and Frerich,[3] *viz.*, 2-alkyl-3-arylthiazolidone. This paper is a further study of nine aryl substituted thiazolidones in order to determine the structure of the alkylation products and to determine the effect both of the aryl groups and of different alkyl halides on the amount of the two possible isomers.

A. Two methods were used in preparing the thiazolidones.

(1) **From $RNHCOCH_2Cl$ and KSCN.**—Equal molecular quantities of the two were dissolved in alcohol and refluxed for one to five hours. In certain cases this method gave a tarry product and a poor yield.

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[1] From a thesis presented to the Graduate School of the University of Kansas by John A. Davis in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Eberly and Dains, THIS JOURNAL, **55**, 3859 (1933).

[3] Beckurts and Frerich, *Arch. Pharm.*, **253**, 233–265 (1915).

(2) **From the Mono-aryl Thiourea.**—This when refluxed in alcohol for one to three hours with equal molecular quantities of pyridine and ethyl chloroacetate usually gave a product free from tar.

B. **Preparation of the Sodium Salt.**—The thiazolidones were soluble in hot 5% sodium hydroxide and on cooling the sodium salts crystallized from the solution.

C. **Alkylation** occurred when an alcohol solution of the sodium salt was heated with an alkyl halide. The 2-alkyl thiazolidone was separated from the 3-alkyl derivatives by the solubility of the former in dilute hydrochloric acid.

Hydrolysis of these alkyl substituted thiazolidones usually resulted in complete rupture of the ring, but it has been found that the 5-benzal derivatives are much more stable, hydrolysis usually yielding 5-benzal-2,4-thiazoledione or 5-benzal-3-alkyl-2,4-thiazoledione, thus affording a convenient method of determining the nature of the group at 2. Hydrolysis was carried out by boiling the benzal derivative in alcoholic hydrochloric acid for five to twenty-five hours.

The benzal derivatives were prepared by a few minutes of heating of a saturated alcohol solution of the thiazolidone and benzaldehyde with a trace of alkali.

Experimental

Following the general methods outlined above, thiazolidones were prepared from the following amines: *o*- and *p*-phenetidines, *o*-, *m*- and *p*-anisidines, pseudocumidine, 2-amino-*p*-cymene, 2,4-diiodoaniline and *p*-iodoaniline. Each of these was then ethylated by heating an alcohol solution of the corresponding sodium salt with ethyl iodide for two or three hours. The alcohol and excess ethyl iodide were then removed with steam and the oily residue dissolved in ether and repeatedly extracted with dilute hydrochloric acid (5–10%). Neutralization of the acid solution caused the separation of the 2-alkyl-2-aryl compound, while evaporation of the ether solution yielded the isomeric 2-aryl-3-alkyl derivative. The latter derivative was also synthesized in each case by two to three hours of heating of an alcohol solution of equal molecular quantities of ethyl chloroacetate, pyridine and the corresponding N-alkyl-N′-aryl thiourea. Ethylation in each case, with the exception of the thiazolidones from pseudocumidine, 2-amino-*p*-cymene and 2,4-diiodoaniline produced two isomeric products: one the 2-ethyl-2-aryl-4-thiazolidone, and the other the 2-aryl-3-ethyl compound. With pseudocumidine and 2-amino-*p*-cymene only the 2-alkyl-2-aryl derivatives were isolated, while with 2,4-diiodoaniline, only the 2-aryl-3-ethyl derivative was isolated.

The following table gives the percentage yields of the isomers obtained on ethylation of the thiazolidones.

Thiazolidone from	% Yield of 2-ethyl-2-aryl compound	% Yield of 3-ethyl-2-aryl compound
o-Phenetidine	68	1
p-Phenetidine	50	1
o-Anisidine	65	0.6
m-Anisidine	46	6
p-Anisidine	55	1
Pseudocumidine	56	0.0
2-Amino-*p*-cymene	65	0.0
p-Iodoaniline	74	16
2,4-Diiodoaniline	0	85

The 2-ethyl-2-aryl compounds obtained from *o*- and *p*-anisidine, *p*-phenetidine and pseudocumidine were identical with the corresponding compounds obtained by Beckurts and Frerich[3] and to which they assigned the erroneous structure, 2-ethyl-imino-3-aryl-4-thiazolidones. However, Beckurts and Frerich in their investigation had overlooked the occurrence of the 2-aryl-3-ethyl isomers.

The sodium salt of the thiazolidone from *p*-iodoaniline was treated with various alkyl halides and the following percentage yields of isomers were obtained.

Alkyl halide	% Yield of 2-alkyl-2-aryl compound	% Yield of 3-alkyl-2-aryl compound
Methyl iodide	60	7.5
Ethyl iodide	74	16
Amyl iodide	34	4
Benzyl chloride	60	4

Proof of structure was obtained in each case by acid hydrolysis of the corresponding 5-benzal derivative using a mixture of equal volumes of alcohol and concentrated hydrochloric acid. The 2-alkyl-2-aryl compounds gave 5-benzal-2,4-thiazoledione[4] and a secondary amine while the 2-aryl-3-alkyl compounds yielded a 5-benzal-3-alkyl-2,4-thiazoledione and the aryl amine. The thiazolediones separated during hydrolysis from the hot solutions, while the amines were obtained by neutralization of the acid after removal of the alcohol.

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(4) Ref. 2, p. 3861.

The thiazolidones were also found to condense with *p*-nitrosodimethylaniline in the same manner as with benzaldehyde. A saturated alcohol solution of 2-ethyl-2-*p*-iodophenylamino-4-thiazolidone when heated with *p*-nitrosodimethylaniline and a trace of alkali gave a dark yellow crys-

PROPERTIES AND ANALYSES

No.	Thioureas	Source	Formula	M. p., °C.	% Nitrogen Calcd.	% Nitrogen Found
I	N-Ethyl-N′-*p*-ethoxyphenyl	5	$C_{11}H_{16}ON_2S$	112	12.50	12.42
II	N-Ethyl-N′-*o*-ethoxyphenyl	5	$C_{11}H_{16}ON_2S$	88	12.50	12.45
III	N-Ethyl-N′-pseudocumyl	6	$C_{12}H_{18}N_2S$	138	12.61	12.45
IV	N-Methyl-N′-pseudocumyl	7	$C_{11}H_{16}N_2S$	179	13.46	13.40
V	N-Ethyl-N′-*o*-methoxyphenyl	5	$C_{10}H_{14}ON_2S$	77	13.33	13.28
VI	N-Ethyl-N′-*p*-methoxyphenyl	5	$C_{10}H_{14}ON_2S$	147	13.33	13.42
VII	N-Ethyl-N′-*m*-methoxyphenyl	5	$C_{10}H_{14}ON_2S$	112	13.33	13.18
VIII	Mono-*p*-cymyl	8	$C_{11}H_{16}N_2S$	152	13.46	13.40
IX	N-Ethyl-N′-*p*-cymyl	5	$C_{13}H_{20}N_2S$	126	11.86	11.71
X	N-Ethyl-N′-2,4-diiodophenyl	9	$C_9H_{10}I_2N_2S$	164	6.49	6.34
XI	N-Methyl-N′-*p*-iodophenyl	10	$C_8H_9IN_2S$	171	9.59	9.49
XII	N-Ethyl-N′-*p*-iodophenyl	5	$C_9H_{11}IN_2S$	147.5	9.15	9.13
XIII	N-Amyl-N′-*p*-iodophenyl	11	$C_{12}H_{17}IN_2S$	130	8.05	7.91
XIV	N-Benzyl-N′-*p*-iodophenyl	12	$C_{14}H_{13}IN_2S$	149	7.61	7.52
	4-Thiazolidone					
XV	2-*p*-Ethoxyphenylimino-3-ethyl-		$C_{13}H_{16}O_2N_2S$	93	10.60	10.58
XVI	2-*o*-Ethoxyphenylamino-[13]		$C_{11}H_{12}O_2N_2S$	172	11.86	11.80
XVII	2-Ethyl-2-*o*-ethoxyphenylamino-		$C_{13}H_{16}O_2N_2S$	99	10.60	10.58
XVIII	2-*o*-Ethoxyphenylimino-3-ethyl-		$C_{13}H_{16}O_2N_2S$	79	10.60	10.48
XIX	2-Pseudocumylimino-3-ethyl-		$C_{14}H_{18}ON_2S$	77	10.68	10.53
XX	2-Pseudocumylimino-3-methyl-[14]		$C_{13}H_{16}ON_2S$	91	11.29	11.27
XXI	2-*o*-Methoxyphenylimino-3-ethyl-		$C_{12}H_{14}O_2N_2S$	114	11.20	11.10
XXII	2-*p*-Methoxyphenylimino-3-ethyl-		$C_{12}H_{14}O_2N_2S$	83	11.20	11.26
XXIII	2-*m*-Methoxyphenylamino-[13]		$C_{10}H_{10}O_2N_2S$	165	12.61	12.65
XXIV	2-Ethyl-2-*m*-methoxyphenylamino-		$C_{12}H_{14}O_2N_2S$	112	11.20	10.89
XXV	2-*m*-Methoxyphenylimino-3-ethyl-		$C_{12}H_{14}O_2N_2S$	65–66	11.20	11.22
XXVI	2-*p*-Cymylamino-[15]		$C_{13}H_{16}ON_2S$	174	11.29	11.28
XXVII	2-Ethyl-2-*p*-cymylamino-		$C_{15}H_{20}ON_2S$	85	10.14	10.04
XXVIII	2-*p*-Cymylimino-3-ethyl-		$C_{15}H_{20}ON_2S$	64	10.14	10.01
XXIX	2-(2,4-Diiodophenylamino)-[16]		$C_9H_6I_2ON_2S$	233	6.31	6.35
XXX	2-(2,4-Diiodophenylimino)-3-ethyl		$C_{11}H_{10}I_2ON_2S$	173	5.94	5.90
XXXI	2-*p*-Iodophenylamino-		$C_9H_7ION_2S$	226	8.81	8.78
XXXII	2-Methyl-2-*p*-iodophenylamino-		$C_{10}H_9ION_2S$	207	8.44	8.42
XXXIII	2-*p*-Iodophenylimino-3-methyl-		$C_{10}H_9ION_2S$	152	8.44	8.46
XXXIV	2-Ethyl-2-*p*-iodophenylamino-		$C_{11}H_{11}ION_2S$	116	8.09	8.02
XXXV	2-*p*-Iodophenylimino-3-ethyl-		$C_{11}H_{11}ION_2S$	103	8.09	8.15
XXXVI	2-Amyl-2-*p*-iodophenylamino-		$C_{14}H_{17}ION_2S$	116	7.22	7.22
XXXVII	2-*p*-Iodophenylimino-3-amyl-		$C_{14}H_{17}ION_2S$	57	7.22	7.17
XXXVIII	2-Phenylimino-3-amyl-[17]		$C_{14}H_{18}ON_2S$	Oil	10.68	10.74
XXXIX	2-Benzyl-2-*p*-iodophenylamino-		$C_{16}H_{13}ION_2S$	176	6.87	6.85
XL	2-*p*-Iodophenylimino-3-benzyl-		$C_{16}H_{13}ION_2S$	137	6.87	6.82
XLI	2-Benzylimino-3-benzyl-[18]		$C_{17}H_{16}ON_2S$	74	9.46	9.42

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(5) Prepared from ethylamine and the corresponding substituted phenyl isothiocyanate.

(6) From ethyl isothiocyanate and pseudocumidine.

(7) From methyl isothiocyanate and pseudocumidine.

(8) Prepared by evaporation to dryness of a water solution of aminocymene hydrochloride and potassium thiocyanate.

(9) From ethyl isothiocyanate and 2,4-diiodoaniline.

(10) From methylamine and *p*-iodophenyl isothiocyanate.

(11) From amyl isothiocyanate and *p*-iodoaniline.

(12) From benzyl isothiocyanate and *p*-iodoaniline.

(13) Best prepared from the corresponding mono-thiourea and ethyl chloroacetate.

(14) Compound XIX first separated as an oil so the corresponding methyl derivative was prepared from IV for comparison.

(15) Best prepared from mono-*p*-cymyl thiourea and ethyl chloroacetate. Attempts to prepare this compound from ω-chloroacetoamino-*p*-cymene and chloroacetyl chloride led to the formation of a very tarry product. ω-Chloroacetoamino-*p*-cymene was prepared by treating an acetone solution of 2-amino-*p*-cymene with equal molecular quantities of chloroacetyl chloride and pyridine, m. p. 85°. *Anal.* Calcd. for $C_{12}H_{16}ClON$: N, 6.21. Found: N, 6.16.

(16) Chloroacetyl chloride added to an acetone solution of 2,4-diiodoaniline and pyridine gave 2,4-diiodo-ω-chloroacetanilide, m. p. 153°. *Anal.* Calcd. for $C_8H_6ClI_2ON$: N, 3.33. Found: N, 3.26. The latter when dissolved in alcohol and heated with KSCN yielded XXIX.

(17) Prepared from N-amyl-N′-phenyl thiourea and ethyl chloroacetate.

(18) Prepared from N-benzyl-N′-phenyl thiourea and ethyl chloroacetate.

No.	5-Benzal-4-thiazolidone	Hydrolysis products[19]	Formula	M. p., °C.	% Nitrogen	
					Calcd.	Found
XLII	2-Ethyl-2-*p*-ethoxyphenylamino-	A, ethyl-*p*-phenetidine[20]	$C_{20}H_{20}O_2N_2S$	210	7.95	7.94
XLIII	2-*p*-Ethoxyphenylimino-3-ethyl-	B, *p*-phenetidine	$C_{20}H_{20}O_2N_2S$	135	7.95	7.89
XLIV	2-*o*-Ethoxyphenylimino-3-ethyl-	B, *o*-phenetidine[21]	$C_{20}H_{20}O_2N_2S$	113	7.95	7.79
XLV	2-Ethyl-2-*o*-ethoxyphenylamino-	A, ethyl-*o*-phenetidine[22]	$C_{20}H_{20}O_2N_2S$	164	7.95	7.86
XLVI	2-Ethyl-2-pseudocumyl-	A	$C_{21}H_{22}ON_2S$	180	8.00	7.98
XLVII	2-Pseudocumylimino-3-ethyl-	B, pseudocumidine	$C_{21}H_{22}ON_2S$	141	8.00	7.95
XLVIII	2-Pseudocumylimino-3-methyl-	Not hydrolyzed	$C_{20}H_{20}ON_2S$	136	8.33	8.28
XLIX	2-Ethyl-2-*o*-methoxyphenylamino-	A, ethyl-*o*-anisidine[23]	$C_{19}H_{18}O_2N_2S$	149	8.28	8.28
L	2-*o*-Methoxyphenylimino-3-ethyl-	B, *o*-anisidine	$C_{19}H_{18}O_2N_2S$	99	8.28	8.27
LI	2-Ethyl-2-*p*-methoxyphenylamino-	A	$C_{19}H_{18}O_2N_2S$	198	8.28	8.26
LII	2-*p*-Methoxyphenylimino-3-ethyl-	B, *p*-anisidine	$C_{19}H_{18}O_2N_2S$	125	8.28	8.24
LIII	2-Ethyl-2-*m*-methoxyphenylamino-	A	$C_{19}H_{18}O_2N_2S$	135	8.28	8.25
LIV	2-*m*-Methoxyphenylimino-3-ethyl-	B, *m*-anisidine	$C_{19}H_{18}O_2N_2S$	109	8.28	8.13
LV	2-Ethyl-2-*p*-cymylamino-	A	$C_{22}H_{24}ON_2S$	169	7.69	7.66
LVI	2-*p*-Cymylimino-3-ethyl-	B, 2-amino-*p*-cymene	$C_{22}H_{24}ON_2S$	73	7.69	7.64
LVII	2-(2,4-Diiodophenylimino)-3-ethyl-[24]	Not hydrolyzed	$C_{18}H_{14}I_2ON_2S$	210–211	5.00	5.01
LVIII	2-Methyl-2-*p*-iodophenylamino-	A, methyl-*p*-iodoaniline[25]	$C_{17}H_{13}ION_2S$	246	6.67	6.70
LIX	2-*p*-Iodophenylimino-3-methyl-	5-Benzal-3-methyl-2,4-thiazoledione,[2] *p*-iodoaniline	$C_{17}H_{13}ION_2S$	167	6.67	6.72
LX	2-Ethyl-2-*p*-iodophenylamino-	A	$C_{18}H_{15}ION_2S$	231	6.45	6.51
LXI	2-*p*-Iodophenylimino-3-ethyl-	B, *p*-iodoaniline	$C_{18}H_{15}ION_2S$	172	6.45	6.43
LXII	2-Amyl-2-*p*-iodophenylamino-	A	$C_{21}H_{21}ION_2S$	202	5.88	5.94
LXIII	2-*p*-Iodophenylimino-3-amyl-	5-Benzal-3-amyl-2,4-thiazoledione,[26] *p*-iodoaniline	$C_{21}H_{21}ION_2S$	105	5.88	5.87
LXIV	2-Phenylimino-3-amyl-	5-Benzal-3-amyl-2,4-thiazoledione[26]	$C_{21}H_{22}ON_2S$	78	8.00	7.95
LXV	2-Benzyl-2-*p*-iodophenylamino-	A, benzylaniline, I_2	$C_{23}H_{17}ION_2S$	221	5.65	5.70
LXVI	2-*p*-Iodophenylimino-3-benzyl-	5-Benzal-3-benzyl-2,4-thiazoledione,[27] *p*-iodoaniline	$C_{23}H_{17}ION_2S$	162	5.65	5.68
LXVII	2-Benzylimino-3-benzyl-	5-Benzal-3-benzyl-2,4-thiazoledione,[27] benzyl amine	$C_{24}H_{20}ON_2S$	109	7.29	7.33

talline product which recrystallized from glacial acetic acid melted with decomposition at 246°.

Anal. Calcd. for $C_{19}H_{19}ION_4S$: N, 11.77. Found: N, 11.68.

Similar treatment of 2-*p*-iodophenylimino-3-ethyl-4-thiazolidone with *p*-nitrosodimethylaniline yielded a slightly soluble, red crystalline product, m. p. 212°.

Anal. Calcd. for $C_{19}H_{19}ION_4S$: N, 11.77. Found: N, 11.58. Hydrolysis of these derivatives with hydrochloric acid in alcohol solution caused complete rupture of the ring.

Summary

The alkylation of nine different aryl substituted thiazolidones has been studied. Certain of the compounds described by Beckurts and Frerich as 2-alkyl-3-aryl thiazolidones were shown, in fact, to be 2-alkyl-2-aryl thiazolidones, thus confirming the work of Eberly and Dains.

In most cases it was found that alkylation produced two isomeric alkyl derivatives: one, the 2-alkyl-2-aryl thiazolidone and the other the 2-aryl-3-alkyl compound. The effect of the aryl group on the amounts of isomers obtained was noted as was also the effect of various alkyl halides.

LAWRENCE, KANSAS

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[19] "A" indicates 5-benzal-2,4-thiazoledione, m. p. 243° and "B," 5-benzal-3-ethyl-2,4-thiazoledione, m. p. 95°. Ref. 2.

[20] Identified by its reaction with phenyl isocyanate to give N-ethyl-N-*p*-ethoxy-phenyl-N′-phenyl urea, m. p. 93°. *Anal.* Calcd. for $C_{17}H_{20}O_2N_2$: N, 9.86. Found: N, 9.91.

[21] With *p*-nitrobenzoyl chloride yielded *p*-nitrobenzoyl-*o*-phenetidide, m. p. 155°. *Anal.* Calcd. for $C_{15}H_{14}O_4N_2$: N, 9.79. Found: N, 9.74. And with *p*-tolyl isocyanate gave N-*p*-tolyl-N′-*o*-ethoxyphenyl urea, m. p. 172°. *Anal.* Calcd. for $C_{16}H_{18}O_2N_2$: N, 10.37. Found: N, 10.31.

[22] With benzene sulfonyl chloride gave ethyl-*o*-phenetidyl-benzene sulfonate, m. p. 61°. *Anal.* Calcd. for $C_{16}H_{19}O_3NS$: N, 4.59. Found: N, 4.79.

[23] Ethyl-*o*-anisidyl-benzene sulfonate formed on addition of benzene sulfonyl chloride, m. p. 90°. *Anal.* Calcd. for $C_{15}H_{17}O_3NS$: N, 4.81. Found: N, 4.93.

[24] Attempts to prepare this compound in alcohol solution were unsuccessful. It was finally obtained by using pyridine as the solvent.

[25] M. p. of product obtained by reaction with benzene sulfonyl chloride was 78°. *Anal.* Calcd. for $C_{13}H_{12}IO_2NS$: N, 3.75. Found: N, 3.90.

[26] M. p. 74°. *Anal.* Calcd. for $C_{15}H_{17}O_2NS$: N, 5.09; S, 11.65. Found: N, 5.24. S, 11.81.

[27] M. p. 134°. *Anal.* Calcd. for $C_{17}H_{13}O_2NS$: N, 4.75. Found: N, 4.82.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

The Development of the Air-Driven Spinning Top as Transparent Ultracentrifuge

BY JAMES W. MCBAIN AND CARROLL M. O'SULLIVAN, S. J.

An ultracentrifuge is any centrifuge of low or high power in which convection does not occur, and in which it is possible to measure any redistribution of the contents.[1] Up to last year, Svedberg alone had developed such convectionless ultracentrifuges. Further, the contents could be submitted to optical observation while in motion. Svedberg and his collaborators have extended their application from the largest respiratory proteins down to the smallest molecules in aqueous solution. To observe sedimentation equilibrium with the former, a very low power is obligatory since sedimentation outward must be exactly balanced by diffusion inward. For sedimentation equilibrium of ordinary molecules, powers ranging from 100,000 to 1,000,000 times gravity are essential. Still higher powers will be required for observing their sedimentation velocity.[2]

The remarkable results obtained at the Upsala laboratories in the last few years have made abundantly evident the important place the ultracentrifuge now occupies in chemical research. Unfortunately, the enormous cost of these elaborate high-powered machines has, up to now, necessarily confined them to one laboratory. The urgent need of a far less expensive type of ultracentrifuge, which would yet completely duplicate the achievements of those of Svedberg, impelled us to attempt during the past four years the task of developing the air-driven spinning top of Henriot and Huguenard[3] as a quantitative ultracentrifuge. One of us has elsewhere called attention to the almost unlimited possibilities in applying their original top to the study of systems which are inherently convectionless, such as jellies, curds and liquid crystals.

The essential features of the air-driven spinning top itself have already been sufficiently described in the literature.[3,4,5,6] The modifications that we have introduced in order to convert it into an ultracentrifuge and the auxiliary apparatus that we have used in the problem can all be discussed under seven heads: Stability, Speed, Transparent Rotor and Stator, Cell, Temperature Control, Light Source and Optical System.

Stability

Any form of vibration in an ultracentrifuge will tend to cause convection currents in the liquid under examination and make sedimentation difficult or impossible, according to the magnitude of the convection in relation to the strength of the restoring field. We found that the instability of the spinning top is of three kinds: precession, vertical vibration and horizontal wobble.

Precession is caused by an unlevel stator or by uneven propulsion (*e. g.*, a plugged air-port or nozzle), and is easily avoided by keeping the stator carefully leveled and by building into the manifold of the stator a very fine mesh strainer. For a stator with air-ports made with a number 73 drill (0.024″), we found a 100 mesh strainer works very well.

Vertical vibration has been treated fully by Girard and Chukri.[5] At high speeds the vacuum under the rotor becomes great enough to overcome the supporting effect of the exhausting air and cause the rotor momentarily to touch the stator. The phenomenon is periodic and produces a loud note of rather low frequency. It is eliminated by simply admitting a little atmospheric air to the space between the rotor and the stator through a valve connected to the apex of the cone of the stator. The method of adjustment is to open the valve rather too much at first, then, when the rotor has attained the desired speed, to close it slowly until the vibration just begins to be heard (or felt in the stator with the hand), at which point the valve is opened again very slightly. This adjustable arrangement is preferable to the uncontrolled opening lately adopted by Beams and his co-workers[4] because the admission of more air than is actually needed slightly reduces the speed and noticeably increases the horizontal wobble.

We have found it impossible to attach to the central air inlet a long tube of any description or a

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[1] The term is due to T. Svedberg who has carefully discussed its definition [*Ber.*, **67A**, 117 (1934)]. It has been used loosely by others.

[2] Only one such measurement has ever been recorded: J. W. McBain and C. M. O'Sullivan, THIS JOURNAL, **57**, 780 (1935), with mercuric chloride.

[3] Henriot and Huguenard, *Compt. rend.*, **180**, 1389 (1925); *J. Phys. Radium*, **8**, 433 (1927).

[4] Beams, *Rev. Sci. Inst.*, **1**, 667 (1930); Beams and Weed, *Science*, **74**, 44 (1931); Beams, *Phys. Rev.*, **A39**, 858 (1932); Beams, Weed and Pickels, *Science*, **78**, 2024 (1933); Pickels and Beams, *ibid.*, **81**, 342 (1935); *Rev. Sci. Instr.*, **6**, 299 (1935).

[5] Girard and Chukri, *Compt. rend.*, [5] **196** (1933).

[6] Garman, *Rev. Sci. Inst.*, **4**, 450 (1933).

short tube of soft rubber without causing excessive wobble. As will be described later, we have taken the air for the central air inlet out of the guard. The connecting tube is of glass, about 15 cm. long, and attached to the inlet by the shortest possible section of rubber tubing. The adjustment is made with a screw clamp on the tubing.

Horizontal wobble is the name we have given to that form of instability in which, while the axis of rotation remains perfectly vertical, the whole rotor moves horizontally in spasmodic jerks. The phenomenon is not periodic. It has two causes. The first results from the fact that the rotor, like any spinning top, rotates not on its center of figure but on its center of gravity. Since these centers do not, in general, coincide, the periphery of the rotor necessarily revolves eccentrically. If the stator is rigidly mounted, this eccentricity becomes cumulative, causing the rotor finally to touch the stator and leap out. If the stator is flexibly mounted it is able to follow the eccentric running of the rotor and the danger of the rotor's jumping out is eliminated. However, the customary slightly flexible stator mounting still leaves another horizontal wobble of smaller amplitude and higher frequency. We found that greatly increasing the flexibility of the stator mounting and reducing the mass of the stator and manifold as much as possible reduced the wobble to about 0.02 or 0.04 mm. (as measured with a low power microscope) a few times a second. The second cause of the horizontal wobble is turbulence in the exhausting air, which becomes quite noticeable when higher pressures and greater volumes of air are used. The turbulence may be eliminated by mounting on the stator (not on the guard) three vertical and radial metal strips which we have called the "baffle strips." Nearly filling the space between the walls of the guard and the sides of the rotor, they are adjusted to clear the sides of the rotor by about 1 mm. As long as they do not extend within the "boundary layer" of air carried by the rotor, which is a little less than 1 mm. thick, their effect on the speed of the rotor is negligible. For a rotor 37 mm. in diameter running in a stator having 12 air-ports made with a number 73 drill, the effect of the baffle strips on the stability was to make the horizontal wobble wholly imperceptible under the microscope at 50 lb. air pressure, and about 0.01 mm. in amplitude at 100 lb. pressure. At still higher pressures the wobble is proportionally greater.

Speed

Measuring the Speed.—Our method of measuring the speed of the rotors is to adjust the note made by a calibrated beat-frequency oscillator to zero-beat with the note made by the running rotor. In order to prove that the note made by the running rotor is quantitatively the same as its number of revolutions per second, and also as an auxiliary method for doubtful cases, we employ the following procedure. The top surface of the rotor is painted black half way around; light from outdoors or from a direct current lamp (flash light) is reflected from the rotor into a photoelectric cell; the resulting pulsating electric current is amplified to audible proportions, the output being connected to the same head-phones to which is connected the output of the beat-frequency oscillator. The amplitudes of both notes can be adjusted to equality, making it easy to bring the two notes to coincidence to within 0.1 beat per second. If the black paint on the top of the rotor is blended out at its edges so that there is really one point of maximum blackness and one point of maximum brightness with regions of gradual change between, the current in the photoelectric cell approximates a sine wave more closely, harmonics are suppressed and it is comparatively easy to select the correct octave of the note of the beat-frequency oscillator. If the correct octave is still doubtful, a mechanical stroboscope used once will settle the doubt permanently, especially if the rotor is marked in one spot only.

Increasing the Speed.—Contrary to first expectations, one cannot achieve unlimited rotational speed with an air-driven spinning top of given diameter by indefinitely increasing the air pressure, because the velocity of air flowing through an orifice quickly approaches a limiting value. For a compressible fluid flowing through a frictionless orifice of ideal design, the relation between the downstream velocity and the upstream and downstream pressures is given by the equation[7,8,9,10,11]

$$u_2 = \sqrt{2gp_1v_1\,[1 - (p_2/p_1)^{k-1/k}]\;k/k - 1}$$

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(7) Wm. Ripper, "Steam Engine Theory and Practice," Longmans, Green and Company, New York City, 1922.

(8) Walker, Lewis and McAdams, "Principles of Chemical Engineering," Chap. III, McGraw-Hill Book Co., Inc., New York City, 1927.

(9) Stodola, "Steam and Gas Turbines," McGraw-Hill Book Co., Inc., 1927.

(10) Ewald, Pöschl and Prandtl, "Physics of Solids and Fluids," Blackie and Son, London, 1930.

(11) Kearton, "Steam Turbine Theory and Design," Sir I. Pitman and Sons, 1931.

where u_2 = downstream velocity (upstream velocity is considered negligible), g = acceleration of gravity, k = ratio C_p/C_v for the gas in question, p_1 = the upstream pressure, p_2 = the downstream pressure and v_1 = the specific volume of the gas at the pressure p_1.

For dry air at 20° this equation reduces to

$$u_2 = 764\sqrt{1 - (p_2/p_1)^{0.288}} \text{ meters per second}$$

If we take p_2 = 0.967 atm. (1 kg./sq. cm.) this equation gives the curve of Fig. 1. The curve shows that it is scarcely economical to use more than 14 kg./sq. cm. (200 lb. per sq. in.). As a matter of fact, we seldom use more than 100 lb. per sq. in. because of the increase in wobble at higher pressures.

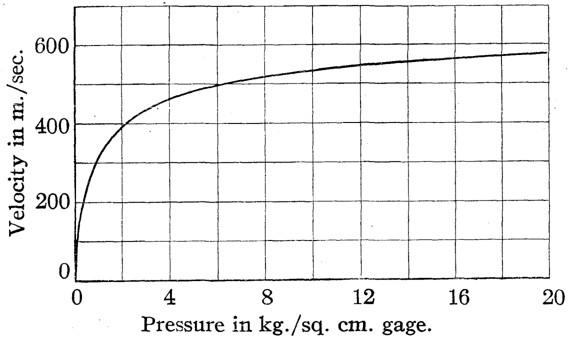

Fig. 1.—Theoretical velocity of air flowing through an ideal orifice as a function of the upstream pressure.

It will be noted from the above equations that the velocity of the air increases not only with increasing p_1 but also with decreasing p_2. We made one attempt to utilize this fact. An ordinary paper pill-box, larger in diameter than the rotor by about 4 mm., and having a hole cut in its bottom over which a glass disk was cemented to serve as a window, was inverted over a rotor while it was running and lightly fastened so that it could not turn. The box was pulled down to the top surface of the stator with great force by the escaping air until it was only a small fraction of a millimeter from it, indicating the establishment of a partial vacuum inside the box. Very low rotors ran about 8% faster inside the pill-box and with no observable instability under the microscope even at 100 lb. pressure. Higher rotors, even those only just high enough to take the lowest of our ultracentrifuge cells, refused to run at all. This, together with the fact that with all rotors there was a noticeable heating of the pill-box due to air friction, induced us temporarily to discontinue experimentation along this line.

The pressure, p_2, between the stator and the rotor can also be reduced and the velocity of the air through the air-ports correspondingly increased by increasing the ratio between the angle of the stator cone and the angle of the rotor cone. Unfortunately, this results in an increase in vertical vibration which can only be eliminated by permitting more air to enter through the central air inlet valve, which in turn increases horizontal wobble. We found the best values for these angles to be 100 to 102° for the rotor cone and 90° for the stator cone.

Since for a given pressure the velocity of the air through the air-ports is constant, it follows that the angular velocity of different rotors will be in inverse proportion to their diameters. For ease of experimentation we chose the comparatively large diameter of 37 mm.

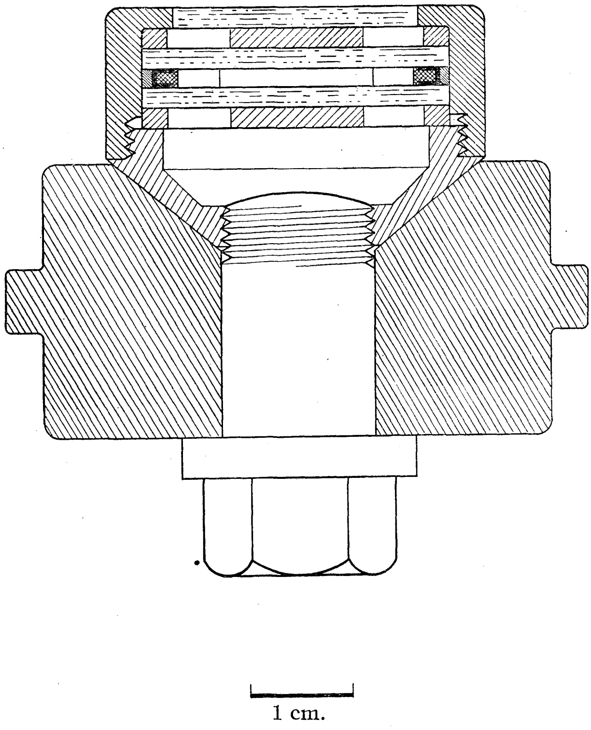

Fig. 2.—The first type of rotor described in the text (shown with the jig which is used to hold the cone of the rotor while the rotor is being assembled—a plumber's strap-wrench is used on the upper part).

Other factors in the design of the stator which affect the speed of the rotors are the total area of the cross sections of the air-ports (regulating the volume of air used), their shape and their orientation. Increasing beyond a certain point the volume of air used increases the horizontal wobble. We found that 12 air-ports 0.024″ in di-

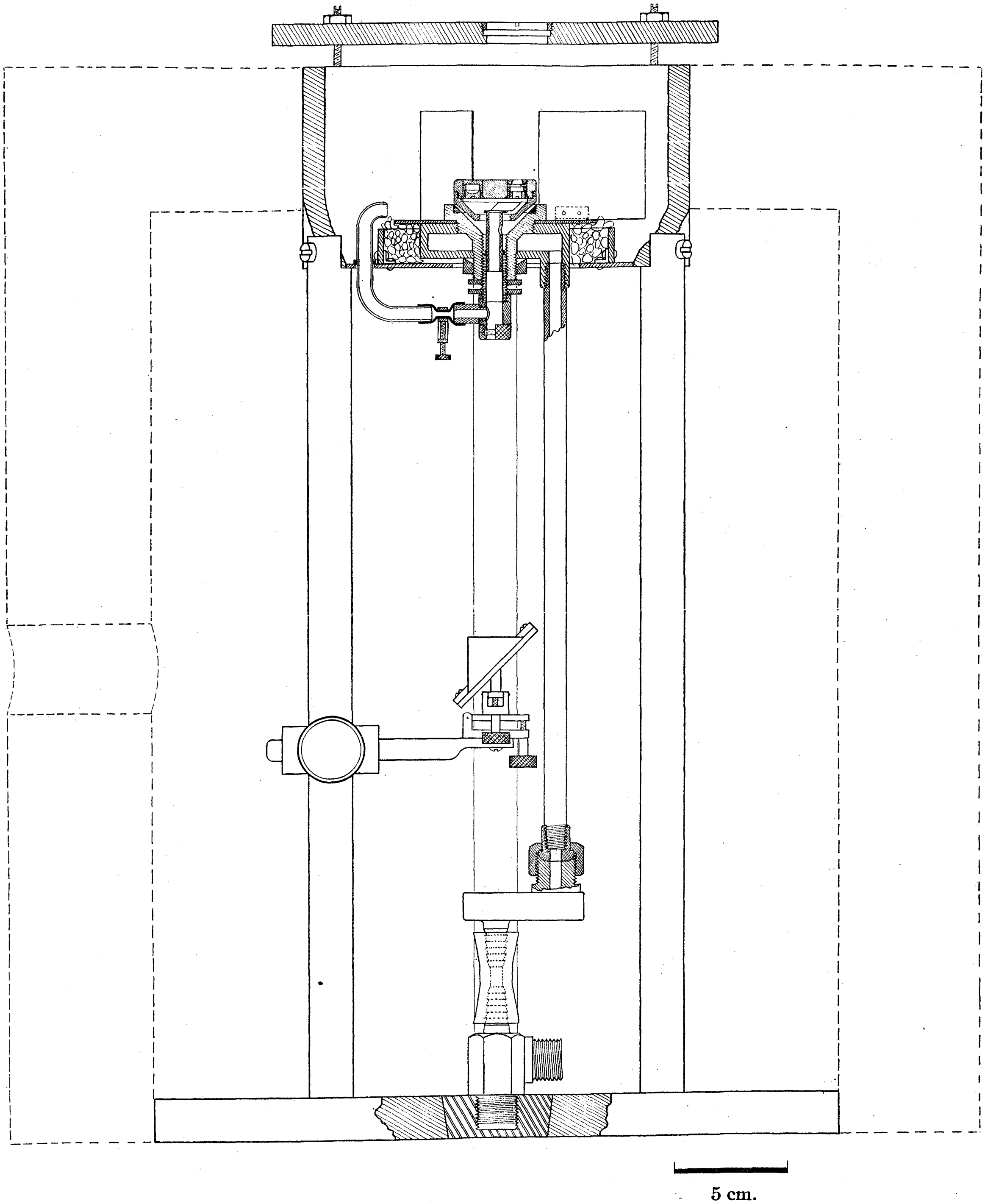

Fig. 3.—The complete assembly. The dashed lines indicate the position of the wool-filled insulating cover.

ameter (No. 73 drill) worked best for a 37-mm. stator.

Theoretically, the air-ports should be shaped like de Laval nozzles, their converging and diverging angles being calculated exactly for the actual conditions of operation. In practice we found that straight drill-hole nozzles, slightly beveled on the upstream side, gave the highest efficiency as far as speed was concerned. Assuming that the mean circle of impact on a 37-mm. rotor is 30 mm. in diameter and that the ratio of the peripheral velocity of the mean circle of impact

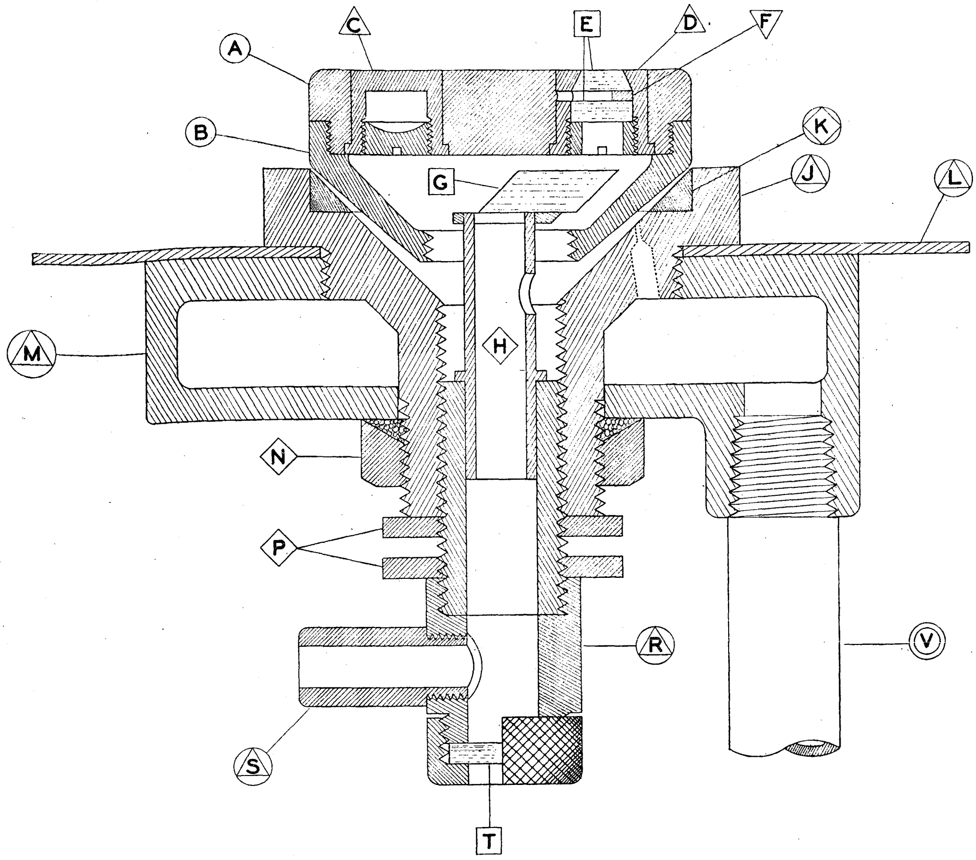

Fig. 4.—Details of rotor (second type described in text), stator, and periscope: A, cell-holder; B, rotor cone; C, dummy cell; D, cell; E, quartz disks; F, hard rubber separator, G, periscope prism; H, periscope tube; J, stator; K, bronze insert; L, disk to which baffle strips are fastened; M, manifold; N, packing nut; P, lock-nuts; R, holder for central air inlet and window; S, connection to central air inlet; T, window; V, high pressure supply tube. The symbols indicate the materials of construction: ○, Republic Steel Corporation's UMA 4, hardened and ground; △, Monel Metal; □, quartz; ▽, hard rubber; ◇, brass; ○△, duralumin (17ST); ⊙◇, bronze; ◎, aluminum.

to the velocity of the air is 1 to 2, the ratio of maximum energy transfer (this neglects the angle the air-jets make with the tangent plane), then a stator with straight drill-hole nozzles has an efficiency of 85%, whereas a stator with nozzles having a divergence of 3° beyond the throat had an efficiency of 71% and a stator with nozzles having a divergence of 6° had an efficiency of only 54%.

The optimum orientation of the air-ports was studied by Garman.[6] Their orientation can be described by two angles, the angle with the horizontal and the angle with a vertical plane through the center of the outlet of the air-port and the axis of the stator. In conformity with our experience, the first should be 35°. For the second we have adopted Garman's value of 65°.

A final and rather obvious factor influencing the speed of the rotors is their skin resistance. To reduce this to a minimum, the rotors must be made as low as possible, be free from anything like eccentric open holes or radial slots and must be highly polished. These features will be noted in the rotors to be described later.

The best material for the construction of the rotors is a high tensile strength alloy tool steel. We have finally adopted Republic Steel Corporation's UMA 4, a chrome–manganese alloy steel. If oil-quenched from 1525°F. and drawn at 600°F., it attains an ultimate tensile strength of 250,000 lb./sq. in. and a yield point of nearly 220,000 lb./sq. in. As the highest speed we have ever attained with a rotor as large as 37 mm. is 3000 r. p. s., and as the stress in a thin steel ring (the shape experiencing maximum stress under rotation) rotating at that speed is only about 130,000

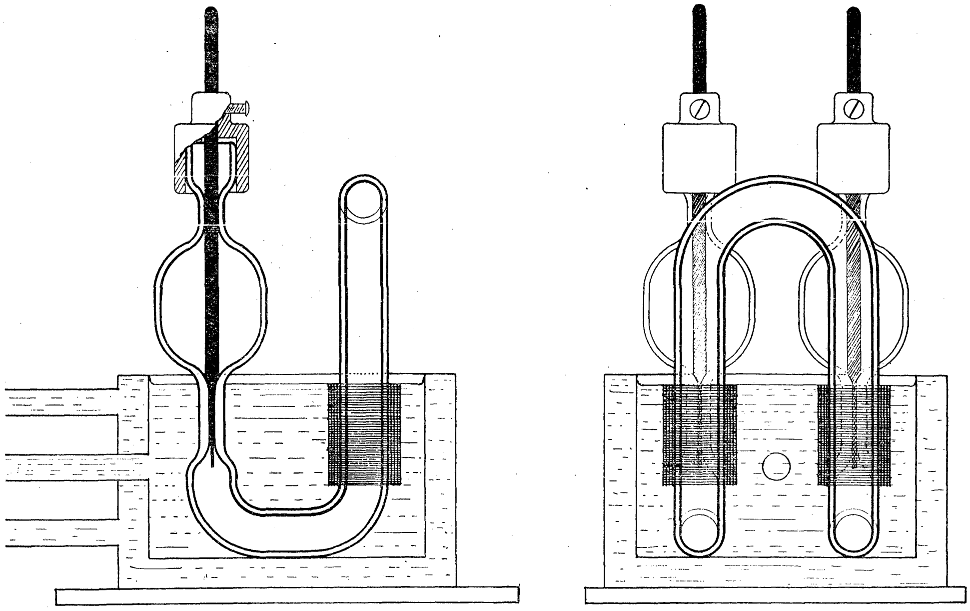

Fig. 5.—Modified Forbes quartz high pressure mercury arc.

lb./sq. in., it is better to draw the steel at 850°F. This gives a tensile strength of about 200,000 and a yield point of about 175,000 lb./sq. in. and an increased resistance to shock. Duralumin, despite the fact that it is nearly three times lighter than steel, compares unfavorably with the alloy steels. The strongest of the wrought Duralumin alloys is 17ST, with an ultimate tensile strength of 58,000 and a yield point of 35,000 lb./sq. in. Its density is 2.79 which is about 0.354 the density of steel. Thus its *effective* tensile strength in the centrifuge in terms of steel is 58,000/0.354 = 163,500 lb./sq. in.

Controlling the Speed.—For any given set of experimental conditions the speed of the rotor is a function only of the air pressure. Hence the attainment of the speed constancy so important in an ultracentrifuge is merely a matter of achieving constant air pressure.[12] Our method is to employ two tanks with a reducing valve between them. A General Electric Co. pressure control switch starts the compressor (a Rix two-stage water-cooled compressor) when the pressure in the first tank falls to 500 lb. and stops it when the pressure reaches 550 lb. The reducing valve, a Fisher Pressure Governor,[13] pilot operated, keeps the second tank at 400 lb. The accuracy of the Fisher valve varies with the load. Under the usual load, the variation of the second tank is ± 0.5 lb., the "hunting" having a period of about five minutes. Under some loads the variation may be as much as ±2 lb., or as little as ±0.05 lb. As a usual operating pressure is 100 lb., the variation of the second tank is reduced to one-fourth at the throttle valve. Furthermore, the pressure–speed curve is already rather flat at 100 lb. so that the final effect on the rotor speed is slight. By setting the beat-frequency oscillator to zero beat with the rotor's note, listening to it for some time and measuring the frequency of the beat note that gradually appears, one can measure exactly the constancy of the rotor speed. The variation is generally much less than 0.1%.

Transparent Rotor and Stator

Two types of transparent rotors were developed. Each consists of two parts, the upper, cylindrical part, containing the cell for the liquid, and the lower, conical part which is the air-turbine proper. In both types the lower part is truncated and hollow and has a 13-mm. threaded hole through the truncated bottom. When the rotor is running, a stationary periscope projects up through the hole into the hollow rotating cone. The head of the periscope is a single quartz prism[14] whose cross section at right angles to the light

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[12] W. R. Hewlett of the Electrical Engineering Department at Stanford University has found definite indication that even with varying air pressure the speed may be held constant by means of synchronous impulses applied to a magnet or probably to laminations carried in the rotor.

[13] Supplied by the Fisher Governor Company, Los Angeles.

[14] We are indebted to the Fred C. Henson Company, Pasadena, Calif., for the care and precision with which crystalline quartz of best optical quality cut so as to be singly refracting has been supplied for all our optical equipment.

beam is a square 4 mm. on a side, and whose cross section parallel to the light beam is a 45° rhomboid with an over-all length of 13.5 mm. The purpose of the periscope is to offset a distance of 9.5 mm. the light beam which comes up through the center of the stator, 9.5 mm. being the distance from the center of the rotor to the average radius of the liquid column in the cell. The head of the periscope has a minimum clearance of 2 mm. inside the hollow cone of the rotor. The presence or absence of the periscope has only a very minute effect on the speed and temperature of the rotor, provided the under side of the upper half of the rotor is smooth. This is insured by inserting a disk of celluloid between the halves (or a disk of cellophane when light of $\lambda < 3000$ Å. is used). An additional advantage of this disk will be described later.

The stator extends entirely through the manifold, being made pressure tight below with a packing nut. This part of the stator is cylindrical and is threaded inside as well as outside. Into it screws a short brass tube, furnished with a lock nut, into which tube, in turn, drops the periscope tube from above with a smooth sliding fit. The periscope tube has a shoulder part way down its side which rests on the top of the other tube, and a key-way which engages a pin near the top of the other tube. The pin determines the orientation of the periscope. The orientation and the height of the periscope can be adjusted by loosening the lock nut on the other tube. The periscope tube has a hole in its side just under the quartz prism to permit the entrance of air to the space between the rotor and stator from the central air inlet valve, as described before. To the other end of the tube into which the periscope tube drops is screwed a Duralumin tube having the central air inlet valve in its side and a small quartz window at the bottom.

The hole in the bottom of the rotor is large enough to permit the passage of the head of the periscope when the periscope is lifted a little and the rotor is tipped slightly to one side.

Below the window in the bottom of the stator a right-angled reflecting quartz prism is attached to one of the legs of the guard by means of an adjustable mounting. The high pressure supply to the manifold is offset, so as to clear the reflecting prism. A high degree of flexibility in the high pressure supply is achieved by making the metal tube attached to the manifold very long, bringing it back to the center line below the reflecting prism, and attaching it to the pressure supply nipple at the base by a very short section of $^1/_4''$ high pressure hose (Linde). The hose is made very short to reduce to a negligible amount the contraction of the hose due to increase in pressure. The manifold is kept centered by the rubber sponge which surrounds it to damp out vibrations.

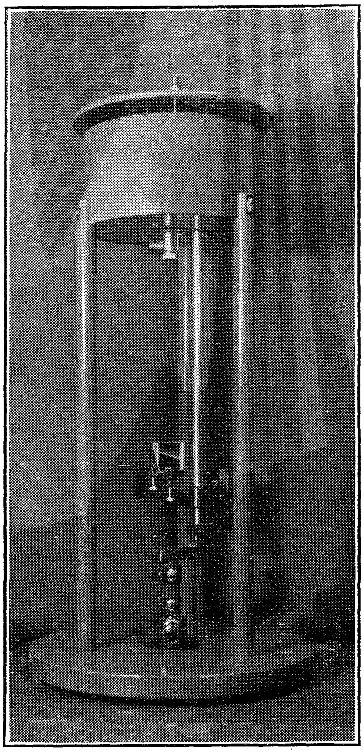

Fig. 6.—The assembly shown in Fig. 3.

Cells

In the first type of transparent rotor the cell is composed of two quartz disks 30 mm. in diameter and 2 mm. thick, fitting into a steel shell which screws on the lower part of the rotor. The liquid is confined between the disks by a special rubber seal made as follows. A 5-mm. slice of a finger of a rubber glove is stretched over the edge of a hard rubber ring 27 mm. outside diameter and 15 mm. inside diameter and about 1.1 mm. thick. The hard rubber ring has four 12° radial slots 4 mm. long cut in it from the inner circumference toward the outer. Outside the hard rubber ring with the soft rubber gasket stretched over its edge is placed an annealed brass ring 30 mm. outside diameter, 28 mm. inside diameter and 1.8 mm. thick. Several brass rings differing in thickness from 1.4 to 1.9 mm. are kept on hand to accommodate different thicknesses of rubber glove. When this assembly is placed between the two quartz disks, (about) three drops of liquid added, and the whole spun in the centrifuge, the hydrostatic pressure of the liquid expands the soft rubber against the quartz above and below and against the brass on the outside, forming a seal that only improves with increasing speed.

At first the brass ring was not used outside the seal. Instead the other parts were made a little larger in diameter and the rubber was allowed to expand against the steel wall of the rotor. Blowouts were frequent because the quartz disks were not perfectly round, because some disks did not fit the rotor exactly, and because the steel of the rotor, being under a stress nine times greater than the stress in the quartz, expanded more than the quartz. The brass ring eliminated these troubles.

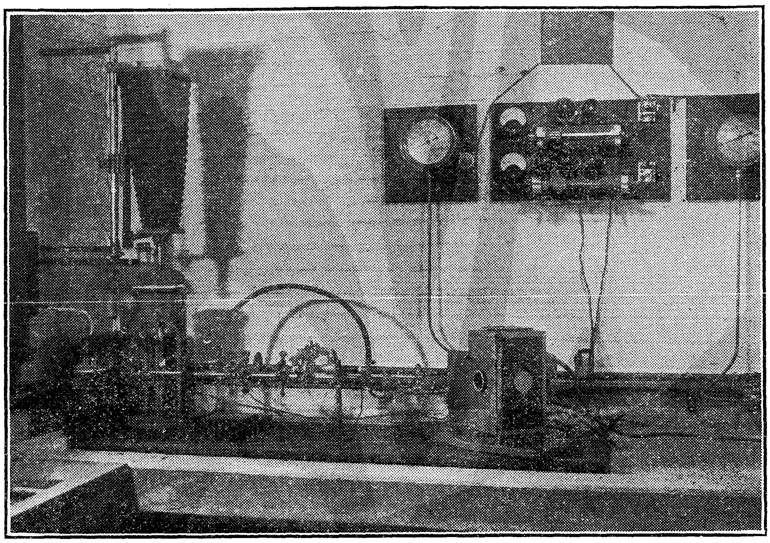

Fig. 7.—The complete centrifuge and optical system before the wool-filled cover and the thermostat for the driving air had been adopted.

To help the quartz disks bear the hydrostatic pressure of the liquid, two steel disks, 30 mm. in diameter and 2 mm. thick, and having four holes each, 6 mm. in diameter, 90° apart and 9.5 mm. from center of disk, are added, one above the upper quartz and one below the lower. The four holes in each disk are aligned with the four slots in the hard rubber ring. The lower steel disk has two pins which engage slots in the steel rotor cover and keep the assembly aligned while the rotor is being screwed together. To eliminate the air friction of the holes in the steel disk, the upper is covered with a 25-mm. disk of quartz and the lower with a 30-mm. disk of celluloid (or cellophane). The addition of these steel disks increases over 30% the speed at which the quartz disks break, giving over a 70% increase in centrifugal acceleration.

Various treatments were tried on the quartz and glass disks in an effort to increase their strength. By far the most successful was the following: besides the plane faces of the disks, their cylindrical sides were also optically polished and the edges formed by the plane faces and the cylindrical sides were slightly rounded and optically polished. Thus the disks were optically polished all over. This made an additional increase in the speed at which they broke of nearly 50%, or an increase in the acceleration of nearly 125%. Thirty-millimeter crystalline quartz disks so polished and supported against hydrostatic pressure by the two steel disks should spin 3000 r. p. s. without breaking (maximum 540,000 times gravity). Despite that fact, however, this type of cell cannot be safely used above 1500 r. p. s. No matter how carefully the quartz disks are handled, it seems impossible to avoid scratching them slightly, thus lowering their breaking speed enormously. Disks that have made many runs at 2500 r. p. s. will unexpectedly burst at 1700 r. p. s. Disk failures are costly because they generally cause the loss of the periscope also. Even at 1500 r. p. s. the factor of safety is low.

The second type of cell is somewhat similar to the cells in Svedberg's latest oil-turbine ultracentrifuges. The upper half of the rotor is a solid steel cylinder 37 mm. in diameter and 8.2 mm. high. Near the bottom it is reduced in diameter and threaded to screw into the rotor cone. The steel cylinder has two vertical holes on a diameter, each 8.6 mm. in diameter and 10 mm. from its center to the center of the cylinder. Into these are pushed from below two monel metal tubes, each of which has a flange 0.5 mm. wide which fits into a recess in the bottom of the large steel cylinder. When pushed all the way in, the tubes are flush with the upper and lower surfaces of the steel cylinder. One of the monel tubes (the dummy) is solid on the upper end and closed on the lower end with a brass screw whose weight is adjusted until the tubes balance. The other monel tube contains the cell, which is composed of seven parts: a slotted hard rubber separator, two thin soft rubber gaskets, two quartz disks, a brass washer and a hollow screw which keeps the assembly under pressure. The hard rubber separator is 6 mm. in diameter and 1 mm. thick. The 6° radial slot which forms the cell proper is 4 mm. long, cut in from the side toward the center of the rotor. The soft rubber gaskets which go between the separator and the quartz windows are cut from very thin sheet rubber to the shape and size of the separator, except that the slot must be a little larger to prevent the soft rubber from being pressed out into the slot in the hard rubber. The upper quartz disk is a truncated cone, 2 mm. thick, its upper diameter being 4 mm., its lower 6 mm. The top 2 mm. of the monel tube is tapered to fit the quartz cone so that the quartz, the monel and the steel are all quite flush on top. The lower quartz disk is a cylinder 2 mm. thick and 6 mm. in diameter. The brass washer is very thin and goes between the lower quartz disk and the hollow screw. In assembling the cell, pressure is applied to the parts by an external press. The office of the hollow screw is merely to maintain this pressure. The liquid is introduced into the cell through a small hole in the side of the monel tube opposite the end of the slot in the hard rubber separator. The liquid is covered with a small amount of pure paraffin oil to prevent evaporation. The cell is quickly taken apart for cleaning and reassembled. No trouble has ever been experienced from leaking, or from breaking of the quartz disk. This rotor, being lower than the previous type, runs 17% faster.

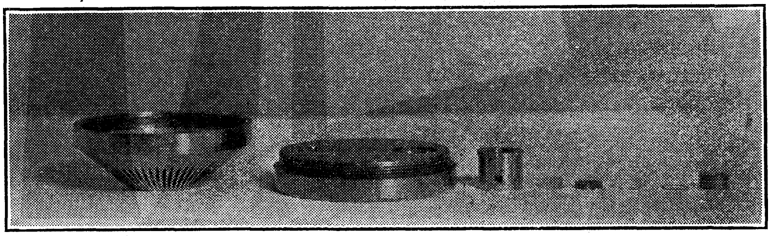

Fig. 8.—The second type rotor apart. From left to right the parts are: the rotor cone, the cell-holder, the shell of the cell, the upper (conical) quartz window, the hard rubber separator with the sectorial slot, the lower (cylindrical) quartz window, the brass washer and the hollow screw.

Temperature Control

In order to determine approximately the temperature of the two walls of the cell, three copper–constantan thermocouples are used. The cold junctions are kept at 0°. One hot junction is suspended directly over the center of the top surface of the spinning rotor, about 0.5 mm. above it. A second hot junction is mounted inside the hollow cone of the rotor, as close as possible to the center of the under side of the upper half of the rotor. Its leads enter through the wall of the stator inside a glass tube about 1 mm. in outside diameter. The glass tube then runs up alongside the periscope tube but without touching it. The third hot junction gives the temperature of the stator.

If the air used to spin the rotor is allowed to expand from room temperature, it will be found that when the rotor is being run at 100 lb. pressure the air in contact with the top of the rotor is about five degrees warmer than the air inside the hollow cone, and about seven degrees warmer than the stator. Such a temperature gradient between the two walls of the cell would cause convection currents and make sedimentation impossible. We eliminate the temperature gradient in the following way. To protect the top of the rotor from the slowly descending current of room air caused by the expanding exhaust, the guard is covered with an asbestos lined metal plate having a quartz window directly over the part of the rotor to be photographed. The plate rests on three screws which raise it about 10 mm. above the top edge of the guard. Less clearance causes instability in the rotor. The high pressure supply is thermally insulated from the stand and guard at the only point where they come in contact, *viz.*, at the base, by a large Bakelite bushing. The stand and guard are further insulated from the room air by a thick hood filled with lamb's wool which slips over the whole assembly, its top being flush with the top edge of the guard.

The driving air is heated by being passed through a large coil of 9.5 mm. copper tubing immersed in a water thermostat. By varying the room temperature, or the temperature of the water thermostat, or the driving pressure (and therefore the speed), it is possible to bring the temperatures above and below the cell to exact equality and to hold them thus indefinitely with a variation of less than ± 0.1°. With the room at 26°, the driving pressure at 100 lb./sq. in. we find that the water thermostat should be at 27°. Only about 70 watts are required to maintain the driving air at this temperature. The air for the central air inlet is taken out of the guard to ensure constancy of temperature.

From the standpoint of uniformity of temperature, the second type of rotor described above has two decided advantages over the first type. (1) In the second type, the cell is as entirely surrounded by metal as the exigencies of transparency will permit. This tends to short-circuit any temperature gradient existing between the top and bottom of the cell. (2) When the disk of celluloid or cellophane is inserted between the halves of the rotor, a dead air space 3 mm. high and 4 mm. in diameter is formed immediately below the lower quartz disk. This helps to insulate the quartz from temperature fluctuations in the cone of the rotor.

Light Source

The light source is a modified form of the high pressure mercury arc developed by Forbes and his collaborators.[15] The bridge placed by Forbes and Heidt between the mercury bulbs to permit the mercury transported to the cathode to flow back to the anode was found unnecessary.[16] If the bridge is omitted, the ionic transfer gradually raises the level of the cathode above the level of the water-bath until the mercury begins to boil. The boiling then compensates for the transfer and the arc reaches a steady state.

The opening used by the same authors for introducing the mercury into the quartz tube, a ground-in plug at the mid-point of the arc, was likewise found unnecessary.

Below each mercury bulb a short section of capillary tubing, about 1.6 mm. inside diameter, has been reintroduced. The electrodes are 3.2 mm. pure iron rods, slipping easily through the small tubing above the bulbs and turned down for part of their length to slip easily also through the capillary tubing below the bulbs. The shoulder on the iron rods where the two diameters meet is turned to a 45° angle and ground into the quartz with very fine carborundum. Across the face of the resulting valve is cut a single slot roughly 0.2 mm. wide and of the same depth. Heavy brass dust caps set-screwed to the top of the iron electrodes keep the valves seated during operation of the arc but permit them to open when the arc is started. The slots permit the pressure in the arc to remain atmospheric. The part of the iron electrodes having the smaller diameter must be long enough to extend entirely through the capillaries to prevent arcing therein.

The water-bath is double, a static bath of distilled water immediately surrounding the arc, and another of circulating tap water outside the first. The constancy of the level of the water-bath is extremely important in maintaining constant intensity. A constant drip and overflow device, situated at a distance from the lamp-house, proved most satisfactory. The water around the quartz tube tends to boil at the surface. It was found advantageous to surround each leg of the tube with several loose turns of copper gauze. This steadies the level of the water around the quartz by lowering the temperature at the surface.

A Weston photronic cell is mounted permanently in a water-cooled holder built into the transite lamp-house and protected from condensation from the water-bath by a Pyrex window. A 0 to 1.5 ma. milliammeter connected to the photronic cell gives a permanent check on the arc's intensity. With the above modifications the arc is as constant as the current source, a 550 volt d. c. motorgenerator whose variation is less than ±1%.

Optical System

The high intensity of the Forbes arc permits the use of a prism monochromator, a valuable asset for absorption photography. Starting from the arc, the optical system consists of a slit 0.3 mm. wide, a quartz collimating lens 5 cm. in diameter and 12 cm. focal length, a pair of 30° right-angled quartz prisms cut from the same crystal with the 60° angles in contact and 120° between the two hypotenuses, a focusing lens 5 cm. in diameter and 12 cm. focal length, a second slit (a hole 0.3 mm. in diameter), a second collimating lens 2 cm. in diameter and 4.8 cm. focal length, a right-angled reflecting quartz prism (directly under the center of the stator), the periscope, cell and camera lens. A fluorescent screen surrounding the second slit facilitates the selection of any line of the mercury arc.

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[15] Forbes and Harrison, *J. Opt. Soc. Am.*, **10**, 1 (1925); *ibid.*, **11**, 99 (1925); THIS JOURNAL, **47**, 2449 (1925); Forbes and Leighton, *J. Phys. Chem.*, **30**, 1628 (1926); *J. Opt. Soc. Am.*, **12**, 58 (1926); Forbes and Heidt, THIS JOURNAL, **53**, 4349 (1931).

[16] Unpublished work of Dr. Philip A. Leighton and collaborators.

Stage of Development

An idea of the range of usefulness of the machine in the present state of its development can be gained from the following. Without heating the air or attempting in any way to control the natural temperature gradient existing in the rotor, the second type of rotor herein described sedimented at every trial such heavy molecules as the respiratory protein of the earthworm (5% solution; 1% in potassium chloride).[17] With the first crude air heating arrangement tried (manually adjusted electric heater inside the air supply tubing) which enabled us to keep the temperatures above and below the cell at the same value to within ± 0.3°, the same rotor easily sedimented molecules as small as the hemp seed protein edestin (molecular weight about 208,000). With the driving air arbitrarily thermostated to within ±0.02° and the room temperature controlled, the same rotor will sometimes sediment molecules as small as purified egg albumin (molecular weight about 35,000).

More remains to be done before the instrument is uniformly reliable for the smallest molecules. The authors are confident that once the exact relations between the temperatures recorded by the thermocouples and the temperatures of the cell walls have been determined, the problem will have been solved completely, for it is comparatively easy to maintain any desired temperature gradient between the air above and below the cell. Devices are contemplated which promise to make the temperature of the air above, within and below the rotor, wholly independent of the room temperature.[18]

Summary

1. The air-driven spinning top has been developed as a transparent convectionless ultracentrifuge.
2. The three types of instability of the air-driven rotor are described, with their causes and remedies.
3. Means are given for measuring, increasing and controlling the speed of the top, with a discussion of the best materials of construction.
4. Spinning top centrifuges are described in which it is possible to photograph the cell by transmitted light of any monochromatic wave length, visible or ultraviolet.
5. Two different types of cells are described.
6. Means are discussed for measuring and controlling the temperature gradient existing between the top and bottom of the cell.
7. The present stage of the development of the instrument is described.

