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Fig. 1. Dehydration of glycols C_4, C_5, and C_6: A—into oxacyclanes at 280° (1), 300° (2), and 320° (3); B—into diolefins at 335° (1), 350° (2), 380° (3), 410° (4), and 420° (5); V—dehydration of oxacyclanes into diolefins at 390° (1), 400° (2), 410° (3), and 420° (4)

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Abstract

Full Text

L. Kh. Freidlin and V. Z. Sharf

STUDY OF THE STEPWISE DEHYDRATION OF GLYCOLS ON A TRICALCIUM PHOSPHATE CATALYST

(Presented by Academician A. A. Balandin, 19.IX.1960)

The catalytic dehydration of dihydric alcohols, in contrast to monohydric alcohols, has been little studied. From trimethylene glycol at 250-350° on Al_2O_3, allyl alcohol, products of its isomerization, disproportionation, and others were obtained. Trimethylene oxide was not detected (^{1}). Complete dehydration of butanediol-1,4 is catalyzed by Al_2O_3, Cr_2O_3, $CaCl_2$, $CaHPO_4$, Na_3PO_4 on carbon (^{2}), and partial dehydration to tetrahydrofuran by ion-exchange resins (^{3}), acids (^{4}), phosphates, chlorides, and others (^{5}). Butene-2-diol-1,4 was dehydrated to dihydrofuran in the presence of acids, Al_2O_3, ThO_2, and $AlPO_4$ (^{6}). Pentanediol-1,5 was dehydrated on phosphorus to pentadiene-1,3 with a yield of 37%, and on Al_2O_3 and kaolin tetrahydropyran was formed, 42% (^{7}). On ion-exchange resins tetrahydropyran is formed (^{3}). Under the action of concentrated sulfuric acid on hexanediol-1,6, α-methyltetrahydropyran was obtained (^{8}), and with 57% H_2SO_4, hexamethylene oxide (^{9}).

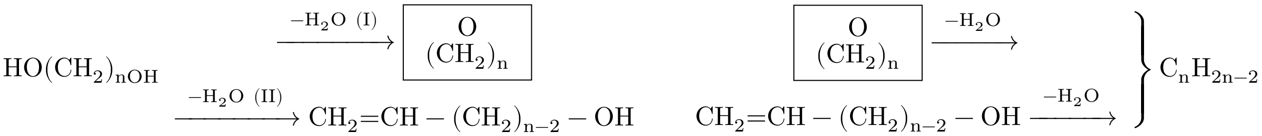
Fig. 1. Dehydration of glycols C_4, C_5, and C_6: A—into oxacyclanes at 280° (1), 300° (2), and 320° (3); B—into diolefins at 335° (1), 350° (2), 380° (3), 410° (4), and 420° (5); V—dehydration of oxacyclanes into diolefins at 390° (1), 400° (2), 410° (3), and 420° (4)

In the present work, the dehydration of a series of diols was investigated over a wide temperature range under identical conditions on the same catalyst. In parallel, the dehydration of possible intermediate reaction products—oxacyclanes and unsaturated alcohols—was studied. The results obtained make it possible to judge the influence of the structure of glycols on the direction of the reaction, the conditions under which they undergo only partial dehydration to an oxide, and the paths of their complete dehydration to a diene hydrocarbon.

In the temperature interval 280-320°, glycols C_4 and C_5 are selectively dehydrated to the corresponding oxides. From Fig. 1A it is seen that the ease of formation of oxacyclanes decreases in the series: $C_4 > C_5 > C_6$. Tetrahydrofuran is obtained in high yield and at a lower temperature than tetrahydropyran, which is obtained more readily than hexamethylene oxide. Above 320° unsaturated alcohols and diolefin hydrocarbons are also formed.

