Geometric Factor in Heterogeneously Catalyzed Dehydration

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Geometric conditions for the dehydration of alcohols on γ-Al$_2$O$_3$ and ThO$_2$ have been studied with the aid of a computer. Computed data rendered it possible to explain some experimental data which have as yet been explicable only with difficulty (the *anti*-elimination mechanism and high *cis/trans* isomer ratio in the dehydration on γ-Al$_2$O$_3$ and the selective formation of 1-alkenes in the dehydration on ThO$_2$). It has been found that the reaction may proceed on the catalyst surface not only as the *syn*-elimination but also as the energetically more favorable *anti*-elimination. Steric demands with respect to the product formation increase in the order: 1-alkene, *cis*-2-alkene, and *trans*-2-alkene. Based on a Monte-Carlo model of coverage of the (100) surface of γ-Al$_2$O$_3$ by hydroxyl groups, the activity of the catalyst, the selectivity of the stereochemical course of the reaction, and the selectivity with respect to the products are discussed in relation to the degree of coverage. On low-index surfaces of ThO$_2$, i.e., (100), (111), and (110), only such adsorption complexes have been identified as lead to preferential formation of 1-alkenes.

INTRODUCTION

Although the reaction mechanism of alcohol dehydration on metal oxides has been studied for several decades, it is not yet fully understood *(1–3)*. The greatest attention has been paid to the course of the dehydration on γ-Al$_2$O$_3$. Not only on this, but also on a number of other oxide catalysts, the radical mechanism or the mechanism involving oxonium or carbonium ions can most probably be excluded in the case of primary or secondary alcohols (for references see *(3)*). Also rejected can be the mechanism involving a surface alcoholate ion (for references see *(3)*). This is supported by the fact that pyridine, which adsorbs specifically on Lewis acidic sites *(4)*, does not affect dehydration *(5–7)*. In addition to this, quantum chemical calculations have shown that the surface alcoholate

is the intermediate product of dehydrogenation reaction *(8, 9)*.

In the light of contemporary knowledge, the course of dehydration on γ-Al$_2$O$_3$ seems to be accounted for in terms of the concerted mechanism of cleavage of hydroxyl group and of hydrogen from the β-carbon with participation of the pair of an acid and a basic site of the catalyst surface *(10)*. Such a *syn*-elimination mechanism has been suggested by Eucken *(11)* and Wicke *(12)* on the basis of the principle of least motion *(13)* and of the fact that the presence of a certain amount of water on the catalyst surface is a prerequisite for the reaction to occur *(14–16)*.

Pillai and Pines *(17)* found and Kibby *et al.* *(18)* have proved that alcohol dehydration on γ-Al$_2$O$_3$ proceeds as the *anti*-elimination. The results of selectivity studies led Schwab and Schwab-Agallidis

(19) to conclude that the reaction proceeds within the pores of the catalyst. This idea has been accepted by Pines and Manassen (2) and Blanc and Pines (20) who assumed that the acid and basic sites are located on the opposite walls of the pore. Under such conditions the steric demands of *anti*-elimination can be easily satisfied. Geometric conditions on a flat catalyst surface were considered earlier to be unfavorable for concerted *anti*-elimination. On the other hand, the dehydration reaction taking place within the pores of molecular size should be controlled by diffusion, which has not been observed.

Another finding which was difficult to explain is the observation that dehydration products contain *cis-* and *trans-*2-alkenes in proportions which do not correspond to thermodynamic equilibrium (2, 3, 21). Infrared spectra measurements of alcohols adsorbed on oxides showed that the center of adsorption activity of alcohols is their hydroxyl group (for references see (3)). Taking into account these facts Knözinger *et al.* (22) have arrived at the following conclusions concerning mechanism of the reaction. A molecule of the alcohol is adsorbed via its hydroxyl group by hydrogen bonding on a surface hydroxyl group (passive bond) and on a surface oxygen ion (active bond). The most favorable configuration is considered to be that in which the C–O bond in the alcohol molecule is pointed away from the surface. Because of this the *anti*-periplanar hydrogen is too remote to be able to interact with the surface basic site. According to the authors, the molecule as a whole exercises vibrational motions by which the $O-C_\alpha-C_\beta-H$ plane inclines to the surface. In this way the β-hydrogen can interact with the surface, which is a prerequisite for the reaction. At the same time, the sterically more favorable conformation for the activated complex is that in which bulky substituents are most remote from the surface. Therefore, forma-

tion of the isomer having substituents in the *cis*-position to each other will be preferred.

Dehydration of alcohols on ThO_2 has been established to be of substantially different type. On this catalyst 1-alkenes are formed highly selectively. Lundeen and van Hoozer (23, 24) ascribed this fact to the steric interaction of substituents in the activated complex of the reaction which is thought to proceed as *syn*-elimination. The structure from which 1-alkene arises via *syn*-elimination is energetically more favorable compared to the structures leading to the formation of 2-alkene. The authors admit, however, that the energy difference is probably not great enough to be an unambiguous evidence for their explanation (24). In this connection Davies and Bray (25) object that "it is difficult to understand why an aluminum oxide surface on which 2-ols eliminate water to give both 1- and 2-olefins, would not have the same steric interaction limitations. . . ." In later works the dehydration of alcohols on ThO_2 is thought to proceed as the E1cB elimination, after adsorption via the hydroxyl group on a surface metal atom (26, 27).

By quantum chemical modeling of alcohol dehydration it was proved that in the dehydration reaction the molecule of alcohol is activated by interaction of the oxygen atom with the electrophilic species (proton) (28, 29). It was further found that by this interaction (which is a model for adsorption by a passive hydrogen bond on a surface hydroxyl group), the most activated hydrogen of all the β-hydrogens is that in the *anti*-periplanar position with respect to the hydroxyl (29).