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[17] The best average value we have obtained for this protein (uncorrected for viscosity and density) is $s = 61.8 \times 10^{-13}$. The value of 72×10^{-13} published by us in THIS JOURNAL, **57**, 780 (1935), proved to be exceptionally high.

[18] Mr. H. J. Fouts in this Laboratory has since found that in order fully to equalize the temperature inside the rotor with the temperature of the slip stream from the driving air (on account of the friction caused by the periscope upon the air within the rotor) it is advisable to draw the air entering the periscope, as well as the air playing upon the top of the rotor, through a much colder thermostat, instead of taking it from the guard ring as described above.

STANFORD UNIVERSITY, CALIF. RECEIVED AUGUST 5, 1935

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

The Photochemical Decomposition of Nitric Oxide[1]

BY PAUL J. FLORY AND HERRICK L. JOHNSTON

Berthelot[2] observed that nitric oxide decomposed when irradiated with light from the quartz mercury arc and concluded that nitrogen and oxygen are the final products of the decomposition. Macdonald,[3] as part of his investigation of the nitrous oxide decomposition, made a brief study of the decomposition of nitric oxide under irradiation from the aluminum spark, between pressures of 50 and 650 mm. He observed that the rate seemed to depend entirely upon the amount of light absorbed and reported a quantum yield of 0.75. He interpreted his data in terms of a primary mechanism of activation. Noyes[4] found good evidence for the decomposition of nitric oxide through the agency of excited mercury atoms. Under the conditions of his experiments he observed no appreciable amount of direct photochemical reaction.

We have investigated the photochemical decomposition of nitric oxide both with the mercury arc and with sparks between various metal elec-

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[1] Presented before the Division of Physical and Inorganic Chemistry at the Cleveland Meeting of the American Chemical Society, Sept., 1934.

[2] Berthelot, *Compt. rend.*, **150**, 1517 (1910).

[3] Macdonald, *J. Chem. Soc.*, 1 (1928).

[4] W. A. Noyes, Jr., THIS JOURNAL, **53**, 514 (1931).

trodes, as sources of radiation, and over a pressure range from 0.02 to 7 mm. We have been successful in correlating the primary process, which proves to be an act of predissociation, with the absorption spectrum of the gas. This interpretation appears, also, to provide a better explanation than that given by Macdonald for the decomposition at the higher pressures.

Experimental

Reaction System.—The reaction system consisted of a cylindrical quartz cell, 75 mm. long by 25 mm. in diameter, with plane end windows. The cell was connected through a graded quartz to Pyrex seal, to a calibrated McLeod gage and to mercury cut-offs which communicated to a high vacuum system and to a preparation line. No stopcocks were contained in the reaction system.

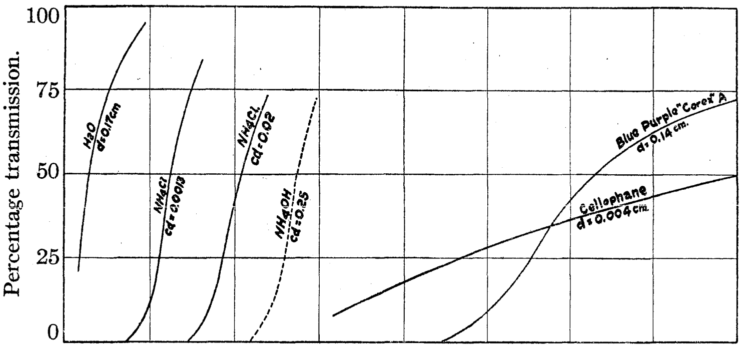

Fig. 1.—Absorption curves of filters (*d*, in centimeters; *c*, in moles per liter).

The reaction system was evacuated to a pressure of 10^{-6} mm. prior to each run, and was usually baked out during evacuation. Nitric oxide, prepared and purified by the method employed by Johnston and Giauque[5] was introduced to the desired pressure and the reaction followed by means of pressure measurements.

In some of the experiments a condenser-diaphragm manometer, similar to the one described by Olson and Hirst[6] was used.

Sources of Illumination.—Most of the experiments were done with a quartz mercury arc which was relatively weak in unreversed λ 2537 resonance radiation. A number of experiments were also made with condensed spark discharges between suitable metal electrodes. It was found necessary to electrically shield the cell, with a tin foil covering, to prevent decomposition under the influence of an induced field set up within the cell.

Filters.—Filters were used to locate the active regions of the spectrum. The absorption characteristics of these filters are shown in Fig. 1. The curves for water and for aqueous ammonium chloride and the solid portion of the curve for ammonium hydroxide are constructed from the absorption data of Ley and Arends.[7] The dotted portion of the ammonium hydroxide curve was constructed from visual estimates obtained with a small ultraviolet fluorescing spectroscope, and is considered reliable to within 25 Å. The curves for cellophane[8] and for the Corex glass were determined by means of a Bausch and Lomb spectrograph equipped with a rotating sector comparator. An under-water spark was the source of continuous radiation.

To prevent photolysis the filter liquids were made to flow through a thin filter cell (one or two mm. liquid thickness) cemented to the reaction cell in such a way that the window of the latter formed one window of the filter cell.

Preliminary Observations

The Gage Reaction.—From considerations of stoichiometry alone nitrogen dioxide, nitrous oxide, nitrogen and oxygen are possibilities as ultimate products of the dissociation.[9] However, Macdonald[3] has shown that nitrous oxide is photochemically decomposed ten times as rapidly as nitric oxide while Norrish[10] has found that nitrogen dioxide is decomposed rapidly into nitric oxide and oxygen at wave lengths shorter than 4000 Å. The reverse thermal reaction is third order and it can be shown from the data of Bodenstein[11] that the rate of recombination of nitric oxide and oxygen is negligible at the pressures of our experiments.

From these considerations it would appear that nitrogen and oxygen should be the final products of the dissociation, regardless of the primary mechanism, and that the final and initial pressures should be equal. Contrary to this expectation preliminary experiments showed that the pressure decreased rapidly to less than one-half of the initial pressure (and went through a minimum at about $^1/_4P_0$).[12] Furthermore, the pressure in the reaction system rose slowly when the arc was shut off but dropped rapidly again, for a short period, when the cell was re-illuminated. As the result of several such alternate periods of light and of dark (*cf.* Fig. 2) the pressure eventually approaches a value which is very near to one-half of the initial pressure.

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[5] Johnston and Giauque, THIS JOURNAL, **51**, 3194 (1929).

[6] Olson and Hirst, *ibid.*, **51**, 2378 (1929).

[7] Ley and Arends, *Z. physik. Chem.*, **B6**, 243 (1929); **B17**, 177 (1932).

[8] The cellophane was placed between two pieces of quartz plate to protect it from the action of ozone. Although the cellophane did show some solarization the effect was not great.

[9] Nitrogen tetroxide and nitrogen trioxide may be excluded since at the low pressures of our experiments these molecules would, themselves, dissociate into the simpler oxides.

[10] Norrish, *J. Chem. Soc.*, 761 (1927).

[11] Bodenstein, *Z. Electrochem.*, **24**, 183 (1918).

[12] The position of the minimum is based on subsequently more careful measurements with the technique finally adopted (*cf. seq.*) for removing the accumulation of oxygen.

A clue to this behavior was found in the observation that a film was deposited on the mercury surface in the stem of the McLeod gage, which indicated that something was being removed from the reaction system during compressions in the gage. This indication was confirmed in a series of runs in which the McLeod gage was replaced by the diaphragm manometer. The results are shown graphically in Fig. 3, for several initial pressures. The broken curve, plotted to the same scale, is from data obtained with the McLeod gage and shows the true course of the decomposition. It is clear that our expectations regarding the constancy of pressure during the early course of the photochemical decomposition[13] are verified.

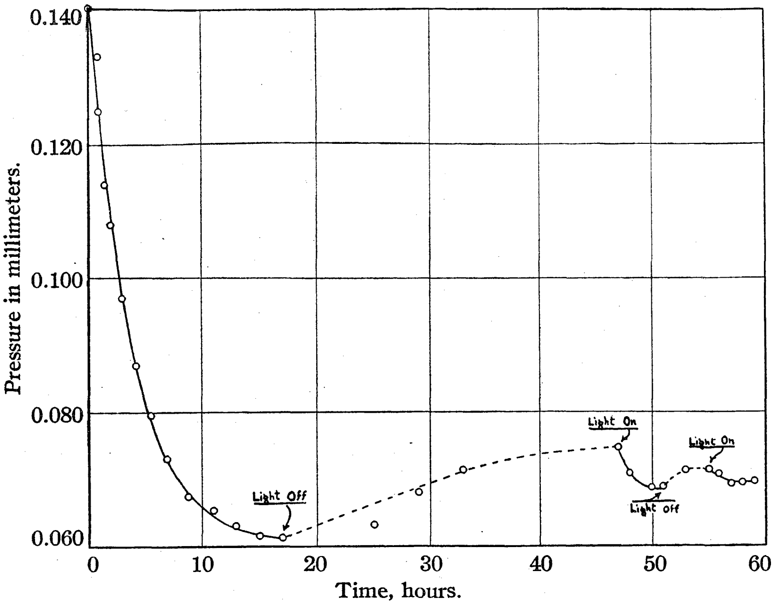

Fig. 2.—Anomalous behavior following the initial period of illumination.

Additional confirmation was obtained in later experiments with the McLeod gage, in which the reaction was allowed to continue for five or six hours without running up the gage. Pressures measured at the end of this period were about $^5/_6$ of the initial pressure, in good accord with the diaphragm gage curves.

The presence of liquid mercury, either on the walls of the connecting tubing or in the reaction cell itself, did not affect the results in either of these experiments.

We interpret this as evidence for the following series of reactions[14]

$$NO + h\nu = {}^1/_2N_2 + {}^1/_2O_2 \qquad (1)$$

$$NO + {}^1/_2O_2 = NO_2 \qquad (2)$$

$$Hg + NO_2 = HgNO_2 \qquad (3)$$

of which (2) and (3) occur only in the gage.

The increase in pressure after the illumination is shut off results from the slow, dark reaction

$$HgNO_2 = HgO + NO \qquad (4)$$

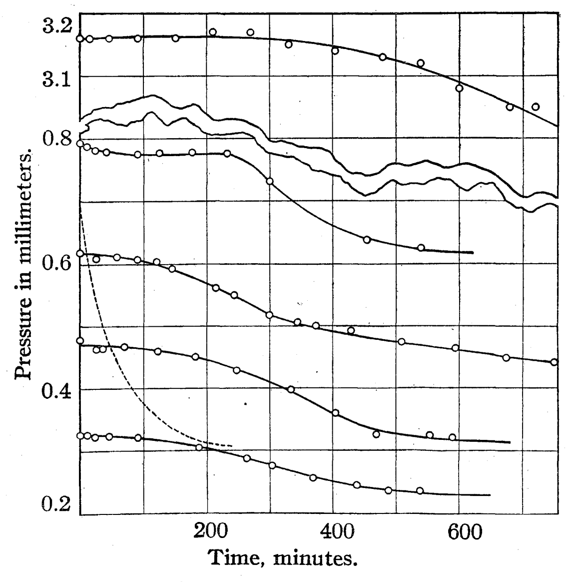

Fig. 3.—Experiments with the membrane manometer; – – – – –, decomposition curve measured with the McLeod gage.

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(13) The marked pressure drop which comes two hours or more after the reaction is initiated is interesting although it appears to be irrelevant to the subject of our investigation since it comes *after* the decomposition of the nitric oxide is ended (comparison with the broken curve). This fact itself is significant since it seems to indicate that the change which produces the decrease in pressure is either prevented, or compensated, through the agency of nitric oxide. It also appears that the change is produced through the action of light, or of excited mercury, on oxygen since we were able to duplicate the pressure decrease, to the correct order of magnitude, with the cell filled with *oxygen alone*. In this experiment the oxygen pressure decreased to about $^3/_4\ P_0$ in seven and one-half hours and was still falling.

Experiments in which a Blue Purple Corex A filter, which prevented decomposition of the nitric oxide, was placed in the path of the radiant energy prevented the appearance of this delayed pressure drop.

The presence of a yellowish-brown deposit (probably mercuric oxide) on the cell window and on the walls for a few millimeters back from the window provided evidence for some reaction, either of oxygen or of ozone, with excited mercury. There is probably some relation between these results and those observed by Neujmin and Popov [*Z. physik. Chem.*, **B27**, 15 (1934)] for illumination of oxygen with light of wave length shorter than λ 1750 but we did not investigate the reaction further.

(14) We refer here only to the stoichiometrical equations for the successive steps. The arguments advanced against the nonoccurrence of (2) in the reaction cell do not apply to the gage, where the pressure reaches 200 millimeters during the compression. Our data do not permit us to assign the formula $HgNO_2$ with certainty although (*cf. seq.*) they do indicate that the nitrogen/oxygen ratio in the compound is very close to $^1/_2$.

This proves to be a first order reaction, as shown in Fig. 5, with a rate constant of 1.5 × 10^{-2} per hour. This figure is based on data obtained in a run, illustrated in Fig. 4, which was taken primarily to study this phase of the process. P_∞ represents the limiting pressure to which the curve of Fig. 4 (dark reaction) extrapolates asymptotically and is indicated in that figure.

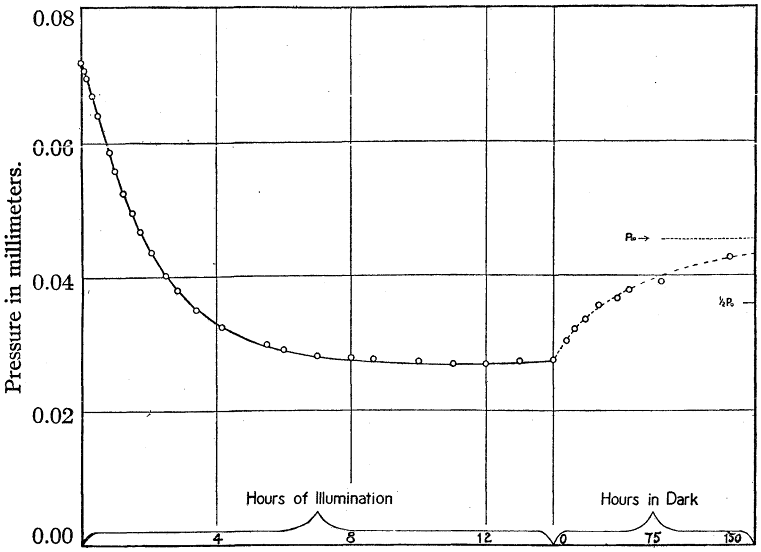

Fig. 4.—Course of a single run, showing the final dark reaction.

Although the reactions which occur in the McLeod gage may appear to be an encumbrance to the study of the photochemical reaction, they actually are an aid since it becomes possible to follow the reaction by measurements of pressure. The expedient was adopted, in all of our later, more careful, quantitative work, of compressing the gas in the gage to a pressure of 200 mm. or more every five minutes, whether pressure readings were wanted or not. Since the gage constituted about 75% of the total volume of the reaction system three-fourths of the accumulated oxygen was thus removed every five minutes. Preliminary trials showed that compression for a period of thirty seconds was more than ample time to remove the oxygen from the gas, and also that the rate of diffusion was sufficient to accomplish removal of the accumulated oxygen by this procedure.

Elimination of Photosensitization as a Mechanism for the Decomposition.—The absence of a mercury sensitized step in the decomposition, under the conditions which pertained to our experiments, was proved by three independent tests.

(1) A mercury vapor filter formed by placing a drop of mercury in the side-arm of an evacuated and baked quartz cell 4.5 cm. long, did not reduce the reaction rate by more than was to be expected for the introduction of two quartz windows into the light path.

(2) The use of a Blue Purple Corex A filter which cuts off the radiation completely below λ 2300 but shows 70% transmission of λ 2537 (*cf.* Fig. 1) reduced the rate to 1.3% of its value without the filter. A similar experiment with a cellophane filter, which cuts out radiation below about λ 2200 but is 45% transparent to λ 2537, reduced the rate to about 1% of its value without the filter.

(3) Insertion of a U-tube cooled with a dry ice–chloroform–carbon tetrachloride bath between the quartz cell (previously baked out thoroughly) and the rest of the reaction system, to keep the cell free of mercury vapor, had no effect on the rate of reaction.

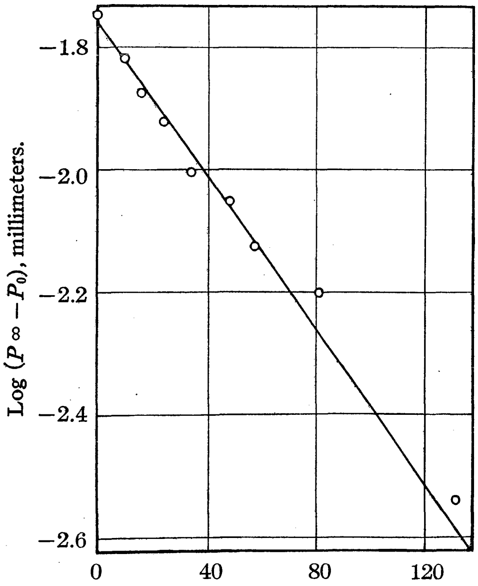

Fig. 5.—The first order gage reaction.

We conclude that the reactions, in our experiments, are at least 98% non-sensitized.[15]

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[15] Our results in no wise contradict those of Noyes (Ref. 4) who reported a mercury sensitized reaction with negligible photochemical reaction. Noyes used a water-cooled arc which doubtless gave a high intensity of λ 2537 while the cooling water, if tap water were used, must have removed almost all of the radiation which we find to be effective for the photochemical process. Our own air-cooled arc

Dependence on Light Intensity.—The influence of the light intensity on the rate of nitric oxide decomposition was determined by the use of calibrated wire screens[16] placed in the light path.

The results of these experiments, with three different screens, are shown in Table I. These runs were all made at about 0.12 mm. initial pressure, which falls in the region (*cf. seq.*) where, for a given light intensity, the percentage decomposition is a function of time and almost independent of the pressure. "t" and "t_0" refer to the times required for the recorded percentage changes in pressure, with and without the screens in the light path, respectively. The last column in the table is obtained from the screen calibrations.

TABLE I

DEPENDENCE OF REACTION RATE ON LIGHT INTENSITY

Screen no.	Change in pressure, %	t, min.	t (min.	t_0/t	I/I_0
1	11.1	30	19.8	0.66	0.681
	16.9	50	31.6	.63	
2	8.9	40	15.6	.39	.361
	12.7	60	22.8	.38	
	19.1	100	36.4	.364	
3	7.5	150	15	.10	.13

The Primary Process

Influence of Pressure on the Rate of Reaction.—In order to obtain information as to the general character of the primary process the dependence of reaction velocity on the pressure of nitric oxide was determined for a series of pressures varying between 0.02 and about 7 mm. So as to minimize the possible influence of the decomposition products on the reaction velocity, the comparisons were made between the *initial* rates of decomposition. The values of $(dP/dt)_0$ for the several individual runs are recorded in Table II, in which the third column gives the probable error in the several determinations, as deduced from a consideration of the accuracy of the McLeod gage, the completeness of oxygen removal, etc.

TABLE II

VARIATION OF REACTION RATE WITH PRESSURE

Initial pressure P_0, mm.	$(dP/dT)_0$, mm./min.	% Error	$\left(\frac{d \ln P}{dt}\right)_0$ Obsd.	Calcd.
0.0215	1.12×10^{-4}	6	5.2×10^{-3}	5.22×10^{-3}
.0428	2.40	4	5.6	5.16
.0677	3.58	2.5	5.28	5.06
.0907	4.54	2	5.00	4.98
.1258	6.14	2	4.88	4.86
.1258	6.00	2	4.76	4.86
.1315	6.50	2	4.94	4.84
.1354	6.72	2	4.96	4.84
.1990	9.4	2	4.72	4.62
.235	10.7	2	4.52	4.52
.306	13.6	2	4.44	4.30
.467	19.4	2	4.12	3.88
.694	22.6	2	3.26	3.36
.977	26.8	2	2.74	2.86
2.24	36.8	3	1.64	1.58
4.37	39	4	0.90	0.84
7.12	44	4	.62	.51

The table indicates that, for very low pressures, $(dP/dt)_0$ is about linear with the pressure and, at high pressures, approaches a constant value. This behavior, together with the linear relationship between rate and light intensity (Table I), suggests at once that the main factor in determining the rate may be the amount of light absorbed. This suggestion is confirmed by the agreement of the experimental values for $(d \ln P/dt)_0$ in column four with those, in column five, which are calculated from the relationship

$$\left(\frac{d \ln P}{dt}\right)_0 = -3/2\, k a I_0 \left(\frac{1 - e^{-aP_0}}{a P_0}\right) \qquad (8)$$

which is derived[17] on the assumption that the decomposition rate is directly proportional to the rate of light absorption and that the absorption of effective radiation obeys Beer's law. The fit is

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gave out very little unreversed radiation of λ 2537, due largely to self reversal in the arc, and accounts for our low mercury sensitized yield. Subsequent experiments with the same arc operated under conditions that very greatly increased the output of λ 2537 resonance radiation gave evidence of a very considerable mercury sensitized reaction.

(16) Forbes, *J. Phys. Chem.*, **32**, 482 (1928).

(17) Here, k is a constant in which is incorporated the quantum yield and the relation of the pressure decrease to the number of molecules which disappear in unit time; I_0 is the intensity of the incident light of effective wave length and a is its absorption coefficient which includes the fixed length of light path applicable to our experiment. P_0 is the initial pressure.

The derivation is as follows.

$$dP/dt = dP_{NO}/dt + dP_{N_2}/dt \qquad (5)$$
$$= -3/2\, kI_{abs} + k_4A \qquad (6)$$

by the stoichiometry of equations 1–3. Here A represents the pressure equivalent of the NO withdrawn by equation (3) and k_4 is the first order velocity constant of reaction (4).

Introduction of Beer's law gives

$$dP/dt = -\,3/2\, kI_0\,(1 - e^{-aP_{NO}}) + k_4A \qquad (7)$$

which reduces, in the limit of $(t = 0)$, to equation (8) above.

The several factors $3/2kaI_0$ were constant under the experimental conditions which we employed and were evaluated collectively, by extrapolation of the experimental values of $(d \ln P/dt)_0$ (*cf.* Fig. 6) to zero pressure. In this limit the quantity in parenthesis, on the right of equation (8), becomes unity.

The values in the fifth column of Table II were then computed through the choice of an arbitrary "best fit" for the absorption coefficient a which proved to be, for these experiments, 1.44 in reciprocal millimeters of pressure. Justification for regarding this fit as a confirmation of the dependence of initial rate on the amount of absorbed light is provided in the excellent agreement with the experimental results over a thirty-five fold change in the initial pressure, obtained with only this one arbitrary constant.

shown graphically in Fig. 6 where the smooth curve is calculated by equation (8) and the circles represent experimental points.

Influence of Nitrogen on the Rate of Reaction.—We find that nitrogen has no effect on the rate of reaction. This was tested both by studying the influence of an excess of nitrogen added at the beginning of an experiment and by studying the effect of nitrogen accumulation on the progress of a full reaction. The latter study also provides additional confirmation of the dependence of rate on the light absorption.

Table III shows the results obtained in two experiments which were run to test the effect of an initial excess of nitrogen. Within the limits of experimental error the rates of nitric oxide decomposition are the same.

TABLE III

COMPARISON OF THE DECOMPOSITION RATES WITH AND WITHOUT NITROGEN AS A DILUENT

$P_0(N_2)$, mm.	$P_0(NO)$, mm.	$(dP/dt)_0$, mm./min.	$(d \ln P_{NO}/dt)_0$,
0	0.1121	4.4×10^{-4}	$3.9\ (\pm 0.1) \times 10^{-3}$ min^{-1}
0.360	.0916	4.0×10^{-4}	$4.3\ (\pm 0.4) \times 10^{-3}$ min^{-1}

Figure 7 shows the course of a complete run (carried out under the more careful conditions of our later experiments) in which the experimental pressures are shown in their relation to a curve calculated from the same basic assumptions that were employed in the preceding section and with the same value of the absorption coefficient which was derived from the initial rates (namely, 1.44 mm.$^{-1}$).[18]

As the graph shows, the experimental values are a little high in the final period of the reaction. Although the discrepancy is definitely greater than the probable error of the rate measurements themselves,[19] the results are, nevertheless, in sufficiently good agreement with the general shape of the calculated curve to show that the rate-controlling factor throughout the decomposition is the absorption of light and that the accumulated nitrogen has no marked influence on the reaction.

Dissociation as the Primary Step.—It is possible from the above results to deduce the general character of the primary process. At 0.1 mm. pressure of nitric oxide the average time between collisions is about 10^{-6} seconds. If the photoreaction involves the collision of an excited and a normal molecule, then at low pressures where only a small fraction of the active radiation is absorbed and where most of the excited molecules would lose their energy by fluorescence, the rate should be proportional to the square of the nitric oxide pressure. The experimental observation (Table II and Fig. 6) that the rate becomes linear with pressure at low pressures therefore rules out the collision process. A primary dissociation of the molecule is the only alternative. Failure of nitrogen, either as an accumulation product or as an initial diluent, to modify the rate also indicates the absence of primary activation.

We may also conclude that any secondary processes which occur subsequent to the dissociation are little influenced by variation in the pressure either of nitric oxide or of nitrogen.

The Active Region of the Spectrum

Effective Mercury Arc Radiation.—It is difficult to be quite certain of the lower limit of the

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(18) This curve was calculated from the equation

$$(P_0 - P) + \frac{3}{4a} \ln \left[\frac{1 - e^{-aP_0}}{1 - e^{-a(4P-P_0)/3}}\right] + \frac{k_4}{2a}\left[\frac{(e^{2akI_0t} - 1)}{2a\,kI_0} - t\right] = 3/2\,kI_0t \qquad (14)$$

This equation is derived from (7) as follows. As a first approximation reaction (4) is neglected so far as it influences either the total absorption of light or the amount of $HgNO_2$ remaining at time t. Then, it follows from the stoichiometry of reactions 1–3 that we may rewrite (7) in the form

$$dP/dt = -3/2\,kI_0(1 - e^{-a(4P-P_0)/3}) + 2/3\,k_4(P_0 - P) \qquad (9)$$

which rearranges to give

$$dP + (3a/4)\,d\ln(1 - e^{-a(4P-P_0)/3}) - \frac{2k_4(P_0 - P)dt}{3(1 - e^{-a(4P-P_0)/3})} + 3/2\,kI_0\,dt = 0 \qquad (10)$$

Expansion of (9) by MacLaurin's theorem with disregard of higher powers of $(P - P_0)$ and of the term in k_4 yields, on integration, the following approximate relationships

$$4P - P_0 = 3\,P_0e^{-2aI_0kt} \qquad (11)$$

and

$$P_0 - P = 3/4\,P_0(1 - e^{-2aI_0kt}) \qquad (12)$$

These values are then substituted in the *third term only* (which is a small correction term) of equation (10) and the denominator of this term is then expanded by MacLaurin's theorem, and powers of the exponent higher than the first are neglected. This treatment yields the equation

$$dP + \frac{3a}{4}\,d\ln(1 - e^{-a(4P-P_0)/3}) - \frac{k_4}{2a}(e^{2aktI_0} - 1)\,dt + 3/2\,kI_0\,dt = 0 \qquad (13)$$

which integrates to give (14) above.

The several approximations introduced in this derivation are exact in the limit of $t = 0$ and remain good throughout the greater portion of the reaction. We cannot expect this equation to reproduce accurately the experimental data in the immediate neighborhood of the pressure minimum (shown in Fig. 4), where reaction (4) plays a relatively great influence.

(19) The formation of a little mercurous nitrate (or other compound with an O to N ratio greater than 2), in the gage may be the cause of the discrepancy.

wave lengths which may have entered our reaction cell but in view of the intense continuous absorption which sets in with air below λ 1750 we are safe in concluding that no radiation below λ 1750 need be considered in seeking the details of the photochemical process. In order to determine what line, or lines, may be responsible for the photochemical decomposition with the mercury arc a number of runs were carried out with the filters whose absorption characteristics are shown in Fig. 1. Reference has already been made to the results obtained with the Corex and the cellophane filters which showed that radiation below λ 2300 is responsible for at least 98% of the reaction, under the conditions which pertained to our experiments. The results obtained with the other filters are given in Table IV, which also includes comparative rates which show the influence of filters on the reaction promoted by radiation from aluminum and zinc sparks. The influence of the ammonium chloride and ammonium hydroxide filters places the effective radiation below λ 1900.[20] The effect of water in reducing the reaction rate by about 50% corresponds to the absorption of water for wave lengths in the neighborhood of λ 1830.

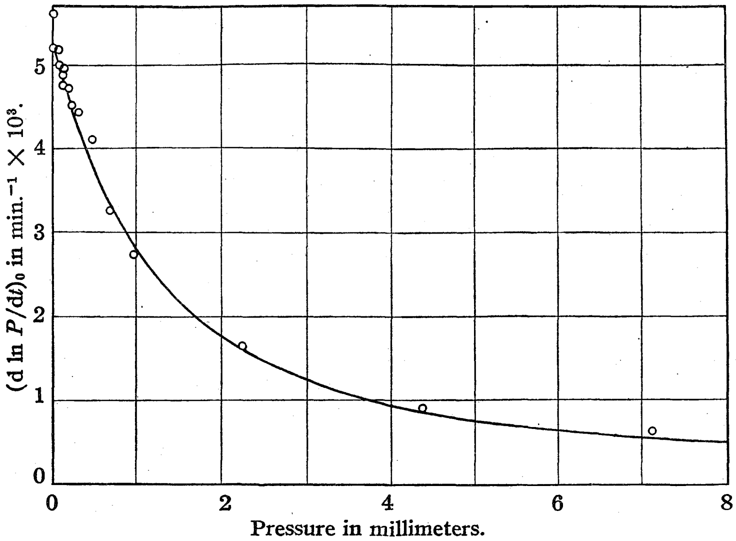

Fig. 6.—Dependence of the initial decomposition rate on the pressure: o, observed: ————, calculated.

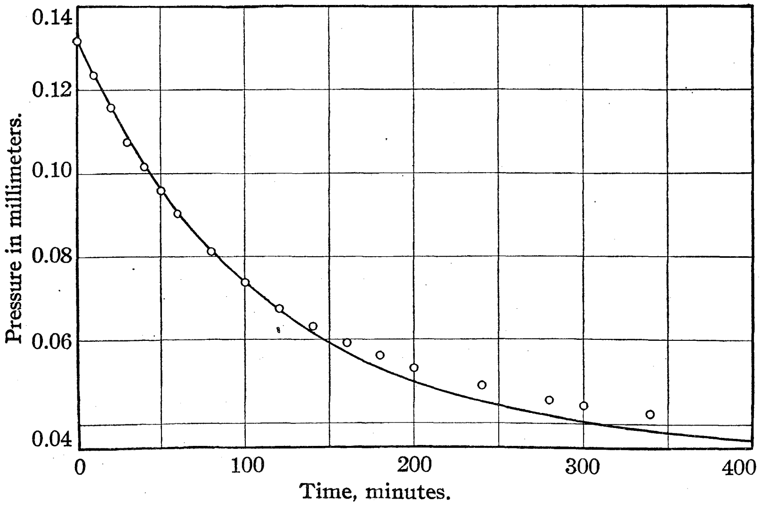

Fig. 7.—Course of a complete run: o, observed; ————, calculated.

The only mercury lines which fall within this active region are those at λλλ 1775, 1832 and 1849, respectively (*cf*. Fig. 8). Hg 1775 falls in a region which is free of nitric oxide absorption. Furthermore, it should be removed completely by the water filter. The results of the several experiments with the mercury arc suggest therefore that the primary process is either the absorption of unreversed radiation from the strong line at λ 1849 in the (9,0) band of the β-system or the absorption of the weak line at λ 1832 (together with continuous radiation surrounding λ 1849) in the (1,0) band of the δ-system. To gain further information on this point an approximate measurement of the absorption coefficient of λ 1849 was carried out spectrographically. An absorption cell 5 cm. long (approximately the mean light path of the divergent light which passed through the 7.5-cm. reaction cell) was placed in front of the spectrograph slit and several exposures of different time lengths were made, both for the evacuated cell and for different pressures of nitric oxide. By visual estimate of the line intensities (all taken on the same plate which was sensitized with Eastman ultraviolet sensitizing solution) the absorption of the λ 1849 line was determined. Application of Beer's Law, which Lambrey[21] has

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(20) Quantitatively, the 3% residual rates with these filters agree, within limits of error, with the 1% rates obtained with the cellophane and Corex filters and indicate: (1) that none of the mercury arc radiation between λ 1900 and λ 2300 is effective in promoting the decomposition and (2) that the small effect due to radiation of longer wave length is due to unreversed radiation of the λ 2537 line.

(21) Lambrey, *Ann. Phys.*, **14**, 95 (1930).

TABLE IV

INFLUENCE OF LIGHT FILTERS ON THE RATES OF NITRIC OXIDE DECOMPOSITION

Source of radiation	Comparative rates (per cent. pressure decrease per minute)			
	Empty cell	H_2O d = 0.15 cm.	NH_4Cl cd = 0.0013	NH_4OH cd = 0.25
Hg arc	0.30	0.14	0.01	0.01
Al spark	..	.70	.05	..
Zn spark	..	.35	.06	..

shown to be applicable to β-band absorption, yielded 1.9 (±0.3) × 10^{-2} mm.$^{-1}$ for el (equivalent to a in equation (8)). The rate dependence on pressure, considered in an earlier section of this paper, yielded 1.4 for the mean absorption coefficient, a, of the active radiation. The absorption of λ 1849 is thus much too weak to account for the observed reaction. No reliable quantitative measurement of the absorption of λ 1832 was possible, due to the low intensity of the line. However, it was found that nitric oxide at only 3 mm. pressure caused almost complete removal of the line. This result is not incompatible with an absorption coefficient of 1.4.

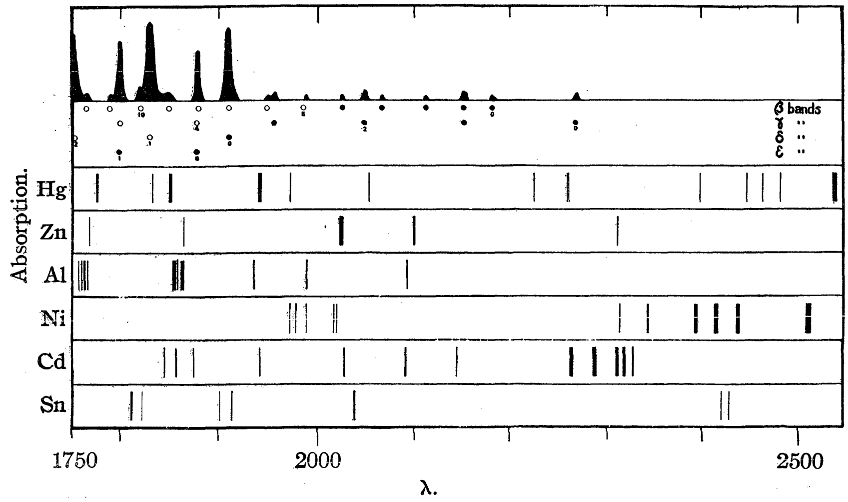

Fig. 8.—Absorption spectrum of nitric oxide in relation to the chief lines of the mercury arc, and of the spark sources employed in this investigation. (The positions and relative intensities of the absorption bands are constructed from the data of Liefson [*Astrophys. J.*, **63**, 73 (1926)] and that of Lambrey [*Ann. phys.*, **14**, 95 (1930)]. The positions and relative intensities of the emission lines are taken from the tabulations in Kayser's "Hauptlinien der Linienspektra aller Elemente." The mercury arc spectrum below λ 1900 is based on the work of Lyman [*Astrophys J.*, **38**, 282 (1913)], who used a mercury arc operated under conditions similar to those we employed except that Lyman's arc was constructed with a fluorite window. Lyman observed that the strong resonance line at λ 1849 was accompanied by continuous radiation extending over more than 40 Å. We confirmed this, for our own arc, by observations taken with a small Gaertner quartz spectrograph. In addition to the broad continuum adjacent to λ 1849 the 1832 line showed up faintly.

The numbers below the circles, which mark the positions of the several absorption bands, represent vibrational quantum numbers of the upper states. White circles mark bands which are absent in emission. Frl. Guillery (*Z. Physik*, **42**, 1212 (1927)) reports emission from the 4′ and 5′ levels of the γ bands but a consideration by one of us (P. J. F.) makes it appear probable that these are, in reality, 0′ and 1′ levels of the ϵ system.

From this we conclude that most, if not all, of the reaction is due to absorption in the δ (1,0) band. Absorption of λ 1849 in the β (9,0) band may have a lesser effect which becomes significant at higher pressures in agreement with the observed rates above 3 mm. pressure (Table II).

Photochemical Effect of Spark Sources.—Results obtained with sparks between metal electrodes confirm the conclusions of the previous section and also indicate some photochemical influence of β-band absorption. The influence of water and ammonium chloride filters on reactions promoted by the aluminum and zinc sparks is included in Table IV. Comparative results obtained with six different spark sources with a 2-mm. water filter are shown in Table V.[22]

The most general observation that we can draw from Table V is that all of the sparks are effective to the same order of magnitude, from which we conclude that their activity is primarily due, not to absorption of their specific lines,[23] but to absorption in the rather considerable continuous background which all of these sources possess.

Removal of the water filter resulted in a two- to four-fold increase in the rates given in Table V. This indicates that most of the active radiation lies below λ 1850. We conclude, therefore, that the same absorption is responsible for dissociation with the several sparks, as with

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[22] The figures in Table V cannot be compared with those in IV since the nature of the power supply, which produced the sparks, was different in the two cases.

[23] The somewhat lesser influence of the ammonium chloride filter in reducing the activity of the zinc spark, than with either mercury or aluminum, may be due to weak absorption of the strong λ 2025 line of zinc in the β (4,0) absorption band of nitric oxide. The low intensity of emission bands with v' = 4 constitutes evidence for some predissociation from this level.

TABLE V

COMPARATIVE RATES OF DECOMPOSITION WITH DIFFERENT SPARKS

Spark source	Rate (% pressure decreases per minute)
Al	0.30
Zn	.23
Cd	.21
Ni	.19
Cu	.11
Sn	.25

the mercury arc—namely, absorption in the δ (1,0) band of nitric oxide, together with some absorption in the hands of the β-system, of which weak absorption of Hg 1849 (and perhaps of Zn 2025) constitute special examples.

The nature of the dependence of the reaction rate on nitric oxide pressure and its independence of nitrogen pressure indicated that the primary step is dissociation. The fact that the active radiation falls in a banded region of the spectrum proves that the dissociation process is one of predissociation.

This conclusion receives support in the emission spectrum of nitric oxide. Thus Kaplan[24] attributes the absence of bands with v' greater than 4 (and the unexpected weakness of ($v' = 4$) bands) to predissociation to a repulsive level which must intersect the upper $^2\Pi$ potential energy curve (*cf.* Fig. 9) somewhere in the neighborhood of $v' = 4$. A similar explanation may be offered to explain the fact that no δ emission bands have been observed[25] with v' greater than zero, although strong emission bands would be expected for higher vibration states, both on the basis of the Franck–Condon principle and of the distribution in absorption.

We expect that radiation absorbed by any of the bands which are marked with open circles in Fig. 8 would be photochemically active while radiation absorbed by bands marked with black circles would be inactive (except for some activity in the β (4,0) band).

Secondary Processes

Nature of the Dissociation Products.—The dissociation energy of nitrogen now seems to be pretty definitely fixed in the neighborhood of 7.34 volts.[26] Combining this value (equivalent to 169,350 calories per mole) with that of the heat of dissociation of oxygen[27] and with the heat of formation of nitric oxide at the absolute zero,[28] we obtain 121,950 calories as the molal heat of dissociation of nitric oxide into atoms, at zero degrees Kelvin. The energy associated with radiation of wave length 1830 Å. exceeds this dissociation energy of nitric oxide by approximately 33,600 calories. Since this is less than the energy necessary to put either atom into an excited electronic state the dissociation products must be the normal atoms. And since momentum, as well as energy, must be conserved in the dissociation, it is a simple matter to compute the kinetic energies given to the respective atoms in the process. These prove to be: for nitrogen, 17,630 calories per gram atom; for oxygen 15,690 calories per gram atom.

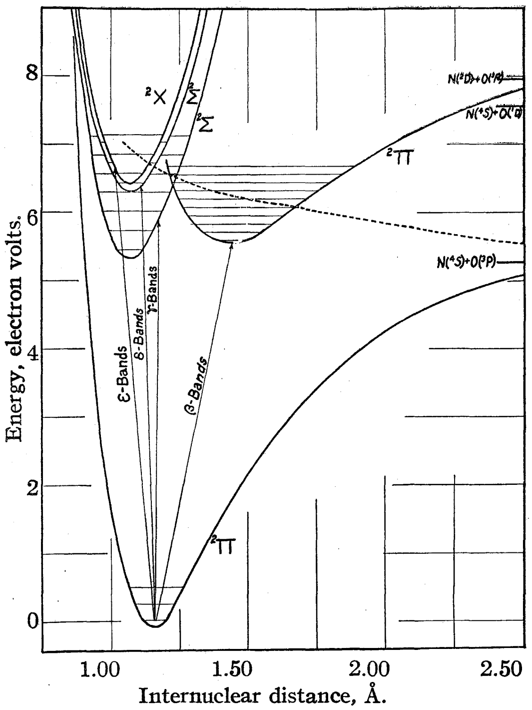

Fig. 9.—Potential energy curves for the known states of nitric oxide: – – – –, estimated position of the $^2\Sigma$ repulsive level responsible for predissociation in the region λ 1800–2000.

Atomic Reactions.—Stoichiometrically possible secondary processes are:

$$N + NO = N_2 + O \qquad + 47{,}400 \tag{15}$$

$$O + NO = O_2 + N \qquad - 4{,}600 \tag{16}$$

$$2N + W = N_2 \qquad +169{,}350 \tag{17}$$

$$2O + W = O_2 \qquad +117{,}350 \tag{18}$$

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[24] Kaplan, *Phys. Rev.*, **37**, 1406 (1931).

[25] Knauss, *ibid.*, **32**, 417 (1928); Schmid, *Z. Physik*, **59**, 42, 850 (1929); *ibid.*, **64**, 279 (1930).

[26] Herzberg and Sponer, *Z. physik. Chem.*, **B26**, 1 (1934); Mulliken, *Phys. Rev.*, **46**, 144 (1934). *Cf.* also Vegard, *Nature*, **134**, 696 (1934), and Lozier, *Phys. Rev.*, **44**, 575 (1933); *ibid.*, **45**, 840 (1934).

[27] Herzberg, *Z. physik. Chem.*, **B10**, 189 (1930).

[28] Giauque and Clayton, THIS JOURNAL, **55**, 4885 (1933).

$N + O + W = NO$ +121,950 (19)
$O + N_2 = NO + N$ − 47,400 (20)
$O + N_2 = N_2O$ − 12,600 (21)
$N + O_2 = NO + O$ + 4,600 (22)
$N + O_2 + W = NO_2$ + 53,250 (23)
$N + NO + W = N_2O$ + 34,800 (24)
$O + NO + W = NO_2$ + 48,650 (25)

where W represents reaction with an adsorbed layer of atoms (or molecules) on the walls.

Of these, (20) and (21) are ruled out completely, and (16) reduced to an improbable occurrence, from energy considerations alone.[29]

A simple calculation, based on the measured rate constants, indicates that the accumulation of oxygen in the reaction system rarely exceeded 1×10^{-3} mm., and was, as a rule, considerably lower than this. This eliminates reaction (22), in comparison with (17) or (19), as a contender for the removal of nitrogen atoms.

At the lowest pressures (0.02 mm.) at which the photodecomposition was studied wall recombination of atoms by reactions (17), (18) and (19) should become a competing process with any gas phase reaction, such as (15). If this latter reaction should occur to an appreciable extent the rate would fall off, at these low pressures, more rapidly than with the first power of the pressure, which is contrary to the experimental results (Fig. 6). Furthermore, the quantum yield at high pressures, where bimolecular gas phase reactions would be favored, is less than unity while reaction (15) would, itself, lead to a quantum yield of two. Therefore we conclude that the recombinations of atoms on the walls, by reactions (17), (18) and (19), constitute nearly the entire secondary process. If the specific velocity constants of (17), (18) and (19) are numerically equal there should be a quantum yield of 0.5, but values from 0 to 1 are possible depending on the ratio of the mean of the rates of (17) and (18) to that of (19).[30]

Correlation with the Decomposition at Higher Pressures

Macdonald,[3] who made a brief study of the decomposition for the pressure range 50 to 650 millimeters, found an extinction coefficient for the active radiation which is only 2% of that we have computed for the active radiation at low pressures and about double that which we have measured for the absorption of λ 1849. From this we conclude that β-band absorption, followed by predissociation, is the primary mechanism of the high pressure decomposition. This is reasonable since, through this range of pressures, absorption in the β-bands must increase in almost direct proportion to the pressure while δ-absorption, already substantially complete even at four or five millimeters, can show little gain.

This conclusion differs from that of Macdonald, who pictured the primary mechanism as one of activation, followed by independent bimolecular reactions between activated and normal molecules. However, we find nothing in Macdonald's work (which was restricted almost entirely to the measurement of quantum yield and to the relation between reaction rate and light absorption) which precludes the predissociation mechanism.

Although the details of the secondary processes appear less certain, most of the arguments advanced in favor of atomic recombinations at the walls, for the low pressure decomposition, appear applicable also at the higher pressures. The one objection to this conclusion is Macdonald's purported observation of appreciable nitrous oxide among the reaction products. This may be accounted for in terms of reaction (24) although to produce 10% nitrous oxide among the products would require a very considerable amount of this reaction since nitrous oxide itself decomposes much faster than nitric oxide. This would require a quantum yield approaching 1.5, which is contrary to the facts. On the basis of what de-

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(29) In collision of a fast oxygen atom, with either nitrogen or nitric oxide in the gas phase, conservation of linear momentum exacts a minimum toll of 35% of the kinetic energy of the oxygen. This leaves only 10,000 calories, as a maximum, for activation. In only a small fraction of the collisions will this maximum energy be available. The great majority of collisions will be elastic due to steric and statistical factors and will dissipate the high energy of the oxygen in successive small losses. A further argument against (16) is the fact that nitrogen as a diluent did not affect the rate.

(30) Reactions (23), (24) and (25) are not excluded on any of the grounds advanced above, although wall reactions of this character appear considerably less probable than (17), (18) or (19). In any case (23), (24) or (25) must be considered in connection with the ultimate products which result from the photodecomposition of the NO_2 or N_2O, which are more rapidly decomposed than the NO. Norrish (ref. 10) has shown that NO_2 decomposes photochemically, by a bimolecular process, to yield NO and O_2. The net effect of (23) would thus be the complete reversal of the initial photodecomposition of nitric oxide, and a consequent quantum yield of zero if this process represented the normal method of removing the nitrogen atoms. It is clearly not of much relative importance in the actual decomposition. The net influence of (25) would be the substitution of a more complex process than (18) for the formation of molecular oxygen. Reactions (17) or (19) would still be required to account for the removal of atomic nitrogen. Macdonald (ref. 3) finds that the photodecomposition of N_2O yields N_2, NO and O_2 in the proportions of 3, 2 and 1. Thus the net effect of (24) is the substitution of a more complex process than (17) or (19) for the removal of nitrogen atoms and would lead to a quantum yield of 1.5, which is double the value observed by Macdonald. Any of these mechanisms (23, 24 or 25) require that one or more of the simple reactions (17, 18 or 19) be operative for the removal of one species of atom. It appears reasonable to credit the entire secondary process, in the main, to the simpler set of reactions.

scription Macdonald gives of his analytical procedure we feel that the presence of nitrous oxide in the reaction products may not be fully established.

Summary

The photochemical decomposition of nitric oxide has been studied, as a function of the pressure, over the pressure range 0.02 to 7 mm. with irradiation both from the mercury arc and from sparks between electrodes of aluminum, zinc, cadmium, nickel, copper and tin, respectively.

The final products of the reaction are nitrogen and oxygen although the latter is removed by a reaction which takes place during compression of the gas in the McLeod gage. This reaction produces a solid product, probably mercurous nitrite, which decomposes to liberate nitric oxide by a first order process which has a velocity constant of 1.5×10^{-2} hr.$^{-1}$.

The rate of decomposition proves to be directly proportional to the rate of light absorption for light of the effective wave length and is, at very low pressures, directly proportional to the pressure. The absorption of effective radiation follows Beer's law and has, for the reaction with the mercury arc, an extinction coefficient of about 2.9×10^{-2} per millimeter light path per millimeter of pressure. Nitrogen as a diluent does not appreciably influence the rate of decomposition. These results, alone, indicate primary dissociation as the first step in the process.

The use of filters containing solutions of ammonium chloride and of ammonium hydroxide places the effective mercury arc radiation below λ 1900. The use of a water filter indicates that the effective region is in the neighborhood of λ 1830. The strong resonance line at λ 1849 is ruled out, except for a relatively small influence at the higher pressures, by measurement of its absorption coefficient which proves to be one hundred times too small for the observed reaction. The alternative is the weak λ 1832 line of mercury which is strongly absorbed by the $(1',0'')$ band of the δ-system of nitric oxide. The essential features of this interpretation are confirmed by the measurement of the decomposition under the influence of both filtered and unfiltered radiation from sparks between metal electrodes. The latter owe the greater portion of their effectiveness to a background of continuous radiation below λ 1900.

This interpretation of the primary process, which must be a predissociation since it occurs in a banded region of the spectrum, agrees well with the evidence for predissociation provided by the emission spectrum of nitric oxide.

Possible secondary processes are considered. All are believed ruled out on theoretical or experimental grounds, in comparison with combination of nitrogen and oxygen atoms on the walls.

Macdonald's work with high pressures of nitric oxide has been considered and it is concluded that the mechanism determined for the low pressure decomposition may also be applied to the results at higher pressures. However, predissociation from the upper levels of the β-bands, rather than the δ-bands, provides the primary step at these higher pressures.

COLUMBUS, OHIO RECEIVED JUNE 25, 1935

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

Reduction Studies in the Morphine Series. VII. Pseudocodeinone[1]

BY ROBERT E. LUTZ AND LYNDON SMALL

Pharmacological studies which have been carried out at the University of Michigan coördinate with the chemical investigations at this Laboratory have shown that as regards general physiological action, the four codeine isomers may be grouped in pairs, codeine with allopseudocodeine, and isocodeine with pseudocodeine.[2] This pairing is based primarily upon the relative degree of convulsive and depressant actions exhibited by each of the drugs, upon their toxicity and upon their effective ratios in other respects when toxicity is taken into account. The same relationship holds for the four corresponding isomeric morphines, and suggests that the spatial arrangement of the alcoholic hydroxyl group may be of

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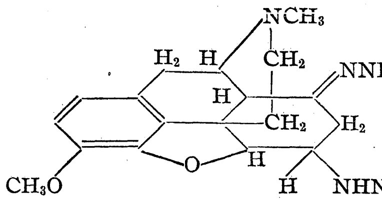
[1] The work reported in this paper is part of a unification of effort by a number of agencies having responsibility for the solution of the problem of drug addiction. The organizations taking part are: The Rockefeller Foundation, the National Research Council, the U. S. Public Health Service, the U. S. Bureau of Narcotics, the University of Virginia and the University of Michigan.

[2] Eddy, *J. Pharmacol.*, **45**, 361 (1932).

more importance for physiological effect than its position (at −6 or −8) on the nucleus.[3] Information on the relative importance of the C-6 and C-8 positions may be expected from the study of derivatives in which the asymmetry at C-6 and C-8 has been destroyed, *i. e.*, compounds whose difference in action must be due to the difference in ring position of the characteristic group present. The present communication deals with the preparation of dihydropseudocodeinone (the "pseudo" analog of Dicodid) and dihydroisomorphinone (the "pseudo"[4] analog of Dilaudid), substances which differ from the well-known drugs cited only in having the keto group at C-8 instead of at C-6. Aside from the practical aspect of the problem, the reduction of pseudocodeinone is of theoretical interest because of the conjugated system involved.

Pseudocodeinone (II) is prepared by oxidation of either pseudocodeine or allopseudocodeine, whereby the secondary alcoholic group at C-8 in these isomers is converted to a carbonyl group, and the stereoisomerism disappears. The location of the carbonyl group at C-8 depends upon the degradation of pseudocodeinone to 3,4,8-trimethoxyphenanthrene.[5] The earlier formulas for pseudocodeine[6] (and hence for pseudocodeinone) placed the alicyclic double linkage at C-13, C-14, whereas the Gulland and Robinson formula[7] locates the unsaturation at C-6, C-7 (formula II). The latter conception is substantiated by the reactions described in the present paper. We have verified the important reaction upon which the Pschorr formula was based, the condensation of pseudocodeinone with benzaldehyde,[8] believed to indicate a methylene group adjacent to the carbonyl. This point of evidence for the Pschorr formula loses most of its weight, however, through our observation that codeine likewise condenses with benzaldehyde under the same conditions.[9]

In favor of the 6,7-position for the pseudocodeinone unsaturation, the reaction with semicarbazide may be advanced. Pseudocodeinone is known to react with semicarbazide to give a monosemicarbazone;[5a] we find that on standing with a large excess of the reagent it reacts with a second molecule in a manner characteristic of α,β-unsaturated ketones[10] to yield a semicarbazino-semicarbazone to which we assign the structure I.



I. Pseudocodeinone semicarbazino-semicarbazone

Hydrogenation of pseudocodeinone in ethanol with a platinum catalyst results largely in formation of the phenolic tetrahydropseudocodeinone,[11] (V), a reaction to be expected from the pseudocodeine type (II) under these conditions. Tetrahydropseudocodeinone still contains the carbonyl group, as is shown by oxime formation.[11] By further reduction, with sodium and alcohol, we obtained only tetrahydropseudocodeine (VI). The diastereomeric tetrahydroallopseudocodeine, whose formation might be anticipated, was not found.

Hydrogenation of pseudocodeinone hydrochloride in glacial acetic acid favors normal saturation of the double linkage, and suppresses reduction of the cyclic ether group. The product consists of nearly equal amounts of the above mentioned tetrahydropseudocodeinone and of the new dihydropseudocodeinone (III).[12] The latter is the desired 8-keto isomer of the 6-keto compound, dihydrocodeinone (Dicodid). In dihydropseudocodeinone the ether bridge is intact, as is shown not only by the lack of phenolic characteristics but also by the reduction (sodium and alcohol) to our previously described non-phenolic dihydropseudocodeine (VII). Through this reduction reaction, as well as by oxime formation, the presence of the carbonyl group in dihydropseudocodeinone is demonstrated. It is notable that the reductions of tetrahydropseudocodeinone and dihydropseudocodeinone are consistent stereochemically in yielding exclusively the reduction product having the pseudocodeine configuration.

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(3) Eddy, *J. Pharmacol.*, **51**, 43 (1934).

(4) The prefix *pseudo* cannot consistently be applied to demethylated analogs of pseudocodeine compounds on account of confusion with the dimolecular products of the pseudomorphine series.

(5) Knorr and Hörlein, *Ber.*, **40**, (a) 2032, (b) 3341 (1907).

(6) Pschorr, *ibid.*, **45**, 2212 (1912).

(7) Gulland and Robinson, *Mem. Proc. Manchester Lit. Phil. Soc.*, **69**, 79 (1925).

(8) Knorr and Hörlein, *Ber.*, **40**, 3341 (1907). See Gulland and Robinson, *J. Chem. Soc.*, **123**, 1001 (1923). *Cf.* Schöpf, *Ann.*, **452**, 212, Note 2 (1927).

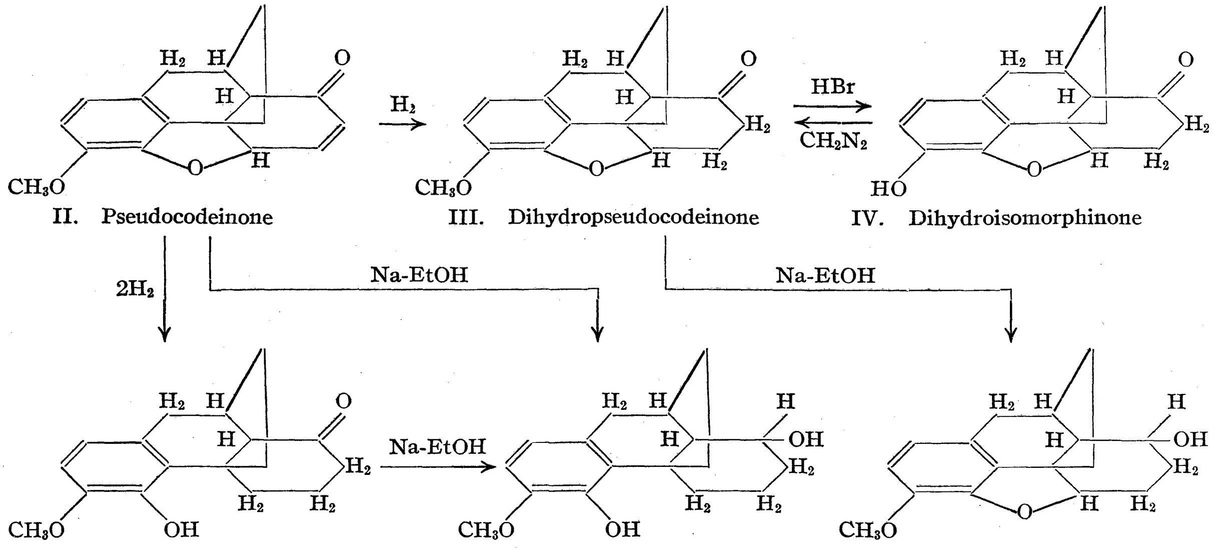
(9) The nature of the reaction is under further investigation.

(10) Houben, "Methoden der org. Chem.," Vol. II, p. 1005.

(11) Karl A. T. Hill, Dissertation, Frankfurt a./M., 1925.

(12) Speyer and Rosenfeld, *Ber.*, **58**, 1117 (1925), obtained from treatment of bromocodeinone with sodium hydrosulfite a compound of formula $C_{18}H_{21}O_3N$, for which they suggested a dihydropseudocodeinone structure. No evidence was advanced to support this suggestion, and the properties of their compound differ from those of our dihydropseudocodeinone.

Sodium and alcohol reduction of pseudocodeinone yields tetrahydropseudocodeine directly, the keto group again being reduced to the favored pseudocodeine configuration as noted above.

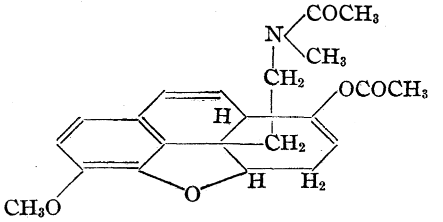


II. Pseudocodeinone III. Dihydropseudocodeinone IV. Dihydroisomorphinone

V. Tetrahydropseudocodeinone VI. Tetrahydropseudocodeine VII. Dihydropseudocodeine

Demethylation of dihydropseudocodeinone gives in good yield dihydroisomorphinone (IV), the 8-keto analog of the 6-keto compound, dihydromorphinone. Dihydroisomorphinone is a strongly phenolic base whose structure is sufficiently demonstrated by the reconversion to dihydropseudocodeinone through the action of diazomethane. The synthesis of dihydroisomorphinone here realized is at present not a practicable one on account of the difficulty involved in the preparation of dihydropseudocodeinone.

An attempt to prepare an 8-enol-acetate analog of the drug "Acedicon" (acetyldemethylodihydrothebaine, or dihydrocodeinone enol acetate) failed because of the lability of the nitrogen-containing ring in dihydropseudocodeinone. The action of acetic anhydride and sodium acetate on dihydropseudocodeinone results in a substance, $C_{22}H_{25}O_5N$, which contains two acetyl groups and which is no longer basic. These facts are best explained by a des-N-acetyldihydropseudocodeinone enol acetate formula, (VIII). This ring opening of dihydropseudocodeinone on acetylation recalls the behavior of apomorphine[13] and morphothebaine,[14] where the driving force of the reaction appears to be the possibility of forming a completely aromatic nucleus.



VIII. Des-N-acetyldihydropseudocodeinone enol acetate

It has long been known that the carbonyl group in codeinone does not react with the Grignard reagent under ordinary conditions[15] or even at temperatures up to 170°, where decomposition occurs.[16] Dihydrocodeinone is attacked only in small degree, yielding traces of a *phenolic* product, and dihydropseudocodeinone is recovered unchanged after treatment with methylmagnesium iodide. Pseudocodeinone, on the other hand, reacts readily with this reagent to yield a substance provisionally named methyldihydropseudocodeinone, which is of interest because of its peculiar properties. It is a strongly phenolic base, whose empirical formula shows that the elements of methane have been added to the starting material. Accordingly, the ether bridge must be open, and the carbonyl group and a double bond still be present. Nevertheless, the new compound resists all attempts at reduction, whether by catalytic methods, sodium in alcohol or cyclohexanol, or the Clemmensen method. None of the other unsaturated or saturated ketones of the morphine series has been found to offer such resist-

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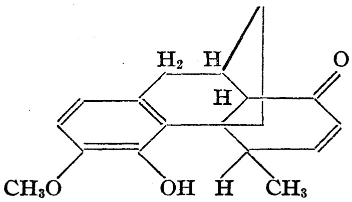
(13) Pschorr, Jaeckel and Fecht, *Ber.*, **35**, 4377 (1902).

(14) Freund, *ibid.*, **32**, 168 (1899); Knorr and Pschorr, *ibid.*, **38**, 3153 (1905).

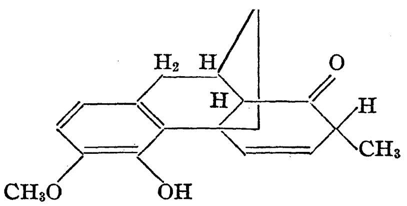
(15) Schneider, Dissertation, Jena, 1906.

(16) Small and Cohen, unpublished results.

ance to reduction at the double linkage or carbonyl group.[17] Furthermore, repeated attempts to prepare an oxime or a semicarbazone failed. We were unable to find any evidence of the presence of either alicyclic double linkage or carbonyl group, although one or both must be present, whatever may be the mechanism by which *one mole* of alkylmagnesium halide adds. We believe that the best interpretation of the reaction is the 1,2- or 1,4-addition of methylmagnesium iodide to the system consisting of an ether linkage and the 6,7-double bond, such as we postulate in the case of desoxycodeine-C and other pseudocodeine types.[18] That the carbonyl group is not involved is not remarkable in view of the indifference of this group in the examples cited above. The structure of methyldihydropseudocodeinone might be expressed by formula IX or X (or a rearranged form of X), of which the α,β-unsaturated ketone formula IX seems the less probable on account of the extraordinary resistance to reduction with sodium and alcohol.



IX. 5-Methyldihydropseudocodeinone



X. 7-Methyldihydropseudocodeinone

In the cases of phenyldihydrothebaine[19] and the methyldihydrothebaines[20] we have a reluctance toward catalytic hydrogenation similar to that here observed, but it should be noted that methyl, ethyl and cyclohexyl dihydro derivatives of desoxycodeine-C, presumably of structure analogous to that of methyldihydropseudocodeinone, can be hydrogenated without difficulty.[18]

Dihydropseudocodeinone is about one-half as toxic as Dicodid, and shows less convulsant action. Its analgesic effect is much less than that of Dicodid, but in effective doses it causes no emesis and almost no excitement. Its activity in general is about one-tenth that of Dicodid. Dihydroisomorphinone presents a similar picture. In respect to analgesia and respiration it is only one-tenth as effective as the 6-keto isomer, Dilaudid; like dihydropseudocodeinone, it has no emetic and but little exciting action. Convulsions occur only with fatal doses. As far as conclusions are justified by the evidence available, it appears that a functional group in the 6-position exerts much more influence on physiological action than one in the 8-position. Pseudocodeine and γ-isomorphine, because of a favorable configuration of the alcoholic hydroxyl, are effective drugs in spite of the disadvantageous ring position of the group; allopseudocodeine and β-isomorphine, the least active of the isomers, have the hydroxyl unfavorably located both in space and in position. In codeine and morphine, the location of the hydroxyl in the active 6-position is of more importance than the unfavorable spatial arrangement, and in the most effective of the isomers, isocodeine and α-isomorphine, both position and configuration intensify physiological action. These conclusions, although drawn from few examples, are offered as a tentative explanation of the consistent relations (in respect to physiological action) of the codeine and morphine isomers and most of their dihydro derivatives.

Experimental

Pseudocodeinone (II) was prepared by chromic acid oxidation of pseudocodeine according to the method of Knorr and Hörlein.[5a] The product was best isolated by cooling the oxidation mixture through addition of ice, making strongly alkaline with sodium hydroxide, and extracting several times with ether. The yield of pure product seldom exceeded 10 to 15%. The important fact reported by Knorr that allopseudocodeine gives the same ketone on oxidation was verified, the yield in one experiment being 30% of that required by theory. The pseudocodeinone base was purified from butanone; occasionally some unchanged pseudocodeine was found, and was removed by utilizing its very slight solubility in ether.

II-Hydrochloride crystallizes from ethanol or from dilute hydrochloric acid; m. p. 201–203° (corr. with dec.); $[\alpha]^{25}_D$ −24° (water, c = 1.0).

