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The Dehydration of Alcohols on Alumina

XIV. Reactivity and Mechanism

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The product distributions and Arrhenius parameters for the zero-order range have been determined for the dehydration on alumina of a series of primary, secondary, and tertiary aliphatic alcohols and for some alicyclic alcohols. The E_2-like transition state structure is thought to be influenced by inductive, hyperconjugative, and steric effects. The elimination of the β-proton from a *trans*-position is assumed to proceed via an "inclination" of the adsorbed structure towards the catalyst surface, which bears the basic center. Thus, the *cis*-preference is easily explained by steric restrictions between certain groups of the adsorbed species and the catalyst surface. The sequence of the activation energies can be explained in the transition state model by the simultaneous influence of ionic, hyperconjugative, and steric effects, while activation entropies probably demonstrate a certain tunnel contribution in the β-proton abstraction.

INTRODUCTION

The majority of alcohols react to form olefins on dehydration over alumina (*1–5*). A large amount of experimental information has been collected in the past. The most striking conclusions with respect to the reaction mechanism are as follows: The dehydration proceeds through an E_2-like reaction intermediate which exhibits a certain ionic character even at low temperatures (*1–3, 6*). This description of the transition state has to be considered according to the bond changes which make most progress initially; they are, however, still concerted in the sense that one bond fission could not proceed without the others.

As stated by Banthorpe (*17*), the molecular events of a particular reaction may belong to a range of transition state types (varying positive charge at C_α), but one of these will predominate in the Boltzmann distribution. This favored structure must be considered as the transition state of the reaction and its nature will be determined by the structure of the reacting molecule and its environment in a predictable manner. With increasing reaction temperature the transition state structure may change from E_2-like to E_1-like (*6, 7*).

The steric course of the reaction is a *trans*-elimination of the elements of water from the α- and β-carbon atoms (*1, 8*). Whenever the formation of *cis*- and *trans*-isomers as primary products is possible, the *cis*-olefin has been observed preferentially (*1–4, 9*). Both these observations seem to be general for heterogeneously catalyzed elimination reactions since they were also obtained for dehydrohalogenation reactions on salt catalysts (*10, 11*).

The explanation of *trans*-elimination and of the *cis*-preference on solid catalyst surfaces are still a matter of controversy. Schwab and Schwab-Agallidis (*12*) postulated on the grounds of selectivity studies that the dehydration would proceed in pores of molecular dimensions and in crevices and channels of the catalyst. This idea was taken over by Pines and Manassen (*1*)

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and Pines and Pillai (*13*) assuming the acidic and basic centers to be located on opposite walls of the crevices. Thus, the adsorbed molecule would not have to turn around. This view has been criticized very recently by Notari (*4*). Notari's cyclic transition state model, however, leads to a *cis*-elimination. Futhermore, the dehydration reaction must always be diffusion controlled when it proceeds only in crevices of molecular size (*37*), a phenomenon which has never been observed for alumina catalysts.

The *cis*-preference was explained by Pines and Haag (*9*) by the assumption of an intermediate proton-olefin complex. Since *cis*-π-complexes are more stable than *trans*-π-complexes, the observed values of the *cis/trans* ratios would be explained.

Noller and co-workers (*14*), relying on dehydrohalogenation reactions, explained the *cis*-preference in E_1-like mechanisms on the grounds of steric considerations. A similar suggestion was made by Notari (*4*) for his cyclic transition state model.

In the present work a new transition state model is proposed that explains the *trans*-elimination as well as the *cis*-preference. The model is deduced from experimental studies on the product distributions, the Arrhenius parameters and reactivities of a series of aliphatic alcohols.

EXPERIMENTAL METHODS

Materials

Most of the alcohols were supplied by C. Roth, Karlsruhe, Germany. They were all p.A. grade and dried over molecular sieve 3A before use. The preparation of the γ-Al_2O_3 catalyst has been described previously (*5*).

Apparatus and procedure

The dehydrations were carried out in a continuous flow reactor at low conversions (*5*). The influence of diffusion phenomena were always avoided. Products were analysed by gas chromatography using two columns in series. The separation of the olefins was performed by either $AgNO_3$/diethylene glycol or dimethylsulfolane. For the quantitative determination of olefins the system was calibrated for each case; the calibration factors showed differences for the various olefins which were too large to be neglected. Product distributions were determined under conditions which guaranteed the formation of primary products. Inhibition by the products is negligible at the low conversions used. The Arrhenius parameters were calculated with only a few exceptions from zero-order rates (partial pressures of alcohols of 100–325 mmHg). The mean errors of the results are given in Tables 1 and 2.