The effect of the electronic factor in the dehydration of alcohols has attracted much attention. On the other hand, the geometric factor, which plays a no less important role in heterogeneous reactions (30–32), has rarely been considered. For this reason, the aim of this work is to investigate in detail the steric conditions of alcohol dehydration

on oxides, to obtain information about possible configurations of the adsorption complex and to find probable reaction mechanisms, taking into account both electronic and geometric factors.

METHODS[1]

In construction of the models used in this work, the general conditions for the dehydration mechanism set out by Knözinger et al. (22) were specified as follows:

(a) The molecule of alcohol adsorbs via its oxygen atom on a surface hydroxyl group by a passive hydrogen bond. (There is another electrophilic site on the surface, i.e., the coordinatively unsaturated Al^{3+} ion. Adsorption on it probably leads quite quickly to the dissociation of the alcohol molecule, yielding the surface alcoholate and hydroxyl. Quantum chemical calculations showed that in the course of dehydration the molecule of alcohol is activated by a decrease of the total electron density, i.e., by interaction with an electron acceptor (28, 29). In contrast to this, the interaction with an electron donor leads to an increase of electron density in the molecule, and according to calculations, it promotes the dehydrogenation reaction (8, 9, 33). The structure proposed by Knözinger et al. (22) which involves passive and active hydrogen bonds probably does not correspond to the transition state of dehydration, since donating and accepting effects of both hydrogen bonds compensate one another. This structure could be the transition state of the exchange of hydrogens between the hydroxyl of an alcohol and the surface, which was established experimentally (34); furthermore, quantum chemical calculation showed that adsorption by a passive hydrogen bond promotes not only dehydration but also the cleavage of the proton from the hydroxyl (29).)

[1] The list of computing programs is available on request from the author.

(b) The alcohol molecule interacts in the adsorption complex through its β-hydrogen with a surface oxygen ion. (According to quantum chemical calculations the adsorption by a passive hydrogen bond increases the ability of the β-hydrogen to be attacked by nucleophilic species (29).)

(c) The O–C_α and C_β–H bonds in the transition state are mutually anti- or syn-periplanar, which determines concerted anti- and syn-elimination, respectively. (According to quantum chemical calculations the activation energy of elimination is lowest for these conformations (29).)

In construction of the models standard bond lengths were used (35): O–H (96 pm), C–H (109 pm), C–O (143 pm), and C–C (154 pm). The length of the hydrogen bond between hydrogen and oxygen has been taken as 160 pm (36). In construction of the fragments of ThO_2 surface the distance between vicinal thorium and oxygen atoms was determined from the lattice constant (37) and had a value of 242.5 pm. Because of controversy in reported lattice constants for γ-Al_2O_3 (38), the distance between vicinal aluminum and oxygen atoms was determined assuming a cubic arrangement of lattice oxygen ions (39) from the density of γ-Al_2O_3 (40) and had a value of 202.1 pm. Bond angles in the alcohol molecule were taken as tetrahedral. With the exception of the C_α–O bond, dihedral angles in the alcohol molecule corresponded to the staggered conformation. In the models of the syn-elimination reaction the conformation along the C_α–C_β bond was eclipsed. Bond and dihedral angles in the fragments of catalysts corresponded to the symmetry of the ideal lattice.

Geometric models of reactant–catalyst complexes were constructed with the aid of a computer in the following way:

(a) Provided that adsorption takes place via formation of two hydrogen bonds, one between the surface hydroxyl group and the alcohol oxygen and the other between
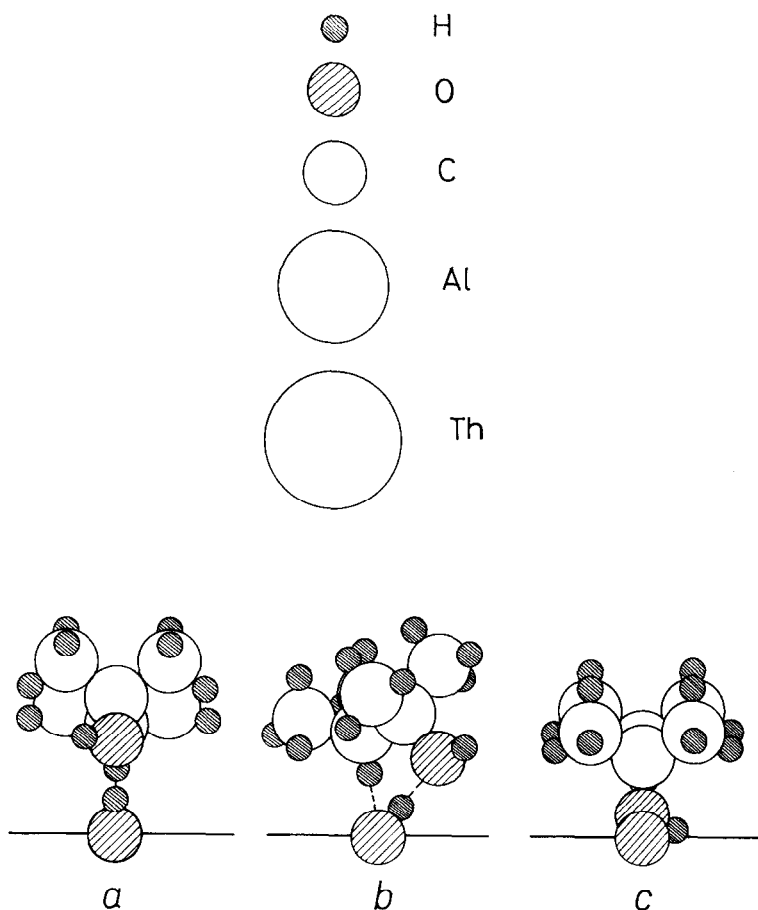
FIG. 1. View of the molecule of 2,3-dimethyl-2-butanol with the conformation corresponding to *syn*-elimination which interacts with the pair of surface sites at a distance of (a) 101 pm, (b) 301 pm, and (c) 560 pm. [The set of circles at the top of the figure designate the atoms and size scale used in this and all later figures.]

the β-hydrogen of the alcohol and the surface oxygen atom and that the atoms $O_{surf}-H \cdots O_{alc}$ and $O_{surf} \cdots H-C_\beta$ are collinear, a conformation of the $C_\alpha-O$ bond of the alcohol has been found for which surface sites have the required distance.