Anal. Calcd. for $C_{18}H_{20}O_3NCl + H_2O$: H_2O, 5.1. Found: H_2O, 4.6. Calcd. for $C_{18}H_{20}O_3NCl$: Cl, 10.63. Found (dried at 120° *in vacuo*): Cl, 10.24.

Pseudocodeinone Semicarbazino-semicarbazone (I).—Two grams of pseudocodeinone with 25 cc. of water, 4 cc. of ethanol and 3 g. of semicarbazide hydrochloride went largely into solution on stirring, and a hydrochloride crystallized out; this showed the constants given by Knorr for pseudocodeinone semicarbazone hydrochloride. When allowed to stand for about three hours with occasional shaking in the presence of the excess semicarbazide, the pre-

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(17) Compare, for example, the reduction of codeinone, dihydrocodeinone, thebainone, metathebainone, dihydrothebainone, pseudocodeinone, dihydropseudocodeinone, tetrahydropseudocodeinone, hydroxycodeinone, dihydrohydroxycodeinone.

(18) Small, Yuen, Fitch and Smith, unpublished results.

(19) Literature review, Small and Lutz, "Chemistry of the Opium Alkaloids," pp. 332–336.

(20) Small and Fry, unpublished results.

cipitate dissolved. After sixty hours the semicarbazinosemicarbazone was thrown out crystalline by ammonia; yield 1.85 g. It is very slightly soluble in most organic solvents, and was purified from 70% alcohol; m. p. 225–227° (unsharp, dec.).

Anal. Calcd. for $C_{20}H_{27}O_4N_7 + H_2O$: H_2O, 4.0. Found: H_2O, 4.1. Calcd. for $C_{20}H_{27}O_4N_7$: C, 55.91; H, 6.34. Found: C, 55.61; H, 6.46.

Dihydropseudocodeinone (III).—A suspension of 13.8 g. of pseudocodeinone hydrochloride in 50 cc. of glacial acetic acid with 0.1 g. of platinum oxide absorbed 1270 cc. (corr.) of hydrogen, or 1.4 moles. The filtered solution was diluted with ice water, made ammoniacal under ether and extracted several times. The oily base thus obtained was dissolved in acetone, from which nearly pure tetrahydropseudocodeinone separated on cooling. Dilution of the filtrate with a little water yielded a second crop of the same product; yield 34%. The acetone solution, partially evaporated in an air blast, gave dihydropseudocodeinone as an oily precipitate, which slowly solidified, m. p. 93–100°, yield 46%. Reduction of pseudocodeinone in alcohol with platinum gave tetrahydropseudocodeinone with only traces of dihydropseudocodeinone.

Dihydropseudocodeinone crystallizes from ethyl acetate or ethyl acetate–ligroin mixtures as balls of rectangular prisms or plates, m. p. 113° (corr.). It may also be purified through the hydriodide. In high vacuum it distils as a colorless glass; $[\alpha]^{25}_D$ +37° (ethanol, c = 0.62).

Anal. Calcd. for $C_{18}H_{21}O_3N$: C, 72.20; H, 7.07. Found: C, 72.19; H, 7.15.

Dihydropseudocodeinone hydrochloride was prepared in acetone with alcoholic hydrogen chloride, and purified from acetone–alcohol mixture. It melts at 172–173° (corr.), and has $[\alpha]^{26}_D$ +13° (water, c = 0.65).

Anal. Calcd. for $C_{18}H_{22}O_3NCl + H_2O$: H_2O, 5.1. Found: H_2O, 4.9. Calcd. for $C_{18}H_{22}O_3NCl$: Cl, 10.57. Found (dried *in vacuo* 120°): Cl, 10.09.

Dihydropseudocodeinone hydriodide crystallizes from water, melts at 250–255° (corr., with dec.), and shows $[\alpha]^{25}_D$ +8.1° (water, c = 0.56).

Anal. Calcd. for $C_{18}H_{22}O_3NI$: I, 29.72. Found (dried *in vacuo* 120°): I, 29.98.

Dihydropseudocodeinone forms a well-crystallized tartrate (from water), m. p. 199–200°, $[\alpha]^{25}_D$ +20° (water, c = 0.91) which gave on analysis values approximating the formula of the acid tartrate.

Dihydropseudocodeinone oxime was prepared by boiling 0.2 g. of base in 2 cc. of water with 1 g. of hydroxylamine hydrochloride; yield nearly quantitative. It was purified from ethanol, and melted at 244–245° (corr.).

Anal. Calcd. for $C_{18}H_{22}O_3N_2$: C, 68.75; H, 7.06. Found: C, 68.69; H, 6.98.

Reduction of dihydropseudocodeinone with sodium in alcohol gave 78% yield of dihydropseudocodeine-A (VII).[21]

Des - N - acetyldihydropseudocodeinone Enol Acetate (VIII).—A solution of 0.5 g. of III in 5 cc. of acetic anhydride with 0.5 g. of sodium acetate, heated for three hours at 100°, gave a nearly quantitative yield of the non-basic product VIII. This crystallized from ethanol as thin six-sided scales of m. p. 191.5–192° (corr.).

Anal. Calcd. for $C_{22}H_{25}O_5N$: C, 68.90; H, 6.57. Found: C, 68.83; H, 6.58.

Tetrahydropseudocodeinone (V).—The physical properties of this compound differ considerably from Hill's description.[11] It behaves like a cryptophenol; it is not readily soluble in dilute sodium hydroxide, and is largely extracted by ether from its solution in alkali. Crystallized from ethanol or acetone it separates as the hemihydrate m. p. 137–138.5° (unsharp, corr.). It sublimes in a high vacuum, yielding the anhydrous form, m. p. 170–171° (corr.); $[\alpha]^{30}_D$ +8.0° (ethanol, c = 0.55).

Anal. Calcd. for $C_{18}H_{23}O_3N + 0.5H_2O$: C, 69.63; H, 7.80. Found: C, 69.64; H, 7.88. Calcd. for $C_{18}H_{23}O_3N$: C, 71.72; H, 7.70. Found (sublimed sample): C, 71.68; H, 8.01.

The base does not react with diazomethane. With acetic anhydride in pyridine (100° for thirty minutes) it forms a monoacetyl derivative which distils as a colorless glass in a high vacuum.

Anal. Calcd. for $C_{18}H_{22}O_3N(COCH_3)$: $COCH_3$, 12.5. Found: $COCH_3$, 12.3.

V-Oxime, crystallized from ethanol, melts at 218–219° (corr.). *Cf.* Hill, m. p. 137° (dec.).

Anal. Calcd. for $C_{18}H_{24}O_3N_2$: C, 68.31; H, 7.65; N, 8.86. Found: C, 68.26; H, 7.81; N, 8.98.

V-Hydrochloride crystallizes hydrated from ethanol, m. p. 165–166° (corr.) with frothing; $[\alpha]^{25}_D$ −6.2° (water, c = 1.29).

Anal. Calcd. for $C_{18}H_{24}O_3NCl + 2H_2O$: H_2O, 9.6; Cl, 9.54. Found: H_2O, 9.7; Cl, 9.36. Calcd. for $C_{18}H_{24}O_3NCl$: Cl, 10.50. Found: Cl, 10.09.

V-Hydriodide crystallizes hydrated from water, m. p. 154–155° (corr.), $[\alpha]^{25}_D$ −5.9° (water, c = 0.85).

Anal. Calcd. for $C_{18}H_{24}O_3NI + H_2O$: H_2O 4.0. Found: H_2O, 3.8. Calcd. for $C_{18}H_{24}O_3NI$: I, 29.58. Found: I, 29.41.

Tetrahydropseudocodeine (VI).—Reduction of either pseudocodeinone or tetrahydropseudocodeinone (0.5 g.) in 50 cc. of absolute alcohol with 5 g. of sodium (nitrogen atmosphere) gave 62% yield of tetrahydropseudocodeine, identified by its two melting points and the melting point of its characteristic methine derivative. Sodium amalgam in dilute acetic acid gave the same product.

Dihydroisomorphinone (IV).—Demethylation of dihydropseudocodeinone with hydriodic acid was unsatisfactory. A solution of 4.5 g. of III in 20 cc. of 48% hydrobromic acid was refluxed for fifteen minutes. An oily base was obtained from ether, and crystallized when digested with ethyl acetate; yield 2.45 g., m. p. 198° (corr.), $[\alpha]^{26}_D$ +46° (ethanol, c = 0.44). The base is soluble in sodium hydroxide, and precipitates on addition of ammonium chloride. The ferric chloride test is intense cobalt blue. IV-Perchlorate crystallizes in rectangular plates; the hydrochloride, hydriodide and tartrate are not crystalline. The base sublimes in a high vacuum at 200°.

Anal. Calcd. for $C_{17}H_{19}O_3N$: C, 71.54; H, 6.72. Found: C, 71.22; H, 6.98.

Methyldihydropseudocodeinone.—Treatment of 12 g. of pseudocodeinone in 1000 cc. of absolute ether with 100 cc. of 1.9 molar methylmagnesium iodide gave an oily base

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[21] Lutz and Small, THIS JOURNAL, **54**, 4715 (1932).

which partly crystallized from ethanol; yield, 3.3 g. It was purified from isopropyl alcohol, m. p. 213.5–214.5° (corr.).

Anal. Calcd. for $C_{19}H_{23}O_3N$: C, 72.82; H, 7.40. Found: C, 72.96, 72.48; H, 7.62, 7.49.

Methyldihydropseudocodeinone was unaffected by treatment with sodium in alcohol or in boiling cyclohexanol, by catalytic hydrogenation in alcohol, acidified alcohol or glacial acetic acid, by zinc and hydrochloric acid (seven hours under reflux), or by hydroxylamine or semicarbazide under various conditions.

The use of ethylmagnesium iodide in the above reaction gave non-crystalline products.

Summary

1. Pseudocodeinone can be reduced under proper conditions to a non-phenolic dihydropseudocodeinone. The relationship of this to dihydropseudocodeine-A establishes its structure.
2. Demethylation of dihydropseudocodeinone results in dihydroisomorphinone, the 8-keto analog of Dilaudid.
3. Dihydropseudocodeinone is indifferent to methylmagnesium iodide, but pseudocodeinone reacts to give a phenolic dihydromethylpseudocodeinone. This product is remarkable in the complete passivity of its carbonyl group and double linkage toward the usual reagents affecting such structures.
4. Comparison of the physiological action of dihydropseudocodeinone and dihydroisomorphinone with that of Dicodid and Dilaudid, and that of the codeine and morphine isomers indicates that morphine derivatives with the functional group at C-6 are more effective than those with the same group at C-8, but that spatial relationships are also very important.

UNIVERSITY, VIRGINIA RECEIVED OCTOBER 11, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Vinyldiazomethane

BY CHARLES D. HURD AND S. C. LUI

Recently, Adamson and Kenner[1] described vinyldiazomethane as if it were new. Nirdlinger and Acree,[2] however, prepared it in 1910. They synthesized it from allylnitrosourethan whereas Kenner employed allyl (acetyl-*t*-butyl)-nitrosamine. In the present work, done in 1933–1934, it was studied to learn whether allyl, cyclopropyl or propenyl esters would be formed during reaction with acids. Actually, it was the ally ester which resulted: $C_6H_5COOH + CH_2{=}CHCHN_2 \longrightarrow N_2 + C_6H_5COOCH_2CH{=}CH_2$. The isomerization of vinyldiazomethane to pyrazole, reported by Adamson and Kenner, was observed. In fact, it was found to isomerize appreciably even during the distillation of the diazo compound.

Vinyldiazomethane was prepared by Nirdlinger and Acree's method, namely, by adding a solution (20%) of potassium hydroxide in methanol to a solution of the nitroso compound (A) in ether (B). When a 1:15 or 1:20 ratio of A:B was maintained, a 22–25% yield of vinyldiazomethane resulted. With a 1:9 ratio, the yield dropped to 13%.

Allylurethan and allylnitrosourethan were prepared by methods closely adapted from those given for methylurethan and methylnitrosourethan in "Organic Syntheses" [Vol. XII, p. 38; XIII. p. 84], the difference being that allylamine was taken instead of methylamine. The yields, respectively, were 81 and 94%. This preparation of allylnitrosourethan is new. Nirdlinger and Acree, who made it from nitrogen trioxide and allylurethan, mentioned no yield and gave no analysis. In the present work, the nitroso compound was analyzed after being thoroughly washed, dried and freed from solvent ether: d^{15}_{15} 1.051 d^{20}_{20} 1.047, d^{25}_{25} 1.044. Decomposition attended efforts to distil it (a red oil) at 3 mm.

Anal. Calcd. for $C_6H_{10}O_3N_2$: N, 17.7. Found: N, 17.4.

To estimate the yields, 10.00 cc. of the ether solution of vinyldiazomethane was mixed in a stoppered flask with a solution of 0.500 g. of *p*-nitrobenzoic acid in 25 cc. of dry ether. When the solution became colorless in 15–25 minutes it was back-titrated with 0.1 *N* barium hydroxide. When the reaction period was extended to twenty-four hours the results were but slightly higher; *e. g.*, a 22.3% value changed to 23.1%. With 2,4,6-trinitrobenzoic acid decolorization occurred immediately and gave quantitative values (23.0% in the case cited) if back-titrated at once.

For comparison of *p*-nitrobenzoic acid and benzoic acid, duplicate experiments were performed with reaction times of one-half, one and twenty-four hours. The yields, respectively, from *p*-nitrobenzoic acid were 22.3, 22.8, 23.1%; from benzoic acid, 12.1, 15.2, 16.2%.

Allyl Benzoate.—Vinyldiazomethane (1.855 g.) and benzoic acid (10 g.) were mixed in 360 cc. of dry ether and left for two days. Then the ether and excess acid were removed. The ester which remained distilled at 228°; yield, 2.90 g. or 65.7%. Two grams of this ester was hy-

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[1] Adamson and Kenner, *J. Chem. Soc.*, 286 (1935).

[2] Nirdlinger and Acree, *Am. Chem. J.*, **43**, 381 (1910).

drolyzed by sodium hydroxide, the alcohol portion ether extracted and a part of it treated with α-naphthyl isocyanate. The allyl α-naphthylcarbamate[3] thus obtained, after two recrystallizations from ligroin, melted at 108°.

Pyrazole.—A vinyldiazomethane solution (0.53 g. in 100 cc. of ether) was set aside for two days, then evaporated. The crystalline residue of pyrazole weighed 0.72 g. This indicates that an appreciable isomerization of the vinyldiazomethane occurs during synthesis in the distillation process. After being twice recrystallized from ether, it melted at 68°. It was identified as pyrazole by converting 0.1 g. of it to pyrazole picrate, m. p. 160°.

Summary

The synthesis and some of the properties of allylnitrosourethan and vinyldiazomethane are discussed.

EVANSTON, ILLINOIS RECEIVED SEPTEMBER 21, 1935

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(3) Neuberg and Kansky, *Biochem. Z.*, **20**, 446 (1909), reported m. p. of 109°.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

The Constitution of Liquid Zinc Amalgams

BY HERMAN A. LIEBHAFSKY

Cells in which the electrodes are zinc amalgams of different concentrations, and the electrolyte is an aqueous solution of a zinc salt, have been investigated frequently during the past fifty years.[1] In three of these investigations,[1,2,3] exceptional care has been employed and the accuracy consequently attained has been so great that the problem of determining the electromotive forces of such cells near room temperature appears to be closed, with these two experimental results definitely established. First, dilute zinc amalgams, even in the absence of oxygen, tend increasingly to lose zinc as they become more dilute,[2a] so that the resulting uncertainties in composition constitute the chief stumbling blocks in obtaining the electromotive forces of zinc amalgam cells to within, say, 0.001 millivolt. And, second, these electromotive forces are actually smaller than the ideal values corresponding to the Nernst equation, so that[4]

$$E_{\text{act}} + \Delta E = E_{\text{id}} = 0.09922T\log[\Sigma(\text{Zn})_1/\Sigma(\text{Zn})_2] \quad (1)$$

ΔE, the departure from ideality, is positive and decreases with the concentration of the more concentrated amalgam in the cell. Richards and Forbes[1] pointed out that this departure from ideality qualitatively indicated a partial polymerization of the zinc. Hildebrand[5] contributed greatly to the problem from the experimental side[5b] when he proved that the vapor pressures of zinc amalgams at 300° exhibit deviations from ideality corresponding to ΔE; and from the theoretical side when he showed, in accord with the ideas of Dolezalek,[6] that both types of deviations could, within certain limits, be *quantitatively* explained on the assumption that

$$\text{Zn}_2 \xrightleftharpoons{K_2} 2\text{Zn};\ K_2 = (\text{Zn})^2/(\text{Zn}_2) \qquad (2)$$

was the only equilibrium existing in these amalgams. More recently the *activities* of zinc amalgams have been calculated from the electromotive force data[2b,3] and the interpretation of ΔE in terms of molecular species (a *concentration* treatment) has lost ground—a state of affairs easy to comprehend if, as Crenshaw[2b] states, the best experimental results for these amalgams agree better with each other than they do with Hildebrand's equation

$$E = 0.19834\,\frac{T}{n}\log\frac{1 + N_2 + \sqrt{N_2^2 + 2AN_2 + A}}{1 + N_1 + \sqrt{N_1^2 + 2AN_1 + A}} \quad (4)$$

where $n = 2$, the N's are the number of moles of mercury for one mole of zinc in amalgams 1 and 2, and $A = 4/(K_2^N + 1)$(see Footnote 4).

It is our purpose here to show that the positive values of ΔE for the zinc amalgams can be quantitatively accounted for without recourse to an activity treatment if we assume the equilibrium

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(1) Richards and Forbes, *Z. physik. Chem.*, **58**, 683 (1907).

(2) Crenshaw, (a) *J. Phys. Chem.*, **14**, 158 (1910); (b) *ibid.*, **34**, 863 (1930).

(3) Pearce and Eversole, *ibid.*, **32**, 209 (1928). For a complete historical summary and additional references, see Ref. 1.

(4) The summation sign, Σ, prefixed to a concentration term indicates that all the zinc in an amalgam is meant; thus, $\Sigma(\text{Zn}) = (\text{Zn}) + (\text{Zn}_2) + (\text{Zn}_3) + \ldots$. Four concentration units have been employed in the investigations referred to above: *viz.*, (1) g. Zn/100 g. Hg, here denoted (as it has just been) by ( ); (2) g. Zn/100 g. amalgam; (3) the units of Richards and Forbes, which we shall designate by $(\text{Zn})^v$—namely, g. Zn/100 g. amalgam for the most concentrated amalgam only; for any other amalgam, this unit with the density change compensated which occurs when the amalgam is prepared by dilution from the most concentrated; (4) the mole fraction of zinc, equal to $1/(1 + N)$, where N is the number of moles of mercury for one mole of zinc; equilibrium constants expressed in this unit will be distinguished by a superscript; thus K_2^N. Electromotive forces will usually be expressed in *millivolts*.

(5) Hildebrand, (a) THIS JOURNAL, **35**, 501 (1913); (b) *Trans. Am. Electrochem. Soc.*, **22**, 335 (1913).

(6) Dolezalek, *Z. physik. Chem.*, (a) **64**, 727 (1908); (b) **71**, 191 (1910).

$$Zn_3 \xrightleftharpoons{K_3} 3Zn;\ K_3 = (Zn)^3/(Zn_3) \qquad (3)$$

to exist in addition to Reaction 2. This means in effect that we assume solutions of Zn, Zn_2, and Zn_3 in mercury at room temperature to be ideal over the entire range of composition.

The Experimental Data

Before proceeding with our interpretation of the experimental data, however, we shall have to re-examine these carefully for the following two reasons. First, all the finally accepted data of Richards and Forbes have never yet been compared with the other accurate experimental results; and, second, although several comparisons have been made, the results thereof are by no means in agreement.[7]

Richards and Forbes measured many combinations of cells at a number of temperatures in the neighborhood of 23° and thus proved beyond doubt that all their final results are concordant; but they did not, as was done in the subsequent investigations, actually measure the electromotive force of every other amalgam against the most concentrated. They did conveniently summarize all their final results, however, when they gave for each value of $(Zn)^{\nu}$ the deviation from ideality (analogous to ΔE, but for which we shall retain their symbols $D\pi$) that they would have obtained had they measured each of the other amalgams against No. 3, the most concentrated. Now, $D\pi$ will not be significantly affected by small changes either in the temperatures of the cells or in the concentrations of the amalgams, and the calculations of E_{act} and ΔE for the data of Richards were based on this fact.[8]

The most serious inaccuracies in these electromotive force investigations are encountered with dilute amalgams since these exhibit the greatest tendency to lose zinc. Crenshaw, and Pearce and Eversole measured all their other amalgams at 25° against the saturated amalgam, for which $\Sigma(Zn) = 2.2200$, as a common reference electrode. We are therefore doubly justified in adopting a method of comparison which places the greatest weight, not upon an arbitrarily chosen dilute amalgam, but upon the most concentrated one in each series. To do this, we modify the procedure of Richards and Forbes slightly by plotting ΔE(Eq. 1) against log $[2.2200/\Sigma(Zn)]$, as in Fig. 1. Their data are for 23.09° (296.2°K.), and have been brought to the same scale as the others (which are for 25°) by adding 2.600 to the ordinate and log 2.2200/0.9173 to the abscissa; this procedure arbitrarily places the point for their No. 1 amalgam on the curve; but it does not similarly constrain the results for their other amalgams, so that the points for these will not agree with the curve unless the corresponding measurements are also in agreement.

An examination of Fig. 1, in which the circles have diameters corresponding to only 0.05 millivolt, immediately reveals that the agreement among all three sets of results is excellent at the higher, and good at the lower, concentrations. The downward deviations for the two most dilute amalgams (Crenshaw's) are undoubtedly caused by loss of zinc,[9] and thus do not indicate a real departure from the horizontal line which ΔE reaches in dilute solution; most of the downward deviations for the other points probably also have their origin in a loss of zinc, so that the actual values of $\Sigma(Zn)$ are less than those employed in

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[7] Hildebrand, and Pearce and Eversole have concluded that Crenshaw's measurements, made over the largest possible concentration range, do not agree with those made by Richards and Forbes over the smaller range (Zn) = 0.9 to 0.05; such disagreement does exist if the most dilute amalgam considered in each set is taken as reference electrode; as Crenshaw[2b] has pointed out, a comparison on this basis is not trustworthy if (as is likely to be the case) the result for either dilute amalgam is in error.

Pearce and Eversole consider that their recent measurements confirm those of Richards and Forbes, but disagree with those of Crenshaw.

Crenshaw[2b] has recently been able to bring all three sets of results into agreement by the following procedure: $[-E/0.00009922T - \log 1/(N+1)]$ is calculated for each value of the mole fraction of zinc in each set of data. To the values of this activity function thus obtained from the data of Pearce and Eversole, 2.0085 is added; a correction of 2.6775 is similarly applied to the values derived from the data of Richards and Forbes. The corrected values corresponding to all three sets of results are then plotted against $1/(N+1)$, the mole fraction of zinc; at the higher mole fractions, a straight line is obtained which, by a somewhat uncertain extrapolation, is extended to infinite dilution. This method of comparing the results necessarily lacks directness and simplicity; although it is perhaps preferable to employing an uncertain dilute reference electrode, it seems definitely less convincing than the straightforward method employed in the text (*cf.* Fig. 1).

[8] π_{id}, the ideal electromotive force for the cells of Richards and Forbes, and E_{id} differ because they involve different concentration units, and slightly different values for the fundamental constants.

E_{act} and ΔE at 23.09° for the *n*th amalgam of Richards and Forbes were calculated as follows. Since

$$\pi_{id} = 29.361 \log [\Sigma(Zn)_3^{\nu}/\Sigma(Zn)_n^{\nu}]$$

and the logarithms of the concentration quotients for all their amalgams are given by these authors, π_{id} was easily obtained. Also,

$$\pi_{id} - D\pi = \pi_{act} = E_{act} = E_{id} - \Delta E$$

so that E_{act} and ΔE are readily calculable by use of the $D\pi$ values, which are also listed in Reference 1.

[9] Crenshaw's detailed experimental results show how rapidly his dilute amalgams were losing zinc; while the electromotive forces of the more concentrated amalgams remained unchanged for weeks, a cell containing a dilute amalgam and the two-phase reference amalgam usually maintained a constant electromotive force for a matter of minutes only; after that the electromotive force increased, indicating loss of zinc from the dilute amalgam.

calculating ΔE. Figure 1 demonstrates convincingly and for the first time that all the final results of the three accurate investigations are in good agreement. Crenshaw[2b] has already reached a similar conclusion, but in a less straightforward manner, by extrapolating an activity function to infinite dilution.[7] Hildebrand has stated[5a] (p. 506) that his equation will not fit Crenshaw's results; since these agree with the others, we must conclude that assuming the existence of Reaction 2 does not suffice to explain the deviations of the electromotive measurements from ideality if the zinc amalgams are in fact ideal solutions. Since Fig. 1 shows them to be ideal solutions within the relatively large concentration range where $\Delta E = 0$ (the range, that is, within which the electromotive forces—losses of zinc neglected—conform to the limiting horizontal line), we assume provisionally that they remain ideal over the entire range of composition; and that the equilibria, Reactions 2 and 3, are wholly responsible for the apparent deviations from ideality encountered at the higher concentrations.

Interpretation of the Experimental Data

Our polymerization hypothesis, which assumes the simultaneous existence of Zn_2 and Zn_3 in rapid equilibrium with monatomic zinc will receive quantitative support if we can show that reasonably constant values of K_2 and K_3 can be calculated from the experimental data. The complex Eq. 4 obviously cannot furnish the point of departure for a simple method of performing these calculations. A simple method, employing Crenshaw's concentration units, has been devised, however, and will now be outlined.

If the zinc amalgams are ideal solutions, Eq. 1 may be written

$$E_{id} = E_{act} = 0.09922T \log [(Zn)_1/(Zn)_2] \quad (5)$$

the concentration of total zinc, $\Sigma(Zn)$, in Eq. 1 being replaced by the concentration of monatomic zinc. Figure 1 shows that $(Zn) = \Sigma(Zn)$ for the more dilute amalgams; if any such dilute amalgam is chosen as common reference electrode, the evaluation of (Zn) for each of the more concentrated amalgams presents no difficulty. These evaluations were accordingly carried out for each set of measurements, and the corresponding values for the "equilibrium quotient," K'', defined by

$$(Zn)^2/[\Sigma(Zn) - (Zn)] = K'' \quad (6)$$

were calculated. K'' would obviously be identical with K_2, the equilibrium constant of Reaction 2, if only this reaction were of importance; under these conditions it should therefore be reasonably constant. Instead, these K'' values showed a pronounced trend in the direction pointing to the existence of a higher polymer, say Zn_3.

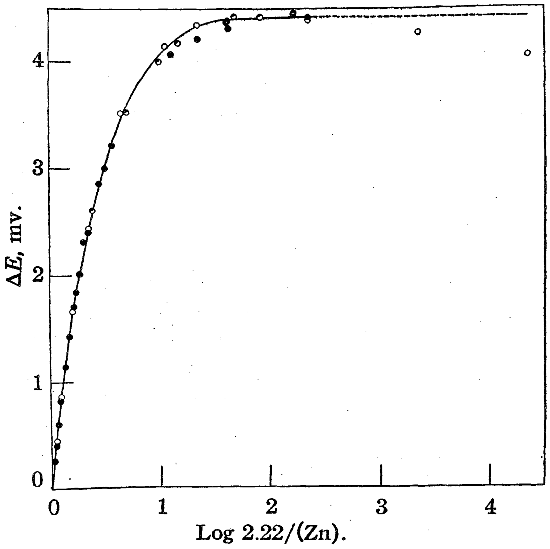

Fig. 1.—Deviations of the electromotive force for zinc amalgams near room temperature. The reference amalgam, for which $\Delta E = 0$, contains 2.220 g. Zn/100 g. Hg. ○, Crenshaw; ●, Pearce and Eversole; ◐, Richards and Forbes.

If Zn_2 and Zn_3 are the only polymers co-existing, then $\Sigma(Zn) = (Zn) + (Zn_2) + (Zn_3)$, and therefore by Eq. 6

$$K'' = (Zn)^2/[(Zn_2) + (Zn_3)] = (Zn)^2/[(Zn)^2/K_2 + (Zn)^3/K_3] \quad (7)$$

the expression on the right being obtained by introducing the equilibrium constants of Reactions 2 and 3. The K'' values for any pair of amalgams, a and b, fix a pair of equilibrium constant values (one for K_2 and one for K_3) because

$$(1/K'')_a = 1/K_2 + (Zn)_a/K_3 \text{ and}$$
$$(1/K'')_b = 1/K_2 + (Zn)_b/K_3 \quad (8)$$
$$\text{whence, } K_3 = \Delta(Zn)/[\Delta(1/K'')] \quad (9)$$

Calculations of K_3 were carried out by reckoning both increments for each of the more dilute amalgams from the most concentrated amalgam in the series; this procedure corresponds to the "long interval" method of evaluating specific rates and also to the experimental method of measuring each of the more dilute amalgams against the most concentrated. Since Fig. 1 shows the data from the three sets of accurate measurements to

TABLE I

K_2 AND K_3 FROM THE RESULTS OF PEARCE AND EVERSOLE AT 25°

No.	1	2	3	4	5	6	7
Σ(Zn)	2.2200	2.0874	1.9968	1.9037	1.8136	1.6353	1.4818
E_{act}	65.160	64.630	64.204	63.789	63.391	62.377	61.393
(Zn)	1.5733	1.5097	1.4604	1.4140	1.3709	1.2668	1.1734
K''	3.827	3.945	3.976	4.084	4.245	4.355	4.464
K_3	....	8.16	11.53	9.72	7.88	9.68	10.72
Σ(Zn) (calcd.)	2.2200[c]	2.0913	1.9945	1.9057	1.8253	1.6388	1.4803

No.	8	9	10	11	12	13
Σ(Zn)	1.3556	1.3052	1.2009	1.1105	1.0096	0.7912
E_{act}	60.528	60.180	59.280	58.467	57.448	54.768
(Zn)	1.0970	1.0676	0.9954	0.9344	0.8631	0.7006
K''	4.653	4.797	4.822	4.958	5.085	5.414
K_3	10.27	9.58	10.72	10.72	11.00	11.39
Σ(Zn) (calcd.)	1.3563	1.3100	1.1992	1.1088	1.0068	0.7877

No.	14	15	16	17	18	19
Σ(Zn)	0.6978	0.6037	0.17633	0.098837	0.051742	0.009858
E_{act}	53.392	51.656	36.700	29.421	21.195	Ref. elec.
(Zn)	0.6294	0.5498	0.17163	0.097383	0.051329	(0.009858)[a]
K''	5.790	5.618	6.267	6.522	6.379	....
K_3	10.65	12.29	13.79[b]	13.66[b]	14.56[b]	....
Σ(Zn) (calcd.)	0.6970	0.5990	0.17535	0.09851	0.05163	0.009869

Final values: $K_2 = 9.09$; $K_3 = 10.4$ (the arithmetic mean of the first fourteen values is 10.3).

[a] Assumed value. [b] Value omitted in taking average. [c] Value determining finally selected K_2.

be in good agreement, it follows that our hypothesis cannot conflict with any of these data if it agrees well with the data from the set of measurements best adapted to testing it, namely, those of Pearce and Eversole. Accordingly, the results of the other calculations will not be given; those corresponding to the data of Pearce and Eversole are summarized in Table I.

The K'' values in Table I clearly show a trend so marked and so consistent that it can scarcely be attributed to experimental errors; this trend, which indicates qualitatively the presence of a polymer higher than Zn_2, might have been predicted from the failure of Eq. 4 in conforming to Crenshaw's results.[10] There is no *trend* in the K_3 values, and the following analysis will show that their constancy is sufficiently good to establish our polymerization hypothesis as highly plausible. We observe first that, in accord with Eqs. 8, a K_3 result higher than the average means that the K_2 value paired with it will be correspondingly lower; the deviations from constancy for these two quantities are thus simply related. Next we notice that slight uncertainties in composition, which appear to be the most serious sources of error in these investigations, will have the greatest effect on K'' (and hence on K_2 and K_3) at the highest concentrations, where the increments in Eq. 9 are very small, and at the lowest, where the differences Σ(Zn)–(Zn) are not much larger than the uncertainties themselves. (To illustrate: if (Zn) for Nos. 2, 10 and 18 were assumed to be only 0.1% higher than in Table I, K_3 would be changed, respectively, to 6.9, 10.4 and 12.3.) The most convincing way to test our polymerization hypothesis is by using the finally selected K_2 and K_3 values to calculate Σ(Zn) for comparison with the amount of zinc used in making each amalgam; these calculations have been performed, with—as Table I shows— excellent results; only in three cases (Nos. 5, 15 and 16) is there an appreciable discrepancy (slightly larger than 0.5%) between the calculated and the experimental values.

Figure 1 indicates that this discrepancy in the last two cases is due to loss of zinc, so that the calculated Σ(Zn) values may well furnish a more reliable estimate of the actual composition of these amalgams than do the amounts of zinc used in preparing them. Since no "smoothing out" of the results has been done, the close agreement of

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(10) To show that assuming the existence of Reaction 2 alone fails to explain the experimental results, we need only attempt to calculate Σ(Zn) for, say, No. 1 on this basis. If only Reaction 2 were of importance, K'' would equal $(Zn)^2/(Zn)_2$; employing $K'' = 4.7$, the arithmetical mean of the first 15 Table I values, we obtain $(Zn_2) = 0.5266$; whence $\Sigma(Zn) = 2.0999$, a value that is unacceptable because it is 6% too low.

the two Σ(Zn) columns is gratifying—not often is it possible to find solutions that can be regarded as ideal over the entire range of composition and described so accurately by the assumption of two simple equilibria. The constitution of the liquid zinc amalgams at room temperature thus seems to be reasonably well established; our polymerization hypothesis, when applied to the results of Pearce and Eversole, gives for the composition of the saturated amalgam at 25°: (Zn) = 1.5733, (Zn_2) = 0.2723 and (Zn_3) = 0.3744.

An examination of the calculations based on the other accurate experimental results does not significantly alter these conclusions. For Crenshaw's data, three series of such calculations—employing as reference electrode the amalgam for which Σ(Zn) was, respectively, 0.1, 0.01 and 0.001—have been carried out; the results of all three sets are substantially in accord. The resulting individual K_3 values do not vary significantly more than those in Table I, but the average thereof is some 10 or 15% *lower* than the value selected from Table I; K_2 is correspondingly higher. The K_3 values from the results of Richards and Forbes are more erratic, and show a trend such that K_3 decreases with Σ(Zn). The average of these would be appreciably *higher* than 10.4, the Table I result; but the concentration range of Richards and Forbes' measurements is restricted, so that this average cannot be given serious weight. Since Pearce and Eversole have by far the greatest number of results extant for the concentration range where K_2 and K_3 can be most accurately determined, we shall adopt the values selected from Table I as final.

Summary and Conclusion

The electromotive force data for zinc amalgams have been re-examined, and it has been shown for the first time that all the final experimental results of the three accurate investigations made near room temperature agree excellently for the more concentrated amalgams and well for the dilute, whose investigation is complicated by their tendency to lose zinc. The deviations of these electromotive forces have been explained on a polymerization hypothesis that assumes the simultaneous existence of Zn_2 and Zn_3 in rapid equilibrium with monatomic zinc. A simple method for calculating the dissociation constants for these polymers has been devised and successfully applied to the electromotive force data; the constants thus obtained are satisfactory, so that the polymerization hypothesis and consequently the constitution of the liquid zinc amalgam at room temperature seem reasonably well established. If the validity of the polymerization hypothesis is granted, then it follows that the zinc amalgams at 25° behave as ideal solutions over the entire range of composition and that the fundamental laws underlying the Nernst equation govern them to within the precision of the measurements. The existing experimental work for other temperatures has permitted only these qualitative conclusions: the heats of dissociation of both polymers are small, that of Zn_3 being the greater.

Since the polymers have heats of dissociation not greatly exceeding RT, they cannot be very stable compounds. We must remember, therefore, that the evidence we have adduced for their existence, although as convincing as evidence of its kind can be, is after all indirect in nature; for we have shown only that zinc amalgams at 25° deviate from the laws of ideal solutions *almost exactly as though* Zn_2 and Zn_3 existed in rapid equilibrium with monatomic zinc. Here, as in the cases of many other solutions, it is difficult to decide whether such deviations, by whatever thermodynamic method they are established, should be attributed to compound formation or to a less definite interaction among the molecules composing the solution; a final decision becomes possible only when more direct experimental methods have "proved" the presence or absence of the compounds in question. Where aqueous solutions are concerned, their Raman spectra are often of service; but corresponding evidence for amalgams does not yet seem to be available.[11] Until it does appear, our indirect evidence would seem sufficiently strong to warrant regarding our polymerization hypothesis as provisionally established: for (1), this hypothesis involves only two equilibria (a much larger number would militate against it); (2), the corresponding equilibrium constants are accurately established (say, to within 5 or 10%); (3), no other set of two equilibria can be formulated that will fit the experimental data so well; and (4), any satisfactory alternative explanation of the deviations in question will have to yield ΔE values practically in-

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[11] In connection with our polymerization hypothesis, it is interesting to observe that many metallic vapors, probably including those of zinc, show band spectra indicating the presence of dimers. See Shawhan, *Phys. Rev.*, **48**, 343 (1935), and Robertson, *Nature*, **135**, 308 (1935), where other references are given.

distinguishable from those given by our polymerization hypothesis; whether any explanation based on intermolecular forces, but not assuming compound formation, will do this becomes doubtful when we remember (see Fig. 1) that ΔE becomes constant long before "infinite dilution" is reached.

It is not claimed, finally, that a *concentration* treatment of amalgams is generally preferable to a treatment in terms of *activities*. The latter quantities are always valuable since they stand, by definition, in simple relation to the free energies of the amalgams, and thus bridge the gap between the thermodynamic functions for an amalgam and its stoichiometric composition. But when amalgams become experimentally indistinguishable from ideal solutions in the manner of Fig. 1, then it seems desirable to try a concentration treatment also, in order to determine whether the deviations from ideality at the higher concentration cannot be quantitatively accounted for by assuming polymerization of the solute; for we may discover in this way what molecular species actually exist in these amalgams.

SCHENECTADY, N. Y. RECEIVED OCTOBER 1, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Energies and Entropies of Activation of the Reaction between Bromoacetate and Thiosulfate Ions[1]

BY VICTOR K. LA MER AND MILDRED E. KAMNER

In the theory of chemical kinetics there are two important quantities which determine the specific rate constant k, namely, the energy of activation E_{act}, defined through the differential form of the well-known Arrhenius equation

$$d \log k/dT = E_{\text{act}}/2.3RT^2 \qquad (1)$$

and the action constant $B = \log \alpha$ in the integrated form, namely

$$k = \alpha\, e^{-E_{\text{act}}/RT} \qquad (2)$$

$$\log k = B - E_{\text{act}}/2.3RT \qquad (3)$$

E_{act} represents the average energy of those molecules which react minus the average energy of all the molecules in the system, all quantities being defined per mole. La Mer[2] has shown as a consequence of this definition of E_{act}, due to Tolman, that

$$B = \log \alpha = \frac{1}{2.3R}\int_0^T \left(\frac{\partial E_{\text{act}}}{\partial T}\right)\frac{dT}{T} + \text{constant} \qquad (4)$$

determines the frequency with which the activated molecules react. In the special case where E_{act} remains independent of T at all temperatures, the integration constant in (4) equals log Z^0. In the case of unimolecular reactions Z^0 is the frequency of breaking the reactive bond in the activated molecule, whereas in a true bimolecular reaction Z° equals the collision frequency at unit concentrations. The dimension of B is time^{-1}.

The first term of B represents the increase in entropy due to the temperature dependence of E_{act} for the process, inactive molecules ⟶ active molecules, and hence has been called[2] the entropy of activation. Further experimental evidence for the temperature dependence of B and E_{act} for a zero type reaction will appear in another paper.[3]

The present paper will deal primarily with the temperature dependence of the kinetic salt effect in a reaction between ions of the same sign to ascertain in how far interionic attraction influences E_{act} and B. The bromoacetate–thiosulfate ion reaction $BrCH_2COO^- + S_2O_3^= \longrightarrow S_2O_3CH_2COO^= + Br^-$ was selected for the experimental study since it is almost unique among ionic reactions for the absence of side reactions and the high precision with which the velocity constant can be determined.[4]

Accordingly, the experiments were designed to test the behavior of E and B for (a) change of temperature at constant concentration of reactants; (b) change of ionic strength (Brönsted–Debye effect) for the same temperature interval; (c) the effect of substituting high valence cations like La^{+++} for the lower valence ions Ba^{++} and Na^+ at the same ionic strength, and (d) the influence of dielectric constant produced by the addition of non-electrolytes.[5]

The Limiting Law for E_{act} and B.—Equation

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[1] A preliminary report of these data was given in THIS JOURNAL, **55**, 1739 (1933). A more complete report was read at the St. Petersburg, Florida, meeting of the Society in March, 1934.

[2] La Mer, *J. Chem. Phys.*, **1**, 289 (1933); THIS JOURNAL, **55**, 1739 (1933).

[3] V. K. La Mer and M. L. Miller, *ibid.*, **57**, 2674 (1935).

[4] La Mer and Fessenden, *ibid.*, **54**, 2351 (1932).

[5] La Mer and Kamner, *ibid.*, **57**, 2669 (1935).

(1) and the Brönsted equation $\log k = \log k^0 + \log f_A f_B/f_X$ yields

$$E_{\text{act}} = E^0_{\text{act}} + [\bar{L}_X - (\bar{L}_A + \bar{L}_B)] \qquad (5)$$
$$= E^0_{\text{act}} + \Delta\bar{L}_{\text{act}}$$

when we recall that $\bar{L} = -RT^2\,\partial \ln f/\partial T$.

The superscript zero refers to the standard state of infinite dilution. $\bar{L} = H - H^0$ is the *relative* partial molal heat content, so that $\Delta\bar{L}_{\text{act}}$ may be called the heat of dilution for the activation process $A + B \rightleftarrows X$.

Similarly by using eq. (4), B can be decomposed into the components.

$$B = B^0 + [\bar{S}_X - (\bar{S}_A + \bar{S}_B)] \qquad (6)$$
$$= \log Z^0 + S^0_{\text{act}}/2.3R + \Delta\bar{S}_{\text{act}}/2.3R$$

$\Delta\bar{S}/2.3R$ is the increase in entropy of activation arising from interionic attraction.

When the thermodynamic operators $\bar{S} = -\partial\bar{F}/\partial T$ and $\bar{H} = \partial(\bar{F}/T)/\partial(1/T)$ are applied to the Debye–Hückel limiting law

$$\bar{F}_i = -N(\epsilon Z)^2\kappa/2D \qquad (7)$$
$$\kappa = C(DTV)^{-1/2}$$

one obtains on substituting Wyman's values[6] of $\partial \ln D/\partial \ln T = -1.371$ for water at 25°, that

$$\bar{L}_i = \bar{F}_i\left[3/2\frac{\partial \ln D}{\partial \ln T} + \frac{1}{2}\frac{\partial \ln V}{\partial \ln T} + 3/2\right] \qquad (8)$$
$$= \bar{F}_i\,[-0.51]$$
$$\bar{S}_i = \bar{F}_i/T\left[3/2\,\partial\ln D/\partial\ln T + \frac{1}{2}\partial \ln V/\partial \ln T + \frac{1}{2}\right] \qquad (9)$$
$$= \bar{F}_i/T[-1.52]$$

It is important to emphasize that in the limit for high dilutions, the *reversible* heat of dilution ($-T\bar{S}_i$) is almost exactly three times greater, *but opposite in sign* to the *irreversible* heat of dilution ($\bar{H}_i$). Now

$$\bar{F}_i/2.3RT = \log f_i = -0.506 Z_i^2\sqrt{\mu} \qquad (10)$$

and $Z_x^2 = (Z_A + Z_B)^2$, hence

$$\Delta\bar{L}_{\text{act}}/2.3RT = 0.51 Z_A Z_B\sqrt{\mu} \qquad (11)$$
$$\Delta\bar{S}_{\text{act}}/2.3R = 1.52\, Z_A Z_B\sqrt{\mu} \qquad (12)$$

The Brönsted–Debye equation, accordingly, can be written

$$\log k = [\log Z^0 + S^0_{\text{act}}/2.3R + 1.52\, Z_A Z_B\sqrt{\mu}]$$
$$- [E^0_{\text{act}}/2.3RT + 0.51 Z_A Z_B]\sqrt{\mu} \qquad (13)$$

The limiting slope of the experimental quantities $\log k$, B, and $E_{\text{act}}/2.3RT$ when plotted against $Z_A Z_B\sqrt{\mu}$ should be, respectively, 1.01, 1.52 and 0.51. Equation (11) thus predicts that in the limit of high dilutions the energy barrier, E_{act}, should increase by 684 $Z_A Z_B\sqrt{\mu}$ calories/mole as a result of interionic attraction.

On the prevailing view[7] that the function of a catalyst is to provide a lower by-pass in the energy barrier, one would be forced to conclude that the addition of a neutral salt should *decrease* the rate of a reaction between ions of the same sign—a conclusion which is contrary to abundant experimental evidence. The explanation is that the action constant B increases concomitantly in the limit about three times as rapidly as E_{act}, and hence B plays the predominant role in determining the magnitude of the neutral salt catalysis.

Preparation of Materials

Bromoacetic acid was redistilled at reduced pressure, sodium thiosulfate was recrystallized and solutions of sodium hydroxide and of potato starch were prepared as in earlier experiments.[8] Iodine was sublimed from a potassium iodide–iodine mixture, resublimed and stored over calcium chloride in a desiccator until used in the preparation of standard iodine solutions. The latter always contained 4% of Mallinckrodt neutral potassium iodide, Analytical Quality, the iodate content of which is not over three parts per million. Sodium chloride and barium chloride were recrystallized once and dried at a temperature exceeding 100°. Lanthanum chloride, precipitated from aqueous solution by hydrogen chloride, was washed with alcohol, air dried and stored over phosphorus pentoxide or calcium chloride. This sample yielded values for velocity constants which checked with those for solutions containing a Welsbach cerium-free lanthanum chloride purified several years earlier.[9]

Experimental Procedure

Two types of technique were employed for the bromoacetate–thiosulfate reactions.

1. For experiments in which the time error in starting and stopping the reaction is negligible, equal volumes of equimolar solutions of the reactants were mixed and the reaction was stopped by iodine titration as described by La Mer and Fessenden.[4]

2. A special type of flask, shown in Fig. 1, was devised to reduce errors in timing the more rapid reactions. The flasks were immersed in the thermostat, 50 cc. of sodium bromoacetate

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(6) Lange and Robinson, *Chem. Rev.*, **9**, 89 (1931).

(7) Getman–Daniels, "Outlines of Theoretical Chemistry," 5th Ed. John Wiley and Sons, Inc., New York City, 1931, p. 348.

(8) V. K. La Mer and M. E. Kamner, THIS JOURNAL, **53**, 2832 (1931).

(9) V. K. La Mer and R. G. Cook, *ibid.*, **51**, 2624 (1929).

solution was pipetted into (a) and 50 cc. of sodium thiosulfate solution of equal molarity was pipetted into (b). After temperature equilibrium had been reached the reaction was started by tipping the flask sidewise and prompt mixing was achieved by pouring the solution back and forth in the two compartments of the flask. To stop the reaction, iodine just insufficient to neutralize the remaining thiosulfate was pipetted into (a), then poured into (b) at a recorded time. The flask was placed in an ice-bath; the stopper and sides were washed down with about 50 cc. of cold distilled water; starch was added and the titration with iodine solution was completed as quickly as possible. The addition of 0.1 cc. of 0.1 *M* acetic acid to the solution before completion of the titration eliminated any possible error due to presence of hypoiodite. With this technique the error in starting and stopping the reaction was reduced to two to three seconds so that reactions involving times ranging from fifteen minutes to an hour yielded velocity constants as reproducible as those of slower reactions.

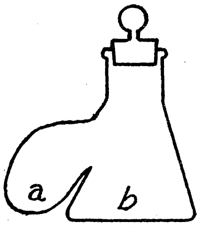

Fig. 1.

Corrections to be made to the end-point of iodine titrations were determined as the volume of the given iodine solution required to produce the same blue color in an equal volume of water containing starch and potassium iodide at the temperature of titration. The use of a daylight lamp improved the precision of the end-point in artificial light.

The fluctuations in the temperature of the thermostat rarely exceeded 0.01° during any of the experiments, except at 50° where the precision of the time average was ±0.01°. Any errors entering into the absolute temperatures, which were determined by the use of the ice-point and of a thermometer calibrated by the Bureau of Standards, cannot be of sufficient magnitude to make any significant difference in the data. For a temperature interval of 25° the uncertainty in E_{act} arising from the uncertainty in temperature is estimated as 0.16% and for a 12.5° interval 0.32%; that is, the order of 24 or 48 calories, respectively.

At 50° eight carefully conducted experiments (no added neutral salts) exhibited a small but reproducible decrease in the velocity constant with the progress of the reaction. The reaction is very rapid at 50° but the drift at this temperature does not appear to be due to errors in timing. We attribute the difficulty to intrusion of the spontaneous water reaction $H_2O + CH_2BrCOO^- \longrightarrow CH_2OHCOO^- + H^+ + Br^-$. This reaction is of entirely negligible velocity at 25 and 37.5° ($k_{25} = 2.8 \times 10^{-6}$) but assumes sufficient importance to vitiate highly precise results at 50°. No data or conclusions are submitted in this paper for temperatures higher than 37.5°.[10]

Recently, Kiss and Vass[11] have reported temperature coefficient data for this reaction over the range 5 to 55°.[12]

The results for the water reaction at 25 and 50° are recorded also in Table I. The method employed consisted in bringing the aqueous solution of sodium bromoacetate to temperature as quickly as possible. The hydrogen ion formed by the hydrolytic reaction was neutralized with sodium hydroxide to a *p*H of 7 at frequent intervals to prevent acid catalysis, using bromthymol blue as indicator. Minor sources of error are incomplete temperature equilibrium at the beginning of the reaction, and the influence of carbon dioxide upon the titration values. To increase the precision, a large number of measurements was made, and the early readings which were burdened with time and temperature errors discarded. The velocity constants for the progressive time intervals were compared with those calculated from the initial time. The $E_{(25-50)}$ for the bromoacetate–water reaction was reproducible to about 0.7% (175 cal.). For typical experiments illustrating the high precision and constancy of the individual velocity constants of the thiosulfate reaction, the reader is referred to the following paper.

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[10] A. N. Kappanna [*J. Indian Chem. Soc.*, **6**, 45 (1929)] reports velocity constants for the thiosulfate reaction at 30, 40 and 50° at eleven concentrations ranging from $\mu = 0.0025$ to 0.085. He states "The *temperature coefficient* of reaction velocity constant on either side of 40° and at different ionic strengths has *almost* the same value, within *narrow* limits 2.2 to 2.3 for a rise in temperature of 10° C." (Italics ours.) Our calculations of his data show that E_{30-40} is 15,320 ± 500 calories an average deviation from the mean which is about ten times as great as ours. *Cf.* Moelwyn-Hughes, "Kinetics of Reactions in Solutions," p. 201, for a similar calculation.

[11] Kiss and Vass, *Z. anorg. allgem. Chem.*, **217**, 305–320 (1934).

[12] They claim that log *k* varies linearly with $1/T$ in all cases. An examination of their Table 8, however, shows that their E_{act} values for 10-degree intervals fluctuate so irregularly and so violently with temperature (800 calories for the interval 5–15° and 15–25°) that one can only conclude that their experimental errors are too large to establish deviations from a temperature independent E_{act}. On the other hand, the data in their Tables 1 and 4 are sufficiently consistent to support our conclusion that the salt catalysis is primarily the result of an increase in the entropy of activation, and certainly does not result from any decrease in the energy of activation.

Calculations

The bimolecular velocity constants were calculated from the formula, $k = \frac{1}{t} \times \frac{1}{a} \times \frac{x}{(a - x)}$ applicable when $a = b$ = moles of reactants per liter of solution. The time, t, is expressed in minutes. All solutions were standardized at room temperature. However, the correct molarity to be substituted in the bimolecular equation at other temperatures differs slightly from the molarity at 25°, because of the expansion or contraction of the solution. To obtain k in moles per liter at the temperature of reaction, the velocity constant at $t°$ was multiplied by the factor

$$\frac{(\text{volume of 1 g. of water at } t°)}{(\text{volume of 1 g. of water at } 25°)}$$

The values of k used in calculation of the energy of activation are the values of k for the molarity at the temperature indicated. This introduces a very small further correction. $\Delta \log k$ must be obtained as the difference of the logarithms of two velocity constants at different temperatures but for identical volume–molar concentrations. Hence, a correction of $\left[\frac{\mathrm{d} \log k}{\mathrm{d}\sqrt{\mu}} (\sqrt{\mu_{t0}} - \sqrt{\mu_{25}})\right]$ has been subtracted from $\log k_{\text{obsd.}}$ at $t°$. It does not exceed 0.0003.

Method of Calculating Precision of E Values

The error in average $\log k$ is estimated so as to take account not only of the error in the mean k in each of one or more experiments, but also the difference between two mean k values for two separate experiments, whenever these were performed. Thus, it is a measure of precision within a given experiment and of the reproducibility of the value. The error in $\Delta \log k$ is evaluated as the square root of the sum of the squares of the errors in the two average $\log k$ values from which it is derived. An error of 25 calories in the determination of E produces an uncertainty of 0.02 units in B in eq. (3).[13]

Discussion of Results

Table I contains the data for $\log k$ for the bromoacetate–thiosulfate ion reaction for various temperatures and additions of neutral salts. These data are plotted in part in Fig. 2 for 0 and 25° to illustrate the specific character of the positive salt catalysis in the presence of Ba^{++} and La^{+++} ions, and the parallelism of the curves at the two temperatures in the absence of these high valence ions.

The values E_{act} are given in the next to the last column. They indicate that $E(0–25°)$ increases by 127 ± 60 calories (15,881 to 16,008) on passing from $\sqrt{\mu} = 0.0895$ to 0.141, and decreases slowly to 15,941 calories at $\sqrt{\mu} = 0.447$. The initial rise in E_{act} appears to be greater than the demands of the limiting law but the probable experimental error is too large for the short interval to warrant a definite conclusion. An examination of the calorimetrically determined values of $\overline{H}$ for salts shows that the individual deviations[14] from the limiting law persist to much lower concentrations than is the case for the function $\overline{F}$. In fact $\overline{H}$ for sodium iodate, potassium nitrate and barium nitrate passes through a maximum in the neighborhood of $\sqrt{\mu} = 0.10$ quite similar to the behavior of E_{act}. The action constant B rises sharply from 11.19 ($\sqrt{\mu} = 0.0895$) to 11.35 ($\sqrt{\mu} = 0.141$) at a rate which is slightly greater than the limiting law prediction. For further increases of μ, B rises less rapidly but steadily to 11.55 at $\sqrt{\mu} = 0.477$. See Figs. 3 and 4. It will be noted that in this case where the ionic strength increase results solely from an increase in concentration of the reactants in the form of their sodium salts, the increase in $\log k$ is due primarily to an increase in B and only secondarily if at all to a variation in E_{act}. In the following paper the rate of this reaction in

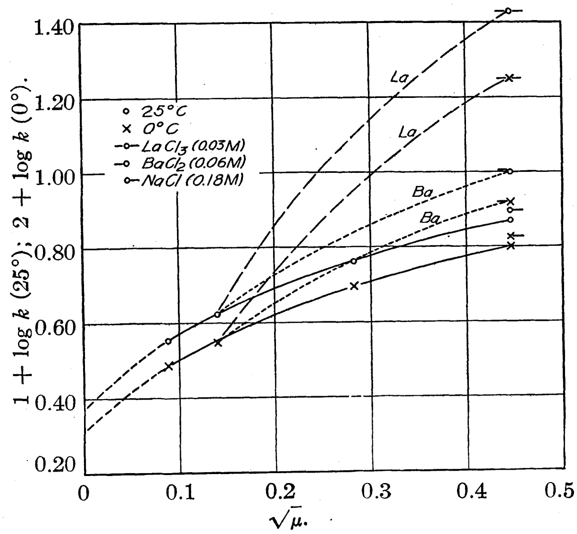

Fig. 2.

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(13) The correction to the energy of activation arising from the dependence of the collision number upon $\sqrt{T}$ amounts to −278 calories for the (0–12.5°) range and to −303 calories for the (25–37.5) range. This correction would magnify the decrease of E with T from 0 to 37.5° by 25 calories and thus strengthens slightly the conclusion that E_{act} is a function of T.

(14) Lange and Robinson, ref. 6, Figs. 8 and 10.

TABLE I

LOG *k*, *E* AND *B* DATA FOR THE REACTION SODIUM BROMOACETATE AND SODIUM THIOSULFATE IN AQUEOUS SOLUTION WITH AND WITHOUT ADDED NEUTRAL SALTS

Sodium Bromoacetate and Sodium Thiosulfate

Concn. moles/liter	*t*, ° C.	Detns.	Conversion range %	*k* Corrected to *m/l* at 25°	2 + log *k*	2 + av. log *k* corr.	Δ log *k*	*E*	*B*
0.002	0	5	12–25	0.03084 ± 0.00007	0.48911 ± 0.001	0.49067	1.06401 ± 0.0018	15,881 ± 30	11.19
.002	0	2	29	.03109 ± .00005	.49262 ± .0007				
.002	25	5	22–68	.3594 ± .0012	1.55558 ± .0015	1.55558			
.005	0	4	39–58	.03523 ± .00003	0.54691 ± .0004	0.54669	0.56244 ± .0011	16,072 ± 30	11.41
.005	12.5	4	7–46	.1286 ± .0003	1.10924 ± .0010	1.10913		(16,008)	
.005	25	4	37–71	.4187 ± .0002	1.62190 ± .0002	1.62034 ± .0013	0.51121 ± .0016	15,946 ± 50	11.30
.005	25	6	40–74	.4162 ± .0006	1.61930 ± .0006		0.46742 ± .0014	15,856 ± 50	11.24
.005	37.5	5	17–60	1.223 ± .0015	2.08743 ± .0005	0.08776			
.02	0	5	47–71	.04902 ± .00007	0.69037 ± .0006	2.68994	1.07176 ± .0007	15,983 ± 10	11.48
.02	25	4	52–59	.5777 ± .0002	1.7610 ± .0002	1.76170			
.05	0	5	18–50	.06344 ± .00029	0.80236 ± .0020	2.80203	1.06896 ± .0021	15,941 ± 30	11.55
.05	25	4	35–72	.743 ± .001	1.87099 ± .0006	1.87099			

Sodium Bromoacetate and Sodium Thiosulfate: 0.18 *M* in NaCl

Concn. moles/liter	*t*, ° C.	Detns.	Conversion range %	*k* Corrected to *m/l* at 25°	2 + log *k*	2 + av. log *k* corr.	Δ log *k*	*E*	*B*
0.005	0	5	9–48	0.06675 ± .00007	0.82445 ± .0005	0.82423	0.56730 ± .0013	16,211 ± 40	11.79
.005	12.5	5	17–62	.2464 ± .0007	1.39164 ± .0012	1.39153		(15,947)	(11.59)
.005	25	4	13–53	.784 ± .005	1.89432 ± .0030	1.89432	.50279 ± .0032	15,683 ± 100	11.38
.005	37.5	3	27–49	2.233 ± .007	2.34889 ± .0014	2.34922	.45490 ± .0033	15,431 ± 120	11.19

( ) Values for 0–25°.

Sodium Bromoacetate and Sodium Thiosulfate: 0.06 *M* in $BaCl_2$

Concn. moles/liter	*t*, ° C.	Detns.	Conversion range %	*k* Corrected to *m/l* at 25°	2 + log *k*	2 + av. log *k* corr.	Δ log *k*	*E*	*B*
0.005	0	5	11–51	0.08212 ± 0.00005	0.91445 ± 0.0003	0.916 ± .001	0.57225 ± .002	16,353 ± 60	12.00
.005	0	4	8–31	.08273 ± .00012	.91766 ± .0006			(16,248)	(11.92)
.005	12.5	5	25–69	.3086 ± .0005	1.48940 ± .0007	1.488 ± 0.001	.51730 ± .002	16,136 ± 60	11.83
.005	12.5	5	31–68	.3069 ± .0006	1.48700 ± .0009				
.005	25	3	23–57	1.014 ± .003	2.00604 ± .0013	2.00530 ± 0.0015			
.005	25	4	23–60	1.011 ± .001	2.00475 ± .0004				
.005	37.5	4	31–48	2.972 ± .009	2.47305 ± .0013	2.473 ± 0.002	.46767 ± .002	15,864 ± 60	11.61
.005	37.5	4	31–61	2.968 ± .014	2.47246 ± .0020				

Sodium Bromoacetate and Sodium Thiosulfate: 0.03 *M* in $LaCl_3$

Concn. moles/liter	*t*, ° C.	Detns.	Conversion range %	*k* Corrected to *m/l* at 25°	2 + log *k*	2 + av. log *k* corr.	Δ log *k*	*E*	*B*
0.005	0	4	18–49	0.117 ± 0.002	1.248 ± .005	1.245 ± 0.005	0.611 ± .005	17,500 ± 150	13.3
.005	0	5	15–54	.174 ± .001	1.241			(17,780)	(13.46)
.005	12.5	4	23–47	.7181 ± .0014	1.85618	1.85622 ± 0.0004			
.005	12.5	4	24–64	.7182 ± .0007	1.85625				
.005	25	4	30–66	2.724 ± .003	2.43521	2.43497 ± 0.0005	0.57875 ± .0007	18,052 ± 25	13.66
.005	25	4	21–69	2.721 ± .009	2.43473				
.005	37.5	10	32–68	8.8 ± 0.2		2.944 ± .010	0.509 ± 0.01	17,270 ± 350	13

Log *k*, *E* and *B* Data for the Reaction Sodium Bromoacetate and Water

Concn. moles/liter	*t*, ° C.	Detns.	Conversion range %	6 + log *k* corr.	Δ log *k*	*E*	*B*
0.05	25	7	10–45	0.4440 ± 0.003	1.4121 ± 0.004	24,915 ± 70	12.69
.05	50	10	18–74	1.8561 ± .0024			
.1	25	7	8–42	0.5276 ± .010	1.4013 ± 0.01	24,725 ± 175	12.64
.1	50	11	9–66	1.9289 ± .001			

the presence of 32.4% sucrose is reported. In this solvent we find that *B* increases from 11.02 to 11.49 or 0.47 units for the same range of concentration of reactants, while E_{act} rises slowly but at a lower level than for water.

The addition of 0.18 *M* sodium chloride to $a = b = 0.005$ *M* to produce $\sqrt{\mu} = 0.447$ yields *E* (0–25) = 15,947 and *B*(0–25) = 11.59. These values do not differ very significantly from those for $a = b = 0.05$ *M* ($\sqrt{\mu} = 0.447$) and we may conclude that chloride ions exercise no specific effect on either *E* or *B*.

On the other hand, the presence of 0.06 *M* barium chloride and particularly 0.03 *M* lanthanum chloride to produce the same $\sqrt{\mu} = 0.447$ produces a marked increase in both *B* and *E*. In the presence of 0.03 *M* lanthanum chloride *E* increases by 1780 cal and *B* increases from 11.55 to 13.46 or almost two logarithmic units.

The substitution of La^{+++} for Na^{+} (and to a less degree Ba^{++} for Na^{+}) creates a situation in which the reactant anions must cluster about the La^{+++} ion. By referring to the Fig. 2 of La Mer and Fessenden, where log *k* (25°) is plotted against $\sqrt{\mu}$, it will be noted that log *k* increases rapidly for small additions of La^{+++} but reaches at low concentrations what appears to be a constant saturation value. This behavior can be explained qualitatively on the basis of the higher terms of the Gronwall–La Mer equation, or when $(Z_1Z_2\epsilon^2/DakT)$ becomes too large for rapid convergence, by the more pictorial but essentially equivalent concept of ion-association as defined by Bjerrum. Thus, the later theory predicts[15] that in the presence of La^{+++} most of the reactants will exist as ion-associated pairs of the type $(LaS_2O_3)^+$ colliding with $BrAc^-$ or as $(LaBrAc)^{++}$ colliding with $S_2O_3^=$ for reaction. The ternary complex $(LaBrAcS_2O_3)^\circ$ may also have a finite life-time. We consider it significant that B increases to a value (13.3) in the presence of La^{+++} which is substantially identical with B for the uncharged methyl ester–thiosulfate-ion reaction. In the next paper we direct attention to a similar state of affairs produced by lowering the dielectric constant to a point where ion-association becomes predominant in the absence of high valence ions. The reaction then behaves substantially as one between uncharged reactants.

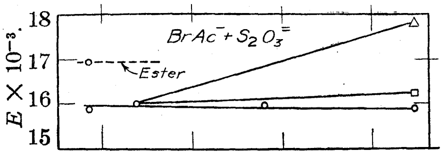

Fig. 3.—○, Sodium salts; □, $BaCl_2$ added; △, $LaCl_3$ added.

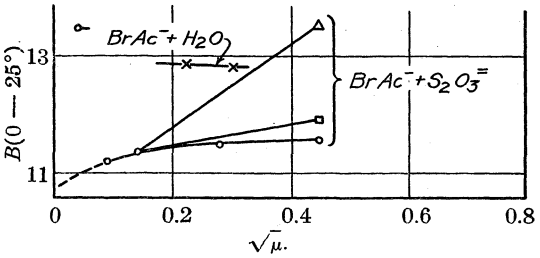

Fig. 4.—-○-, Methyl ester–thiosulfate reaction; ○, reactants present as sodium salts; □, $BaCl_2$ added; △, $LaCl_3$ added.