RESULTS AND DISCUSSION

1. Product Distribution

The products formed on dehydration of various aliphatic and alicyclic alcohols have been determined as a function of contact time under various conditions. The composition of olefins given in Table 1 is always based on the distribution of primary products.

Isobutanol gave only isobutene on dehydration even at temperatures up to 300°C, i.e., methyl migration, as observed by Herling and Pines (*15*), could not be found. In the case of cyclohexanol a secondary isomerization of cyclohexene to methylcyclopentene, as reported by Kochloefl and Bažant (*33*) and by Pines and Haag (*9*), did not occur, cyclohexene being the only product. The absence of skeletal isomerization, which is in contradiction with the results of the above-mentioned workers (*9, 15, 33*) may easily be explained by the different experimental conditions used in the present work. The product distributions belong to the primary products and were observed at low conversions (<10%) and at low temperatures, i.e., in the range of 160 to 300°C for the dehyration of isobutanol and of 140 to 190°C for that of cyclohexanol. Since skeletal isomerization is expected to occur at elevated temperatures, it may well have contributed under the more severe conditions used by Pines and Haag (*9*) and Herling and Pines (*15*), i.e., 350°C for the dehydration of isobutanol and 350 to 410°C for that of cyclohexanol. Furthermore, the activity for

TABLE 1
Product Distributions

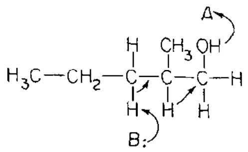
Alcohol	Olefins	T(°C)	(%)	*cis/trans* ratio
2-Methyl-1-pentanol	2-Methyl-1-pentene	255	92	
	2-Methyl-2-pentene		8	
Neopentyl alcohol	2-Methyl-2-butene	307	28.7	
	2-Methyl-1-butene		71.3	
	2-Methyl-2-butene	351	35.6	
	2-Methyl-1-bentene		64.4	
2-Butanol	*cis*-2-Butene	188	83.7	5.1
	trans-2-Butene		16.3	
	1-Butene		Not detectable	
3-Methyl-2-butanol	2-Methyl-2-butene	205	79.4	
	3-Methyl-1-butene		20.6	
2-Pentanol	1-Pentene	240	26.2	
	cis-2-Pentene		57.4	3.5
	trans-2-Pentene		16.4	
3-Pentanol	*cis*-2-Pentene	230	70.6	2.4
	trans-2-Pentene		29.4	
2-Methyl-3-pentanol	2-Methyl-2-pentene	233	41.8	
	cis-4-Methyl-2-pentene		46.5	4.0
	trans-4-Methyl-2-pentene		11.6	
2-Methyl-2-butanol	2-Methyl-2-butene	180	44.8	
	2-Methyl-1-butene		55.2	
	2-Methyl-2-butene	157	49.9	
	2-Methyl-1-butene		50.1	
3-Methyl-3-pentanol	2-Ethyl-1-butene	169	20	
	cis-3-Methyl-2-pentene		56	2.3
	trans-3-Methyl-2-pentene		24	

skeletal isomerization may be different for various alumina catalysts.

Cyclopentanol and cycloheptanol yielded only cyclopentene and cycloheptene, respectively. Isopropyl and *tert*-butyl alcohol yielded only propylene and isobutene, respectively. α- and β-phenylethanol gave styrene as the only product.

The product distribution of the other alcohols studied in the present work are given in Table 1, generally for one temperature. These distributions change for different temperatures according to the Arrhenius parameters (see Table 2). Table 1, column 5 also gives the *cis/trans* ratios for the respective isomeric products.

The dehydration of 2-methyl-1-pentanol yields mainly 2-methyl-1-pentene and to a minor extent 2-methyl-2-pentene (approx 8%). The formation of the 2-olefin from a primary alcohol can be explained by a γ-elimination aided by anchimeric assistance of the β-hydrogen as shown by Pines and Manassen (*1*):



The absence of methyl migration can be understood because of the higher mobility of hydrogen compared to the methyl group. Methyl migration, however, must occur on dehydration of neopentyl alcohol to form 2-methyl-2-butene and 2-methyl-1-butene,

