Pyridine.—No reaction took place with this reagent and the high-melting bromide in ether or alcohol even after long boiling. The low-melting bromide with the same reagent gave a trace of unsaturated compound after boiling for 5 hours in alcohol; the rest of the material was unchanged.

Summary

1. Diphenylchlorophosphine reacts with benzaldehyde and benzalacetophenone in the presence of glacial acetic acid. The products are an hydroxy and a keto-phosphine oxide, respectively.

2. The mechanism of the reaction with the unsaturated ketone has been established, as in the previous work with the trichloride, by using acetic anhydride. With this reagent an unsaturated intermediate compound is formed; it combines with bromine and after treatment with water yields 2 stereo-isomeric α-bromo-keto-phosphine oxides.

3. The stereo-isomeric bromides on treatment with alkaline reagents either lose hydrogen bromide or are reduced to the halogen-free keto-phosphine oxide. A study of the behavior of 2 pairs of closely related isomeric bromides has shown that each isomer may either be reduced or lose hydrogen bromide, according to the reagent employed.

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

THE OXIDATION OF PROPYLENE GLYCOL WITH POTASSIUM PERMANGANATE[1]

BY WILLIAM LLOYD EVANS

Received July 31, 1922

The experiments described here are a continuation of a series of oxidation studies being made in this Laboratory, the principal purpose of which is to establish from exact quantitative data the molecular stages through which organic compounds of the more simple structure pass when they undergo this type of chemical change. Obviously many factors, such as temperature, the nature of oxidizing agents, concentration of reacting materials and time, exercise a marked influence on the nature of the results obtained both from the qualitative and quantitative standpoints. The oxidation of propylene glycol with potassium permanganate in both neutral and alkaline solutions has been previously studied by Witzemann and the author.[2] The results of those experiments showed that carbon dioxide, acetic and oxalic acids were the final oxidation products in alkaline solutions, while carbon dioxide and acetic acid were the only products obtained in neutral solutions. In this paper an account is given of the results that were obtained by the oxidation of propylene glycol at conditions of con-

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[1] This paper was read at the Chicago Meeting of the American Chemical Society, 1920.

[2] Evans and Witzemann, THIS JOURNAL, 34, 1086 (1912).

stant temperature, 50° and 75°, and with various concentrations of alkali. Qualitatively, the final oxidation products were found to be the same as those which were obtained previously.

Experimental Part

Materials.—The propylene glycol used in these experiments was imported. A standard solution containing 152 g. (2 moles) per liter was made from the fraction boiling at 86° at 12 mm. These experiments were carried out essentially in the same manner as those which have been described by Day, Adkins, Hoover, Sefton,[3] and the author. After the oxidizing mixture, consisting of 30 g. of potassium permanganate and the chosen amount of alkali dissolved in a liter of carbon-dioxide-free water, had attained the temperature of the thermostat, 20 cc. of the standard solution of propylene glycol was immediately added. In contradistinction to acetol, there is no marked local heating on the addition of the propylene glycol solution. The usual precautions were taken with reference to ascertaining the oxidizing value of the permanganate, the content of carbon dioxide of the water and alkali, and the volatile component content of the phosphoric acid used in the distillation of acetic acid.

Analysis.—The usual methods of analysis were employed in the determination of carbon dioxide, and acetic and oxalic acids.

Results.—The results which were obtained by calculating all the experimental data to the basis of a solution containing a 0.1 mole of propylene glycol at the same concentration as was actually used (3.04 g. per 1020 cc.) are shown in Fig. 1, from which can be seen the general effect of both temperature and concentration of alkali upon the amount of the various oxidation products obtained. The materials at 50° were allowed to interact for 192 hours, those at 75°, 48 hours.