In any case the highly abnormal local accumulation of reactant anions around a La^{+++} ion will operate to increase $\Delta\bar{L}_{act}$ well above the demands of the limiting law so that E_{act} will be increased. On the theory that the height of the energy barrier is the sole regulator of the rate of reaction, one would be tempted to predict that the rate should be decreased.

The clustering of the reactant anions about a central La^{+++} ion, however, provides a greatly enhanced opportunity for collisions between the bromoacetate and thiosulfate ions. This increase in total number of collisions will be reflected in $\Delta\bar{S}_{act}$, the increase in entropy of activation due to interionic attraction. In Section 2 it was shown that the limiting form of the Debye theory predicts that $\Delta\bar{S}_{act}/2.3R$ increases three times as rapidly as $\Delta\bar{L}_{act}/2.3RT$; it is reasonable to assume that a similar qualitative relation will hold in the high valence mixtures, even though an exact calculation cannot be made.[16]

Hence the increase in B is of sufficient magnitude to more than counterbalance the rate-depressing effect of an increase in E_{act}. The temperature dependence of these marked catalytic effects of high valence ions of sign opposite to the reacting ions furnishes convincing evidence of the importance of taking into account the variations in the entropy of activation as well as the energy of activation in developing a satisfactory theory of catalytic behavior. The previous theories appear to have neglected the most important factor.

Influence of Concentration and Temperature

A closer examination of the data reveals for $a = b = 0.005\ M$ where the reaction has been studied at 12.5° intervals that E_{act} decreases (see Fig. 5) by a small but significant amount (216 cal.), which of course is exactly paralleled by the decrease in B from 11.41 to 11.24. The parallel decrease in B[17] is a result of the relation $\partial E_{act}/\partial B = 2.3RT$ which holds when the solvent is constant. This decrease of E_{act} and B values with rising temperature is more definite in the data for

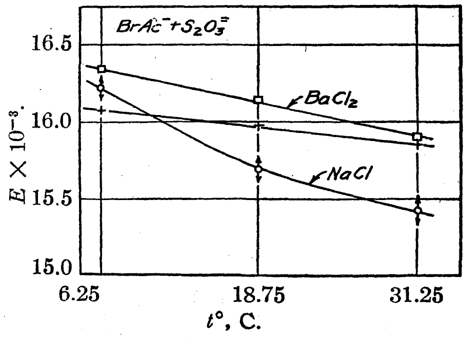

Fig. 5.—+ No added salt.

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[15] Fuoss and Kraus, THIS JOURNAL, series of papers from 1933 on; Fuoss, *Chem. Rev.*, **17**, 27 (1935).

[16] For the complications involved in the calculation, see La Mer and Parks [THIS JOURNAL, **55**, 4343 (1933)], particularly pages 4352–3.

[17] See Mary L. Miller, Thesis, Columbia University, 1934, for a more elaborate discussion of the necessity of parallel E and B values for a constant solvent at different temperature intervals.

0.18 *M* sodium chloride additions, where the heat capacity of activation is of the order of -12 cal./deg./mole (see Fig. 5).

In Eyring's theory,[18] which appeared after this work was completed, the activated complex is defined in terms of the partition function (sum of state) of the activated complex. In this theory the attempt is made to dispense completely with the concept of collisions and steric factors in reaction kinetics. Any changes in collision frequency, therefore, will be reflected entirely in terms of an entropy of activation. While this view has the advantage of being independent of any molecular picture, and may prove fruitful in the present case, we incline to the view supported by O. K. Rice and Gershinowitz that the collision mechanism has pictorial merit and should not be entirely discarded.[19]

Rodebush[20] has also pointed out that the collisional mechanism and Eyring's treatment are different but essentially equivalent ways of describing the same phenomenon, a conclusion which is evident from our eq. (4).

One may say, depending upon the point of view, that the reaction proceeds more rapidly as a result of an increase in the number of effective collisions, produced in the present data by an increase in the concentration of positive ions, or that the rate increases because of an increase in the entropy of activation,[21] which means that the number of systems crossing the energy barrier per unit of time is increased as a result of the increased number of reactive complexes per unit of volume of phase space.

Summary

1. An equation has been derived, based upon the limiting form of the Debye–Hückel theory, which predicts that E_{act}, the energy of activation of a reaction, and the entropy of activation (action constant B), will vary for water at 25° with the square root of ionic strength according to the law $E_{\text{act}}/2.3RT = E^0_{\text{act}}/2.3RT + 0.51\ Z_AZ_B\ \sqrt{\mu}$ and $B = B^0 + 1.52\ Z_AZ_B\ \sqrt{\mu}$.

2. The temperature coefficients of the reaction bromoacetate ion plus thiosulfate ion have been studied precisely over a range of temperature and concentration to obtain significant data for the effect of temperature and ionic environment upon E_{act} and B. For the sodium salts at $a = b = 0.005\ M$, $\partial E_{\text{act}}/\partial T = C_{\text{act}} \cong -8.6$ for the range 0–37.5°, in the presence of 0.18 *M* NaCl $C_{\text{act}} \cong -12$ cal./deg. mole.

3. The increase in log *k* produced by the addition of low valence ions (Na^+) is closely correlated with an increase in *B*.

4. In the presence of high valence ions (Ba^{++} and La^{+++}) of sign opposite to the reacting anions, E_{act} is considerably increased, but this retarding effect of an increase of height of the energy barrier is more than compensated for by an increase in the entropy of activation.

This example represents an interesting exception to the theory of catalytic action as usually stated and is discussed in the terms of the picture of ion-association.

NEW YORK, N. Y. RECEIVED AUGUST 15, 1935

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[18] Eyring, *J. Chem. Phys.*, **3**, 107 (1935). See also the very recent paper of Wynne-Jones and Eyring [*ibid.*, **3**, 492 (1935)] which reached us after this paper was written.

[19] O. K. Rice and Gershinowitz, *ibid.*, **2**, 273, 853 (1934); Evans and Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1935); *J. Chem. Phys.*, **3**, 479, 490 (1935).

[20] Rodebush, *J. Chem. Phys.*, **3**, 242 (1935).

[21] Brandsma appears to have been the first to identify the collision frequency and steric factors as entropy quantities. Brandsma, Thesis, Delft, 1925; *Rec. trav. chim.*, **47**, 94 (1928); **48**, 1205 (1929).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Influence of Non-Electrolytes upon the Kinetics of the Reaction between Bromoacetate and Thiosulfate Ions[1,2]

BY VICTOR K. LA MER AND MILDRED E. KAMNER[3]

Introduction

The literature contains few precise values of the energy of activation for non-ionic reactions and still fewer values in the case of ionic reactions. The problem of solvent influence upon the kinetics of ionic reactions has been approached only through the change in velocity constant and with one exception[4] the data are limited to a single temperature and usually to one concentration of reactants.[5] In this investigation, both the energy and the entropy of activation calculated from experimental data for reaction velocity constants are utilized as a means of approach to the problem of solvent effect upon reaction velocity. The purpose of this investigation was to compare the data in terms of E_{act} and B for the bromoacetate–thiosulfate reaction after addition of urea, sucrose, glycerol or dioxane with the corresponding data for aqueous solution.

Materials

The purification of reacting materials has been described previously.[6]

Urea.—Pure carbamide was recrystallized from distilled water. The solution was not warmed above room temperature as Wyman[7] found that urea solutions allowed to stand for several hours at a temperature of 30 or 35° undergo a change associated with a change in conductivity. The urea was thoroughly air-dried and kept in a calcium chloride desiccator overnight before use.

Sucrose.—Commercial packaged cane sugar was used.

Glycerol.—Kahlbaum twice-distilled glycerol, density 1.26, was employed.

Dioxane.—The commercial product was purified as described by Kraus and Fuoss.[8]

Experimental

The reacting solutions were prepared as follows.

After a solution of bromoacetic acid had been neutralized with sodium hydroxide solution, a weighed quantity of non-electrolyte was added and the solution was made up to volume and weighed. Sodium thiosulfate solution was prepared so as to contain the same weight per cent. of non-electrolyte as the bromoacetate solution and its molarity was determined by titration against a primary iodine standard and adjusted to that of bromoacetate solution.

For the velocity measurements, the two types of technique described in the previous paper were employed. Analytical errors are not greater than one part per thousand.

Experiments were carried out at 25.00 ± 0.01° and at 0.00 ± 0.02°. The 25.00° point was determined on two Beckmann thermometers by means of a platinum resistance thermometer (kindness of Dr. Shedlovsky of The Rockefeller Institute for Medical Research); the readings agreed throughout the work. For zero degrees, two Beckmann thermometers were set at the ice-point of water and the settings were checked frequently. A refrigeration unit maintained the temperature of a water–ethylene glycol bath at zero degrees. Two or more hours were allowed for temperature equilibrium at 25° and at least three hours at 0° before mixing the reactants.

Concentrations of reactants are expressed in moles per liter of solution at 25°. Concentrations of non-electrolytes are in grams of non-electrolyte per 100 g. of solution.

Analytical Precision and Controls

Sodium thiosulfate solutions were freshly prepared for each experiment. Much has been written about the instability of dilute solutions of sodium thiosulfate but the possibility of decomposition in the solid state seems to have been disregarded. A sample of $Na_2S_2O_3 \cdot 5H_2O$ which had been recrystallized several years before and yielded excellent results at that time, gave drifting velocity constants. The cause may have been a slight decomposition to form sulfur and sulfite ion; then, in solution, thiosulfate ions and sulfite ions reacted with bromoacetate simultaneously during the early part of the reaction, accounting for the drift in velocity constants. This source of error does not enter into any of the data presented here.

Commercial dioxane gave an acid solution with water and contained an impurity which oxidized iodide to iodine. After treatment with sodium hydroxide, drying with barium oxide and refluxing over sodium, a non-oxidizing sample was obtained. From an aqueous solution of this dioxane, thiosulfate measured by iodine titration gave 100.2% recovery after twenty-four hours and 100.6% recovery after two weeks. However, the iodine end-point is yellow in the presence of starch and dioxane! Whether dioxane samples remained free of oxidizing impurity and for what period of time was unpredictable and seemingly without relation to their having been protected from light or stored with or without water. It appeared to be not merely a matter of sufficiently long treatment with sodium.

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(1) This paper is abstracted from the dissertation of Mildred E. Kamner presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, at Columbia University, July, 1934. For details, the reader is referred to The Dissertation.

(2) Read at the New York meeting of the American Chemical Society, April, 1935.

(3) Fellow, American Association of University Women (Dorothy Bridgman Atkinson Fellowship of the Northwest Central Section) 1933–34.

(4) A. N. Kappanna, *J. Indian Chem. Soc.*, **6**, 419 (1929).

(5) M. Prasad, C. L. Mankodi and R. D. Godbole, *ibid.*, **7**, 59 (1930); C. V. King and O. F. Steinbach, THIS JOURNAL, **52**, 4779 (1930); A. v. Kiss, *Acta Chemica, Mineralogica, Physica*, **3**, 20 (1933); D. Straup and E. J. Cohn, Preliminary Note, *J. Biol. Chem.*, **105**, Scientific Proc. LXXXVII (1934).

(6) La Mer and Kamner, THIS JOURNAL, **57**, 2662 (1935).

(7) J. Wyman, Jr., *ibid.*, **55**, 4116 (1933).

(8) C. A. Kraus and R. M. Fuoss, *ibid.*, **55**, 21 (1933).

Malone and Ferguson[9] reported that different samples of dioxane showed different dielectric constants depending upon the length of time the dioxane was allowed to stand over sodium. The data for the experiment with a dioxane–water mixture are presented as being only semi-quantitative; the reaction mixture was of *p*H about 5.5 to 6, assuming the same indicator colors for dioxane–water as for water.

The starch–iodine end-point was more easily detected by placing the solutions in an ice-bath. Blanks were usually from 0.01 to 0.04 cc. of iodine solution. If the total blank were due to the added non-electrolyte or an impurity in it, a mole of urea, sucrose or glycerol would react with 10^{-5} to 10^{-6} equivalents of iodine.

Thiosulfate ion does not react with urea, sucrose or glycerol in aqueous solution as shown by iodine titration values which agreed to within less than a part per thousand with the values in the absence of non-electrolyte. The following data show no indication of appreciable side reactions of bromoacetate ion in the presence of these non-electrolytes either with them or with water.

TABLE I

Concn. of reactants, *M* $a = b$	Non-electrolyte, %	% Completion of reaction Obs.	% Completion of reaction Theoretical[a]	Moles of bromoacetate reacting with one mole of thiosulfate
0.02	21.2 Urea	98.6	99.6	0.989
.05	21.2 Urea	99.2	99.9	.993
.05	21.0 Urea	98.6	99.2	.994
.02	32.4 Sucrose	99.97	99.7	1.003
.05	32.3 Sucrose	99.5	99.7	0.998
.02	67.9 Glycerol	98.6	98.9	.997

[a] Calculated on basis of initial quantities of reactants.

Calculations

The precision of *k* is expressed as the average deviation of a single value from the mean. The reliability of E_{act} was calculated using the maximum k_{25} value and minimum k_0 value as indicated by the individual precisions of *k* less the E_{act} using the average *k* values. This estimate of the deviations of E_{act} is thus a maximum for this pair of experiments. $\Delta E_{\text{act}} = (E_{\text{act}}$, non-electrolyte $- E_{\text{act}}$, water). The precision measure of ΔE_{act}, $=$ [(precision in E_{act}, water)^2 + (precision in E_{act}, non-electrolyte)^2]$^{1/2}$. An error of 25 calories in E_{act} produces an error of about 0.02 logarithmic unit in *B*.

The detailed data for the velocity constants of four representative experiments are in Table II; the solvent in each case is water and the non-electrolyte indicated. Table III contains values of E_{act} and *B* for the reaction in aqueous solution quoted from the previous paper.[10] The values of E_{act} and *B* for the reaction in solutions containing non-electrolytes and the deviations of E_{act}, *B* and *k* from the values for aqueous solutions appear in Table IV.

TABLE II

t, min.	$(a - x)$ in cc. iodine,	% Reactants converted	*k*
Urea = 21.2%. $a = b = 0.05$, $T = 0°$			
0	44.09	..	...
84.4	33.31	24.4	0.0767
139.4	28.65	35.0	.0773
213.9	24.19	45.1	.0769
274.2	21.40	51.5	.0773
Average			.0771 ± 0.0003
Corrected for volume change			.0765
Sucrose = 32.4%, $T = 25°$. $a = b = 0.005$			
0	40.74	..	...
137.5	31.58	22.5	0.4219
177.6	29.63	27.3	.4223
378.9	22.66	44.4	.4214
1129.2	12.06	70.4	.4212
		Average	.4217 ± 0.0005
Glycerol 67.9%, $T = 0°$. $a = b = 0.02$			
0	49.50	..	...
247.5	36.81	25.6	0.0696
248.5	36.70	25.9	.0702
1042	20.28	59.0	.0691
1042	20.30	59.0	.0690
1092	19.67	60.3	.0694
Average			.0695 ± 0.0004
Corrected for volume change			.0690
Dioxane 50.3%, $T = 25°$. $a = b = 0.005$			
0	46.50	..	...
76	38.17	17.9	0.574
285	25.79	44.5	.564
334	23.95	48.5	.564
1154	10.90	76.6	.566
		Average	.567 ± 0.004

TABLE III

Concn. of reactants $a = b$ in aqueous soln.	$E_{(0-25)}$	*B*
0.002	15,880 ± 70	11.19
.005	16,010 ± 30	11.35
.02	15,980 ± 10	11.48
.05	15,940 ± 40	11.55

Discussion

The addition of urea, sucrose, glycerol or dioxane increased the rate of the bromoacetate–thiosulfate reaction in water at 25 and 0°, the only exception being the 2% decrease in *k* at 25° when a 0.002 *M* solution of reactants is 1.08 *M* in sucrose. These results are shown in Fig. 1. The change in velocity constant is not determined by the ratio of sucrose to reactants.

An interpretation of the changes in velocity constant can be obtained through consideration

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[9] M. G. Malone and A. L. Ferguson, *J. Chem. Phys.*, **2**, 99 (1934).

[10] V. K. La Mer and M. E. Kamner, Paper read at the March, 1934, meeting of the American Chemical Society.

TABLE IV

Concn. $a = b$ M	t, °C.	Average k	Log k + 2	E	ΔE from water	ΔE accounted for by errors	B	ΔB from water	% Δk from water 25°	% Δk from water 0°
Urea = 21.2% = 3.73 M										
0.05	25	0.903								
.05	25	.897[a] ± 0.003	1.9542	15,970 ± 40	+ 30	60	11.65	+0.10	+21.1	+20.7
.05	0	.0765 ± .0003	0.8837							
.02	25	.726 ± .0003	1.8609	16,000 ± 10	+ 20	15	11.58	+ .10	+25.6	+25.2
.02	0	.0613 ± .00005	0.7880							
Sucrose = 32.4% = 1.08 M										
0.05	25	0.795 ± 0.003	1.9004	15,820 ± 50	− 120	65	11.49	−0.06	+ 7.0	+ 9.0
.05	0	.0691 ± .0003	0.8395							
.02	25	.605 ± .001	1.7818	15,750 ± 30	− 230	30	11.32	− .16	+ 4.7	+ 8.6
.02	0	.0532 ± .0002	0.7259							
.02	25	.602 ± .002	1.7796	15,740 ± 30	− 240	30	11.31	− .17	+ 4.2	+ 8.2
.02	0	.0530 ± .0001	0.7243							
.005	25	.4217 ± .0005	1.6250	15,730 ± 40	− 280	50	11.15	− .20	+ 1.0	+ 5.7
.005	0	.0372 ± .0002	0.5705							
.002	25	.352 ± .002	1.5465	15,650 ± 100	− 230	125	11.02	− .17	− 2.0	+ 1.3
.002	0	.0314 ± .0003	0.4969							
Sucrose = 1.47%										
0.002	25	0.358 ± 0.001	1.5539	15,930 ± 40	+ 50	80	11.22	+0.03	+ 0.3	− 1.3
.002	0	.0306 ± .0001	0.4857							
Glycerol 68.5% = 8.78 M; 69.7% (last two expts.)										
0.05	25	0.879 ± 0.007	1.9440	14,770 ± 120	−1170	125	10.76	−0.79	+18.3	+41.8
.05	0	.0899 ± .001	0.9538							
.02	25	.677 ± .002	1.8306	14,790 ± 60	−1190	60	10.67	− .81	+17.1	+40.8
.02	0	.0690 ± .0004	0.8389							
Dioxane 50.3% = 5.92 M										
0.005	25	0.567 ± 0.004	1.7536	14,820	−1190	..	10.61	−0.74	+36	+63
.005	0	.0575 ± .0004	0.7597							

[a] k = 0.896 with 21.0% urea ≈ 0.897 with 21.2% urea.

of other properties of the reaction system; namely, the energy of activation and its change with temperature. If the Arrhenius equation, $d \ln k = (E_{\text{act}}/RT^2)dT$ is integrated by assuming that E_{act} is a function of temperature, *i. e.*, $E_{\text{act}} = E^0_{\text{act}} + \int_0^T (\partial E_{\text{act}}/(\partial T)dT$, then

$$\int_0^T (E_{\text{act}}/RT^2)dT = \frac{-E^0_{\text{act}} + \int_0^T (\partial E_{\text{act}}/\partial T)dT}{RT} + \frac{1}{R}\int_0^T \left(\frac{\partial E_{\text{act}}}{\partial T}\right) d \ln T \quad (1)$$

La Mer[11] has defined the change in energy of activation with temperature as the heat capacity of activation and by analogy with thermodynamic heat capacities has designated the last term as the entropy of activation divided by R. Thus

$$\ln k = -E_{\text{act}}/RT + (S_{\text{act}} - S_{0\,\text{act}})/RT + \ln \text{const.} \quad (2)$$

the constant having the dimensions of a frequency (time^{-1}). If the reactants require no activation for reaction, E_{act} becomes zero, and every collision results in reaction. If the reactants are ideal gases the constant becomes the gas kinetic collision frequency at unit concentrations designated as Z^0

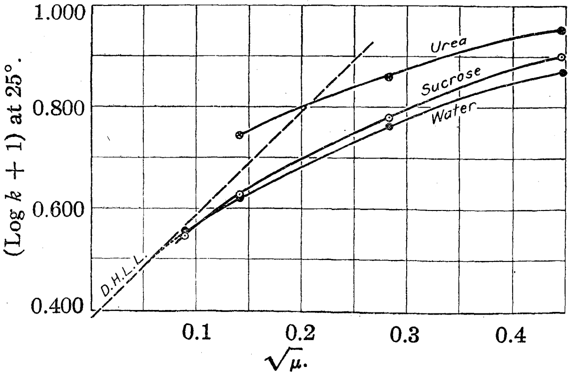

Fig. 1.

$$\log k = -E_{\text{act}}/2.3RT + \underbrace{(S_{\text{act}} - S_{0\,\text{act}})/2.3R + \log Z^0}_{B} \quad (3$$

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(11) V. K. La Mer, *J. Chem. Phys.*, **1**, No. 5, 289 (1933).

B thus consists of two terms, one involving entropy of activation and the other a collision frequency. A change in the value of B may be attributed, in general, to a change in one or both of the quantities which determine its numerical magnitude, the collision frequency and the derivative of E_{act} with respect to temperature integrated with respect to ln T.

The experimental data show that when urea is added to the aqueous solvent for the bromoacetate–thiosulfate reaction, B is increased, E_{act} is unchanged and k is increased. The addition of sucrose, glycerol or dioxane to the aqueous solvent for the reaction causes a decrease in B, but this decrease in B in the cases of glycerol, dioxane and sucrose (at higher concentrations of reactants) is more than compensated for by the decrease in E_{act} and thus k is increased.

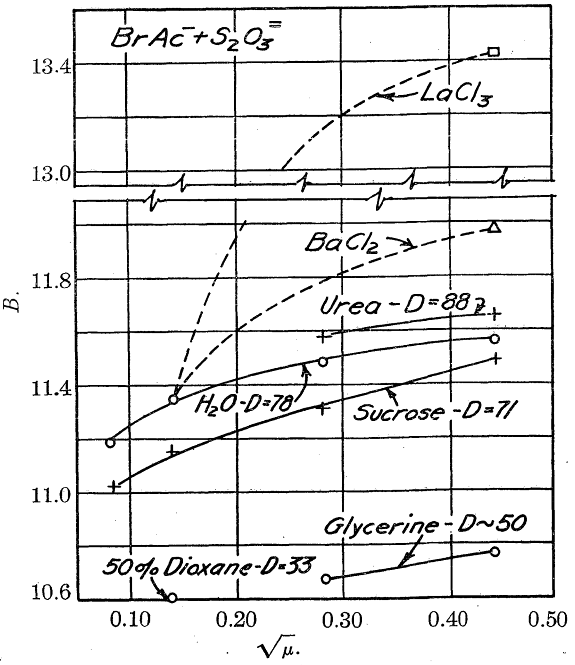

Fig. 2.

In the sucrose solutions as in the case of water (Table III and Fig. 2) B decreases significantly in passing from 0.05 to 0.002 M in reactants. The decrease in E_{act} over this same range may or may not be real; it exceeds but slightly the amount which can be accounted for by experimental errors. One cannot do more than suggest the possibility that the presence of 540 long chain sucrose molecules for a molecule of each reactant diminishes the velocity constant at $a = b = 0.002$ M by having decreased the number of collisions between reactants.

Kappanna[4] has studied the effect of sucrose addition to the bromoacetate–thiosulfate reaction; his data agree with those presented here in respect to the fact that sucrose increases the velocity constant at high concentrations of reactants and decreases it at low concentrations. Calculations made from his velocity constant data show that the addition of alcohol to the aqueous solvent decreases both E_{act} and B.

Influence of Dielectric Constant

For the case of reactions between an ion and a neutral molecule, Harned and Samaras[12] have shown that log k is frequently but not always proportional to D. For the reaction $NH_4^+ + CNO^- \longrightarrow$ urea which involves the collision of ions of opposite sign, Warner and Warrick[13] found that log k is roughly proportional to $1/D$ when the dielectric is decreased by addition of various alcohols or of dioxane to water.

However, no simple relation is revealed by plotting log k against D or $1/D$ either for our data or for those of Kappanna for the bromoacetate–thiosulfate reaction in aqueous alcohol solutions. Kappanna's data show a minimum k value at 40% ethyl alcohol for low concentrations of reactants. The minimum is displaced to lower alcohol concentrations as the ionic strength of the reactants is increased.

Although the dielectric constants of the solvents employed in this research range from urea, D = 98.1 (0°) = 88.4 (25°); water, D = 88.2 (0°) = 78.5 (25°); sucrose (32.4%) D = 78.4 (0°) = 70 (25°); glycerol D = 63.2 (0°) = 55.7 (25°); to dioxane $D \doteq 33$ (25°), the velocity constants in the presence of non-electrolytes exceed those for water. Scatchard's theory[14] of the effect of D obviously does not hold for the present data. Straup-Cope and Cohn[15] report that amino acids which increase the dielectric constant increase the velocity of this reaction.

Since the magnitude of k is determined by the quantities E and B it is appropriate to attempt to correlate E and B rather than k with the dielectric constant of the solvent. In Fig. 3 (E_{act} − 16,000) and B are plotted against $1/D$. B decreases with decreasing dielectric constant of the

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[12] Harned and Samaras, THIS JOURNAL, **54**, 1 and 9 (1932).

[13] Warner and Warrick, *ibid.*, **57**, 1491 (1935); see also Piter Vass [*Magyar Chem. Folyoirat*, **37**, 217 (1931) through *C. A.*] who claims that the $Fe^{+++} + I^-$ reaction follows the Grube-Schmid law.

[14] Scatchard, *Chem. Rev.*, **10**, 229 (1932). See Eq. (9), p. 235.

[15] Straup-Cope and Cohn, *J. Biol. Chem.*, **105**, Proc. LXXXVII (1934); THIS JOURNAL, **57**, 1794 (1935).

solvent to a value of $D \simeq 55$; the lowering of D from 55 to $\simeq 33$ produces no further decrease. Except for the urea solutions, the E curve follows a parallel course to B but is distinctly less sensitive to changes in the concentration of reactants. The increasing value of B with increasing concentration of reactants in sucrose solutions would be interpreted as a result of the increased number of collisions arising from the interionic attraction effect. Our analysis thus supports the Christiansen[16] interpretation of the Brönsted–Debye effect. We suggest that the decrease in B values with decreasing values of D results from a decrease in the number of effective collisions as a result of the increased electrostatic repulsion between reacting ions of the same sign. Finally, with decrease of dielectric a point must be reached in which the reacting ions are no longer dissociated from the sodium ions. When the dielectric constant falls below about 50 the phenomenon of ion association of the sodium ions with the bromoacetate and the thiosulfate ions becomes very important. Fuoss and Kraus[17] claim that for uni-univalent electrolytes in solvents where D is less than 43.6 the behavior of ions of opposite sign is most easily accounted for in terms of a mass action dissociation constant of the salt. In the case of 50% dioxane–water where $D = 33$ the reactants will exist principally in the form of their neutral salt pairs. Somewhere in the neighborhood of $D = 50$, the repulsive effect of lowering the dielectric is exhausted and consequently no further decrease in B can be expected. The reaction now behaves substantially as a reaction between two uncharged molecules, though of course a considerable dipole interaction will still persist at close distances.

In solvents of extremely low dielectric constant the ternary and higher order ion-pairs become stable. It is conceivable that under such conditions the order of the reaction may change. In fact Brönsted and Bell[18] found that the diazoacetic ethyl ester reaction proceeds in benzene at a rate which is proportional to the square of the concentration of the catalyzing acid, whereas in water it is proportional to the first power of the hydrogen-ion concentration.

The kinetic data for the bromoacetate–thiosulfate reaction furnish examples of an increase in velocity constant with (1) an increase in E_{act}, (2) a decrease in E_{act}, (3) E_{act} remaining unchanged.

(1) The increase in E_{act} resulting from the addition of barium chloride or lanthanum chloride was more than compensated for by an increase in B, and k was increased.[10]

(2) In the present work, the addition of sucrose, glycerol or dioxane lowered E_{act} by such an amount that although B was also lowered, k was increased.

(3) E_{act} is unaffected by the addition of urea and the increase in velocity constant results entirely from an increase in B.

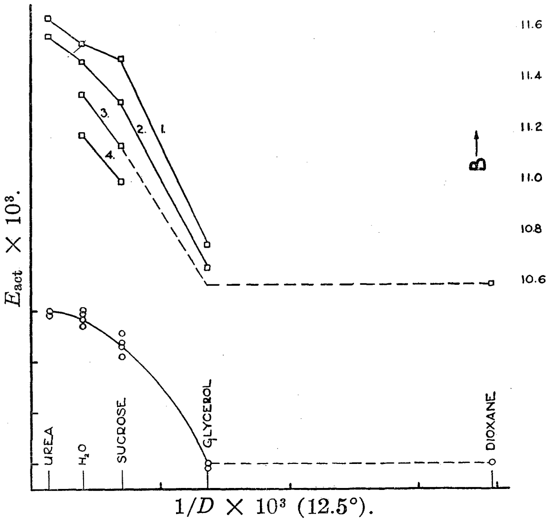

Fig. 3.—1, 0.05 *M;* 2, 0.02 *M;* 3, 0.005 *M;* 4, 0.002 *M.*

Summary

1. The kinetics of the reaction between bromoacetate ions and thiosulfate ions have been studied at 0 and at 25° in the presence of non-electrolytes; the precision of the experimental data is ±0.5%. The velocity constant is increased by addition of urea, sucrose, glycerol or dioxane to the aqueous solvent, in spite of the fact that urea raises the dielectric constant while the others lower it.

2. The energy of activation remains the same in the case of urea but is decreased by addition of each of the other non-electrolytes. The action constant B decreases almost linearly as a function of $1/D$ from $D = 88$ to 55.7.

3. In 32% sucrose solutions ($D = 70$ at 25°), as in water, the positive salt catalysis arises from an increase in the entropy of activation which more than compensates for the retarding influence of an increase in the energy of activation.

NEW YORK, N. Y. RECEIVED AUGUST 15, 1935

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[16] Christiansen, *Z. physik. Chem.*, **113**, 35 (1924).

[17] Fuoss and Kraus, THIS JOURNAL, **55**, 2387 (1933), and later papers of this series; Fuoss, *Chem. Rev.*, **17**, 27 (1935).

[18] Brönsted and Bell, *ibid.*, **53**, 2478 (1931).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Temperature Dependence of the Energy of Activation in the Dealdolization of Diacetone Alcohol

BY VICTOR K. LA MER AND MARY L. MILLER[1]

Introduction

For many reactions the temperature dependence of the velocity constant can be satisfactorily described by the Arrhenius equation

$$d \ln k/dT = E_{act}/RT^2 \qquad (1)$$

by considering the energy of activation E_{act} to be a constant independent of temperature. Under this assumption equation (1) becomes, on integration

$$\ln k = (-E_{act}/RT) + 2.3B \qquad (2)$$

$2.3B$ is the constant of integration, which likewise should be independent of temperature. If we accept, however, the statistical interpretation of E_{act} as exemplified in Tolman's treatment,[2] namely, that E_{act} is the difference between the average energy of those molecules *which react* and the average energy of all the molecules, then as La Mer[3] has pointed out, E_{act} and B must necessarily be functions of the temperature,[4] and for consistency with thermodynamics B must involve a quantity which he called the entropy of activation. The slope of the $E_{act} - T$ curve will give

$$dE_{act}/dT = (\bar{c}_{j,\,act} - \bar{c}_i) \qquad (3)$$

where $\bar{c}_i$ is the partial molal heat capacity of all the molecules and $\bar{c}_j$ is the partial molal heat capacity of all the molecules *which react.* $\bar{c}_j$ includes the k_j factors or specific reactivity rates for different reacting levels involved in the process of statistical averaging. Whether the temperature dependence will be of significant magnitude is a question which must be decided for each reaction by experiments covering as wide a temperature range as possible. This was the primary purpose of the research. The prevailing view as epitomized in the statement of Moelwyn-Hughes[5] "*As a general rule examples which appear to contradict the Arrhenius law may also be omitted for experience has shown that such seeming deviations can usually be attributed to the presence of impurities or inadequate control of temperature,*" is primarily a result of the difficulties inherent in precise temperature coefficient measurement and an unwarranted faith in the constancy of E_{act}. Since the temperature variation of E_{act} is frequently within the limits of experimental error, it is usually detectable only in those cases where the analytical method can be considerably refined as in the case of solution reactions, or where the temperature interval can be made comparatively large. Furthermore, it is recognized that relatively small errors in the temperature scale can produce a trend in E_{act}, which is without significance.

Although the literature contains a number of carefully investigated reactions,[3,6] which yield values for E_{act} which certainly are not independent of temperature, yet in most instances the authors have either ignored the effect or have drawn unduly conservative conclusions.[7] An important exception is to be noted in the recent papers of Semerano,[8] of Liebhafsky and Mohammed, and of Harned and Seltz.[9]

On recalculating the data of G. M. Murphy[10] on the dealdolization of diacetone alcohol $(CH_3)_2COHCH_2COCH_3 + OH^- = 2CH_3COCH_3 + OH^-$, carried out at 20, 25, 30 and 35°, one of us

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[1] This paper is abstracted from a dissertation submitted by Mary L. Miller in July, 1934, to the Faculty of Pure Science, Columbia University, in partial fulfilment of the requirements of the degree of Doctor of Philosophy.

[2] R. C. Tolman, "Statistical Mechanics with Applications to Physics and Chemistry," Chemical Catalog Co., New York City, 1927.

[3] V. K. La Mer, (a) *J. Chem. Phys.*, **1**, 289 (1933); (b) THIS JOURNAL, **55**, 1739 (1933).

[4] The necessity of some temperature dependence of E_{act} was first pointed out by Trautz, whose treatment recognized the role of specific heats but became rather involved. See also Kassel, and Scheffer and Brandsma. M. Trautz, (a) *Z. physik. Chem.*, **66**, 496 (1909); (b) *Z. Electrochem.*, **15**, 692 (1909); (c) *Z. anorg. allgem. Chem.*, **102**, 81 (1918); L. S. Kassel, *Proc. Nat. Acad. Sci.*, **16**, 358 (1930); Scheffer and Brandsma, *Rec. Trav. Chim.*, **45**, 522 (1926), and earlier papers.

[5] E. A. Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford University Press, London, 1933, p. 80.

[6] E. R. Schierz and H. T. Ward, THIS JOURNAL, **50**, 3240 (1928); E. L. Whitford, *ibid.*, **47**, 953 (1925); J. C. Crocker and F. H. Lowe, *Trans. Chem. Soc.*, **91**, 953 (1907); H. Olsson, *Z. physik. Chem.*, **133**, 233 (1928); A. Skrabal, *Monatsh.*, **63**, 23 (1933); M. Kilpatrick, THIS JOURNAL, **48**, 2091 (1926); F. O. Rice and M. Kilpatrick, *ibid.*, **45**, 1401 (1923); H. Essex and O. Gelormini, *ibid.*, **48**, 882 (1926).

[7] For example, for the formic acid decomposition, the statement "... there is a general tendency (for E_{act}) to increase but slightly with increase in temperature," is hardly a fitting description of the data when E_{act} increases by about 1800 cal. quite consistently in four solvents, 94.4, 92.78, 91.49 and 89.53% H_2SO_4, for the range 20 to 40° corresponding to $C_{act} > 90$ cal. [Schierz and Ward (*loc. cit.*)].

[8] G. Semerano, *Gazz. chim. ital.*, **61**, 921 (1931).

[9] H. A. Liebhafsky and A. Mohammed, THIS JOURNAL, **55**, 3977 (1933); Harned and Seltz, *ibid.*, **44**, 1475 (1922).

[10] G. M. Murphy, *ibid.*, **53**, 977 (1931). See Ref. 3 (a) for calculations.

noted that they required a value for $C_{act} \cong 200$ cal. mol.$^{-1}$ deg.$^{-1}$. Since a heat capacity of activation of this magnitude is astonishingly large, and could arise from an error in measurement at a single temperature, we have reinvestigated the kinetics of this reaction at 5-degree intervals from 0 to 50°.

The dealdolization reaction has been investigated extensively by Koelichen, Åkerlöf, French, John Miller and Kilpatrick at 25°. It is free from complicating side reactions and is pseudo unimolecular for constant concentrations of bases. The absolute velocity can be varied over wide limits by varying the concentration of the base used as catalyst; hence the reaction is well suited for investigation over a wide range of temperature.

II. Experimental Method

The velocity was measured by the dilatometric method. A solution prepared by diluting an appropriate volume of 0.25 *N* sodium hydroxide to about 250 cc. was evacuated and kept in a thermostat regulated to 0.01° (at 0.0 and 5 to 0.02°) for at least two and one-half hours. The reaction was initiated by adding 2%[11] by volume of diacetone alcohol. After boiling under vacuum, the mixture was transferred by pressure to the dilatometer. Vacuum was reapplied until no bubbles were visible. Pressure was again applied momentarily, about 8 cm. of mercury was introduced into the capillary, and after a predetermined time readings were begun. The equilibrium value was taken at a time appropriate to the given velocity and about an hour thereafter. The capillary was water-jacketed and kept within one or two degrees of the surrounding bath.

An important innovation in the present work was the determination of the concentration of alkali after completion of the reaction by titration of an aliquot with standard acid. The customary procedure is open to the objection that the concentrations calculated from the weight of water, alkali and substrate used in preparing the mixture, may be altered during the degassing process. After the equilibrium value had been obtained the solution was brought to room temperature in the dilatometer. The first aliquot was removed for density determination and a second withdrawn in an atmosphere of carbon dioxide-free air directly into the weight buret. For the slower reactions measurements were taken at equal time intervals. Thus it was not always necessary to obtain an equilibrium value since the Guggenheim method for calculating the constant[12] could then be used. Our procedure differs from that of Åkerlöf principally in the determination of the concentrations and in the filling of the dilatometer. Åkerlöf filled his dilatometer by suction, a method which involves considerable foaming. We minimized foaming by transferring the mixture using pressure as did John Miller and Kilpatrick.[13] Since these measurements are to be interpreted from the point of view of the collision theory, concentrations are expressed in terms of normality of the final solution rather than molality of the initial solution. Time is in minutes.

The results of some preliminary experiments involving distinct variations in the experimental procedure are given in Table I. Although of lower precision than the subsequent data, they serve to indicate that the factors investigated are relatively unimportant.

TABLE I

PRELIMINARY RUNS TO INVESTIGATE THE EFFECT OF MISCELLANEOUS FACTORS AT 25.00°

Factor investigated	Concn. NaOH	$k/c \times 10^3$
Darkened reaction tube	0.02993	226
Darkened reaction tube	.03971	221
Darkened reaction tube and light protection during distn.	.03381	228
	.04382	222
Previous sun exposure (9 hrs.) of diacetone alcohol	.02909	240
Sun exposure as above (94 hrs.)	.03033	225
In the presence of 0.0002 *M* Ba^{++}	.02474	228
In the presence of 0.002 *M* Ba^{++}	.03145	222
With excess acetone (2% by vol.)	.07724	225
Measurements using cathetometer	.05720	223
Three months later	.05622	223
Foaming method	.03666	219
Foaming method	.03321	219

The velocity constants *k* were calculated by the well-known equation for first order reactions, or at low temperatures, 0 and 5°, by the Guggenheim method; in many cases by both. Typical experiments illustrating the character of the results at 50° for high and low concentrations of sodium hydroxide are to be found in the Dissertation.

Preparation and Purity of Materials

Sodium Hydroxide.—An approximately 0.25 *N* stock solution was prepared with Kahlbaum "sodium hydroxide from sodium." This was freed from carbonate with barium hydroxide[14] and stored in a paraffin lined bottle.

Water.—The water was redistilled and freed from carbon dioxide by boiling.

Hydrochloric Acid.—0.05 *N* HCl was made up by weight from constant boiling acid[15] and standardized gravimetrically as chloride.

Methyl Alcohol.—An analyzed product from Eimer and Amend was distilled from sodium hydroxide and iodine[16] and fractionated with a 38-cm. Hempel column; sp. gr.$^{25}_{0}$ 0.800. The alcohol was not dried.

Diacetone Alcohol.—Diacetone alcohol, Eastman No. 1084, was distilled under about 20 mm. pressure (b. p.

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[11] Up to 5% was used in some of the faster reactions at 50°.

[12] E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

[13] J. Miller and M. Kilpatrick, THIS JOURNAL, **53**, 3217 (1931).

[14] J. E. S. Han and T. Y. Chao, *J. Ind. Eng. Chem., Anal. Ed.*, **4**, 229 (1932).

[15] G. A. Hulett and W. D. Bonner, THIS JOURNAL, **31**, 390 (1909).

[16] A. V. Rakovskiĭ and A. V. Frost, *Trav. Inst. Pure Chem. Reagents* (Moscow), **9**, 95 (1930), courtesy of *Chemical Abstracts*.

164°, uncorr.) and kept in resistance-glass bottles for not over a week. Table II gives the results of several runs at 0.0° using samples of diacetone alcohol which had been subjected to further purification processes. The preparation yielded a solution neutral to litmus.

TABLE II

VELOCITY CONSTANTS AT 0.00° USING DIACETONE ALCOHOL PURIFIED BY DIFFERENT METHODS

Method of purification	Concn. NaOH	$k/c \times 10^4$
A commercial product		
Two distillations	0.1026	177.6
Two distillations	.1050	177.2
Three distillations	.1045	176.6
Two distillations, one crystn.	.1047	177.0
Eastman Kodak Co. product		
One distillation	.06740	176.5
One distillation, one crystn.	.07895	176.0
One distillation and one crystn.	.08328	176.0

Precision

Temperature.—A 24-junction copper–constantan thermocouple[17] which had previously been calibrated by Dr. Eichelberger in terms of the platinum resistance thermometer at Rockefeller Institute for Medical Research, was used for the temperature standard. During the course of these experiments it was recalibrated against the freezing point of benzene[18] 5.83°, the transition point of sodium sulfate[19] 32.384°, and against Baudin Thermometer No. 18537 at 25.00 and 40.15°. Temperatures so obtained are believed to be accurate to 0.01°.

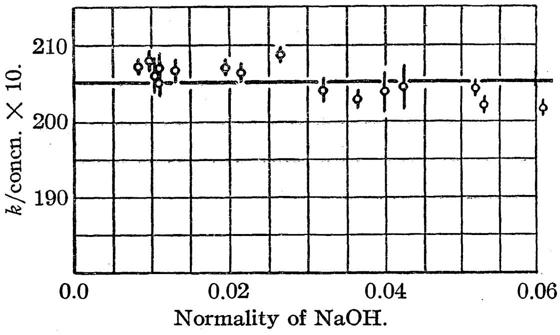

Fig. 1.—Concentration dependence of k/c values at 49.97°.

Concentration.—A precision of 0.1% was easily obtained in the titration of the sodium hydroxide content of the final solution, using weight burets and brom cresol purple as indicator.

Velocity.—The dilatometers[20] differed from those of Åkerlöf only in being equipped with a smaller water-jacket, graduated in millimeters. The reaction tube contained about 90 cc. and the capillary was usually 70 cm. long and 0.7 mm. in diameter. The height of the mercury was read to 0.1 mm. All dilatometers were calibrated to correct for irregularities in scale and bore. The readings were precise to 0.1% when at least 10 cm. from the initial and final values, which is the optimum precision to be expected in the k values.

Concentration Dependence.—From his measurements at 25° French[21] concludes that the ratio of velocity constant to molality is independent of sodium hydroxide concentration from 0.01 to 0.10 *M*, a conclusion which Murphy states that he has confirmed. From the point of view of temperature coefficient measurements it is important to ascertain whether this concentration independence of k/c obtains at the extremes of temperature to be examined. At 0.0° the relationship holds for the concentrations in Table II. Although runs at lower concentrations are undoubtedly possible, they were not made since the range already investigated covers a region readily measurable at 25°.

TABLE III

DEPENDENCE OF k/c ON NaOH CONCENTRATION AT 49.97°

Concn. of NaOH	$k/c \times 10^2$	Concn. of NaOH	$k/c \times 10^2$
0.008275	207.3 ± 1.0	0.02647	208.6 ± 0.8
.009849	208.0 ± 1.5	.03230	203.8 ± 1.4
.01052	205.8 ± 2.7	.03662	202.7 ± 1.1
.01073	205.1 ± 2.0	.03976	203.9 ± 2.8
.01091	207.1 ± 3.2	.04228	204.5 ± 3.3
.01354	206.9 ± 1.5	.05190	204.2 ± 0.6
.01963	207.1 ± 0.8	.05323	202.0 ± 1.0
.02153	206.6 ± 1.3	.06087	201.4 ± 1.0

The data of Table III for k/c at 49.97° (see Fig. 1) reveal a decrease with rising concentration which is barely outside the experimental error.

Above 0.06 *N* sodium hydroxide the method of measurement becomes inapplicable, the constants being no longer reproducible and the solutions becoming slightly yellow. Åkerlöf,[22] while studying the effect of higher concentrations of sodium hydroxide, over 2 *m*, at 25°, found that at a velocity constant about equal to 0.1 (at 50° $k = 0.1$ when $c = 0.05$ *N*) the simple method broke down. He attributes this behavior to failure to maintain temperature equilibrium during the course of the reaction. Therefore for higher velocities he used a dilatometer containing a spiral through which the bath water was circulated.

In Fig. 2 we plot our data (Table IV) for k/c at 25° (circles) as a function of the concentration of sodium hydroxide, along with Koelichen's values[23]

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[17] W. C. Eichelberger, THIS JOURNAL, **54**, 3105 (1932).

[18] T. W. Richards and J. W. Shipley, *ibid.*, **36**, 1825 (1914).

[19] H. C. Dickinson and Mueller, *Bull. Bur. Standards*, **3**, 656 (1907).

[20] Some of these dilatometers were kindly loaned by Prof. H. S. Harned and Dr. Åkerlöf, to whom we extend our thanks.

[21] C. C. French, THIS JOURNAL, **51**, 3215 (1929).

[22] G. Åkerlöf, (a) *ibid.*, **48**, 3046 (1926); (b) *ibid.*, **49**, 2955 (1927); (c) *ibid.*, **50**, 733 (1928).

[23] K. Koelichen, *Z. physik. Chem.*, **33**, 129 (1900).

TABLE IV

DEPENDENCE OF k/c ON NaOH CONCENTRATION AT 25.00°

Concn. NaOH	$k/c \times 10^3$
0.02052	221.9 ± 0.3
.02920	223.3 ± 1.2
.05180	224.3 ± 0.6
.06160	221.8 ± 0.2
.07099	222.2 ± 0.8
.08637	219.4 ± 0.1
.1045	221.0 ± 0.8
	221.9 ± 1.0

(crosses) for k/c obtained by averaging his closely agreeing values for sodium hydroxide and barium hydroxide at 25.2° and reducing by 2% for comparison at 25°. Both sets of data are in excellent agreement and amply verify the linear dependence of k upon the concentration of sodium hydroxide.

On the other hand, the k/m values of French,[24] of Murphy,[25] and of Åkerlöf,[22] although agreeing fairly well among themselves are distinctly lower (6% at 0.1 N and 10% at 0.01 N) than ours, and furthermore exhibit a concentration dependence. The discrepancy persists even after we correct our k/c values to the k/m concentration scale as indicated by the dashed line in Fig. 2.

Incomplete removal of bubbles or leakage at the stopcock is not the explanation although in individual cases these factors may contribute to the scattering of the k/c values. We suspect that the discrepancy arises in the determination of the concentration of alkali. Our method of direct determination by titration at the conclusion of the reaction eliminates any possibility of reporting incorrect values for the concentration due to absorption of carbon dioxide during the process of filling the dilatometer and to the presence of acid impurities in the diacetone alcohol.

None of the previous investigators, except Koelichen, gives the method of preparation or the characteristics of the diacetone alcohol used. We find that 20 g. of the Eastman product contains 1.2×10^{-4} mole of acid, whereas the preparation Diacetone (Commercial Solvents) contains 2×10^{-3} mole of acid. The presence of acid impurities would lead to a decrease in k/m values with decreasing molality of sodium hydroxide, and is consistent with the hypothesis that these errors enter in the data of French, Murphy and Åkerlöf.

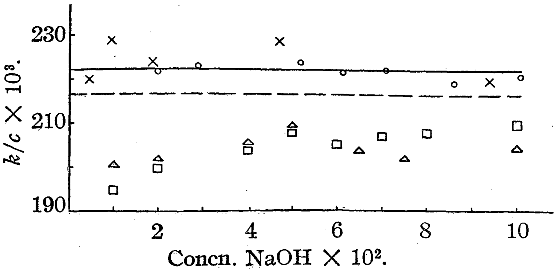


Fig. 2.—Concentration dependence of k/c at 25.00°: ○, this investigation, Table IV; ×, Koelichen k/c; △, French k/m; □, Murphy k/m; ——, mean of Table IV; ----, Table IV corrected to k/m scale.

Methyl Alcohol Effect

Since the recalculation of Murphy's data indicated a change in C_{act} with addition of methyl alcohol to the solvent, it seemed desirable to obtain a few points on the energy of activation–temperature curve for a water–methyl alcohol mixture, with a view, not only of affording a check on the general character of the water curve but possibly of shedding light on the mechanism of the reaction.

Tests showed that the final titration was unaffected by the quantity of alcohol used. Since the procedure of boiling by vacuum would remove slightly different amounts of alcohol at different temperatures, it was necessary to measure the methyl alcohol concentration in the final solution. This was accomplished by constructing density–alcohol concentration curves at each temperature, using a fixed quantity of diacetone alcohol in the mixture and allowing the sodium hydroxide concentration to vary only over narrow limits.

Experimental Results

A summary of the velocity constants obtained at eleven different temperatures is given in Table V.

TABLE V

VELOCITY CONSTANTS WITH AQUEOUS SODIUM HYDROXIDE

T., °C.	No. of expts. in average	Average k for 0.1 N NaOH
0.00	7	$(176.7 \pm 0.5) \times 10^{-5}$
5.86	2	$(322.1 \pm 2.2) \times 10^{-5}$
9.79	2	$(484.9 \pm 2.3) \times 10^{-5}$
14.98	2	$(825.7 \pm 3.7) \times 10^{-5}$
19.92	2	$(134.7 \pm 0.8) \times 10^{-4}$
25.00	7	$(221.9 \pm 1.0) \times 10^{-4}$
29.90	3	$(357 \pm 2) \times 10^{-4}$
34.97	2	$(568.8 \pm 1.0) \times 10^{-4}$
40.01	2	$(896.8 \pm 2.8) \times 10^{-4}$
45.11	4	$(140.2 \pm 1.1) \times 10^{-3}$
49.97	16	$(205.2 \pm 1.9) \times 10^{-3}$

The velocity constants, corrected to 18.5%

(24) C. C. French, THIS JOURNAL, **51**, 3215 (1929).

(25) G. M. Murphy, *ibid.*, **53**, 977 (1931).

by volume of methyl alcohol in the final solution, are given in Table VI.

TABLE VI

VELOCITY CONSTANTS USING 18.5% OF METHYL ALCOHOL

T., °C.	No. of expt. in average	Average k for 0.1 N NaOH
0.00	2	$(93.14 \pm 0.64) \times 10^{-5}$
11.22	2	$(339.7 \pm 0.9) \times 10^{-5}$
14.84	2	$(507.7 \pm 2.8) \times 10^{-5}$
25.04	2	$(152.6 \pm 1.0) \times 10^{-4}$
29.98	1	256.1×10^{-4}
34.99	1	428.0×10^{-4}
49.95	2	$(183.2 \pm 0.1) \times 10^{-3}$

For comparison with the collision theory, the values of E_{act} and the integration constant B are given in Tables VII and VIII. The nature of the temperature dependence is strikingly exhibited by plotting these E_{act} and B values against temperature as in Figs. 3 and 4. From these curves the following points are observed. (1) E_{act} increases by nearly 1400 calories from 5 to 32.5° and then decreases by 500 calories (over five times the probable error) to 45°. (2) In the presence of 18.5% methyl alcohol E_{act} follows a similar course to 32.5°. (3) E_{act} increases by 1500 calories at 20° on the addition of 18.5% methyl alcohol. (4) Addition of 18.5% methyl alcohol produces an increase of one logarithmic unit in B. (5) The B values parallel the E_{act} values very closely.

TABLE VII

E AND B VALUES FROM THE ARRHENIUS EQUATION AT DIFFERENT TEMPERATURES

(′ for 15° interval, ″ for 20°, others for 10°)

Mid-point of temp. interval, °C.	E_{act}, cal.	B moles liter/min.
4.89	15850	10.92
7.49	16100′	11.13′
9.96	16230″	11.22″
10.42	16500	11.42
12.89	16550′	11.46′
14.85	16620	11.52
15.43	16680″	11.56″
17.39	16770′	11.63
19.84	16920″	11.75″
19.99	16850	11.69
22.44	17040′	11.83′
24.91	17250	11.97
24.97	17040″	11.84″
27.44	17180′	11.93
29.96	17220″	11.96″
29.98	17240	11.98
32.50	17270′	12.00′
34.95	17190	11.94
35.05	17290″	12.02″
37.50	17250′	11.98′
39.93	16960″	11.78″
40.04	17350	12.05
42.47	16930′	11.76′
44.99	16720	11.61

TABLE VIII

E AND B VALUES FROM THE ARRHENIUS EQUATION FOR DIFFERENT TEMPERATURE INTERVALS IN THE PRESENCE OF 18.5 VOLUME PER CENT. OF METHYL ALCOHOL

Interval, °C.	Mid-point of temp. interval	E_{act}[a] cal.	B moles liter-min.
0–11.22	5.61	17810	12.21
0–14.84	7.42	17870	12.27
0–25.04	12.52	18090	12.43
11.22–14.84	13.03	(18070)	(12.41)
11.22–25.04	18.13	18330	12.61
14.84–25.04	19.94	18420	12.68
25.04–29.98	27.51	(18840)	(12.98)
25.04–34.99	30.01	18930	13.05
29.98–34.99	32.48	(19040)	13.12
25.04–49.95	37.49	19110	13.18
29.98–49.95	39.96	19190	13.23
34.99–49.95	42.47	19240	13.27

[a] The precision of E is estimated at 90 cal. and that of B at 0.07 unit in B, the estimate being obtained as follows. The "average error" of the mean is averaged for all temperatures and used to obtain the ∂k_1. The $\partial E)_{\text{k}_1\text{k}_2\text{T}\Delta\text{T}} \cong 0$ and $\Delta T = 10°$ $\partial(\Delta T) = 0.02°$. Numerical values are taken at 25°.

$$\partial E)_{\text{k}_1\text{k}_2\text{T}_1\text{T}_2} = \frac{-RT_1T_2 \ln k_1/k_2 \, \partial(\Delta T)}{(\Delta T)^2} = 34 \text{ cal.}$$

$$\partial B)_{\text{kT}} = \frac{\partial E}{2.3RT} = 0.067$$

$$\partial E)_{\text{k}_2(\Delta\text{T})\text{T}_1\text{T}_2} = \frac{-RT_1T_2 \, \partial k_1}{\Delta T k_1} = 60 \text{ cal.}$$

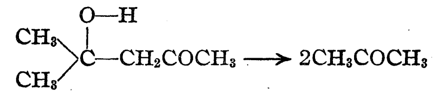
$$\partial B)_{\text{ET}} = 2.3\partial k/k = 0.008$$

$$\partial B)_{\text{Ek}} \cong 0$$

$$\partial E)_{\text{k}_1(\Delta\text{T})\text{T}_1\text{T}_2} = 60 \text{ cal.}$$

$$\Delta E = 90 \text{ cal.} \qquad \Delta B = 0.07 \text{ unit of } B$$

A survey of the literatures shows that reactions which have so far demonstrated a marked temperature dependence of E_{act} fall roughly into two classes; namely, those involving a halogen compound and those which are either a hydrolysis or a proton change.[26] The present reaction is of the latter type being the reversal of an aldol process.



$$(CH_3)_2C(OH){-}CH_2COCH_3 \longrightarrow 2CH_3COCH_3$$

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[26] A. (1) Decomposition of acetone dicarboxylic acid, E. Wiig, *J. Phys. Chem.*, **32**, 961 (1928); (2) Dehydration of citric,[a] formic,[b] and malic acids,[c] (a) E. J. Wiig, THIS JOURNAL, **52**, 4729 (1930); (b) E. R. Schierz and H. T. Ward, *ibid.*, **50**, 3240 (1928); (c) E. L. Whitford, *ibid.*, **47**, 953 (1925); (3) Alkaline hydrolysis of amides, J. C. Crocker and F. H. Lowe, *Trans. Chem. Soc.*, **91**, 953 (1907); (4) Alkaline hydrolysis of esters, H. Olsson, *Z. physik. Chem.*, **133**, 233 (1928); (5) Hydrolysis of ethers, A. Skrabal, *Monatsh.*, **63**, 23 (1933); (6) Decomposition of nitrosotriacetonamine (possibly), M. Kilpatrick, THIS JOURNAL, **48**, 2091 (1926); (7) Inversion of cane sugar, E. A. Moelwyn-Hughes, *Z. physik. Chem.*, **B26**, 281 (1934); B. (1) Sodium phenolates plus alkyl iodides, D. Segaller, *J. Chem. Soc.*, **105**, 106 (1914); (2) Bromoacetates plus thiosulfates (very slight), V. K. La Mer, THIS JOURNAL, **55**, 1739 (1933); La Mer and Kamner, *ibid.*, **57**, 2662 (1935); (3) Acetone plus iodine (very slight), F. O. Rice and M. Kilpatrick, *ibid.*, **45**, 1401 (1923).

It was pointed out in the previous theoretical paper[27] that when E_{act} is strictly independent of temperature B reduces to log Z^0, where Z^0 is the gas kinetic collision number, since in the expression

$$B = \log Z^0 + \frac{1}{2.3R}\int_0^T \left(\frac{\partial E_{\text{act}}}{\partial T}\right)\frac{\mathrm{d}T}{T} \tag{4}$$

the last term to the right involving the change in energy of activation with temperature vanishes. It should be remarked that although B for this reaction is not far from the order of magnitude predicted for a pure collision number,[28] however, its behavior with temperature is not at all the $T^{1/2}$ effect which would be demanded and the constant increment on the addition of methyl alcohol indicates its complex nature. Obviously the increase of one logarithmic unit in B can hardly be interpreted as arising solely from a ten-fold increase in the number of collisions.

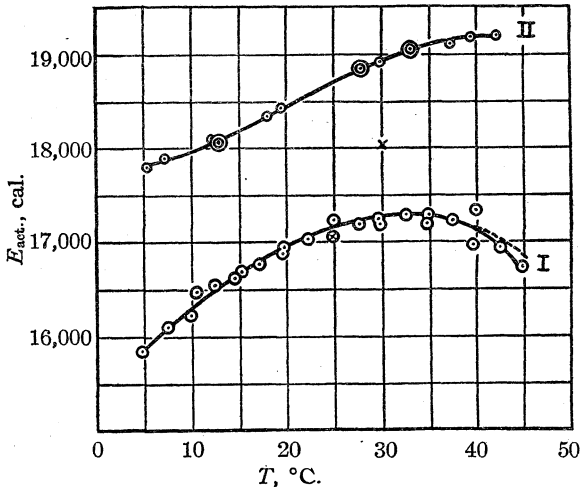

Fig. 3.—Temperature dependence of the Arrhenius E: I, water solution; II, 18.5% methyl alcohol; ×, Murphy's data; ◉, very small temperature interval.

The presence of such difficulties is recognized even by the proponents of the extreme form of the collision theory. Since the linear extrapolation of the log k − $1/T$ curve to infinite temperature, by which the collision number, Z, is obtained, cannot be made unless E_{act} is independent of temperature, some authors have attempted to correct E_{act} and others to correct B to justify this procedure. Moelwyn-Hughes' theory[29] would obtain the "true" E_{act} for reactions of this type (*i. e.*, involving a neutral molecule and an ion), which exhibit a marked discrepancy between the calculated and observed collision frequency by using for the calculation, not k, but k divided by the viscosity coefficient. Such a procedure implies that if the corrected E_{act} is to be independent of temperature the measured E_{act} was not. It may be recalled that the reactions which required this interpretation include the acid hydrolysis of esters and amides, the decomposition of nitrosotriacetoneamine, hydrolysis of sugars and the hydrolysis of γ stearolactone. A like treatment, applied to the present reaction,[30] gives E^*_{act} = 21,300 cal. and B^* = 13.9, a good correlation. However, in methyl alcohol solution E^*_{act} = 23,800 cal. and B^* = 14.9, making the former agreement seem purely fortuitous.

The parallel behavior of E_{act} and B previously pointed out is not surprising in the special case where T is the independent variable, but is a consequence of equation (4) relating B to the entropy of activation.

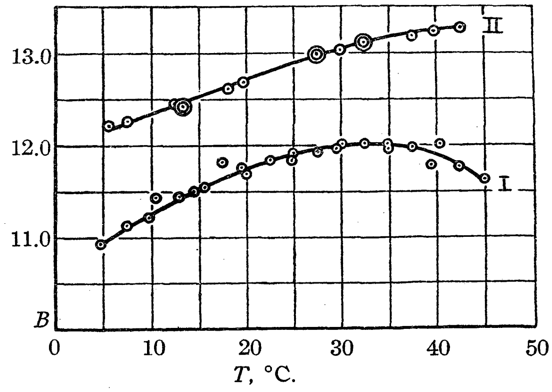

Fig. 4.—Diacetone alcohol: I, solvent water; II, solvent 18.5% methyl alcohol.

Thus, by differentiating the expressions for E_{act} and 2.3 B in respect to temperature and forming the ratio, we get

$$2.3\,\frac{\mathrm{d}B}{\mathrm{d}E} = 2.3\,\frac{\mathrm{d}B}{\mathrm{d}T}\bigg/\frac{\mathrm{d}E_{\text{act}}}{\mathrm{d}T} = \frac{1}{RT}$$

The above considerations apply solely to the dB/dE resulting from a change in temperature and are not to be confused with the rough parallelisms between E_{act} and B[31] observed when either the solvent or one of the reactants is changed.

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(27) V. K. La Mer, (a) *J. Chem. Phys.*, **1**, 289 (1933); (b) THIS JOURNAL, **55**, 1739 (1933).

(28) The fortuitous nature of such agreement has been emphasized by Polissar, and by D. T. Lewis and Hudleston: M. J. Polissar, *ibid.*, **54**, 3105 (1932); D. T. Lewis and L. J. Hudleston, *Trans. Chem. Soc.*, 1398 (1932).

(29) E. A. Moelwyn-Hughes, *Phil. Mag.*, **14**, 112 (1932).

(30) Since the following approximations were made in order to use the viscosity data ("I. C. T."), a constancy of E^*_{act} of better than ±300 cal. can hardly be expected: (1) graphical interpolation for concentration and temperature; (2) additivity of η for acetone and methyl alcohol solutions; (3) negligible change in η due to the small amount of sodium hydroxide present.

(31) W. A. Holzschmidt, *Z. anorg. allgem. Chem.*, **200**, 82 (1931); S. Roginsky and L. Rosenkewitsch, *Z. physik. Chem.*, **10B**, 47 (1930); J. K. Syrkin, *Z. anorg. allgem. Chem.*, **199**, 28 (1931).

Summary

1. The velocity constant for the diacetone alcohol decomposition in the presence of dilute sodium hydroxide has been measured at 5° intervals from 0 to 50°.

2. The constancy of ratio of velocity constant to sodium hydroxide concentration has been confirmed over a limited concentration range at 25°.

3. The energy of activation, calculated from the Arrhenius equation for a series of temperature intervals, has been shown to be a function of temperature well outside the limits of error. E_{act} increases consistently from a value of 15,850 cal. at 5° to 17,250 at 32.5 and then decreases by about 400 cal. at 45°.

4. On the addition of 18.5% of methyl alcohol E_{act} increases by over 1700 cal. but the general character of the E_{act}–T curve remains little changed to 30°.

5. The corresponding B values from the integrated Arrhenius equation, $\ln k = 2.3\,B - (E_{\text{act}}/RT)$, both in water and the methyl alcohol solution parallel these E_{act} values and furnish experimental evidence for abandoning the unfortunate term "temperature independent constant" for this quantity.

6. The data show that the collision theory is inadequate and that the entropy of activation is an important quantity in considering solution reactions.

NEW YORK, N. Y. RECEIVED AUGUST 15, 1935

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 506]

The Structure and Entropy of Ice and of Other Crystals with Some Randomness of Atomic Arrangement

BY LINUS PAULING

Investigations of the entropy of substances at low temperatures have produced very important information regarding the structure of crystals, the work of Giauque and his collaborators being particularly noteworthy. For example, the observed entropy of crystalline hydrogen shows that even at very low temperatures the molecules of orthohydrogen in the crystal are rotating about as freely as in the gas;[1] subsequent to this discovery the phenomenon of rotation of molecules in crystals was found to be not uncommon. Also the entropy values of carbon monoxide[2] and nitrous oxide[3] show that in crystals of these substances the molecules are not uniquely oriented, but have instead a choice between two orientations, presumably the opposed orientations CO and OC or NNO and ONN along fixed axes. It is pointed out in this note that the observed entropy of ice at low temperatures provides strong support for a particular structure of ice, and thus gives an answer to a question which has been extensively discussed during the past few years.

