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Study of the Interaction of Aliphatic Alcohols with TiO_2

I. Decomposition of Ethanol, 2-Propanol, and tert-Butanol on Anatase

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Adsorption of ethanol 2-propanol, and tert-butanol has been studied on a well-characterized anatase sample using volumetric and ir techniques. Differences in the adsorption capacities for the three alcohols have been interpreted as due to the same electronic and steric effects that determine changes in the maximum coordination for the Ti^{IV} ions in titanium alkoxides. Decomposition of the adsorbed phase was followed by ir and TPD (temperature-programmed decomposition) methods and was compared with the catalytic dehydration of the respective alcohols. The agreement between the kinetic parameters for both processes indicates that the slowest step for the catalytic reaction corresponds to a monomolecular decomposition of the adsorbed species, as supported by studies of water displacement from the anatase surface by all three alcohols.

INTRODUCTION

In spite of the considerable attention paid to the study of the adsorption of alcohols on TiO_2 (*1–8*), little is known about the decomposition of these alcohols catalyzed by TiO_2, in contrast to the number of papers dealing with this reaction on Al_2O_3 and SiO_2 (*9*). Some time ago, Wheeler *et al.* (*10*) reported gc data on the desorption of ethanol and 2-propanol from metal oxides, including rutile and anatase, from which they concluded that TiO_2 has dehydrogenating activity. This actually contrasts with the more recent results of Jackson and Parfitt (*7*), who observed that ethyl, *n*-butyl, and *n*-hexyl alkoxides formed during adsorption of the corresponding alcohols on rutile surfaces are thermally decomposed at 300°C, producing surface carbonate species with water and the respective 1-alkene in the gas phase, in agreement with the monomolecular dehydration reported by Knözinger and Kochloefl (*11*) for several deutero-2-propanols on anatase.

In the present paper we have studied the adsorption and decomposition of ethanol (EtOH), 2-propanol (2-PrOH), and tert-butanol (*t*-BuOH) on a well-characterized anatase sample, for which a model of the surface has been previously proposed by us (*12*). The aim of this work was to obtain further information on the behavior of TiO_2 as a catalyst in the dehydration of such alcohols and, at the same time, to check the use of ir spectroscopy and temperature-programmed decomposition methods in the study of catalytic processes.

EXPERIMENTAL

Materials. TiO_2 (anatase) had been kindly supplied by British Tioxide (Code No. CL/D 173/2), having been prepared by hydrolysis of titanyl sulfate, followed by heating in air at 700°C. The surface area (25 ± 0.3 m^2 g^{-1}) was obtained by the BET

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method using N_2 at 77°K. A detailed study of the porosity of this sample has been published elsewhere (*13*) and has shown that the sample has open V-shaped pores with $\bar{d}$ = 28–29 Å.

Conductivity water and EtOH, 2-PrOH, and t-BuOH from Merck (99% purity and redistilled on anhydrous $CuSO_4$) were subjected to several freeze–pump–thaw cycles before use.

Apparatus and procedures. Adsorption isotherms up to 400 N m^{-2} were determined volumetrically, using 0.7 g of sample in a small-volume system (67 ml) with a silicon oil manometer. Infrared spectra were recorded at room temperature with a Perkin–Elmer 621 double-beam grating spectrometer, using a vacuum cell (*14*) with a small appendage which could be cooled at 77°K to condense vapors, and a gas sampling device providing gc analysis of the evolved gases. TiO_2 specimens were used in the form of self-supporting disks (40 mg cm^{-2} and 13 mmϕ), and a weighed amount of powdered sample was also included, attached to the disk holder to enable simultaneous volumetric adsorption measurements to be made.

Temperature-programmed decomposition (TPD) experiments were carried out in a cell similar to that described by Amenomiya and Cvetanovic (*15*) using N_2 as carrier gas. A sufficiently high flow rate was selected so that the temperature of the TPD peaks remained flow independent, while the readsorption of products became eliminated. Pulses of the evolved gases were gc analyzed throughout these experiments.

Catalytic activity was measured in a flow system provided with a Pyrex glass reactor. Helium, at a flow rate of 80 ml min^{-1}, was used as carrier gas under diffusion-free conditions, always using an excess of alcohol in the gas phase to ensure a fully covered surface (pseudo-zero-order reaction). Under such conditions, the reaction rate did not depend on the alcohol pressure, conversions always being lower than 10%. In both TPD and catalytic experiments, the products were gc analyzed using a Perkin–Elmer F-7 chromatograph with FID detection, provided with a Par-I (Hewlett–Packard) column (2-m length, $\frac{1}{4}$-in. diameter).