(b) The molecule of the alcohol was subjected to translation and rotation operations such that the positions of adsorption sites obtained in the preceding step were identified with the positions of the corresponding sites on the fragment of the catalyst surface.

(c) By rotating the alcohol molecule along the joint between adsorption sites a

configuration has been found in which the two shortest distances between the molecule atoms and the surface atoms are equal and maximal (the term distance refers here to the distance between the centers of atoms from which the sum of the radii of the atoms is subtracted).

In the figures illustrating the structures found in this way we used parallel projections to the draft plane. Atoms were taken as balls whose radii were chosen so that the atoms bonded together (in the alcohol molecule) or vicinal atoms (in the catalyst fragment) touched each other.

(Note: The radii of atoms defined as above differ significantly from the ionic radii (41) used most frequently in depicting crystal structure. Their values are close, however, to those of covalent radii with which they have a similar definition (42). The sums of the chosen radii are understood in this work as the distance limits which cannot be surmounted by atoms without distinct repulsion).

The structure of the hydrated γ-Al_2O_3 (100) surface was modeled analogously to Peri (43). This means that we considered only a portion of surface in the form of a square with dimensions 50 × 50 hydroxyl groups. The sides of this square, the upper and lower and the right and left, have been considered as neighboring, in order to exclude the edge effects. The initially fully hydroxylated surface was progressively dehydrated and its structure analyzed at fixed intervals. The program which simulated dehydration worked in two stages. In the first stage the process was directed so that the structures containing two or

more vicinal vacancies have not been formed on the surface. Nor were two or more vicinal oxygen atoms. At the moment in which the modeled surface could not be further dehydrated under given conditions, the computation adopted the second stage, the dehydration proceeding to the final stage in which there were only isolated hydroxyl groups on the model surface. The program worked in the following way.

In the first step, a group to be cleaved as a whole has been selected from the list of suitable groups with the aid of the generator of pseudorandom numbers. (In the beginning of the first and second stages of the work of the program the list of suitable groups contained all the hydroxyl groups present on the surface. During computation the groups already cleaved and those which were found to be isolated have been taken out. Also taken out of the list of suitable groups in the first stage of the program were the groups in the vicinity of which a vacancy was just formed as well as the groups which were found not to have in
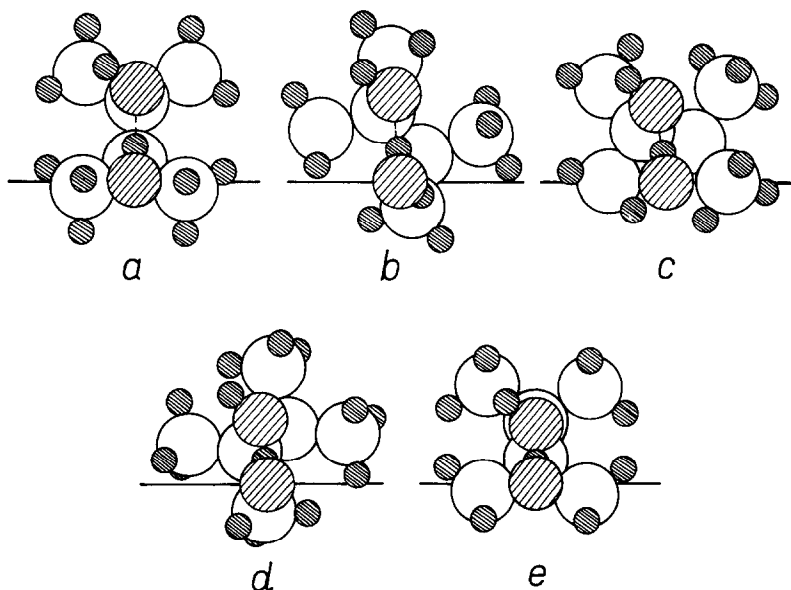

FIG. 2. View of the molecule of 2,3-dimethyl-2-butanol with the conformation corresponding to *anti*-elimination which interacts with the pair of surface sites at a distance of (a) 557 pm. (b) 577 pm, (c) 617 pm, (d) 657 pm, and (e) 671 pm.

their vicinity a group from which proton cleavage is possible without formation of vicinal oxygen ions. The list constructed in this way was meant to ensure a constant dehydration rate during computation and thus to ensure convergency of the process to the final stage, in contrast to the procedure adopted by Peri (43).) In the case that the conditions valid for a given stage of dehydration did not make the cleavage of a selected group possible, the random choice according to the first step was repeated. In the favorable case the second step was performed.

In the second step, one of the groups vicinal to the group selected in the first step has been selected by the random choice. In the case that the conditions valid for a given stage of dehydration allowed the proton to be cleaved from this group, the dehydration process has been realized on the pair of selected groups. In the opposite case another vicinal group was selected. If none of such groups was available, the choice according to the first step was repeated.