TABLE 2
ARRHENIUS PARAMETERS

Alcohol	Olefins	Temp range (°C)	ΔE (kcal/mole)	$\Delta S^{\ddagger}$ (eu)	n^a
Primary					
Isobutanol	Isobutene	158–204	30.5 ± 0.5	−12.4 ± 1.1	28
2-Methyl-1-pentanol	2-Methyl-1-pentene^b	217–275	24.8 ± 0.6	−27.6 ± 1.2	50
	2-Methyl-2-pentene^{b,c}	231–275	37.2 ± 1.7	−8.4 ± 3.2	39
β-Phenylethanol	Styrene	202–253	24.9 ± 0.5	−27.7 ± 0.6	13
Secondary					
2-Propanol	Propylene	173–224	27.0 ± 0.7	−20.2 ± 1.5	29
2-Butanol	*trans*-2-Butene	155–198	30.6 ± 0.8	−12.5 ± 1.8	37
	cis-2-Butene	155–198	25.4 ± 0.8	−20.2 ± 1.8	40
3-Methyl-2-butanol	2-Methyl-2-butene	154–204	24.2 ± 0.3	−22.1 ± 0.6	28
	3-Methyl-1-butene	154–204	27.0 ± 0.3	−18.8 ± 0.8	28
2-Pentanol	1-Pentene	203–249	22.3 ± 0.4	−29.8 ± 0.7	33
	trans-2-Pentene	203–249	29.2 ± 0.5	−18.4 ± 0.9	33
	cis-2-Pentene	203–249	26.2 ± 0.3	−21.6 ± 0.6	33
3-Pentanol	*trans*-2-Pentene	191–244	23.4 ± 0.3	−27.4 ± 0.5	38
	cis-2-Pentene	191–244	22.8 ± 0.3	−26.9 ± 0.5	38
2-Methyl-3-pentanol	2-Methyl-2-pentene	196–253	24.4 ± 0.4	−25.6 ± 0.8	25
	trans-4-Methyl-2-pentene	196–253	28.5 ± 0.4	−20.4 ± 0.7	25
	cis-4-Methyl-2-pentene	196–253	26.0 ± 0.3	−22.2 ± 0.6	25
α-Phenylethanol	Styrene	141–178	24.9 ± 1.0	−18.2 ± 2.3	18
Alicyclic					
Cyclopentanol	Cyclopentene	144–189	26.9 ± 0.7	−15.1 ± 1.5	35
Cyclohexanol	Cyclohexene	144–178	25.6 ± 0.6	−17.1 ± 1.5	8
Cycloheptanol	Cycloheptene	137–178	26.0 ± 0.6	−16.4 ± 1.5	25
Tertiary					
t-Butanol	Isobutene	117–185	24.3 ± 0.4	−19.0 ± 0.5	62
2-Methyl-2-butanol	2-Methyl-2-butene	128–172	21.3 ± 0.5	−25.7 ± 0.7	17
	2-Methyl-1-butene	128–172	22.4 ± 0.4	−23.4 ± 0.9	17
3-Methyl-3-pentanol	*cis*-3-Methyl-2-pentene	136–189	17.4 ± 0.5	−35.6 ± 0.6	25
	trans-3-methyl-2-pentene	136–189	17.6 ± 0.5	−36.7 ± 0.5	25
	2-Ethyl-1-butene	136–189	20.0 ± 0.5	−32.1 ± 0.5	25

[a] Number of experimental values.

[b] Zero order not reached.

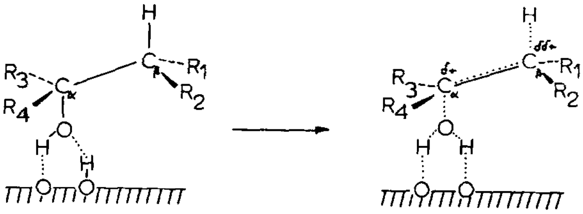
[c] Formed by γ-elimination.

the 1-olefin predominating. The olefin ratio of 1:2 to 1:2.5 agrees quite well with those reported by Pillai and Pines (*16*). These authors explained the mechanism of dehydration of neopentyl-type alcohols on alumina by assuming a concerted γ-elimination with methyl migration. A carbonium ion mechanism is excluded because of the different distribution of products in the dehydration of *tert*-pentanol.

The tendency of the product distributions for secondary and tertiary alcohols as shown in Table 1 proves that the more stable Saytzeff-products are, in general, formed preferentially. The second obvious fact is the high *cis*-preference, *cis*/*trans* olefin ratios being formed between 2.3 and 5.1. Both these observations agree with those of other authors (*1*).