A treatment of the TiO_2, consisting of heating in air at 400°C followed by outgassing at 350°C for 4 hr, was used as the standard treatment before adsorption, ir, and TPD experiments, while the same treatment in a He flow (30 ml min^{-1}) was used in the catalytic studies after oxidation in air. After such treatment, the surface has characteristic ir and TPD patterns (*12*), showing only a small number of OH groups ($\simeq$0.3 OH nm^{-2}) giving bands at 3730, 3680, and 3620 cm^{-1} and a weak shoulder at 1600 cm^{-1} due to traces of molecular water that were removed only during the TPD scanning at $t > 450$°C.

RESULTS

Isotherms and Infrared Spectra

Figure 1 shows characteristic adsorption isotherms of water and the three alcohols at room temperature on a standard TiO_2 surface. From these isotherms, "irreversible adsorptions" were obtained by substraction of branch *b* from *a*. In all cases, the "irreversible adsorption" was roughly the value of the adsorption amount at negligible pressure ($\sim$2.5 N m^{-2}), indicating that strong interaction of the adsorbed molecules with the surface occurs. The most noticeable difference between water and the alcohols was the higher capacity of the sample for retaining weakly adsorbed water; this can be related to the possibility of formation of multi-hydrogen-bonded species. Thus, after trapping the gas phase at 77°K, ca. 3 H_2O nm^{-2} remained on the surface.

The "irreversible adsorption" for EtOH was slightly higher than that for water, while 2-PrOH and t-BuOH show "irreversible adsorptions" (1.6 and 1.3 molecules nm^{-2}), much lower than for EtOH and water.

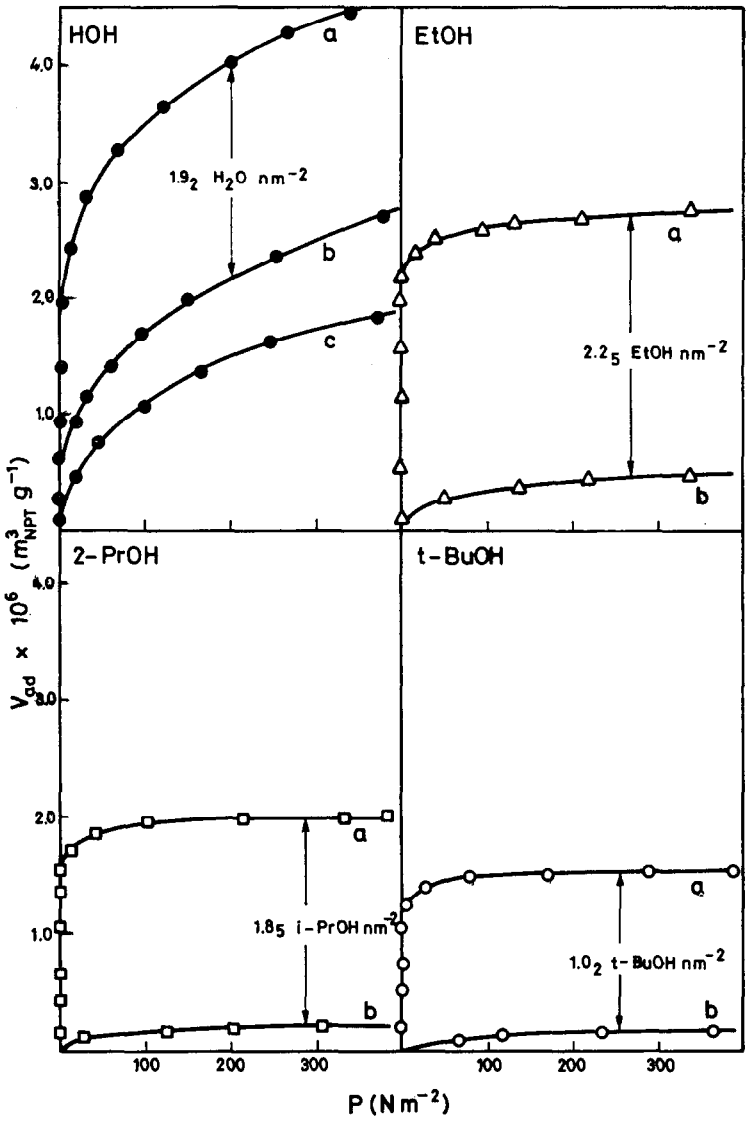


FIG. 1. Adsorption isotherms of water, ethanol, 2-propanol, and tert-butanol on anatase at room temperature. (a) On a standard treated surface; (b) after (a) and evacuation at room temperature for 1 hr; (c) adsorption of water on a sample covered with 2 EtOH nm^{-2}.