RESULTS[2] AND DISCUSSION

The assumption about two-center adsorption of an alcohol raises the question as to whether there are pairs of sites (hydroxyl and oxygen ions) on the catalyst surface which at a given degree of freedom (free rotation around the $O-C_\alpha$ bond) could be spanned with the molecule of the alcohol. At the same time, as far as the $C_\alpha-C_\beta$ bond is concerned, due to through-space and through-bond interaction of the sp^3 hybrid carbon orbitals involved originally in the $O-C_\alpha$ and $C_\beta-H$ bonds, such conformations are stabilized in which O, C_α, C_β, and H atoms are coplanar (44). Thus anti-elimination is energetically favorable and somewhat less so is syn-elimination (29, 44). The activation energy of elimina-

[2] The numerical results are available on request from the author.
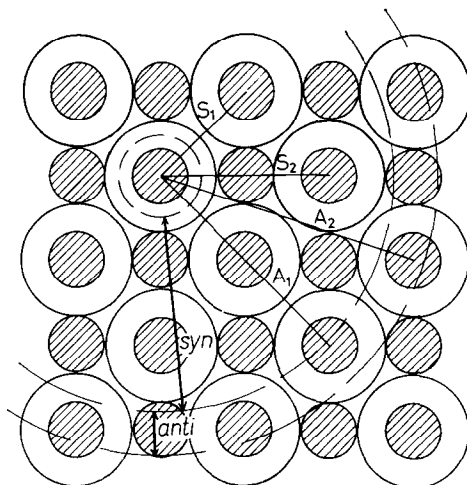

FIG. 3. Scheme of the fully hydrated (100) surface of γ-Al$_2$O$_3$ (43); all types of suitable surface oxygen atoms pairs are marked which were found in distance regions for the syn-periplanar (101–560 pm) and the anti-periplanar (557–671 pm) conformation of the alcohol molecule.

tion for all the other mutual positions of the cleaved $O-C_\alpha$ and $C_\beta-H$ bond is higher, since stabilization interaction of the activated complex is partially or completely restricted (44).

The computation has shown that under accepted assumptions about the geometry of the activated complex the syn-elimination may proceed on the hydroxy ion–oxygen ion pair with a distance between these species of 101–560 pm. As represented in Fig. 1 the character of steric interactions of the adsorbate with the surface remains preserved over the whole range of distances. The α- and β-carbons may be substituted by methyls, without inducing steric hinderance. In the case of anti-elimination the situation is more complicated, although the range of suitable distances is markedly narrower, i.e., 557–671 pm. In anti-elimination structures some of the bonds of substituents on the α- or β-carbon point always to the surface. Figure 2 shows that on going through the region of suitable distances the configuration of the surface
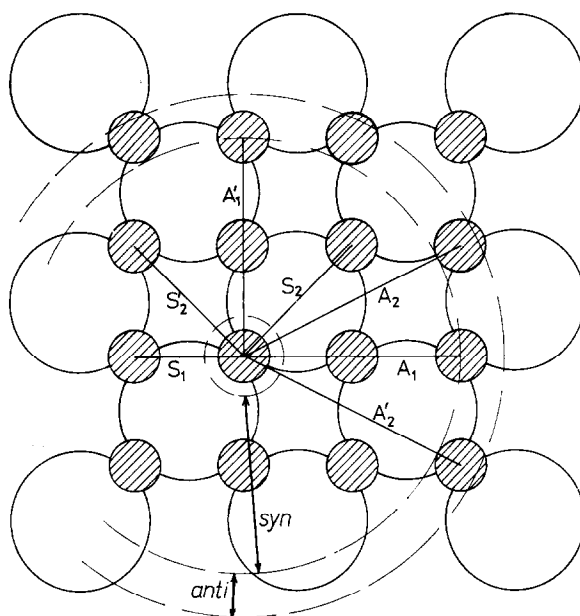
FIG. 4. Scheme of the fully hydrated (100) surface of ThO_2 (45); see legend of Fig. 3.

complex changes dramatically, since the molecule of the alcohol turns through 180°.

For the shortest possible distance the β-carbon is nearer to the surface than the α-carbon (Fig. 2a) and the bonds to β-substituents point to the surface. One can thus expect that on the pair of sites at these distances only α,α-disubstituted ethanols would adsorb without steric hinderance. Relatively small changes in the distance between sites lead to substantially different configurations of the surface complex. As the distance increases, α,α,β-trisubstituted (Fig. 2b), α,β-disubstituted
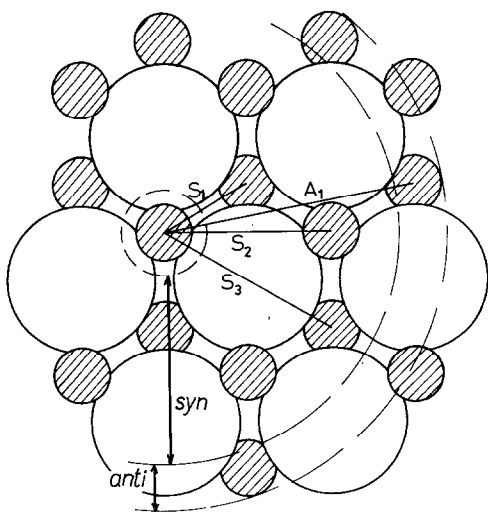

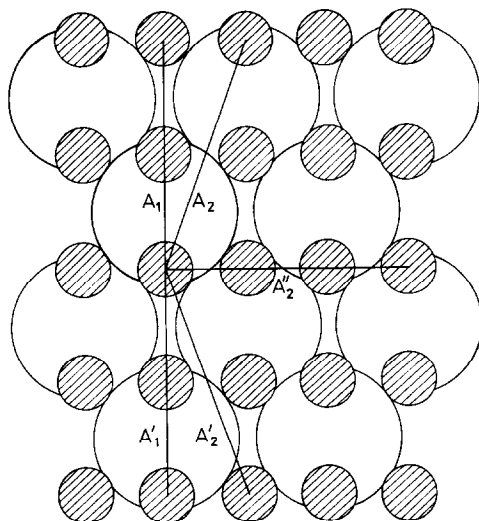FIG. 5. Scheme of the fully hydrated (111) surface of ThO_2 (45); see legend of Fig. 3.