Theoretical Part

In order to ascertain the mechanism followed in the oxidation reactions of propylene glycol, the various dissociation possibilities of this alcohol may be considered. These may be represented by the following equations.[4]

$$\mathrm{CH_3.CHOH.CH_2OH \rightleftharpoons CH_3.CH_2OH + CH_2O} \qquad (1)$$

$$\mathrm{CH_3.CHOH.CH_2OH \rightleftharpoons CH_3.CHO + CH_3OH} \qquad (2)$$

$$\mathrm{CH_3.CHOH.CH_2OH \rightleftharpoons CH_3.CHOH.CH{<} + H_2O} \qquad (3)$$

$$\mathrm{CH_3.CHOH.CH_2OH \rightleftharpoons CH_3.\overset{\vee}{C}.CH_2OH + H_2O} \qquad (4)$$

$$\mathrm{CH_3.CHOH.CH_2OH \rightleftharpoons CH_3.\underset{\wedge}{C}.CH{<} + 2H_2O} \qquad (5)$$

In addition to these, there are four other ways in which this compound may react, when considered from the standpoint of the methyl group. All of these would lead to reactions which would result in the absence of acetic acid, an oxidation product which was present in both neutral and alkaline solutions.

Acetic acid and carbon dioxide are the sole reaction products when propylene glycol is oxidized with neutral permanganate solutions at 50° and 75°. In considering the above dissociation equations in connection

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[3] Evans and others, THIS JOURNAL, (a) **41,** 1267, 1385 (1919); (b) **44,** 1730 (1922); (c) **44,** 2271, 2276 (1922).

[4] (a) Nef, *Ann.*, **335,** 191, 303 (1904). (b) Ref. 2, p. 1101. (c) Evans and Morgan, THIS JOURNAL, **35,** 54 (1913).

with the oxidation mechanism of propylene glycol, it is necessary to know the behavior of the various dissociation products towards the oxidizing agent used.

Equations 1 and 2.—Ethyl alcohol and acetaldehyde are oxidized exclusively to acetic acid in neutral permanganate solutions[5] at 50° and 75°, while carbon dioxide is the final oxidation product of both formaldehyde and methyl alcohol with the same reagent. Hence, the reactions indicated by Equations 1 and 2 would seem to account for the formation of acetic acid and carbon dioxide from propylene glycol, were it not for the known facts in reference to the behavior of aqueous solutions of propylene glycol towards silver oxide both in the absence and presence of alkalies. Witzemann[6] found that propylene glycol was oxidized by these reagents to acetic acid and carbon dioxide although the reactions were apparently incomplete. Furthermore, it was found that ethyl and methyl alcohol were unacted upon with silver oxide both in the presence and absence of alkalies. Witzemann also showed that formic acid was not present as an oxidation product of propylene glycol with silver oxide, although this acid was always present with carbon dioxide when formaldehyde was oxidized under the same conditions. In the presence of alkalies formic acid was the only oxidation product of formaldehyde with silver oxide. Therefore, it is clear from these facts that propylene glycol does not exist in either neutral or alkaline solutions in the state of dissociation indicated by Equations 1 and 2, and hence these equations are rigidly excluded as possible mechanisms in the oxidation of propylene glycol. Furthermore, the reactions indicated by Equations 1 and 2 would not account for maxima in the curves for carbon dioxide.

Equations 3, 4 and 5.—The first oxidation product arising from the dissociation indicated in Equation 3 would be lactic aldehyde; in Equation 4, acetol; in Equation 5, pyruvic aldehyde. Although the action of alkaline permanganates towards lactic and pyruvic aldehydes is not known, it is undoubtedly the same as that towards lactic and pyruvic acids, the soluble salts of which are oxidized to carbon dioxide, acetic and oxalic acids by this reagent. These are also the oxidation products of propylene glycol with alkaline permanganate and hence, on the basis of the results obtained solely from the use of neutral and alkaline permanganates, no definite choice can be made between Equations 3, 4 and 5, as to the one expressing the exact course followed in these reactions.

Pyruvic aldehyde may arise in the oxidation of propylene glycol from the following sources: (a) the oxidation of lactic aldehyde (Equation 3), the oxidation of acetol[2,3b] (Equation 4), and by the simultaneous oxidation

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[5] Ref. 3a, pp. 1273, 1390.