When the alcohols were adsorbed on the standard surface, two facts were worthy of note and can be seen in Fig. 2. There is, first, the loss of the OH stretch of the unperturbed alcoholic hydroxyl group and, second, the development of a broad band at 3480 cm^{-1}, suggesting OH interactions between the adsorbed species and the surface. In order to elucidate the type of interactions involved in the alcohol adsorption, and until reaching the "irreversible adsorption" coverages, small doses were adsorbed at room temperature on the standard treated surface, and ir spectra were recorded in the usual way, as shown in Fig. 3 for EtOH. By plotting the absorbances of ν_{OH} and $\nu^{asym}_{CH_3}$ stretching bands against the coverage (Fig. 4), several features for the three alcohols could be observed. For all alcohols, the absorbances of both the broad

band at 3480 cm^{-1} and the $\nu^{asym}_{CH_3}$ band increase linearly with the alcohol coverages, fulfilling Beer's Law, until a "critical coverage" is reached. As shown in Fig. 4, this "break point" for EtOH was at a coverage of ca. 2 molecules nm^{-2}, while, in the case of 2-PrOH and t-BuOH, it was at ca. 1 molecule nm^{-2}. Similar behavior was observed for the surface OH band at 3730 cm^{-1} that, in this case, decreased slowly with a constant slope up to the "break point" and, thereafter, more sharply.

In spite of the difficulty of determining these actual absorbances with accuracy, the two small bands at 3680 and 3620 cm^{-1} follow a rather similar pattern, first increasing up to the "break point" and then decreasing. However, the relative changes of these two bands were different from primary, secondary, and tertiary alcohols,

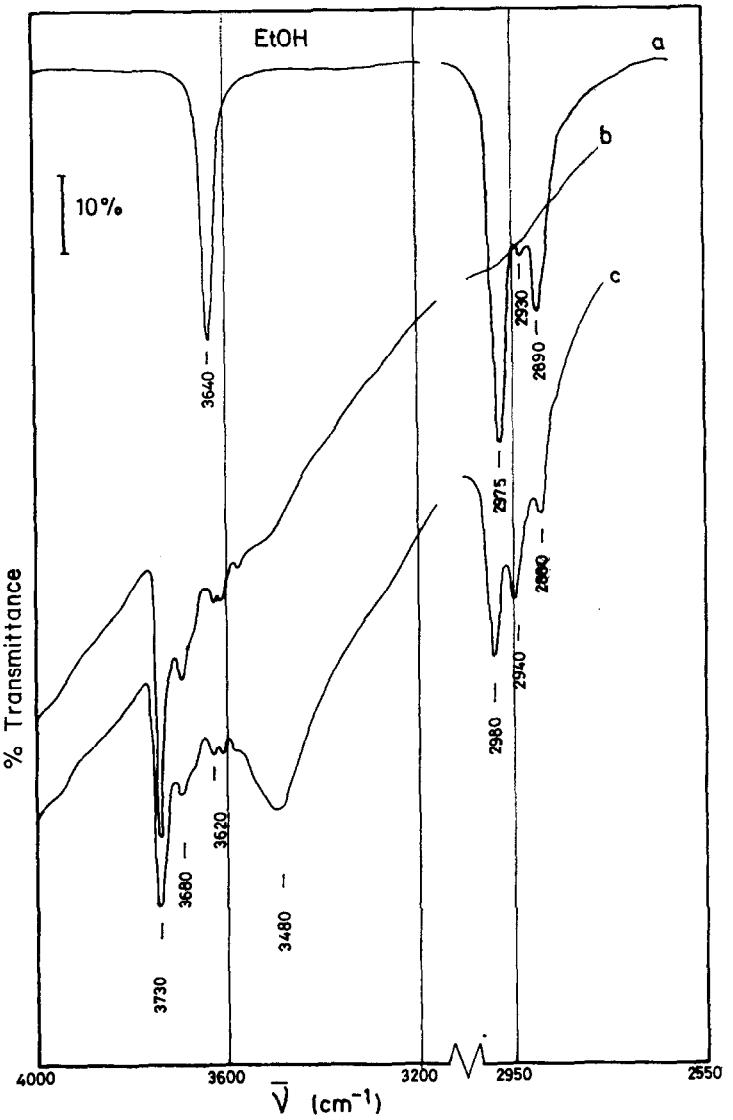


FIG. 2. Infrared spectra of: (a) EtOH diluted in CCl_4; (b) anatase standard surface; (c) EtOH adsorbed on anatase (coverage, 0.80 EtOH nm^{-2}).