To explain the observed product distributions, one has to take into consideration the various possible transition state structures, which determine the reaction course. It has been proved very recently (*6*), by means of kinetic isotope effects, that the elements of water are eliminated from primary, secondary, and tertiary alcohols through an E_2-like reaction intermediate which, depending on temperature and reactant structure, contains ionic contributions even at low temperatures. Furthermore, it is well known that simple β-eliminations on alumina are predominantly *trans*-eliminations. This has been shown by Pines and Manassen (*1*) and Blanc and Pines (*19*) for cyclic systems. The predominance of *trans*-elimination for the dehydration of aliphatic alcohols was clearly established by Hall (*8*) and by Kibby *et al.* (*38*), who used the diastereomeric alcohols *d,l-erythro-* and *d,l-threo-*deutero-2-butanol-d_1, as reactants. The dehydration of these molecules over alumina at 200°C proceeds in a nearly stereospecific fashion; the olefinic products which are formed, prove the assumption of a *trans*-elimination (predominating to approx 80%), which was further supported by ^{14}C-tracer studies (*1*). Possible transition state structures, therefore, are only those which show an E_2-like structure with the developing double bond being preformed to a certain degree and which bear the hydroxyl group and the β-proton in a coplanar conformation. The transition state structures must furthermore allow the interaction of the β-proton with a basic site (oxygen ion) on the surface and it must explain the observed *cis/trans* ratios for the respective isomeric olefins. Generally speaking, the transition state model has to take into account the properties of the reactant molecule and of the products and also the very specific geometric requirements brought about by the transition state being developed on the surface of a solid. The elimination of the elements of water from such a transition state is certainly influenced by inductive effects, olefin stabilizing effects (hyperconjugation), statistical effects (number of β-hydrogens available for elimination) and steric effects. Since Saytzeff and Hofmann products, generally with a clear preponderance of the more stable Saytzeff olefin, are formed, it must be concluded that inductive effects and olefin stabilizing effects of the substituent groups attached to C_α and C_β play an important role. The importance of inductive effects is well known from reactions in solution (*17*). The effect of hyperconjugation is still not accepted generally. Dewar (*18*), however, has shown that hyperconjugation, though it is not necessarily important in ground electronic states, plays an important role in transition states of chemical reactions. Since the dehydration of alcohols proceeds through an E_2-like reaction intermediate which bears a positive charge at the C_α-atom, the influence of both inductive and olefin stabilizing effects seems quite plausible and therefore the statistical effect plays only a minor role. This conclusion is in good accordance with observations of Kochloefl and coworkers (*20*). The importance of steric effects has been previously assumed by various authors (*14*, *19*, *20*). For reactions on solid surfaces, one has to distinguish between a steric hindrance of the adsorbed alcohol molecule (or certain groups of the molecule) and the catalyst surface, and a steric compression within the reacting molecule or the transition state. This latter type of steric effect is relatively unimportant in solution reactions (*17*). On solid catalyst surfaces, however, steric effects should, at least in certain cases, not be neglected. Most probably the first of the above-mentioned two types of steric effects predominates, while the second may possibly contribute to a lesser extent.

The experimental results in Table 1 seem to indicate that the inductive effect and hyperconjugation predominate over steric effects in determining the preference of Hofmann or Saytzeff products. The observed *cis/trans* ratios, however, cannot be explained by these effects. The assumption of an intermediate π-complex, on the other hand, is not fully in concordance with the experimental kinetic isotope effects as shown by Knözinger and Scheglila (*6*). However, steric restrictions in the transition state are most likely to determine the *cis/trans* ratio of the respective isomeric olefins. This suggestion will now be explained by means of a transition state model.