It has been generally recognized since the discovery of the hydrogen bond[4] that the unusual properties of water and ice (high melting and boiling points, low density, association, high dielectric constants, etc.) owe their existence to hydrogen bonds between water molecules. The arrangement of oxygen atoms (but not of hydrogen atoms) in crystals of ice is known from x-ray studies;[5] it is not a close-packed arrangement (as of sulfur atoms in the high-temperature form of hydrogen sulfide), but a very open one, like that of the silicon atoms in high-tridymite. Each oxygen atom in ice is tetrahedrally surrounded by four other oxygen atoms at the distance 2.76 Å., and it has been assumed that it is bonded to these atoms by hydrogen bonds, the number of hydrogen atoms being just that required to place one hydrogen atom between each pair of oxygen atoms. (Similarly in high-tridymite there is an oxygen atom between each pair of silicon atoms; we might say that each silicon atom is attached to four others by oxygen bonds.)

The question now arises as to whether a given hydrogen atom is midway between the two oxygen

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(1) W. F. Giauque and H. L. Johnston, THIS JOURNAL, **50**, 3221 (1928); L. Pauling, *Phys. Rev.*, **36**, 430 (1930).

(2) J. O. Clayton and W. F. Giauque, THIS JOURNAL, **54**, 2610 (1932).

(3) R. W. Blue and W. F. Giauque, *ibid.*, **57**, 991 (1935); K. Clusius, *Z. Elektrochem.*, **40**, 99 (1934).

(4) W. M. Latimer and W. H. Rodebush, THIS JOURNAL, **42**, 1419 (1920).

(5) D. M. Dennison, *Phys. Rev.*, **17**, 20 (1921); W. H. Bragg, *Proc. Phys. Soc.* (London), **34**, 98 (1922); W. H. Barnes, *Proc. Roy. Soc.* (London), **A125**, 670 (1929).

atoms it connects or closer to one than to the other. The answer to this is that it is closer to one than to the other. In the gas molecule the O–H distance is 0.95 Å., and the magnitudes of the changes in properties from steam to ice are not sufficiently great to permit us to assume that this distance is increased to 1.38 Å. In ice each hydrogen atom is about 0.95 Å. from one oxygen atom and 1.81 Å. from another.

We now ask whether each hydrogen atom (or rather hydrogen nucleus) has a choice of two positions along its oxygen–oxygen axis, independent of the positions of the other hydrogen nuclei. The answer is in the negative; for we know that the concentration of $(OH)^-$ and $(H_3O)^+$ ions in water is very small, and we expect the situation to be essentially unchanged in ice. Hence the hydrogen nuclei will assume positions such that each oxygen atom (with at most very few exceptions) will have two hydrogen atoms attached to it.

Let us now make the following assumptions (to be supported later by a discussion of the entropy) regarding the structure of ice.

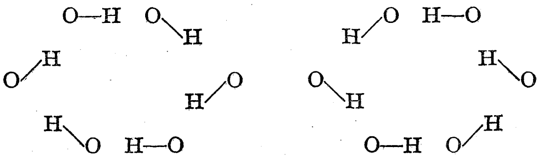
(1) In ice each oxygen atom has two hydrogen atoms attached to it at distances of about 0.95 Å., forming a water molecule, the HOH angle being about 105° as in the gas molecule.

(2) Each water molecule is oriented so that its two hydrogen atoms are directed approximately toward two of the four oxygen atoms which surround it tetrahedrally, forming hydrogen bonds.

(3) The orientations of adjacent water molecules are such that only one hydrogen atom lies approximately along each oxygen–oxygen axis.

(4) Under ordinary conditions the interaction of non-adjacent molecules is not such as to appreciably stabilize any one of the many configurations satisfying the preceding conditions with reference to the others.

Thus we assume that an ice crystal can exist in any one of a large number of configurations,[6] each corresponding to certain orientations of the water molecules. The crystal can change from one configuration to another by rotation of some of the molecules or by the motion of some of the hydrogen nuclei, each moving a distance of about 0.86 Å. from a potential minimum 0.95 Å. from one oxygen atom to another one 0.95 Å. from an adjacent oxygen atom. It is probable that both processes occur. As an example of a change from one to another configuration, we may consider one of the puckered rings of six oxygen atoms occurring in ice



Change from one of the two cyclic arrangements of hydrogen nuclei to the other is permitted by our postulates. The fact that at temperatures above about 200Å. the dielectric constant of ice is of the order of magnitude of that of water shows that the molecules can orient themselves with considerable freedom, the crystal changing under the influence of the electric field from unpolarized to polarized configurations satisfying the above conditions. On cooling the crystal to low temperatures it freezes into some one of the possible configurations; but it does not go over (in a reasonable period of time) to a perfect crystal with no randomness of molecular orientation. It will have at very low temperatures the entropy $k \ln W$, in which W is the number of configurations accessible to the crystal.

Let us now calculate W, using two different methods.

There are N molecules in a mole of ice. A given molecule can orient itself in six ways satisfying condition 2. However, the chance that the adjacent molecules will permit a given orientation is $^1/_4$; inasmuch as each adjacent molecule has two hydrogen-occupied and two unoccupied tetrahedral directions, making the chance that a given direction is available for each hydrogen of the original molecule $^1/_2$, and the chance that both can be located in accordance with the given orientation $^1/_4$. The total number of configurations for N molecules is thus $W = (^6/_4)^N = (^3/_2)^N$.

The same result is given by the following equivalent argument. Ignoring condition 1, there are 2^{2N} configurations with hydrogen bonds between adjacent oxygen atoms, each hydrogen nucleus having the choice of two positions, one near one oxygen atom and the other near the other. Some of these are ruled out by condition 1. Let us now consider a given oxygen atom and the four surrounding hydrogen atoms. There are sixteen arrangements of the four hydrogen nuclei. Of

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(6) One of the large number of configurations is represented by the structure of ice suggested by J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, 1, 515 (1933); these authors also suggested that at temperatures just below the melting point (but not at lower temperatures) the molecular arrangement might be partially or largely irregular.

these ten are ruled out by condition 1—one gives $(H_4O)^{++}$, four give $(H_3O)^+$, four $(OH)^-$ and one O^{--}. This condition for each oxygen atom thus permits only $^6/_{16} = {}^3/_8$ of the configurations, the total number of permitted configurations being accordingly $W = 2^{2N}(^3/_8)^N = (^3/_2)^N$.

The contribution of this lack of regularity to the entropy of ice is thus R ln $^3/_2 = 0.805$ E. U. The observed entropy discrepancy of ice at low temperatures is 0.87 E. U., obtained by subtracting the entropy difference of ice at very low temperatures and water vapor at standard conditions, for which the value 44.23 E. U. has been calculated from thermal data by Giauque and Ashley,[7] from the spectroscopic value 45.101 E. U. for the entropy of water vapor given by Gordon.[8] The agreement in the experimental and theoretical entropy values provides strong support of the postulated structure of ice.[9]

The structure of ice is seen to be of a type intermediate between that of carbon monoxide and nitrous oxide, in which each molecule can assume either one of two orientations essentially independently of the orientations of the other molecules in the crystal, and that of a perfect molecular crystal, in which the position and orientation of each molecule are uniquely determined by the other molecules. In ice the orientation of a given molecule is dependent on the orientations of its four immediate neighbors, but not directly on the orientations of the more distant molecules.

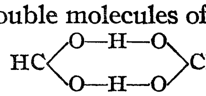
It should be pointed out that a finite residual entropy calculated for a substance from experimental data obtained at temperatures extending down to a certain temperature, with extrapolation below that point, may arise either from failure of the experimenter to obtain thermodynamic equilibrium in his calorimetric measurements or from error in the extrapolation. Measurements made under ideal conditions and extended to sufficiently low temperatures would presumably lead to zero entropy for any system.

Other Crystals with Residual Entropy

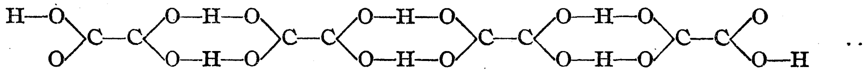
Our knowledge of the structure of crystals permits the prediction to be made that many other crystals will be found to have residual entropy at very low temperatures as a result of some randomness of atomic arrangement. It is probable, however, that experimental verification of the residual entropy would be difficult for most of the cases mentioned below.

Diaspore, $AlHO_2$, contains groups OHO with hydrogen bonds.[10] As in water, we expect the hydrogen nucleus to be closer to one oxygen atom than to the other. Inasmuch as there is no restriction on the choice of the two positions, each oxygen atom forming only one hydrogen bond, this would lead to a residual entropy of R ln 2 per mole of $AlHO_2$. The same residual entropy is expected per HO_2 group for other crystals containing this group (staurolite).

Hydrogen bonds may not always lead to residual entropy. For example, the crystal lepidocrocite,[11] FeOOH, contains infinite strings of oxygen atoms joined by hydrogen bonds, $^{\rm O}{\rm H}_{\rm O}{\rm H}^{\rm O}{\rm H}_{\rm O}{\rm H}^{\rm O}{\rm H}$. If we assume that the choice of two positions by a hydrogen nucleus is restricted by the requirement that each oxygen have one and only one attached hydrogen, then there are two accessible configurations per string. This lack of definiteness does not lead to an appreciable residual entropy for a large crystal.

In the double molecules of formic acid, with the structure[12]  and in other monocarboxylic acids forming double molecules, we expect that the interaction within a carboxyl group is strong enough to permit only the two configurations in which one hydrogen nucleus is attached to each carboxyl group to be stable at low temperatures. This would lead to a residual entropy of $^1/_2$ R ln 2 per RCOOH.

By a similar argument we calculate for β-oxalic acid (anhydrous), which contain finite strings[13] of molecules



the residual entropy R ln 2 per mole of $(COOH)_2$, whereas α-oxalic acid, containing layers with the dealized structure[13] in which there are infinite sequences of carboxyl groups attached by hydrogen bonds, would have no appreciable residual

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[7] W. F. Giauque and M. F. Ashley, *Phys. Rev.*, **43**, 81 (1933).

[8] A. R. Gordon, *J. Chem. Phys.*, **2**, 65 (1934).

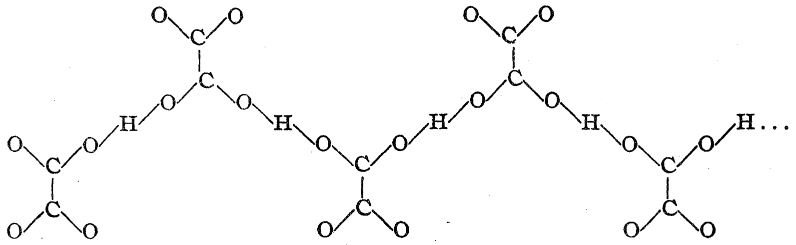
[9] The existence of this residual entropy of ice at very low temperatures was discovered by Giauque and Ashley (ref. 7), who preliminarily ascribed it to the persistance of rotation of ortho-water molecules (comprising $^3/_4$ of the total) about their electric-moment axes, giving an entropy of $^3/_4$ R ln $2 = 1.03$ E. U.

[10] F. J. Ewing, *J. Chem. Phys.*, **3**, 203 (1935).

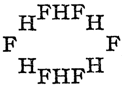
[11] F. J. Ewing, *ibid.*, **3**, 420 (1935).

[12] L. Pauling and L. O. Brockway, *Proc. Nat. Acad. Sci.*, **20**, 336 (1934).

[13] S. B. Hendricks, *Z. Krist.*, **91**, 48 (1935).



entropy. The experimental verification of this prediction by heat capacity measurements and the study of the equilibrium between the two forms might be practicable.

At present it is not possible to predict with confidence whether the hydrogen nucleus between two fluorine atoms connected by a hydrogen bond has the choice of two positions (as for oxygen atoms) or not. The FHF distance of 2.35 Å. is somewhat greater than twice the H–F distance in HF, 0.91 Å., although the difference (29%) is not so great as for OHO and H–O (45%). The question would be answered by a determination of the residual entropy of potassium hydrogen fluoride, KHF_2, or of some other crystal containing the HF_2 group; the residual entropy would be $R \ln 2$ if the potential function for the hydrogen nucleus has two minima rather than one. The same residual entropy would also be shown by KH_2F_3, KH_3F_4, etc. If crystalline hydrofluoric acid contains cyclic molecules $(HF)_6$, with the structure  $\begin{matrix} & {}_{\mathrm{H}}{}^{\mathrm{FHF}}{}_{\mathrm{H}} & \\ \mathrm{F} & & \mathrm{F} \\ & {}^{\mathrm{H}}{}_{\mathrm{FHF}}{}^{\mathrm{H}} & \end{matrix}$, the two-minimum function and the restriction that one hydrogen is attached to each fluorine would lead to a residual entropy of $^1/_6\, R \ln 2$ per mole of HF.

Hydrogen bonds between unlike atoms, as in NH_4F, would not lead to residual entropy.

Residual entropy may also result from the multiplicity of stable positions for atoms other than hydrogen. In γ-Al_2O_3 and γ-Fe_2O_3 the oxygen ions are arranged in a close-packed framework, which provides nine positions for every eight cations. The x-ray data[14] indicate that the cations are distributed essentially at random among these positions, leading to a residual entropy of $^3/_2\, R \ln {}^{27}/_{16} = 1.558$ E. U. per mole of R_2O_3. In pyrrhotite,[15] $Fe_{1-\delta}S$, the sulfur atoms have a hexagonal arrangement, the iron atoms being distributed apparently at random among the positions provided, of which they occupy the fraction $1 - \delta$. In the cubic tungsten bronzes,[16] Na_xWO_3, the sodium ions occupy the fraction x of the available positions. These crystals would presumably show residual entropy of mixing of the ions W^{5+} and W^{6+} as well as the entropy of random distribution of the sodium ions. A somewhat similar case is provided by the hexagonal form of silver iodide,[17] in which at room temperature each silver atom has the choice of four or five positions a few tenths of an Ångström apart. At liquid air temperatures, however, most of the atoms settle into one position, so that no residual entropy would be shown.

Many crystals show an uncertainty in structure similar to that of CO and NNO or of solid solutions. For potassium cyanate the x-ray data[18] indicate that each cyanate ion has the choice of two orientations, NCO and OCN, which would lead to the residual entropy $R \ln 2$. In spinel, $MgAl_2O_4$, and other crystals with the spinel structure, the bivalent and trivalent cations are distributed with considerable randomness among the available positions,[19] leading to a residual entropy corresponding to a crystalline solution. In muscovite,[20] $KAl_2(AlSi_3)O_{10}(OH)_2$, one aluminum and three silicon atoms per formula are distributed, presumably with considerable randomness, among the available tetrahedral positions. The same phenomenon, leading to residual entropy, without doubt occurs in many aluminosilicates.

Crystals of cadmium bromide[21] and nickel bromide[22] prepared in certain ways show a type of randomness which does not lead to any appreciable residual entropy, provided that the crystals are not extremely small. This randomness of structure ("Wechselstruktur," alternating layer structure) consists in a choice between two positions for each layer of a layer structure, leading to an entropy of $k \ln 2$ for each layer, which remains

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[14] G. Hägg and G. Söderhohn, *Z. physik. Chem.*, **B29**, 88 (1935); G. Hägg, *ibid.*, **B29**, 95 (1935); E. J. W. Verwey, *Z. Krist.*, **91**, 65 (1935); E. Kordes, *ibid.*, **91**, 193 (1935).

[15] G. Hägg and I. Sucksdorff, *Z. physik. Chem.*, **B22**, 444 (1933).

[16] G. Hägg, *ibid.*, **B29**, 192 (1935).

[17] L. Helmholz, *J. Chem. Phys.*, **3**, 740 (1935).

[18] S. B. Hendricks and L. Pauling, THIS JOURNAL, **47**, 2904 (1925).

[19] T. F. W. Barth and E. Posnjak, *J. Washington Acad. Sci.*, **21**, 255 (1931); F. Machatschki, *Z. Krist.*, **80**, 416 (1931).

[20] L. Pauling, *Proc. Nat. Acad. Sci.*, **16**, 123 (1930); W. W. Jackson and J. West, *Z. Krist.*, **76**, 211 (1930).

[21] J. M. Bijvoet and W. Nieuwenkamp, *ibid.*, **86**, 466 (1933).

[22] J. A. A. Ketelaar, *ibid.*, **88**, 26 (1934).

inappreciable, inasmuch as the number of layers in a crystal (other than an extremely small crystal) is very small compared with the number of atoms.

In this connection it might be mentioned that there exists the possibility that ice may crystallize with such an alternating layer structure. The oxygen-atom arrangement assigned to ice corresponds to superimposing double oxygen layers in the sequence ABAB—(A at 00, B at $^1/_3\ ^2/_3$, C at $^2/_3\ ^1/_3$ of a hexagonal net). The sequence ABCABCABC— would also lead to an arrangement (diamond) such that each oxygen atom is surrounded by four others arranged tetrahedrally, which is indeed, so far as I can see, just as satisfactory as the reported arrangement. There is no good evidence that such a cubic modification of ice has been observed. However, the arbitrariness of orientation which we have found to exist for the water molecules in ice suggests that there may also be an arbitrariness in the sequence of double oxygen layers, with configurations such as ABABABCBCB— occurring. Such an alternating layer structure would have hexagonal symmetry, might develop faces at angles corresponding to the axial ratio $c/a = 1.63$, and would not be distinguishable so far as residual entropy is concerned from a crystal with fixed oxygen atom arrangement. The x-ray data show that the sequence of layers is not completely random, the structure being essentially ABABAB—; it is possible, however, that a change in the sequence, corresponding to twinning on the basal plane, occurs occasionally.

I am indebted to Professor W. F. Giauque for discussing the question of the structure and entropy of ice, as well as related questions, with me.

Summary

It is suggested that ice consists of water molecules arranged so that each is surrounded by four others, each molecule being oriented in such a way as to direct its two hydrogen atoms toward two of the four neighbors, forming hydrogen bonds. The orientations are further restricted by the requirement that only one hydrogen atom lie near each O–O axis. There are $(^3/_2)^N$ such configurations for N molecules, leading to a residual entropy of $R \ln {}^3/_2 = 0.805$ E. U., in good agreement with the experimental value 0.87 E. U.

The structure and entropy of other crystals showing randomness of atom arrangement are discussed.

PASADENA, CALIF. RECEIVED SEPTEMBER 24, 1935

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 507]

The Radial Distribution Method of Interpretation of Electron Diffraction Photographs of Gas Molecules

BY LINUS PAULING AND L. O. BROCKWAY

Introduction

The only method of interpretation of electron diffraction photographs of gas molecules which has been used to any great extent is the so-called *visual method*, involving the correlation of apparent maxima and minima on the photographs with maxima and minima on simplified theoretical curves calculated for various models of the molecule under consideration. This method of interpretation, originally developed by Wierl,[1] has been thoroughly tested by Pauling and Brockway[2] who have shown it to yield values of interatomic distances accurate to within about 1% (estimated probable error). The main disadvantage of the method is that it does not involve a straightforward process of determining the structure of a molecule from the analysis of experimental results, but consists instead in the testing (and rejection or acceptance) of any structures which may be formulated, a tedious calculation being required for each structure.

We have developed a new method of interpretation of the photographs which does not suffer from this disadvantage. This *radial distribution method*, which is closely related to the method of interpretation of x-ray diffraction data developed by Zernike and Prins[3] for the study of the structure of liquids and applied by Warren and Gingrich[4] to crystals, consists in the calculation (from

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[1] R. Wierl, *Ann. Physik*, **8**, 521 (1931); **13**, 453 (1932).

[2] L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

[3] F. Zernike and J. A. Prins, *Z. Physik*, **41**, 184 (1927); see also P. Debye and H. Menke, *Ergeb. Tech. Röntgenkunde*, Akad. Verlagsges., Leipzig, Vol. II, 1931.

[4] B. E. Warren and N. S. Gingrich, *Phys. Rev.*, **46**, 368 (1934).

data provided by the electron diffraction photograph) of a distribution function for scattering power, representing the product of the scattering powers in volume elements the distance l apart as a function of l. Since the scattering power of an atom for fast electrons is large only in the neighborhood of the nucleus, a maximum in this distribution function indicates that the internuclear distance for two atoms in the molecule is given by the corresponding value of l. The radial distribution method thus leads directly to values of the internuclear distances and hence to the structure of the molecule.

Because of the difficulty of obtaining satisfactory photometer records of electron diffraction photographs of gas molecules, we have adapted and extended the visual method to the calculation of radial distribution curves, by making use of the values of $(4\pi \sin \vartheta/2)/\lambda$ obtained by the measurement of ring diameters (as in the usual visual method) in conjunction with visually estimated intensities of the rings, as described below. Various tests of the method indicate that the important interatomic distances can be determined in this way to within 1 or 2% (probable error).

The radial distribution method, while thus not completely independent of the usual visual method, is sufficiently different from it to lead in some cases to somewhat different values for interatomic distances. We feel that these values carry some weight, and we have accordingly discussed by the new method a number of molecules whose structures as determined by the usual visual method have been reported in earlier publications, and have then combined the results of the two methods in presenting a revised set of values of interatomic distances for these molecules.

The radial distribution method is especially satisfying in that it leads directly to the values of the principal interatomic distances, and so immediately rules out all structures for the molecule except those compatible with these values. Moreover, the method can be applied unchanged to those molecules for which the investigator is unable to formulate a reasonable structure (such as S_2Cl_2, in which the rotation about the S–S bond may be restricted to some extent, leading to difficultly predictable variation in the Cl–Cl distance), yielding a distribution curve which reveals the information provided by the photograph regarding the structure of the molecule.

We are greatly indebted to Dr. S. Weinbaum, Dr. J. Sherman, and Mr. J. Y. Beach for assistance in the preparation of this paper.

Description of the Method

The intensity of the coherent electron scattering at the angle ϑ by gas molecules is usually represented by the expression

$$I(\vartheta) = K \sum_i \sum_j \psi_i \psi_j \frac{\sin x_{ij}}{x_{ij}} \qquad (1)$$

in which K is a constant, and

$$x_{ij} = \frac{4\pi \sin \vartheta/2}{\lambda} l_{ij} \qquad (2)$$

with l_{ij} the distance between atoms i and j in the molecule, λ the wave length of the electrons, and ψ_i the scattering function for the ith atom. A more general expression is

$$s^4 I(s) = K' \int_0^\infty l^2 D(l) \frac{\sin sl}{sl} \, dl \qquad (3)$$

in which we have introduced the new angle variable

$$s = (4\pi \sin \vartheta/2)/\lambda \qquad (4)$$

and have replaced the double sum by an integral, writing in place of the product of atomic scattering powers $\psi_i\psi_j$ the function $l^2 D(l)/s^4$, representing, aside from the factor $1/s^4$ (the scattering factor for electrons by a unit charge), the product of scattering powers in all volume elements the distance l apart. This expression is a Fourier integral for $s^5 I(s)$, the coefficients of the Fourier terms being $lD(l)$. On inverting the Fourier integral we obtain the following expression for $D(l)$ in terms of $I(s)$

$$D(l) = K'' \int_0^\infty s^6 I(s) \frac{\sin sl}{sl} \, ds \qquad (5)$$

Instead of attempting to apply the expression in this form, we simplify it radically in a way suggested by the appearance of the electron diffraction photographs, which to the eye show a succession of rings; namely, by replacing the integral by a finite sum of terms, including one term for each ring. We accordingly write, ignoring the constant K''

$$D(l) = \sum_{k=1}^{n} I_k \frac{\sin s_k l}{s_k l} \qquad (6)$$

in which

$$s_k = (4\pi \sin \vartheta_k/2)/\lambda$$

ϑ_k being the scattering angle for the kth ring as measured in the usual way,[2] and I_k an estimated value[5] for the integrated intensity of the kth ring

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(5) It is our experience that the intensities as estimated visually (the change from ring to ring being small, as seen in the tables) are satisfactory, despite neglect of the factor s^6. This may be due in part to the comparison by the eye of each ring with the adjacent background, which falls off in intensity approximately with $1/s^4$.

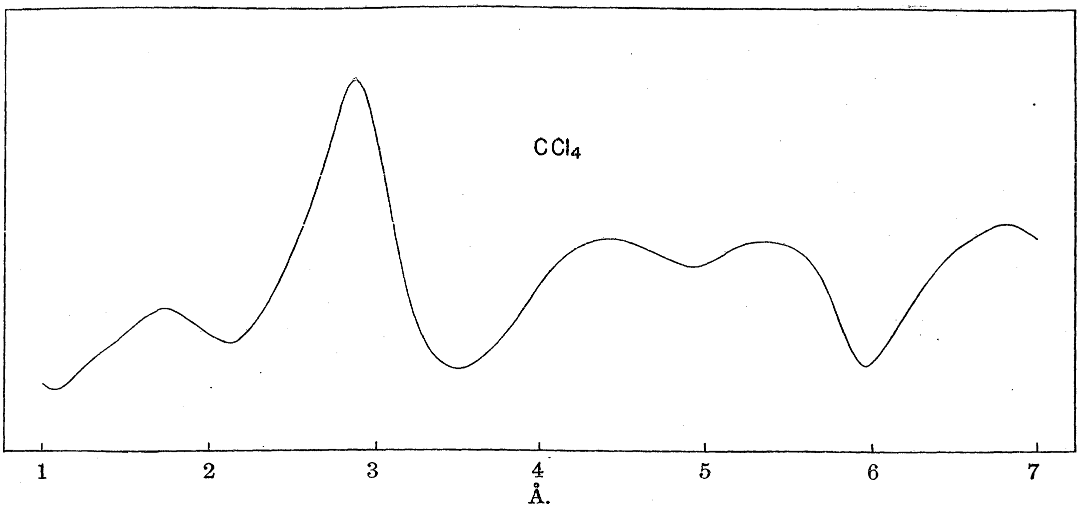

Fig. 1.—Radial distribution function for carbon tetrachloride. The part of the curve beyond 4 Å. is without significance.

(the factor s^6 being included in I_k). This simplification, which at first seems extreme, is seen on analysis not to be unreasonable; each section of the integral, corresponding to the range of angles between successive apparent minima, is replaced by a single Fourier term, whose frequency is in the middle of the frequencies for the range replaced, the coefficient of the single term being an integrated coefficient over the range. For values of l in the region of importance (corresponding to interatomic distances in the molecule) this simplification will not change the form of $D(l)$ very much; at smaller and larger values of l, however, it will introduce false maxima, instead of falling asymptotically to zero.

It is seen that the calculation of a radial distribution curve is closely similar to the calculation of a simplified theoretical intensity curve for the usual visual method, the summation being over the rings seen on the photograph instead of over the interatomic distances in the assumed model; but whereas in the usual treatment the calculation may need to be repeated for many models, a single curve only is required for the new method.

In the usual treatment the apparent intensities of the rings play only a minor part, in that some use is made of them in the decision among models by qualitative comparison of photograph and curves. Numerical values of estimated intensities are needed for the new method; it is found empirically, however, that the positions of the principal maxima are not very sensitive to changes in the estimated intensities, as long as the rings are kept in correct qualitative relation to one another. It is sometimes necessary to introduce a term in the series to represent a shelf on one side of a ring, or some similar feature of the photograph.[6]

In the calculations reported in this paper the curves were evaluated at intervals of 0.1 Å. except in the neighborhood of the principal maxima, where smaller intervals (usually 0.02 Å.) were used. The values of (sin sl)/sl were obtained from tables prepared by Dr. P. C. Cross with the aid of Sherman's (sin x)/x tables.[7]

Tests of the Method

Carbon Tetrachloride.—By the usual visual method and by other methods involving microphotometer records, we have assigned[8] to the carbon tetrachloride molecule the value 1.760 ± 0.005 Å. for the C–Cl distance, a value supported by other recent work.[9] The radial distribution function for this molecule calculated by Equation 6, using the ten terms for which data are given in Table I, is shown in Fig. 1.

It is seen that the six Cl–Cl terms are shown by a very sharp peak, the four C–Cl terms appearing

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(6) Dr. Simon Bauer has suggested that it may sometimes be convenient to introduce terms corresponding to the apparent minima between rings, using negative coefficients.

(7) J. Sherman, *Z. Krist.*, **85**, 404 (1933). The tables prepared by Dr. Cross give values of (sin sl)/sl for $0.80 \leqslant s \leqslant 4.00$ at intervals of 0.01, for values of l up to 40, and $4.02 \leqslant s \leqslant 8.00$ at intervals of 0.02, for values of l up to 20. the intervals for l being 0.2.

(8) L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

(9) V. E. Cosslett and H. de Laszlo [*Nature*, **134**, 63 (1934)] report 1.754 ± 0.02 Å. and V. E. Cosslett [*Trans. Faraday Soc.*, **30**, 981 (1934)] reports 1.74 ± 0.02 Å. C. Degard, J. Pierard and W. van der Grinten give the values 1.75 ± 0.02 Å. (electron diffraction) and 1.74 ± 0.02 Å. (x-ray diffraction) in a letter to *Nature*, **136**, 142 (1935).

TABLE I

CARBON TETRACHLORIDE

k	I_k	s_k
1	20	2.93
2	30	4.91
3	15	7.13
4	10	9.23
5	10	11.34
6	5	13.54
7	4	15.79
8	2	17.82
9	1	19.98
10	1	22.34

as a small peak at a smaller value of l; in addition some broad peaks occur at larger values of l. The complete Fourier integral representing the radial distribution would, of course, fall asymptotically to zero after the Cl–Cl maximum. Because of the crudity of our approximation to the integral by a series of ten terms we can expect our function to continue to vary appreciably in this region, the maxima there having no significance.

The l value given by the small C–Cl peak, about 1.74 Å., is unreliable, inasmuch as it is rather sensitive to change in the number of rings considered. That given by the Cl–Cl hump, however, is reliable. It is Cl–Cl = 2.856 Å., which corresponds to C–Cl = 1.749 Å., in good agreement with the earlier value, the deviation being in the direction of the values of Cosslett and de Laszlo.

The effect of including successive rings is shown in Fig. 2, the first curve including only one term (ring 1), the second two (rings 1 and 2), and so on. It is seen that the principal peak assumes its position and shape very quickly, the Cl–Cl distance being given to within 2% (2.81 Å.) by two terms alone, and quickly rising to a constant value (2.85 Å. for five terms, 2.86 Å. for six and more terms). The small C–Cl peak, on the other hand, fluctuates considerably, the l value varying between 1.72 and 1.78 Å. for curves 5 to 10.

Bromine and Chlorine.—Accurate values of the internuclear distances in the molecules Br_2 and Cl_2 are known from band spectral studies, namely, Br–Br = 2.281 Å. and Cl–Cl = 1.988 Å. The visual method led to results (2.289 Å. and 2.009 Å., respectively) in satisfactory agreement with these.[8] Radial distribution curves for these substances are shown in Fig. 3, the data used being given in Tables II and III. For bromine, with seven rings, three different estimates of intensities lead to the same Br–Br distance, 2.270 Å., less than 0.5% from the band spectral value. The Cl–Cl distance, given by the curve, 1.995 Å., is still closer to that found from band spectra. The agreement for these two molecules indicates that there is no large error inherent in the radial distribution method.

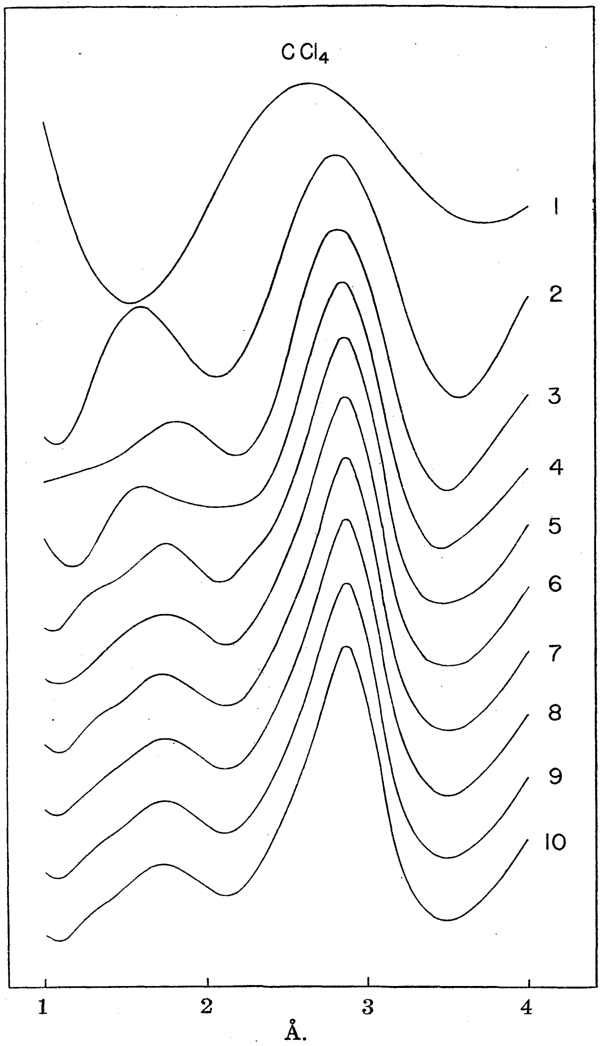

Fig. 2.—Radial distribution curves for carbon tetrachloride, calculated with one term (1), two terms (2) and so on.

Benzene.—A careful study of photographs of benzene both by the visual method and by the analysis of microphotometer records[8] has led to the value C–C = 1.390 ± 0.005 Å. for the edge of the plane hexagon formed by the carbon atoms, in agreement with the values 1.39 ± 0.03 Å. and 1.40 ± 0.03 Å. reported by Wierl.[1] The accuracy of this determination and the fact that the various carbon–carbon distances are geometrically related

TABLE II

BROMINE

	I_k			
k	A	B	C	s_k
1	6	32	16	3.50
2	5	16	12	6.17
3	4	8	8	8.90
4	3	4	4	11.67
5	2	2	2	14.44
6	1	1	1	17.19

TABLE III

CHLORINE

k	I_k	s_k
1	10	3.94
2	5	6.99
3	2	10.08
4	1	13.30

make benzene a suitable substance for testing the new method.

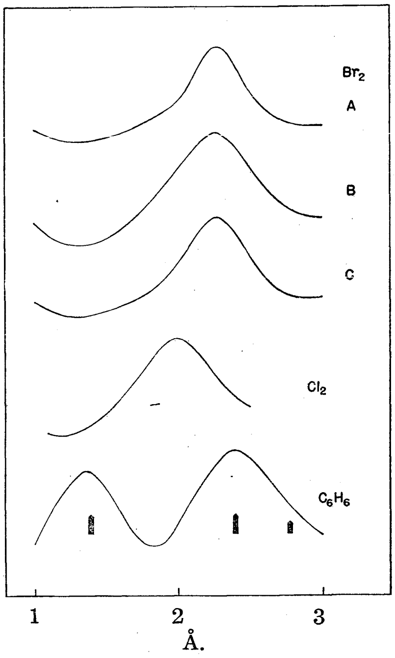

Fig. 3.—Radial distribution curves for bromine, chlorine and benzene.

The radial distribution curve calculated with the inclusion of seven terms, for which data are given in Table IV (the fourth and sixth terms corresponding to apparent shelves rather than well-defined rings), is shown in Fig. 3.

Only the two principal distances, corresponding to the six ortho C–C interactions and the six meta C–C interactions, are represented by maxima, the three para C–C interactions (which should yield a hump about one-half as pronounced as the others at the position indicated by the smallest arrow) and the various C–H interactions not being indicated on the curve. This is in agreement with our experience in general with the radial distribution method, which usually can be relied on (in the form in which we are using it) to provide information regarding only the two or three most important interactions, the peaks for which must also be separated by at least about 0.5 Å. in order to be resolved.

TABLE IV

BENZENE

k	I_k	s_k
1	50	3.35
2	160	5.805
3	20	9.55
4	5	11.50
5	15	13.83
6	3	16.23
7	8	18.66

The two maxima occur at the distances 1.381 and 2.390 Å., their ratio being 1:1.731. The close approximation of this ratio to the value $1:\sqrt{3}$ required by the hexagonal configuration of the molecule provides an interesting check on the method.

The value 1.381 Å. is 0.009 Å. less than that found in the earlier treatment. We believe that in this case the earlier treatment, involving the analysis of microphotometer records as well as the application of the usual visual method, is the more reliable, and we prefer not to change from the value 1.390 ± 0.005 Å. Indeed, we think that the usual visual method is itself somewhat more reliable than the radial distribution method in the case of benzene, inasmuch as the photographs show some precisely measurable features (very sharp fourth minimum and fourth maximum) as well as some rather diffuse rings which can be measured only with less precision; in the usual visual method great weight can be given to the results calculated from the precisely measured features, whereas in the radial distribution method the weighting is determined by the intensities of the rings, the result being dependent on the diffuse as well as the sharp ones.

Tetrahedral Molecules.—The tetrahedral molecules MX_4 permit an interesting test of the radial distribution method in that the ratio of the two distances X–X and M–X should be $2\sqrt{2}/\sqrt{3} = 1.633$. We have seen that in carbon tetrachloride this ratio is given by the curve to within about 1%. The compounds CF_4, SiF_4,

$SiCl_4$, $GeCl_4$ and $SnCl_4$ provide better tests, inasmuch as the two maxima arise from more nearly equal interactions. The curves for these five molecules, calculated for the constants[10] given in Table V, are shown in Fig. 4. It is seen that each curve shows two well-defined peaks, that for X–X being stronger than that for M–X in CF_4 and $SiCl_4$, and weaker in the other three. The lack of symmetry of the peaks (particularly pronounced for $GeCl_4$) could presumably be remedied by changing the estimated values of I_k; though such a procedure might be justified, we have not adopted it, retaining instead the original estimates in every case.

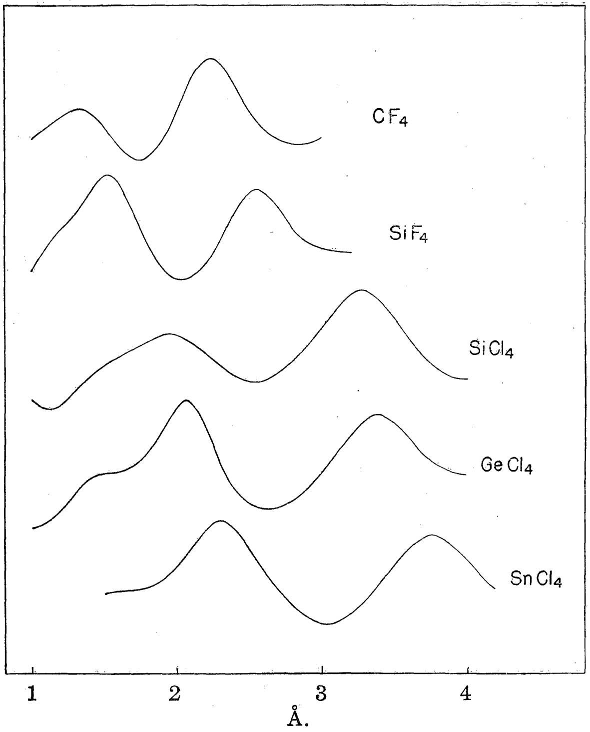

Fig. 4.—Radial distribution curves for carbon and silicon tetrafluorides and silicon, germanium and tin tetrachloride.

The values of l for the X–X and M–X peaks are given in Table VI, together with their ratios. It is seen that the ratio is in every case slightly higher than the correct value 1.633. The deviations of 0.3 to 2.7% provide some indication as to the reliability of the method; there seems to be some tendency for the maxima of the two peaks to be displaced away from one another.

TABLE V

TETRAHALIDES

	CF_4		SiF_4		$SiCl_4$		$GeCl_4$		$SnCl_4$	
k	I_k	s_k	I_k	s_k	I_k	s_k	I_k	s_k	I_k	s_k
1	10	3.56	40	5.41	15	2.55	3	2.29	60	3.67
2	25	6.18	20	8.27	40	4.25	30	4.09	60	5.62
3	10	9.28	5	9.97	15	6.29	20	6.27	20	6.70
4	3	12.06	10	13.02	5	8.04	8	7.22	16	8.78
5	3	14.49	3	17.27	8	9.90	15	9.75	8	11.67
6			1	21.34	1	11.89	6	12.75	4	14.23
7					3	13.85	3	15.46	2	16.79
8					1	15.93	2	18.51		

TABLE VI

DISTANCES IN TETRAHALIDE MOLECULES

Compound	CF_4	SiF_4	CCl_4	$SiCl_4$	$GeCl_4$	$SnCl_4$
X–X, Å.	2.235	2.555	2.870	3.274	3.385	3.760
M–X, Å.	1.335	1.527	1.74	1.963	2.070	2.295
Ratio	1.674	1.673	1.649	1.668	1.635	1.638

Carbon Disulfide and Carbon Oxysulfide.—Radial distribution curves for carbon disulfide and carbon oxysulfide (treated by the usual method by Cross and Brockway[11]) are shown in Fig. 5. For carbon disulfide the maxima of the two peaks occur at 1.60 and 3.07 Å. In this symmetrical linear molecule the C–S distance is just one-half the S–S distance; the values found deviate from this ratio by 4%. Similarly in carbon oxysulfide the sum of two interatomic distances equals the third. The values C–S = 1.60 Å. and O–S = 2.70 Å. given by the two maxima differ by 1.10 Å. The C–O distance is not given by the curve (being indicated only by a hump at the point indicated by the arrow); there is little doubt that the value 1.16 ± 0.02 Å. found by Cross and Brockway is

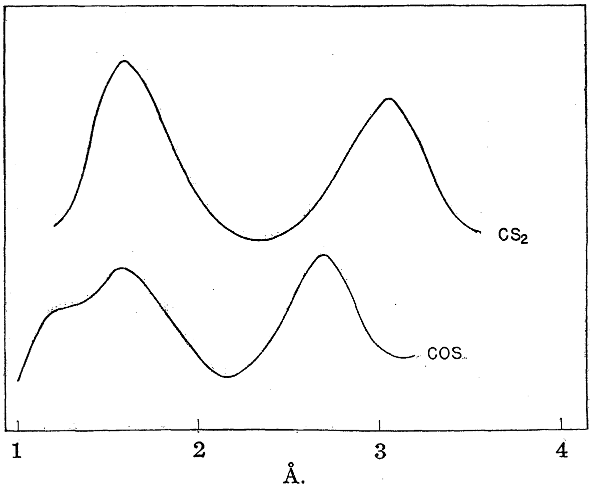

Fig. 5.—Radial distribution curves for carbon disulfide and carbon oxysulfide.

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(10) The s_k values are in the main taken from (a) L. O. Brockway and F. T. Wall, THIS JOURNAL, **56**, 2373 (1934), and (b) L. O. Brockway, *ibid.*, **57**, 958 (1935), with values for shelves (not given in these papers) obtained by measurement of the original photographs.

(11) P. C. Cross and L. O. Brockway, *J. Chem. Phys.*, **3**, December (1935).

reliable, however, showing that there is an error of about 3% in the values given by the maxima. It is interesting to note that the two peaks for these curves are displaced toward one another, rather than away from one another as for the tetrahalides.

The comparison with the interatomic distance values reported by Cross and Brockway, C–S = 1.54 ± 0.03 Å. and S–S = 3.08 ± 0.06 Å. in CS_2, C–O = 1.16 ± 0.02 Å., C–S = 1.56 ± 0.03 Å., and O–S = 2.72 ± 0.05 Å. in COS, indicates that of the two peaks of these radial distribution curves the outer one is somewhat more reliable than the inner one.

TABLE VII

CARBON DISULFIDE AND CARBONYL SULFIDE

	CS_2		COS	
Ring	I	s	I	s
1	50	4.713	15	5.23
2	12	6.312	10	7.67
3	16	8.698	4	9.82
4	4	10.63	6	12.20
5	8	12.65	2	14.04
6	2	14.58	3	16.65
7	4	16.81		
8	1	18.7		
9	2	21.0		

Discussion of the Method

From the examples given we see that the radial distribution method in the simplified form which we have developed for the treatment of electron diffraction photographs of gas molecules is reasonably reliable and accurate, usually providing values of the two or three most important interatomic distances in the molecule (that is, those which contribute most to the diffraction pattern) with an accuracy of 1 or 2%. Probably the principal advantage of the method is that its application is straightforward; no previous information or hypothesis regarding the structure of the molecule (or, in fact, regarding even the chemical composition of the scattering gas) is needed. The information provided by a radial distribution curve usually eliminates all models of the molecule under consideration except those defined by a narrow range of values of the structural parameters; these models can then be considered in detail by the usual method, this consideration usually leading to a further restriction in the parameter values. The calculation of a radial distribution curve is thus the logical first step in the analysis of an electron diffraction photograph. Examples showing the use of these curves are included in the following paper.

We recommend that in general values of interatomic distances given by the two methods be averaged, with about equal weights unless it is felt that in a special case one method is more satisfactory than the other. The usual visual method is superior to the radial distribution method under circumstances such as the following: (1) when there are geometrical relations among interatomic distances (CS_2, C_3O_2, benzene, etc.); (2) when the photographs show some especially precisely measurable features, such as some very sharp rings (benzene); (3) when knowledge regarding certain structural parameters is available and it is desired to vary only the others; (4) when the molecule contains two or more important interatomic distances with values so close to one another that the corresponding peaks are not resolved on the radial distribution curves. On the other hand, the radial distribution method is superior in cases such as the following: (1) when the molecule contains rotating groups or some other structural feature making the detailed formulation of a model difficult (S_2Cl_2, etc.); (2) when the decision as to the model depends on quantitative intensity estimates and small changes in ring diameters (ClO_2, SO_2, etc.).

Revised Values of Structural Parameters of Molecules

On calculating radial distribution curves for molecules for which structures have been previously reported from this Laboratory on the basis of the usual method of interpretation, we have in some cases obtained interatomic distance values agreeing exactly with the earlier values and in some cases values which deviate by a small amount (rarely more than 3%). For a few molecules the new method has provided information (bond angles in ClO_2 and SO_2) not before available. We feel that it is worth while to present a table of revised values of structural parameters for these molecules, giving weight to the results of both methods. The revision includes most of the substances which have been studied in this Laboratory; some (methyl azide, diacetylene, carbon suboxide, dioxane, etc.) are omitted because of the small number of rings shown on the photographs or the unsuitability of the radial distribution method (for reasons such as those mentioned above).

Benzene.—We recommend no change in the value C–C = 1.390 ± 0.005 Å. in benzene.

Tetrahalides.—Values of M–X and (X–X)/1.633 given by the maxima on the radial distribution curves (Figs. 1 and 4) for six tetrahalides are shown in the second and third columns of Table XI, with the values obtained by the usual visual method[10a] in the fourth column. In averaging these we have assigned weights to the two radial distribution peaks as indicated by their prominence, and have given the two distinct methods about equal weight. It is seen that in no case is the change made greater than 1%.

Trihalides of Phosphorus and Arsenic.—Radial distribution curves for PF_3, AsF_3, PCl_3 and $AsCl_3$, calculated with the data given in Table VIII, are shown in Fig. 6. Each curve shows two peaks, corresponding to M–X and X–X; values for their maxima (except for X–X in AsF_3, this peak being so broad as to make its maximum unreliable) are given in Table XII, together with the values obtained by the usual visual method in an earlier investigation.[10a] The weighted averages for M–X, X–X and the X–M–X angle are given in the last three columns.

TABLE VIII

TRIHALIDE MOLECULES

	PF_3		AsF_3		PCl_3		$AsCl_3$	
Ring	*I*	*s*	*I*	*s*	*I*	*s*	*I*	*s*
1	4	5.74	10	4.73	5	2.76	2	2.33
2	2	8.82	5	8.09	15	4.54	20	3.944
3	1	13.45	2	11.77	10	6.66	10	6.234
4			1	15.26	1	8.75	3	9.55
5					4	10.38	2	12.13
6					3	12.58		

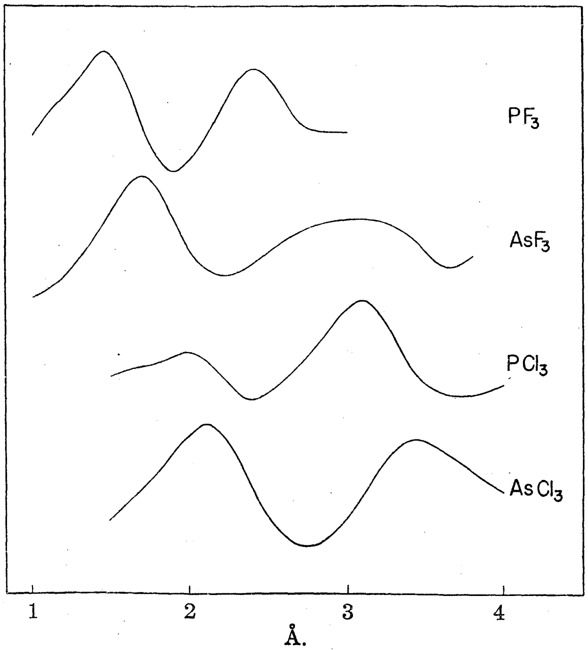

Fig. 6.—Radial distribution curves for triflourides and trichlorides of phosphorus and arsenic.

Methylene Chloride and Chloroform.—Curves for CH_3Cl, CH_2Cl_2 and $CHCl_3$ (Table IX) are shown in Fig. 7. The maximum for methyl chloride lies at 1.80 Å.; we do not consider this value sufficiently reliable to warrant a change from the value C–Cl = 1.77 ± 0.02 Å. previously reported.[12] The M–X and X–X values given by the maxima for methylene chloride and chloroform (Table XII) are in excellent agreement with those found by the usual method.

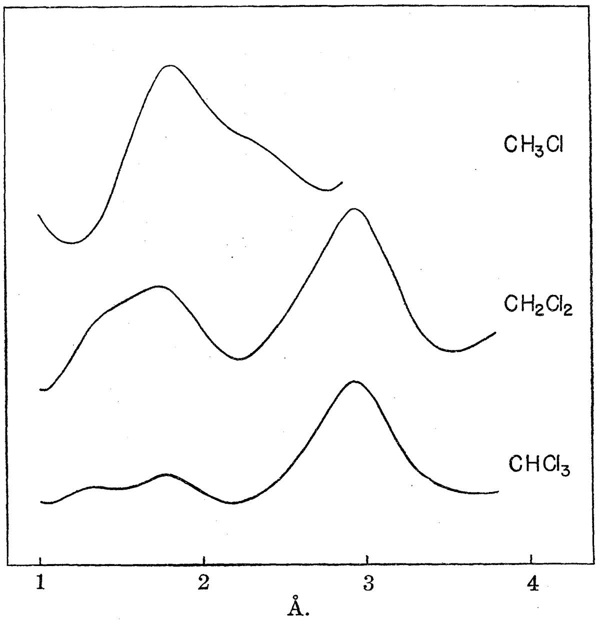

Fig. 7.—Radial distribution curves for methyl chloride, methylene chloride and chloroform.

TABLE IX

	CH_3Cl		CH_2Cl_2		$CHCl_3$	
Ring	*I*	*s*	*I*	*s*	*I*	*s*
1	15	4.07	15	2.81	25	2.74
2	8	8.12	40	4.81	40	4.78
3	3	11.24	15	7.00	20	6.99
4	1	14.49	8	8.84	10	9.04
5			10	11.01	15	11.16
6			3	13.28	3	13.32
7			5	15.41	3	15.32
8			1	17.94	1	17.47

Chlorine Monoxide, Dimethyl Ether, Chlorine Dioxide and Sulfur Dioxide.—The radial distribution curves for Cl_2O, $(CH_3)_2O$, ClO_2 and SO_2 (Fig. 8) show two peaks, the positions of the

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[12] Sutton and Brockway, THIS JOURNAL, **57**, 473 (1935).

maxima being recorded in Table XII. For chlorine monoxide we have averaged the results of the two methods with equal weights (the agreement being less satisfactory than usual). In the case of dimethyl ether smaller weight is given to the results of the radial distribution method because of the lack of symmetry of the first peak, which may cause the maximum to be displaced. It is interesting to note that the radial distribution method provides values of the angles in ClO_2 and SO_2, whereas the usual method of interpretation failed in this respect, presumably because the qualitative comparisons must be supplemented by quantitative considerations in order to obtain this information.

TABLE X

	ClO_2		$(CH_3)_2O$		ClO_2		SO_2	
Ring	*I*	*s*	*I*	*s*	*I*	*s*	*I*	*s*
1	5	2.801	10	6.024	5	4.98	10	5.625
2	15	4.835	4	9.744	2	9.25	6	9.66
3	3	7.328	2	13.63	1	13.68	2	13.76
4	1	9.14	1	17.78			1	18.15
5	1	11.45						

TABLE XI

M–X DISTANCES IN TETRAHALIDE MOLECULES

	Radial distribution M–X	Radial distribution X–X/1.633	Visual method	Final values of M–X
CF_4	1.335 Å.	1.369 Å.	1.360 Å.	1.36 ± 0.02 Å.
SiF_4	1.527	1.565	1.544	1.54 ± 0.02
CCl_4	(1.74)	1.749	1.760	1.755 ± 0.005
$SiCl_4$	1.963	2.005	2.016	2.00 ± 0.02
$GeCl_4$	2.070	2.073	2.103	2.08 ± 0.02
$SnCl_4$	2.295	2.303	2.289	2.30 ± 0.02

Summary

It is shown by empirical tests that the radial distribution function given by a sum of Fourier terms corresponding to the rings observed on an electron diffraction photograph of gas molecules (using visually measured ring diameters and estimated intensities) provides values of the important interatomic distances accurate to one or two per cent. (probable error). The substances used in the tests include carbon tetrachloride and other tetrahalides, bromine, chlorine, benzene, carbon disulfide and carbon oxysulfide.

The radial distribution method of interpretation is applied to a number of molecules previously investigated, and revised values of interatomic distances and bond angles, obtained by considering the results of this method as well as of the usual visual method, are presented (Tables XI and XII).

It is pointed out that the radial distribution method is particularly satisfying in that it leads directly to the values of the important interatomic distances in the molecule, thus eliminating many possible models and usually limiting the molecule to the structures represented by small ranges of values of the structural parameters.

TABLE XII

INTERATOMIC DISTANCES IN MOLECULES MX_2 AND MX_3

	Radial distribution			Visual method			Final values		
	M–X	X–X	Angle	M–X	X–X	Angle	M–X	X–X	Angle
PF_3	1.47 Å.	2.41 Å.	110°	1.56 Å.	2.37 Å.	99°	1.52 ± 0.04 Å.	2.39 ± 0.03 Å.	104 ± 4°
AsF_3	1.70	...	...	1.73	...	...	1.72 ± .02	... ...	... ..
PCl_3	1.98	3.08	102	2.02	3.09	100	2.00 ± .02	3.09 ± 0.02	101 ± 2
$AsCl_3$	2.13	3.43	107	2.18	3.36	101	2.16 ± .03	3.39 ± .04	103 ± 3
CH_2Cl_2	(1.73)	2.935	...	1.77	2.92	111	1.77 ± .02	2.93 ± .02	112 ± 2
$CHCl_3$	(1.77)	2.931	...	1.78	2.93	111	1.77 ± .02	2.93 ± .02	112 ± 2
Cl_2O	1.65	2.86	120	1.71	2.82	111	1.68 ± .03	2.84 ± .03	115 ± 4
$(CH_3)_2O$	1.38	2.28	111	1.44	2.39	111	1.42 ± .03	2.35 ± .05	111 ± 4
ClO_2	1.53	2.85	137	1.53	...	...	1.53 ± .02	2.85 ± .15	137 ± 15
SO_2	1.43	2.56	127	1.46	...	...	1.45 ± .02	2.56 ± .15	124 ± 15

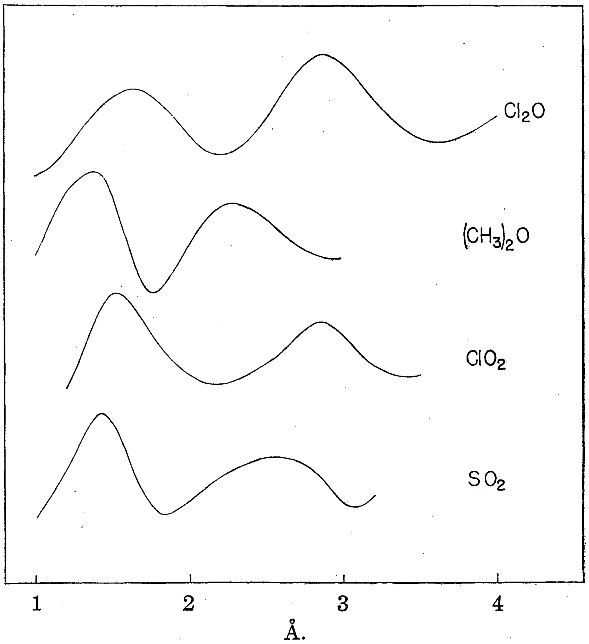


Fig. 8.—Radial distribution curves for chlorine monoxide, dimethyl ether, chlorine dioxide, and sulfur dioxide.

PASADENA, CALIFORNIA RECEIVED SEPTEMBER 24, 1935

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 508]

The Electron Diffraction Investigation of Phosgene, the Six Chloroethylenes, Thiophosgene, α-Methylhydroxylamine and Nitromethane[1]

BY L. O. BROCKWAY, J. Y. BEACH AND LINUS PAULING

Introduction

The importance of the use of interatomic distances as a test for resonance of molecules among several valence-bond structures has been mentioned in earlier papers,[2] in which it was pointed out that the interatomic distance for two bonded atoms in a resonating molecule is determined mainly by the strongest of the bonds between the two atoms provided by the resonating structures. We have now obtained evidence regarding the quantitative dependence of interatomic distance on bond type for resonance between a single bond and a double bond, and have made use of this relation in the discussion of the electronic structure of a number of molecules involving single bond–double bond resonance. The investigation is based largely on the determination of the atomic configuration of molecules by the diffraction of electrons; the description of this work is given in this paper, and the interpretation and discussion of results in the following one.

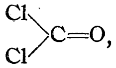
Electron diffraction photographs of the gas molecules investigated were prepared in the usual way,[3] with film distances of about 12, 20 or 30 cm., the electron wave lengths being about 0.06 Å. The photographs were measured on a comparator and interpreted both by the radial distribution method[4] and the usual visual method.[5] The results are given below; in each case the interatomic distances and bond angles are provided with estimated probable errors, which indicate the extent to which we consider them to be reliable.

We are indebted to Dr. S. Weinbaum and Dr. J. Sherman for aid in connection with the extensive calculations involved in the interpretation of the photographs.

Phosgene.—The phosgene used was prepared by the action of fuming sulfuric acid on carbon tetrachloride in the presence of a catalyst (infusorial earth), and was purified by distillation.

The photographs show eight rings, with values of $s = (4\pi \sin \Theta/2)/\lambda$ (averages for eleven photographs measured by two observers) and estimated intensities given in Table I.

The eight-term radial distribution function (Fig. 1) shows two peaks, the first, with maximum at 1.79 Å., representing C–Cl, and the second, a broad peak with maximum at 2.74 Å., representing Cl–Cl and Cl–O (unresolved).

In applying the usual visual method we calculated curves for sixteen plane symmetric models. Three parameters are involved, the Cl–C–Cl angle, the C–O distance, and the C–Cl distance, the qualitative appearance of the curves being dependent on the angle and the ratio of the distances. The angle was varied from 110 to 125° and the ratio C–Cl/C–O from 1.23 to 1.60. Most of the models are eliminated at once by qualitative comparisons. The model corresponding to the valence bond structure  $\mathrm{Cl_2C{=}O}$, with C–Cl = 1.76, C–O = 1.28, and the angle Cl–C–Cl = 110°, leads to curve A of Fig. 2, which is unsatisfactory in regard to the fourth and sixth rings, each of which is observed to be close to the preceding one. Curve B of Fig. 2 represents the model (with C–O = 1.12, C–Cl = 1.80, angle Cl–C–Cl = 110°) reported by Dornte[6] as the result of the study of electron diffraction photographs showing only four rings; it is seen that this curve is unsatisfactory, showing no maximum corresponding to our observed fourth ring.

It was found that models with the Cl–C–Cl angle equal to about 117° and the ratio of distances C–O/C–Cl equal to about 1.28/1.66 lead to curves in reasonably good qualitative agreement with experiment, all other models tried being unsatisfactory. Thus in Fig. 3 the curve for α = 117° (C) is reasonably satisfactory, the fourth and sixth rings being represented by humps rather than maxima; the curve for α = 115° (D) shows no sign of the sixth ring, and that for 120° (B) is unsatisfactory with regard to the clearly ob-

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[1] Some of the results communicated in this paper were presented at the meeting of the A. A. A. S. in Berkeley, June, 1934.

[2] L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293, 498 (1932); L. O. Brockway, *ibid.*, **19**, 860 (1930); L. O. Brockway and L. Pauling, *ibid.*, **19**, 868 (1933); L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

[3] R. Wierl, *Ann. Physik*, **8**, 521 (1931); L. O. Brockway and L. Pauling, *Proc. Nat. Acad. Sci.*, **19**, 69 (1933).

[4] L. Pauling and L. O. Brockway, THIS JOURNAL, **57**, 2684 (1935).

[5] See L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

[6] R. W. Dornte, THIS JOURNAL, **55**, 4126 (1933).

TABLE I

PHOSGENE, $COCl_2$

Max.	Min.	*I*	*s*	Values of *x* C	D	F	Values of C–Cl C	D	F
1		20	3.00	2.88	2.84	2.90	(1.574 Å.)	(1.590 Å.)	(1.605 Å.)
	2		3.95	3.88	3.83	3.88	(1.610)	(1.629)	(1.631)
2		15	5.05	5.15	5.07	5.11	1.672	1.687	1.680
	3		6.33	6.50	6.35	6.40	1.684	1.685	1.678
3		10	7.44	7.70	7.66	7.74	1.697	1.730	1.727
	4		8.53	8.90		8.87	1.711		1.726
4		2	9.34	9.63		9.30	1.691		1.653
	5		10.33	10.76	10.25	10.50	1.708	1.667	1.687
5		5	11.51	12.25	11.75	11.95	1.745	1.715	1.723
	6		12.54						
6		1	13.51[a]						
	7		14.52	14.50	14.25	14.40	1.638	1.649	1.646
7		3	15.70	16.00	15.62	15.76	1.671	1.671	1.666
	8		16.94	17.38	16.88	17.12	1.683	1.674	1.678
8		1	18.10	18.25	17.80	18.00	1.654	1.652	1.651
						Average	1.687 Å.	1.681 Å.	1.683 Å.

Model C: Cl–C–Cl = 117° C–O = 1.28 Å. C–Cl = 1.64 Å
D: Cl–C–Cl = 117° 1.28 1.68
F: Cl–C–Cl = 118° 1.28 1.66

Results: C–Cl = 1.68 ± 0.02 Å.
Cl–Cl = 2.87 ± .02 Å.
C–O = 1.28 ± .03 Å.
Angle Cl–C–Cl = 117 ± 2°
Angle Cl–C–O = 121°30′ ± 1°

[a] This ring or shelf does not appear as a maximum on the simplified theoretical curves for these models.

served fourth ring. The effect of changing the C–O/C–Cl ratio is shown by the lower four curves in Fig. 2. Of these the curves for 117°, 1.28/1.64, and 117°, 1.28/1.68, agree very well with the photographs in qualitative appearance except that the sixth ring is not quite so well represented as expected, appearing only as a shelf on the curves.

In the figures of this paper showing intensity curves the observed values of *s* for apparent maxima and minima are indicated by small vertical lines. In comparing these with the calculated intensity curves it must be borne in mind that a linear change of scale may be made; the indicated *s* values are shown in each case for the *x*/*s* ratio determined by quantitative comparison for the model finally accepted.

The results of the quantitative comparison of the photographs with the curves for three models are given in Table I. Bearing in mind the qualitative comparison, we write as the probable configuration of the phosgene molecule $\alpha = 117 \pm 2°$ (angle Cl–C–Cl), C–Cl = 1.68 ± 0.02 Å., C–O = 1.28 ± 0.03 Å., and Cl–Cl = 2.87 ± 0.02 Å.

The values of Dornte (whose work has been referred to above), $\alpha = 110 \pm 5°$, C–Cl = 1.80 ± 0.04 Å., and C–O = 1.12 ± 0.02 Å., we believe to be less accurate than the errors assigned to them indicate.

Vinyl Chloride.—Photographs of vinyl chloride (from the Carbide and Carbon Chemical Company) were taken with a film distance of 12.19 cm. (the same distance being used also for the other chloroethylenes). The photographs show about six rings: the first very weak, the second strong, the third and fourth medium, the fifth weak and the sixth very weak. In addition there is apparent a very weak ring or shelf be-

TABLE II

VINYL CHLORIDE

Max.	Min.	*I*	*s*	*x* for model D	C–Cl
2		30	5.19	5.14	1.663 Å.
	3		6.45	6.48	1.687
3		20	7.61	7.77	1.714
Shelf		5	9.84		
	4		10.76	10.76	1.680
4		15	12.15	12.21	1.687
	5		13.51	13.48	1.676
5		10	15.27	15.01	1.653
6		5	19.10	19.40	1.707
				Average	1.683 Å.

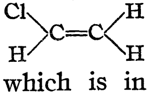
Results: C–C = 1.38 Å. (assumed)
C_1–Cl = 1.69 ± 0.02 Å.
C_2–Cl = 2.70 ± .02 Å.
α = 122 ± 2°

tween the third and fourth rings, somewhat closer to the third than to the fourth. Measured values of *s* obtained by two observers from nine photographs are given in the fourth column of Table II and estimated intensities for the rings in the third column.

The six-term radial distribution curve is given in Fig. 1. It shows two pronounced peaks, with maxima at 1.695 and 2.69 Å., with indication of a subsidiary peak at 1.35 or 1.40 Å. The first two we associate with the two carbon–chlorine interactions, and the last with carbon–carbon. If we accept the value 1.38 Å. for C–C, the distances 1.695 and 2.69 Å. lead to the value 121° for the C–C–Cl bond angle α.

