differences are too large to be explained solely by differences in the conductivities of the electrolyte. The cell reactions when the salts are used are the same as those given for sodium hydroxide except that the corresponding magnesium salts are formed.

The same principles should apply to cells constructed with salts of lower melting points than those used in this investigation. Eutectic salt mixtures should serve this purpose. As the voltages were measured when there was a net flow of electric current, thermodynamic data cannot be given. It may be stated, however, that different voltages obtained for different electrolytes must correspond, in part, to the differences in the free energy of formation of the various magnesium salts. The cell reaction is exothermic at high temperatures but insufficient heat is evolved to maintain the cell reaction.

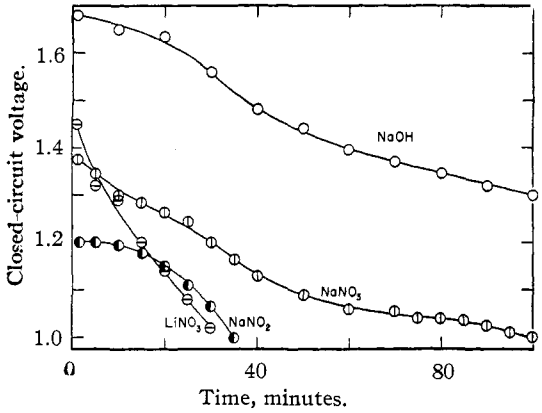


Fig. 9.—Long discharges of the cells Mg: molten electrolyte: MnO_2: C.

Summary

Data are presented for the galvanic cell, magnesium: solid or molten electrolyte: manganese dioxide: C over a temperature range extending from room temperature to and above the melting point of the solid. Several electrolytes were studied with sodium hydroxide being the best. The cell has open-circuit voltages which increase as a function of temperature. However, the cell does not sustain a voltage until the melting point of the electrolyte is reached and exceeded. Cells of this type may be activated by heat.

The difference between the open- and closed-circuit voltages of the cell becomes negligible at temperatures considerably above the melting point of the electrolyte.

The cell reaction was postulated for an electrolyte of molten sodium hydroxide and was confirmed in part by X-ray diffraction studies.

WASHINGTON, D. C. RECEIVED JUNE 22, 1948

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, MERCK & CO., INC.]

The Catalytic Reduction of the Esters of Tartaric Acid to the Erythritols

BY NELSON R. TRENNER AND FREDERICK A. BACHER

A perusal of the literature prior to 1940 concerning the catalytic reduction of the esters of α-hydroxy aliphatic dibasic acids to the corresponding glycols reveals the opinion that in general such reductions cannot be successfully accomplished in the presence of a copper chromite catalyst and at about 250° since marked hydrogenolysis at one or more of the C–O bonds takes place.[1] In view, however, of the possibility, also suggested by Adkins, that the hydrogenolytic reactions take place subsequent to the formation of the glycol and of the further possibility that such hydrogenolytic reactions require a higher activation energy[2] than does the ester reduction, there would follow the possibility that the use of lower temperatures would result in the desired reduction of the ester groups without the occurrence of significant hydrogenolysis. An investigation of the behavior of the dialkyl tartrates in the presence of copper chromite catalyst and in the temperature range of 150 to 200° revealed that these speculations are indeed confirmed and that successful ester reductions to the corresponding tetrahydroxybutanes may be achieved without significant hydrogenolysis.

(1) H. Adkins, "Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts," The University of Wisconsin Press, Madison, Wis., 1937, p. 104.

(2) In referring to the activation energy concept we here assume that this quantity *essentially* determines the relative reaction rates involved and that other factors such as relative degrees of adsorption on the catalyst surface, the nature of the rate determining steps, etc., are substantially constant for the various reactants involved in this investigation. This would seem reasonably justified provided we confine our speculations to molecules of the same general type and size and to a relatively small temperature range.

Experimental

Dialkyl Tartrates.—*meso*-Tartaric acid was prepared from *d*-tartaric acid by means of hot alkali isomerization followed by removal of the *d*- and *l*-isomers as the potassium salts and precipitation of lead *meso*-tartrate.[3] Esterification of the lead salt was effected through the use of alcoholic hydrogen chloride. The crystalline esters were isolated, purified and identified in the usual manner. The dialkyl *meso*-tartrates used in the reductions reported here had the following melting points: dimethyl ester 113–114° (capillary); diethyl ester 56–57° (capillary). The diethyl *d*-tartrate diacetate melted 67–68° (capillary). Diethyl *d*-tartrate is a liquid and it was characterized by means of its ultimate analysis and optical rotation $[\alpha]^{23}D$ +7.5°.