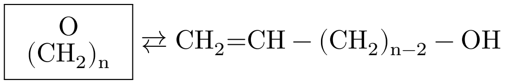
The strain of oxacyclanes (in kcal/mol) is 4.6 for C_4 and 0 for C_5. For C_3 and C_6 it is probably close to the strain of thiacyclanes, respectively C_3 19.8 and C_6 3.9 (^{10}). However, as is seen from Fig. 1B, the degree of dehydration of oxacyclanes C_4 and C_5 under identical conditions proved to be approximately the same, and for C_6 it is noticeably greater. From comparison of Figs. 1B and 1V it follows that oxacyclanes are dehydrated to diolefins with more difficulty than the corresponding glycols. Tetrahydrofuran begins to dehydrate to divinyl at a temperature that is 100° higher than the temperature of dehydration of butanediol to divinyl. Analogously, tetrahydropyran is noticeably more difficult to dehydra–

is converted into pentadiene than pentanediol-1,5. As can be seen from Fig. 2B, the maximum yield of hexenol–17% (curve 2)–was obtained at 350°, of hexamethylene oxide–32% at 380° (curve 1), and of hexadienes–60% at 400° (curve 3). The intensive formation of diolefin at temperatures above 350°, with simultaneous increase in the yield of hexamethylene oxide and decrease in the yield of hexenol, shows that the diolefin is formed chiefly from hexenol, which is less stable than the oxide. Indeed, when passed over the catalyst at 400°, the degree of conversion of hexenol into hexadiene was 75-80%, while that of hexamethylene oxide was 18%. Thus, the formation of diolefins in this process proceeds predominantly through the stage of unsaturated alcohols (II), and not through the stage of oxacyclanes (I):



$$HO(CH_2)_{nOH} \begin{matrix} \xrightarrow{-H_2O\ (I)} \boxed{\begin{matrix} O \\ (CH_2)_n \end{matrix}} \\ \xrightarrow{-H_2O\ (II)} CH_2{=}CH-(CH_2)_{n-2}-OH \end{matrix} \qquad \left. \begin{matrix} \boxed{\begin{matrix} O \\ (CH_2)_n \end{matrix}} \xrightarrow{-H_2O} \\ CH_2{=}CH-(CH_2)_{n-2}-OH \xrightarrow{-H_2O} \end{matrix} \right\} C_nH_{2n-2}$$

As for the unsaturated alcohol, it may be formed by isomerization of the oxacyclane:



$$\boxed{\begin{matrix} O \\ (CH_2)_n \end{matrix}} \rightleftarrows CH_2{=}CH-(CH_2)_{n-2}-OH$$

or directly by dehydration of the diol. In our experiments, at 340° and above, diolefins were formed from oxacyclanes, whereas unsaturated alcohols were not detected. In the dehydration of glycols under the same conditions, along with diolefins, unsaturated alcohols were also obtained. It is therefore necessary to assume that at elevated temperatures the reaction mechanism changes and pathway II appears, with a considerably higher temperature coefficient than pathway I. In the case of pentanediol, the temperature coefficient of reaction (II) is relatively small; therefore the rate of diolefin formation is lower than from the C_4 and C_6 diols, Fig. 1B.

Experimental Part

The experiments were carried out under flow conditions in a quartz tube. The catalyst volume was 25 ml, and the grain size was 2 × 3 mm. Preparation of the catalyst is described in (11). Diols (oxacyclanes, unsaturated alcohols) were passed uniformly at a rate of 17.5 ml/hr. The liquid reaction products were dried over ignited potassium carbonate and fractionated on a 15-t.p. column. The content of carbonyl groups and unsaturated bonds in them was determined. The position of the double bonds was determined by the k. r. s. method. The yield was calculated on the compound passed through.

Dehydration of trimethylene glycol (b.p. 95°/5 mm, n_D^{20} 1.4396). The degree of its conversion at 250, 300, and 350° was respectively 5, 20, and 49%. The main reaction products were allyl alcohol (b.p. 96-97°, d_4^{20} 0.8569, n_D^{20} 1.4136) and propionaldehyde (b.p. 47-49°, d_4^{20} 0.7970, n_D^{20} 1.3644). Trimethylene oxide was not detected.

Dehydration of butene-2-diol-1,4 (b.p. 115-122°/8 mm, d_4^{20} 1.067, n_D^{20} 1.4732). At 280° the degree of conversion was 60%. The main reaction products were 2,5-dihydrofuran (b.p. 66-67°, d_4^{20} 0.9560; n_D^{20} 1.4275, yield 25.8%) and crotonaldehyde (b.p. 102-103°, d_4^{20} 0.8519, n_D^{20} 1.4370, yield 11.5%):

$$CH_2OH-CH{=}CH-CH_2OH \rightarrow H_2O+\boxed{}>O\,(CH_2{=}CH-CH_2-C(=O)H)\,.$$