In applying the usual visual method, we have found that the photographs do not provide enough information to permit us to evaluate simultaneously the two distances C–Cl and C–C and the angle Cl–C–C with much accuracy. Accordingly we have assumed the C–C distance to have the double bond value 1.38 Å., and have calculated curves for C–Cl = 1.68, C–C = 1.38 and the angle α = 130, 125, 122.5 and 120°. These are shown as B, C, D and E in Fig. 4. Of these B and C are qualitatively unsatisfactory in that the hump corresponding to the faint ring or shelf observed between the third and fourth rings is too large, and E in that the hump is too small. Comparison of measured values of *s* with the *x* values for model D (Table II) leads to the carbon–chlorine distances 1.683 and 2.70 Å.

Combining the results of the two methods, we write C–C = 1.38 Å. (assumed), C_1–Cl = 1.69 ± 0.02 Å., C_2–Cl = 2.70 ± 0.02 Å., α = 122 ± 2°. No earlier electron diffraction work on this substance has been reported.

It is of interest to consider also the model with C_1–Cl = 1.76, C–C = 1.38 and α = 125°, corresponding to the non-resonating structure  $\mathrm{ClHC{=}CH_2}$. This gives the curve A of Fig. 4, which is in satisfactory qualitative agreement with the photographs. The quantitative comparison leads to the distances C–Cl = 1.68 Å. and C–C = 1.32 Å., however, and since the latter distance should not fall below 1.38 Å., the experimentally established value for the carbon–carbon double bond, the non-resonating structure is unsatisfactory.

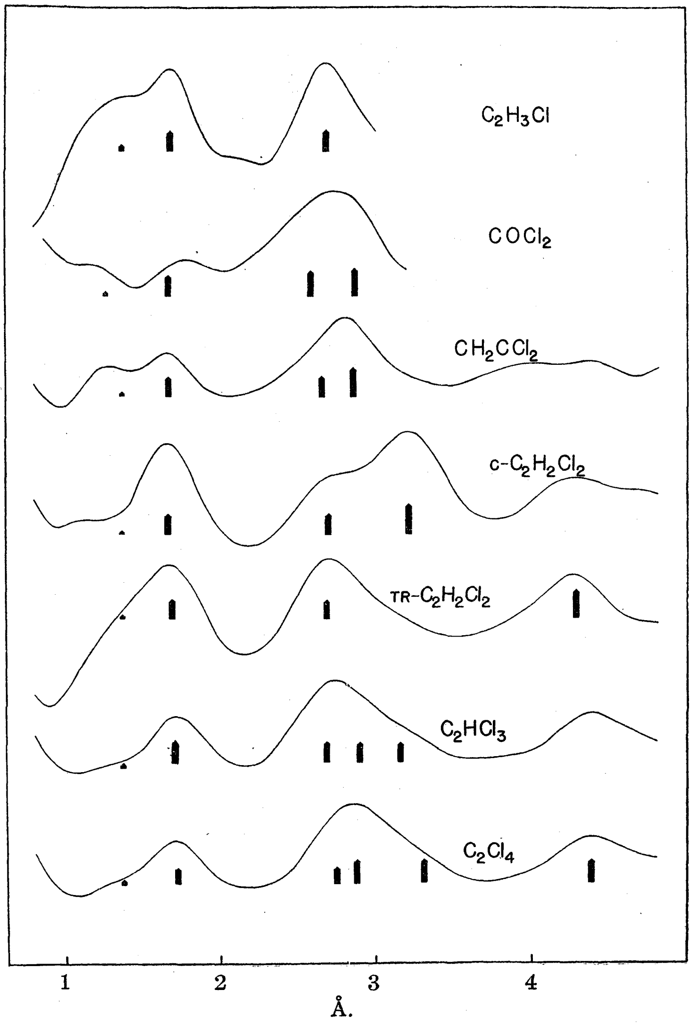


Fig. 1.—Radial distribution curves for phosgene and the six chloroethylenes.

1,1-Dichloroethylene.—The substance was prepared by treating 1,1,2-trichloroethane (made by passing vinyl chloride into antimony pentachloride) with alcoholic potassium hydroxide, and was purified by fractional distillation.

The photographs, showing seven well-defined rings, have the following qualitative appearance: the first medium, the second strong, the third medium, the fourth weak and the fifth medium weak, these five being about equally spaced; then a wide minimum and a weak ring, and another wide minimum and weak ring. Measured values of *s* (averages for four photographs) and estimates of *I* are given in Table III.

Table III

1,1-Dichloroethylene

Max.	Min.	I	s	x for Model C	D	C–Cl for Model C	D
1		15	2.87	2.75	2.74	(1.629 Å.)	(1.623 Å.)
	2		3.83	3.73	3.67	(1.656)	(1.629)
2		40	5.02	4.96	4.95	1.679	1.676
	3		6.28	6.23	6.20	1.687	1.679
3		15	7.33	7.40	7.34	1.717	1.702
	4		8.42	8.33	8.22	1.681	1.660
4		8	9.38	9.24	9.15	1.674	1.659
	5		10.52	10.50	10.33	1.697	1.670
5		20	11.76	11.78	11.73	1.703	1.696
6		10	15.55	15.75	15.56	1.722	1.701
					Average C–Cl =	1.695 Å.	1.680 Å.
					Cl–Cl =	2.858 Å.	2.870 Å.

Model C: C–Cl/C–C = 1.70/1.38, β = 115°
Model D: C–Cl/C–C = 1.70/1.38, β = 117.5°
Results: C–C = 1.38 Å. (assumed)
C–Cl = 1.69 ± 0.02 Å.
Cl–Cl = 2.86 ± 0.02 Å.
Angle Cl–C–Cl = 116 ± 2°
Angle Cl–C–C = 122 ± 1°

The six-term radial distribution function (Fig. 1) shows a C–Cl peak with maximum at 1.67 Å., and a large peak due to both Cl–Cl and C–Cl interactions. The lack of resolution of this peak (maximum at 2.81 Å.) makes its interpretation difficult.

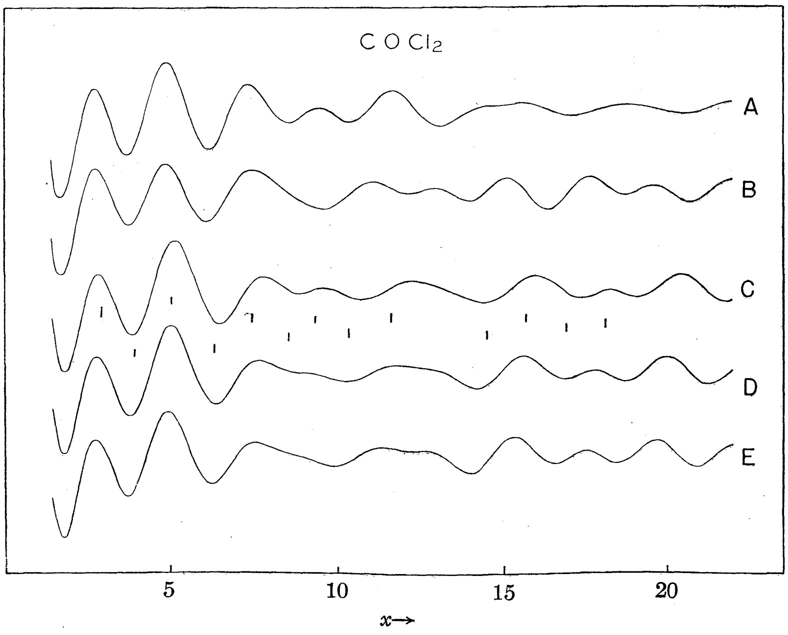
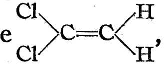


Fig. 2.—Simplified intensity curves for phosgene. A, α (angle Cl–C–Cl) = 110°, r (ratio C–O/C–Cl) = 1.28/1.76; B, α = 110°, r = 1.12/1.80; C, α = 117°, r = 1.28/1.64; D, α = 117°, r = 1.28/1.68; E, α = 117°, r = 1.28/1.72.

We have calculated intensity curves for twelve models, with the Cl–C–Cl angle β varied between 110 and 125° and the C–Cl/C–C ratio varied between 1.76/1.38 and 1.64/1.38. It was not found possible to evaluate the C–Cl/C–C ratio as well as the angle β with much accuracy; accordingly we have assumed the C–C distance to have the double bond value 1.38 Å. Of the models tried, only those with β equal to about 115° agree qualitatively with the photographs. For example, the model with C–Cl = 1.76 Å., C–C = 1.38 Å., and β = 110°, corresponding to the valence-bond structure , is unsatisfactory in that the fourth maximum on the curve (curve A of Fig. 5) is higher than the third, whereas the fourth ring is observed to be much weaker than the third and fifth. Quantitative comparison with this and other curves shows the C–Cl distance to be about 1.70 Å. Curves B, C, D and E of Fig. 5 are calculated for C–Cl = 1.70, C–C = 1.38, and the angle β = 112.5, 115, 117.5 and 120°, respectively. Of these curve B is unsatisfactory in that it shows an additional maximum between those corresponding to the fifth and sixth rings, and curve E in that the fourth maximum is too high. Curves C and D are satisfactory, and we accordingly accept for the Cl–C–Cl angle the value $\beta = 116 \pm 2°$.

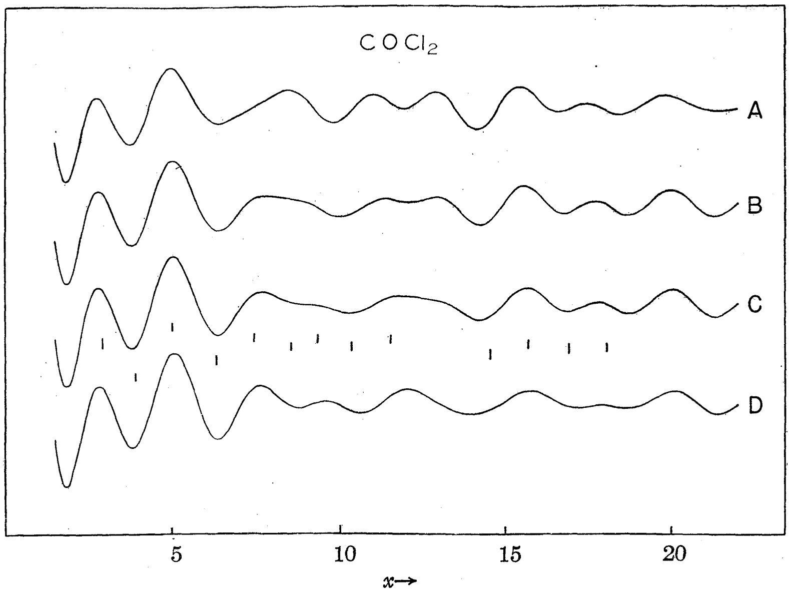


Fig. 3.—Intensity curves for phosgene, with $r = 1.28/1.68$, and $\alpha = 125$, 120, 117 and 115° for A, B, C and D, respectively.

The quantitative comparison of the measured values of s and the x values for models C and D, given in Table III, leads to the interatomic distances C–Cl = 1.69 ± 0.02 Å., Cl–Cl = 2.86 ± 0.02 A., with the angle Cl–C–Cl = 116 ± 2° and C–C = 1.38 Å. (assumed).

The only previous investigation of this substance, that of Wierl[7] by electron diffraction, gave the value Cl–Cl = 2.9 ± 0.3 Å.

cis-Dichloroethylene.—The sample of *cis*-dichloroethylene used was obtained from a mixture of the *cis* and *trans* compounds by fractional distillation with a 90-cm. column.

The photographs show five well-defined rings, with the following qualitative appearance: the first ring medium; the second strong, with an outer shelf; the third medium; the fourth weak, and somewhat closer to the third than to the fifth; the fifth medium weak. Observed values of s (averages for nine photographs) and estimated intensities are given in Table IV.

The six-term radial distribution function is shown in Fig. 1. It shows two well-defined peaks, with maxima at 1.67 Å. (C–Cl) and 3.21 Å. (Cl–Cl). These correspond to the value 123°15′ for the angle Cl–C–C, and to another C–Cl distance of 2.69 Å., some indication of which is visible in the curve.

On calculation of theoretical intensity curves it was found that all models giving rough qualitative agreement with the photographs lead to a Cl–Cl distance close to 3.23 Å. In order to determine the C–Cl distance, curves were calculated for a series of models with C–C = 1.38 and Cl–Cl = 3.23, the value of C–Cl being varied. It was found that the shelf beyond the second ring changes rapidly in this series; only for C–Cl = 1.68 (curve C in Fig. 6) does the shelf correspond to its appearance on the photograph (about one-fourth as pronounced as the second ring). Decrease by 3% wipes it out entirely. We accordingly accept model C. The comparison of observed s values and x values for this model, given in Table IV, leads to C–Cl = 1.671 Å., Cl–Cl = 3.223 Å.

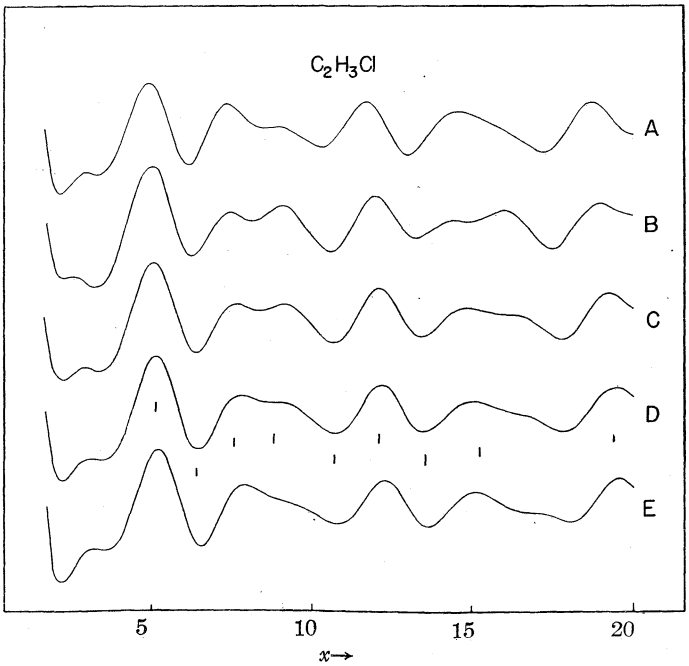


Fig. 4.—Intensity curves for five models of vinyl chloride.

Curve A, calculated for the non-resonating

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(7) R. Wierl, *Ann. Physik*, **13**, 453 (1932).

Table IV

cis-Dichloroethylene

Max.	Min.	*I*	*s*	*x* for Model A	*x* for C	C–Cl for Model A	C–Cl for C
1		10	2.480	2.36	2.46	(1.675 Å.)	(1.666 Å.)
	2		3.489	3.20	3.35	(1.614)	(1.613)
2		30	4.652	4.33	4.62	(1.639)	(1.668)
Shelf		8	6.00				
	3		6.958	6.57	6.88	1.662	1.661
3		20	8.095	7.74	8.14	1.682	1.689
	4		9.22	8.78	9.23	1.675	1.681
4		3	10.10	9.62	10.01	1.677	1.665
	5		11.16	10.54	10.98	1.664	1.653
5		10	12.17	11.63	12.15	1.682	1.677
					Average	1.674 Å.	1.671 Å.

Model A: C–C = 1.38, C–Cl = 1.76, β = 125°
Model C: C–C = 1.38, C–Cl = 1.68, β = 123.7°
Results: C–C = 1.38 Å. (assumed)
C–Cl = 1.67 ± 0.03 Å.
Cl–Cl = 3.22 ± 0.02 Å.
Angle Cl–C–C = 123.5 ± 1°

model with the Cl–C–C angle β = 125°, C–C = 1.38, and C–Cl = 1.76, is in satisfactory qualitative agreement with the photographs, quantitative comparison, however, giving C–Cl = 1.674 Å. and Cl–Cl = 3.233 Å. (Table IV), the only essential difference from the results for model C being in the C–C distance, for which the low value 1.30 Å. is obtained. Curve D, calculated for β = 130°, C–Cl = 1.72, and C–C = 1.38, shows the extreme qualitative disagreement caused by a relatively small change in model.

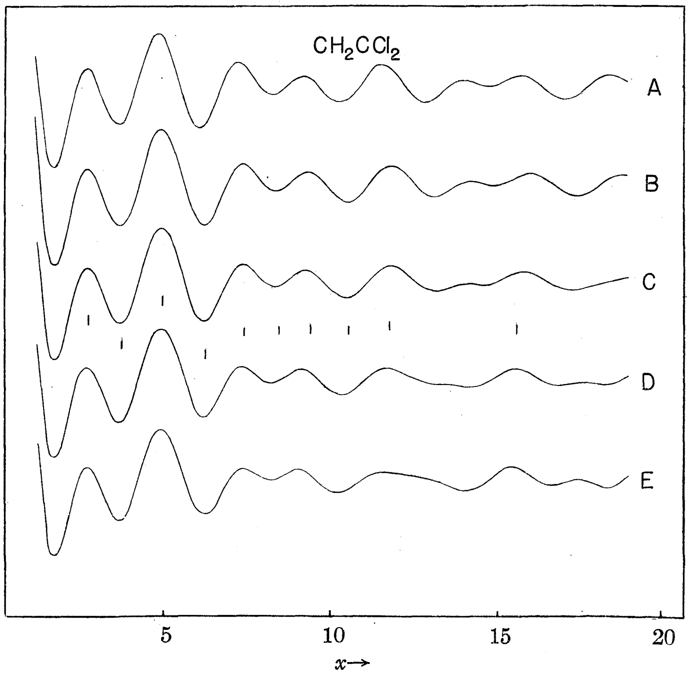

Fig. 5.—Intensity curves for 1,1-dichloroethylene.

Combining the results of the two methods, we accept for the structural constants the values C–C = 1.38 Å. (assumed), C–Cl = 1.67 ± 0.03 Å., Cl–Cl = 3.22 ± 0.02 Å., β (angle Cl–C–C) = 123.5 ± 1°. Previous investigations have given the less accurate values Cl–Cl = 3.30 ± 0.1 Å. (Wierl,[7] electron diffraction) and Cl–Cl = 3.6 Å. (Debye,[8] x-ray diffraction).

trans-Dichloroethylene.—The sample of *trans*-dichloroethylene was separated from a mixture with the *cis* compound by fractional distillation.

The photographs show seven measurable rings, with apparent intensities as given in Table V (the second ring showing an outer shelf). Values of *s* (averages for ten photographs) are also given in the table for the features which could be measured with accuracy.

The eight-term radial distribution function, given in Fig. 1, shows three well-defined peaks, with maxima at 1.675, 2.70 and 4.27 Å. These we correlate with the two C–Cl interactions and the Cl–Cl interaction, the three interactions being of about equal importance. The distances correspond to the values C–C = 1.38 Å., β (angle Cl–C–C) = 123°.

In applying the usual visual method we observed that the quantitative comparison with the photographs of all the models tried gave values close to 4.27 Å. for the Cl–Cl distance. We then

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(8) P. Debye, *Physik. Z.*, **31**, 142 (1930).

TABLE V

trans-DICHLOROETHYLENE

Max.	Min.		*s*	*x* for Model C	D	C–Cl for Model C	D
1		5	3.11	3.25	3.26	(1.777 Å.)	(1.803 Å.)
	2		3.98	3.95	3.95	1.687	1.707
2		20	4.90	4.87	4.87	1.690	1.716
Shelf		5	5.68				
	3		6.78	6.71	6.77	1.682	1.717
3		10	7.74	7.75	7.74	1.702	1.720
4		1	9.18	9.17	9.18	1.698	1.720
5		1	10.59	10.63	10.62	1.706	1.724
6		5	12.11	12.10	12.11	1.699	1.720
7		2	14.97	15.05	15.02	1.709	1.725
					Average C–Cl	1.697 Å.	1.719 Å.
					Cl–Cl	4.272 Å.	4.277 Å.

Results:

C–C = 1.38 Å. (assumed)

C–Cl = 1.69 ± 0.02 Å.

Cl–Cl = 4.27 ± 0.02 Å.

Angle Cl–C–C = 122.5 ± 1°

calculated curves for models with Cl–Cl = 4.28, C–C = 1.38, and C–Cl = 1.68, 1.70, 1.72 and 1.76 (curves B, C, D and E, respectively, of Fig. 7). All of these agree qualitatively with the photographs except in so far as the weak fourth and fifth rings are concerned; the approximate equality of these rings is best represented by curve D. The results of the quantitative comparison for C and D are given in Table V; it is seen that the value of the Cl–Cl distance is essentially independent of the model.

Averaging the results of the two methods, with about equal weights, we assign to the structural parameters the values C–C = 1.38 Å. (assumed), C–Cl = 1.69 ± 0.02 Å., Cl–Cl = 4.27 ± 0.02 Å., β (angle Cl–C–C) = 122.5 ± 1°. Previous studies gave the values Cl–Cl = 4.33 ± 0.1 Å. (Wierl,[7] electron diffraction) and Cl–Cl = 4.1 Å. (Debye,[8] x-ray diffraction). In addition a note has been published by de Laszlo[9] in which the C–Cl distance in this molecule is given as 1.74 Å.

Trichloroethylene.—The photographs of trichloroethylene (Eastman) show six rings, with intensities weak, strong, medium, weak, medium weak, weak. Characteristic features are that there is some indication of a small shelf between the second and third rings (closer to the second than to the third) and that the weak fourth ring is closer to the third than to the fifth. The measured values of *s* (average for three photographs, two observers) are given in Table VI.

The five-term radial distribution function (Fig. 1) shows three peaks, with maxima at 1.73, 2.85 and 4.37 Å., the first corresponding to the small C–Cl distances, the second to the larger C–Cl distances and to two Cl–Cl distances, and the third to the *trans* Cl–Cl distance. The lack of resolution of the second peak makes it of little value.

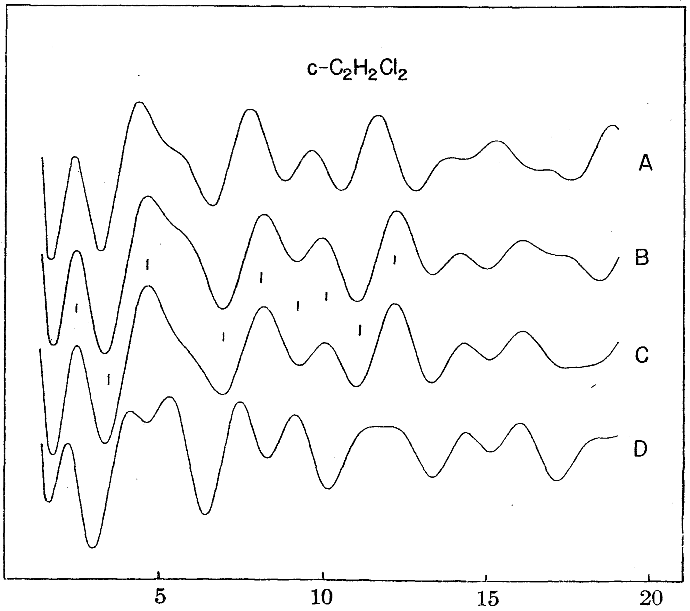

Fig. 6.—Intensity curves for *cis*-dichloroethylene.

In discussing the possible molecular models we have restricted ourselves mainly to those in which

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(9) H. de Laszlo, *Nature*, **135**, 474 (1935).

the three Cl–C–C angles are equal. Curve A (Fig. 8) is calculated for C–C = 1.38, C–Cl = 1.76 and the angles Cl–C–C = 125° for the CCl_2 group and 123° for the CHCl group. This curve agrees with the photographs qualitatively, and leads on quantitative comparison to the value 1.69 Å. for C–Cl (and hence 1.32 Å. for C–C).

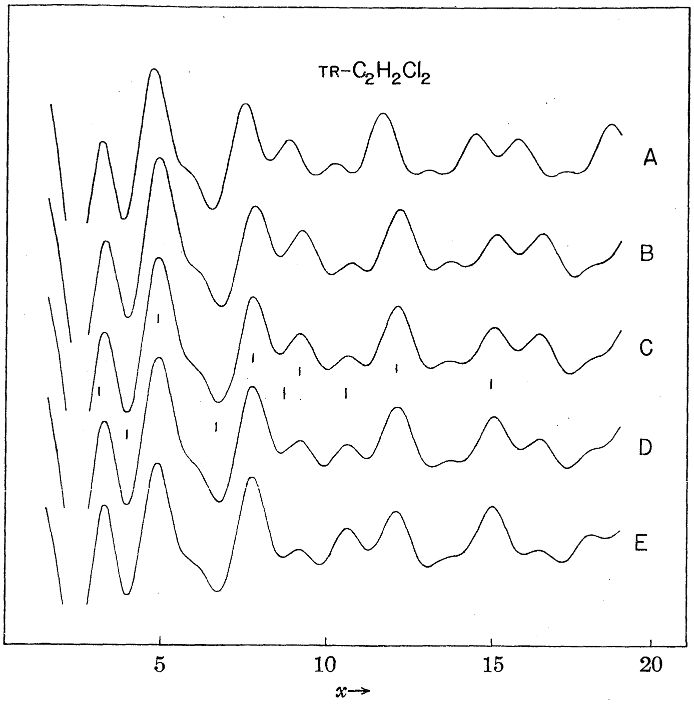

Fig. 7.—Intensity curves for *trans*-dichloroethylene.

Other models lead to about the same C–Cl value. Curves B, C, D and E of Fig. 8 are calculated for C–C = 1.38, C–Cl = 1.70 and the angles Cl–C–C = 125, 122.5, 121.5 and 120°, respectively. Of these curves C alone is in satisfactory qualitative agreement with the photographs. Quantitative comparison (Table VI) leads to the values C–Cl = 1.69 Å., Cl–Cl = 2.85, 3.19 and 4.27 Å. Giving somewhat more weight to these than to the radial distribution values, we accept as representing the configuration of the molecule the values C–C = 1.38 Å. (assumed), C–Cl = 1.71 ± 0.03 Å., Cl–Cl = 2.72 ± 0.04 Å. (in the CCl_2 group), and Cl–Cl = 3.23 ± 0.05 Å. and 4.33 ± 0.05 Å. (between CCl_2 and CHCl), with the angles Cl–C–C = 123 ± 2°.

Table VI

Trichloroethylene

Max.	Min.	*I*	*s*	*x*	Model C C–Cl
1			2.91	2.80	(1.639 Å.)
	2		3.88	3.73	(1.633)
2		30	4.86	4.79	1.675
	3		6.43		
3		15	7.81	7.73	1.683
	4		8.68	8.59	1.682
4		4	9.67	9.11	1.602
	5		10.91	10.97	1.709
5		10	12.04	12.03	1.699
6		4	15.49	16.20	1.778
				Average	1.690 Å.

Results: C–C = 1.38 Å. (assumed)
C–Cl = 1.71 ± 0.03 Å.
Cl–Cl = 2.72 ± 0.04 Å.
3.23 ± 0.05 Å.
4.33 ± 0.05 Å.
Angles Cl–C–C = 123 ± 2°

Trichloroethylene previously has been studied by this method by Dornte,[10] who reported the values C–C = 1.32 ± 0.08 Å., C–Cl = 1.82 ± 0.08 Å., Cl–Cl = 3.41 ± 0.08 Å., and Cl–Cl = 4.52 ± 0.08 Å., in approximate agreement with our values.

Tetrachloroethylene.—The rather weak photographs of tetrachloroethylene (Eastman) obtained at room temperature show six rings, the first medium, the second strong, the third medium, the fourth weak, the fifth medium weak and the sixth weak. Averaged values of *s* (for four photographs) and estimated intensities are given in Table VII.

The six-term radial distribution function (Fig. 9) shows three peaks, with maxima at 1.72, 2.86 and 4.37 Å., the first representing a C–Cl distance, the third the *trans* Cl–Cl distance, and the large second peak representing three distances.

Curves A, B, C and D of Fig. 9 are calculated

Table VII

Tetrachloroethylene

Max.	Min.	*I*	*s*	*x* for model B	C–Cl
1		15	2.78	2.70	(1.69 Å.)
	2		3.81	3.68	(1.68)
2		30	4.76	4.63	1.691
3		10	7.46	7.52	1.753
4		3	9.00	9.12	1.761
5		8	11.84	11.72	1.722
6		3	15.17		
				Average	1.732 Å.

Results: C–C = 1.38 Å. (assumed)
C–Cl = 1.73 ± 0.02 Å.
Cl–Cl = 2.87 ± 0.03 Å.
3.30 ± 0.03 Å.
4.28 ± 0.03 Å.
Angle Cl–C–C = 123° 45′ ± 1°

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[10] R. W. Dornte, *J. Chem. Phys.*, **1**, 566 (1933).

for models with C–C = 1.38, C–Cl = 1.74 and the angles Cl–C–C = 125°, 123°45′, 122°30′ and 121°15′, respectively. It is seen that the curves change very rapidly with change in angle. The appearance of the photograph is closely reproduced by curve B, and not so well by C or A; the latter is unsatisfactory only in that the fourth peak is not sufficiently displaced toward the third. We accordingly accept for the Cl–C–C angle the value 123°45′ ± 1°.

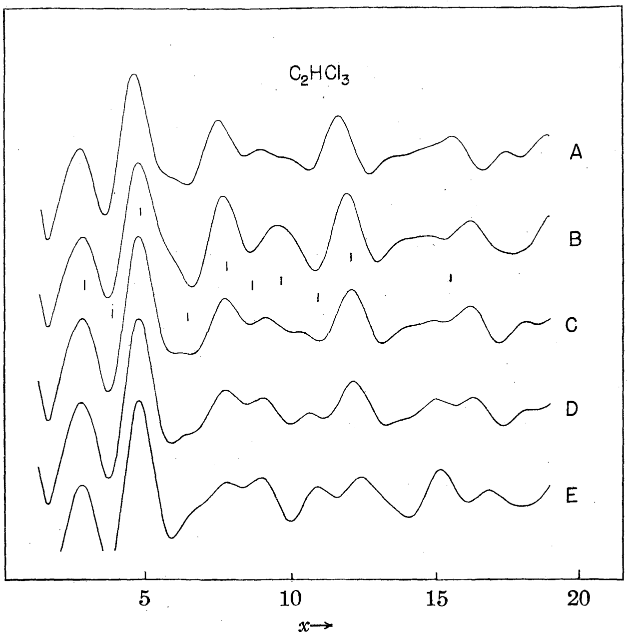

Fig. 8.—Intensity curves for trichloroethylene.

TABLE VIII

THIOPHOSGENE

Max.	Min.	*I*	*s*	*x* for model B	C–Cl
1		10	2.84	2.67	(1.598 Å.)
	2		3.75	3.67	(1.664)
2		25	5.00	4.84	(1.646)
	3		6.08	6.04	1.689
3		12	7.16	7.13	1.693
	4		8.10	8.06	1.692
4		12	9.17	9.09	1.685
	5		10.25	10.29	1.707
5		6	11.40	11.49	1.713
	6		12.43	12.51	1.711
6		3	13.41	13.48	1.709
	7		14.51	14.56	1.706
7		3	15.56	15.75	1.721
	8		16.78	16.88	1.710
8		1	17.79	17.90	1.711
	9		18.90	18.87	1.697
9		1	19.90	19.97	1.706
				Average	1.704 Å.

Results: C–S = 1.63 Å. (assumed)
Angle Cl–C–Cl = 116 ± 2° (assumed)
C–Cl = 1.70 ± 0.02 Å.
Cl–Cl = 2.88 ± 0.04 Å.
Cl–S = 2.90 ± 0.04 Å.

The quantitative comparison leads to C–Cl = 1.732 Å. and Cl–Cl (*trans*) = 4.38 Å., in essential agreement with the results of the radial distribution treatment. We accordingly accept for the structural parameters of the molecule the values C–C = 1.38 Å. (assumed), C–Cl = 1.73 ± 0.02 Å., Cl–Cl = 2.87 ± 0.03 Å. (in the same CCl_2 group), and Cl–Cl = 3.30 ± 0.03 Å. and 4.28 ± 0.03 Å. (between CCl_2 groups), with the angle Cl–C–C = 123°45′ ± 1°.

A previous electron diffraction investigation by Dornte[10] gave the values C–C = 1.32 ± 0.08 Å., C–Cl = 1.82 ± 0.08 Å., and Cl–Cl = 3.41 ± 0.08 Å. and 4.52 ± 0.08 Å., in approximate agreement with our results. De Laszlo has also reported the value C–Cl = 1.74 Å. in a preliminary note.[9]

Thiophosgene.—The thiophosgene used was prepared by the chlorination of carbon disulfide and subsequent reduction, and purified by fractional distillation.[11]

The photographs show nine rings, for which measured *s* values and estimated intensities are given in Table VIII (averages for four photo-

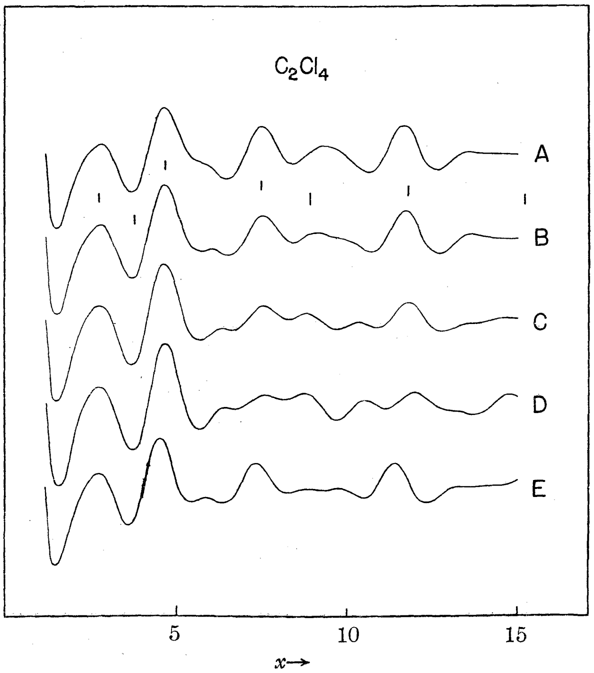

Fig. 9.—Intensity curves for tetrachloroethylene.

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[11] "Organic Syntheses," John Wiley and Sons, Inc., New York City Coll., Vol. I, p. 493.

graphs[12]). The nine-term radial distribution curve (Fig. 10) shows two well-defined peaks, the first, with maximum at 1.59 Å., corresponding to the C–S and C–Cl distances, and the second, with maximum at 2.87 Å., to the Cl–Cl and Cl–S distances. The sharpness of the second peak (which closely resembles the Cl–Cl peak for carbon tetrachloride) indicates strongly that the Cl–Cl and Cl–S distances are nearly equal. The position of the first maximum is unreliable, being strongly dependent on the estimated intensity values.

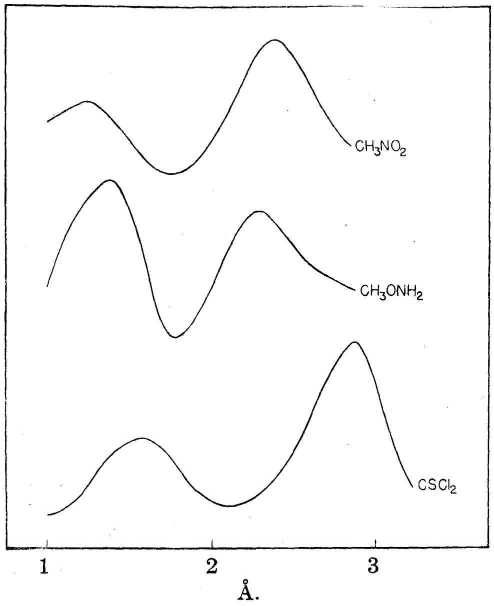

Fig. 10.—Radial distribution curves for nitromethane, α-methylhydroxylamine and thiophosgene.

On calculating simplified intensity curves for eight models it was found that all of the parameters determining the structure of the molecule could not be evaluated. The curves out to the tenth ring are affected very little by small changes in the Cl–Cl/Cl–S ratio, no perceptible differences existing between those calculated for C–S = 1.63, C–Cl = 1.70, and the angle Cl–C–Cl = 114, 116, 118 and 120°, respectively, the Cl–Cl/Cl–S ratio changing from 0.97 to 1.02. All of these curves agree satisfactorily with the photographs in qualitative appearance; the 116° curve is shown as A in Fig. 11. The curves are also not very sensitive to small changes in the position of the light carbon atom; however, the curve for C–Cl = 1.76, C–S = 1.44 and the angle Cl–C–Cl = 110° (B of Fig. 11) is qualitatively unsatisfactory in regard to the fourth ring, which is observed to be as strong as the third.

We have assumed for the C–S distance the double bond value 1.63 Å., as given by the table of covalent radii (and verified by the value 1.64 Å. reported for crystals of thiourea),[13] and for the angle Cl–C–Cl the value 116 ± 2°, as in phosgene and 1,1-dichloroethylene. The observed size of the Cl–Cl–S triangle then requires that C–Cl be close to 1.70 Å. The quantitative comparison with curve A leads to C–Cl = 1.704 Å.; taking some cognizance of the 2.87 Å. peak on the radial distribution curve, we accept for the structural parameters the values C–S = 1.63 Å. (assumed), angle Cl–C–Cl = 116 ± 2° (assumed), C–Cl = 1.70 ± 0.02 Å., Cl–Cl = 2.88 ± 0.04 Å., and Cl–S = 2.90 ± 0.04 Å.

α-Methylhydroxylamine.—The photographs of α-methylhydroxylamine (Eastman) show three well-defined rings, with *s* values (average for four films) and estimated intensities given in Table IX. The three-term radial distribution function (Fig. 10) shows peaks with maxima at 1.39 and 2.31 Å. The first we interpret as showing the C–O and O–N distances, unresolved, the table of covalent radii giving for them the values 1.43 and 1.36 Å., respectively. The C–N distance 2.31 Å. then leads to the value 112° for the C–O–N angle.

Intensity curves were calculated for the following values of the angle: 114, 110 and 106°. In these the ratio of the O–N and C–O distances was taken as 1.36/1.43. The curves for the first two are shown in Fig. 12 and the *x* values in Table IX. Model A (110° angle) is superior to Model B (114° angle) as indicated by the poor agreement between the *x* and *s* values for the second maxi-

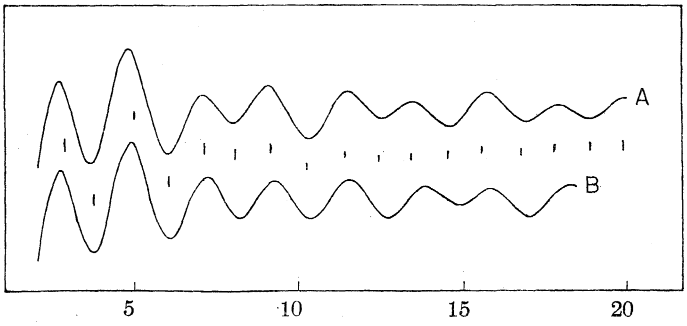

Fig. 11.—Intensity curves for thiophosgene.

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[12] Some measurements made on five rings of very weak photographs, disagreeing with those in the table by about 2%, were discarded.

[13] R. W. G. Wyckoff and R. B. Corey, *Z. Krist.*, **81**, 386 (1932).

TABLE IX

α-METHYLHYDROXYLAMINE

				Model A		Model B	
Max.	Min.	*I*	*s*	*x*	N–O	*x*	N–O
1		5	6.00	6.10	1.383 Å.	6.04	1.369 Å.
	2		7.95	7.93	1.357	7.88	1.349
2		2	9.49	9.93	1.418	10.20	(1.461)
	3		12.13	12.20	1.367	12.17	1.362
3		1	13.94	14.30	1.393	14.18	1.381
				Average	1.384 Å.		1.365 Å.

Results: N–O = 1.37 ± 0.02 Å.
C–O = 1.44 ± 0.02 Å.
C–N = 2.31 ± 0.03 Å.
Angle C–O–N = 111 ± 3°

mum in Model B. The 106° model was rejected because it leads to widely fluctuating values for the size of the molecule as calculated from the various maxima and minima. The quantitative comparison for Model A leads to N–O = 1.38 Å., C–O = 1.45 Å. and C–N = 2.31 Å.

Combining the results of the two methods we obtain the values N–O = 1.37 ± 0.02 Å., C–O = 1.44 ± 0.02 Å., angle C–O–N = 111 ± 3°, C–N = 2.31 ± 0.03 Å.

Nitromethane.—The photographs of nitromethane (Eastman) show four well-defined rings followed by a very wide minimum and two more very faint maxima. The *s* values averaged from six photographs and the estimated intensities are given in Table X. The six-term radial distribution function (Fig. 10) shows two peaks with maxima at 1.19 and 2.18 Å., the first corresponding to the N–O distance with the N–C distance unresolved and the second to the O–O and C–O distances.

TABLE X

NITROMETHANE

Max.	Min.	*I*	*s*	*x*	$N–O_{125°}$
1		10	3.65	3.27	(1.09 Å.)
	2		5.04	4.43	(1.07)
2		30	6.50	6.26	1.175
	3		7.96	8.00	1.226
3		12	9.29	9.28	1.219
	4		10.54	10.17	1.178
4		12	11.75	11.83	1.228
	5		13.47	13.61	1.231
5		3	17.77	17.21	1.181
	6		19.37	19.50	1.227
6		2	21.02		
				Average	1.208 Å.

Results: N–O = 1.21 ± 0.02 Å.
C–N = 1.46 ± 0.02 Å.
Angle O–N–O = 127 ± 3°

The photographs do not permit the evaluation of all the structural parameters. We expect, however, that the C–N distance has the single bond value 1.47 Å. and the N–O distances approximately the double bond value 1.22 Å. The three curves in Fig. 13 correspond to models having the relative dimensions determined by the above distances and the three values of the O–N–O angle, 120, 125 and 130°, respectively. The qualitative features of the photographs fix the angle at about 127°. Thus, the prominence of the third maximum relative to the fourth and the position and character of the fifth minimum as observed on the photograph eliminate the 120° model. In the 130° curve the position of the seventh maximum is a little better than in the one for 125° but the hump following the fifth minimum is too pronounced. The quantitative comparison (Table X) leads to the values C–N = 1.46 ± 0.02 Å. and N–O = 1.21 ± 0.02 Å., with the angle O–N–O = 127 ± 3°.

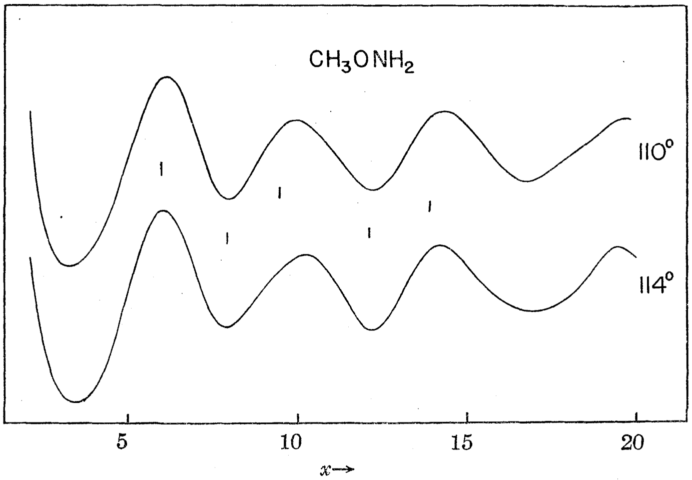


Fig. 12.—Intensity curves for α-methylhydroxylamine.

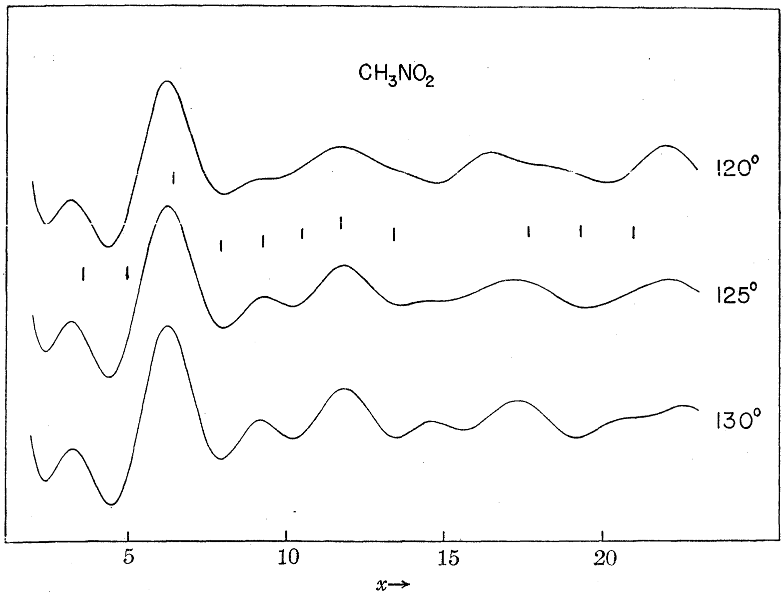


Fig. 13.—Intensity curves for nitromethane.

Discussion of Results

In phosgene, thiophosgene and the six chloroethylenes the carbon–chlorine distances vary between 1.67 and 1.73 Å., being between 5 and 2% less than the normal single bond value 1.76 Å. This decrease is due to the partial double bond character caused by resonance resulting from the conjugation of an unshared pair of electrons on the chlorine atom with the adjacent double bond. The values found for the angle Cl–C–X are somewhat smaller than the tetrahedral value 125°16′ for the angle between a single bond and a double bond, as a result of the same phenomenon. A detailed discussion of these effects is given in the following paper.

For the other interatomic distances the values found are in good agreement with the table of covalent radii. In phosgene the carbon–oxygen distance has the double bond value 1.28 ± 0.02 Å. (1.28 Å. from the table), and for thiophosgene the double bond value 1.63 Å. for the carbon–sulfur distance leads to a satisfactory interpretation of the photographs. The N–O distance 1.21 ± 0.02 Å. for the nitro group in nitromethane is close to the double bond value 1.22 Å. The distances N–O = 1.37 ± 0.02 Å. and C–O = 1.44 ± 0.02 Å. in α-methylhydroxylamine and C–N = 1.46 ± 0.02 Å. in nitromethane agree well with the single bond values 1.36, 1.43 and 1.47 Å., respectively, given by the table of radii.

Summary

The arrangements of atoms in molecules of phosgene, the six chloroethylenes, thiophosgene, α-methylhydroxylamine and nitromethane have been determined by the use of electron diffraction photographs, interpreted both by the radial distribution method and the usual visual method, with the following results. (Values given without attached probable errors were assumed to be correct in the investigation.)

Phosgene: C–Cl = 1.68 ± 0.02 Å.; C–O = 1.28 ± 0.02 Å.; angle Cl–C–O = 121.5 ± 1°.

	C—C	C—Cl	Angle Cl—C—C
Vinyl chloride	1.38 Å.	1.69 ± 0.02 Å.	122 ± 2°
1,1-Dichloroethylene	1.38	1.69 ± 0.02	122 ± 1°
cis-Dichloroethylene	1.38	1.67 ± 0.03	123.5 ± 1°
trans-Dichloroethylene	1.38	1.69 ± 0.02	122.5 ± 1°
Trichloroethylene	1.38	1.71 ± 0.03	123 ± 2°
Tetrachloroethylene	1.38	1.73 ± 0.02	123.75 ± 1°

Thiophosgene: C–Cl = 1.70 ± 0.02 Å.; C–S = 1.63 Å.; angle Cl–C–S = 122°.
α-Methylhydroxylamine: N–O = 1.37 ± 0.02 Å.; O—C = 1.44 ± 0.02 Å.; angle C–O–N = 111 ± 3°.
Nitromethane: N–O = 1.21 ± 0.02 Å.; C–N = 1.46 ± 0.02 Å.; angle O–N–O = 127 ± 3°.

The discussion and interpretation of these results are given in the following paper.

Pasadena, California Received September 24, 1935

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 509]

The Dependence of Interatomic Distance on Single Bond–Double Bond Resonance[1]

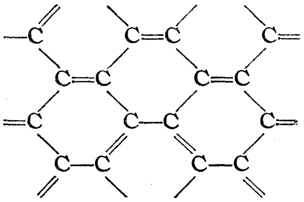
BY LINUS PAULING, L. O. BROCKWAY AND J. Y. BEACH

Introduction

Three years ago it was pointed out[2] that observed values of interatomic distances provide useful information regarding the electronic structures of molecules, and especially regarding resonance between two or more valence bond structures. On the basis of the available information it was concluded that resonance between two or more structures leads to interatomic distances nearly as small as the smallest of those for the individual structures.[3] For example, in benzene each carbon–carbon bond resonates about equally between a single bond and a double bond (as given by the two Kekulé structures); the observed carbon–carbon distance, 1.39 Å., is much closer to the carbon–carbon double bond distance, 1.38 Å., than to the single bond distance, 1.54 Å.

In benzene the two Kekulé structures contribute equally. In general, however, the coefficients of the functions corresponding to different structures in the approximate wave function of a molecule may have arbitrary values, and a bond between two atoms may have any intermediate character between the extremes of a pure single bond and a pure double bond. For a series of bonds covering the range between a pure single bond and a pure double bond we expect the interatomic distance to change continuously from the single bond value to the double bond value. In this paper we present evidence regarding the nature of the function expressing the dependence of interatomic distance on single bond–double bond resonance, and then make use of the function in order to obtain information regarding the electronic structures of resonating molecules for which experimental interatomic distance values are available. The effect of resonance on bond angles is also discussed.

The Interatomic Distance Function for Single Bond–Double Bond Resonance.—The carbon–carbon single bond distance is 1.54 Å. (diamond, aliphatic compounds). For the carbon–carbon double bond distance we shall use the value 1.38 Å. given by the table of covalent radii;[4] some support for this is given by Badger's value[5] 1.37 Å. for ethylene. These give the two extreme points of the interatomic distance function for single bond–double bond resonance. The midway point, for fifty per cent. double bond character, is provided by the value 1.39 Å. for benzene;[6] the electronic structure of benzene is represented in the main by resonance between the two Kekulé structures (the contribution of excited structures being small[7]), and this makes each bond resonate equally between a double and a single bond. Another point on the curve is provided by graphite (C–C = 1.42 Å.), in which each bond has one-third double bond character, corresponding to resonance among many structures such as



Through these four points we draw a smooth curve, as shown in Fig. 1, which we accept as representing the dependence of carbon–carbon interatomic distance on double-bond character for single bond–double bond resonance. We believe that by a suitable translation and a change of vertical scale (to give the correct end-points) the same function can be used for bonds between other atoms, and probably also for double bond–triple bond resonance. This use of the curve will be illustrated below.

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[1] Part of the material in this paper was presented at the meeting of the A. A. A. S. in Berkeley, June, 1934.

[2] L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932).

[3] The following argument, suggested by Professor P. M. Morse, shows that this conclusion is reasonable. Of two potential functions corresponding to two structures, the one with the smaller value of the equilibrium internuclear distance will have the greater curvature in the neighborhood of the minimum [see for example, R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934)]. Hence the more stable of the two resultant potential functions corresponding to resonance between these two structures will tend to have its minimum in the position determined by the original curve of greater curvature, that is, near the smaller value of the internuclear distance.

[4] L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932); L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

[5] R. M. Badger, *Phys. Rev.*, **45**, 648 (1934).

[6] L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

[7] A possibly more accurate value for the double bond character of the bonds in benzene (0.46) is obtained by considering all five canonical structures with weights equal to the squares of their coefficients in the wave function. There is some uncertainty as to the significance of this, however, because of the non-orthogonality of the wave functions for the canonical structures, and for chemical purposes it is sufficiently accurate to follow the simple procedure adopted above.

It is seen that a small amount of double bond character causes a large decrease in interatomic distance below the single bond value, whereas only a small change from the double bond value is caused by even as much as fifty per cent. single bond character.[8] In consequence, the interatomic distance criterion for resonance provides quantitative information only through about one-half of the bond character region.

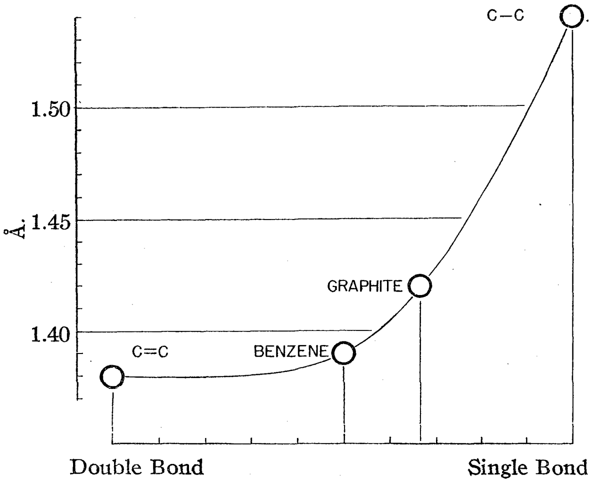

Fig. 1.—The empirical function expressing the dependence of carbon–carbon interatomic distance on bond character for single bond–double bond resonance.

The applicability of the curve to bonds other than carbon–carbon can be tested with the data for carbon–oxygen and nitrogen–oxygen bonds given in Table I, the predicted distances being obtained from the table of covalent radii for pure single and double bonds, and from the curve (with end-points determined by the table) for bonds of intermediate type. The carbonate and nitrate ions resemble graphite in that the double bond resonates among three positions, whereas in the carboxyl and nitro groups, as in benzene, the double bond resonates between two positions. It is seen that there is approximate agreement between predicted and observed values.

TABLE I

COMPARISON OF PREDICTED AND OBSERVED INTERATOMIC DISTANCES

Amount of double bond character	Predicted distance	Observed distance
Carbon–Oxygen Bonds		
0	1.43 Å.	1.42 Å. in $(CH_3)_2O$[a]
		1.44 in CH_3ONH_2[a]
$^1/_3$	1.32	1.31 (1.26) in $(CO_3)^{=b}$
$^1/_2$	1.29	1.29 in $(HCOOH)_2$[c]
1	1.28	
Nitrogen–Oxygen Bonds		
0	1.36 Å.	1.37 Å. in CH_3ONH_2[a]
$^1/_3$	1.26	1.22 (1.26) in $(NO_3)^{-b}$
$^1/_2$	1.23	1.21 in CH_3NO_2[a]
1	1.22	

[a] Preceding papers. [b] Preliminary values obtained through redetermination of parameters in crystals (calcite and sodium nitrate) by Mr. Norman Elliot. The values in parentheses are based on older parameter determinations. [c] L. Pauling and L. O. Brockway, *Proc. Nat. Acad. Sci.*, **20**, 336 (1934). The value 1.25 Å. reported in crystals of oxalic acids and oxalates is probably less reliable.

The Use of the Interatomic Distance Function in Discussing the Electronic Structure of Molecules.—The observed interatomic distances listed in Table II are interpreted with the aid of the curve of Fig. 1 to lead to the assignment of fractional double bond character as given in the last column. It is seen that a single bond between conjugated double bonds (cyclopentadiene) or conjugated benzene rings (biphenyl) *p*-diphenylbenzene, has about 15 or 20% double bond character,[9] whereas a single bond between conjugated

TABLE II

INTERATOMIC DISTANCES AND BOND TYPE

Molecule	Bond	Observed distance	Amount of double bond character
Cyclopentadiene	C—C	1.46 Å.[a]	0.20
p-Diphenylbenzene	C—C	1.48[b]	.14
Biphenyl	C—C	1.48[c]	.14
Cyanogen	C—C	1.43[d]	.29
Diacetylene	C—C	1.43[d]	.29
Urea	C—N	1.37[e]	.28
Thiourea	C—N	1.37[f]	.28
Cyanuric triazide	C—N	1.38[g]	.25
Carbon suboxide	C═C	1.30[h]	.20[i]
	C═O	1.20[h]	.20[i]

[a] Preliminary result of electron diffraction study in this Laboratory. [b] L. W. Pickett, *Proc. Roy. Soc.* (London), **A142**, 333 (1933). [c] J. Dhar, *Indian J. Phys.*, **7**, 43 (1932). [d] L. O. Brockway, *Proc. Nat. Acad. Sci.*, **19**, 868 (1933). [e] R. W. G. Wyckoff and R. B. Corey, *Z. Krist.*, **89**, 462 (1934). [f] R. W. G. Wyckoff and R. B. Corey, *ibid.*, **81**, 386 (1932). [g] I. E. Knaggs, *Proc. Roy. Soc.* (London), **A150**, 576 (1935). [h] L. O. Brockway and L. Pauling, *Proc. Nat. Acad. Sci.*, **19**, 860 (1933). [i] Triple-bond character.

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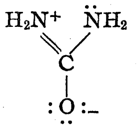
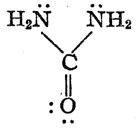
[8] Verification of the shape of the curve has been obtained with the collaboration of Dr. J. Sherman by the theoretical treatment of a somewhat similar problem (the effect of *s-p* hybridization of bond orbitals on interatomic distance).

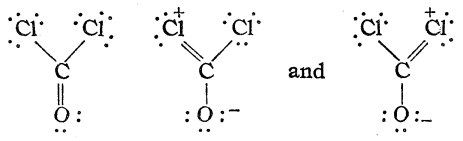
[9] The comparison of these results with the simple theory of conjugated systems [Pauling and Sherman, *J. Chem. Phys.*, **1**, 679 (1933)] is not straightforward because of non-orthogonality of the canonical structures. If we assume that the double bond character is given by the square of the coefficient of the structure — = — in the normalized wave function for a system of two conjugated double bonds the simple theory leads to the value 0.25, in approximate agreement with the experimental result.

triple bonds (cyanogen, diacetylene) has about 30% double bond character. In cyanuric triazide the reported distance for the bond linking an azide group to the cyanuric ring corresponds to about 25% double bond character.

In urea and thiourea the ionic structures such as  are of sufficient importance to give each C–N bond about 28% double bond character. In case these structures were equivalent to the structure  giving complete resonance, each bond would have one-third double bond character, as in the carbonate, nitrate, and guanidonium ions. The experimental result shows that resonance is nearly complete.

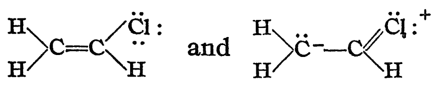
In carbon suboxide, for which the structure $:\ddot{O}=C=C=C=\ddot{O}:$ is most important, structures such as $^{-}:\underset{\cdot\cdot}{\ddot{O}}-C\equiv C-C\equiv O:^{+}$ contribute about 20% triple bond character to each bond.

Resonance of a Carbon–Chlorine Bond and an Adjacent Double Bond.—We expect the phosgene molecule to resonate among the structures



of which the first is the most important, the second and third making only small contributions to the normal state of the molecule. The value 1.68 ± 0.02 Å. for the C–Cl distance, reported in the preceding paper,(10) corresponds to 17% double bond character for the carbon–chlorine bonds, calculated with the curve of Fig. 1, with end points C–Cl = 1.76 Å. and C=Cl = 1.58 Å. The value C–Cl = 1.70 ± 0.02 Å. in thiophosgene leads to 12% double bond character, indicating that the ionic structures make a smaller contribution for this molecule than for phosgene.

We might predict that of the six chloroethylenes the C–Cl distance would be smallest in vinyl chloride, which resonates between the structures



and largest in tetrachloroethylene, in which the effect of the double bond is divided among four carbon–chlorine bonds. This is found experimentally (Table III), except that the distance reported for *cis*-dichloroethylene is about 0.02 Å. smaller and that for vinyl chloride somewhat larger than expected. The amounts of double bond character shown in the table are reasonable—about 15% for mono- and dichloroethylenes, 10% for trichloroethylene, and 6% for tetrachloroethylene.

TABLE III

INTERATOMIC DISTANCES AND BOND TYPE FOR CARBON–CHLORINE BONDS

Molecule	C–Cl distance	Double bond character
Phosgene	1.68 ± 0.02 Å.	0.17
Thiophosgene	1.70 ± .02	.12
CH_2CHCl	1.69 ± .02	.14
CH_2CCl_2	1.69 ± .02	.14
cis-CHClCHCl	1.67 ± .03	.20
trans-CHClCHCl	1.69 ± .02	.14
$CHClCCl_2$	1.71 ± .03	.10
C_2Cl_4	1.73 ± .02	.06

The effect of this partial double bond character on the chemical properties of chlorine atoms conjugated to double bonds is well known; it corresponds in the main to a diminution in reactivity. The correlation with bond angles is discussed in a later section of this paper.

Inasmuch as the conjugation properties of a double bond and a benzene ring are closely similar,(11) we expect for the halogen substituted benzenes interatomic distances similar to those for the halogen ethylenes. De Laszlo(12) has reported the values C–Cl = 1.69 Å., C–Br = 1.88 Å., and C–I = 2.05 Å., corresponding to 14, 6, and 10% double bond character, respectively.(13)

The Dependence of Bond Angles on Single Bond–Double Bond Resonance.—In a molecule such as phosgene or 1,1-dichloroethylene the value 125°16′ for the angle Cl–C–O (β) is predicted by the theory of the tetrahedral carbon atom in case that the C–Cl bonds have no double bond character. If the double bond resonates equally among all three positions, giving the Cl–C bond one-third double bond character, we expect from symmetry

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(10) Brockway, Beach and Pauling, THIS JOURNAL, **57**, 2693 1935).

(11) L. Pauling and J. Sherman, *J. Chem. Phys.*, **1**, 679 (1933).

(12) H. de Laszlo, *Proc. Roy. Soc.* (London), **A146**, 690 (1934).

(13) The interatomic distance values given are stated to hold for hexahalogen, *sym*-trihalogen and *p*-dihalogen benzenes. We expect the distances in these different compounds to be different, however; and investigation of these and other halogen compounds is under way in this Laboratory. De Laszlo has also reported values of C–Br and C–I distances in ethylenic and acetylenic compounds in a letter to *Nature*, **135**, 474 (1935).

the value 120° for β. Between these limits the dependence of β on the amount of double bond character of the C–Cl bonds may be postulated to be given by a curve similar in shape to the interatomic distance curve of Fig. 1. If this is so, there would be a linear relation connecting the angle β and the C–Cl distance, between the points β = 125°16′, C–Cl = 1.76 Å. and β = 120°, C–Cl = 1.64 Å. (as given by the curve for one-third double bond character). From a similar discussion, the other chloroethylenes (except vinyl chloride) would be expected to fall roughly on the same line.

A test of this relation is shown in Fig. 2, the seven points being those determined experimentally for phosgene and the six chloroethylenes.

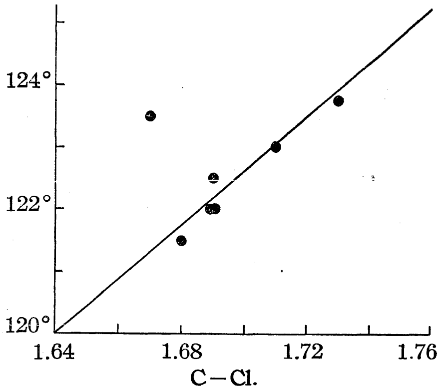
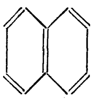
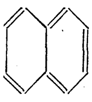
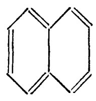


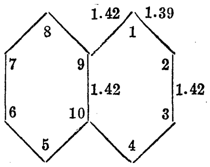
Fig. 2.—The relation between bond angle and carbon-chlorine distance for phosgene and the chloroethylenes.

It is seen that, with one exception, the points lie very close to the straight line drawn according to our assumptions, the displacements being much less than the probable errors of the experimental values. The exceptional point is that for *cis*-dichloroethylene, the discrepancy confirms the suggestion made in the preceding section that our results for this substance are slightly in error.[14] It is surprising that vinyl chloride obeys the same relation, as there is no apparent reason for the angle to be much different from 125°16′.

Interatomic Distances in Polynuclear Aromatic Hydrocarbons.—As a further example of the use of the interatomic distance function we shall discuss the polynuclear aromatic hydrocarbons.

For naphthalene there are three unexcited structures   and 

Giving these equal weights, we obtain the result that the 1–2 bonds have $^2/_3$ double bond character and all others $^1/_3$. These correspond to the values 1.39 Å. for the 1–2 interatomic distances (including 3–4, 5–6 and 7–8), and 1.42 Å. for all others, giving the configuration



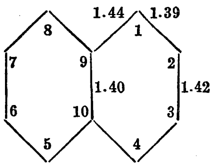
A possibly more reliable prediction can be made on the basis of Sherman's wave function for naphthalene,[15] by considering all 42 canonical structures. The fractional double bond character of a bond can be considered to be given approximately (neglecting non-orthogonality of the canonical wave functions) by the expression

$$\sum_i' a_i^2 \Big/ \sum_i a_i^2$$

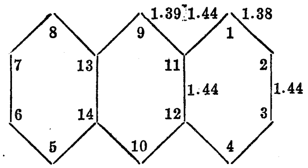
in which a_i represents the coefficient for the *i*th structure; the unprimed sum includes all structures of the set of 42, and the primed sum those for which the bond in question is a double bond. The results of this calculation are the following:[16]

Bond	1–2	2–3	9–1	9–10
Double bond character	0.60	0.33	0.26	0.43
C–C distance	1.39 Å.	1.42 Å.	1.44 Å.	1.40 Å.

corresponding to the configuration



The four unexcited structures for anthracene, given equal weights, lead to $^3/_4$ double bond character for the 1–2 bonds, $^1/_2$ for the 9–11 bonds and $^1/_4$ for others, the predicted configuration being



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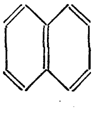
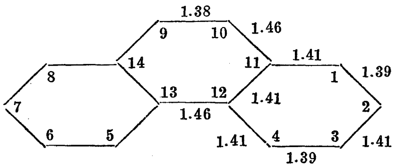
[14] The discrepancies are removed by increasing the C–Cl distance by 0.02 Å., to 1.69 Å., and decreasing the angle by 1°, to 122°30′. These changes are within the estimated probable errors of our determination, ±0.03 Å. and ±1°, respectively.

