JOURNAL OF CATALYSIS 17, 252-263 (1970)

The Dehydration of Alcohols on Alumina

XII. Kinetic Isotope Effects in the Olefin Formation from Butanols

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Received October 3, 1969

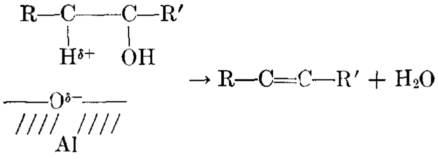
Primary kinetic isotope effects of the dehydration from the gas phase of tertiary, secondary and iso-butanol on alumina have been measured in a temperature range between 120 and 230°C. The deuteration of the hydroxyl group does not give rise to an isotope effect, whereas substitution of the β-proton by deuterium produces an appreciable effect. From the dependence of the isotope effects on substrate structure and temperature it can be concluded that at temperatures below 200°C primary, secondary, and tertiary alcohols are dehydrated via E 2-like reaction intermediates over alumina which presumably contain a certain degree of ionic contributions. With increasing temperature these ionic contributions are favored so that at elevated temperatures—depending on the reactant structure—the reaction may proceed via a E 1-mechanism.

INTRODUCTION

The majority of alcohols leads to the formation of olefins on dehydration over alumina (*1–4*). This reaction has been studied with respect to its mechanism for many years which nevertheless is not fully understood until today.

Pines and Haag (*6*) and later Krylov (*7*) and Jain and Pillai (*8*) prefer an adsorption of the alcohol through the oxygen of the alcoholic hydroxyl group on an incompletely coordinated surface aluminum ion (Lewis center). The C-O bond of the alcohol can therefore be polarized, making the OH-group a better leaving group. The β-hydrogen can be abstracted by a basic site. The participation of basic sites in the dehydration of alcohols has recently been proved by poisoning experiments with tetracyanoethylene (*9*, *10*). The active participation of Lewis acid sites, on the other hand, could be ruled out by selectively poisoning the alumina with pyridine (*2*, *3*, *11*, *12*). The adsorption of alcohol by surface hydroxyl groups and oxygen ions via H-bonds has therefore been preferred over the adsorption on Lewis acid sites (*2*, *3*). Each alcohol molecule most probably forms more than one H-bond, thus preforming the water molecule to be eliminated.

Pisman and co-workers (*5*) postulated a reaction intermediate which is H-bonded to a surface oxygen ion via the C_β-proton:



$$\underset{\overset{|}{H^{\delta+}}}{R{-}C}{-}\underset{\overset{|}{OH}}{C}{-}R' \cdots \underset{Al}{O^{\delta-}} \rightarrow R{-}C{=}C{-}R' + H_2O$$

As a possible pathway of the elimination of water from ethanol, the decomposition through surface alkoxide species has also been discussed (*13*, *14*). Surface alkoxide species are indeed formed during the adsorption of certain, but by far not all alcohols. In particular, most of the alcohols which solely form olefins on dehydration

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at low temperatures do not form surface alkoxides (*15*). Also for the dehydration of secondary alicyclic alcohols could the participation of surface alkoxide species be rejected very recently (*46*). Makarov and Shtschekotschichin (*16*) and Arai and coworkers (*17*) on the other hand tried to prove the alkoxide mechanism by thermal desorption studies of ethanol. It seems, however, questionable whether conclusions can be drawn concerning the mechanism of the heterogeneously catalyzed dehydration from the results of this experimental technique. During the reaction from the gas phase alcohol molecules adsorbed by H-bonds are present in the adsorbed phase which can take part in the reaction course, contrary to the thermal desorption experiments (*2*, *3*).

Thus, at the moment, an alcohol molecule held to the surface by more than one non-linear H-bond seems to be the most probable adsorption state in which the elimination of water is initiated. According to Krylov (*7*), the desorption of water is the slowest process. There is, however, strong kinetic evidence which proves the reaction itself to be the rate-determining process (*47*). Regarding the mechanism, one of the most important questions is the timing of the elementary steps. Pines and coworkers (*4*) from studies of the product distributions at relatively elevated temperatures arrived at the conclusion that the dehydration of primary and secondary aliphatic alcohols proceeds via an E 2-like reaction intermediate whereas the elimination of water from tertiary alcohols goes through an E 1-mechanism. Recently, however, it was shown with the aid of product distributions (*18*) and of kinetic isotope effects (*19*) that even tertiary alcohols are dehydrated via an E 2-like mechanism at low temperatures. To elucidate further these very important questions which are still a matter of controversy, the kinetic β-deuterium isotope effect on the dehydration over alumina has been studied. Isobutanol, sec-butanol, and tertiary butanol were chosen as substrates to cover the groups of primary, secondary, and tertiary alcohols.

