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

THE MECHANISM OF CARBOHYDRATE OXIDATION. III. THE OXIDATION OF THE HEXITOLS *d*-MANNITOL, *d*-SORBITOL AND DULCITOL

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In view of the results that have been obtained[2] with *d*-glucose, *d*-mannose *d*-galactose, and *d*-fructose it became of much interest to ascertain the behavior of these more commonly known hexahydric alcohols when they were oxidized with neutral and alkaline potassium permanganate under the same experimental conditions that were used with the carbohydrates mentioned above. In the preceding paper it was pointed out that the oxidation products of the glucose (mannose) series and the allose (altrose) series *would probably show different quantitative relationships* when oxidized with permanganates at the lower concentrations of alkali, while at the higher concentrations of the base these relationships should be practically identical. The same general relationship was also predicted for the galactose (talose) series and the gulose (idose) series of carbohydrates. From a consideration of the formulas of *d*-mannitol, *d*-sorbitol, and dulcitol, it is clear that the oxidation of only one of the primary alcohol groups in these compounds will yield optical antipodes in the case of both *d*-mannitol and dulcitol, and two different aldohexoses, namely *d*-glucose and *l*-gulose, in the case of *d*-sorbitol. It has previously been shown[3] that *d*- and *l*-arabinose behave in a practically identical manner when they are oxidized with neutral and alkaline permanganate. Hence, it is fair to assume that the mannose optical antipodes as well as those of galactose should comport themselves similarly. In the case of *d*-sorbitol it is clear that the yield of a given oxidation product depends on the manner in which the *d*-sorbitol is attacked; that is (a) whether it would be oxidized exclusively to either *d*-glucose alone or *l*-gulose alone, or to a mixture of both aldohexoses, or (b) whether both primary alcohol groups are oxidized simultaneously. To shed light on this matter was one of the reasons for studying *d*-sorbitol. Should these hexitols be oxidized only at one end of the carbon chain, then it is obvious that the general mechanism of oxidation should be the same as that of the corresponding aldohexoses. To ascertain whether this was true was one of the main purposes of these experiments.

Experimental Part

Materials and Procedure.—The dulcitol, *d*-sorbitol and *d*-mannitol were purchased

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[1] Du Pont Fellow, 1923.

[2] See preceding papers, THIS JOURNAL, 47, (a) 3085, (b) 3098 (1925).

[3] THIS JOURNAL, 47, 3090 (1925).

on the market with the assurance that they were of the very highest degree of purity. These claims were verified experimentally. The experimental conditions, methods of oxidation and analytical procedure were exactly the same as those employed in previously reported investigations of this character.[4] The temperatures chosen were 25°, 50° and 75°. The oxidation mixture was of such a character that it contained 14 g. of potassium permanganate (98.7%) and the alkali of chosen normality in 500 cc. of water. This amount of permanganate was slightly in excess of that necessary to convert all of the carbon of the hexitols to carbon dioxide. On account of the cost of the materials to be oxidized, a flask was calibrated to contain 102 cc. Four burets were calibrated to deliver 25 cc. when *completely drained.* The concentration of the hexitol solution was such that 25 cc. of it contained the amount (1.8214 g.) to be oxidized. This weight (0.01 mole) of the hexitols contains the same amount of carbon as do the portions of hexoses previously studied under the same experimental conditions. Then by making four oxidations simultaneously, it was possible to utilize 100 out of every 102 cc. of solution prepared.