Anal. Calcd. for $C_8H_{14}O_6$: C, 46.6; H, 6.80. Found: C, 46.7; H, 6.86.

(3) Beilstein III, fourth edition, 1921, p. 529.

General Procedure.—The following is a description of the procedure used in a typical hydrogenation experiment. Into the copper liner of a typical hydrogenation bomb was charged 4 g. of the dialkyl tartrate in 100 cc. of absolute methanol, 2 g. of copper chromite catalyst (prepared according to the directions given by Adkins[1] p. 13) and the bomb sealed. Hydrogen gas was introduced to a pressure such that, after raising the temperature of the bomb to 165°, a pressure of about 5000 pounds per square inch was developed. By means of a thermostat, the temperature could be held constant during the reaction. Usually from five to six hours of shaking were required for completion of the hydrogenation. After cooling to room temperature, the excess hydrogen was bled off and the bomb contents washed with methanol into centrifuge bottles. After making to a known volume and centrifugation of the catalyst, an aliquot of the clear methanol solution was removed, evaporated to a small volume on the steam-bath, cooled and seeded or agitated to induce crystallization of the *meso*-erythritol. Finally diethyl ether was added to complete the crystallization and the solid was filtered and washed with hot ethyl acetate or ether. After drying, the solid was weighed. The combined mother liquors from the *meso*-erythritol crystallization were evaporated to a sirup on the steam-bath and then washed and triturated with relatively large volumes of hot ether to remove any unreduced ester. These ether washings were combined and evaporated to dryness leaving a crystalline residue of dialkyl *meso*-tartrate. The triturated sirupy residue was heated and pumped off and then weighed. This sirup proved to be a mixture of isomeric erythritols. Each product was characterized by analysis, melting point and, in the case of the erythritols, by preparation of the solid dibenzal derivatives. The analysis of a typical sirup is: *Anal.* Calcd. for $C_4H_{10}O_4$: C, 39.3; H, 8.25. Found: C, 39.2, 39.2; H, 8.6, 8.7. For the dibenzal derivative of the above: *Anal.* Calcd. for $C_{18}H_{18}O_4$: C, 72.5; H, 6.05. Found: C, 72.7; H, 6.2.

Discussion

Catalytic hydrogenations of dimethyl *meso*-tartrate in methanol using copper oxide–chromium oxide catalysts were studied over a temperature range from 150 to 200° and over a hydrogen pressure range from 2000 to 5100 pounds per square inch. The results of these experiments indicated that the optimum conditions for *meso*-erythritol formation occur at about 165° and 5000 p.s.i. hydrogen pressure when a catalyst weight to reactant weight ratio of 0.5 is employed. After five to six hours under these conditions the average composition of the reaction product was found to be 5–10% unreacted dimethyl *meso*-tartrate and 95–90% mixed erythritols from the latter of which about 70% was isolated as pure *meso*-erythritol (m.p. 120–121°; accepted value 120°[4]) leaving about 30% as a sirup of non-crystallizable, isomerized erythritols. Below 150° the hydrogenation rate becomes excessively slow while at 200° there is evidence that appreciable hydrogenolysis takes place, at least with our catalyst preparations. Experiment showed that the substitution of ethanol for methanol as solvent is without effect upon these results. A more drastic change in the character of the solvent, such as the substitution of diethyl ether or of no solvent at all results in almost complete failure to hydrogenate, only 3–4% of reduction being observed even after thirteen to fourteen hours at 165°. Hydrogen pressures of about 5000 p.s.i. seem prerequisite for satisfactory reduction since at 2000 p.s.i. no reduction was found to have taken place after six hours at 165° and the catalyst was found to have undergone a change from the black reactive form to a red inactive form. This observation was found to be true regardless of whether the catalyst was studied in the presence of dimethyl *meso*-tartrate or of *meso*-erythritol (which undergoes isomerization at 5000 p.s.i., see below). As expected diethyl esters were found to give the same results as their dimethyl analogs.

An investigation of diethyl *d*-tartrate under the same general conditions used for the *meso*-tartrates revealed that an entirely analogous set of reactions take place. The only observed reaction product from this reactant was *partially* isomerized *d*-erythritol obtained in 95–97% yields. This partially isomerized product was fractionated into a crystalline solid (65%) and a non-crystallizable sirup (30%). One such crystalline solid, analyzed as a $C_4H_{10}O_4$ compound, was found to melt at 88–90°[4] and to have the following optical rotation: $[\alpha]^{27}D$ −3.9° (*c*, 6; water) (accepted value for *d*-erythritol is $[\alpha]^{25}D$ − 4.3 (water)[4]). The sirupy fraction, analyzed as a $C_4H_{10}O_4$ compound, gave a dibenzal derivative of correct analysis and was found to be optically inactive, from which it was judged to be a mixture of *isomerized* erythritols similar to those given by the *meso*-tartrates.