EXPERIMENTAL

Materials

Protonated and deuterated alcohols were all prepared by Grignard-reactions. The deuterated reagents were supplied by C. Roth, Karlsruhe, Germany. They were all 99% deuterated in the position in question. The other reagents were p. A. grade from Riedel-de-Haen, Hannover, Germany.

Tertiary butanols. A Grignard-compound was made from magnesium turnings and normal or deuterated methyl iodide which was then reacted with normal or perdeuterated acetone, respectively, to give tertiary butanols. The OH-alcohols were distilled over Na_2SO_4 and then kept over molecular sieve 3A. The OD-alcohols were prepared from OH-alcohols by deuterium exchange with D_2O and subsequent drying over $BaSO_4$.

Secondary butanols. The Grignard-compound formed from magnesium and ethyl bromide was reacted with acetaldehyde in absolute ether to give secondary butanol. For the preparation of $CD_3CD_2CH(OH)$-CH_3, perdeuterated ethyl bromide was used. The alcohols were dried following the procedure described for tertiary alcohols.

Isobutanols. Isopropyl bromide needed for the preparation of the isobutanols was prepared by reaction of PBr_3 with isopropanol at −10°C (*20*). The product was distilled, the unreacted alcohol extracted with concentrated sulfuric acid and dried at 0°C over K_2CO_3. The Grignard-compound made from the isopropyl bromide and magnesium was reacted with paraformaldehyde to introduce a methyl group in the carbon chain and then hydrolyzed in ether with ice and diluted hydrochloric acid. The solution of ether and isobutanol was dried over K_2CO_3, filtered and distilled. For the preparation of $(CH_3)_2$-$CDCH_2OH$ and $(CD_3)_2CDCH_2OH$ the respective isopropyl bromides $(CH_3)_2CDBr$ and $(CD_3)_2CDBr$ were made from $(CH_3)_2$-$CDOH$ and $(CD_3)_2CDOH$, respectively, and then treated as described above.

The purity and degree of deuteration of the resulting alcohols was proved by IR-spectroscopy and NMR. The purity was

TABLE 1
C—H(D)-STRETCHING VIBRATIONS OF THE ALCOHOLS

	Iso-BuOH		sec-BuOH		tert-BuOH	
Wave-number (cm^{-1})	$-\overset{\overset{\text{H}}{\vert}}{\underset{\vert}{\text{C}}}-$	$-\overset{\overset{\text{D}}{\vert}}{\underset{\vert}{\text{C}}}-$	$>CH_2$	$>CD_2$	$-CH_3$	$-CD_3$
ν	2850	2100	—	—	—	—
ν_{as}	—	—	2926	2185	2962	2221
ν_s	—	—	2853	2070	2872	2130

better than 99%. The degree of deuteration was 97% for $(CD_3)_3COH$, 92% for $(CH_3)_2CDCH_2OH$, 90% for $(CD_3)_2CDCH_2OH$ and 84% for $C_2D_5CH(OH)CH_3$. The wave numbers of the respective symmetric and asymmetric C-H(D) stretching vibrations are given in Table 1.

The γ-Al_2O_3 used as catalyst has been described elsewhere (*1*). 700–1000 mg of catalyst was used in each run depending on temperature and reactivity of the alcohol.

Apparatus. The reactions were carried out in a quasi-static system as previously described (*21*), which contained a re-circulating pump (*22*) and which was connected to a conventional vacuum system. The circulating feed velocity was about 600 ml/min. No inhibition by external diffusion could be detected under these conditions even at the highest temperatures used. The whole system was thermostated at 71 ± 2°C to prevent condensation of the substrate. The reaction temperature was kept constant to ±0.2° at the desired value and measured by a thermocouple. The reaction rate was followed by measuring the total pressure with a mercury manometer.

Procedure. The catalyst was evacuated to 10^{-5} mm Hg at the highest reaction temperature before each series of measurements. After a few successive runs the activity of the catalyst was constant and reproducible. Each run was about 30 min, the catalyst was evacuated between successive runs.

The olefin formation from alcohols follows the formal equation

$$A \rightarrow R + S,$$

so that the pressure increase per unity of time directly gives the reaction velocity. It is known from preceding kinetic studies (*15*, *23*) that the olefin formation is a zero order reaction at 80 mm Hg in the whole temperature range covered in this work. Thus, plots of the total pressure increase against reaction time are straight lines whose slopes $\Delta p/\Delta t$ determines the zero order rate constant r.