FIG. 6. Scheme of the fully hydrated (110) surface of ThO_2; see legend of Fig. 3.

(Fig. 2c), α,β,β-trisubstituted (Fig. 2d), and β,β-disubstituted ethanol (Fig. 2e) may adsorb gradually. This conclusion is not valid in general, since the assumption that the situation of the molecule adsorbed on the surface is analogous to the situation of, for example, a scale model situated on a desk is not correct. The adsorbent and adsorbate are composed of particles of roughly the same size (in order of magnitude). Therefore, as will be seen later, the catalyst does not represent a *flat* base, but a very uneven base to the molecule of the reactant.

Figures 3 to 6 show the fragments of ideal, fully hydroxylated surfaces of γ-Al$_2$O$_3$ *(43)* and ThO$_2$ *(45)*. For the sake of simplicity the hydrogen atoms of hydroxyl groups are not depicted in the figures. In Figs. 4 and 5 all the depicted oxygen atoms

are parts of the surface hydroxyl groups. In Figs. 3 and 6 this is true only for oxygen atoms located above the metal atoms. The oxygen atoms located between the metal atoms are the oxygen ions of the crystal lattice. In Figs. 3 to 6 were found all the positions which could be occupied by oxygen ion after partial dehydration of the surface, this being made for the corresponding distance regions (101–560 pm for *syn*-elimination and 557–671 pm for *anti*-elimination). The pairs of oxygen atoms of the hydroxyl ion–oxygen ion pairs were designated as S or A according to their relevance to the region of *syn*- or *anti*-elimination distances and were further denoted by numerical indices increasing with distance between sites.

The use of the procedure described in the Methods section above yielded the struc-
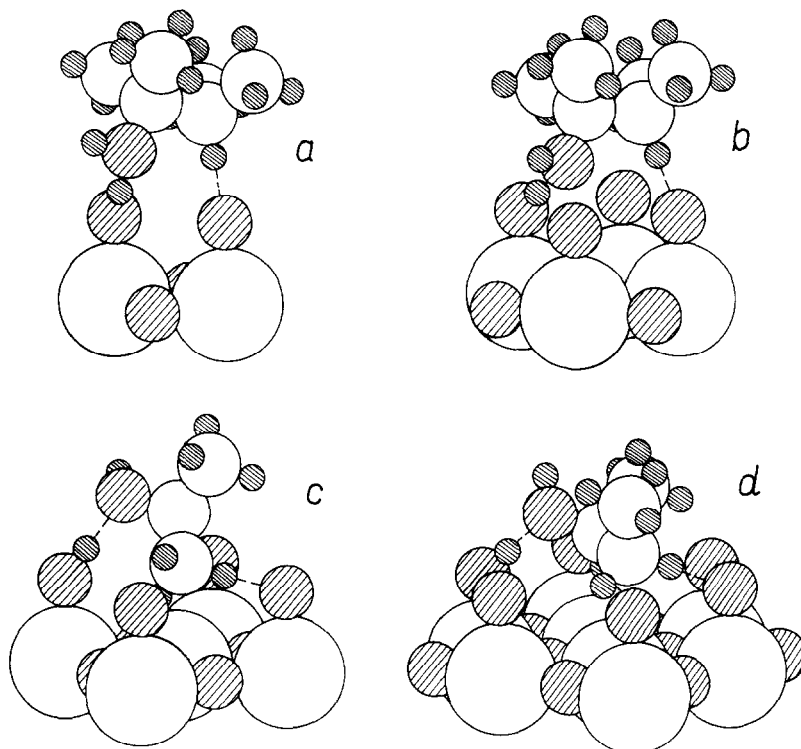

FIG. 7. Molecules of alcohols interacting with the pairs of differently distant sites of the (100) surface of γ-Al$_2$O$_3$ (see Fig. 3). (a) S_1—286 pm, (b) S_2—404 pm, (c) A_1—572 pm, and (d) A_2—639 pm.
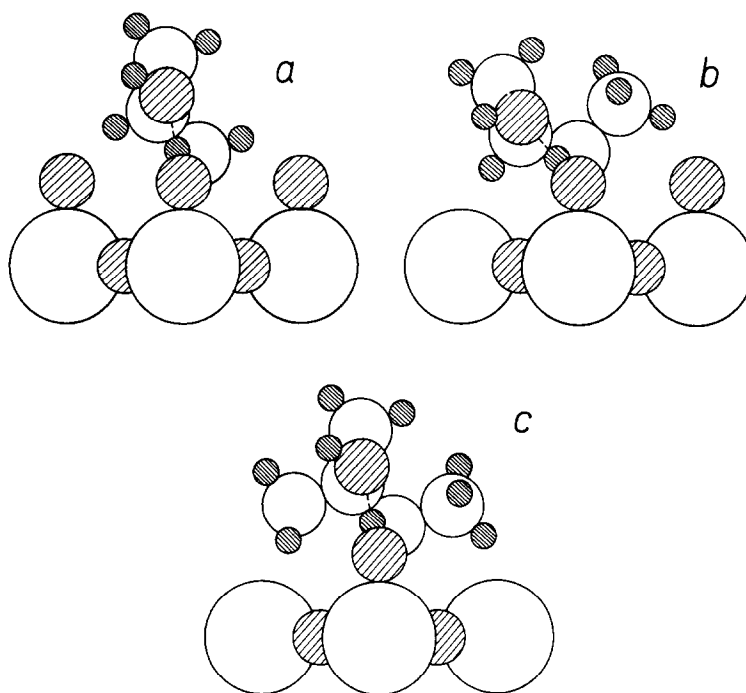
FIG. 8. Molecules of alcohols interacting with pairs of sites of the (100) surface of γ-Al$_2$O$_3$ (A_1—572 pm, see Fig. 3) at varying degrees of surface hydration.

