

The Dehydration of Alcohols over Alumina

VII. The Dependence of Reaction Direction on the Substrate Structure

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The kinetics of the dehydration of *n*-propanol, benzyl alcohol, isobutanol, and cyclohexanol on γ -Al₂O₃ have been studied and the structures of the adsorption complexes have been investigated by IR spectroscopy. The same rate equation as in the case of the dehydration of methanol and ethanol to ether and of *tert*-butanol to olefin is found empirically. The selectivity with respect to ether and olefin formation is regarded to be a function of the thermal stability of the respective surface alkoxides. There is IR spectroscopic evidence of such surface alkoxides on the adsorption of alcohols which form ethers, whereas with olefin-forming alcohols no such compounds are detectable.

1. INTRODUCTION

The dehydration of alcohols on alumina leads either to ether or to olefin (1). The ether formation from straight-chain aliphatic C₁-C₄ alcohols (1) and benzyl alcohol (2) in particular can be investigated, albeit in a somewhat narrow temperature range, without interference from side or consecutive reactions. On the other hand the dehydration of isobutanol, *tert*-butanol (1), and cyclohexanol (3, 4) yields only olefin. The kinetics of the dehydration of methanol (5), ethanol (6), and *tert*-butanol (7) has already been investigated and an explanation of the empirically determined rate equation given (8). With the help of IR investigations of the ethanol adsorption on alumina (9-12) we suggested (6, 8) that if the ether formation goes through a surface alkoxide stage, whereas the olefin formation goes through E1- or E2-like reaction intermediates (13). In order to test this hypothesis we have investigated the IR spectra and the dehydration kinetics of a few other alcohols on alumina. *n*-Propanol and benzyl alcohol were chosen as representative of the ether-forming alcohols and isobutanol and cyclohexanol of the olefin-forming alcohols.

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2. EXPERIMENTAL

Materials

The alcohols and aluminum tertiary butylate were AR grade from Fluka AG (Buchs, Switzerland). Residual water was removed from the alcohols before use by drying over 3-Å molecular sieve. The other aluminum alcoholates used for registration of reference spectra were prepared as follows:

Aluminum isobutylate. Five grams of aluminum powder was heated in a mixture of 30 cc of benzene and 30 cc of isobutanol. The hot solution was filtered and the excess alcohol and benzene distilled off. The remaining paraffin-like mass had a melting point of 221°C compared to 215-225°C as reported by Robinson and Peak (14). The C/H analysis gave 54.9% C and 10.8% H (theoretical values: 58.5% C and 11.0% H).

Aluminum cyclohexylate. Six grams of aluminum ethylate (Merck, Darmstadt, Germany) was allowed to react with 20 cc of cyclohexanol. The ethyl alcohol produced and the excess cyclohexanol were distilled off. The brownish-colored, prism-formed crystals so obtained were recrystallized in xylene. As the substance became unstable before melting its melting point could not

be determined (15). The C/H analysis gave 61.9% C and 6.51% H (theoretical values: 61.3% C and 6.35% H).

Aluminum benzylate. Aluminum benzylate was prepared in the same way as the cyclohexylate. During the recrystallization from a low-boiling petroleum ether large transparent prisms were formed. They had a melting point of 57°C as compared to the value of 59–60°C reported in the literature (16). NMR spectra, which were made in a hexadeuterobenzene solution, indicated that the substance was the benzylate.

Catalysts

The γ -Al₂O₃ used as catalyst in the kinetic measurements has been described elsewhere (1). About 300 mg of catalyst was used in each run. Because of the particle size and the large intensity losses this oxide was unsuitable for the spectroscopic investigations. A γ -Al₂O₃ type P110c1 (Degussa, Hanau, Germany) prepared by flame hydrolysis was therefore used. The particle size ranged between 5 and 30 m μ and the BET surface was 100 \pm 10 m²/g. The oxide was heated to 500°C in vacuum (10⁻³ mm Hg) for 1 hr before use. This oxide shows the same catalytic behavior as the catalyst used in the kinetic measurements. The activity, however, is somewhat lower.