Wall reactions could not be observed even at the highest temperatures. Applying the formula (*24*)

$$\phi = \frac{R_k^2}{p \cdot D_{\text{eff}}}\left(-\frac{V_R}{V_k}\right)\frac{dp}{dt}, \qquad (1)$$

where R_k is the radius of the catalyst grains, p the alcohol pressure in mm Hg, D_{eff} the effective diffusion coefficient, V_R the volume of the reactor, V_k the volume of the catalyst, $\frac{dp}{dt}$ the reaction rate, inhibition by internal diffusion could be excluded. For zero order reactions ϕ should not exceed a value of 6:

$$\phi \leq 6. \qquad (2)$$

Assuming Knudsen molecular flow to work and suggesting pore radii of 25 Å, one calculates $\phi = 0.4$ for the most extreme conditions so that the Eq. (2) is fulfilled.

The zero order rate constants were plotted in Arrhenius diagrams and the optimal straight line calculated by means of a least squares method. The activation energies ΔE were thus obtained from the slope and the activation entropies $\Delta S^{\ddagger}$ from the ordinate value at $1/T = 0$. According to Eq. (3) which is given by the transition state theory: (*30*)

$$r = \frac{kT}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta E/RT} C_a e^{-(\Delta n^{\ddagger} - 1)} \qquad (3)$$

k	Boltzmann constant
h	Planck's constant
R	gas constant
c_a	surface concentration of the substrate
$\Delta n^\ddagger$	change in number of molecules by the transition to the transition state (here $\Delta n^\ddagger = 0$)

The surface concentration of the alcohols in a completely filled surface was calculated from the liquid density according to Emmett and Brunauer (*25*) to be 3.7×10^{-4} Mol/g. This result is in good agreement with experimental values of saturation concentrations in the precatalytic temperature range (*26*). The entropy at a surface concentration of 1 Mol/g is taken as the standard state.

The kinetic isotope effect, defined as

$$\alpha = \frac{r_H}{r_D}, \qquad (4)$$

is calculated taking the values of the rate constants r_H and r_D of protonated and deuterated substrates, from the calculated optimal straight line of the Arrhenius diagrams. Since the substrate alcohols are not totally deuterated in the position in question the experimental isotope effects α_{exp} were corrected to 100% deuteration by the equation

$$\alpha = \frac{a\alpha_{\text{exp}}}{1 - b\alpha_{\text{exp}}}, \qquad (5)$$

a and b being the fractions of the deuterated and protonated substrate alcohol, respectively.

From the isotope effects the differences of the activation entropies $\Delta(\Delta S^\ddagger)$ between protonated and deuterated alcohols can be easily calculated from

$$\alpha = \frac{r_H}{r_D} = \frac{e^{\Delta S_H{}^\ddagger/R} e^{-\Delta E_H/RT}}{e^{\Delta S_D{}^\ddagger/R} e^{-\Delta E_D/RT}} \qquad (6a)$$

$$\Delta(\Delta S^\ddagger) = 4.576 \log \alpha + \frac{\Delta E_H - \Delta E_D}{T}, \qquad (6b)$$

if equal surface concentrations $c_{aH} = c_{aD}$ for the two alcohols are assumed.

The mean error of the kinetic isotope effects is approximately 10% in all cases as calculated from the mean errors of the individual rate constants of protonated and deuterated substrates (see Figs. 1–3). The relative mean errors of activation energies and entropies are given in the tables. The absolute activation entropies as calculated from Eq. (3), however, contain a systematic error induced by the calculation of the surface concentration from the liquid density.

RESULTS

Product distribution

Since the reaction was followed by measurements of the pressure increase only, it

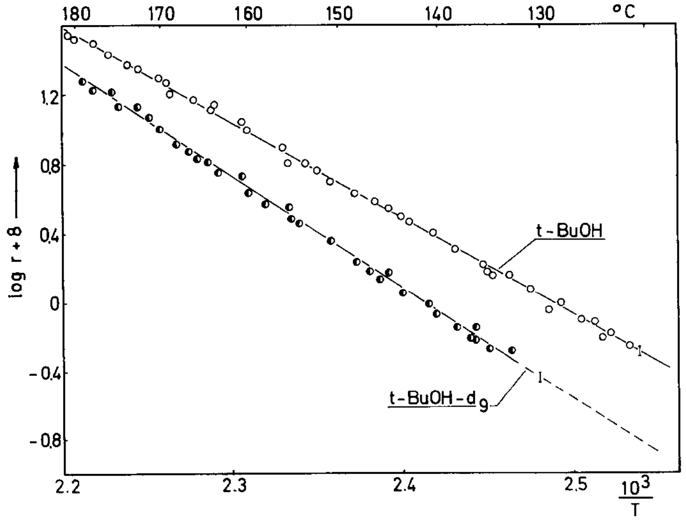


FIG. 1. Arrhenius plots for the dehydration of tertiary butanol and tertiary butanol-d$_9$.