[15] J. Sherman, *J. Chem. Phys.*, **2**, 488 (1934).

[16] It may be pointed out that the changes from the simple calculation given above result mainly from the fact that the coefficient for the structure  is larger than that for the other unexcited structures.

For phenanthrene the five unexcited structures lead to $^4/_5$ double bond character for the 9–10 bonds, $^3/_5$ for the 1–2 bonds, $^2/_5$ for the 1–11, 11–12 and 4–12 bonds, and $^1/_5$ for the 10–11 and 12–13 bonds, and the predicted configuration is



Similar prediction can be made for larger molecules. It must be pointed out that the contributions of excited structures become important for bonds with small double bond character, inasmuch as in conjugated systems excited structures alone may lead to as much as 20% double bond character; it is probable that the maximum carbon–carbon bond distance in aromatic hydrocarbons is about 1.46 Å., the minimum being the double bond distance 1.38 Å.

The predicted average interatomic distance is 1.41 Å. in naphthalene, anthracene and phenanthrene, this value being somewhat larger than the benzene value (1.39 Å.). With increase in size of the hydrocarbon the carbon–carbon distances should all approach the graphite value 1.42 Å.

The only experimental values of sufficient accuracy to permit a test of the predicted values are those obtained by Robertson in his careful and thorough x-ray investigations of the structure of crystals of naphthalene[17] and anthracene.[18] In each of these molecules Robertson reports the value 1.41 Å. for the average carbon–carbon bond distance, in complete agreement with the predicted value.[19] He does not discuss individual variations from the average; however, measurements made on his reproduced electron distribution projections (Fig. 2 for naphthalene, Fig. 2 for anthracene) show differences of 2 or 3% in the predicted directions.[20]

Summary

Using experimental values for carbon–carbon bonds, a function is plotted showing the dependence of interatomic distance on bond character for single bond–double bond resonance. This function is tested with data for other bonds, and used in the discussion of the electronic structure of molecules containing conjugated double or triple bonds or aromatic nuclei and of molecules containing carbon–chlorine bonds adjacent to double bonds. The dependence of bond angles on single bond–double bond resonance is discussed. Values of carbon–carbon bond distances in polynuclear aromatic hydrocarbons are predicted and compared with the existent experimental data.

[17] J. M. Robertson, *Proc. Roy. Soc.* (London), **A142**, 674 (1933).

[18] J. M. Robertson, *ibid.*, **A140**, 79 (1933).

[19] The data for chrysene [J. Iball, *ibid.*, **A146**, 140 (1934)] are also compatible with this value.

[20] The value 1.41 Å. has also been reported for the carbon–carbon distance in benzene derivatives. We think it probable that this is 0.02 Å. too large.

PASADENA, CALIFORNIA RECEIVED SEPTEMBER 24, 1935

[CONTRIBUTION FROM THE ONTARIO RESEARCH FOUNDATION]

Vapor Pressures of Certain Glycols

BY O. J. SCHIERHOLTZ AND M. L. STAPLES

In connection with other current research work, the authors have had occasion to determine the vapor pressure curves for the following glycols: ethylene, 1,2-propylene, 1,3-propylene, 1,3-butylene and 2,3-butylene.

A search of the literature for physical constants of these compounds revealed the fact that comparatively little has been published. With the exception of ethylene glycol, no vapor pressure data could be found, and many of the physical constants which are recorded are not at all concordant. The densities and refractive indices have been determined for all the above glycols, and are tabulated below.

All the compounds used in the determinations were purified by distillation, suitable neutralizing agents being used to obtain completely neutral, colorless, odorless products. The purities were such that the refractive index of successive fractions did not differ by more than 0.00038, and in most cases the difference was considerably less.

The starting materials for those glycols not synthesized in this laboratory were as follows: ethylene glycol and 1,2-propylene glycol, Carbide and Carbon Chemicals Corporation; 1,3-propylene glycol, Eastman Kodak Company.

Preparation of 2,3-Butylene Glycol.—This compound was prepared by the hydrolysis of 2,3-dibromobutylene, $CH_3CHBrCHBrCH_3$ (Eastman, b. p. 155–157°) in the presence of lead oxide. A similar method has been used by Dr. Harold Hibbert of McGill University, in the synthesis of a number of polyhydroxy compounds.

The following procedure was used: 30 cc. of 2,3-dibromobutylene and 300 g. of finely ground lead oxide were agitated in 2 liters of water for twenty-four hours at room temperature, with a high-speed stirrer. The precipitated lead bromide and excess lead oxide were then filtered off and the liquid concentrated under vacuum to about 500 cc. By chilling with ice, as much as possible of the lead bromide still in solution was precipitated and removed by filtration. To remove any lead remaining in solution, the filtrate was treated with hydrogen sulfide. After filtering, the liquid was further concentrated in the presence of a small amount of silver carbonate, to eliminate the last traces of halogen. The yield of glycol obtained was 50% of the theoretical. Prompt reaction of any liberated hydrogen bromide with the lead oxide seems to be essential to obtain good yields. Efficient agitation is an aid to this end. With the same point in view, the use of freshly precipitated lead hydroxide has been advocated.

Preparation of 1,3-Butylene Glycol.—The synthesis of this compound was carried out by using a slight modification of the method described by Halpern.[1] The procedure consisted of the reduction of acetaldol with aluminum amalgam. In the present case, 200 cc. of acetaldol (Eastman, Tech.) was distilled at 20 mm. pressure into 2 liters of water, in order to avoid the usual strongly exothermic reaction which is noted in the receiver when aldol is distilled alone. The solution was further diluted to 3.5 liters and cooled to 18°. Aluminum amalgam was then added at intervals to avoid rise in temperature, and the mixture allowed to stand for three days in order to complete the reaction. A yield of 75% of the theoretical amount of glycol was finally obtained.

Method of Determining Vapor Pressures.—The vapor pressures were studied by boiling the liquid under different pressures. The apparatus consisted of a Claisen distilling flask with a specially wide side-arm bent down at right angles and attached, by means of an adapter, to a receiver which was packed in ice. A cone-type electrical heater was placed under the distilling flask, and the whole assembly mounted on a shaking machine of the reciprocating type.

With the use of agitation, practically all superheating was overcome, as indicated by the difference between the liquid and vapor temperatures which was found to be of the order of about 0.5°. The vapor temperatures were determined by a short-range type precision thermometer. With this type of thermometer, the mercury column was surrounded completely by vapor, and stem corrections were avoided. The usual practice of bleeding a fine stream of air into the boiling liquid, in order to overcome bumping, could not be used, for this was shown to produce a considerable effect on the boiling point. Constant pressures were obtained by including a 10-liter chamber in the apparatus train, and using a pressure regulator.[10] The temperatures were determined to an accuracy of 0.1°, while the pressures could be read to 0.3 mm. All pressures are recorded in mm. of mercury at 0°.

TABLE I

PHYSICAL CONSTANTS OF THE GLYCOLS

Source of data	B. p., °C. (760 mm.)	Refr. index n_D	°C.	Density d_4	°C.
		Ethylene			
Taylor and Rinkenbach[2]	197.2			1.1132	20
Karvonen[3]		1.43178	20		
Authors	197.2	1.43192	20	1.1140	20
		1.43072	25		
		1,2-Propylene			
Wurtz[4]	188–189			1.051	0
Authors	187.4	1.43162	25	1.0354	23
		1,3-Propylene			
Rayner[5]	210–211			1.0554^{20}	20
Karvonen[3]		1.43983	20	1.0597	20
Wurtz and Reboul[6]	216			1.053	19
Authors	214.7	1.43847	25	1.0538	20
		1.43940	21		
		1,3-Butylene			
Bergmann, Miekeley and von Lippmann[7]	108–109(12)	1.4418	19.5		
Wurtz[8]	207–208(769)			1.0259	
Authors	207.5	1.44252	19.5	1.0053	20
		1.44098	25		
		2,3-Butylene			
Kling[9]	178–180				
Wurtz[4]	183–184			1.048	0
Authors	182.5	1.43637	25	1.0033	20

TABLE II

VALUES FOR GLYCOLS

Temperature range, °C.	Constant A	Constant B
	Ethylene	
90–130	3193.6	9.7423
130–197.2	2994.4	9.2477
	1,2-Propylene	
80–130	3039.0	9.5157
130–187.5	2925.2	9.2317
	1,3-Propylene	
110–160	3305.4	9.6951
160–214.7	3154.9	9.3484
	1,3-Butylene	
100–150	3116.7	9.3890
150–207.5	3035.6	9.1979
	2,3-Butylene	
80–130	3023.9	9.5521
130–182.5	2907.1	9.2616

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(1) Halpern, *Monatsh.*, **22**, 63 (1901).

(2) Taylor and Rinkenbach, *Ind. Eng. Chem.*, **18**, 676 (1926).

(3) Karvonen, *Ann. Acad. Sci. Fennicae*, **A10**, No. 10, 9 (1918).

(4) Würtz, *Ann. chim. phys.*, [3] **55**, 438–454 (1859).

(5) A. Rayner, *J. Soc. Chem. Ind.*, **45**, 265–266, 287–288T (1926).

(6) Wurtz and Reboul, *C. E., Compt. rend.*, **79**, 169 (1874).

(7) Max Bergmann, A. Miekeley and E. von Lippmann, *Ber.*, **62**, 1467–1474 (1929).

(8) Wurtz, *Bull. soc. chim.*, [2] **41**, 362 (1884).

(9) A. Kling, *Ann. chim. phys.*, [8] **5**, 553 (1905).

(10) O. J. Schierholtz, *Ind. Eng. Chem., Anal. Ed.*, **7**, 284 (1935).

Experimental Results

In the case of each compound, determinations were made at from twelve to fifteen different pressures over the range 10–760 mm. By plotting the logarithm of the vapor pressure against the reciprocal of the absolute temperature, an almost straight line relationship was obtained. The constants for the conventional equation

$$\log_{10} p_{\text{mm.}} = -(A/T) + B$$

were evaluated, and are recorded in Table II. Vapor pressures calculated by means of this equation fall within the limit of error of the experimental results.

Summary

1. The vapor pressure curves over the range 10–760 mm. have been determined for the following glycols: ethylene, 1,2-propylene, 1,3-propylene, 1,3-butylene and 2,3-butylene. With the exception of ethylene glycol, these data are here reported for the first time.

2. The densities and refractive indices are given for all the above compounds.

3. The methods used for the preparation of 1,3-butylene and 2,3-butylene glycols are also described.

TORONTO, CANADA RECEIVED JUNE 28, 1935

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

The Mercury–Mercuric Oxide–Saturated Barium Hydroxide and Calcium Hydroxide Electrodes

BY G. J. SAMUELSON AND D. J. BROWN

It was the purpose of this research to study the mercury, mercuric oxide, barium hydroxide electrode with a view to its being used as a reference electrode. A saturated solution of the base was used to avoid troublesome preparation of standard solutions, thus permitting of easier preparation than is possible with the unsaturated type. Brown and Andrews[1] used Ming Chow's[2] electrode, containing sodium hydroxide, as a standard in their work and found its use very satisfactory.

The cell studied was, according to the common convention in designating it, as follows

$$\text{Hg}/(\text{HgO(s)}, \text{Ba(OH)}_2\text{(s)}/m\ \text{KCl}/\text{KCl(s)}, \text{Hg}_2\text{Cl}_2\text{(s)}/\text{Hg}$$

In the spontaneous reaction within the cell, an electron current flows in the external circuit from left to right, the complete reaction being

$$\text{Hg} + \text{Ba(OH)}_2 + \text{Hg}_2\text{Cl}_2 \rightleftharpoons 2\text{Hg} + \text{BaCl}_2 + \text{HgO} + \text{H}_2\text{O}$$

Mercuric Oxide.—Mercuric oxide was prepared by decomposing pure mercuric nitrate. However, electrodes containing this oxide gave potentials not differing sensibly from those obtained with half-cells containing "chemically pure" commercial mercuric oxide.

Barium Hydroxide.—The best available grade of barium hydroxide was recrystallized from distilled water.

Potassium Chloride.—This was prepared by recrystallization of "chemically pure" potassium chloride from distilled water.

Mercurous Chloride.—Calomel was prepared electrolytically by the method of Lipscomb and Hulett.[3]

Agar-Agar.—This was an ordinary commercial form of the substance.

Water.—The water used was twice distilled, once from alkaline permanganate, Pyrex containers and a block-tin condenser being employed.

Electrode Vessels.—Electrode vessels similar to type to those of Lewis, Brighton and Sebastian.[4]

Reference Half-Cell.—A layer of mercury in the chamber was covered with a layer of electrolytically prepared calomel containing crystals of potassium chloride. Over this was poured a saturated solution of potassium chloride to within a few centimeters of the top of the chamber.

Experimental Half-Cells.—A flask containing water and excess barium hydroxide and mercuric oxide was shaken frequently, the contents of the flask being kept near the temperature at which measurements were to be made. This mixture was poured into the electrode chamber in which were a layer of mercury and additional barium hydroxide and mercuric oxide.

Half-Cell Chamber.—A glass jar, 6 cm. in diameter and similar to a hydrometer jar, was nearly filled with a saturated solution the same as that used in the electrode, excess of the solute being added. The jar was fitted with a large rubber stopper. The lower part of the long straight arm of an h-shaped glass tube passed through the large rubber stopper and dipped into the solution within the jar. The bent side-arm of the tube passed through a one-holed rubber stopper which was inserted into the mouth of the electrode vessel, the tube dipping beneath the surface of the solution in the vessel. The arrangement was such that the small stopper and h-tube suspended the electrode vessel in a position parallel to the jar, and on about the same

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[1] Brown and Andrews, THIS JOURNAL, **42**, 488 (1920).

[2] Ming Chow, *ibid.*, **56**, 388 (1934); **57**, 254 (1935).

[3] Lipscomb and Hulett, *ibid.*, **38**, 22 (1916).

[4] Lewis, Brighton and Sebastian, *ibid.*, **39**, 2245 (1917).

level, so that when the apparatus was immersed in the water-bath, the level of the water just reached the top of the jar and of the electrode vessel. The upper end of the longer straight arm of the h-shaped tube was closed with a short piece of rubber tubing containing a glass bead as a valve. Connection between the solution in the electrode vessel and that in the jar was effected whenever desired by sucking on the rubber tube at the upper end of the h-tube, the glass bead preventing the return of air and so making the solutions continuous.

Several such nests of four to eight electrodes each were made for both experimental and reference electrodes. Thus the electrodes could be checked against each other simply by connecting any pair of them to the potentiometer.

Baths.—Measurements on the electrodes were made at temperatures of 0, 15, 25 and 35 ± 0.02°.

Standard Cell.—A Weston standard cell recently calibrated by the Bureau of Standards.

Potentiometer.—All potential measurements were made with a Leeds and Northrup Type K potentiometer calibrated by the Bureau of Standards and equipped with a Type R reflecting galvanometer.

Salt Bridge.—Several methods of effecting contact between the saturated solutions of barium hydroxide in the one electrode and of potassium chloride in the reference electrode were tried.[5] Finally the gel–salt bridge method was adopted. The bridge used in this work consisted of a gel of 2.5% agar–agar in molar potassium chloride solution.

Several bridges were tried in every set of measurements to establish the reproducibility and constancy of the agar–salt bridge. Table I gives representative data for the cell

$Hg/HgO(s),\ Ba(OH)_2(s)/bridge/KCl(s),\ Hg_2Cl_2(s)/Hg$

at 25° with four changes of the agar–salt bridge, the time elapsed from insertion of the bridge being also indicated in hours and electromotive force in volts. The same combination of half-cells was used with all of these bridges, the different bridges being used successively.

TABLE I

AGAR BRIDGES WITH SAME CELL

Bridge 1 Time	Bridge 1 E. m. f.	Bridge 2 Time	Bridge 2 E. m. f.
0	0.0965	0	0.0972
2½	.0975	5	.0979
15	.0982	21	.0981
23	.0982	95	.0980
64	.0981		
Bridge 3		**Bridge 4**	
0	0.0984	0	0.0982
4	.0985	1	.0984
18	.0985	7	.0985
30	.0985	23	.0984

From these data it appears that the whole cell, which includes the reference and experimental electrodes and the agar–salt bridge, becomes relatively constant within a short time after insertion of the bridge, and for an indefinite period of time.

Before comparison of the experimental half-cell with the reference electrode was made, it was customary to check the latter against the other members of the reference nest (consisting of four saturated calomel electrodes, an occasional exchange of one of these for a freshly prepared one being made). At all times the maximum variation between the various calomel half-cells used was within 0.1 millivolt. These were found also to be very nearly constant and reproducible if made of highly purified materials exactly as directed.

The usual procedure with the experimental electrodes was to compare the several ones with one another, Table II, and to compare only one of these with the reference half-cell.

TABLE II

E. M. F. COMPARISON OF BARIUM HYDROXIDE HALF-CELLS

Cell	Hours 1	18	42	87
2–6	0.00018	0.00019	0.00019	0.00019
3–6	.00007	.00010	.00007	.00007
4–6	.00004	.00004	.00005	.00005
5–6	.00013	.00011	.00011	.00011
3–4	.00005	.00004	.00004	.00004

The first column indicates the half-cell combination read, the electrodes being numbered, the one on the left being negative to the one on the right. The potential differences in volts are given at the indicated time elapsed from the insertion of the nest of electrodes in the bath.

These half-cells, when measured against the reference electrode, gave values, from the beginning of the period of measurement to the end, which were more nearly constant than the bridge itself. From Table II it may be seen that the barium hydroxide half-cells reached almost at once, and maintained for indefinite periods of time, steady relationship with each other. Moreover, the greatest difference between any pair of the freshly prepared half-cells containing purified substances is less than 0.2 millivolt. A summary of data for representative determinations on electrodes of the type mercury-mercuric oxide-saturated barium hydroxide, where the material used were of the highest quality available, is given in Table III.

This electrode is negative to the saturated calomel electrode, according to convention, and since the latter has been established as ±0.2446 volt

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[5] Lamb and Larson, THIS JOURNAL, **42**, 229 (1920); Ferguson and co-workers, *ibid.*, **54**, 1279 (1932); Guggenheim, *ibid.*, **52**, 1331 (1930).

TABLE III

CELLS, $Hg/HgO(s)$, $Ba(OH)_2(s)//KCl(s)$, $Hg_2Cl_2/(s)Hg$

T., °C.	Electrodes	Period of meas. days	Max. deviation, v.	Av. e. m. f. as read, v.	Av. e. m. f. *vs.* cal. at 25°	Temp. coefficient volts deg.
0	6	5	0.0004	0.0794	0.0844	−0.00052
15	6	5	.0002	.0902	.0922	− .00062
25	6	16	.0003	.0984	.0984	− .00062
35	5	18	.0002	.1066	.1046	

at 25° in comparison with the normal hydrogen electrode,[6] the former may be seen from Table III to have a value of +0.1562 volt at 25° against the hydrogen electrode. With an increase in temperature, the mercuric oxide–saturated barium hydroxide electrode becomes more negative to the calomel electrode and so less positive to the hydrogen electrode by 0.00060 volt per degree. Hence, the true potential of the electrode against the normal hydrogen electrode is given by the expression

$$E_t = 0.1462 - 0.00060(t - 25°)$$

A number of rapid exchanges from one bath to another were tried on this electrode to establish the effect of a sudden change of temperature on its potential. In all of these, whether the temperature change was positive or negative, the electrode assumed potentials within an hour which varied not more than 0.0003 volt from those of the ones already in the bath.

It has been seen from the data in Table II, which are representative of those obtained for various determinations, that the experimental electrode under investigation attained equilibrium very rapidly and then was almost constant in potential for an indefinite period of time. This was found to be the case whether chemically pure or further purified materials were employed in its preparation. The electrode was very easily prepared. A mixture of the oxide, barium hydroxide and water, shaken for a few minutes to ensure saturation, and then poured over a layer of mercury in the half-cell chamber constituted an electrode the potential of which, within an hour after it was placed in the bath, was not sensibly different from that of another prepared by mechanically shaking the mixture for several hours, or by occasionally agitating it for several days.

The electrode was readily reproducible in potential value when made of the purest materials. However, with the less pure materials the potentials, though constant to within 0.0002 volt for any half-cell were noticeably different for various half-cells from those obtained when the purest materials were used. In all the electrodes of ordinary "chemically pure" barium hydroxide and mercuric oxide, red and yellow, secured from various sources, and once-distilled water that were studied, the potentials were within a maximum variation of ±0.001 volt of those attained by electrodes of repurified materials.

The Mercury, Mercuric Oxide, Saturated Calcium Hydroxide Electrode

Other factors influencing the electromotive forces of the half-cells being constant, the mercury–mercuric oxide electrode containing saturated calcium hydroxide should have a temperature coefficient less negative than that of the one containing saturated barium hydroxide.

The study of the mercury, mercuric oxide, calcium hydroxide electrode was carried out, in general, in the same manner as that of the barium hydroxide electrode. The calcium hydroxide was prepared from pure calcium carbonate. Pure sodium carbonate and calcium chloride were allowed to react and the carbonate was filtered, washed free of chlorides and calcined until no carbonate remained. The resulting oxide was then used in the half-cell. The $Hg/HgO(s)$ $Ca(OH)(s)$ electrode is negative to the saturated calomel electrode. From the table the electromotive force of the mercury–mercuric oxide–saturated calcium electrode at 25° is −0.0523 volt against the saturated calomel at 25°. Accordingly, it should have a value of +0.1923 volt against the normal hydrogen electrode at that temperature. With an increase in temperature the electrode becomes less negative to the saturated calomel electrode at 25° by 0.00010 volt per degree.

CELLS, $Hg//HgO(s)$, $Ca(OH)_2(s)//KCl(s)$, $Hg_2Cl_2/(s)Hg$

T., °C.	Electrodes	Period of meas. days	Max. dev., v.	Av. e. m. f. as read v.	Av. e. m. f. *vs.* cal. at 25°	Temp. coefficient volts/deg.
0	8	2	0.0022	0.0497	0.0547	+0.00010
15	7	3	.0014	.0512	.0532	+ .00009
25	12	7	.0018	.0523	.0523	+ .00010
35	10	7	.0016	.0533	.0513	

In the most extreme cases the agar–salt bridge showed a reproducibility, with the calcium hydroxide electrodes, which was within ±0.0010 volt—not as good as with the barium hydroxide

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[6] Ewing, THIS JOURNAL, **47**, 301 (1925).

electrodes. However, the mercury, mercuric oxide, calcium hydroxide electrodes compared very favorably in speed of reaching equilibrium and in constancy with those containing barium hydroxide. It may be seen from the table that the maximum deviations between the electrodes read at the various temperatures is considerably greater than with the barium hydroxide half-cells, reaching a maximum of about two millivolts. This was the usual situation with these half-cells. A number of electrodes were made up using ordinary materials, "technical" calcium oxide, ordinary C. P. red and yellow mercuric oxide, etc., and these were found to give potentials usually well within ±0.002 volt of the above value.

Summary

1. The electrode $Hg/HgO(s)$, $Ba(OH)_2(s)$ has been studied from the standpoints of ease of preparation, constancy, reproducibility and effect of temperature change.

2. The potential of the electrode including a liquid junction, compared to the hydrogen electrode at zero is $+0.1462 - 0.00060(t - 25°) \pm 0.0002$ volt.

3. Likewise the potential of the electrode using ordinary materials is $\pm 0.1462 - 0.00060 (t - 25°) \pm 0.001$ volt.

4. The electrode using ordinary materials is very satisfactory for ordinary work.

5. The electrode $Hg/HgO(s)$, $Ca(OH)_2(s)$ has been studied from the standpoint of ease of preparation, constancy, reproducibility and temperature coefficient.

6. The potential of the electrode against the normal hydrogen electrode is $+0.1923 + 0.00010 (t - 25°) \pm 0.0010$ volt.

LINCOLN, NEBRASKA RECEIVED JULY 29, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, UNIVERSITY OF TORONTO]

The Diffusion of Helium through Fused Silica

BY E. O. BRAATEN AND G. F. CLARK

Introduction

It has been established by many observers[1] that the lighter gases can diffuse readily through fused silica. Over a wide range of temperatures and pressures it has been found that the rate of diffusion is proportional to the pressure, and that the diffusion process has a temperature coefficient expressed by an exponential relation (equation 1). Most of the results have been obtained at high temperatures where rates of diffusion are larger and experimental procedure less tedious. Sufficient data are not yet available at the lower temperatures to permit of construction of a theory valid over the whole temperature range where diffusion occurs.

Theory

It has been shown that when the Lennard-Jones[2] theory for diffusion is applied to systems of inert gases in silica the resulting equations do not fit experimental results. It appears, therefore, that the diffusion of monatomic gases through silica does not involve the mechanism of surface adsorption followed by subsequent diffusion. An extension of the theory was made by Alty,[3] who postulated that the gas enters the solid directly from the gas phase after which it penetrates the solid in the manner described by Lennard-Jones. Before the gas can enter the cracks in the solid it must have an energy, W_0, sufficient to overcome a potential barrier composed of two overlapping fields at the entrance to each pore, a comparatively small energy E_0 being also required for the atom to diffuse along the cracks.

The diffusion equation which Alty derived is

$$M = Bp\, e^{-(W_0 + E_0)/kT} \qquad (1)$$

where $E_0 \ll kT$, p is the pressure, M is the mass flowing through the solid per unit time, k is Boltzmann's constant, B is a constant, and T the absolute temperature. Equation (1) is found to be valid for temperatures above 200°, but below this temperature the rates are higher than would be expected according to the equation. Barrer[4]

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(1) P. Villard, *Compt. rend.*, **130**, 1752 (1900); A. Jacquerod and F. L. Perrot, *ibid.*, **139**, 789 (1905); E. C. Mayer, *Phys. Rev.*, **6**, 283 (1915); G. A. Williams and J. B. Ferguson, THIS JOURNAL, **44**, 2160 (1922); Johnson and Burt, *J. Opt. Soc. Am.*, **6**, 734 (1922); Steacie and Johnson, *Proc. Roy. Soc.* (London), **117A**, 662 (1927); J. W. McBain, "The Sorption of Gases by Solids," Geo. Routledge & Sons, Ltd., London, 1932, where a complete bibliography is given up to the date of publication; *Trans. Faraday Soc.*, "A General Discussion on the Adsorption of Gases by Solids," 1932.

(2) J. E. Lennard-Jones, *Trans. Faraday Soc.*, **28**, 333 (1928).

(3) T. Alty, *Phil. Mag.*, **15**, 1035 (1933).

(4) R. M. Barrer, *J. Chem. Soc.*, 376 (1934).

has shown that one may expect a decrease in energy of activation E_0 below 200°, this decrease being attributed to the formation of a new surface phase removable by treatment of the surface with hydrofluoric acid.

Experimental

Two different types of apparatus were used. The first arrangement, Fig. 1a, consisted of two tubes, the inner one of fused silica and the outer of soft glass, held together by means of a waxed ground joint. The capillary neck between the silica bulb and the ground joint prevented any appreciable error in the measurements if the top part of the system should be at a slightly lower temperature than the bulb itself. (This error would, in any case, be small between the temperatures 25 and 130°.) The second apparatus, Fig. 1b, was designed to work over all ranges of temperature. It consisted of a silica bulb attached to a Pyrex bulb by means of a graded seal which permitted the complete submersion of the bulb in the heating bath.

In the first apparatus bulbs of thicknesses 1.8, 1.0 and 0.5 mm. were used. They were made from the same sample of clear fused silica of good quality.[5] A further silica bulb 20 cm. long, 2 cm. diam. and 0.19 mm. thick was used in the second apparatus. An estimate of the average thickness of a bulb was made both by averaging the measured wall thicknesses, and by calculation from the weight of the bulb. The gas used was helium (99.9% pure).

The systems were heated by an electric furnace and the temperature, measured on a mercury thermometer, was kept constant to about 1° by means of a brass–invar thermostat. The pressure measurements were made on a sensitive McLeod gage and the mass of gas diffusing through the bulbs was calculated from the volumes of the different parts of the system and the densities of the gas in those parts. A small amount of gas diffuses through the Pyrex–silica graded seal connecting the silica bulb to the McLeod gage. This has been calculated to be less than 0.1% of the mass of gas diffusing through the silica bulb. Calculations show that no corrections were necessary for thermomolecular flow. It may be noted that in Fig. 1a the gas diffuses from the inside out while in Fig. 1b the diffusion is from outside the fused silica to the inside.

Results

Tables I to V show the values obtained for the mass of helium in grams diffusing through 1 sq. cm. of silica surface per hour for different pressures, sets of values being given for several temperatures and thicknesses of silica.

These values have been plotted in Fig. 2 and show that the rate of diffusion varies linearly with pressure, in agreement with earlier work. Fig. 3 shows that the rate of diffusion is inversely proportional to the thickness, the graph being linear within the limits of experimental error.

Table VI shows the values for the mass diffusing through 1 sq. cm. at a fixed pressure of 76 cm. for different temperatures. A set of values has been obtained for each thickness of silica. In Fig. 4 it will be observed that when the logarithm of the mass of gas diffusing is plotted against $1/T$ a

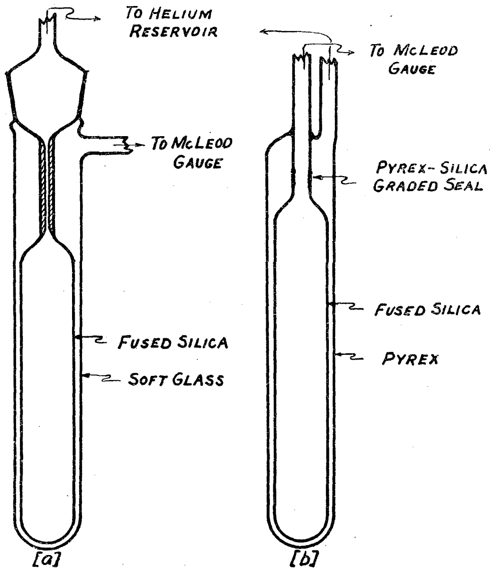

Fig. 1.

TABLE I

0.5 MM.

Press., cm.	Mass × 10^{10}
42.8°	
75.5	107.0
57.0	83.0
33.0	48.1
19.4	27.5
7.4	10.4
102.7°	
75.7	371.0
47.1	231.3
29.6	140.5
10.7	50.6

TABLE II

1.0 MM.

Press., cm.	Mass × 10^{10}
42.8°	
75.5	47.4
57.0	36.5
33.0	22.9
19.4	13.9
7.4	5.3
102.7°	
75.7	166.5
47.1	105.9
29.6	63.8
10.7	22.9

TABLE III

1.8 MM.

Press., cm.	Mass × 10^{10}
134.5°	
75.8	157.2
34.1	68.7
9.2	16.4

TABLE IV

1.0 MM. (Ground)

Press., cm.	Mass × 10^{10}
134.5°	
75.8	274.6
34.1	118.5
9.2	36.0

TABLE V

0.19 MM.

Press., cm.	Mass × 10^{10}
42.8°	
75.3	293.2
60.6	236.4
39.0	154.2
20.7	81.4
8.1	31.5

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(5) Made by the Thermal Syndicate, England.

TABLE VI

PRESSURE CONSTANT AT 76.0 CM.

Thickness, mm.	T, °C.	Mass (grams) × 10^{10}
0.5	0.0	32.9
	25.4	68.0
	60.5	155.2
	79.5	234.4
	131.0	574.0
1.0	0.0	13.6
	25.4	31.2
	60.5	71.1
	79.5	106.0
	131.0	255.3
1.0 (ground)	42.9	51.4
	80.0	110.0
	134.5	274.6
1.8	42.9	27.4
	80.0	62.4
	134.5	157.2

straight line is obtained in every case over the whole temperature range, namely, from 0 to 135°. Curves A, B, C and D are all parallel which suggests that the energies of activation are the same for samples of fused silica with the same silicate content. The energy of activation determined from the graph is 4800 cal./gram atom. The data for curve E obtained previously[5] lead to an activation energy of 4120 cal. E was not from the same melt as the other samples; Barrer[4] has already reported that the activation energy depends on the sample.

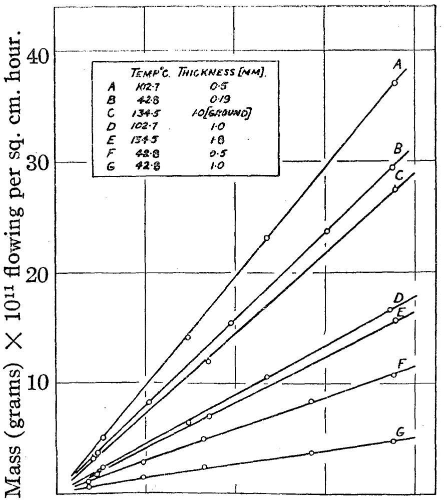

Fig. 2.

After measurements had been completed on the tube of thickness 1.0 mm., its outer surface was ground with fine carborundum and the measurements repeated. The rates were very slightly higher but the same value of $W_0 + E_0$ was obtained. (These results are not in the graph.)

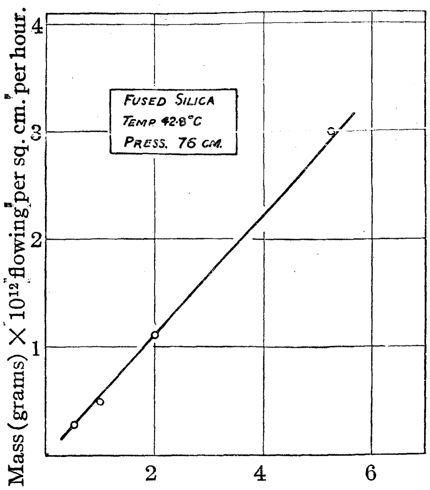

Fig. 3.

Table VII shows the values obtained for the 0.19-mm. bulb at a constant pressure and a wide range of temperatures.

TABLE VII

T, °C.	Mass in g. × 10^{10}	T, °C.	Mass in g. × 10^{10}
−78.0	2.47	121.6	1362
−58.4	8.24	164	2478
−42.9	17.2	231	5520
−21.0	43.5	314	11720
0.0	90.4	412	23000
42.8	296	497	36050
80.4	660	562	46720

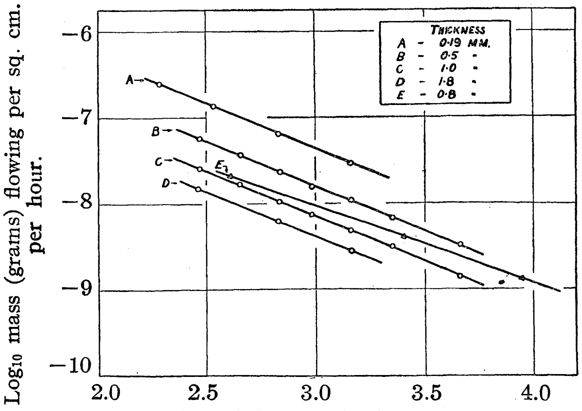

Fig. 4.

Theory[3] predicts that, at least at higher temperatures, the graph showing the relation between the logarithm of the mass and $1/T$ should be a straight line. These results have been plotted in Fig. 5 and certainly a straight line is indicated above 180°. At this temperature there seems to be a change of slope, the points corresponding to lower temperatures apparently fitting a second straight line. The value for the activation energy as calculated for the region between 180 and 562° is 5390 cal., in fair agreement with the results of other observers who worked in this temperature range, while the magnitude of $W_0 + E_0$ for the region 180 to −78° is 4800 cal. per gram atom. It should be noted that no decrease of activation energy is found below −20°. Previous results suggesting a decrease[6] were not corroborated, and it appears that the discrepancy is due to the use of a bulb which could not be kept at sufficiently uniform temperature.

The change in the slope for the graph in Fig. 5 has also been obtained by Van Voorhis[7] and T'sai and Hogness[8] for the passage of helium through fused silica, although no values were obtained by them for temperatures below 180°. It is generally agreed upon that the activation energy remains constant for temperatures from 250 to 1000°.

The heat treatment which the thin bulb received did not appear to affect its properties for diffusion.[4] In obtaining the results for the thin-walled tube the initial temperature 42.9° was gradually increased to 562°. The rates of diffusion were measured again while changing from high to low temperature. The appearance of the tube remained unchanged during the work.

It is a pleasure to thank Professor E. F. Burton for his valuable advice and encouragement throughout this work, and Mr. Chappell for his assistance in constructing the apparatus.

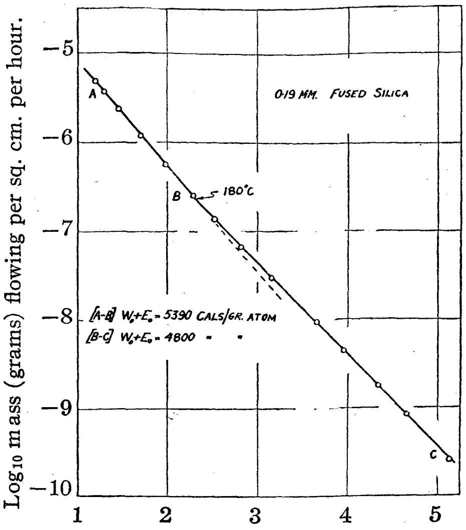

Fig. 5.

Summary

It has been found for the diffusion of helium through fused silica that (a) the gas passing through is proportional to the pressure, (b) increasing the emergent surface many times only slightly increases the rate of diffusion and (c) the rate of diffusion is inversely proportional to the thickness, which is in accord with Fick's law of diffusion.

Two values for the activation energy have been obtained depending on the temperature region for which the experiments were carried out. The magnitude for $W_0 + E_0$ was found to be independent of the thickness of the sample and to depend on the silicate content.

TORONTO, CANADA RECEIVED OCTOBER 1, 1935

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(6) E. F. Burton, E. O. Braaten and J. O. Wilhelm, *Can. J. of Res.*, **8**, 463 (1933).

(7) C. C. Van Voorhis, *Phys.*, **A32**, 557 (1924).

(8) T'sai and Hogness, *J. Phys. Chem.*, **36**, 2595 (1932).

[CONTRIBUTION FROM THE LABORATORY OF CATALYSIS, CHARKOW INSTITUTE OF CHEMICAL TECHNOLOGY]

Catalysis by Fusions

BY I. E. ADADUROW AND P. D. DIDENKO

The problem of the part played by solid surfaces in the catalytic process has been repeatedly the object of many discussions. Owing to the work of Schwab and Pietsch,[1] it has been more often repeated recently that not all places on the surface of the catalyzer possess an equal catalytic activity and that the latter is particularly inherent to places possessed of an elevated energy. Nevertheless, in a recent paper, Steacie and Elkin[2] attempted to demonstrate, on the example of the decomposition of methanol by solid and liquid zinc, that these places of elevated energy, active centers, etc., do not play any substantial part in the catalytic process. In their investigation these authors proceed from the conjecture that, if the activity of the catalyzer is essentially based on irregularities and disturbances of the crystalline surface (active places, edges and angles of crystals, etc.), it must fall abruptly if the catalyzer becomes fused. To verify this conjecture, Steacie and Elkin measured the dependence of the speed of decomposition of methyl alcohol vapors by zinc from the change of temperature between 360 and 440°, the size of the surface of the zinc remaining constant (for example, 0.5 sq. cm.). The time of increase of total pressure for a determined percentage rate was used by the authors as a standard of catalytic activity. An uninterrupted increase of activity with the rise of temperature was thus obtained, without interruption of this increase at the fusion point, *i. e.*, at 420°. The authors conclude from this that the surface of zinc is regularly active and that in general the activity of a solid substance cannot be attributed to a limited part of its surface.

We have repeatedly expressed[3] the idea that the nature of the catalytic action of a solid on the molecules of the catalyzed components of the reaction represents an influence of the field of the surface that deforms the molecules, which results in the obtaining of an active reacting condition by the molecules. But, for such a deformation to take place, two basic conditions are required. The first consists in a sufficient deforming power of the field to bring the molecule in an active condition. The second consists merely in the correspondence of the field of pertinent active places (edges, angles of disturbances, etc.) or centers (active points, points of the network) to the fields of the molecules that are being catalyzed, *i. e.*, in their possessing a necessary and definite texture and shape.[4]

From this point of view it is possible to agree with Steacie and Elkin only in the case if the form of the field that is necessary for the activation be maintained not only when approximating the fusing point, 420°, but also in the fused zinc; the power of the field yet retaining a value sufficient for the necessary deformation of the molecule that is being catalyzed.

Recently, in 1933, Randall and Rooksby[5] undertook an x-ray investigation of a whole series of liquid metals near their fusing points with the result that sodium, potassium, rubidium and cesium show in the Röntgenogram maxima at the points where intensive lines of these metals in solid condition are situated. Otherwise, near the fusing point fused metals can keep or obtain the reciprocal disposition of molecules which the metal possesses in the solid phase. It is clear that such a disposition of molecules can be fixed only by the field that is prevalent in the fusion. If not by the value of its tension, the field must in any case correspond in shape and texture to the shape and texture of the field of the crystalline network. Thus it is only necessary that its value be sufficient for the deformation of the molecule called forth by it to be able to produce in it the proper reacting power, and then the cata-

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(1) G. M. Schwab and E. Pietsch, *Z. physik. Chem.*, **1B**, 385 (1929); *Z. Elektrochem.*, **35**, 573 (1929); E. Pietsch, A. Kotowsky and G. Berend, *ibid.*, **35**, 582 (1929); *Z. physik. Chem.*, **5B**, 1 (1929); Smekal, *Z. Elektrochem.*, **35**, 567 (1929).

(2) Steacie and Elkin, *Proc. Roy. Soc.* (London), **A142**, 457 (1933).

(3) I. E. Adadurow, lectures on "Theory of Heterogeneous Catalysis" read in 1933–1934 at the Charkow University (stenotyped); I. E. Adadurow and W. A. Dzisco, *J. Phys. Chem. U. S. S. R.*, **3**, 489 (1932); I. E. Adadurow and P. J. Krainii, *ibid.*, **3**, 496 (1932); I. E. Adadurow, *ibid.*, **4**, 907 (1933); **5**, no. 7 (1934); and a series of other works by I. E. Adadurow and collaborators on vanadium and chrome catalyzers, published in *J. Applied Chem. U. S. S. R.*, 1930–1935.

(4) C. S. Taylor and D. B. Jones, "Variable Activity of Catalytic Surfaces," *Uspechi Chimii*, **2**, 701 (1934); Taylor, *Z. Elektrochem.*, **35**, 542 (1929).

(5) J. T. Randall and H. R. Rooksby, *Physik. Z.*, **33**, 473 (1932); W. I. Danilow, "Dispersion of x-Rays in Liquid Metals and Alloys," *Uspechi fisitch. nauk*, **14**, 449 (1934); *ibid.*, other literature on the same problem.

TABLE I

OXIDATION OF AMMONIA BY FUSED TIN

T, °C.	Velocity of air	Velocity of NH_3	Determined analytically % of NH_3	Determined analytically % of NO	% of contacting	Notes
300	300	30	10	...	..	A white vapor of nitrite appears
420	160	16	...	...	..	White nitrite vapor
460	143	55	...	...	..	Simultaneously with the vapor
540	143	28	...	...	..	a marked white grayish de-
610	179	55	...	...	..	posit appears on the discharge
640	197	55	...	...	..	tube growing as the temper-
650	210	58	7.6	2.3	32	ature increases
800	1300	70	4.4	1.8	40.9	Typical curve
800	1300	70	5.0	2.4	48.0	of the contact process
840	1300	70	5.0	4.0	80.0	
865	1300	70	4.6	1.7	36.9	See Fig. 2
900	1300	70	5.0	0.92	18.5	

lytic process by the fusion will result, in the same way that it had been secured by the solid body.

As a subject for investigation of catalysis by fusion we selected the catalytic oxidation of ammonia by fusions of metallic tin and silver, which melt at 231.8 and 960°, respectively. The oxidation was carried out in the apparatus schematically shown in Fig. 1. The apparatus consists of a test-tube (a), in whose neck a quartz tube (b), soldered at one end, for the thermocouple used in measuring the temperature of the fusion, is inserted through a stopper consisting of an acid-proof and thermally resistant plaster. Another quartz tube (c) is reserved for the introduction of the air–ammonia mixture that bubbles through the fused liquid metal or passes through the solid metal. To make it possible for the gas to pass through the solid metal (silver), it is first fused and then allowed to cool very slowly without interrupting the flow of the air–ammonia mixture, which thus works a series of thin channels through the hardening metal, through which the gas mixture passes afterward when the metal has completely solidified. Besides these two tubes, a quartz tube (d) for discharging the gases is also soldered into the stopper. The whole apparatus is put into an electric furnace and heated to the temperature required. In the lower part of the test-tube (c) is introduced the catalyzing metal. The analysis of the air–ammonia mixture and of the gases leaving the conversion apparatus was made by the usual method.

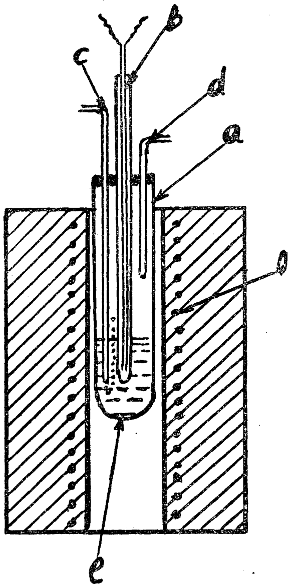

Fig. 1.

The experiments with tin gave the following results at about 300° and at a rate of 0.03 liter per minute of ammonia and 0.30 liter per minute of air: at a ratio of 10% ammonia to 90% air, a white vapor of the nitrite appears. With the increase of the velocity of the gas current to 0.05 liter/minute for ammonia and 0.50 liter/minute for the air, the development of ammonium nitrite increases. Only at about 650° the contacting action begins to be evident and the nitrite vapor disappears. But it is to be noted that simultaneously with the appearance of nitrite a grayish-white deposit forms on the tube discharging the converted gases, which upon investigation proved to be a mixture of tin oxide and tin dioxide ($SnO + SnO_2$). The results of the investigation are shown in Table I.

After opening the contact tube, it was found that nearly all the metal had been transformed to a grayish-white-green mixture of particles of metal that did not have time to oxidize with tin oxide and tin dioxide.

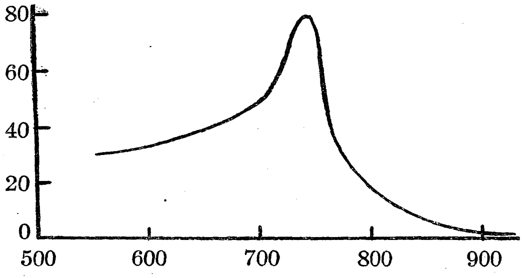

Fig. 2.

Thus the catalyzing effect here is obtained not by metallic tin, but by tin oxide, which has been used already by Wortmann[6] as a contact mass for the oxidation of ammonia. The appearance of tin oxide here is also not unexpected, because tin that is resistant to the oxidizing action of atmospheric oxygen at an ordinary temperature goes over to oxides easily enough at temperatures above the fusing point.

Thus a metal should be selected which would not form compounds with oxygen at elevated temperatures approximating the melting point or

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(6) Oskar Kausch, "Catalyzers for the Production of Sulfuric and Nitric Acids and Synthetic Ammonia," NTWU, 1934, p. 140; also An., p. 79049.

above and at the same time would catalyze the reaction of oxidation of ammonia nitrogen compounds. Such a substance is silver, which, as has been said by D. I. Mendelejew, "is a metal that does not oxidize in the heat."[7] The silver is not oxidized by atmospheric oxygen at any temperature and its oxide, Ag_2O, decomposes when heated. According to Le Chatelier, the dissociation pressure of oxygen isolated by silver oxide at 300° is a trifle over 10 atm.; silver peroxide decomposes when being dried and heated to 150°, giving off oxygen.

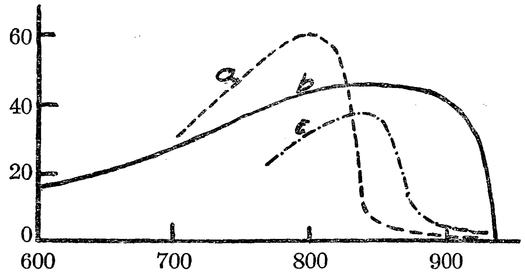

Fig. 3.

Because of the catalytic properties of silver W. Manchot and I. Haas[8] proposed to use it for the oxidation of ammonia, indicating that an active catalyst is obtained by reducing dry silver oxide at a temperature under 100°. The results of the experiments are shown in Table II.

TABLE II

T, °C.	% NH_3	% of conversion	T, °C.	% NH_3	% of conversion
Velocity 1700 cc./min.			680	10.5	25.8
Curve A, Fig. 3.			700	10.5	28.6
710	10.4	32.6	720	10.1	31.0
720	9.9	37.5	740	10.1	35.6
730	10.1	41.0	770	10.1	40.2
740	10.4	45.1	790	8.0	45.1
750	10.0	47.9	800	8.0	45.3
760	10.9	52.7	820	9.7	46.7
770	11.0	54.8	880	11.2	46.4
780	10.4	58.5	900	11.2	42.1
790	9.4	61.7	920	11.2	38.4
800	9.4	61.7	940	11.0	2.3
810	9.4	61.6	960	10.4	1.4
820	10.1	55.3	1000	5.0	2.0
830	9.8	42.0	Velocity, 3900 cc./min.		
840	9.9	17.9	Curve C, Fig. 3		
850	11	7.2	770	8	21.2
900	10.4	2.6	800	10.2	31.3
940	10.2	1.2	820	10.1	35.6
960	9.6	0.7	840	9.7	37.6
1000	6	1.9	860	9.4	23.4
Velocity, 2340 cc./min.			880	10.0	6.7
Curve C, Fig. 3			920	10.1	2.7
600	11.5	16.5	940	9.4	1.3
620	11.0	17.3	1000	9.4	1.9
660	10.5	22.3			

Curve C

These data form in certain temperature limits curves (a, b, c, Fig. 3) that are very like the conversion curves obtained by Andrusow[9] for the influence of velocity.

They differ, however, from the curves of Andrusow in that there is an abrupt fall in the rate of conversion in certain temperature intervals and that near the fusing point of silver the pyrometer always indicates an abrupt rise of temperature to 1000 or more degrees. This points to the fact that the reaction of oxidation of ammonia to nitric oxide is here substituted at the moment when the network dissociates owing to the transformation of the metal from the solid to liquid state by the reaction of dissociation of ammonia to elementary nitrogen and hydrogen, which oxidizes afterward to water. As can be seen from the equations, the latter reaction goes on with a much greater evolution of heat as compared with the first.

$$4NH_3 + 5O_2 = 4NO + 6H_2O + 215 \text{ cal.} \quad (1)$$
$$4NH_3 + 3O_2 = 2N_2 + 6H_2O + 315 \text{ cal.} \quad (2)$$

In the present case, therefore, an oxidation of ammonia by liquid fused metals cannot be brought about. In the case of tin the oxidation begins at the start of the oxidation of the fused metal and of the forming of a slow-fusing mixture of tin oxide and dioxide.

By making tests with such a metal as silver, for which the forming of slow-fusing oxides is excluded owing to the natural properties of this metal, we see that at temperatures below the melting point the reaction of oxidation of ammonia goes on with a greater or lower percentage of conversion, but near the fusing point the rate of oxidation falls abruptly, what is most clearly seen from Curve C, Fig. 3, for the velocity 2340. At the fusing point the reaction changes its character, being substituted by the reaction of decomposition of ammonia to elementary nitrogen with an abrupt change in the rise of the temperature of the reaction.

This fact, independently or not of our admitting a catalytic inhomogeneity of the surface, is con-

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[7] D. I. Mendelejew, "Principles of Chemistry," Vol. II, 1932, p. 228.

[8] M. Manchot and I. Haas, German Patent 30,065.

[9] Z. Andrusow, *Z. angew. Chem.*, **39**, 321 (1926); **40**, 166 (1926); **59**, 458 (1927); **60**, 536 (1927).

nected with an abrupt change of the field of the elements of the network under the influence of temperature at the fusing point, when the energy of the structure has fallen to naught and when further on the attractive power between the elements of the network is substituted by a repulsing power. It is quite clear that at this moment the potential of the outer field ceases to be adequate not only to the intramolecular field of the molecule that is being catalyzed, but it changes not only by size, but also by form and therefore it is difficult to admit that the catalytic process that takes place when a solid catalyzer is being used takes place also if it is substituted by a liquid fusion.

Therefore the work of Steacie and Elkin appears to us as not irreproachable. The dissociation of methyl alcohol takes place according to Bone and Davies[10] by the equation $CH_3OH = CH_4 + O$, and it is quite certain that the cause of the uninterrupted growth of activity in the limits of 360 to 440°, with no exception for the fusing point of zinc at 420°, does not lie in the equal activity of the surface of zinc; similarly to the case of the attempt with the catalytic oxidation of ammonia by fused tin, where the catalysis takes place not on the surface of the fused metal, but on the oxide, in the case of zinc the catalysis takes place not on the fused metal, but on the surface of the solid zinc oxide that forms in proportion to the atomic oxygen that separates the moment the dissociation of methyl alcohol takes place.

The higher the temperature, the more zinc oxide is being formed, and it is plain why the work of Steacie and Elkin demonstrates here an uninterrupted growth of activity with the increase of temperature. A check test made of the dissociation of methyl alcohol by zinc chips demonstrated quite clearly that at 360–400° the zinc chips are transformed first from the surface and then nearly completely (depending on the quantity of the vapor passed), to zinc oxide when methyl alcohol vapors are passed through them. Furthermore with the growth of the quantity of zinc oxide that is being formed the speed of the reaction of the dissociation of methyl alcohol increases. The fact that finely ground zinc or zinc dust acts as a reducing agent even on water, which is easily decomposed at low temperatures (100°) with simultaneous formation of zinc oxide being known, it was easy to foresee this result. What concerns the catalytic action of the zinc oxide that is being formed on the decomposition of methyl alcohol, it has been investigated by Adkins and Perkins,[11] who indicated that zinc oxide, under 350°, possesses a nearly imperceptible catalytic faculty for the decomposition of methyl alcohol. If the temperature is being raised, an increasing amount of gaseous products is being formed such as methane, hydrogen, ethane, carbon monoxide and carbon dioxide, which are being obtained also when the decomposition over aluminum oxide (Al_2O_3) is carried out.

Messrs. Deutsh and Prozorowsky, scientific laborers of the laboratory, took part in the experimental part of the work.

Conclusions

1. The work of Steacie and Elkin is subject to no objections as to its principal points, if it will be taken into consideration that x-ray investigations demonstrate that the orientation of the elements of the network is retained by some metals near the fusing point and in fused condition, which indicates that the shape of the field is being retained in any case. And if its potential is sufficient for the needed deformation of the catalyzed molecule, there is no impossibility of catalysis by fusions near the fusing point.

2. But in the special case of decomposition by Steacie and Elkin of methyl alcohol in the temperature range of 360 to 440° attention is attracted by the too great interval of temperature and the growing activity with the increase of temperature inherent to the solid as to the fused catalyzer, which does not take place in usual catalytic processes and calls forth a doubt as to the correctness of the explanation of the causes given by the authors.

3. The oxidation of ammonia by fused tin as carried out by us demonstrates the same increasing activity of the liquid catalyst at high temperatures (up to 840°), where nothing similar to an orientation of the crystalline network can last. The growth of the catalytic activity with time as with the increase of temperature clearly indicates the necessity of searching for other causes of its growth.

4. In the course of the investigation it has been quite clearly demonstrated that the oxidation of ammonia begins only from the moment of the formation of tin oxide and dioxide, which

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[10] W. A. Bone and H. Davies, *J. Chem. Soc.*, **105**, 1691 (1914).

[11] H. Adkins and P. D. Perkins, *J. Phys. Chem.*, **32**, 221 (1929).

has been recommended as a catalyzer for the oxidation of ammonia by Wortmann.

5. The example of silver taken as a catalyzer which does not form oxides and does not change its metallic individuality with rise of temperature demonstrated that near the fusing point the catalytic activity falls abruptly simultaneously with a change of the type of the reaction itself at the fusing point.

6. From this it becomes likely that in the process of decomposition of methyl alcohol by zinc the nature of the increasing activity may be explained by the formation of zinc oxide similarly to what had been demonstrated by us in the case of oxidation of ammonia by fused tin, where the increasing activity is related to the formation of tin oxide.

7. The formation of tin oxide in the process of decomposition of methyl alcohol is very probable, as Bone and Davies have demonstrated that its thermal decomposition takes place according to the equation $CH_3OH \longrightarrow CH_4 + O$, and the reaction takes place according to the equation $2CH_3OH \longrightarrow CH_3OCH_3 + H_2O$.

The formation of zinc oxide in proportion to water vapor is also quite evident, as in the case of $CH_3OCH_3 \longrightarrow C_2H_6 + O$; the formation of zinc oxide is inevitable.

8. The attempted decomposition of methyl alcohol vapor by zinc chips at 360–400° undertaken by us showed experimentally that zinc chips either are partially covered by zinc oxide on their surface or go over to it completely, depending on the quantity of methyl alcohol that has been passed and the time this has taken.

9. From the aforesaid, it is to be acknowledged that the conclusion of Steacie and Elkin that the surface of zinc is equally active and that in general the catalytic activity of a solid matter cannot be ascribed to a limited part of its surface, is baseless and results from an insufficient cleanness of the experiment.

CHARKOW, RUSSIA

RECEIVED MARCH 15, 1935

NOTES

Thermocouples from 2 to 90° Absolute

BY J. ELSTON AHLBERG AND WALTER O. LUNDBERG

In the establishment of temperature scales, several methods are being employed. Due to the necessity of setting up an accurate temperature scale between 20 and 70°K. it was thought desirable to test mathematical equations relating the electromotive force of thermocouples to temperature. The general trend of the data given by Giauque and associates[1,2] for a copper–constantan thermocouple (ice reference junction) between 13 and 90° K. made it apparent that the following simple equation might accurately represent the results

$$E = A + BT^2 + CT^3 + DT^4$$

E is the thermocouple voltage in microvolts, T is the absolute temperature, A, B, C and D are constants. The third law of thermodynamics requires that the term associated with the first power of temperature be equal to zero. Terms associated with powers of temperature higher than the fourth are assumed negligible.

Using the values by Giauque and associates[1,2] at 15, 20, 70 and 90°K. we find $A = 6681.26$, $B = -1.6547 \times 10^{-1}$, $C = 5.5460 \times 10^{-4}$ and $D = -9.878 \times 10^{-7}$. The agreement between the data of Giauque and associates and the above equation is as follows: from 13 to 23°K. better than 0.008°; from 24 to 35°K. better than 0.05°; and from 40 to 90°K. better than 0.03°. The agreements are well within the limits of accuracy claimed by them. The agreements additionally indicate the validity of the temperature scale at the University of California and of the data used in its establishment.[3] Moreover, the average deviation of the temperature coefficients of voltage from the calculated values is but 0.3%.

At the Johns Hopkins University we have experimentally compared a copper–constantan ther-

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[1] Giauque, Buffington and Schulze, THIS JOURNAL, **49**, 2343 (1927).

[2] Giauque, Johnston and Kelley, *ibid.*, **49**, 2367 (1927).

[3] Onnes, Keesom and Associates, *Comm. Phys. Lab. Univ. Leiden*; Simon and Lange, *Z. Physik*, **15**, 312 (1923).

mocouple (ice reference junction) with a helium gas thermometer between 2 and 20°K. and with oxygen vapor pressures between 70 and 90°K. The average deviation of the thermocouple voltages from the above equation is less than 0.01%. The constants determined are $A = 6039.9$, $B = -1.5475 \times 10^{-1}$, $C = 6.2064 \times 10^{-4}$ and $D = -1.5652 \times 10^{-6}$.

Comparisons of the above sets of experimental data, and of other thermocouples, show, to a first approximation, that the differences in voltages of two different thermocouples are proportional to their average voltage. The limitations of this last rule can be estimated from the two sets of constants given in this report.

The data discussed suggest that only four isolated comparisons of voltage and temperature are necessary in the calibration of thermocouples for use below 90°K.[4] However, when time and equipment are available, direct experimental calibration of thermocouples is to be preferred to the method suggested in this report.

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(4) At temperatures lower than 20°K. the temperature coefficient of voltage of thermocouples becomes very small making it advisable to resort to other methods for temperature measurement.

CHEMICAL LABORATORY
THE JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND

RECEIVED JULY 16, 1935

The Thermal Reaction between Gaseous Iodine Monochloride and Hydrogen

BY W. D. BONNER, W. L. GORE AND DON M. YOST

It has been found that at about 200° and above, gaseous iodine monochloride and hydrogen react slowly to form hydrogen chloride and iodine. That no hydrogen iodide is present in the reacting mixture is shown by the results of some unpublished experiments made by the late Prof. H. P. Ramsperger, who found that iodine monochloride and hydrogen iodide react very rapidly to form iodine and hydrogen chloride. A simple free energy calculation shows that this reaction goes practically to completion. The main reaction between iodine monochloride and hydrogen is then

$$2\mathrm{ICl(g)} + \mathrm{H_2(g)} = \mathrm{I_2(g)} + 2\mathrm{HCl(g)}$$

Inasmuch as no pressure change accompanies the reaction, the compositions of the reacting mixtures were determined iodimetrically. Weighed quantities of best quality liquid chlorine and solid iodine in small breakable capsules were placed in 100-cc. bulbs. The bulbs were evacuated and then filled to the desired pressure with hydrogen which had been carefully freed from oxygen and water vapor. After sealing off, the bulbs were shaken to break the capsules and were then immersed in a thermostat filled with molten Crisco. At suitable time intervals a bulb was removed from the thermostat, and the reaction was stopped by cooling the bulb rapidly in an air blast. Independent experiments had shown that no detectable reaction takes place below 100°. The cooled bulbs were opened under a solution of potassium iodide and the resulting iodine titrated with 0.1 N thiosulfate.

The best constants were obtained when the rate equation was assumed to be

$$-d(\mathrm{ICl})/dt = k(\mathrm{H_2})(\mathrm{ICl})$$

$$k = \frac{2 \times 2.303}{t(c_1 - 2c_2)} \log \frac{2c_2(1 - B)}{2c_2 - c_1B}$$

where c_1 and c_2 are the initial concentrations of ICl(g) and H_2(g), respectively, and B is the fraction of ICl consumed in time t. At 205°, $k = 0.031 \pm 0.006$; at 230°, $k = 0.17 \pm 0.06$; and at 240°, $k = 0.35 \pm 0.06$. The concentrations of ICl and H_2 are here expressed in moles per liter, and the time is given in minutes. Experiments in which the bulbs were filled with powdered Pyrex glass yielded, within the errors indicated, the same values for the specific rate constants. Representative results of the experiments are presented in Table I.

TABLE I

RESULTS OF REACTION RATE EXPERIMENTS

Temp., °C.	t, min.	Moles per liter $c_1 \times 10^2$	$c_2 \times 10^2$	Fraction ICl reacted B	k
205	360	3.12	3.19	0.329	0.033
	360	4.43	3.19	.199	.021
	60	2.20	3.15	.0674	.038
230	120	3.09	3.42	.402	.139
	60	2.53	3.43	.376	.248
	60	2.04	3.43	.202	.113
	31	1.49	3.43	.131	.138
	31	2.66	3.45	.113	.116
	30	2.68	3.13	.155	.180
	15	2.24	3.43	.098	.208
240	85	2.41	3.44	.466	.322
	50	1.38	1.94	.241	.298
	48	2.13	2.73	.375	.414
	39	1.68	1.94	.188	.284
	31	1.62	3.44	.350	.420

The mechanism suggested by these results is the following, which is put forward as a purely tentative one

$$\mathrm{H_2} + \mathrm{ICl} = \mathrm{HI} + \mathrm{HCl} \qquad \text{(slow)}$$
$$\mathrm{HI} + \mathrm{ICl} = \mathrm{HCl} + \mathrm{I_2} \qquad \text{(rapid)}$$

The deviation of the values of individual rate constants from the mean is appreciably greater than is usually found where a single mixture can be followed with time, yet no correlation between the deviations and the concentrations of reactants or products is evident.

It must be pointed out that iodine monochloride dissociates[1] somewhat (3% at 210°) into iodine and chlorine, and that a mechanism involving the possible reaction of hydrogen with chlorine must be considered. Inasmuch as the dissociation is greatly repressed as soon as some free iodine is formed, and since mixtures initially containing excess iodine gave sensibly the same results, such a mechanism does not seem likely. The direct reaction between hydrogen and iodine is very slow at 240° and below.[2]

When the average values of the specific reaction rate constants are plotted against $1/T$ a straight line results. The energy of activation for the assumed slow reaction is 33,900 cal.

[1] McMorris and Yost, THIS JOURNAL, **54**, 2247 (1932).

[2] Bodenstein, *Z. physik. Chem.*, **29**, 295 (1899).

CONTRIBUTION FROM
GATES CHEMICAL LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 484
AND FROM THE CHEMICAL LABORATORIES
UNIVERSITY OF UTAH, NO. 46

RECEIVED JUNE 25, 1935

Specific Heat and Binding Conditions of Adsorbed Argon on Charcoal

BY HANS M. CASSEL

When a monoatomic gas is adsorbed at the surface of an elementary solid, the first adsorption layer represents a more or less perfect continuation of the crystal lattice. Accordingly, the "adatoms"[1] behave as being bound by certain centers of attraction around which they move similarly as the atoms of the adsorbent. But, due to the anisotropy of the situation, the oscillation perpendicular to the surface freezes in, if the temperature is enough decreased, whereas the degrees of freedom parallel to the surface, corresponding to weaker binding forces, remain still excited at much lower temperatures.