tures for the (100) surface of γ-Al$_2$O$_3$ which are depicted in Fig. 7. It was found that *syn*-elimination on the given catalyst surface may proceed without distinct steric hinderance for fully methyl-substituted ethanol on the pair of active sites S_1 (Fig. 7a) and S_2 (Fig. 7b). In both cases the positions of hydroxyl groups on the surface may be completely occupied. However, also *anti*-elimination can proceed on the (100) surface of γ-Al$_2$O$_3$. In this case the steric demands are more complicated. Thus on a uniform surface subjected to partial dehydration (*43*) only α-mono-substituted ethanol can react on the pair of sites A_1 to give 1-alkenes (Fig. 7c). *Anti*-elimination can take place also on the pair of sites A_2 (Fig. 7d). This requires, however, the existence of two vicinal vacancies in the hydroxyl coverage, i.e., deviation from the uniform arrangement (*43*). On this pair of sites the reaction proceeds starting with α,β-disubstituted ethanol to

give *cis*-2-alkenes. The formation of *trans*-2-alkenes is eliminated by geometric conditions of the arrangement given.

The relationship between the degree and uniformity of coverage of the (100) surface of γ-Al$_2$O$_3$ by hydroxyl groups on the one hand and the number and position of substituents in the reactant molecule on the other hand can be explained by the example of the pair of sites A_1. The situation is depicted in Fig. 8. As shown earlier (Fig. 7c), α-monosubstituted ethanol can react on the pair A_1 if there is a vacancy between both sites (Fig. 8a). Only 1-alkenes can be formed under these conditions. If another hydroxyl group is removed at the expense of regularity in the surface coverage (*43*), geometric conditions on the pair A_1 allow the reaction of α,β-disubstituted ethanol to occur (Fig. 8b). The conformation of methyl leads, however, only to *cis*-2-alkenes. If the degree of hydration and the regularity of the surface is further

lowered by cleaving another hydroxyl group, the reaction on the pair A_1 can proceed with α,α,β-trisubstituted ethanol (Fig. 8c). In this case trans-2-alkenes can be produced. For anti-elimination it therefore holds that with respect to the product, the steric demands of the reaction increase in the order 1-alkene, cis-2-alkene, and trans-2-alkene.

By means of the Monte-Carlo model of dehydration of the (100) surface of γ-Al$_2$O$_3$ we have studied the effect of hydroxyl group concentration on the proportion of the sites suitable for syn- and anti-elimination. The calculation was performed repeatedly for the sample of the surface containing 2500 hydroxyl groups and the resulting values were averaged, until statistical fluctuations have been smoothed. Figure 9 shows that the results of calculation for 10,000 sites, made by Peri (43), may not be statistically smoothed. The values presented in this work are based on the surface with 67,500 sites which, according to Fig. 9, is the sample sufficiently representative for the purpose given.
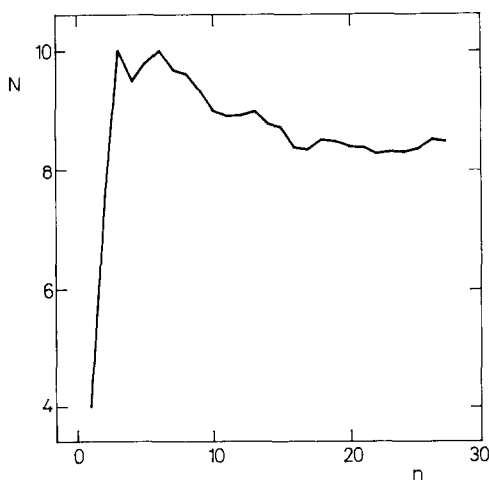

FIG. 9. The number of pairs N of sites of type A_1 with the surrounding according to Fig. 8c on the surface occupied by only isolated hydroxyl groups in dependence upon the number of experiments n for the Monte-Carlo model.

TABLE 1

Surface Concentrations of Pairs of Sites on the (100) Surface of γ-Al$_2$O$_3$ According to the Monte-Carlo Model after 27 Experiments on 2500 Centers (in numbers per 1 nm^2) for Varying Degree of Coverage of the Surface by Hydroxyl Groups (in %)

Coverage	Concentration of pairs of the type					
	S_1	S_2	$A_1{}^a$	$A_1{}^b$	$A_1{}^c$	A_2
100.00	0.000	0.000	0.000	0.000	0.000	0.000
90.00	1.754	2.280	0.637	0.000	0.000	0.000
80.00	3.277	4.142	1.354	0.000	0.000	0.000
70.00	4.548	5.571	2.095	0.000	0.000	0.000
60.00	5.460	6.420	2.870	0.000	0.000	0.000
50.00	5.909	6.605	3.578	0.000	0.000	0.000
40.00	5.839	6.166	4.027	0.000	0.000	0.000
33.54^d	5.447	5.532	4.063	0.000	0.000	0.000
30.00	5.083	5.148	3.630	0.196	0.003	0.142
20.00	3.916	3.808	2.427	0.553	0.019	0.402
10.00	2.437	2.087	1.265	0.581	0.040	0.426
8.52^e	2.180	1.799	1.101	0.552	0.042	0.404
0.00	0.000	0.000	0.000	0.000	0.000	0.000

^{a} Pairs of sites with the surrounding according to Figs. 7c and 8a (formation of 1-alkenes possible).

^{b} Pairs of sites with the surrounding according to Fig. 8b (formation of cis-2-alkenes possible).

^{c} Pairs of sites with the surrounding according to Fig. 8c (formation of trans-2-alkenes possible).

^{d} The lowest degree of coverage achieved without formation of irregularities (i.e., vicinal oxygen ions or vacancies).

^{e} The coverage at which only isolated hydroxyl groups are present on the surface.