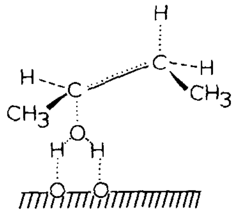


I

II

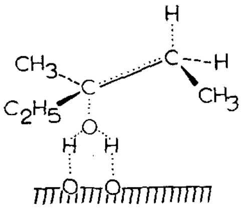
As previously postulated (*2*) the alcohol molecule is assumed to be adsorbed via 2 or 3 H bonds between a hydroxyl proton of the alcohol and an oxygen ion of the surface and between hydroxyl protons of surface hydroxyl groups and free electron pairs of the hydroxyl oxygen of the alcohol (I). The H bond formation will polarize the C–O bond to a certain extent, depending mainly on the nature of the α-substituents. This is the most probable adsorption structure since the alkyl groups attached to C_α are removed from the surface as far as possible with the C_α–O bond vertical to the catalyst surface (*21*). The reaction may be induced in this adsorbed molecule whenever two hydroxyl protons come close to the hydroxyl oxygen of the alcohol at the same time and a β-proton is found in *trans*-position at that instant. By this random fluctuation of two protons to the respective oxygen the C_α-atom becomes highly positively polarized and the water molecule is preformed. This time-dependent polarization may be compared to inductomeric effects, which influence the reactivity of reacting molecules (*22*). The preformation of the water molecule is in agreement with the early dehydration mechanism proposed by Eucken and Wicke (*23–25*) and with the principle of least motion (*26*). Once the C_α-atom has become positively polarized, a positive charge is also induced on the C_β-atom, which is influenced by the β-substituents. The hybridization of C_α and C_β is changed towards sp^2; p-orbitals and thus the double bond between C_α and C_β are developing, the β-proton becoming more and more acidic at the same time. The reaction can be successful whenever the β-proton comes into interaction with the basic center before the initiating polarization of the C_α-atom returns to its original state. Since no basic center is available for interaction with a β-proton in the *trans*-position and the rotation of C_β–H around the C_α–C_β axis (which furthermore would lead to a *cis*-elimination) is precluded by the developing double bond, the transition state structure must necessarily involve some type of motion relative to the catalyst surface such that the β-hydrogen comes close to a basic site. This basic site may be located in cracks or at any edge or corner of the "rough" surface in the neighborhood of the adsorbed alcohol molecule. Such a type of molecular motion can indeed be suggested as being caused by a vibrational degree of freedom "parallel" to the surface if a localized adsorption of the reacting molecule is assumed. The respective vibrational mode may be understood as a rocking vibration of the whole molecule, i.e., a periodical inclination of the plane which is defined by the O–C_α–C_β–H bonds. This motion then leads to an approach to the above-mentioned appropriately located basic site. In the following discussion, the motion of the adsorbed molecule which we have just described will be termed "inclination." The frequency factors of the reactions studied in the present work lie in the range between 5×10^5 and 2×10^{11} sec^{-1}. These values require frequencies of the rocking vibration of the order of magnitude of 10^{11} sec^{-1} in the most extreme case. Frequencies of this magnitude (up to 10^{12} sec^{-1}) for vibrations parallel to the surface are reasonable (*40*, *41*). Furthermore, vibrations with frequencies of this order of magnitude are certainly excited at the elevated temperatures used. The proposed motion of the adsorbed molecule is thus at least not in contradiction to the model of a rocking vibration mode. Thus, the inclination of the whole structure leads to an approach of the β-hydrogen to a basic site and renders an interaction possible, while the C_α-O bond fission is still not complete. An interaction between β-proton and the basic site involved in the β-proton abstraction is certainly necessary in either case, the proton passing over the potential well or tunneling through it. A concerted elimination of the elements of water under the influence of the attacking basic center is thus preserved, and the observed *trans*-elimination can be explained.*

The inclination towards the surface is in both cases certainly highly restricted by bulky substituent groups attached to C_α and C_β. The inclination therefore will occur most probably and with the higher effectiveness to that side of the transition state structure that leads to the lower steric hindrance. This suggestion can explain the observed *cis/trans* ratios, and is consistent with all the experimental results offered. We illustrate it with reference to two examples, 2-butanol and 3-methyl-3-pentanol. Though for the initial state structure certainly the *trans*-conformation is preferred, the most favorable conformation for the transition state of 2-butanol is III with the methyl groups in the *cis*-position:



III

This structure may easily incline backwards towards the surface, whereas a structure with the methyl groups in *trans*-position would bring about a high steric restriction to inclination towards each side. *Cis*-2-Butene is therefore the preferred 2-olefin. For the dehydration of 3-methyl-3-pentanol, on the other hand, the most favorable transition state structure is the one with the methyl groups in the *trans*-position (IV):



IV

since otherwise the more bulky ethyl group would more strongly hinder the "backward inclination" of the surface complex. In this case therefore the *cis*-isomer is sterically preferred.*

Thus the present model of the transition state for concerted dehydration reactions on alumina explains not only the *trans*-elimination course but also the observed *cis/trans* ratios. On the grounds of these suggestions it seems justified to explain the *cis*-preference by steric effects.