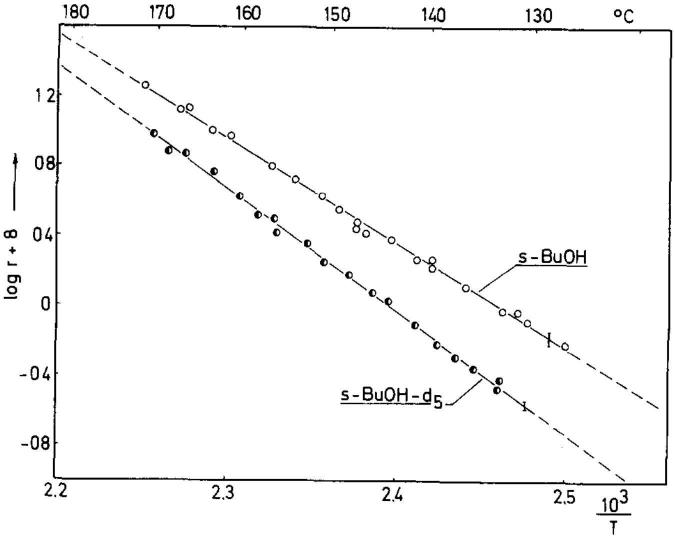


FIG. 2. Arrhenius plots for the dehydration of secondary butanol and secondary butanol-d_5.

must be ascertained that the dehydration produces only one olefinic main product to which the pressure increase can be attributed. This were not the case if an isomeric mixture of primary products would be formed. There are no problems at all for the dehydration of tertiary butanol since the only possible product formed is isobutylene (*23*). As shown by Pines and Haag (*6*) 1-butene, *cis-* and *trans*-2-butene with clear preference of the *cis*-product are formed on dehydration of 2-butanol at 350°C. For the alumina catalyst used in the present work and in a temperature range up to 200°C it has been shown, however, that *cis-* and *trans*-2-butene are the only products formed and that the *cis*-preference is about 10:1 (*18*). The reaction can therefore be considered as proceding simply by

$$\text{2-BuOH} \rightarrow \textit{cis}\text{-2-butene} + H_2O.$$

Furthermore the dehydration of the deuterated alcohol $CD_3CD_2CH(OH)CH_3$ will give the kinetic isotope effect of this re-

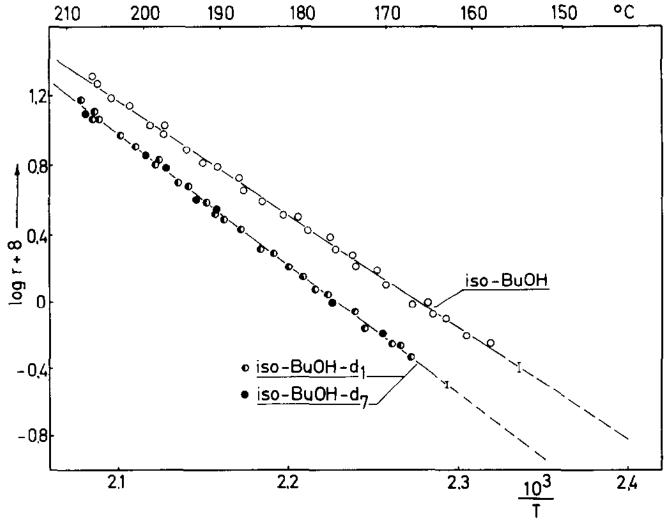


FIG. 3. Arrhenius plots for the dehydration of isobutanol, isobutanol-d_1, and isobutanol-d_7.

action, since no α- or β-exo-elimination occurred.

With respect to the dehydration of isobutanol, Herling and Pines (*27*) found 1-butene as a product at 350°C besides the main product isobutene. This indicates the contribution of a certain degree of γ-elimination. For the presently used catalyst, however, no formation of 1-butene could be observed even at temperatures up to 300°C. Thus, the dehydration of isobutanol proceeds via a pure β-elimination. This is confirmed by mass-spectrometric determinations of the deuterium content in the isobutene formed from the C_β-deuterated isobutanol-d_1 $(CH_3)_2CDCH_2OH$. The isobutene formed from this substrate by β-elimination should not be deuterated. The reaction product, however, contained isobutene-d_1 and even several fold deuterated isobutenes. It could be shown by contacting normal isobutylene with a deuterated alumina surface with and without heavy water in the gas phase that deuterium exchange takes place between the catalyst surface and the olefin at the temperatures applied. Thus, the appearance of deuterated isobutylene in the reaction products results from a secondary deuteration of the primary product. Similarly deuterium exchange with alumina surfaces has been observed for ethylene (*28*) and butenes (*29*). The deuterium exchange with paraffins and alkyl groups on the other hand should, if possible, proceed comparably slowly (*48*), so that a deuteration of the substrate alcohol can be ruled out. The dehydration of isobutanol therefore is a clean β-elimination. This will also be confirmed by the results of the kinetic isotope effects. The relative rate of dehydration of $(CH_3)_2$-$CDCH_2OH$ measures the kinetic isotope effect and the comparison of rates of dehydration of $(CH_3)_2CDCH_2OH$ and $(CD_3)_2CDCH_2OH$ allows the estimation of possible contributions of secondary isotope effects.