Results.—The qualitative results obtained in these experiments were the same as those found for *d*-glucose, *d*-mannose, *d*-galactose and *d*-fructose. As with these carbohydrates, oxalic acid, carbon dioxide and a trace of a volatile substance calculated as acetic acid were the final reaction products. In a later paper it will be shown that this acid is undoubtedly acetic. In neutral solutions no oxalic acid was present, the hexitols being oxidized practically quantitatively (98%) to carbon dioxide. In alkaline solutions oxalic acid was always present as a final reaction product. The results obtained in these oxidations showed a carbon return ranging from 97.6 to 101.9%, the average of all our work being 99.8%. Our general experience proved that the hexitols were more resistant to oxidation than were the familiar hexoses. All of our data are shown in the accompanying figures in which the carbon equivalents of the oxidation products are expressed as functions of the alkali

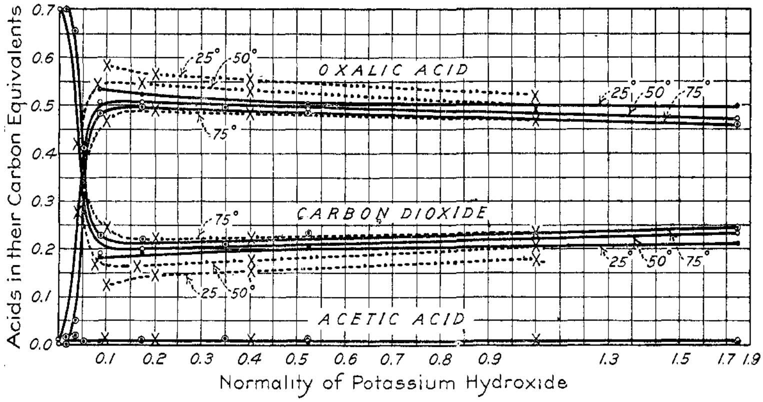

Fig. 1.—Oxidation of *d*- galactose (X) and dulcitol (●, ○, ◉) at 25, 50 and 75°.

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[4] This Journal, 47, 3088 (1925).

normality. Previously published results on the oxidation of *d*-mannose, *d*-glucose and *d*-galactose are quoted in the diagrams for *d*-mannitol, *d*-sorbitol and dulcitol, respectively.

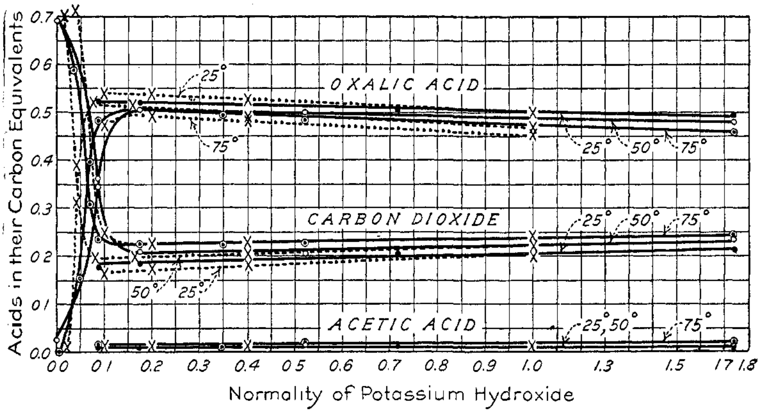

Fig. 2.—Oxidation of *d*-glucose (X) and sorbitol (●, ○, ◉) at 25, 50 and 75°.

In conclusion we wish to thank E. I. du Pont de Nemours and Company whose kindly interest and good will have made this work possible.

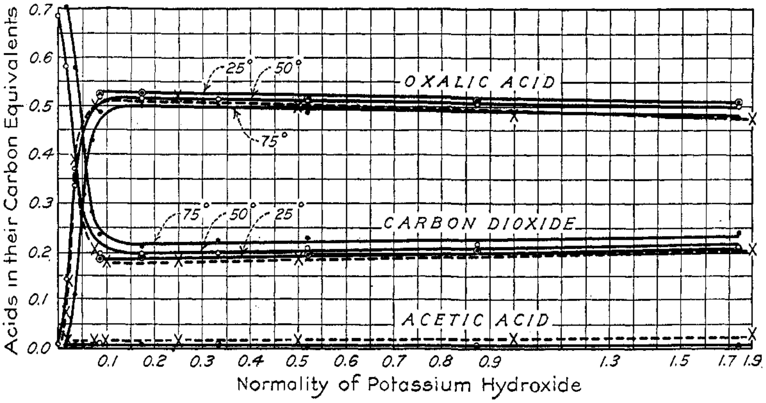

Fig. 3.—Oxidation of *d*-mannose at 50° (X) and *d*-mannitol at 25, 50 and 75° (◉, ○, ●).

