[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 293]

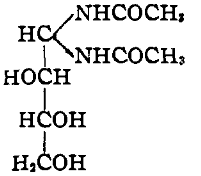
Lead Tetraacetate Oxidations in the Sugar Group. V.[1] The Rates of Oxidation of Open-Chain Polyalcohols in Dry Acetic Acid Solution[2]

BY ROBERT C. HOCKETT, MARGARET T. DIENES, HEWITT G. FLETCHER, JR.,[3] AND HUGH E. RAMSDEN

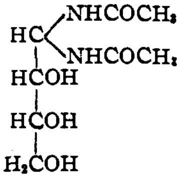
In a series of recent papers,[1,4] we have shown the behavior toward lead tetraacetate, of a number of vicinal triols in which the three carbinol groups form part of a six-membered ring. In such structures, the configurations of the carbon atoms are responsible for definite and predictable space relations among the hydroxyl groups and it has been found possible to correlate the shape of the oxidation curves obtained under standard conditions, with these space relations and certain other structural features. It appears possible from these correlations, to predict which of three types of oxidation curve will be found for a given glycopyranoside or, conversely, to deduce certain structural features from the type of curve observed. Moreover, the same considerations apply to anhydrides of polyalcohols[4] as to glycopyranosides of like ring type.

It now becomes of interest to determine the types of oxidation curve which will be obtained from open-chain polyalcohols with various numbers of hydroxyl groups, when these substances are oxidized under the same standardized conditions.[5] In such compounds there would appear to be no fixed space relations among the various hydroxyl groups because of the possibility of free rotation around the carbon-to-carbon single bonds. A definite relation between the amount of oxidant consumed and the number of carbinol groups present in an unbroken row, might be expected.

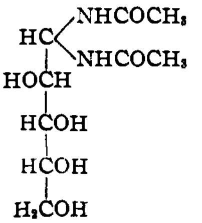
In the present paper, we report such oxidations of glycol, glycerol, erythritol, arabitol, mannitol, sorbitol and dulcitol. Another group of open-chain compounds is provided by the diacetamide derivatives of the sugars which are obtained in the course of the Wohl degradation.[6] Four of these were on hand from previous studies: "D-threose diacetamide,"[7] "D-erythrose diacetamide,"[8] "D-arabinose diacetamide"[9] and "D-lyxose diacetamide."[9]



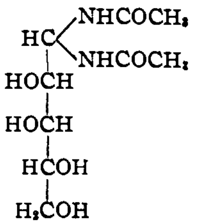
"D-Threose diacetamide"



"D-Erythrose diacetamide"



"D-Arabinose diacetamide"



"D-Lyxose diacetamide"

The results are shown in two figures. First, it may be noted that the configuration of an open-chain polyalcohol has no effect upon the course of oxidation in the present cases. Mannitol, dulcitol and sorbitol do not differ beyond the limits of experimental error, so that the curve shown for mannitol expresses equally well the behavior of the other hexitols. Second, the curves when examined in a purely empirical manner, seem to show a striking family relationship which indicates that the position of the curve with respect to the coördinates is a function of the number of free COH groups in an *unbroken* series. Nevertheless, the curves do not indicate a simple stoichiometric relation between amount of oxidant used and the number of such alcohol groups. We have many evidences that the reactions are complex and do not accept for the oxidation of polyalcohols by lead tetraacetate in dry acetic acid, the simple mechanism proposed by Malaprade[10] for the oxidation of such polyols by periodic acid in water. One of the several disturbing elements is the oxidation of by-product formic acid by lead tetraacetate. The rate of this reaction, measured under comparable conditions, is recorded for comparison. Only glycol which produces no formic acid ceases to consume oxidant at the "theoretical" level of one mole.

Nevertheless, if standard conditions are used, it is probable that open-chain polyalcohols containing the same number of C–OH groups in a series, will give similar curves so long as substituents of extreme difference in polarity are absent. A case in point is the striking similarity between the oxidation curves of glycerol and the two "tetrose diacetamides" on the one hand and

---

[1] Number IV of this series, THIS JOURNAL, 65, 1474 (1943).

[2] The material in this paper is taken in part from theses submitted by Margaret T. Dienes in May, 1940, by Hewitt G. Fletcher, Jr., in September, 1942, and by Hugh E. Ramsden in February, 1943, in partial fulfillment of the requirements for the degrees, respectively, of Bachelor of Science, Doctor of Philosophy and Bachelor of Science.

[3] Moore Fellow in Chemistry, 1941–1942.

[4] Hockett and Conley, THIS JOURNAL, 66, 464 (1944).

[5] *Cf.* Criegee, *Sitz. Ges. Beförder. ges. Naturw. Marburg*, 69, 25 (1934).

[6] Wohl, *Ber.*, 32, 3666 (1899).

[7] Hockett, THIS JOURNAL, 57, 2265 (1935).

[8] Hockett and Maynard, *ibid.*, 61, 2111 (1939).

[9] Hockett, Deulofeu, Sedoff and Mendive, *ibid.*, 60, 278 (1938).

[10] Malaprade, *Compt. rend.*, 186, 382 (1928).

those of erythritol and the two "pentose diacetamides" on the other.