2. Arrhenius Parameters

If the proposed transition state model comes close to the real situation it must also explain the sequence of the Arrhenius parameters. The zero-order rate is given by the transition state theory (*27*):

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

where k is Boltzmann's constant, h is Planck's constant, R is the gas constant, c_a is the surface concentration of the reactant and $\Delta n^\ddagger$ is the change in number of molecules during the formation of the transition state (here $\Delta n^\ddagger = 0$). The surface concentration of the alcohols in a complete monolayer was calculated from the liquid density according to Emmett and Brunauer (*28*). Results from such calculations agree very well with experimental values of saturation concentrations in the precatalytic temperature range (*29*). Activation energies were obtained from the slope and the acti-

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* All the conclusions remain valid if alternatively a reaction intermediate is assumed whose structure comes close to a nonclassical bridged carbonium ion.

* The prefixes *cis* and *trans* are used upon consideration of the longest chain in the olefin in agreement with the IUPAC Definitive Rules for Nomenclature (*30*).

vation entropies from the intercept at $1/T = 0$ of Arrhenius plots, applying a least squares method. The entropy at a surface concentration of 1 mole/g is taken as the standard state. As an example, the Arrhenius diagram for the dehydration of *tert*-butanol between 117 and 185°C is shown in Fig. 1. The Arrhenius parameters obtained are given in Table 2 for each primary product. The last column of Table 2 gives the numbers n of experimental points used for the calculations. Recently Bagg (*30*) discussed the significance of differences of Arrhenius parameters, which were determined with the assumption of their temperature independence. From his results, one calculates that, for the most extreme temperature ranges of the present work, differences greater than approximately 0.5 kcal/mole for the activation energies and greater than approximately 5 eu for the activation entropy should be significant. Lateral interactions between adsorbed molecules may also influence the Arrhenius parameters. However, at least for the comparison of the formation of different products from the same reactant, these influences should be negligible. Differences of the activation energies of more than 1–2 kcal/mole and of the activation entropies of more than 5 eu may, therefore, be considered to be significant. The Arrhenius parameters given in Table 2 are all related to the transition from the ground state to an E_2-like reaction intermediate. Thus, the differences between the various activation energies and entropies must be attributed to the details of the E_2 transition state as determined by the substrate structure in the sense mentioned in the introduction (i.e., degree of C_α-polarization, degree of double bond preformation). Environments and basic centers are at least qualitatively equal in all cases.

If the values for 2-methyl-1-pentanol and for neopentanol, which could not be measured in the zero order range, are excluded, Table 2 shows roughly the following trends:

$$\Delta E_{\text{primary}} > \Delta E_{sec} > \Delta E_{tert}$$

$$\Delta S^{\ddagger}_{\text{primary}} > \Delta S^{\ddagger}_{sec} > \Delta S^{\ddagger}_{tert}$$

i.e., the lower the C_α-polarization and the higher the double bond preformation in

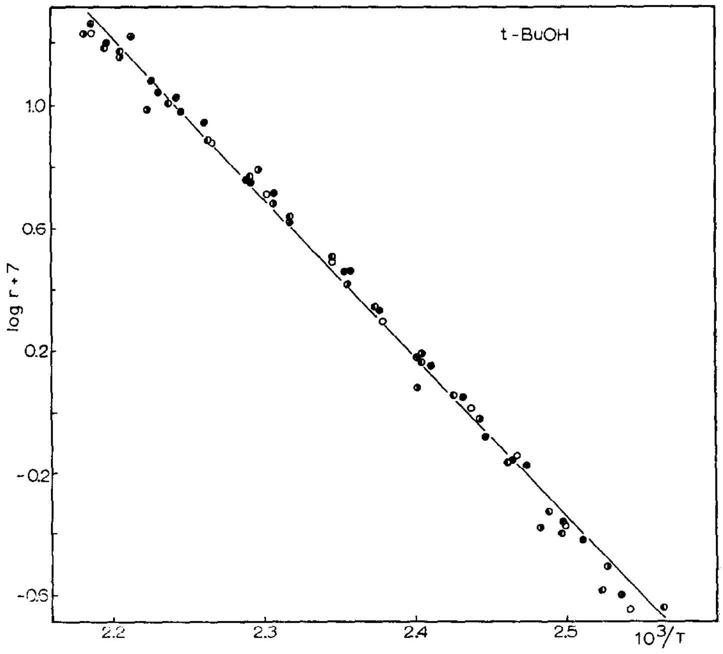


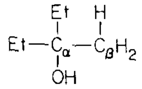
FIG. 1. Arrhenius plot for the dehydration of *tert*-butanol in the temperature range between 117 and 185°C.

the E_2-like transition state the higher is the activation energy and the less negative the activation entropy [see also (*6*, *7*)].