Discussion and Summary

1. The graphical representation of our results points very strongly to the conclusion that the hexitols are oxidized by neutral and alkaline potassium permanganate through the intermediate formation of aldohexoses. Were the reaction taking place by the simultaneous oxidation of both primary alcohol groups in the hexitol molecule, the yield of carbon dioxide would be much higher than it is in the case of the corresponding carbohydrates.

2. Furthermore, the results obtained in the oxidation of *d*-sorbitol show that this hexitol is oxidized through the intermediate formation of *d*-glucose rather than *l*-gulose. Were the latter aldohexose involved wholly or in part, the curve for oxalic acid should bear some resemblance to that for *d*-galactose under the same conditions.[2b]

3. The points of view given in Paragraphs 1 and 2 of this summary find confirmation in the literature of this field of work. When Fenton[5] oxidized *d*-mannitol, *d*-sorbitol, and dulcitol with hydrogen peroxide in the presence of ferrous sulfate he obtained osones which were converted into the osazones of *d*-mannose, *d*-glucose and *d*-galactose, respectively. Fischer[6] treated *d*-sorbitol with bromine water and obtained a sugar which formed glucosazone. He obtained a sugar from mannitol which gave the same osazone. More recently Votocék and Krauz[7] have shown that aqueous solutions of mannitol are oxidized to a mixture of mannose and fructose with nitrous acid fumes. This is exceptionally interesting because it shows the stability of the primary alcohol group even under the acid condition used by these investigators.

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ADDITIONS AND CORRECTIONS

1924, VOLUME 46

The Adsorption of Arsenious Acid by Hydrous Aluminum Oxide, by John H. Yoe.

Pp. 2393 and 2394. In Figs. 1 and 4, the ordinates should read, "0.1, 0.2, 0.3," etc., instead of "10, 20, 30," etc.

1925, VOLUME 47

The Solubility of Ferrous Hydroxide and its Effect upon Corrosion, by W. G. Whitman, R. P. Russell and G. H. B. Davis.

P. 74. In lines 25 and 26, instead of "formation of ferrous hydroxide from the elements," read "formation of ferrous hydroxide from iron, oxygen and water."

In lines 27 and 28, in place of "$-(I/N_a + I/N_k) \times 0.0591 \log K$," read "$-(0.0591/2) \log (Fe^{++})(OH^-)^2$," and in place of "$-1.5 \times 0.0591 \times (-4.4)$," read "$-(0.0591/2) \times (-13.5)$."

P. 77. In Fig. 9, the word "Initial" should be inserted, so that the abscissas will read, "Initial *P*H of NaOH solutions."

The Activity Coefficients of Hydrochloric Acid in Solutions of Ethyl Alcohol, by Herbert S. Harned and Maurice H. Fleysher.

P. 89. In line 18, instead of "log γ is inversely proportional to the dielectric constant," read "log γ is inversely proportional to the three-halves power of the dielectric constant." Equation 2 should read, "$\log \gamma_1/\log \gamma_2 = (D_2/D_1)^{3/2}$." If, according to the following paragraph, $1/D^{3/2}$ had been plotted instead of $1/D$, the values of γ_3 would have been about 1–2% higher than those given.

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[5] Fenton, *J. Chem. Soc.*, **75**, 9 (1899).

[6] Fischer, *Ber.*, **23**, 3686 (1890).

[7] Votocék and Krauz, *Z. Zuckerind. Bohmen*, **43**, 577 (1919).