[6] The Oxidation of Propylene Glycol, p. 26, *Dissertation*, The Ohio State University, 1912.

of the primary and secondary groups (Equation 5). The pyruvic aldehyde so formed would be converted by means of alkalies into lactic acid. Since lactates are oxidized to pyruvates by means of permanganates,[7] and furthermore since lactates and pyruvates[2] are in turn oxidized by alkaline permanganates to the same final oxidation products as propylene glycol, it is clear that lactic and pyruvic acids are two of the intermediate compounds formed in these oxidations. The same result would be obtained by the direct oxidation of lactic aldehyde to lactic acid or to the rearrangement of lactic aldehyde to acetal. The mechanism whereby oxalic acid is obtained as one of the final oxidation products of pyruvic acid has been recently pointed out in a paper by Hoover[8] and the writer, in which it was shown that pyruvic acid is oxidized to oxalic acid and carbon dioxide through the successive formation of hydroxy-pyruvic, formylglyoxylic, and glyoxylic acids. As is well known, pyruvic acid is oxidized in part to acetic acid and carbon dioxide.

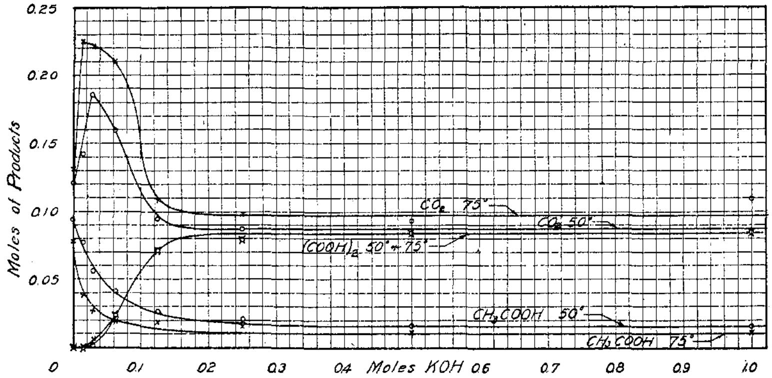

Fig. 1.—Effect of temperature and alkali on the formation of carbon dioxide, oxalic and acetic acids from 0.10 mole of propylene glycol.

In these experiments it was found that more than one carbon atom equivalent (0.1 mole) of carbon dioxide is formed in the oxidation of propylene glycol at certain concentrations of alkali (See Fig. 1). If it is true that lactic and pyruvic acids are intermediate compounds in the oxidation of propylene glycol, then these two acids should also yield more than one carbon atom equivalent of carbon dioxide when they are oxidized under the same conditions as were used here. In some earlier experiments Witzemann and the writer[9] found that these acids were really oxidized in the same manner with the formation of this excessive amount of carbon dioxide. Nef[10] found that lactic acid was one of the products of reaction

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[7] Beilstein and Wiegand, *Ber.*, **17**, 841 (1884).

[8] Ref. 3b, p. 1739.

[9] Ref. 2, pp. 1097, 1099; Ref. 6, p. 33.

[10] Ref. 4a, pp. 305–306.

of alkalies on propylene glycol at 200–230°. In some experiments[11] on the oxidation of propylene glycol with silver oxide and silver chloride in the presence of soluble bases he obtained carbon dioxide, acetic acid, and small amounts of a product resembling lactates.

An examination of Fig. 1, shows that acetic acid and carbon dioxide would be the sole oxidation products of propylene glycol, were it not for the presence of increasing concentrations of alkali. When the concentrations of the alkali reach a definite value, vinyl alcohol is present, due to the action of alkalies on the acetaldehyde formed from the dissociation of lactic and pyruvic aldehyde, and acetol. The vinyl alcohol so formed is immediately oxidized by permanganates to oxalic acid and carbon dioxide. The increase in oxalic acid production is accompanied by a decrease in that of carbon dioxide. The maximum in the carbon dioxide production is due to the direct oxidation of pyruvic aldehyde to pyruvic acid from which hydroxypyruvic acid may be obtained. In neutral solutions and in those of low alkalinity, hydroxypyruvic acid is dissociated into glyoxylic acid and formaldehyde, which in turn are oxidized exclusively to carbon dioxide. As the concentration of the alkali is increased, the dissociation in this direction is decreased, and the reactivity of the primary alcohol[12] group of hydroxypyruvic acid is greatly increased, thus leading to the formation of formylglyoxylic acid.