Arrhenius parameters and isotope effects

In Table 2, the Arrhenius parameters are given. Columns 3 and 4 represent the activation energies of normal and deuterated alcohols, respectively, columns 5 and 6 the respective activation entropies, column 7 the difference $\Delta S_H{}^\ddagger - \Delta S_D{}^\ddagger$ of these values and column 8 the difference $\Delta(\Delta S^\ddagger)$ as calculated directly from the kinetic isotope effect according to Eq. (6b). The mean errors and the number of experimental points to which the least squares method was applied are also given. These experimental rate data were reproducibly obtained on various catalyst samples and on the same sample at a couple of subsequent days. The entropies of activation $\Delta S_H{}^\ddagger$ and $\Delta S_D{}^\ddagger$ are given for mean temperatures of the temperature ranges covered. Reaction rates and activation energies as measured with prepared and commercial normal alcohols agree within the error limits. These activation energies also agree excellently with those measured in a dynamic reactor i.e., 25,5, 27,5, and 30,0 kcal/Mol for the dehydration of tertiary butanol (*23*), secondary butanol (*18*), and isobutanol (*15*), resp. Figures 1–3 show the Arrhenius plots for the 3 pairs of substrate alcohols. The mean derivations of the (log *r*)-values from the optimal straight line are indicated in the figures. The corrected kinetic isotope effects as calculated from these straight lines—which in some cases were extrapolated to higher or lower temperatures are shown in Table 3 together with the theoretical values of the maximum isotope ef-

TABLE 3
KINETIC ISOTOPE EFFECTS OF THE DEHYDRATION OF BUTYL ALCOHOLS ON γ-Al_2O_3

T (°C)	α_{max}	Experimental Isotope Effect α		
		t-BuOH	sec-BuOH	iso-BuOH
120	4.15	3.67	—	—
130	4.01	3.26	4.10	—
140	3.87	2.77	3.28	—
150	3.76	2.42	2.70	3.44
160	3.64	2.14	2.28	2.92
170	3.54	1.89	1.94	2.55
180	3.44	1.67	1.64	2.10
190	3.35	1.51	—	1.91
200	3.26	1.37	—	1.67
210	3.18	—	—	1.49

TABLE 2

ARRHENIUS-PARAMETERS

Alcohol	ΔT (°C)	ΔE(H) (kcal/Mol)	ΔE(D) (kcal/Mol)	$\Delta S_H^\ddagger$ (e.u.)	$\Delta S_D^\ddagger$ (e.u.)	$\Delta S_H^\ddagger - \Delta S_D^\ddagger$ (e.u.)	$\Delta(\Delta S^\ddagger)$ (e.u.)	n
$(CH_3)_3COH$	121 – 180	25.3 ± 0.2	—	−18.8 ± 1.1	—			38
$(CD_3)_3COH$	132 – 178	—	29.5 ± 0.4	—	−10.6 ± 2.0	−8.2	−8.3 ± 0.6	32
$C_2H_5CH(OH)CH_3$	127 – 171	27.3 ± 0.4	—	−14.5 ± 0.6	—			21
$C_2D_5CH(OH)CH_3$	133 – 170	—	32.0 ± 0.3	—	−5.0 ± 0.6	−9.5	−9.3 ± 0.6	19
$(CH_3)_2CHCH_2OH$	158 – 204	30.5 ± 0.3	—	−12.4 ± 1.1	—			28
$(CD_3)_2CDCH_2OH$ $(CH_3)_2CDCH_2OH$	167 – 208	—	35.1 ± 0.3	—	−3.7 ± 1.6	−8.7	−8.6 ± 0.6	32

fect $\alpha_{\max}$ given by the difference in zero point energies for normal and deuterated alcohols (e.g., Eq. (9)). As expected $\alpha_{\max}$ is nearly independent of the substrate structure and diminishes slightly with increasing temperature. The experimental isotope effects on the other hand exhibit a much more pronounced temperature dependence and are apparently determined by the substrate structure. It should be mentioned that in neither case the deuteration of the hydroxyl group caused a detectable effect, secondary effects by γ-C deuteration could not be observed either as shown by the exact coincidence of the effects for $(CH_3)_2CDCH_2OH$ and $(CD_3)_2$-$CDCH_2OH$ (see Fig. 3). If present, these secondary effects must be too low to be detected with the system used.