A given specimen of catalyst could be used in repeated reductions without apparent change of activity.

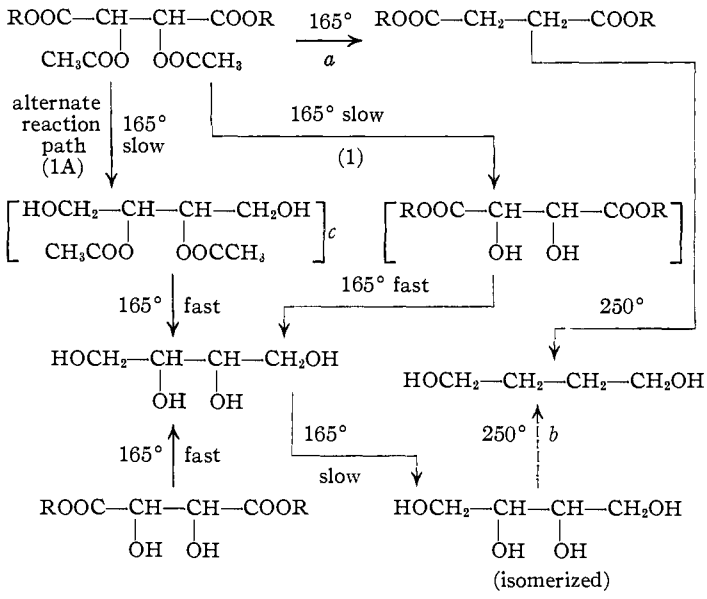
In view of the repeated appearance of isomerized erythritols in these hydrogenations, it became of interest to determine whether such changes took place before or subsequent to formation of the erythritol. Accordingly, therefore, experiments were carried out with pure *meso*-erythritol which revealed that in six hours at 165°, 5100 p.s.i. hydrogen pressure and a catalyst ratio of 0.5 (methanol as solvent) a gross product is obtained which analyzed for 100% $C_4H_{10}O_4$ but which could be fractioned to give 60% crystalline *meso*-erythritol (m. p. 120°) and 40% of non-crystallizable sirup (composition $C_4H_{10}O_4$; dibenzal derivative $C_{18}H_{10}O_4$). Evidently *meso*-erythritol is partially isomerized under these conditions.

Finally, for reasons discussed later, the behavior of diethyl *d*-tartrate diacetate was also studied under the above conditions. Here a product was obtained after four hours which contained 32% of unreacted starting material. Of the 68% which had reacted, 42% was isolated in the form of partially isomerized *d*-erythritol [$[\alpha]^{25}D$ − 4.0° (*c*, 5; methanol); accepted value $[\alpha]^{25}D$ − 11.8° (*c*, 5; methanol)] and 59% as diethyl succinate.

(4) F. Micheel, "Chemie der Zucker und Polysaccharide," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1939, p. 20.

These data taken together with the findings of Adkins and his co-workers throw more definite light upon some features of the mechanism of the reactions involved. Our experiments have indicated that the isomerization process can take place in the case of erythritol and, consequently, it would seem reasonable to suppose that the isomerizations, always observed to accompany our tartrate reductions, take place subsequent to the reduction of the ester groups. Attention is called to the fact that the ratio of total isomerized products to un-isomerized product is roughly the same regardless of whether one starts with *meso*-erythritol or with the dialkyl *d*- or *meso*-tartrate, a consequence which would be expected in terms of the above postulate. Adkins and his co-workers found (see reference 1, page 105) at 250°, and over copper–chromium oxide catalysts, that the hydrogenations of diethyl α-hydroxy-β-methyl succinate and of ethyl β-hydroxybutyrate yield only 1,2- and 1,4-butanediols and 1- and 2-butanols, respectively. From these observations one may reasonably conclude that under the same conditions only 1,2- and 1,4-butanediols would be obtained from the dialkyl tartrates. In view of our results, which indicate that the activation energy of reduction of an ester group alpha to a CH–OH group is lower than the activation energy of the hydrogenolysis of a beta C–OH group, one might conclude that in going from the dialkyl tartrates to the corresponding 1,2- and 1,4-butanediols the reaction passes through the tetrahydroxybutanes as an intermediate. In addition, the activation energy for the isomerization process of the tetrahydroxybutanes is lower than that of the hydrogenolysis of the beta C–OH groups.