Kinetic Investigations

The kinetic measurements were carried out in a continuous flow reactor in which the feed flows over a vessel containing the catalyst (5, 6). The feed consists of a helium carrier gas containing substrate vapor which is introduced by a saturator (6). All disturbing transport phenomena can be eliminated by keeping the conversion low (<3%). A second saturator, which allows the introduction of a higher concentration of reaction products into the gas stream, can be used to determine the dependence of the reaction rate on the concentration of products (6).

The analysis and the quantitative determination of the reaction products were made by gas chromatography. A 2-m column, 5-mm ID, packed with carbowax 1500 (20% by wt) on Teflon was usually used.

The reaction rates have been calculated as described elsewhere (5, 6).

IR Spectroscopic Investigations

The IR spectra of the adsorbed alcohols were obtained in a vacuum-proof, heatable metal cell with silver chloride windows (8). The spacing of the windows (1–2 mm) determined the thickness of the alumina powder. The weight of the samples was 10–13 mg for every cm² of the infrared beam. The spectra were recorded on an IR spectrometer type 225 from Perkin-Elmer at the adsorption temperature.

3. RESULTS AND DISCUSSION

Kinetic Measurements

Under the chosen experimental conditions the catalytic dehydration of *n*-propanol, benzyl alcohol, and cyclohexanol could be observed above 130°C, while for isobutanol a temperature of 160°C was necessary. The pressure dependence of the reaction rate of the ether and olefin formation was measured between 40 and 300 mm Hg. Because of the low vapor pressure of benzyl alcohol the dehydration could only be followed up to 120 mm Hg. The zero order could be verified in all cases for the following ranges:

<i>n</i> -Propanol	Up to 200°C above 50 mm Hg
Benzyl alcohol	Up to 170°C above 30 mm Hg
Isobutanol	Up to 240°C above 80 mm Hg
Cyclohexanol	Up to 180°C above 80 mm Hg

Figure 1 gives a few examples of these measurements. Reaction rates are given in moles of product per gram of catalyst per second. In the case of the ether formation we therefore have a bimolecular reaction in the adsorbed phase, that is a Langmuir-Hinshelwood mechanism. This result has also been obtained for the ether formation from methanol (5) and ethanol (6). In the zero order range the Arrhenius plots lead directly to the "true" activation energies. A few values of the activation energies for the dehydration of four alcohols investigated are listed in Table 1 for various catalyst samples and at various substrate pressures.

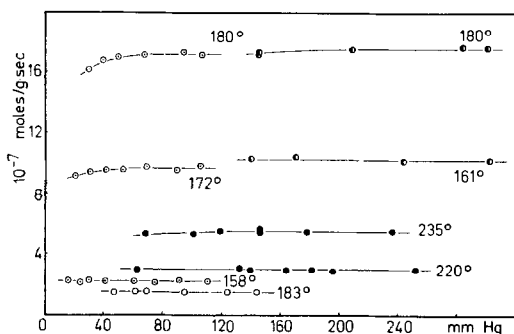


Fig. 1. Pressure dependence of the reaction rate for the dehydration of isobutanol (●), cyclohexanol (○), *n*-propanol (○), and benzyl alcohol (○).

Mean values and maximum errors are also given.

Ether and olefin formation are both strongly inhibited by water. No inhibition by the other products could be observed. The kinetics were determined by measuring the reaction rates at various constant alcohol pressures as a function of the water pressure. The latter could be established by introduc-

TABLE I
TRUE ACTIVATION ENERGIES OF THE ETHER
AND OLEFIN FORMATION

Alcohol	Pressure (mm Hg)	Activation energy (kcal/mole)	Mean values
<i>n</i> -Propanol	54	24.6	25.1 ± 0.6
	86	25.2	
	112	24.6	
	125	25.2	
	136	25.7	
Benzyl alcohol	20	24.6	25.5 ± 0.7
	50	26.0	
	50	26.2	
	61	25.9	
	75	25.7	
Isobutanol	100	24.9	30.0 ± 0.6
	79	30.6	
	98	29.9	
	120	29.6	
	137	29.7	
Cyclohexanol	160	29.9	25.7 ± 0.3
	200	29.7	
	75	25.6	
	95	25.9	
	120	25.5	
	120	26.0	
	158	25.5	
	240	25.6	