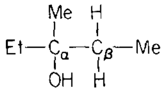
2.1. Activation Energies

Since all the reactions studied go through an E_2-like reaction intermediate, which, depending on the reactant structure, more or less resembles the structure of the final products, the rate of the C_β–H bond fission mainly determines the overall reaction rate and the Arrhenius parameters. The above mentioned trend of the activation energies may then be explained roughly by the increasing β-proton acidity in the sequence of primary, secondary, and tertiary structures, since the higher the initial β-proton acidity, the lower is the energy necessary to promote the proton to a position that is favorable for its complete abstraction.

Inductive effects apparently play an important role in the determination of the activation energy. As shown in the previous paragraph, however, olefin stabilizing effects (hyperconjugation) must also be taken into account in the proposed transition state model. Since the olefin stabilizing effect of alkyl groups follows the reverse order to the inductive effect, the order of activation energies may also be reversed if the differences of inductive influences are not predominating too much. This observation is made for a number of dehydrations, in particular those in which various products are formed from one and the same alcohol. The point has already been discussed for the formation of Hofmann and Saytzeff products from 3-methyl-2-butanol and 2-methyl-2-butanol (*7*). The dehydration of 3-methyl-3-pentanol is therefore chosen as an example here. Considering the inductive effect alone, one would expect a lower activation energy for the formation of 2-ethyl-1-butene than for the formation of the 3-methyl-2-pentenes. Experimentally, however, the reverse order is found (see Table 2), which can only be explained by the simultaneous influence of inductive effects and hyperconjugation. In the case of 2-ethyl-1-butene formation the β-proton acidity is not reduced by the inductive effect of alkyl groups attached to C_β, while olefin stabilization is relatively poor, since only two ethyl groups are C_α-linked (4 protons available for hyperconjugation):


$$\mathrm{Et{-}\overset{\overset{Et}{|}}{\underset{\underset{OH}{|}}{C_\alpha}}{-}\overset{\overset{H}{|}}{C_\beta}H_2}$$

In the formation of the 3-methyl-2-pentenes on the other hand, one methyl group at C_β reduces the β-proton acidity; the developing double bond, however, is stabilized much more effectively than in the former case, by two methyl groups and one ethyl group (8 protons available for hyperconjugation):


$$\mathrm{Et{-}\overset{\overset{Me}{|}}{\underset{\underset{OH}{|}}{C_\alpha}}{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C_\beta}}{-}Me}$$

Thus, hyperconjugation reverses the order of the activation energies as predicted by the inductive effect alone.

Similarly, all the activation energies given in Table 2 can be explained. It is worth mentioning that the charges induced on the β-hydrogen are generally small; differences of only one thousandth of the electronic charge, however, can cause differences in the free energy of activation of about 1 kcal/mole (*31*).

The observed differences in the activation energies between *cis*- and *trans*-olefins cannot be explained by these effects. As a third contribution to the activation energies steric hindrance to the inclination of the transition state structure must therefore be taken into account. This contribution will increase the activation energy for the formation of the sterically less preferred isomer. The difference in steric hindrance to inclination between the transition state conformations for the formation of *cis*- and *trans*-2-butene from 2-butanol are very strong and thus the differences in the respective activation energies are high. For the formation of *trans*- and *cis*-3-methyl-2-pentene from 3-methyl-3-pentanol the activation energies are practically equal; this fact must be caused by the relatively small differences of steric hindrance to the inclination in the two respective transition state conformations (see formula IV). The *cis*-preference is therefore not greatly pronounced in this case, the ratio being only 2.3 (see Table 1).

2.2. Activation Entropies

The activation entropies cannot be as easily discussed. Assuming the localized adsorbed reactant to be the initial state and neglecting rotational contributions, the above-mentioned order may be explained to a first approximation by differences of the vibrational partition functions in the ground and transition states. The higher the E_1-character (tertiary structures) the more pronounced is the C_α–O bond fission which results in a relatively high loss of vibrational degrees of freedom and therefore leads to a highly negative entropy of activation. With increasing E_2-character (secondary and primary structures) the C_α–O bond loosening is weaker, the double bond is preformed, and the β-hydrogen forms a bond to the basic center. Thus, in such cases, some bonds are weakened and the respective force constants are lowered; other bonds, however, are strengthened or even new bonds are formed. Completely different sets of force constants and frequencies, therefore, have to be considered for the ground and transition state and one might suppose that the entropy loss in the formation of the transition state is the lower, the higher the E_2-character of the transition state. Since the geometrical situation determines the inclination probability and thus the preexponential factor of the Arrhenius equation, steric effects must be also incorporated in the experimentally found activation entropies.