The results obtained using the diacetate of diethyl *d*-tartrate indicate some facts concerning the relative ease of hydrogenolysis at the beta C–OH and C–$OCOCH_3$ groups. It will be noted that in the hydrogenation of the diacetate, two products are produced in roughly equal amounts, namely, erythritol and diethyl succinate. Thus it would appear that the activation energy required for the hydrogenolysis at the C–O bond of the C–$OCOCH_3$ group is lower than that required for the C–O bond of the beta C–OH group and, moreover, that it is about the same as that required for the reduction of the C–O bonds of the terminal ester groups in the dialkyl tartrates and lower than that required for the reduction of the C–O bonds of the ester groups in the dialkyl succinates (see reference 1, page 99). Briefly the interrelationships for these reactions may be summarized as follows:



[a] All the above reaction steps are to be assumed as taking place in the presence of copper–chromium oxide catalyst and 5000 p. s. i. hydrogen pressure. [b] This reaction is conjectural. It is assumed that 1,2-butanediol would probably be formed from the erythritols at 250°. [c] The formulas in brackets are assumed to be intermediates.

In view of the fact that we failed to isolate any intermediate between diethyl *d*-tartrate diacetate and its final products, we are inclined to believe that the rate determining step in the reaction mechanism which leads to erythritol must be either of the two reactions (1) or (1A) indicated above. The alternate reaction path (1A) which goes through tetrahydroxybutane-2,3-diacetate seems less probable in view of the facts that this investigation as well as that of Adkins on benzilic ester (see ref. 1, p. 101) have shown that reductions of α hydroxy esters take place quite readily at low temperatures while reductions of α-substituted esters appear not to take place readily at such low temperatures (the diethyl succinate formed in our diacetate reduction survived our reaction conditions as no significant amount of 1,4-butanediol was observed to be present).

Summary

The high pressure reduction of the simple dialkyl tartrates over copper–chromium oxide catalyst has been investigated at temperatures near 165° and has been found to yield the erythritols (tetrahydroxybutanes) without significant hydrogenolysis of the β-hydroxyl groups. Evidence is presented which indicates that the ester groups in α-hydroxy esters are more readily reduced (*i. e.*, at lower temperatures) than the ester groups in α-unsubstituted esters. Evidence is also presented which shows that the hydrogenolysis at the C–O bond of the C–$OCOCH_3$ group takes place more readily (*i. e.*, at a lower temperature) than

at the C–O bond of a β-hydroxy group. Finally, evidence is presented which shows that isomerization of the erythritols takes place at 165° over a copper–chromium oxide catalyst. The interrelationships of these reactions are briefly discussed and some of the pioneering concepts of Adkins and his co-workers are confirmed and extended.

RAHWAY, NEW JERSEY RECEIVED NOVEMBER 26, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Action of Sulfuric Acid, Ethanesulfonic Acid and Chlorosulfonic Acid on Aliphatic Hydrocarbons

BY GEORGE S. GORDON III[1] AND ROBERT L. BURWELL, JR.

In a recent investigation of the action of sulfuric acid on (+)3-methylheptane,[2] it was found that sulfuric acid-d_2 caused hydrogen exchange, racemization and isomerization to occur at rates strongly influenced by the water content of the acid. With 80 mole per cent. sulfuric acid, the reactions proceeded at convenient rates at 60° with relative rates of 30:2:1. The rate of exchange of 2-methylheptane was about the same as that of 3-methylheptane but that of octane was over a hundred-fold slower.

It was proposed that these reactions involve an intermediate formed by the oxidation of the hydrocarbon, and that this intermediate acts as a chain initiator for a reaction of a chain length of about twenty.

It appeared desirable to extend these experiments to hydrocarbons of lower and higher molecular weight, to study the effect of the addition of materials which might be presumed to act as initiators and to investigate the action of some other acids. The results of these experiments are reported in the present paper.