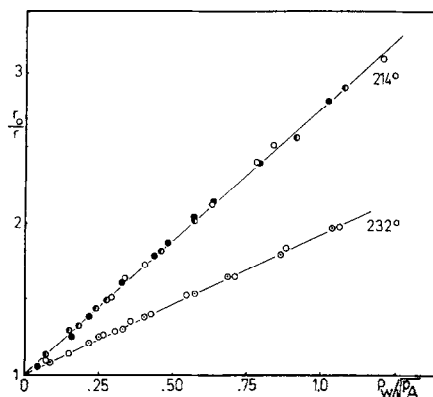


Fig. 2. Water inhibition for the olefin formation from isobutanol at 90 (○), 120 (●), 172 (○), and 185 (●) mm Hg.

ing a second helium stream saturated with a known amount of water to the reaction feed. The results for the olefin formation from isobutanol and the ether formation from benzyl alcohol at various temperatures and pressures are shown in Figs. 2 and 3, respectively. In the range measured (up to a maximum ratio of water to alcohol of about 15 to 85) the reaction rates for the ether and also for the olefin formation can be represented by the equation

$$r = r_0 \frac{P_A^{1/2}}{P_A^{1/2} + bP_W} = r_0 \theta_A \quad (1)$$

or in the linearized form

$$\frac{r_0}{r} = 1 + b \frac{P_W}{P_A^{1/2}} \quad (2)$$

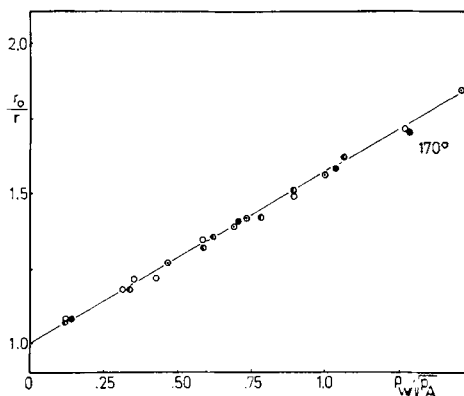


Fig. 3. Water inhibition for the ether formation from benzyl alcohol at 25 (●), 40 (○), 50 (●), and 78 (○) mm Hg.

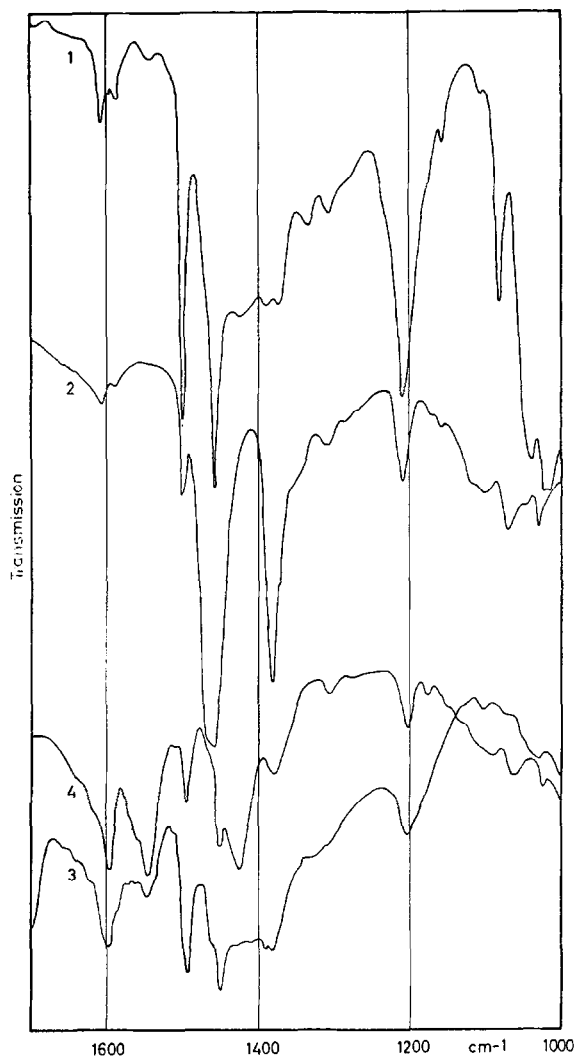


Fig. 4. IR spectra of benzyl alcohol adsorbed on alumina: (1) liquid benzyl alcohol; (2) aluminum benzylate; (3) benzyl alcohol adsorbed on alumina at 160°C; (4) benzyl alcohol on alumina after desorption at 170°C.

