ACCELERATION OF THE CATALYTIC DEHYDRATION
OF ISOPROPANOL ON ALUMINUM OXIDE
BY ADDITION OF EXTRANEOUS SUBSTANCES*

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The dehydration of alcohol upon aluminum oxide is extremely sensitive to the presence of many extraneous substances when the process is conducted in an adsorption layer [1-3]. The active intermediate forms produced as a result of the adsorption of alcohol on the surface of the catalyst interacts with neighboring molecules; both inhibition (for example, when acetone or dioxane is added to i-C₃H₇OH) and acceleration of the reaction (for example, "coupled dehydration" of C₂H₅OH in the presence of i-C₃H₇OH) are observed. In view of the importance of these phenomena for an understanding of the mechanism of catalytic dehydration, it seemed interesting to study the influence of additions of certain extraneous substances when the dehydration of i-C₃H₇OH was conducted over Al₂O₃ under the usual circulating conditions at atmospheric pressure. When the substances added do not participate in the intermediate stages of the reaction, the only expected result might be greater or lesser inhibition, due to adsorption displacement and competition for the active sites of the surface; otherwise one might expect both acceleration and deceleration of the reaction. There are no data on the literature on the accelerating action of additives on the reaction under consideration, if we disregard the indications in [4] of a slight acceleration by chloroform.

EXPERIMENTAL

The work was conducted in the apparatus depicted in Fig. 1, after preliminary displacement of air from it by nitrogen or helium. The initial mixture (alcohol with dissolved additive) was delivered through an electrolytic burette [5] into an evaporator, and then into a circulating-type reactor. To prevent losses of C₃H₆ on account of dissolution in the catalyzate, the reaction products were sent through a condenser into a receiver, the lower portion of which, where the liquid catalyzate accumulated, was warmed in such a way as to provide for slight boiling of the liquid. The gaseous portion of the reaction products, together with the dissolved propylene isolated, passed again through a condenser and entered calibrated bottles for collection and subsequent chromatographic analysis. After the end of the experiment, the system was purged with a standard amount of helium or nitrogen to remove residual gases from the reaction and transfer them to a gas-collecting bottle.

To verify the constance of the catalyst activity - the absence of stable promotion or poisoning by the substances added - experiments were always conducted preliminarily, delivering substances to the reactor in the following sequence: pure alcohol (15 min) - alcohol + additive (15 min) - pure alcohol (15 min) without intermediate regeneration of the catalyst. In this case, the activity at the end of the experiment, as a rule, differed little from the initial value. When certain additives were introduced (for example, butyl nitrite, tetraethyllead, tetrabutyl titanate), the activity still changed; therefore, for greater assurance the bulk of the measurements were always performed with a fresh portion of the catalyst. All the figures indicated in Table 1 represent averages of two to three determinations and were obtained precisely according to a procedure ensuring sufficiently good reproducibility (the maximum discrepancies between parallel experiments are 10% rel. for low degrees of conversion and 5% rel. for high degrees of conversion).

The catalyst was brand A-1 Al₂O₃ with a specific surface of 180 m²/g, used in [1-3]. The amount of the catalyst was 0.5 g, mixed with 5 ml of pulverized glass - to reduce the influence of the endothermic

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character of the reaction; the temperature of the experiments was 190–270°, duration 15 min, volume velocity of alcohol vapors about 300 h⁻¹ (10 h⁻¹ calculated on the basis of the liquid).

In addition to the circulating method, we also used a pulsed chromatographic method in the work (catalyst A-1, sample weight 0.2 g). These experiments were conducted to determine the conditions and products of the decomposition of the individual substances added, as well as to detect the possibility of acceleration or inhibition of the reaction during the passage of mixtures of these substances with alcohol in a pulsed system.

Analysis of the gas was conducted in a chromatograph with a column filled with Al₂O₃, impregnated with 3% NaOH. In certain experiments, in addition, the liquid portion of the catalyze was investigated chromatographically (column with polyethylene glycol-2000 on celite 545), and radiochromatographic investigations were conducted. L. A. Maklizh, whom the authors would like thank, took part in this last portion of the work.

In the work we used "rienst" brand abs. i-C₃H₇OH, produced by VEB Laborchemie Apolda, grade pure and analytical grade dihexyl oxalate and alkyl halides; oxalic acid esters were synthesized according to the procedures: diethyl oxalate [6], dimethyl diisopropyl oxalates [7], and di-tert-butyloxyl oxide [8]. The constants of all the compounds used corresponded to the literature data.

Preliminary experiments conducted at temperature of 190–230° indicated that the addition of certain substances to i-C₃H₇OH in amounts of 10 mole% leads to a substantial (from 2- to 12-fold) increase in the amount of C₃H₆ formed. Such substances include acetals [HC(O)₂C₂H₅ and CH₃CH(O)₂C₂H₅], esters of weak acids (diethyl carbonate, orthoformic ester, tetrabutyl titanate), alkyl halides (CH₃I, C₂H₅I, i-C₃H₇Br, C₂H₅Br, n-, i-, and t-C₃H₇Br, C₆H₅Br, cyclohexyl bromide, n-C₄H₉Cl, CHCl₃), and certain others. Additions of CH₃NO₂, C₂H₅NO₂, methyl formate, butyl acetate, tetraethyllead, butyl nitrite, tert–butyl peroxide, propylene oxide, malonic ester, and acetic acid had no effect (or produced an inhibition). The acceleration of the reaction noted apparently may be due to various factors. First of all, in certain cases the addition of substantial (10 mole%) amounts of the accelerator led only to a small increase in the absolute amount of propylene formed—by 1–2%. Since the degree of decomposition of pure i-C₃H₇OH under these conditions was only 0.1–2.5%, such an increase in the amount of C₃H₆, especially at low temperatures, might correspond to a tenfold acceleration of the reaction. Apparently such an increase in the degree of conversion could be explained entirely by assuming the occurrence of the process in two steps with an intermediate exchange of hydrocarbon radicals (for example, on account of alcoholysis of esters), where from the originally added ethyl, methyl, butyl, etc. esters of halogen derivatives, on the one hand, and isopropanol, on the other, the corresponding isopropyl derivatives are formed. In the case when the stability of these isopropyl derivatives will be lower under the reaction conditions (high temperatures, presence of a catalyst) than the stability of the starting materials, this leads to a certain slight increase in the amount of propylene formed, which may be interpreted as an apparent acceleration of the dehydroyation of i-C₃H₇OH.

Actually, the stability, for example, of pure diisopropyl oxalate under the conditions of our experiments was substantially lower than that of diethyl oxalate—the degree of conversion to the olefin in a circulating apparatus at 190° in the presence of Al₂O₃ was 80 and 0.2%, respectively. Therefore, during the passage of a mixture of i-C₃H₇OH+diethyl oxalate over the catalyst under these conditions, there could be a formation of diisopropyl oxalate as a result of alcoholysis or transesterification, and this substance could then instantaneously decompose on Al₂O₃, liberating propylene. Direct radiochemical experiments indicated that in the case of the passage of i-C₃H₇OH, i-C₃H₇OH, or sec-C₃H₇OH with an addition of 10% diethyl oxalate, labeled with radiocarbon [we synthesized the preparation from (COOH)₂ and ¹⁴C₂H₅OH] was passed over Al₂O₃ at 190–230°, a substantial increase was observed in the amount of propylene or butylenes formed. However, in this case practically all the radioactivity remained in the liquid catalyze in the form of ¹⁴C₂H₅OH, which confirms the assumption of the presence of an intermediate stage of exchange of hydrocarbon radicals.