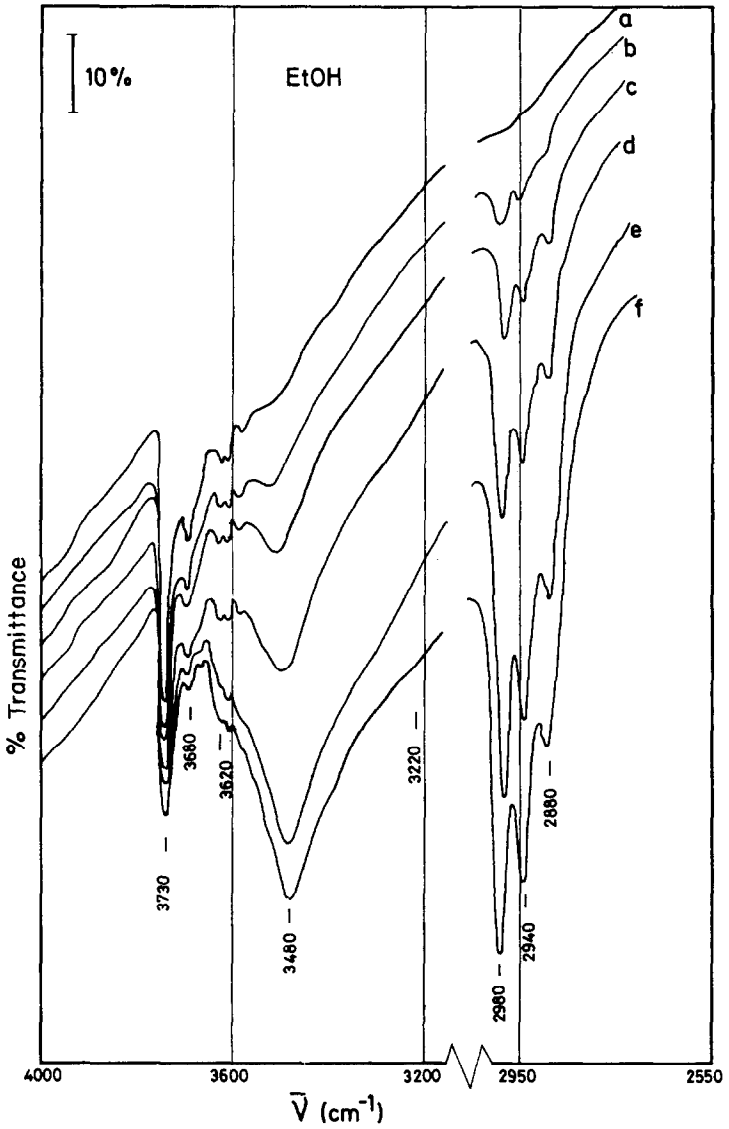


FIG. 3. Infrared spectra of ethanol adsorbed on anatase (coverages in EtOH nm^{-2}): (a) standard surface; (b) 0.49; (c) 1.07; (d) 1.76; (e) 2.30; (f) 2.58.

as can be seen in Fig. 4. The behavior of the OH bands during adsorption of doses of water is shown for comparative purposes. It can be seen that bands at 3680 and 3620 cm^{-1} sharply increase for coverages higher than 1 H_2O nm^{-2}, though the band at 3730 cm^{-1} remains at the same intensity up to coverages of 2 H_2O nm^{-2}.