The results of the calculations for the Monte-Carlo model are presented in Table 1. The primary fact is a trivial finding that both fully occupied and completely dehydroxylated surfaces do not contain the pairs of sites and are therefore inactive for the dehydration of alcohols. This phenomenon has been established experimentally by a number of authors. It was found that the presence of a certain amount of water on the catalyst surface is a prerequisite (14–16) and that, on the other hand, water when present in greater amounts retards the reaction (46–48).

From Table 1 it is seen that the concentration of pairs of sites passes through a maximum. As steric demands of the reaction increase, the maximum is progressively more shifted to zero coverage. This is due to the fact that in the dehydration of alcohols on γ-Al$_2$O$_3$ the existence of active
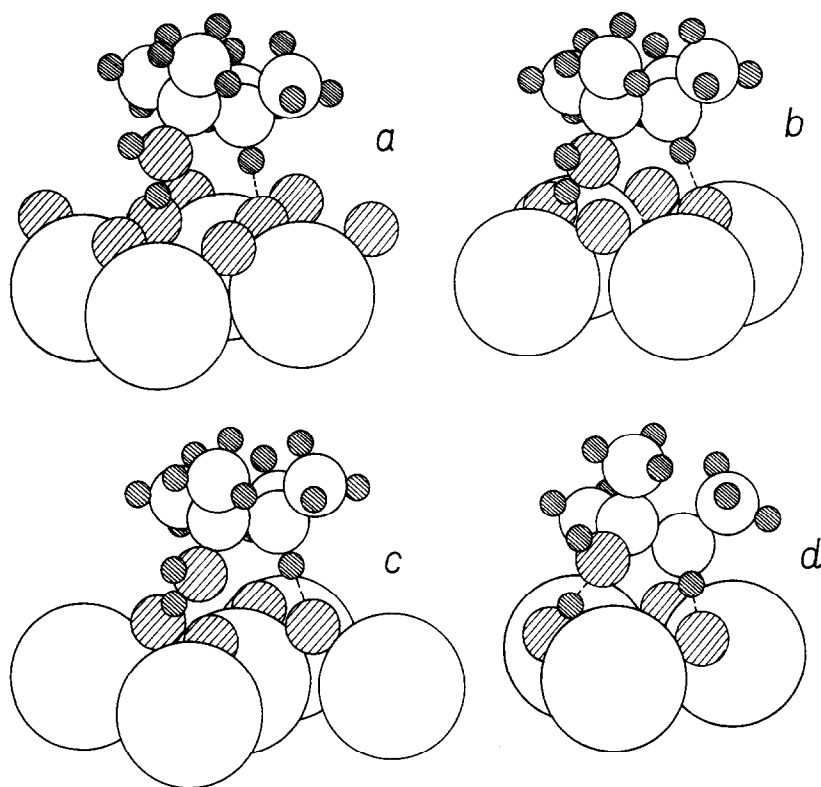
FIG. 10. Molecules of alcohols interacting with the pairs of differently distant sites of the (100) surface of ThO$_2$ (see Fig. 4) (a) S_1—280 pm, (b) S_2—396 pm, (c) S_2'—396 pm, and the pairs of sites of the (111) surface of ThO$_2$ (see Fig. 5), (d) S_2—396 pm.

sites is conditioned by the presence of water on the catalyst surface. On the other hand, the higher coverage by hydroxyl groups results in the lack of surface oxygen ions which participate also in the reaction. In addition, hydroxyl groups which do not operate as adsorption sites may act as steric hinderance.

Maximum activity for the *syn*-elimination reaction is exhibited by the ideal (100) surface of γ-Al$_2$O$_3$ at about 50% coverage by hydroxyl groups. The most suitable conditions for formation of 1-alkenes has been found to be the surface covered to 30–40%. Finally, 2-alkenes are formed in maximum amounts at a coverage equal to 10 to 20%. Temperatures used in pretreatment of the catalyst (*2*) correspond to 5–15% coverage (*49*). According to Table 1,

at 10% coverage the concentrations of sites for 1-alkenes and 2-alkenes are comparable and the concentration of *syn*-elimination sites is two times higher compared with the concentration of *anti*-elimination sites. The difference in the activation energies of the *syn*- and *anti*-elimination can be estimated as 6.3 × 10^4 J/mol (15 kcal/mol) (*29*). Providing that the frequency factor is comparable within an order of magnitude, the rate constant of *anti*-elimination at 600 to 700 K is higher by five orders of magnitude. At a given degree of coverage the reaction will therefore proceed via the energetically more favorable path (*29, 44*), i.e., as *anti*-elimination. This has already been shown (*2, 3, 17, 18*).

In addition to the selectivity of the steric

course of the reaction, our models render it possible to also explain the selectivity with respect to the products. Formation of *cis*-2-alkenes on the surface is less sterically demanding than formation of *trans*-alkenes (see Figs. 7 and 8). The concentration of "*cis*-sites" on the (100) surface of γ-Al$_2$O$_3$ is thus higher than that of "*trans*-sites" (Table 1). This accounts for a high *cis/trans* ratio of isomers in the products (*2, 3, 21*). The stereoselectivity of the reaction course and the higher than equilibrium *cis/trans* ratio of isomers seem to be the properties common for a series of heterogeneously catalyzed eliminations (*50, 51*). It has been found for elimination of HCl on salt catalysts that the *cis/trans* ratio decreases with decreasing amount of water present on the catalyst surface (*52*). It deserves to be mentioned that also in the model used the ratio of "*cis*-" to "*trans*-site" concentrations decreases with decreasing amount of water present on the surface (Table 1). The following values of the ratio correspond, respectively, to the coverage 30; 20; 10, and 8.52%: 123, 52, 25, and 23. Discussing the surface coverage model one should keep in mind that alcohol chemisorbed as alcoholate can block a great part of the surface as can water which is the reaction product. Including of these effects
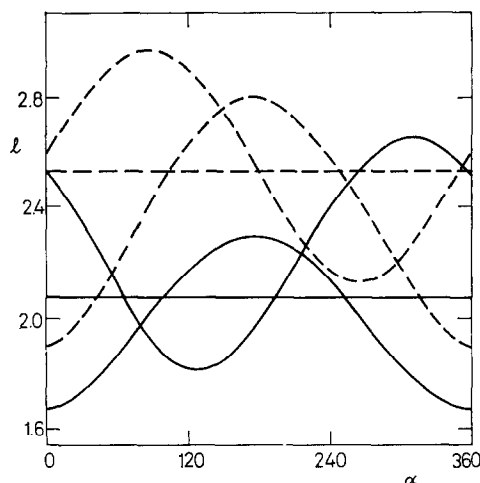

