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The Dehydration of Alcohols over Alumina

I. The Reaction Scheme

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For a number of straight-chained and branched alcohols the reaction scheme for the dehydration reaction on γ-Al_2O_3 is established. Assuming the "principle of least motion" is valid, the comparability of analogous reaction steps of different substrates with respect to a still unknown mechanism is proposed.

Since the beginning of the 20th century the dehydration of alcohols, in particular ethanol, on alumina has often been investigated. Only few of these investigations concern themselves with the influence of the substrate structure on the activation energy of the reaction. Dohse (*1*) and Bork (*2*), contrary to Stauffer and Kranich (*3*), find a systematic connection between activation energy and chain length or chain branching. It would appear, however, that in the above-mentioned publications the primary step of the reaction was not clearly understood. In addition, the question arises whether a comparison of the activation energies of various reactions is allowed. In principle, this will only be allowable when the experimental conditions and the reaction mechanisms are comparable.

Since Winfield (*4*) has given an excellent review of dehydration reactions, only two references are given here. Balaceanu and Jungers (*5*) suggest a primary ether formation with a possible attainment of equilibrium for the dehydration of ethanol. The olefin is formed as a secondary product with a reformation of the alcohol. At higher temperatures the olefin can also be formed directly. This scheme should also be valid for the higher members of the homologous series of primary aliphatic alcohols. Isagulyants and co-workers (*6*) come to the same scheme for the ethanol dehydration with the difference that the secondary olefin formation is thought to occur through water elimination from the ether.

We have attempted to determine the reaction steps of a series of straight-chain and branched alcohols on alumina. Very similar reaction schemes will be found for the different substrates. Assuming the "principle of least motion" is valid, one should be able to conclude whether a comparison of the activation energies of an analogous reaction step, for the same reaction order, of various substrates is really justified.

EXPERIMENTAL

a. Materials. The majority of the substrates were preparations for gas chromatography from Merck, Darmstadt. Ethanol A. R. was from Riedel de Haen, Seelze-Hannover. The purity of all substrates was >99%. The helium carrier gas from Linde contained 0.01% impurities.

b. Catalyst preparation and pretreatment. Only a catalyst which was selective for the dehydration and gave a reproducible activity could be considered. The choice fell on alumina, which, depending on structure and pretreatment, gives up to 100%

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dehydration (*7*). Bayerit-type R. D. 6176 from P. Spence (Lancs.) with 0.12 wt % foreign cations (*8*) was used as the starting material for the alumina. After 15 hr sintering at 800°C in a nitrogen stream a γ modification (*8*) of the alumina with a BET surface of 110 m^2/g (*9*) was obtained. The so-prepared oxide samples were sealed off in glass tubes and before use as catalysts were pretreated for 12–20 hr at the highest temperature used under reaction conditions. To control the activity during a series of experiments, the individual measurements were taken at alternatively high and low values of the altered parameter (e.g., temperature or contact time). The quantity of catalyst used was between 0.3 and 0.35 g.

c. Apparatus. The differential flow reactor in conjunction with a gas chromatograph has been described elsewhere (*10*). The gas chromatographic analyses were made with an apparatus of type GC-2 from Beckman Instruments. This commercial instrument has been slightly modified in so far as the sample valve has been heated to prevent any condensation of the sample. The separation of the reaction products was effected on the following column: 2 m Carbowax 1500, 20 wt % on Teflon at 130°C and 88 ml/min (30°C). The olefin composition was investigated on a 2-m column of $AgNO_3$ in diethylene glycol after freezing out the condensable products.

d. Evaluation. The partial pressures of the various components were obtained by comparing the peak areas or heights with a calibration curve. In every case the calibration curve was linear over the total range in which measurements were taken.

The contact time τ is defined as the ratio of catalyst quantity m in grams to the space velocity of the gas mixture v in ml (STP)/sec. Assuming the gas mixture to be ideal, the space velocity can be calculated from an equation by Damköhler (*11*) as

$$v = v_0[\bar{p}/(\bar{p} - p_s)] \qquad (1)$$

if one considers the evaporation as a type of monomolecular reaction; v_0 is the space velocity of the pure carrier gas, p_s the partial pressure of the substrate, and $\bar{p} = 720$ Torr the mean atmospheric pressure in Munich. τ then becomes

$$\tau = m/v_0[(\bar{p} - p_s)/\bar{p}] \qquad (2)$$

with the dimension g sec/ml(STP). For reactions with volume changes v must be corrected according to the change in the number of moles during the reaction. The carrier gas velocity v_0 must also be corrected for the water vapor pressure of the soap solution in the flow meter and for the fraction of uncondensable reaction products. While the water vapor pressure constitutes an error of less than 5% in all cases and could therefore be neglected, experiments with a high percentage of olefin in the gas mixture had to be appropriately corrected.

e. Errors. The glass reaction in the measured range was at the most 3% of the reaction on the catalyst. The mean error for a single determination (peak area → partial pressure) under constant reaction conditions is about 6%. This scattering can be attributed to small changes in catalyst temperature (± 1°C) and in flow velocity, as well as some uncontrollable activity changes of the catalyst.