Discussion

The fact that deuteration of the hydroxyl group does not cause an isotope effect, even when the alcohol is admitted to a deuterium exchanged catalyst surface, excludes any rate determining participation of the hydroxyl proton and also a rate determining desorption of water, at least for the case that the water molecule is adsorbed via H-bonds to surface hydroxyl or deuteroxyl groups. This adsorption structure must exist, however, if the proposed reaction mechanism with the alcohol molecules being adsorbed via H-bonds (*2*, *3*) is accepted. Thus, a rate determining desorption of water from Lewis acid sites as postulated by Krylov (7) must also be rejected at least for low temperatures, since a β-deuterium isotope is observed. This is in agreement with pyridine poisoning experiments which show that Lewis acid sites do not take part in the olefin formation (*2*, *3*, *11*, *12*). The high isotope effects which result from deuteration in β-position imply a rate determining participation of the C_β-H(D) bond fission during the dehydration course. These β-elimination reactions can be considered as H-transfer reactions.

For monomolecular zero order surface reactions Eq. (7) follows from the transition state theory: (*30*)

$$r = c_a \cdot \frac{kT}{h} \cdot \frac{f_a^\ddagger}{f_a} e^{-\Delta E/RT}, \qquad (7)$$

where ΔE is the classical activation energy and f_a and $f_a^\ddagger$ the partition functions of the substrate in the adsorbed and in the activated adsorbed states, respectively. Assuming the surface concentrations and the partition functions of the activated complex of normal and deuterated compounds to be equal, Block and Kral (*31*) deduced for the kinetic isotope effect

$$\alpha = \frac{r_H}{r_D} = \frac{\exp[h\nu_H/2kT] - \exp[-h\nu_H/2kT]}{\exp[h\nu_D/2kT] - \exp[-h\nu_D/2kT]}. \qquad (8)$$

μ_H and μ_D are the frequencies of the stretching vibrations of the C-H(D) bonds in question. From this equation one obtains for temperatures below 400°C

$$\alpha = e^{\Delta E_0/RT}, \qquad (9)$$

which corresponds to the maximum possible isotope effect $\alpha_{\max}$. ΔE_0 in Eq. (9) means the difference between the zero point energies of the respective vibrations in normal and deuterated reactants. At higher temperatures the minimum isotope effect is then given by

$$\alpha_{\min} = \frac{\nu_H}{\nu_D} = \sqrt{\frac{m_H}{m_D}} \approx 1.4, \qquad (10)$$

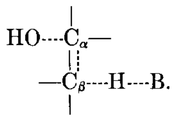
where m_H and m_D are the reduced masses of the normal and deuterated substrates. The maximum isotope effect $\alpha_{\max}$ and its temperature dependence is given in Table 3, the wave numbers ν_H and ν_D being taken from Table 1 for calculation. In the above mentioned deduction of Eq. (9) only the zero point energies of the C_β-H and C_β-D stretching vibrations have been taken into account and these bonds are assumed to be completely broken in the transition state. Thus, the transition state does not contribute to the zero point energy differences. This picture leads to relatively high kinetic isotope effects ($\alpha_{\max} > \alpha$) and does not allow for influences of the reactant structure which in fact are observed (see Table 3). This treatment is apparently too oversimplified and cannot be applied to discuss the present results. Such observations of so-called "small" isotope effects are well known for homogeneous systems and have often been attributed to incompletely broken bonds in the transition state, a picture which has been shown by Westheimer (*32*) to be inadequate in terms of the transition state theory.

Elimination reactions such as the dehydration of alcohols can be described as proton transfer reactions of the type

$$A - H + B \rightleftharpoons [A\ldots H\ldots B]^{\ddagger} \rightarrow A + BH,$$

where the base B in the case of the heterogeneously catalyzed reaction is a surface oxygen ion of the alumina catalyst. The primary kinetic isotope effect of this class of reactions is a function of the differences between the zero point energies of normal and deuterated compounds in the ground and transition states. The transition state of a trans-elimination following an E 2-mechanism may be written as

(I)



$$\begin{array}{l} \qquad | \\ HO{\cdots}C_{\alpha}{-} \\ \qquad \|\!\vdots \\ \;\;{-}C_{\beta}{\cdots}H{\cdots}B. \\ \qquad | \end{array}$$