Standard conditions, of course, must be chosen arbitrarily and such a choice has been recorded in the fourth paper of this series.[1] It may also be helpful to attempt an expression in words of the position where the curve of any polyol should be found if it is determined under the standard conditions: At a time between five and ten hours under these conditions, each polyol will reach a consumption of $n - 1$ moles of lead tetraacetate if it contains n free COH groups in an unbroken series. However, no stoichiometric significance is to be attached to this statement and progressive deviations are to be expected as we ascend the series since the excess of oxidant cannot be made infinite in practice. Nevertheless, the curves recorded in Fig. 1 may provide a valuable frame of reference in solving the structures of polyalcohol derivatives when used judiciously. In a previous paper[11] several glycols of widely differing structures were shown to be similar enough in behavior so that no difficulty would be experienced in identifying them as compounds containing one adjacent pair of C–OH groups.

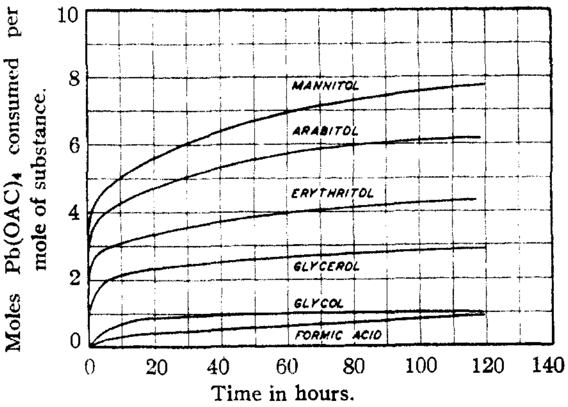


Fig. 1.—Oxidations in dry acetic acid: samples 0.0025 molar; ratio of oxidant, 15.2/1.

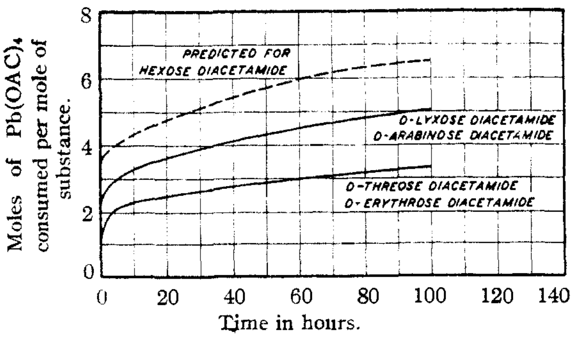


Fig. 2.—Oxidations in dry acetic acid: samples 0.0025 molar; ratio of oxidant, 15.2/1.

We are indebted to the Atlas Powder Company for samples of pure mannitol and sorbitol.

Experimental

Procedure.—These experiments were carried out under the exact conditions described by Hockett, Dienes and Ramsden.[1]

Materials

Mannitol and Sorbitol.—Highly pure samples were supplied by the Atlas Powder Company of Wilmington, Delaware.

Dulcitol.—Eastman Kodak Company material was used.

Arabitol.—This substance was prepared by deacetylation of the pure pentaacetate.[12]

Erythritol.—A sample from the Eastman Kodak Company was found to be highly pure.

Glycerol.—A sample of C. P. grade was fractionated in an efficient column under reduced pressure. Because of the hygroscopic nature of this substance, an analysis was made for water. A few drops were placed in a 25.0-cc. volumetric flask which was immediately stoppered and weighed. The glycerol was then dissolved and made up to the mark with dry acetic acid which had been analyzed for water by the method of Almy, Griffin and Wilcox.[13] An aliquot of the acetic acid solution was analyzed for water and the dry weight of the glycerol calculated. The water content of the glycerol was found to be only 1.32%. Then a volume sufficient to give the desired sample weight of glycerol (0.0230 g.) was measured from a dry buret into a 100.0-cc. volumetric flask. The oxidation was carried out as usual.

Glycol.—Eastman C. P. ethylene glycol was fractionated under reduced pressure.

Formic Acid.—Mallinckrodt Analytical Reagent grade of specific gravity 1.20, containing about 13% water, was allowed to stand in contact with anhydrous oxalic acid for several days and was then decanted and distilled under reduced pressure. The distillate was kept for several days in contact with boric anhydride and then distilled from boric anhydride.[14]

Summary

1. The oxidation of open-chain polyalcohols by lead tetraacetate in dry acetic acid under standard conditions, has been measured.

2. An empirical relation between the position of the oxidation curve and the number of carbinol groups present in a continuous chain is stated.

3. The lack of effect of configuration on the oxidation behavior of open-chain polyalcohols is noted.

4. The action of lead tetraacetate upon dry formic acid under the standard conditions is described.

Cambridge, Mass. Received September 29, 1943

---

[11] Hockett and McClenahan, This Journal, 61, 1670 (1939).

[12] Hockett and Hudson, *ibid.*, 57, 1753 (1935).

[13] Almy, Griffin and Wilcox, *Ind. Eng. Chem.*, *Anal. Ed.*, 12, 392 (1940).

[14] Schlesinger, This Journal, 36, 1589 (1914).