where r means the reaction rate in moles/g sec; r_0 , the reaction rate for the zero order; P_A and P_W , the partial pressures of alcohol and water; and b , a constant. This expression has already been found for the dehydration of methanol (5), ethanol (6), and *tert*-butanol (7) on γ - Al_2O_3 , as well as for the dehydration of methanol on α - Al_2O_3 (17). θ_A in Eq. (1) represents the catalyst surface coverage with alcohol. To explain this expression we assumed that at high temperatures the alcohol was preferentially adsorbed over two nonlinear H bonds (8). This was verified by

IR spectroscopic investigations on the H-bond systems during the adsorption of alcohols (18). The square-root expressions in Eqs. (1) and (2) are brought about by this two-point adsorption. On the other hand, the temperature dependence of the deformation band of molecularly adsorbed water clearly shows an adsorption of water on a single center (OH-group) by a passive H-bond at low surface coverages of water (8). The water pressure therefore appears linear in the rate equation.

In the rate equation for the bimolecular

ether formation the surface concentration of the alcohol appears linear and not, as one might expect, squared. We therefore postulated (6) that one of the reaction partners for the ether formation from ethanol is in the form of a surface alkoxide of finite lifetime, whose concentration during the reaction can be regarded as constant and which can be detected with IR spectroscopy. For this reason only the surface concentration of the second reaction partner, a molecularly adsorbed alcohol molecule bound over two nonlinear H bonds, appears in the rate equation. These considerations would also seem to be valid for the alcohols investigated here. In addition the selectivity with respect to ether and olefin formation can be explained by the thermal stability of the surface alkoxides, insofar as it can be shown that only the ether-forming alcohols can lead to a surface alkoxide.

IR Spectroscopic Investigations

In order to test the above considerations the adsorption of *tert*-butanol, isobutanol, cyclohexanol, and benzyl alcohol was investigated by IR spectroscopy, particular emphasis being placed on the surface alkoxide formation. The spectra, henceforth called "adsorption spectra," were taken after adsorption of the alcohols at pressures of 40 to 60 mm Hg and temperatures between 50° and 180°C, at the adsorption temperature. Only in the case of benzyl alcohol adsorption was the Al₂O₃ sample wet with the alcohol prior to the heat treatment. Finally "desorption spectra" were measured at the highest adsorption temperature by evacuating to 10⁻³ mm Hg for 1 hr. The spectra of the alcohols and the respective solid aluminum alkoxides which were suspended in paraffin oil, were used for

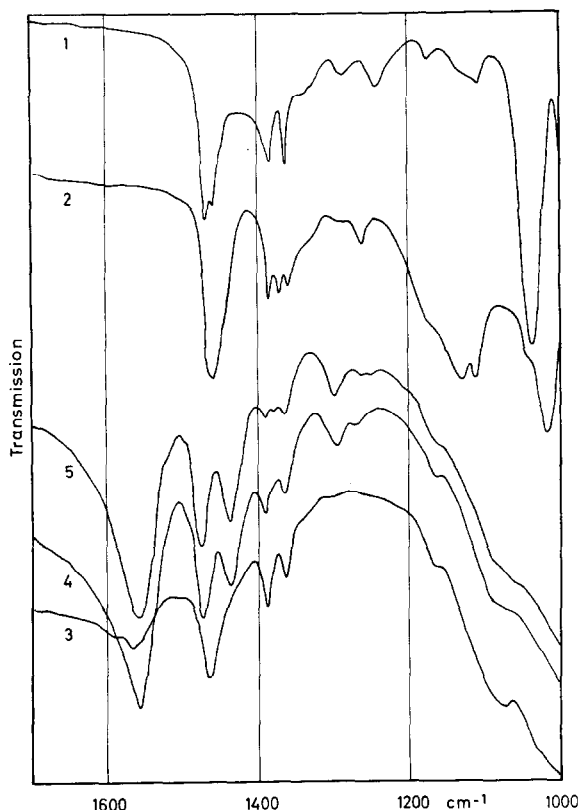


Fig. 5. IR spectra of isobutanol adsorbed on alumina: (1) liquid isobutanol; (2) aluminum isobutylate; (3) isobutanol adsorbed on alumina at 110°C; (4) isobutanol adsorbed on alumina at 170°C; (5) after desorption at 170°C.