The relative bond loosening of the C_α-O and the C_β-H bonds and correspondingly the preformation of $C_\alpha{=}C_\beta$ double bonds may vary over wide ranges (*33*, *34*). Thus, asymmetric transition states with the proton near C_β and the C-O bond nearly completely broken (E 1-like transition state) and with the proton near the base and the C-O bond nearly unaffected (E1cB-like transition state) are possible. In these two cases the double bond is only weakly preformed. A comparably high degree of preformation of the double bond (quantitatively depending on the degree of bond loosening of C_α-O and C_β-H bonds) is reached for the synchronous E 2-mechanism, for which the bond breaking of C_α-O and C_β-H proceeds to equal extents in the transition state. Transition states of this type now allow obviously for influences of the substrate structure, since protons may stabilize the preformation of the double bond, whereas substituents at C_α or C_β may favor ionic contributions. These structure influences must necessarily reflect themselves also in the kinetic isotope effects. In a first approximation the transition state (I) can be simplified by considering only the linear part

$$C_\beta \overset{f_{11}}{\cdots\cdots} H \overset{f_{22}}{\cdots\cdots} B.$$

This three-center model apparently exhibits its three normal vibrations. The asymmetric stretching mode is considered to be the reaction coordinate. The various possible transition states can be described by the relative values of the force constants f_{11} and f_{22} and the coupling constant f_{12}. It has been shown, that the highest isotope effects can be expected for symmetrical E 2-like transition states ($f_{11} \approx f_{22}$), i.e., when the proton is approximately half transferred, whereas E 1-like ($f_{11} > f_{22}$) and E1cB-like ($f_{11} < f_{22}$) transition states lead to lower effects (*32*, *35–39*). These considerations and estimations have been done for homogeneous systems but may equally well be applied to heterogeneously catalyzed elimination reactions.

Dependence on reactant structure

The observed isotope effects are all smaller than $\alpha_{\max}$, but at least at low temperatures not much. Such high kinetic isotope effects make an E 2-like transition state highly probable even in the case of the dehydration of tertiary alcohols. At equal temperatures, the sequence of the isotope effects is

$$\text{t-BuOH} < \text{sec-BuOH} < \text{iso-BuOH}.$$

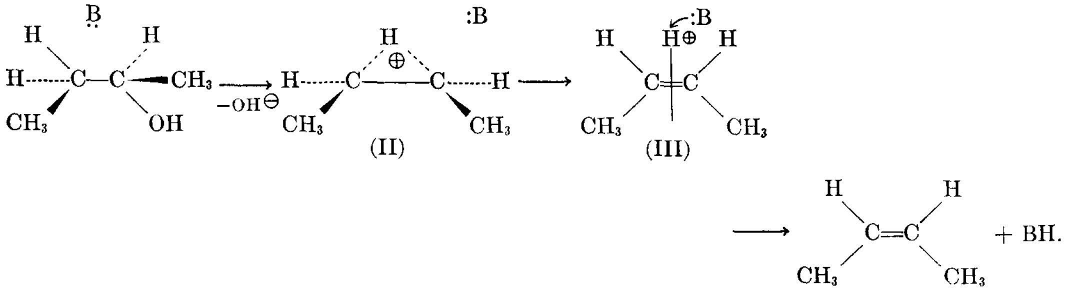
This sequence suggests the highest E 2-character for the dehydration mechanism of the primary alcohol, while ionic contributions to the transition state apparently progressively increase when changing to the secondary and tertiary alcohol, i.e., the transition state becomes more E 1-like for the secondary and tertiary alcohol. This conclusion agrees quite well with the sequence of the ionization potentials of the alkyl groups

$$\text{t-Bu} < \text{sec-Bu} < \text{iso-Bu},$$

since the lower the ionization potential the more favored is the formation of an E 1-

like transition state (*40*). The same conclusion was reached by a discussion of the sequence of the activation energies (*2*, *3*, *18*). The mechanisms of the dehydration of the three alcohols on alumina is thus apparently E 2-like, which at low temperatures contains only small ionic contributions whose percentage is determined mainly by the ionization potential of the alkyl rest.

There are two further points related to the influence of the substrate structure which appear well worth to be mentioned. The high preference of the *cis*-product on dehydration of secondary butanol has been explained by Pines and Haag (*6*) by the intermediate formation of a proton-olefin π-complex:



As stated by Lewis and coworkers (*41*, *42*), the formation of "triangular" transition states such as (II) leads to small kinetic isotope effects. For such transition states it seems more likely that a bending rather than a stretching vibration is converted to translational motion. Since normally bending frequencies are lower than stretching frequencies, the loss of zero point energy is smaller and hence the isotope effect. Since the experimental isotope effect for the dehydration of secondary butanol fits very well in the sequence of alcohols studied such an explanation seems unlikely. If the intermediate formation of a π-complex (III) at low temperatures is accepted, a preceding rate determining formation of an E 2-like transition state seems necessary rather than that of a triangular structure (II) to explain the high isotope effect. This transition state may then be followed by the π-complex before desorption to *cis*-2-butene. It may, however, be speculated that the mechanism proposed by Pines and Haag with a triangular transition state operates at the elevated temperatures used by them, since at these temperatures the ionic contributions to the transition state structure will predominate (see next paragraph). The stronger temperature dependence of the isotope effect of the dehydration of secondary butanol than of tertiary butanol may then be explained by the superposition of two contributions: the decrease in isotope effect according to the increase in ionic character and according to the formation of a bridged intermediate in competition with its unbridged counterpart; this latter effect is unlikely in the case of tertiary butanol.