Decomposition of the Adsorbed Phase

Decomposition of the adsorbed alcohols was studied by the TPD technique, using several heating rates in order to evaluate the kinetic parameters. Characteristic TPD traces for water and the three alcohols are shown in Fig. 5. Analysis of pulses of the evolved gases during TPD scanning (shown only for ethanol in this figure) indicates that all three alcohols decompose, giving olefins and water as the main products. In the case of EtOH, the first broad TPD peak at 250°C corresponds to desorption of the alcohol. A simple calculation from

the flow rate of the carrier gas and the gc calibration indicated that the recovered alcohol was about 50% of the total coverage; thus, only ca. 1 EtOH nm^{-2} should decompose during TPD scanning. The sharper TPD peak at 340°C was due to ethylene and water, as shown by the gc analysis of the pulses. However, butenes and diethyl ether were also detected in this range of temperatures, though the amounts of these products were always lower than 5% of the evolved olefin at each particular temperature. In the cases of 2-PrOH and t-BuOH, the TPD traces in Fig. 5 indicate that a small amount of alcohol was also desorbed, unreacted as confirmed by gc analysis (not shown in the figure), leaving coverages of ca. 1 *R*OH nm^{-2}.

In connection with these alcohols, it is noteworthy that, in the case of t-BuOH, the olefin isobutene evolves at 180°C, a temperature considerably lower than that for water desorption, which gives the peak at 250°C in the same TPD trace. For 2-PrOH, water and propylene evolve at almost the same temperature, giving a single peak at ca. 280°C.

Using different heating rates (β between 4 and 30°C min^{-1}) and assuming a first-order reaction for the olefin formation, the kinetic parameters for the decomposition of the three alcohols were obtained from the temperatures of the TPD peaks (T_M) due to olefin evolution, by using the

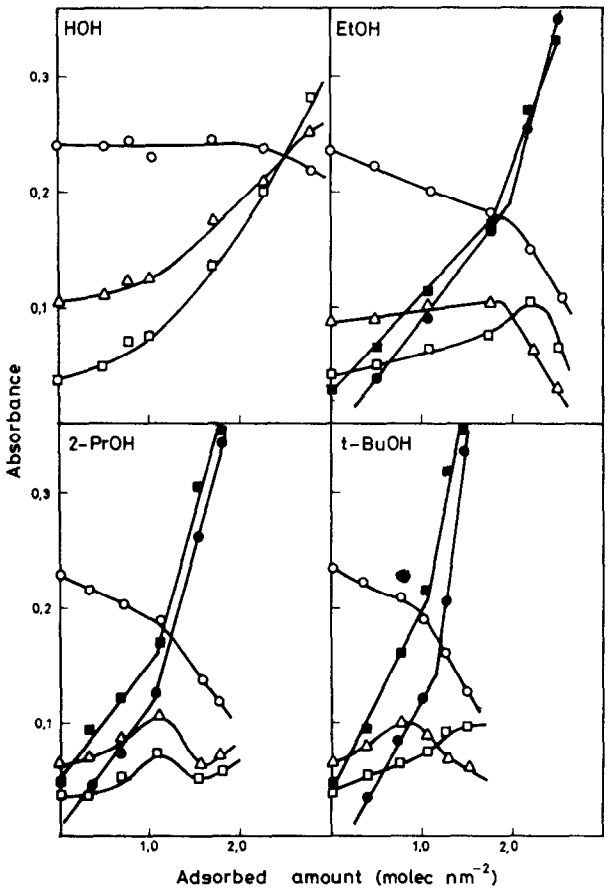


FIG. 4. Changes of absorbance for the ν_{OH} of the free surface OH groups and the $\nu^{asym}_{CH_3}$ against adsorption coverages of alcohols. (○) 3730; (△) 3680; (□) 3260; (●) 2975; (■) 3480 cm^{-1}.