Another contribution to the entropies of activation furthermore complicates the discussion. It has been found that the entropies of activation for the dehydration of normal and β-deuterated alcohols are quite different (*6*). Theory predicts that the isotope effect should appear mainly in the activation energy and should have only a minor effect upon the preexponential factor of the Arrhenius equation. Bell (*32*) has shown that generally the ratio of the preexponential factors should lie within the limits 0.5–1 for proton transfer reactions. Ratios $A_H/A_D < 0.5$ are considered to provide strong evidence of an appreciable degree of tunneling. The ratios obtained for the presently considered dehydration reactions were approximately (*6*) $A_H/A_D = 0.01 \pm 0.006$, so that one has to assume certain tunnel contributions to β-proton abstraction. The magnitude of the tunnel effect, as well as the vibrational frequencies of the transition state and the inclination frequency, strongly depend on the shape and dimensions of the energy hyperplanes. These are, however, unknown and we will therefore restrict ourselves to the foregoing qualitative consideration.

As an important result, it can only be emphasized that most probably the tunnel effect in the proton transfer from C_β to the basic center plays an important role in the dehydration of alcohols on alumina. Thus, Noller's suggestion (*11*, *37*), which assumed a considerably high β-proton mobility, finds some support. This property of the leaving β-proton also suggests that it can be abstracted from the presently proposed structure, after being in interaction with the basic center, while the reaction intermediate has not to turn totally around in concordance with the discussion in paragraph 1.

3. Linear Free Energy Relationships

Linear free energy relationships have been shown to give information on the mechanism of heterogenously catalyzed reactions (*34*). For the dehydration of a series of secondary alcohols on alumina at 300°C the Taft equation was found to correlate the rates when an E_1-like transition state model with the reaction center at C_α was adopted (*35*). The reaction constant ρ^* had a low positive value. The Hammett equation was fulfilled for the dehydration of substituted 1-phenylethanols, the ρ^*-constant being negative (*36*). The low positive and the negative reaction constants provide strong evidence for a highly ionic character of the transition state, which is caused by the phenyl group and the high reaction temperature applied in agreement with the proposed transition state model.

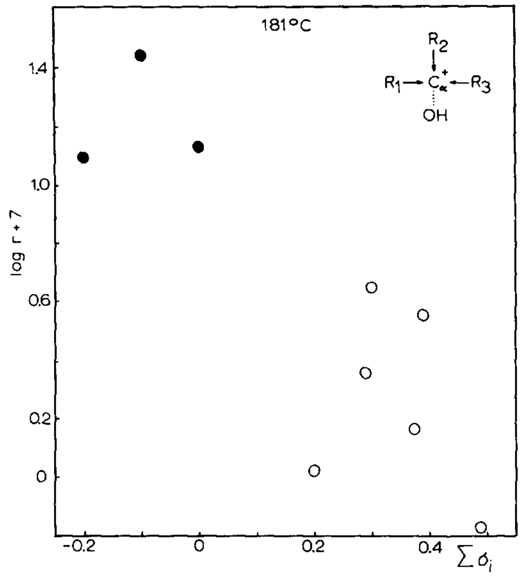


FIG. 2. Taft correlation for the dehydration of aliphatic alcohols at 181°C.

As shown in Fig. 2, the Taft equation does not correlate the rates of dehydration at lower temperatures, if the σ^*-constants are calculated on the assumption that the C_α-atom is the reaction center (E_1-type). This result proves that the E_1-character does not predominate in the dehydration of alcohols on alumina at low temperatures.

For an E_2-mechanism a correlation of the data by a simple two parameter Taft equation cannot be expected because of the simultaneous influence of hyperconjugation in the E_2-like transition state. Furthermore, the ionic character must be dependent on the α- and β-substitution, so that the exact mechanism may change from molecule to molecule. Another difficulty in E_2-reactions arises since the reaction center is not clearly defined. The C_α–C_β grouping could be considered as the reaction center, where inductive and hyperconjugation effects of α- and β-substituents, would have to be considered. Since, however, α-substituents also have inductive effects on C_β and vice versa, their influence being damped by an unknown factor, the σ^*-constants cannot be calculated correctly for the respective model. It thus seems that Taft relationships cannot be verified for E_2-like reactions at the moment.

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