As for the dehydration of isobutanol, the absence of differences between the kinetic isotope effects measured for $(CH_3)_2CDCH_2OH$ and $(CD_3)_2CDCH_2OH$ seem to exclude a contribution of γ-elimination as found by Herling and Pines (*27*), at least for the catalyst used in the present work. This result agrees with the conclusions from the product distributions as mentioned in paragraph 3.

Dependence on reaction temperature

As previously stated, the experimental isotope effects are all smaller than the $\alpha_{\max}$ values. This behavior is still more pronounced as the temperature increases. Thus, the temperature dependence of the isotope effect is much stronger than the theoretically predictable dependence (see Table 3). It is therefore proposed that the E-character of the transition state becomes more and more pronounced as the temperature is raised. At high temperatures the mechanism may therefore be a pure E 1-mechanism, the temperature of the complete change naturally depends on the reactant structure and will be higher for secondary and primary alcohols than for tertiary. The limiting value of approximately 1.3 of the isotope effect for the dehydration of tertiary butanol is reached near 200°C and remains constant at higher temperatures. This value is close to the magnitude of secondary isotope effects and may thus well indicate an E 1-like mechanism at temperatures higher than 200°C. The results therefore agree quite well with the mechanistic proposals of Pines and coworkers (*4*), which were mainly based on studies of the product distributions at temperatures above 250°C. Kinetic isotope effects of the order of 1.4 to 1.5 were found by Blanc and Pines (*49*) for the dehydration of *cis*-2-methylcyclohexanol-2-d between 200 and 240°C; this result was taken as evidence for a concerted *trans*-elimination.

A similar change in mechanism from E 2-to E 1-like with increasing temperature has also been observed and explained by Noller, Andreu and coworkers (*43, 44*) for the dehydrohalogenation of halogen hydrocarbons over salt and oxide catalysts.

It has been mentioned that E 1-like as well as E1cB-like transition states lead to lower isotope effects than such of the E 2-type. Since E 1-contributions have been preferred in the foregoing discussion, the general possibility of E1cB-like transition states, which may correspond to Pisman's mechanism (*5*) as mentioned in the introduction, must be excluded. Since the isotope effects are not conclusive in this point, other considerations must be taken into account. There are two facts which appear to be in favor of the E 1-like transition state. Firstly, the basicity of the surface oxygen ions seems to be too low to initiate a proton abstraction from a C-H bond. Secondly, the bond dissociation energy for a heterolytic bond rupture of the C-H bond to form a carbanion (E1cB-like transition state) is considerably higher than that for the heterolytic bond rupture of the C-O bond, which leads to the formation of a carbonium ion (E 1-like transition state).

On the other hand, the still high bond dissociation energy of the heterolytic rupture of the latter bond may account for the high temperature preference of an E-like over an E 2-like transition state (for an analogous discussion for the dehydrohalogenation see (*44, 45*)). Another explanation, however, seems also possible. The formation of a carbonium ion depends not only on the substrate structure of the reactant but also on the Brönsted acidity of the surface hydroxyl groups. Thus, on silica-alumina and various other oxides which are known to develop Brönsted acidity, alcohols are dehydrated via an E 1-like mechanism (*3, 50*). It may be possible that the Brönsted acidity of the surface hydroxyl groups on alumina increases with increasing temperature and thus slightly favors ionic contributions to the mechanism at higher temperatures. This point, however, is not yet clear.

The entropy values $\Delta S_H{}^\ddagger - \Delta S_D{}^\ddagger$ and $\Delta(\Delta S^\ddagger)$ as calculated according to Eqs. (3) and (6b), respectively, agree very well (see Table 2). It seems, however, difficult if not impossible at the moment to draw any definite conclusion from the entropies of activation with respect to the mechanism of the reactions under consideration. We hope to be able in the near future to present the results of model calculations including isotope effects and entropies of activation, which are presently carried out.

ACKNOWLEDGMENTS

We are indebted to Prof. Dr. G.-M. Schwab for his continual interest in our work. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support. Furthermore, we thank Dr. K. Kochloefl for valuable discussions.

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