Dehydration of butanediol-1,4 (b.p. 106°/5 mm, d_4^{20} 1.015, n_D^{20} 1.4478), Fig. 2A. In the interval 260–320° only tetrahydrofuran is formed (b.p. 64–65°, d_4^{20} 0.8878, n_D^{20} 1.4075), the yield of which reaches 98% (curve 1):

$$HO-(CH_2)_4-OH \rightarrow H_2O+O.$$

At higher temperatures the yield of tetrahydrofuran decreases, and divinyl is also formed (determined chromatographically), buten-1-ol-4 (b.p. 113–115°, d_4^{20} 0.8460, n_D^{20} 1.4244), buten-2-ol-4, and butyraldehyde. At 336° the yield of gaseous products was 14%, and at 426°, 73%, if all the gas is taken as divinyl (Fig. 2, 2). In the experiment at 426°, 73% divinyl was determined in the gaseous products. Tetrahydrofuran at 340° is completely recovered unchanged. Its dehydration to divinyl begins at temperatures above 380° (curve 3):

$$\text{tetrahydrofuran} \rightarrow H_2O + CH_2{=}CH - CH{=}CH_2.$$

Fig. 2. Dehydration of butanediol-1,4 and tetrahydrofuran (A), pentanediol-1,5 and tetrahydropyran (B), hexanediol-1,6 (V), 3,7-dimethyloctanediol-1,7, and citronellol (G): *a*—oxacyclanes, *b*—unsaturated alcohols, *v*—diolefins.

At 380–494°, only tetrahydrofuran and water were detected in the liquid catalyzate.

Dehydration of pentanediol-1,5 (b.p. 115°/5 mm, d_4^{20} 0.9850, n_D^{20} 1.4512), Fig. 2B. In the interval 280–343°, pentanediol is selectively dehydrated to tetrahydropyran (b.p. 86.5–87.5°, d_4^{20} 0.8634, n_D^{20} 1.4280), curve 1:

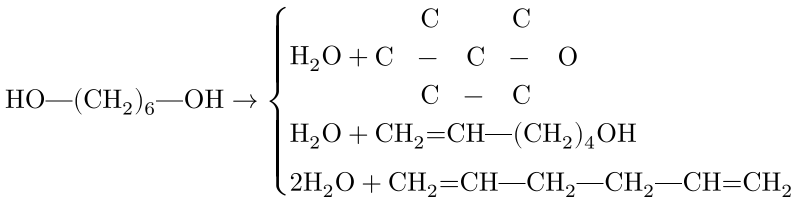
$$HO - (CH_2)_5 - OH \rightarrow H_2O\text{+tetrahydropyranO}.$$

Its yield at 343° was 72%. At higher temperatures pentenols are also formed (b.p. 135–139°, d_4^{20} 0.8412, n_D^{20} 1.4377) and pentadienes (I, b.p. 23–26°, n_D^{20} 1.3895, Raman spectral frequency 1647.3 cm^{-1}; II, b.p. 41–42°, n_D^{20} 1.4320, Raman spectral frequency 1651.1 cm^{-1}; on hydrogenation the diene absorbs $\sim$ 2 moles of H_2), curve 2. At 423° the yield of pentadienes is 33%. In the absence of catalyst, pentanediol at this temperature did not change. At 389–418°, pentadienes were formed from tetrahydropyran (curve 3):

$$\text{tetrahydropyran} \rightarrow H_2O + CH_2{=}CH - CH_2 - CH{=}CH_2.$$

Dehydration of hexanediol-1,6 (b.p. 127°/5 mm, m.p. 40°), Fig. 2V. The reaction products are: hexamethylene oxide, curve 1 (b.p. 119–120°, d_4^{20} 0.9037, n_D^{20} 1.4394, C 71.59%, H 12.00%, IR spectrum as in (^{12})), hexenols (b.p. 155–158°, d_4^{20} 0.8418, n_D^{20} 1.4375, Raman spectral frequencies: 1642 cm^{-1} and 1678 cm^{-1}), curve 2, and hexadiene-1,5 (b.p. 61–64°, d_4^{20} 0.7031, n_D^{20} 1.4110, on hydrogenation absorbs