Fig. 11. Distance between selected Th atoms of the (100) surface of ThO$_2$ and C (dashed line) and H atoms (full line) of the molecule of ethanol while rotating around the joint between surface sites (A_1—see Fig. 4). Horizontal lines denote a minimum admissible distance given by the sum of the radii used for graphical representation.

would require a dynamic model of the reaction.

Substantially different results have been obtained in modeling the dehydration of alcohols on ThO$_2$. Although on this catalyst, as already found (*26, 27*), the cleavage of the key bonds of the molecule does not proceed in the concerted manner but step-
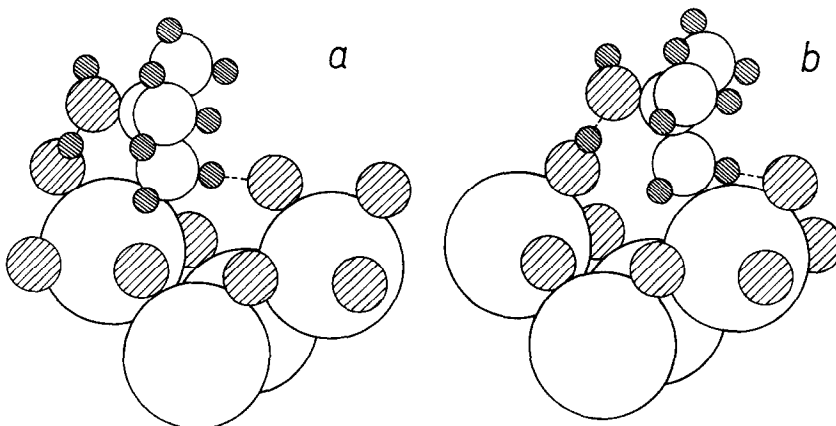

Fig. 12. Molecules of alcohols interacting with the pairs of sites of the (110) surface of ThO$_2$ (see Fig. 6). (a) A_1—560 pm and (b) A_1'—560 pm.

wise according to the E1cB mechanism, also here a two-center adsorption should take place. The conformation of the molecule of the reactant in this stage of the reaction is thus worth elucidating. ThO_2 seems to possess on its surface above all the (100) and (111) faces (45). On the pairs of sites with a suitable distance (Figs. 4 and 5) we have constructed the structures shown in Fig. 10, using the procedure described in the Methods section. It is of interest that in spite of the fact that on the (100) and (111) surfaces of ThO_2 one can find pairs of sites with distance suitable also for *anti*-periplanar conformation, under the structural assumptions accepted the reaction can be realized only in the *syn*-periplanar conformation. Attempts at constructing *anti*-periplanar structures have been unsuccessful because of too short distances between C_α, C_β, and H_β atoms of the alcohol molecule and of Th atoms of the surface which create the nearest surrounding of the pair of adsorption sites. This is illustrated in Fig. 11 for the pair A_1 of the (100) surface of ThO_2.

The situation is not changed when hydroxyl groups are placed on the (111) surface even in positions corresponding to another layer of oxygen atoms, i.e., above Th atoms. The choice of considered faces has thus been extended to the residual low-index surface, i.e., (110) (Fig. 6). In addition to further *syn*-periplanar structures (quantitatively identical with those already mentioned—see Fig. 10) two *anti*-periplanar structures have been found on this surface (Fig. 12) which belong to the pairs of sites A_1 and A_1' (see Fig. 6). From Fig. 12 it becomes obvious that in both cases geometric conditions allow only 1-alkene formation to take place.

The (100), (110), and (111) surfaces of ThO_2 thus provide conditions which are suitable above all for the *syn*-periplanar conformation. So they differ significantly from the (100) surface of γ-Al_2O_3. This finding answers the objection raised by

Davies and Bray (25) which was mentioned in the Introduction and supports Lundeen and van Hoozer's (23, 24) explanation of the preferred formation of 1-alkene on ThO_2. One can assume further that due to high energetic preference the reaction will proceed to a great extent also as the *anti*-periplanar conformation, irrespective of the small number of suitable pairs of sites. Also this reaction path yields 1-alkenes which are the main product of the dehydration of alcohols on ThO_2 (23–27).

Relatively simple calculations thus render it possible to consider in detail the actual geometric conditions for heterogeneously catalyzed reactions and to explain a number of observations as a consequence of the effect of geometric factor. Conclusions drawn from these calculations are frequently in surprisingly good agreement with experimental findings. On considering the results one should keep in mind a number of simplified assumptions about the structure of the adsorbent and the adsorbate at the moment of their mutual interaction which were adopted in constructing the models. In the case of the dehydration on γ-Al_2O_3 a question arises about the correctness of the choice of especially the (100) surface. Nevertheless, the inclusion of other surfaces of γ-Al_2O_3, on which adsorption conditions probably differ from those on (100) surface, cannot change the main fact, i.e., the alcohol molecule in the *anti*-periplanar conformation can be adsorbed on two surface sites simultaneously. The limitations and inaccuracy of the models employed would most probably affect the results quantitatively rather than qualitatively. We believe therefore that the conclusions concerning the role and effect of geometric factor in the heterogeneously catalyzed reactions under study are justified.

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