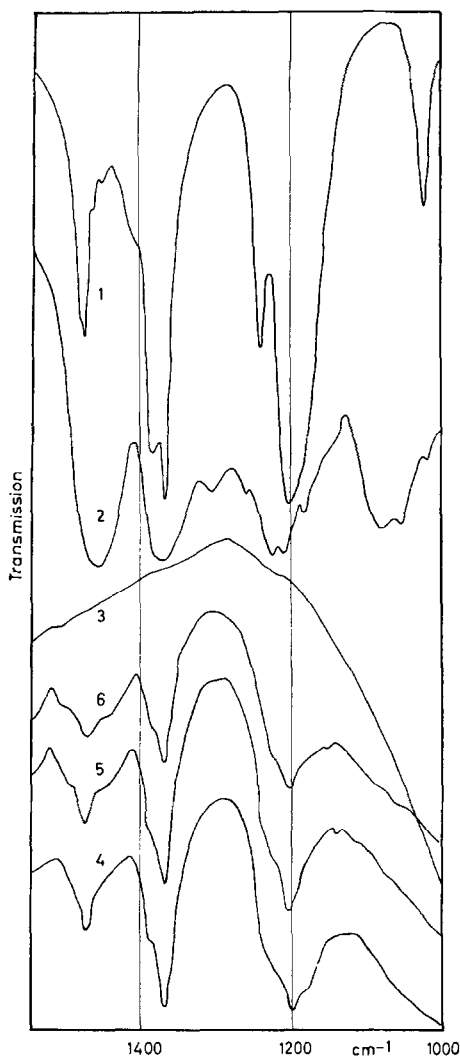


FIG. 6. IR spectra of tertiary butanol adsorbed on alumina: (1) liquid tertiary butanol; (2) aluminum *tert*-butylate; (3) γ - Al_2O_3 , background; (4) *tert*-butanol adsorbed on alumina at 84°C; (5) at 123°C; (6) at 161°C.

comparison. The spectra between 1600 and 1000 cm^{-1} for the ether-forming benzyl alcohol and the olefin-forming alcohols isobutanol and tertiary butanol are given in Figs. 4, 5, and 6. Since the IR spectra of the alkoxides are not available in the literature, the assignment of the various bands cannot be given.

Aluminum benzylate has characteristic bands at 1028, 1069, 1090, 1170, 1208, and 1307 cm^{-1} ; liquid benzyl alcohol on the other

hand at 1028, 1040, 1083, 1160, 1212, 1308 and 1338 cm^{-1} (Fig. 4). While in the adsorption and desorption spectra the alcohol bands (mainly those at 1040, 1083, 1160, 1212, and 1338 cm^{-1}) diminish with increasing temperature, most of the aluminum benzylate bands become larger (mainly those at 1022, 1060, 1090, 1170, and 1304 cm^{-1}). The "desorption spectrum" of benzyl alcohol on alumina at 170° (Fig. 4) is very close to that of the aluminum benzylate in the range between 1200 and 1000 cm^{-1} . The existence of a surface benzylate can be implied from this information.

At higher temperatures, as can be seen from the "desorption spectrum" (see Fig. 4), very intensive bands appear at 1600, 1550, and 1425 cm^{-1} . These bands can be assigned to a surface carboxylate structure, as has been shown by reference spectra of sodium and potassium benzoate. Analogous carboxylate structures have been observed during the adsorption of methanol and ethanol by Greenler (9), and of *n*-propanol and *n*-butanol by Corso (19), and by Kagel (12). In the case of benzyl alcohol adsorption the bands of the carboxylate structure do not disturb the identification of the alcoholate structure.