It depends on the size and shape of the potential box in which the adatom may be regarded as contained,[2] whether the movement is a two-dimensional translation or a two-dimensional harmonic oscillation. Accordingly, the specific heat of the adatoms, in the first case, has the value, R, remaining constant except at extremely low temperatures, and, in the second case, the value, $2R$, decreasing with decreasing temperature in analogy to the Debye function of the three-dimensional oscillator.

F. Simon and R. C. Swain[3] recently having measured the heat capacity of argon adsorbed on charcoal observed the rather constant value, R, between 80 and 60°K., but, at lower temperatures, a decrease leading to an almost imperceptible amount below 20°K. Thus, the experimental result agrees neither with the first nor with the second possibility explained above. Instead, the appearance of the sloping-down perfectly resembles the Debye function of a one-dimensional oscillator.

This view, indeed, is justified, since it is much more probable that an argon atom is adsorbed in the hollow edges or steps of the very cleavable material than on the smooth surfaces of the netplanes. Adatoms bound by two vicinal crystal planes, at low temperatures, are capable of only one-dimensional vibrations parallel to both surfaces. The specific heat measurements, therefore, back the suggestion that the majority of the argon atoms is adsorbed in this way.

[1] I. Langmuir, *J. Chem. Physics*, **1**, 3 (1933).

[2] The author is very much indebted to Dr. L. Pauling, Cal. Tech., for the calculation of the degeneracy temperature.

[3] F. Simon and R. C. Swain, *Z. physik. Chem.*, **B28**, 189 (1935).

STANFORD UNIVERSITY
STANFORD UNIV., CALIF.

RECEIVED SEPTEMBER 3, 1935

Areametric Analysis. A Useful Technique in Estimating Small Amounts of Heavy Precipitates

BY V. R. DAMERELL AND M. AXELROD

In attempting to measure small amounts (0.01 to 5 mg.) of lead sulfate in contact with sulfuric acid, the authors were able to develop a simple technique whereby compact circular (or square) piles of precipitate could be obtained, of reproducible dimensions, in the center of the flask bottom (see Fig. 1). The apparent areas of these "spots" (as viewed from above, and assuming them to be flat circles or squares) could be readily measured and compared to the areas produced by known amounts of precipitate. This method of analysis is new, according to the authors' best knowledge, and since it involves the measurement of an area, the term areametric analysis is proposed.

The method is generally applicable to heavy precipitates of the lead sulfate type, such as barium sulfate, lead arsenate, lead chromate, etc. The determination is made right in the precipitation beaker or flask, and the procedure is of such simplicity that the authors feel the method may be of considerable use in the estimation of small amounts of many substances.

The technique used in the formation of these "spots" was as follows. The liquid in the flask was first swirled twenty or thirty times, to loosen the precipitate and cause part of it to go to the center. Then after allowing the precipitate to settle for a minute or two, the flask was tipped so that the line made by the edge of the liquid crept nearly to the center of the flask bottom. Sufficient liquid was present in the flask so that the flask bottom made a maximum angle of about 60° with the desk top. This was done ten times to the left, ten times to the right, and ten times each backward and forward. The precipitate was brought to the center of the flask bottom by this procedure.

Finally the flask was held by the thumb and finger of the right hand near the bottom and the thumb and finger of the left hand near the top, over a black surface. The right hand now made a series of short backward and forward movements (about ten to a series, at the rate of three or four a second). During these movements the flask did not move more than a millimeter or two, and the force was applied by the whole forearm, the wrist being held practically stiff. After each series of shakes the flask was rotated 30 or 40°. These vibrational movements caused the precipitate to be swept into a compact circular pile. Photographs of spots obtained are given in Fig. 1.

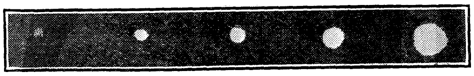

Fig. 1.—Lead sulfate "spots."

After a few minutes of such shaking the spot reached an essentially constant, minimum size. The flask was then placed on the "standard spot" card (Fig. 2) and moved along until a spot was reached which matched the unknown spot in size. This card was simply a reduced copy of a contact photograph of a twist drill and steel wire gage. It was calibrated with known amounts of precipitate. A sheet of millimeter graph paper can be substituted for occasional determinations.

This vibration method was used to obtain circles having an apparent area up to about twenty square millimeters. For larger amounts than this the minimum area of the square was obtained by the tipping process described above. The dimensions of the square could be rapidly obtained by placing the flask on millimeter graph paper.

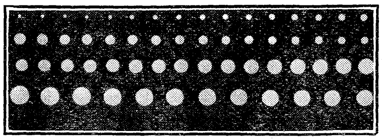

Fig. 2.

Quantitative results are given in Table I for lead sulfate in contact with 10 cc. of 40% sulfuric acid, measured in a 50-cc. Pyrex Erlenmeyer flask.

TABLE I

Mg. lead present	Mg. lead found	Impurities present, mg.	Mg. lead present	Mg. lead found	Impurities present, mg.
0.08	0.08	None	0.06	0.08	Sn (10)
.20	.19	None	.10	.13[a]	As (10) Bi (1)
.13	.14	None	.20	.19[a]	Cu (10) Cd (1)
.10	.09	None	.30	.32[a]	As (1) Bi (1) Cu (1)
.04	.06	None			Sb (1) Sn (1)
.02	.03	None	.40	.37[a]	Cu (1) Cd (1)
.04	.05	None	.50	.54[a]	Cu (10) Cd (10)
.20	.15	Cd (10)	1.0	1.3[a]	As (10) Bi (10)
.12	.10	Cu (50)			Cu (10)
.09	.10	Bi (10)	2.0	1.8[a]	Cu (5) Cd (5)
.08	.08	Bi (50)	3.0	2.7[a]	As (5) Sb (10)
.06	.12	As (50)			Sn (10)
.17	.18	Sb (10)	4.0	4.2[a]	Cu (4) Cd (4)

[a] Precipitate washed three times, redissolved and reprecipitated.

MORLEY CHEMICAL LABORATORY
WESTERN RESERVE UNIVERSITY
CLEVELAND, OHIO

RECEIVED SEPTEMBER 3, 1935

The Catalytic Oxidation of Carbon

BY JESSE E. DAY,[1] RICHARD F. ROBEY AND HYP J. DAUBEN

A few years ago, Taylor[2] reported a means of demonstrating the peculiar catalytic effect of sodium chloride on the oxidation of soot carbon, a phenomenon well known to the layman in its practical application.

We have successfully performed the demonstration of Taylor many times; it was discovered, however, that not only sodium chloride is effec-

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(1) Because of the untimely death of Professor Jesse E. Day, on April 19, 1935, the junior authors have been deprived of the benefits of his kindly guidance and criticism in the preparation of this paper.—R. F. R. and H. J. D.

(2) R. K. Taylor, THIS JOURNAL, 52, 3025 (1930).

tive, but other salts apparently equally as well. This seemed so striking that we immediately endeavored to verify this observation in a somewhat more exact manner.

A small tube (2.4 cm. in diameter) was rotated (3 r. p. m.) on its long axis inside a split type laboratory combustion furnace. A short (4 cm.) length of the tube, in the center of the furnace, and having a negligible temperature gradient, was coated completely with the salt in question. Thus the concentration of the salt was assumed to be constant at the carbon–salt interface. The temperature of the furnace was then increased to and maintained at a predetermined convenient value (±3°). Carbon film deposition, mirror reflected observation, and air admittance were made through a narrow longitudinal slot (2 cm. wide) in the under portion of the surrounding furnace. The apparatus was entirely enclosed in a small glass-fronted cabinet to protect it from drafts.

Carbon deposition was carried out by means of a wide flame of enriched natural gas from a Pyrex glass burner which moved mechanically along the slot in the furnace at a uniform rate (0.02 cm./sec.). The flame deposited the carbon film uniformly, as evidenced by the manner in which it disappeared on oxidation, and at a rate of 3.5 micromoles/sec., reproducible within 10%.

The lengths of time required for the disappearance of the carbon film from the 4 cm. sector were determined when deposited on bare glass as well as on the following c. p. salts: lithium, sodium, potassium, calcium, strontium and barium chlorides, calcium and barium hydroxides, sodium and potassium sulfates.

At 575° the carbon burned off the bare glass in about 180 sec. This was cut down by all of the salts to between 20 and 30 sec., as far as could be discerned by the method of observation. At 550° the oxidation of the carbon from the bare surface required 280 sec. It was reduced by the presence of the salts to 130–150 sec. At 515°, the oxidation from the bare surface required 630 sec. This was cut down by the barium and strontium salts to about 300, by the calcium salts and sodium chloride to about 230, and by the potassium and lithium chlorides, and sodium and potassium sulfates to about 170 sec. The values given are the averages of two or more observations usually agreeing within 10% or less. This agreement evidences a fair reproducibility of oxidizable surface area.

The most ready explanation of the effect of salts in the oxidation of carbon is that offered by Taylor and Neville.[3] They pointed out that the probable function of salts in the reaction of steam on carbon is in hastening the decomposition of the C_xO_y surface complex. With this barrier removed, a carbon surface is more readily attacked by oxidizing gases.

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[3] H. S. Taylor and H. A. Neville, This Journal, **43**, 2055 (1921).

Chemical Laboratory
The Ohio State University
Columbus, Ohio

Received August 5, 1935

The Isolation and Identification of a Paraffin Hydrocarbon from Urine of Pregnancy

By William Forris Hart and M. Allen Northup

Marrian[1] has mentioned that a paraffin hydrocarbon which is physiologically inactive, occurs in urine of pregnancy. Schwenk[2] also states that he has encountered a physiologically inactive hydrocarbon in urine of pregnancy.

We have isolated and identified one hydrocarbon, heptacosane, from urine of pregnancy, and have evidence of the presence of another, pentacosane, in the same material.

Experimental.—Twelve liters of urine were aged for several months and acidified to Congo red with concentrated hydrochloric acid, the acidified urine was then treated with 28 g. of fuller's earth per liter, agitated thoroughly, and allowed to stand overnight. The fuller's earth was then filtered off, and a second absorption on 14 g. per liter was applied. The combined fuller's earth fractions were air dried and extracted seven times with convenient volumes of low boiling petroleum ether (below 70°). The combined petroleum ether residue was taken up in 50 cc. of ethyl acetate. This solution, on chilling, deposited 1.4 g. of white plate-like crystals. It was found on recrystallizing from methanol that this material could be separated into two fractions, one soluble, and the other insoluble, in warm methanol.

The fraction insoluble in warm methanol was recrystallized repeatedly from ethyl acetate. The final melting point was 58–59° (uncorrected). Analysis gave: C, 85.83 and 84.56, H, 14.62 and 14.62; molecular weight (micro Rast), 391, 391. Calcd. for heptacosane ($C_{27}H_{56}$): C, 85.16,

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[1] Marrian, *Physiol. Rev.*, **13**, 185 (1933).

[2] E. Schwenk, private communication.

H, 14.83; molecular weight, 380; melting point, 59°.[3]

The fraction soluble in warm methanol was recrystallized repeatedly from ethyl acetate. The final melting point was 52–54° (uncorrected). Analysis gave: C, 85.07; H, 15.08%. Calcd. for pentacosane ($C_{25}H_{52}$): C, 85.37; H, 14.63; melting point, 54°.[3]

It is not certain whether this fraction consists of a pure hydrocarbon, or a mixture of two or more hydrocarbons. On crystallizing from ethyl acetate on a microscope slide it has the form of homogeneous hexagonal plates.

Besides the solubilities mentioned above, these fractions are very soluble in chloroform and benzene, soluble in hot and insoluble in cold acetone and ethanol, and insoluble in water and alkali.

They contain no nitrogen or phosphorus, have no acid or saponification number, do not reduce Fehling's solution, and do not absorb bromine from chloroform solution. They have been found to have no oestrogenic activity.

The procedure outlined above was applied to eight liters of non-pregnant female urine which had been aged for two weeks. From the petroleum ether was obtained 3.8 mg. of an impure waxy substance from which it was not possible to isolate any crystalline material melting below 120°.

The same procedure was also applied to two samples of male urine of eight liters each. One of these was a year old; the other had been aged two weeks. Like the non-pregnant female urine each yielded a few milligrams of impure waxy substance from which no crystalline material melting below 120° could be isolated. If these hydrocarbons occur in non-pregnant female, and male, urine they must do so in an amount far less than in urine of pregnancy. The physiological source of these hydrocarbons during pregnancy raises many interesting speculations.

The authors regret that factors beyond their control have prevented an extension of this investigation. They wish to thank Dr. F. R. Eldred, Director of Research, of Reed and Carnrick, for his kind permission to publish this work, and Dr. J. B. Niederl of Washington Square College, New York University, for the micro analyses and molecular weight determinations.

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[3] Hildebrand and Wachter, THIS JOURNAL, **51**, 2487 (1929).

A CONTRIBUTION FROM THE
LABORATORIES OF REED AND CARNRICK
JERSEY CITY, N. J.

RECEIVED OCTOBER 25, 1935

Preparation of Alpha-Naphthoic Acid

BY D. J. LODER[1] AND F. C. WHITMORE

During some work which demanded the preparation of a considerable amount of pure alpha-naphthoic acid, all of the regular methods of preparing this substance were tried with only mediocre success. At the same time some studies were being carried out on the preparation of tertiary alcohols by the action of the Grignard reagent with diethyl carbonate and it had been observed that when the Grignard reagent was "sterically hindered" the reaction could be stopped at the ketone stage or even at the ester stage. Consequently, alpha-naphthylmagnesium bromide (5 moles in 2.5 liters of absolute ether) was added slowly to a solution of ethyl carbonate (7.5 moles in 500 cc. of dry ether). Treatment of the mixture with a slight excess of 30% sulfuric acid, separation of the ether layer and isolation in the usual way gave a 70% yield of redistilled ethyl alpha-naphthoate boiling at 143–144.5° at 3 mm. Hydrolysis of the ester gave over a 90% yield of pure alpha-naphthoic acid.

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[1] Present address: Ammonia Department, du Pont Experimental Station, Wilmington, Delaware.

NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS AND
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA

RECEIVED SEPTEMBER 12, 1935

The Mechanism of the Addition of Halogens to Ethylenic Linkages

BY RICHARD A. OGG, JR.

The addition in solution of halogens to an ethylenic linkage is assumed by Ingold[1] to proceed through the formation of an intermediate positive carbonium ion, as RCHBr—C^+HR, which subsequently adds a halide ion. Experiment indicates positive carbonium ions to be configuratively unstable,[2,3] and hence this mechanism would lead one to expect identical products (*i. e.*, a mixture of meso and *dl* dihalides) from *cis–trans* isomers, in contradiction to experimental fact.

Carothers[4] has proposed that addition reactions of ethylenic linkages are initiated by an internal ionization of the double bond, followed by addition of the reagent molecule at the positive end,

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[1] C. K. Ingold, *Chem. Reviews*, **15**, 225 (1934).
[2] E. S. Wallis and F. H. Adams, THIS JOURNAL, **55**, 3838 (1933).
[3] E. Bergmann and M. Polanyi, *Naturwissenschaften*, **21**, 378 (1933).
[4] W. H. Carothers, THIS JOURNAL, **46**, 2227 (1924).

and subsequent rearrangement to the stable addition product. Such an internal ionization of double linkages, in view of the rapid racemization of positive carbonium ions, would cause a rapid *cis–trans* isomerization of ethylene derivatives even in the absence of reagents. Hence this mechanism is open to the same objection as that of Ingold, *i. e.*, in leading to identical addition products from *cis–trans* isomers. Both mechanisms infer the addition reactions in question to be uncatalyzed.

The following mechanism is suggested as more plausible. Using bromine, for example, the consecutive reactions are

(1) $Br^- + RCH{=}CHR \longrightarrow RCHBr{-}C^-HR$
(2) $RCHBr{-}C^-HR + Br{-}Br \longrightarrow RCHBr{-}CBrHR + Br^-$

That is, the addition is catalyzed by halide ion, and the intermediate is a carbanion. Carbanions have been shown[2] to have stable configurations, and hence stereochemically different products should result from *cis–trans* isomers. Further, explanation is afforded of the generally observed *trans* addition of halogens to ethylenic linkages. Reaction (1) is to be regarded as a substitution reaction of the halide ion with one of the electron pair bonds of the ethylenic linkage, and hence as attended by *optical inversion* of the intermediate carbon atom.[5] The carbanion thus has a *trans* configuration, and since no configuration change attends reaction (2), the final addition product should be *trans*.

Experimental evidence for the proposed mechanism is found in a number of cases in which addition or removal of halogens from an ethylenic linkage is catalyzed by halide ions. Thus Slator[6] found the decomposition of ethylene diiodide to be catalyzed by iodide ions in alcoholic solution. Obviously the addition of iodine to ethylene must be similarly catalyzed. Reaction of a 1,2-dibromo compound with iodide ions to yield the corresponding unsaturated compound is a well-known typical reaction. Halogen addition to simple ethylenic hydrocarbons in solution is ordinarily exceedingly rapid. However, the marked slowness of the addition of bromine to ethylene in rigorously purified and dried solvents[7] indicates the ordinary reaction to be catalyzed by impurities, of which halide ions appear most likely. The otherwise immeasurably slow addition of bromine to maleic and fumaric esters was found by Hanson and Williams[8] to be catalyzed by a trace of hydrogen bromide. Finally, the author has observed, using glacial acetic acid as a solvent, that the normally slow addition of bromine to maleic and fumaric acids, stilbene, cinnamic acid and tetrachloroethylene is markedly catalyzed by dissolved lithium and potassium bromides.

A very similar mechanism to the above probably obtains for addition of hydrogen halides to ethylenic linkages, step (2) being replaced by addition of a hydrogen ion to the carbanion. *Trans* addition should also occur in this case. Likewise the addition of halogens and hydrogen halides to acetylenic linkages should proceed in analogous fashion, giving *trans* addition products, as is actually observed.

It is to be emphasized that the above mechanism applies to reactions in solution, and in the dark. Gas phase addition of halogens to double bonds cannot of course be caused by ionic catalysis, and it is significant that no homogeneous reaction of gaseous ethylene with bromine or chlorine[9,10] is observed at low temperatures. In the photochemical reaction the chains are carried by free halogen atoms and the radicals RCHBr—CHR. The rapid racemization of the latter, followed by loss of halogen atoms, explains the well-known halogen-sensitized *cis–trans* isomerization of ethylene derivatives. Likewise, the photochemical reaction is to be expected to lead to a mixture of *cis* and *trans* addition products.

Cases in which marked *cis* addition of halogens occurs practically all involve the *ions* of maleic and fumaric acids.[11] Due to the Coulomb repulsion between the negative charges of the halide ion and of the acid ions, the above mechanism could hardly be expected to obtain. It is much more probable that intermediate lactone formation occurs, in which case the *cis* addition is readily explicable.

The recent communication of Anantakrishnan and Ingold[12] substantiates the above suggestion that halogen addition to ethylenic hydrocarbons is catalyzed by halide ions.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY, CALIF.
RECEIVED JULY 22, 1935

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[5] N. Meer and M. Polanyi, *Z. physik. Chem.*, **19B**, 164 (1932); A. R. Olson, *J. Chem. Phys.*, **1**, 418 (1933).

[6] A. Slator, *J. Chem. Soc.*, **85**, 1697 (1904).

[7] H. S. Davis, THIS JOURNAL, **50**, 2769 (1928).

[8] N. W. Hanson and D. M. Williams, *J. Chem. Soc.*, 1059 (1930).

[9] Stewart and Edlund, THIS JOURNAL, **45**, 1014 (1923).

[10] R. G. W. Norrish, *J. Chem. Soc.*, **123**, 3006 (1923).

[11] Terry and Eichelberger, THIS JOURNAL, **47**, 1067 (1925).

[12] S. V. Anantakrishnan and C. K. Ingold, *J. Chem. Soc.*, 984 (1935).

Catalysis in Organic Chemistry. V. Decompositions of Esters and Acids by Anhydrous Zinc Chloride[1]

BY H. W. UNDERWOOD, JR., AND O. L. BARIL

The catalytic decomposition of esters and acids by anhydrous zinc chloride has been described in previous papers.[2] The transformations observed were represented by three different types of decomposition which involved the elimination of an aliphatic unsaturated hydrocarbon or carbon dioxide or both. In order to substantiate these results, additional experiments of a similar nature were performed, from which the following regularities and generalities may be concluded.

The methyl, ethyl, propyl and butyl esters of monobasic aliphatic acids were not affected by the catalyst under the conditions of the experiment. The esters derived from amyl alcohol and from a monobasic aliphatic acid decomposed very slowly into an unsaturated hydrocarbon and the aliphatic acid. The rate of decomposition increases with a rise in the number of carbon atoms in the alcohol group. The aliphatic monobasic acids themselves are not affected by the catalyst. Esters of aliphatic dibasic acids are all decomposed, the dibasic acid reacting with the zinc chloride to form the zinc salt of the dibasic acid with evolution of hydrogen chloride. The hydrogen chloride in turn forms the alkyl halide with the liberated unsaturated hydrocarbon.

Esters of aromatic acids decompose into an unsaturated hydrocarbon and the aromatic acid, which in turn decomposes into carbon dioxide and a saturated aromatic hydrocarbon, providing the aromatic acid is monobasic. If the aromatic acid is a dibasic acid, the anhydride of the acid is formed. Benzyl esters decompose into the acid, and the benzyl groups polymerize, forming a dark tarry residue. All unsaturated hydrocarbons evolved, whether aliphatic or aromatic, polymerize, the polymerization increasing with the rise in the number of carbon atoms in the hydrocarbon.

Esters and acids readily decomposed by heat were not used. Those which were used could be distilled or fused without decomposition. In every case, decomposition of the ester or acid was effected, in the presence of anhydrous zinc chloride, at a much lower temperature than if heated alone. Zinc chloride dissolved in the ester or acid before any evidence of decomposition appeared. Esters and acids which did not dissolve the zinc chloride on heating were not themselves decomposed. This peculiar phenomenon was also noted in the experiments described in previous papers. During the decomposition, there was always a color change from colorless to yellow to orange to red to brown and finally black. The temperature in every case was raised until the ester or acid dropped freely from the end of the reflux condenser. There was often evidence of decomposition in the reaction flask before this temperature was reached. The tests described by Mulliken ["Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York City, 1904, 1916, 1922, Vols. I, II and IV] were used for the identification of all the products of decomposition.

Experimental

No evidence of decomposition was found in experiments with ethyl chloroacetate, dichloroethyl acetate, trichloroethyl acetate, ethyl isovalerate, *n*-butyl formate, *n*-propyl acetate, propyl formate, isopropyl formate and methyl *m*-nitrobenzoate.

Esters Decomposing with Evolution of Carbon Dioxide.—Methyl cinnamate yielded styrene and its polymers; ethyl cyanoacetate gave ethylene and methyl cyanide; amyl chlorocarbonate decomposed into amylene and its polymers, amyl chloride and hydrogen chloride; amyl chloroacetate into amylene and its polymers, chloroacetic acid and hydrogen chloride; ethyl anisate into ethylene, anisic acid, anisole and *p*-ethyl cresyl ether; ethyl phenylacetate into ethylene, phenylacetic acid, propylbenzene and acetic acid; isoamyl valerate into valeric acid, isopropylethylene and its dimer; *n*-amyl acetate into acetic acid, amylene and its polymers; isoamyl propionate into propionic acid, isopropyl ethylene and its dimer; ethyl *m*-aminobenzoate into ethylene and aniline; and ethyl *p*-nitrobenzoate into ethylene and *p*-nitrobenzoic acid.

Ethyl acetoacetate yielded acetone, ethyl acetate and propyl methyl ketone; and isobutyl acetoacetate gave isobutylene, acetone, isobutyl acetate and methyl isoamyl ketone. Ethyl diethylmalonate gave ethylene and ethyl diethylacetate; while ethyl dipropylmalonate gave ethylene and ethyl dipropylacetate. Methyl carbonate yielded methyl alcohol; cyclohexyl acetate gave cyclohexane and acetic anhydride; while ethyl orthoformate decomposed into ethyl ether and ethyl formate when distilled over anhydrous zinc chloride, but on refluxing the mixture for one hour at 60°, ethyl alcohol and paraldehyde were obtained.

Acetal and ethylal gave ethyl alcohol and paraform, whereas dimethyl acetal yielded methyl alcohol and par-

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[1] Due to the death of Professor Underwood, this paper has been prepared by the junior author.

[2] Underwood and Baril, THIS JOURNAL, **52**, 395 (1930); **53**, 2200 (1931).

aldehyde. Benzene was obtained from both the iso- and terephthalic acids. Anisic acid gave anisole; *p*-toluic acid yielded toluene and the zinc salt of *p*-toluic acid; and diphenylacetic acid decomposed into diphenylmethane.

Esters Decomposing without Evolution of Carbon Dioxide.—Benzyl benzoate and benzyl butyrate decomposed into their respective acids, benzoic and butyric. The benzyl groups polymerized, forming a dark colored and tarry residue. Dimethyl phthalate gave phthalic anhydride, and *n*-amyl phthalate gave phthalic anhydride, amylene and its polymers. Phenyl acetate yielded phenol; and phenyl salicylate gave phenol at a temperature of 177° in presence of the catalyst, although a temperature of 280° is required to decompose it without a catalyst. Phenylacetic acid yielded acetic acid; *m*- and *p*-nitrobenzoic acid reacted with the catalyst to form the zinc salt of the acid with evolution of hydrogen chloride. The *p*-nitrobenzoic acid mixture blew up after fifteen minutes of heating, leaving a deposit of soot over the entire apparatus.

A new type of decomposition has been observed with the elimination of carbon monoxide instead of carbon dioxide from halogenated aliphatic acids. Monochloroacetic acid decomposed into carbon monoxide, formaldehyde and hydrogen chloride; and the trichloroacetic acid decomposed into carbon monoxide, carbonyl chloride and hydrogen chloride.

The authors wish to express their thanks for a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences which partly defrayed the cost of this work.

CONTRIBUTION NO. 131 FROM THE
RESEARCH LABORATORY OF ORGANIC CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS.
RECEIVED JULY 17, 1935

Reduction of Nitroguanidine. III. Synthesis of Aminoguanidine[1]

BY G. B. L. SMITH AND EDWARD ANZELMI

Aminoguanidine has been prepared by the reduction of nitroguanidine with zinc in a solution of acetic acid,[2] by the interaction of hydrazine hydrochloride and cyanamide,[3] and by the electrolytic reduction of nitroguanidine.[4] We have prepared aminoguanidine in high purity and excellent yield by the hydrazinolysis of methyl isothiourea sulfate. To 139 g. of methyl isothiourea sulfate in 200 ml. of water at 10° is added 119 ml. of a 42% solution of hydrazine hydrate[5] diluted with an equal volume of water. The methyl mercaptan liberated can be absorbed in a solution of sodium hydroxide.[6] Finally the aminoguanidine sulfate is precipitated by addition of an equal volume of 95% ethanol to the solution concentrated to 200 ml. A second crop of crystals separates on concentration of the filtered solution. The water of crystallization (1 molecule) may be removed by drying *in vacuo* or at 105°; yield 90%; m. p. 206° with decomposition (Thiele, 207–208°). Aminoguanidine sulfate was identified through conversion to the picrate and bicarbonate, by liberation in alkaline solution of one-half of the nitrogen as ammonia and by hydrolysis to hydrazine.[7] *Anal.* calcd. for $(CH_6N_4)_2H_2SO_4$: SO_4, 39.83; NH_3, 27.67; N_2H_4, 26.02. Found: SO_4, 39.3, 39.7; NH_3, 27.2, 27.5, 27.7; N_2H_4, 26.03, 25.93. The fact that aminoguanidine bicarbonate has the composition $CN_4H_6H_2CO_3$ has been established by analysis. A solution of aminoguanidine is a strong base K_B estimated as 1.1×10^{-3}. Further work on aminoguanidine and alkylaminoguanidines is in progress.

POLYTECHNIC INSTITUTE OF BROOKLYN
BROOKLYN, N. Y.
RECEIVED MAY 3, 1935

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[1] For more full details see B.S. thesis by Edward Anzelmi, Polytechnic Institute of Brooklyn, 1933. Contribution No. 27 from the Department of Chemistry of the Polytechnic Institute of Brooklyn.

[2] Thiele, *Ann.*, **270**, 1 (1892).

[3] Pellizzarri and Cuneo, *Gazz. chim. ital.*, [2] **21**, 405 (1901).

[4] Boehringer, German Patent 167,637. We have as yet been unable to confirm this observation.

[5] From the Eastman Kodak Company.

[6] Phillips and Clarke, THIS JOURNAL, **45**, 1755 (1923).

[7] Jamieson, *Am. J. Sci.*, [4] **33**, 353 (1912).

COMMUNICATIONS TO THE EDITOR

THE RELATIVE ATOMIC WEIGHT OF OXYGEN IN WATER AND IN AIR

Sir:

Washburn, Smith and Smith [*Bur. Standards J. Res.*, **13,** 599 (1934)] burned oxygen and hydrogen from an electrolytic cell separately with "normal" hydrogen and oxygen, respectively, obtaining in the first fraction a difference of density in p. p. m., γ, between these waters and normal water -13.2 for the cell oxygen plus "normal" hydrogen and -7.8 for the cell hydrogen plus atmospheric oxygen. The cell hydrogen and oxygen burned together gave water of γ value, -20.5, approximately the sum of the first two data. A little reflection will show that if this work is correct, there is no difference between the atomic weight of oxygen in air and in water. Unfortunately it now appears that due to an unlucky compensation of effects this agreement is merely a coincidence and that there is a significant difference in the atomic weight of oxygen from the two sources.

I have electrolyzed water made from tank hydrogen and Linde oxygen (whose atomic weight in reference to atmospheric oxygen was corrected for) and burned the oxygen with tank hydrogen. Two electrolyses gave γ equal to -6.9 for this water. Two electrolyses of normal water, followed by combustion of the oxygen with the same tank hydrogen gave water having a γ value of -11.5; the difference between the results is 4.6, from which the atomic weight of oxygen in the air can be calculated to be 16.00008 if the atomic weight of oxygen in Lake Michigan water is 16.00000.

Understanding this fact makes easy the explanation of several anomalous and unexplained results of other workers. In the work of Washburn mentioned above neither his tank hydrogen nor his oxygen was "normal," *i. e.*, had the same atomic weight as the two elements in water, the hydrogen being too light and the oxygen too heavy. It is also clear why Washburn, Smith and Smith's conclusion that the oxygen isotopes fractionate more rapidly than those of hydrogen on electrolysis is erroneous. Greene and Voskuyl's [This Journal 56, 1649 (1934)] anomalous finding that tank hydrogen burned with air resulted in water denser than normal is explained, and the results of W. Heinlen Hall and Johnston [This Journal, **57,** 1515 (1935)] indicating that the isotopes of hydrogen fractionate on combustion will now have to be largely modified. The increase in density of water obtained by myself and many others in the combustion of organic substances will have to be reinterpreted.

Incidentally the data reported here confirm the prediction of Urey and Greiff [This Journal, **57,** 321 (1935)] that when water and oxygen are brought into equilibrium, the O^{18} concentrates in the oxygen, and the conclusion that it is meaningless to express the atomic weight of oxygen to more than four decimal places.

It is hoped to repeat more accurately the experimental work described in this paper.

Department of Chemistry
Northwestern University
Evanston, Illinois
Malcolm Dole

Received November 18, 1935

THE PREPARATION OF 9,10-DIHYDROPHENANTHRENE AND ITS DERIVATIVES

Sir:

The selective activity of copper–chromium–barium oxide catalyst permits the expectation that in phenanthrene only, or chiefly the 9,10-double bond, which in some respects exhibits a decidedly olefinic character, would be saturated by hydrogenation in the presence of this catalyst.

Phenanthrene, purified according to Cohen and Cormier [This Journal, **52,** 4363 (1930)] and treated with, and distilled over sodium, was dissolved in 2 to 3 parts of absolute alcohol and mixed with about 10% (by weight) of catalyst 37 KAF [Connor, Folkers and Adkins, *ibid.*, **54,** 1138 (1932)]. The hydrogenation was carried out at pressures from 2000 to 4000 lb./sq. in., maintaining a temperature of 220° for twenty-four to thirty-six hours. After separating from the reaction mixture 10 to 20% of unchanged phenanthrene (as the picrate), 60 to 80% of crude 9,10-dihydrophenanthrene was obtained (after distillation *in vacuo*). No tetrahydro- or octahydrophenanthrene could be detected. The

Substance	M. p., °C.	Formula	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found
2-Acetyl-9,10-dihydrophenanthrene	51–52	$C_{16}H_{14}O$	86.44	86.77	6.35	6.64
-Oxime	146–147.5	$C_{16}H_{15}NO$	80.97	80.61	6.38	6.43
-Semicarbazone	236–237	$C_{17}H_{17}N_3O$	73.07	73.05	6.14	6.14
9,10-Dihydro-2-bromoacetylphenanthrene	93.5–95	$C_{16}H_{13}BrO$	63.78	63.71	4.35	4.49
9,10-Dihydrophenanthrene-2-carboxylic acid	211.5–212.5	$C_{15}H_{12}O_2$	80.32	80.34	5.39	5.42
-Methyl ester	Oil	$C_{16}H_{14}O_2$	80.63	80.50	5.93	5.66
2-Acetyl-9,10-phenanthrenequinone	223–224	$C_{16}H_{10}O_3$	76.78	76.67	4.03	4.36

compound thus obtained is sufficiently pure for the reactions described below. After further purification, the 9,10-dihydrophenanthrene melted at 31–32° and showed $n^{25}{}_D$ 1.6464 [*cf.* Schroeter, *Ber.*, **62**, 645 (1929)].

In the Friedel–Crafts reaction, which proceeds equally well in carbon disulfide or nitrobenzene, only one acetyl compound is formed (purified through the semicarbazone, yield, about 90%). The acetyl group enters the 2-position of the dihydrophenanthrene, which resembles in respect to this reaction diphenyl rather than phenanthrene. Structural proof: (A) acetyldihydrophenanthrene $\xrightarrow{CrO_3}$ 2-acetyl-9,10-phenanthrene quinone; (B) acetyldihydrophenanthrene $\xrightarrow{NaOCl}$ dihydrophenanthrene carboxylic acid $\longrightarrow$ methyl ester $\xrightarrow[20\text{ hrs., }300°]{Se}$ phenanthrene-2-carboxylic acid.

We intend to study substitution products of 9,10-dihydrophenanthrene prepared either by introducing substituents into dihydrophenanthrene or by partial hydrogenation of substituted phenanthrenes. We are interested in particular in the synthesis of compounds with nitrogen-containing side chains and rings similar to the phenanthrene and dibenzofuran derivatives previously described from this Laboratory. The preference shown by the acetyl group for position 2 (and this will undoubtedly hold true for similar substituents) makes starting materials for the synthesis of substances related to sterols and sex hormones easily accessible.

Anthracene, submitted to high pressure hydrogenation with copper chromite, is reduced nearly quantitatively to 9,10-dihydroanthracene. In this case the reduction is completed at a considerably lower temperature (160°) within a few hours. This demonstrates again the marked difference between the reactivities of the meso-positions in anthracene and phenanthrene, respectively.

COBB CHEMICAL LABORATORY
UNIVERSITY OF VIRGINIA
UNIVERSITY, VA.

ALFRED BURGER
ERICH MOSETTIG

RECEIVED NOVEMBER 23, 1935

THE APPLICATION OF POLANYI'S POTENTIAL THEORY TO THE VAN DER WAALS ADSORPTION OF GASES ON IRON SYNTHETIC AMMONIA CATALYSTS

Sir:

Polanyi's "potential theory" of gas adsorption by solids [*Verhandl. deut. phys. Ges.*, **18,** 55 (1916)] in its original form was interpreted in terms of a postulated thick film of compressed or liquefied gas on the surface of the solid. In 1928 Polanyi and Goldman [*Z. physik. Chem.*, **132,** 321 (1928)] pointed out that the theory can be applied to adsorption in monomolecular layers. Thus far the theory has been applied exclusively to the adsorption of organic vapors, carbon dioxide and sulfur dioxide on amorphous adsorbents like charcoal and silica gel. The present communication shows the applicability of the theory to some low temperature isotherms that we have been obtaining on iron catalysts.

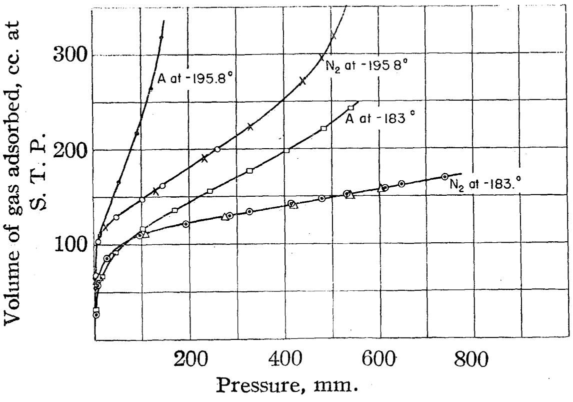


Fig. 1.

Figure 1 shows isotherms obtained for argon and nitrogen on a 25-cc. sample (43.6 g. of iron) of a singly promoted (10.2% Al_2O_3) iron synthetic ammonia catalyst at −183° and −195.8°. These adsorption data plotted according to Polanyi's theory are shown in Fig. 2. As abscissas are plotted $RT\log_{10}P_s/P$; these abscissa values when multiplied by 2.303 give the free energy of compression of the gas from the pressure P, at which a particular adsorption point is obtained, to the liquefaction pressure P_s of the gas at temperature T. Nitrogen isotherms for the above two temperatures have also been obtained for a pure iron and a doubly promoted iron catalyst. In all of these cases the adsorption of a given gas on a particular catalyst at two or more temperatures could be represented by a single potential curve of the type shown in Fig. 2.

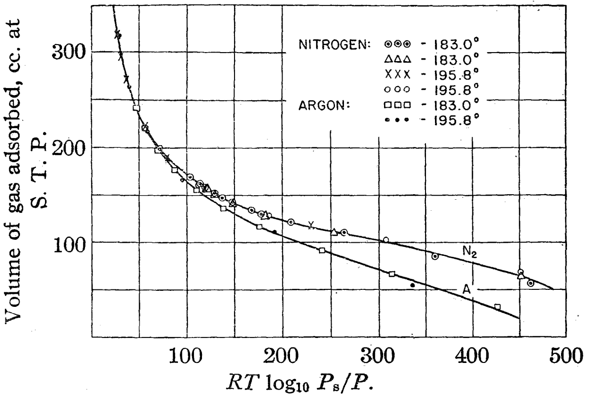


Fig. 2.—Potential–volume curves for the adsorption of nitrogen and argon on a single promoted iron synthetic ammonia catalyst.

The potential plots seem to represent the isotherms very closely throughout the entire pressure range covered, including: (a) the region concave to the pressure axis where probably less than a molecular layer of gas exists, (b) the linear portion which we have postulated represents the building up of a second layer of gas on the catalyst surface [THIS JOURNAL, **57,** 1754 (1935)], and (c) the higher pressure portion which is convex to the pressure axis and which, it is generally believed, represents the condensation of the gas to liquid in the capillaries of the adsorbent. The inclusion of this last region in the portions represented by the potential theory is rather unexpected since the theory was not intended to include such capillary condensations.

One other characteristic of the potential curves is worth noting. Polanyi and Goldman found that for their data the adsorbed mass-potential plots did not coincide at different temperatures, the higher temperature curves being slightly below the lower temperature curves in every case. They explained this displacement by postulating constancy of adsorption volume and thermal expansion of the adsorbed gas, so that less gas was required to fill the adsorption volume at higher temperatures than at lower. As shown in Fig. 2 our potential curves exhibit no such variation with temperature, the −183 and −195.8° points falling on the same curve. The significance of this result is not certain as yet.

BUREAU OF CHEMISTRY AND SOILS P. H. EMMETT
U. S. DEPARTMENT OF AGRICULTURE STEPHEN BRUNAUER
WASHINGTON, D. C.

RECEIVED NOVEMBER 1, 1935

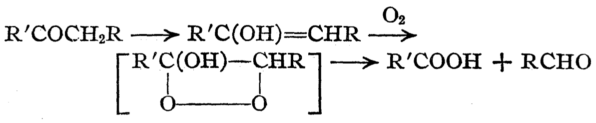
THE AUTO-OXIDATION OF KETONES

Sir:

Several ketones of the type $R'COCH_2R$ (R = phenyl) on standing in the presence of light and air for varying periods of time were observed to acquire an aldehyde-like odor. On further investigation it was found that an acid $R'COOH$ and an aldehyde $RCHO$ could be isolated.

Benzyl-2-chlorophenyl ketone, which is a liquid [Jenkins and Richardson, THIS JOURNAL, **55,** 1618 (1933)] on standing slowly solidifies and acquires a strong odor of benzaldehyde. The solid is shaken up with dilute sodium carbonate solution and extracted with ether. The aqueous layer is acidified with hydrochloric acid and 2-chlorobenzoic acid is obtained. The ether is distilled and the oil which remains is steam distilled. The distillate is treated with phenylhydrazine acetate and benzalphenylhydrazone is obtained. The solid gives a strong peroxide reaction using the test of Kharasch [Kharasch, McNab and Mayo, *ibid.*, **55,** 2523 (1933)].

The course of the reaction may be illustrated as



$$R'COCH_2R \longrightarrow R'C(OH){=}CHR \xrightarrow{O_2} \left[\begin{array}{c} R'C(OH){-}CHR \\ |\qquad\quad | \\ O{-\!-\!-\!-}O \end{array}\right] \longrightarrow R'COOH + RCHO$$

These reactions are being fully investigated and the results will be reported later.

THE CHEMISTRY DEPARTMENT OF SANFORD S. JENKINS
THE JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND

RECEIVED OCTOBER 24, 1935

CHEMICAL STUDIES ON TOAD POISONS. VIII. THE DEHYDROGENATION OF CINOBUFAGIN

Sir:

In our investigation of the chemical relationship of the bufagins (cardiac principles present in toad secretions) to the cardiac plant aglucones, possessing similar pharmacological and chemical properties, and to the sterols, it seemed of interest to ascertain whether the bufagins, on dehydrogenation with selenium, would yield methylcyclopentenophenanthrene. The formation of this hydrocarbon, $C_{18}H_{16}$, is generally considered a characteristic of the sterol ring system. Cinobufagin, $C_{25}H_{32}O_6$ [Jensen and Evans, *J. Biol. Chem.*, **104**, 307 (1934)] (the analytical data obtained for cinobufagin and certain of its derivatives would also agree with $C_{26}H_{34}O_6$ [Crowfoot, *Chem. and Ind.*, **54**, 568 (1935)]), was therefore subjected to dehydrogenation by the procedure of Diels [Diels, Gaedke and Koerding, *Ann.*, **459**, 1 (1927)]. As only a limited amount of material was available for this study, and losses were involved in the separation of compounds closely related chemically, the quantity of the hydrocarbon finally obtained was so small that a complete characterization was impossible. From the mixture of the reaction products about 10 mg. of a hydrocarbon fraction was secured which melted at 120–121°. This hydrocarbon is believed to be identical with methylcyclopentenophenanthrene. Its analytical data agree with the formula $C_{18}H_{16}$, and on mixing it with methylcyclopentenophenanthrene obtained by Elderfield and Jacobs [*J. Biol. Chem.*, **107**, 143 (1934)] by dehydrogenation of strophanthidin, no melting point depression was observed. It appears, therefore, that cinobufagin and probably also the various other bufagins contain the same ring system as the cardiac plant aglucones and the sterols. After completing this work, a paper by Ikawa [*J. Pharm. Soc. Japan*, **55**, 144 (German abstract), 748 (original Japanese) (1935)] appeared, in which he reports the isolation of the Diels hydrocarbon $C_{18}H_{16}$ from the dehydrogenation mixture of ψ-bufotaline. In this connection it might be mentioned that Wieland and Hesse [*Ann.*, **517** 22 (1935)] recently have obtained a hydrocarbon from the dehydrogenation mixture of bufotaline which they believe to be identical with chrysene. Investigations are now in progress to determine, in the bufagins, the exact nature of the side chain which contains the lactone ring.

Five grams of cinobufagin, dried at 110° *in vacuo*, was mixed with 6 g. of selenium and heated in a flask with a glass joint ascending tube for thirty-five hours at 310–320° and then for ten hours at 320–340°. The reaction mass was extracted with ether and the residue from evaporation of the solvent was subjected to fractional distillation at 12 mm. The fraction distilling at 200–230° was semi-crystalline and was fractionally recrystallized from alcohol according to the triangle scheme. After numerous crystallizations a hydrocarbon fraction was secured which melted at 120–121° and showed a m. p. of 121–122° when mixed with methylcyclopentenophenanthrene (m. p. 123–124°) prepared from strophanthidin (Elderfield and Jacobs). *Anal.* (by Dr. Ing. A. Schoeller, Berlin-Schmargendorf, Germany). Calcd. for $C_{18}H_{16}$: C, 93.05; H, 6.95. Found: C, 92.81; H, 6.82.

The author is greatly indebted to Dr. W. A. Jacobs, of the Rockefeller Institute for Medical Research, New York, for a sample of methylcyclopentenophenanthrene, and would like also to express his thanks to Dr. K. K. Chen, Lilly Research Laboratories, Indianapolis, for a supply of an extract of Ch'an Su.

LABORATORY FOR ENDOCRINE RESEARCH H. JENSEN
SCHOOL OF MEDICINE
THE JOHNS HOPKINS UNIVERSITY
BALTIMORE, MD.

RECEIVED NOVEMBER 22, 1935

THE COLLAPSE OF MONOMOLECULAR FILMS OF PALMITIC ACID UPON ACID SOLUTIONS

Sir:

When monomolecular films of palmitic acid were compressed on very pure hydrochloric acid or phosphate buffer solutions contained in a Langmuir film-pressure trough, in the range 15–20°, it was noticed that after each increment of weight had been placed in the balance pan, and the barrier advanced to establish equilibrium, a slow shrinkage followed, the area, however, finally attaining a value which was reproducible to a high degree. When the compression was carried out in this manner, with an attempt to obtain "equilibrium areas" at every point of the force–area curve, the films collapsed at a pressure apparently connected with the hydrogen-ion concentration (*i. e.*, the films could be compressed without limit when a definite pressure was reached, the value of which has been called the "collapse pressure" in the literature). When the collapse pressure values were plotted against *p*H values of the substrate (which varied from *p*H 1 to *p*H 6) an S-shaped curve resulted, similar to the percentage neutralization curve in the case of a weak organic acid in water solution. However, the mid-point of this curve was about *p*H 3, as compared to *p*H 5, the mid-point of neutralization curves of fatty acids. Since the variation of collapse pressure with *p*H may be considered as related to neutralization, this appears to be evidence of increased activity of palmitic acid when oriented on a water surface.

The collapse pressure was specific for hydrogen ions alone, although increased spread at low pressures was noticed when calcium or magnesium ions were present in the hydrochloric acid solution. A specific effect, in causing what may be either collapse or solution of the film at room temperatures, has been noticed in the case of neutral potassium permanganate solutions. This was not noticed with hydrogen peroxide, potassium ferricyanide or potassium dichromate solutions.

In view of the work of Cary and Rideal [*Proc. Roy. Soc.* (London), **A109,** 301 (1925)] on the spreading of fatty acid crystals on acid solutions, which indicates that many of the films should be thermodynamically unstable above 8 dynes, in the neighborhood of 20°, work is now in progress on a repetition of the above studies, using mixtures of higher hydrocarbons, such as tetradecane, with palmitic and other acids, to determine whether this relation between collapse pressure and hydrogen-ion concentration holds for an interface where the acid film may collapse in a reversible manner. It is planned further to apply thermodynamic interpretation, such as Harkins' spreading coefficient to the collapse phenomena. The results with the monomolecular films alone will be reported more fully in the near future, together with those obtained with mixed films.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS
ROBERT J. MYERS

RECEIVED OCTOBER 17, 1935

THE ACTIVATION OF SPECIFIC BONDS IN COMPLEX MOLECULES AT CATALYTIC SURFACES

Sir:

It has now become possible to examine the activation of specific bonds in complex molecules at catalytic surfaces, a fundamental problem in surface catalysis, that of specificity. We shall illustrate a method capable of quite general applicability by a specific example, that of the molecule ethane. In this we are concerned with two types of bond, the C–C and the C–H bond. We have followed the activation of these bonds on an active nickel surface by the study of the two reactions (a) the exchange reaction $C_2H_6 + mD_2 \longrightarrow C_2H_xD_y$ where $x + y = 6$ and m may be varied arbitrarily; (b) $C_2H_6 + H_2 = 2CH_4$. The former involves only the C–H, the latter the C–C bond, the other reactant in each case being hydrogen (or deuterium) adsorbed on the surface in the activated form. We find that, on this catalyst, the exchange reaction proceeds quantitatively at 138° under conditions in which reaction (b) is quite negligible. The production of methane sets in, under our conditions about 150° and is sensibly complete around 200°. We thus define the temperature, catalyst and reactant concentration conditions necessary to activated adsorption of ethane molecules producing either the C–H or the C–C bond split or both. By extension of these studies to other catalyst surfaces, to molecules which contain a wide variety of other bonds, *e. g.*, O–H, N–H, C–O, C–N, etc., and to varied operating conditions we plan to determine in detail the factors which produce specific activity of catalysts in general.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, N. J.
HUGH S. TAYLOR
KIYOSHI MORIKAWA
W. S. BENEDICT

RECEIVED NOVEMBER 8, 1935

SYNTHESIS OF DEUTERO-ACETALDEHYDE

Sir:

By absorbing deutero-acetylene in an acid solution of mercury salts in deuterium oxide we have succeeded in synthesizing deutero-acetaldehyde. About 25 cc. have been prepared so far. The aldehyde freed from deuterium oxide by repeated distillations at low temperatures is a colorless mobile liquid. Preliminary determinations indicate a vapor pressure of 327 mm. at 0°. It shows the usual aldehyde reactions: reducing ammoniacal silver solutions, forming a white crystalline compound with ammonia and a phenylhydrazone with phenylhydrazine.

The D_2O used in generating the acetylene and in the absorbing solution was 99.6% pure. The burning of about 2 cc. of the aldehyde over copper oxide in a current of oxygen gave D_2O of 99.2% purity, both values determined by the interferometer method.

The determination of the physical constants of this compound as well as its chemical properties is proceeding in this Laboratory.

HAVEMEYER LABORATORY
COLUMBIA UNIVERSITY
NEW YORK CITY
J. ENRIQUE ZANETTI
DARRELL V. SICKMAN

RECEIVED OCTOBER 23, 1935

NEW BOOKS

The Chemistry of Solids. By CECIL H. DESCH. The George Fisher Baker Non-Resident Lectureship in Chemistry at Cornell University. Cornell University Press, 124 Roberts Place, Ithaca, N. Y., 1934. 196 pages. 15 × 22 cm. Price, $2.50.

This volume, which contains the substance of lectures delivered by the author as George Fisher Baker non-resident lecturer in Chemistry at Cornell University, comprises seventeen chapters, of which about one half deal with topics more familiar to metallographers than to chemists, the other half with views less unfamiliar to chemists than to metallographers. It brings together and examines, from a single viewpoint, a great deal of diverse information; its style is clear and simple, as would be expected by those familiar with the author's publications; and altogether it is to be recommended as a very interesting readable book which deserves to be widely read and pondered. For this general subject of the make-up and behavior of solids touches every one interested in physical science, pure or applied; far less is known about it than is commonly supposed, and much remains to be ascertained before we can claim to have even a passable knowledge and command of the behavior of solids. Perusal of this book should stimulate a more widespread interest in these important questions.

JOHN JOHNSTON

Life and Experiences of a Bengali Chemist. Vol. II. By PRAFULLA CHANDRA RÂY. Chuckervertty, Chatterjee and Company, Ltd., 15 College Square, Calcutta, India, 1935. viii + 469 pp. 15 × 22.5 cm. Price, 6s.

A review of the first Volume of this autobiography of Rây has already appeared in THIS JOURNAL (**55**, 1298 (1933)). This second and concluding Volume contains a collection of the author's essays on diverse educational, political, social and economic problems of Hindu civilization.

In the Introduction the author assures us that . . . "throughout my active career, now extending over half-a-century, I have served Chemistry as the Goddess of my idolatry; to her I have been a whole-hearted devotee . . . ." In spite of this, it is evident that the author has also been an active participant in the public life of his country.

These essays are written in a spirited and lucid style, and like the more connected contents of the previous Volume, disclose a keen and courageous personality, passionately devoted to the welfare of India.

ARTHUR B. LAMB

BOOKS RECEIVED

October 15, 1935–November 15, 1935

ARTHUR K. ANDERSON. "Essentials of Physiological Chemistry." John Wiley and Sons, Inc., 440 Fourth Ave., New York, N. Y. 257 pp. $2.75.

A. A. BENEDETTI-PICHLER and W. F. SPIKES. "Introduction to the Microtechnique of Inorganic Qualitative Analysis." Microchemical Service, 30 Van Zandt Ave., Douglaston, New York. 180 pp. $3.00.

H. E. CLEAVES and J. G. THOMPSON. "The Metal—Iron." Published for the Engineering Foundation by McGraw-Hill Book Company, Inc., 330 West 42d St., New York, N. Y. 574 pp. $6.00.

ALEXANDER FINDLAY. "The Teaching of Chemistry in the Universities of Aberdeen." The Aberdeen University Press, Ltd., 6 Upperkirkgate, Aberdeen, Scotland. 92 pp.

W. A. KOEHLER. "Principles and Applications of Electrochemistry. Vol. II. Applications." John Wiley and Sons, Inc., 440 Fourth Ave., New York, N. Y. 545 pp. $5.00.

A. C. LEEMANN. "Le Pausoma et la Géométrie de l'Énergie." Georg & Co., S. A. Libraires—Éditeurs, Corraterie 5, Genève, Switzerland. 257 pp. Francs suisses 15.

PRAFULLA CHANDRA RÂY. "Life and Experiences of a Bengali Chemist." Vol. II. Chuckervertty, Chatterjee & Co., Ltd., 15 College Square, Calcutta, India. 469 pp. $1.50 or 6s.

"Richter-Anschütz Chemie der Kohlenstoffverbindungen. Carbocyclische Verbindungen, Naturstoffe und freie organische Radikale. Zweite Hälfte. Aromatische Verbindungen. Freie organische Radikale." Akademische Verlagsgesellschaft m. b. H., Markgrafenstrasse 6, Leipzig C 1, Germany. 915 pp. RM. 54; bound, RM. 56.

"Statistical Appendix to Minerals Yearbook, 1934." Bureau of Mines, U. S. Department of the Interior. Superintendent of Documents, Government Printing Office, Washington, D. C. 434 pp. $1.00.

"Suggestions to Authors of Papers Submitted for Publication by the United States Geological Survey." Fourth edition. Superintendent of Documents, Government Printing Office, Washington, D. C. 126 pp. $0.15.

ADDITIONS AND CORRECTIONS

Notice to Readers.—For the convenience of those who may wish to cut out the corrections and attach them to the margins of the articles corrected, they have been printed only upon one side of the page.

1932, Vol. 54

Aliphatic Tertiary Alcohols and Chlorides Containing the Normal Amyl Group and the Related Olefins and their Ozonolysis. By Frank C. Whitmore and F. E. Williams.

Page 408. "The density reported for tri-*n*-amylcarbinol, d^{25}_{4} 0.8293, was abnormally low when compared with those recorded for other di-*n*-amylcarbinols. The refractive index, n^{20}_{D} 1.4470, was recorded for the same carbinol.

"A more recent preparation of tri-*n*-amylcarbinol showed d^{25}_{4} 0.8349, which is in complete accord with the densities of the homologs. The refractive index obtained on the present sample, n^{20}_{D} 1.4484, indicates that the first sample of carbinol contained olefin."—Frank C. Whitmore, F. E. Williams and A. H. Popkin.

The Photolysis of Hydrogen Peroxide in Aqueous Solution. By Lawrence Joseph Heidt.

Page 2842. Table I, col. 5, "I/I_0" should read: 100 I/I_0.

Line 19 of the text, $\epsilon(1/cd \log I/I_0$. . . should read $\epsilon = (1/cd)$ [log (I_0/I)].

Line 20, cm.), should read: cm., .

Line 23, "Using the method of Forbes, Heidt and Boissonannas[10]" should read: Using the method described in later work by the author.[10]. . ."—Lawrence Joseph Heidt.

1933, Vol. 55

The Desoxymorphines. By Lyndon F. Small and David E. Morris.

Page 2885. In the seventh line from the top $[\alpha]_{\mathrm{D}}$ $-118.8°$ should read $[\alpha]_{\mathrm{D}}$ $+118.8°$.—Lyndon F. Small.

1934, Vol. 56

Low Pressure Data of State of Nitric Oxide and of Nitrous Oxide between their Boiling Points and Room Temperature. By Herrick L. Johnston and Harry R. Weimer.

Page 628. A misplaced decimal point occurs in the second term of Equation (6). The coefficient of this term should be 56115.0.—H. L. Johnston.

The Interaction of the Acid Chloride of 2-Benzoylbenzoic Acid with Phenols. II. Diarylphthalides. By F. F. Blicke and R. D. Swisher.

Page 924. The third phthalide in Table I should be named 2′-hydroxy-5′-bromodiphenyl instead of 2′-hydroxy-4′-bromodiphenyl.—F. F. Blicke.

The Vapor Pressure of Certain Ketones. By M. Glenn Mayberry and John G. Aston.

Page 2682. ". . . The range of the measurements was not given due to an oversight in revision. This was approximately the same for all ketones and extended from room temperature to the boiling point except in the case of the ketones of lower vapor pressure, when the range was from 10 or 20 mm. to 735 mm. In one exceptional case, namely, that of diisopropyl ketone, the range was 49–123°."—J. G. Aston.

1935, Vol. 57

Preparation of Deuterium Free Water. Deuterium Content of Ordinary Water and the Atomic Weight of Hydrogen. Electrolytic Separation of the Oxygen Isotopes. By Herrick L. Johnston.

Page 485. "Dr. Malcolm Dole has kindly called our attention to the significance of a small correction for thermal expansion of the Pyrex float, which we did not apply in our original computations. With this correction applied, which amounts to 11 p. p. m. in density for each full degree of temperature (or 4.0% on the uncorrected density increments), our figure 19.1 ± 1 p. p. m. should be replaced by 18.3 ± 1 p. p. m.

"There was also a small computation error in the H/D ratio, 5750 ± 250. The correct H/D ratio, computed for the density difference of 18.3 ± 1 p. p. m., is 5815 ± 250, based on Taylor and Selwood's value, 1.1079, for the density of pure D_2O or 5790 ± 250, based on the value 1.1074 recently published by Tronstad, Nordhagen and Brun [*Nature*, **136**, 515 (1935)]. Obviously 5800 ± 250 is the best representation of our results. These computations take account of the slight non-additivity of D_2O and H_2O volumes found by Luten [*Phys. Rev.*, **45**, 161 (1934)].

"These slight changes are without significance in the further computations in our paper."—H. L. Johnston.

Heat Capacities and Dissociation Equilibria of Gases. By Bernard Lewis and Guenther von Elbe.

Page 612. "Due to several typographical errors and also to the recent exact determination of the $'\Delta$ level of the oxygen molecule by spectroscopic methods as 0.97 volt [Herzberg, *Nature*, **133**, 759 (1934); Ellis and Kneser, *Phys. Rev.*, **45**, 133 (1934)] we wish to make corrections to Table I of this paper. The new oxygen values are obtained by adding $^3/_2$ RT to the numbers given in Table II of Johnston and Walker's paper [This Journal, **57**, 682 (1935)]. We have improved the values for other molecules by a more precise method of interpolation for temperatures intermediate between published values. In the revised table given herewith the values of NO, O_3, Br_2 and HBr are omitted because they could not be improved upon.

"Log K of oxygen at 5000°K. in Table II should read 1.715."—Bernard Lewis.

ENERGY CONTENT ($E^\circ_T - E^\circ_0$) OF GASES

Temp, °K.	H_2	O_2	N_2	CO	OH	CO_2	H_2O
200	965	987	992	992	...	...	1192
250	1197	...	...	...	...	...	...
300	1440	1486	1489	1489	1523	1660	1791
400	1936	1998	1987	1989	2034	2403	2409
600	2936	3088	3006	3017	3048	4135	3687
800	3947	4265	4078	4110	4069	6107	5073
1000	4978	5511	5216	5270	5118	8247	6577
1200	6044	6802	6410	6485	6200	10503	8200
1400	7151	8123	7646	7741	7340	12844	9920
1600	8293	9476	8912	9025	8525	15246	11740
1800	9478	10852	10207	10334	9740	17698	13655
2000	10700	12248	11528	11665	10985	20187	15650
2200	11954	13667	12857	13011	12255	22703	17700
2400	13234	15110	14200	14365	13565	25248	19800
2600	14545	16570	15550	15725	14890	27819	21945
2800	15881	18049	16914	17096	16235	30406	24125
3000	17231	19544	18287	18476	17607	33012	26330
3200	18593	21061	19668	19860	19000		
3500	20650	23366	21743	21947	21105		

Homoamines and Homoacids. By Percy L. Julian and Bernard M. Sturgis.

Pages 1126–1127. "An unfortunate omission in our details concerning the preparation of rhodanine has just been discovered. After precipitating a mixture of thiocarbamylthioglycolic acid and rhodanine (not pure rhodanine) with the hydrochloric acid heated to 80–90°, the precipitate is filtered, dissolved in the least possible quantity of warm glacial acetic acid and boiled for five minutes. From this cooled solution the rhodanine separates fairly pure, and may be recrystallized either from alcohol or from glacial acetic acid. The latter is preferable." —PERCY L. JULIAN and BERNARD M. STURGIS.

Arsenated Phenoxyethanols. By Melvin R. Stevinson and Cliff S. Hamilton.

Page 1601. In Table I, for Compound 9 (sodium salt of 7), the calculated percentage of arsenic should be 23.93 instead of 23.65.—MELVIN R. STEVINSON.

The Photolysis of Dry Ozone at λλ208, 254, 280 and 313 mμ. II. Reaction Kinetics. By Lawrence Joseph Heidt.

Page 1711. Col. 1, line 31, "log $I_0/I/p_{O_3}d$" should read: [log $(I_0/I)]/p_{O_3}d$. Col. 2, line 38, "the data of" should read: "the plots of the data of . . . ."

Page 1713. The first sentence of the legend under Fig. 1, should read: The curves resulted from calculations based upon our hypothesis. Col. 1, line 1, "The curves are hypothetical" should read: "The curves resulted from calculations based upon the hypothesis below." Col. 2, lines 16 and 17, "...in the presence of" should read: "...compared to that of...."

Page 1714. Col. 1, line 22, "$i = 0.14 \pm 1$" should read: "$i_{\text{minimum}} = 0.14 \pm 1$. Col. 1, footnote, line 3, "$1/\phi$ with p_{O_2}/p_{O_3}" should read: "$1/\phi$ against p_{O_2}/p_{O_3}." Col. 2, line 22, "...difference between the long wave length...." should read: "difference between the energies corresponding to the long wave length...."

Page 1715. Col. 2, line 5, "...varies widely..." should read: "...varied widely...," and, "It is approxi-" should read: "It was approxi-." Col. 2, line 17, "...also $k_3/k_2 \ll 1$..." should read: "...also from the data, $k_3/k_2 \ll 1$...."

Page 1716. Col. 1, after paragraph ending with "...heated to softness." Insert the following paragraph: "The large erratic fluctuations in the experimentally determined values of $1/\phi$ may now be attributed mainly to the enormous momentary fluctuations in the light intensity during the course of an experiment when the spark was used as a light source. This was reassuring in view of the care taken to improve the accuracy of the results."—LAWRENCE JOSEPH HEIDT.

Androsterone (Communication to the Editor). By Russell E. Marker.

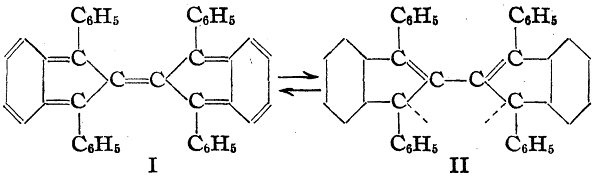
Page 1755. "In Table I, one important transformation was omitted, namely, the conversion of beta-cholestanol by means of thionyl chloride to alpha-cholestyl chloride."—RUSSELL E. MARKER.

The Decomposition of Nitramide in Acid and Salt Solutions. By Charles A. Marlies and Victor K. La Mer.

Page 1812. The characteristic of log $k^*_{\text{corr.}}$ in Fig. 3 should be one arithmetical unit smaller, the total range in the diagram being −5.8 to −3.0.—CHARLES A. MARLIES.

The Synthesis of Bis-2,2′-(1,3-diphenylindenol-3). A Contribution to the Rubrene Problem. By J. C. Eck and C. S. Marvel.

Page 1898. The formulas in the reaction shown in column two are erroneously printed and should be



I II

See also in this connection the Communication to the Editor, by A. Schönberg, to appear in the January, 1936, JOURNAL.—C. S. MARVEL.

Acetylene Polymers and their Derivatives. XXXIII. Cyano-4-butadiene-1,3. By Donald D. Coffman.

Page 1982. In the second paragraph of the Experimental Part, the *MR* (obsd.) of cyano-4-butadiene-1,3 is recorded as 24.57. This is erroneous and as a matter of fact this value is 26.40, which agrees well with the structure of the compound, which, because of its progressively conjugated system of three multiple bonds, should have considerably increased refraction.—DONALD D. COFFMAN.

Author Index to Volume LVII, 1935[1]

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[1] This index was prepared in the Editorial Offices of *Chemical Abstracts* through the courtesy of E. J. Crane and under his direction.

Subject Index to Volume LVII, 1935[1]

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