RESULTS

1. Straight-Chain Primary Aliphatic Alcohols

a. Methanol (A). In the investigated temperature range up to 320°C, only water (W) and dimethyl ether (E) were found as reaction products. The dehydration of methanol, therefore, occurs according to the equation

$$2A \rightarrow E + W \qquad (3)$$

b. Ethanol (A). Diethyl ether (E), ethylene (O), and water (W) are found as reaction products. In Fig. 1 the temperature dependence of the partial pressures of these substances with a gas flow of 51 ml (STP)/min helium and an initial ethanol pressure of 99 Torr is shown. It is clear that at low temperatures the dehydration involves a bimolecular reaction with ether formation, analogous to Eq. (3). First at temperatures of 240°C and above ethylene formation—

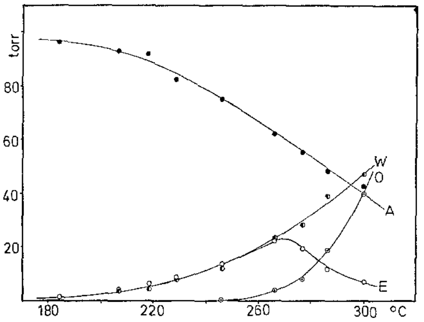


FIG. 1. Dependence of the ethanol decomposition on catalyst temperature.

dependent on the contact time—takes place. The finding of a temperature maximum for the ether formation indicates a secondary decomposition of the ether to olefin, since olefin first appears just near the inflection point of the ether curve.

On the same contact diethyl ether gives ethanol and ethylene as reaction products. In Fig. 2 the alteration of the partial pressures with temperature is shown. The gas flow was 51 ml (STP)/min helium and the initial ether pressure was 47 Torr. Initially the ethanol and ethylene pressures increase similarly. Above 260°C the slope of the ethylene curve becomes steeper and simultaneously water appears. Both diagrams (Figs. 1 and 2) show that the ether decomposition begins in the same temperature range, between 240° and 250°C.

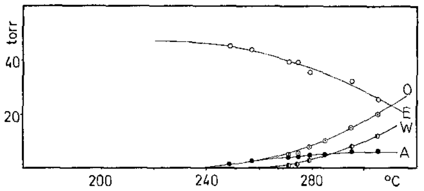


FIG. 2. Dependence of the diethyl ether decomposition on catalyst temperature.

The dependence of the degree of ethanol decomposition on the contact time furnishes further information about the various reaction steps. Figures 3–6 show this dependence at temperatures of 211°, 256°, 298°, and 343°C and an initial ethanol pressure of 106 Torr. Even with large con-

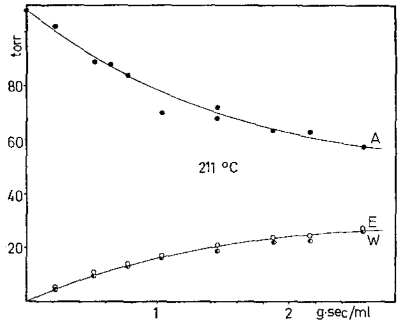


FIG. 3

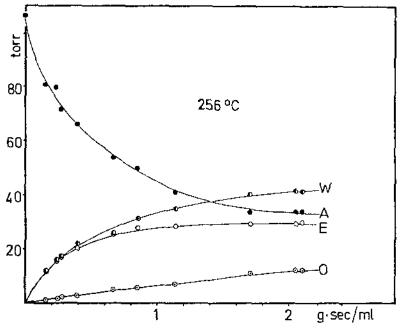


FIG. 4

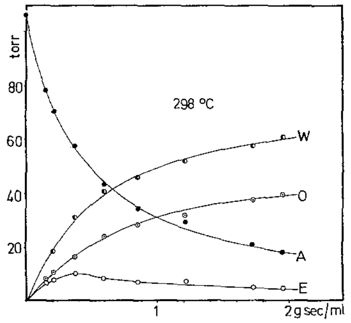


FIG. 5

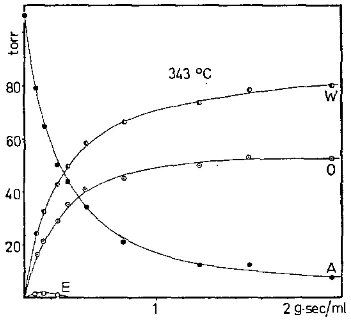


FIG. 6

FIGS. 3–6. Dependence of the ethanol decomposition on contact time at temperatures indicated.

tact times only ether formation is found at 211°C. At 256°C ethylene is found with a slight induction period, typical for a consecutive reaction. The ether pressure at 298°C shows a maximum on variation of the contact times while at 343°C the ether is found in small concentrations and only for short contact times. The induction period in the ethylene curves disappears.