A similar oxidation of the alcohol to a surface carboxylate can be observed for the adsorption of isobutanol on alumina as shown in Fig. 5. At relatively low adsorption temperatures the "adsorption spectrum" is very close to that of liquid isobutanol. With increasing temperature intensive bands appear at 1560, 1475, 1440 cm^{-1} , while at the same time the band of the CH_2 deformation vibration at 1460 cm^{-1} diminishes. Comparison with the spectra of various metal salts of isobutyric acid shows that these bands ought to be typical for a surface carboxylate. Characteristic bands which on the other hand could indicate the formation of a surface alcoholate could not be observed. Such bands should appear at 1020, 1115, 1135, and 1260 cm^{-1} (see Fig. 5).

Aluminum tertiary butylate shows intensive characteristic bands at 1060, 1085, and 1358 cm^{-1} (Fig. 6). *tert*-Butanol has no absorption at these wave numbers so that the formation of a surface alcoholate by

tert-butanol should be clearly seen. The adsorption spectra, however, give no evidence of any bands other than those of liquid *tert*-butanol. The formation of an alcoholate by the adsorption of *tert*-butanol on alumina can therefore be negated. In addition, no indication of a surface carboxylate was found, for the formation of which a reorganization of the carbon skeleton would have been necessary.

No aluminum alcoholate was formed by the adsorption of cyclohexanol on alumina. The formation of this surface compound should be indicated by the appearance of bands at 1015 and 1055 cm^{-1} , whereas only spectra very similar to those of liquid cyclohexanol could be obtained under the conditions used.

Since the adsorption of methanol (9), ethanol (9-12), *n*-propanol (11, 12), isopropanol (11), *n*-butanol (12), and benzyl alcohol shows the existence of surface alcoholate structures and all these alcohols, at least at low temperatures, yield ether (1), it can be seen as proven that all the ether-forming alcohols, which have been investigated up to now, form an aluminum alcoholate during adsorption.

The ether-forming and the olefin-forming alcohols are therefore clearly distinguished from one another by the fact that the first group has the ability to form a relatively stable aluminum alkoxide. Thermochemical investigations of the alkoxide stability show analogous distinctions (20). These findings do not of course prove the active participation of the observed surface alkoxides in the ether formation. However, since up to now no contrary evidence has been found we come to the conclusion that the surface alkoxides are intimately concerned with the selectivity during the dehydration of alcohols on alumina.

An olefin formation by dissociation of alkoxide groups with a short lifetime has also been discussed (21). The alkoxide formation presumably occurs on incompletely coordinated surface aluminum ions through dissociative adsorption of the alcohol as stated by Kagel (12). Such Lewis centers can be selectively poisoned by pyridine. The activity of pyridine-poisoned

alumina catalysts for the olefin formation from *tert*-butanol remains unaltered (21, 23). Therefore the olefin formation cannot proceed over the dissociation of a surface alkoxide. The behavior of a tertiary alcohol may appear to be not necessarily characteristic of primary and secondary alcohols as regarding the dehydration mechanism. However, Treibmann and Simon (24) could recently prove the above mentioned conclusion. By comparing the IR spectra of adsorbed isopropanol and kinetic data of the olefin formation from this alcohol, they could preclude an active participation of a surface alkoxide in the case of the dehydration of a secondary alcohol though this compound was really formed under catalytical conditions. The ether formation from ethanol on the other hand is inhibited on the addition of pyridine to the alumina (23). This is a further point in evidence of the active participation of surface alkoxides in the ether formation.

For the mechanism of ether formation we come therefore to the conclusion that a surface alcoholate group reacts with an alcohol molecule in the adsorbed phase by an electrophilic attack on the hydroxyl oxygen. The details of this mechanistic concept are discussed in two prior publications (8, 25). The monomolecular olefin formation at higher temperatures can go through similar stages as in the dehydration in dilute acid solutions, as Pines and Manassen (13) suggest, i.e., tertiary alcohols form more or less free carbonium ions, secondary alcohols form stabilized intermediates which can be considered as being between carbonium ions and the transition state of a concerted reaction, and primary alcohols are dehydrated via a concerted mechanism. Current work, however, seems to prove an E2-like reaction intermediate at low temperatures for the olefin formation even from tertiary alcohols so that, depending on the temperature, dehydration goes through a concerted or carbonium ion mechanism. This work will be published later.

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