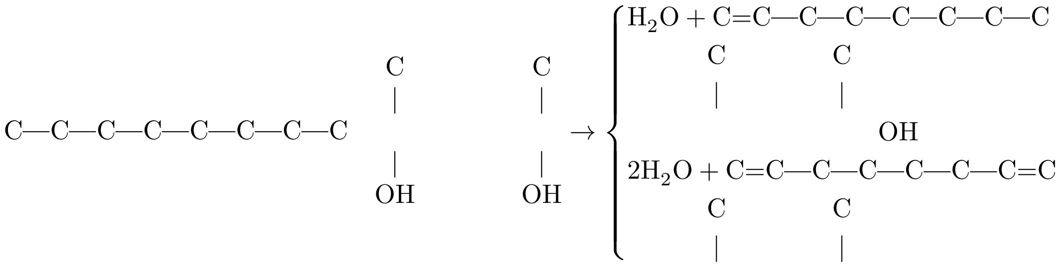
2 moles of H_2, Raman spectrum frequency 1642 cm^{-1}); curve 3:



$$HO—(CH_2)_6—OH \rightarrow \begin{cases} \begin{array}{lcccc} & C & & C & \\ H_2O + C & - & C & - & O \\ & C & - & C & \end{array} \\ H_2O + CH_2{=}CH—(CH_2)_4OH \\ 2H_2O + CH_2{=}CH—CH_2—CH_2—CH{=}CH_2 \end{cases}$$

At the same time, isomerization products are formed: α-methyltetrahydropyran, α-ethyltetrahydrofuran, hexadiene-1,4, etc.

Dehydration of 3,7-dimethyloctanediol-1,7 (b.p. 133°/4 mm, d_4^{20} 0.9274, n_D^{20} 1.4609), Fig. 2G. The reaction was carried out in vacuum (20 mm), catalyst amount 100 ml, rate of passage of the diol 90 ml/hr. At 200° the diol is selectively dehydrated to citronellol (b.p. 128–129°/22 mm, d_4^{20} 0.8547, n_D^{20} 1.4609), curve 1, in 84% yield. The yield of the diolefin (b.p. 162–164°, d_4^{20} 0.7984, n_D^{20} 1.4522, Raman spectrum frequencies: 1644 cm^{-1} and 1669 cm^{-1}) was 5%:



$$\mathrm{C{-}C{-}C{-}C{-}C{-}C{-}C{-}C}\quad \overset{\displaystyle \mathrm{C}}{\underset{\displaystyle \mathrm{OH}}{|}}\qquad \overset{\displaystyle \mathrm{C}}{\underset{\displaystyle \mathrm{OH}}{|}} \rightarrow \begin{cases} \mathrm{H_2O + C{=}C{-}C{-}C{-}C{-}C{-}C{-}C} \\ \qquad \overset{\displaystyle \mathrm{C}}{|} \qquad \overset{\displaystyle \mathrm{C}}{|} \qquad \mathrm{OH} \\ \mathrm{2H_2O + C{=}C{-}C{-}C{-}C{-}C{-}C{=}C} \\ \qquad \overset{\displaystyle \mathrm{C}}{|} \qquad \overset{\displaystyle \mathrm{C}}{|} \end{cases}$$

With increasing temperature, the yield of citronellol decreases, while that of the diolefin correspondingly increases (curve 2) and at 290° amounts to 90%. Under similar conditions citronellol is dehydrated to diolefins with approximately the same yield as the diol (curve 3).

Thus, dehydration of $\alpha\omega$-glycols C_4, C_5, and C_6 proceeds stepwise. In the first stage of the process an oxacyclane is formed. In the second stage an isomeric unsaturated monohydric alcohol is also formed. The final product of the dehydration reaction of diols—the diolefin—is obtained predominantly through the stage of formation of the unsaturated alcohol (II), and not through the oxide (I).

Butene-2-diol-1,4 is dehydrated mainly with formation of the oxide. In the dehydration products of the C_3 and C_8 diols the corresponding oxides were not detected. However, by analogy with (^{1}), it is possible that upon dehydration of trimethylene glycol, trimethylene oxide is formed, but it rapidly isomerizes into allyl alcohol and propionaldehyde. In the case of octanediol, the oxide is probably not formed owing to the non-equivalence of its OH groups, of which the tertiary one is split off at a lower temperature than the primary one.

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Note: Figure translations are in progress. See original paper for figures.

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