If the slight induction period shown in Fig. 4 is only apparent this would mean that the primary and secondary olefin formation occurs simultaneously.

The mass balances for the conditions shown in Figs. 5 and 6 are faulty. Further gas chromatographic and infrared investigations show that in both cases (high temperatures) dehydrogenation, resulting in an error in the mass balance, has occurred. Acetaldehyde and hydrogen, as well as ethane, which presumably arises from a hydrogenation of the ethylene (*12*), were detected. Under the conditions normally used for the gas chromatographic separation, hydrogen, ethane, and ethylene came as a single peak and since the thermal conductivities of hydrogen and ethylene are, respectively, positive and negative compared to the helium carrier gas, the mixture of these gases gives a deflection which is smaller than that of pure ethylene. The apparent loss of ethylene shown in Figs. 5 and 6 may be attributed to this effect. However, since the dehydration can be considered to be independent of the dehydrogenation, the partial pressures of ether and water may be considered to give characteristic plots.

c. Higher homologs. The straight-chained alcohols up to *n*-hexanol show a completely similar behavior. The temperature range in which solely ether formation takes place becomes progressively smaller with increasing chain length. A consecutive reaction with the higher homologs is the isomerization of the initial 1-olefins. In agreement with other authors (*13*), for the *n*-butanol dehydration, an isomerization of the 1-butene initially formed, giving *cis*- and *trans*-2-butene with a clear preference for the *cis* product, was found. Skeletal isomerization could not be observed.

2. Branched Alcohols

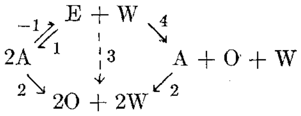
Isopropanol and the butanol isomers—butanol-2, isobutanol, and *tert*-butanol—were the branched alcohols investigated. The dehydration of isopropanol yields only minute quantities of diisopropyl ether along with propene formation. With water elimination from isobutanol and *tert*-butanol, isobutene is obtained as 95% of the reaction products, while with butanol-2 a mixture of the isomers 1-, *cis*-, and *trans*-2-butene is found, which according to Pines and Haag (*14*) form in primary parallel reaction steps. For none of the branched butanols could ether be detected.

DISCUSSION

1. Reaction Scheme

It follows from the results obtained by the dehydration of primary straight-chain alcohols that at low temperatures and small conversions the primary reaction step (1) is a bimolecular ether formation. Typical for this is the appearance of only ether and water at low temperatures and the induction period of olefin partial pressure against contact time. At higher degrees of decomposition the back reaction (—1) will become important. With increasing temperatures the induction period of the olefin curve disappears while at the same time the ether concentration in the contact time diagram goes through a maximum. This indicates that with increasing temperature a primary olefin elimination (2), in addition to the secondary olefin elimination from ether, becomes more important. The question whether the consecutive reaction for the olefin formation from ether occurs with water (3) or with alcohol elimination (4) cannot be definitely answered for the whole temperature range. At lower temperatures the alcohol elimination (4) is certainly preferred (compare Fig. 2), while from the steep rise in olefin pressure and the simultaneous appearance of water with increasing temperature, the water elimination cannot be excluded. However, the reaction step (3) would appear to be much less probable, than step (4). Experience has shown that the probability is very small that more than one bond of a reactive molecule is directly concerned during a chemical reaction. For reaction step (3) four bonds would have to be broken and four new ones formed. On the other hand, if one considers a transition state in the form of an oxonium ion RO^+RH, only one bond is required to dissociate to give step (4). It would therefore appear that also for higher temperatures the ethylene formation from ether goes through the stages (4)–(2), although step (3) cannot be completely excluded.

For the straight-chain primary alcohols the following reaction scheme can therefore be set up:



The contributions of the single reaction steps are temperature-dependent and for step (—1) also concentration-dependent. This scheme is in agreement with the previously mentioned scheme from Balaceanu and Jungers (*5*).

For isopropanol the same scheme as for the straight-chain alcohols is valid, with the difference that the reaction step (1) cannot be isolated. The dehydration of the isomeric butanols takes place according to step (2) with ensuing isomerization.