Experimental

Materials.—(+)4-Methyl-2-hexanol (the diastereoisomeric pair in unknown ratio) was prepared from (+)2-methyl-1-bromobutane[2] and acetaldehyde by the Grignard reaction and distilled in a 25-plate Stedman column to give a 77% yield in a 0.8-mole run, $[\alpha]^{25}D$ +11.7°, b. p. 150–151°. The bromide, d^{25}_4 1.2173 and $n^{20}D$ 1.4452, had been prepared as previously described[2] from protracted action of phosphorus tribromide on active amyl alcohol and had not been distilled. Its rotation, $[\alpha]^{25}D$ +3.89° was less than that of the probable maximum value of 4.05° consistent with the work of Marckwald[3] and Brauns[4] and confirmed in this research on a fractionated sample prepared by the action of phosphorus tribromide in the conventional way.

(+)3-Methylhexane was prepared from (+)4-methyl-2-hexanol in two ways. The latter compound was converted into the bromide by the method previously described[2] in 96% yield. This (0.46 mole) was converted to the Grignard reagent, hydrolyzed with 20% sulfuric acid, washed with concentrated sulfuric acid and fractionated to give a 30% yield based on the carbinol, $[\alpha]^{25}D$ +9.10°. In the second method, the alcohol was dehydrated by passage over activated alumina (Puralox, Harshaw Chemical Company) at 450° at a rate of one cc. of alcohol per cc. of catalyst per hour. The resulting heptylene ($\alpha^{26}D$ +13.70°, 1 dm.) was hydrogenated in methanol with the Adams platinum oxide catalyst to give an over-all yield of 55%, $[\alpha]^{25}D$ +9.12°; d^{25}_4 0.6824 and $n^{20}D$ 1.3889.[5]

(+)3-Methylhendecane was made via the Grignard reaction between (+)2-methyl-1-bromobutane and heptanal, dehydration of the resulting carbinol and hydrogenation of the resulting dodecylene by the methods described above, $[\alpha]^{25}D$ +7.45°, $n^{20}D$ 1.4229.

2,2-Dimethylhexane was obtained from the American Petroleum Institute Research Project 45 at The Ohio State University through the kindness of Dr. Kenneth Greenlee. Its purity was estimated as 99.58 ± 0.13% by A. P. I. project 6 at the National Bureau of Standards.

2-Methylpentane was prepared by hydrogenating, with the platinum oxide catalyst, 2-methylpentadiene from the Commercial Solvents Corporation. After distillation (b. p. 59.8–60.0°, 750 mm.), this showed $n^{20}D$ 1.3717.

The preparation of (+)3-methylheptane, *n*-octane and sulfuric acid-d_2 has been described.[2] A sample of triply distilled ethanesulfonic acid from the Standard Oil Company (Indiana) was mixed with 99.8% deuterium oxide and dehydrated by warming under vacuum. Upon analysis of the water produced by neutralization with sodium hydroxide, 45.8% of the acidic hydrogen was found to have been replaced by deuterium. The ethanesulfonic acid was free from sulfuric acid to the degree detectable by barium chloride.

Vacuum distillation of a solution of sulfuric acid whose deuterium content was 25 mole per cent. and chlorosulfonic acid gave chlorosulfonic acid of 11.5% deuterium content.

Apparatus and Procedure.—The former apparatus[2] was employed. The reactants were stirred together at a fixed temperature under an atmosphere of nitrogen. The hydrocarbon layer was then removed by distillation under vacuum at low temperatures for examination in the polarimeter and infrared spectrograph and for combustion to permit deuterium analysis. However, where the hydrocarbon had too low a vapor pressure (3-methylhendecane) or the acid had too high a vapor pressure (chlorosulfonic acid), the products were pipetted directly from the reaction vessel to a graduated tube and were immediately washed to remove acidic impurities. Save as otherwise indicated, 4.2 cc. of acid and 3.0 cc. of hydrocarbon were used. Stirring corresponding to that of the higher speed of the previous paper[2] was used save as otherwise specified.

Experimental Results

The former experiments with (+)3-methylheptane and sulfuric acid have been extended to an investigation of the effects of the addition of small amounts of butylene and of sodium *s*-butyl sulfate. A temperature of 60° and 95.3% sulfuric acid was employed. Results are given in Table I.

(1) Standard Oil Company (Indiana) Fellow, 1946–1948. Present address, General Electric Company, Pittsfield, Massachusetts.

(2) Burwell and Gordon, THIS JOURNAL, **70**, 3128 (1948).

(3) Marckwald and Nolda, *Ber.*, **42**, 1583 (1909).

(4) Brauns, *J. Research Nat. Bur. Standards*, **18**, 315 (1937).

(5) American Petroleum Institute, Research Project 44 at the National Bureau of Standards, Selected Values of Properties of Hydrocarbons, Table 2a (part 2) gives $n^{20}D$ 1.38865 and d^{25}_4 0.6828.