Summary

1. Propylene glycol is oxidized with neutral permanganate solutions at 50° and 75° to acetic acid and carbon dioxide. Above certain minimum concentrations of alkali, oxalic acid is also an oxidation product.

2. Lactic and pyruvic acids are probably 2 of the intermediate compounds formed in these oxidations. The lactic acid arises from either (a) the oxidation of lactic aldehyde, or (b) the rearrangement of pyruvic aldehyde in the presence of alkalies. Pyruvic acid is an oxidation product of lactic acid.

3. The acetic acid in these oxidations is probably obtained from two sources: (a) the oxidation of acetaldehyde, which is present as a dissociation product; (b) the oxidation of pyruvic acid.

4. The oxalic acid is probably formed as follows: (a) the oxidation of glycolic acid obtained by the oxidation of vinyl alcohol; (b) the oxidation of glyoxylic acid which is formed from pyruvic acid by the successive formation of dioxypyruvic and formylglyoxylic acid.

5. Carbon dioxide is probably formed as follows: (a) by the oxidation of formaldehyde; (b) by the oxidation of pyruvic acid; (c) by the oxidation of glyoxylic acid, which in neutral solutions and those of exceedingly small concentrations of alkali is converted exclusively to carbon dioxide.

[11] Ref. 4a, pp. 312–315.

[12] Ref. 4a, p. 313.

6. The effect of temperature is to increase the carbon dioxide production and diminish that of acetic acid.

7. The alkali functions as follows: (a) it neutralizes the acids formed; (b) it increases the enolization of acetaldehyde and pyruvic acid; (c) it causes the rearrangement of pyruvic aldehyde to lactic acid. As the concentration of the alkali is increased the dissociation of the 3-carbon atom compounds into 2 other compounds is suppressed in that direction. This is caused by the increased reactivity of the alcohol groups in propylene glycol, due to the lower point of dissociation of the alcoholates formed in comparison with that of the alcohol itself.

In conclusion the author desires to thank the following persons: Mr. Paul R. Hines, whose valuable assistance has made this work possible, and Dr. J. E. Day of the University of Wisconsin and Mr. W. R. Stemen, for some earlier preliminary investigations with propylene glycol and potassium permanganate.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

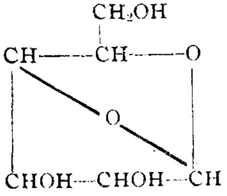
STUDIES ON CELLULOSE CHEMISTRY

II. THE ACTION OF DRY HYDROGEN BROMIDE ON CARBOHYDRATES AND POLYSACCHARIDES[1,2]

BY HAROLD HIBBERT AND HAROLD S. HILL

Received August 17, 1922

The theoretical considerations as to the constitution of cellulose put forward by one of us[3] some two years ago were based on the supposition that its reactions are explained most satisfactorily on the assumption that it represents a polymerized form of an anhydro glucose, which was termed the cellulose "nucleus" [I]. Cotton cellulose is to be regarded as a polymeric form of this (II).



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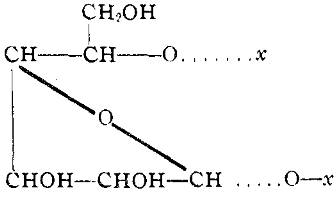

II

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[1] This paper is constructed from Part I of a dissertation presented by Harold Sanford Hill in June, 1922, to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy. The thesis gves a review of previous work on the conversion of carbohydrates and polysaccharides into furfuraldehyde derivatives.

[2] Communicated to the Cellulose Section of the American Chemical Society, at the Rochester Meeting, April, 1921.

[3] Hibbert, *J. Ind. Eng. Chem.*, **13**, 256, 334 (1921).