2. Thermodynamical Considerations

Since the values of the free enthalpy for the various reaction steps are not tabulated, we have calculated them using the free enthalpy of formation $\Delta G_f^{\mathrm{norm}}$ in the standard state, which can be evaluated using an increment method (*15*). $\Delta G_f^{\mathrm{norm}}$ (T) means the free enthalpy of formation of 1 mole at temperature T, for a standard pressure of 1 atm. From these values the free enthalpies of the reaction steps $\Delta G_R^{\mathrm{norm}}$ (analogous definition) can be calculated. The relation

$$\Delta G_R^{\mathrm{norm}}(T) = -RT \ln K_p \qquad (4)$$

now allows the equilibrium constants K_p, in particular for reaction (1) ↔ (—1) to be calculated. In Table 1 experimental values of K_p, obtained from Fig. 3 (211°C), Fig. 4 (256°C), and measurements at 196°C, are compared with the calculated values.

TABLE 1
COMPARISON OF CALCULATED AND EXPERIMENTAL EQUILIBRIUM CONSTANTS

T (°C)	K_p (calc.)	K_p (exp)
196°	0.05	0.06
211°	0.08	0.26
256°	0.22	0.97

Considering the fact that some of the plots had to be extrapolated to longer contact times and that the calculated ΔG values are not exact, which greatly affects the K_p values, a better agreement can hardly be expected. In any case, experiment and calculation show the same temperature dependence, contrary to the values of Pease and Yung (*16*), who find a displacement of the equilibrium in favor of the alcohol at higher temperatures. From the values of K_p one can also evaluate the ratio of the reaction velocity w for steps (1) and (—1). It can be shown that for small degrees of decomposition and not too large contact times the back reaction is negligible (e.g., at 211°C and 10% decomposition the ratio w_1/w_{-1} lies between 8 and 26).

In Table 2 the free enthalpies of reaction $\Delta G_R^{\mathrm{norm}}$ of reaction steps (1) and (2) for some straight-chained and branched alcohols at two different temperatures are shown. On correcting these values to the partial pressure values existing under experimental conditions, the values for step (1) with the straight-chain alcohols also become negative, but the over-all tendency remains the same. It would therefore appear that for all alcohols the direct olefin formation should be preferred to the ether formation, because of the greater negative free enthalpies of reaction. In spite of this ether formation is observed for the straight-chain alcohols on alumina at low temperatures. With increasing temperature the free enthalpy of reaction values for step (2) decrease more rapidly than for step (1) and the course of the reaction is

TABLE 2

Free Enthalpies of Reaction for Ether [step (1)] and Olefin [step (2)] Formation from Various Alcohols

Alcohol	T (°abs)	ΔG_R^{norm} (kcal/mole) (1) $2A \rightarrow E + W$	ΔG_R^{norm} (kcal/mole) (2) $A \rightarrow O + W$
C_2H_5OH	500°	+2.24	−2.75
	600°	+0.33	−5.64
n-C_3H_7OH	500°	+2.24	−6.5
	600°	+0.33	−9.5
n-C_4H_9OH	500°	+2.24	−6.36
	600°	+0.33	−9.48
n-$C_5H_{11}OH$	500°	+2.24	−7.03
	600°	+0.33	−10.08
iso-C_3H_7OH	500°	+5.44	−5.04
	600°	+3.37	−8.34
iso-C_4H_9OH	500°	+2.24	−8.54
	600°	+0.33	−11.39
tert-C_4H_9OH	500°	+16.28	−1.93
	600°	+14.39	−5.18

displaced in favor of direct olefin formation. For the branched alcohols either step (1) has positive free enthalpy values or step (2) strongly negative values. Even the presence of catalyst does not lead to ether formation, so that in these cases the selectivity of the alumina is not strong enough to allow the thermodynamically unfavored reaction course to be taken.

3. Comparability of the Dehydration of Various Alcohols

The "principle of least motion," as postulated by Rice and Teller (*17*), states that from a number of possible reaction mechanisms with a high degree of probability, the mechanism in which the position of the individual atoms (least motion of atoms) and the electron configuration of the reacting system (least motion of electronic configuration) is least altered is chosen. In our case the question is, whether analogous reaction steps of the various substrates, as characterized by the activation energies, can be compared with one another, i.e., whether the reactions take place with the same mechanism. Since the alcohols investigated here differ only in chain length or chain branching and the same reaction scheme is valid for all of them, i.e., analogous products are formed, one can assume that analogous reaction steps of the various substrates occur by the same still unknown mechanism. For if the "principle of least motion" is valid and the path of least structure alteration of the reacting system is chosen, it is unlikely that for so similar reactions several equivalent paths for the same recation direction are available. We therefore arrive at the conclusion that analogous reaction steps of the reaction scheme found here for various substrates, e.g., the ether formation, occur with a high degree of probability, if not with certainty, with the same mechanism and the same elementary step is rate-determining. The activation energies are then, for the same reaction order, comparable with one another.

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