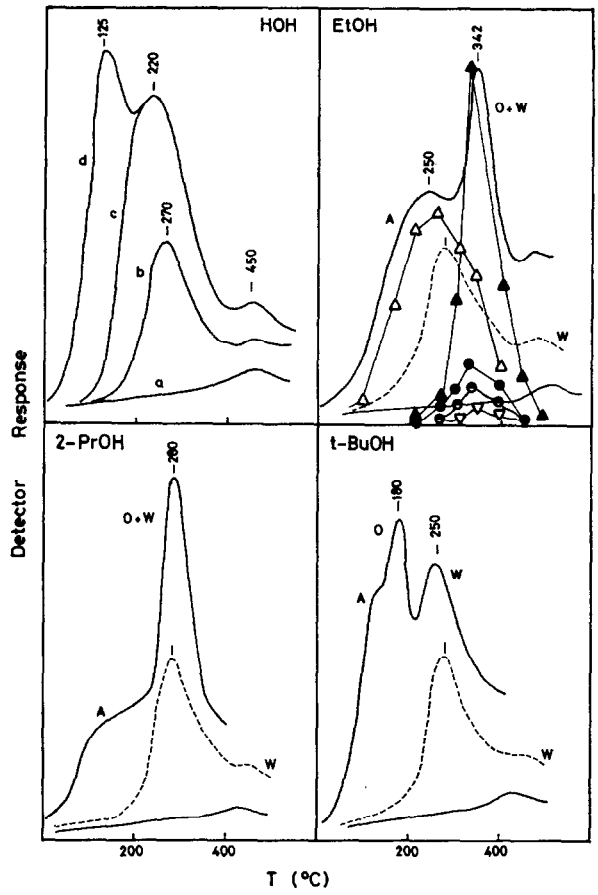


FIG. 5. TPD traces of water and alcohols adsorbed on anatase (β = 16°C min^{-1}). Water: (a) standard surface; (b) covered with 1 H_2O nm^{-2}; (c) covered with 2 H_2O nm^{-2}; (d) covered with 3 H_2O nm^{-2}. Alcohols: in all cases, the dashed line corresponds to the TPD trace of 1 H_2O nm^{-2}, and the TPD trace of the standard sample is included. A, Alcohol; O, olefin; W, water. Analyses of pulses for ethanol: (△) ethanol; (▽) diethyl ether; (▲) ethylene; (●) 1-butene; (◓)*trans*-2-butene.

equation:

$$2 \log T_M - \log \beta = E/2.3RT_M + \log (E/AR),$$

E being the activation energy and A the frequency factor. The calculated values for E and A are given in Table 1, together with the kinetic parameters for the desorption of water with an initial coverage of 1 H_2O nm^{-2} from the standard surface (*16*). This latter value was somewhat higher than the 32 kJ mol^{-1} obtained for the desorption of water formed during TPD experiments with t-butanol.

Data in Table 1 show that values of A (in seconds)$^{-1}$ are rather low for all three alcohols, though of the same order as those reported by other authors (*17*) for this type of reaction on metal oxides.

In order to check the credibility gap of the above values and their independence of the experimental technique (TPD method), a set of experiments was carried out to determine the kinetic parameters from the thermal evolution of ν_{CH} bands in the ir spectra of the adsorbed species. In these experiments, EtOH, 2-PrOH, and t-BuOH were adsorbed on a standard

TABLE 1

TPD Kinetic Parameters for Alcohol Dehydration and Water Desorption from an Anatase Surface

Preadsorbed species	Activation energy (kJ mol^{-1})	Frequency factor (s^{-1})
EtOH	76.5 ± 2	1.4×10^4
2-PrOH	92.4 ± 2	4.7×10^6
t-BuOH	53.9 ± 2	9.8×10^3
Water	50–54	1.0×10^3

TABLE 2

Infrared Kinetic Parameters for Alcohol Dehydration on an Anatase Surface

Preadsorbed species	Activation energy (kJ mol^{-1})	Frequency factor (s^{-1})
EtOH	78.6 ± 5	1.0×10^4
2-PrOH	92.8 ± 5	4.8×10^6
t-BuOH	56.0 ± 5	2.0×10^4

surface and were decomposed at several temperatures, while the reaction was monitored by recording changes of the ν^{asym}_{CH} band at 2980–2975 cm^{-1}. Initial coverages were in all cases kept lower than 1 molecule nm^{-2}, thus allowing only a single species to exist on the surface, so that Beer's Law can be applied. In these experiments the TiO_2 disk was moved, for a measured short time, into the furnace of the ir cell, previously stabilized at a preset temperature, and was then quenched at room temperature, and the absorbance of the ν_{CH} band was recorded. During the experiment, the evolved gases were trapped at 77°K and then were gc analyzed at the end of the experiment, thus confirming that the main products were olefins. However, small traces of butenes and diethyl ether were detected when using EtOH, as previously observed during the TPD experiments.

After heating at 400°C for 1 hr, the ir spectrum of the original surface was restored, showing its hydroxyl bands at 3730, 3680, and 3620 cm^{-1} with their original intensities.

Straight lines were obtained when values of log A (A is absorbance of the ν^{asym}_{CH} band) were plotted against the total time of heating at each particular temperature, thus confirming the first-order reaction in all cases. The rate constant values ob-

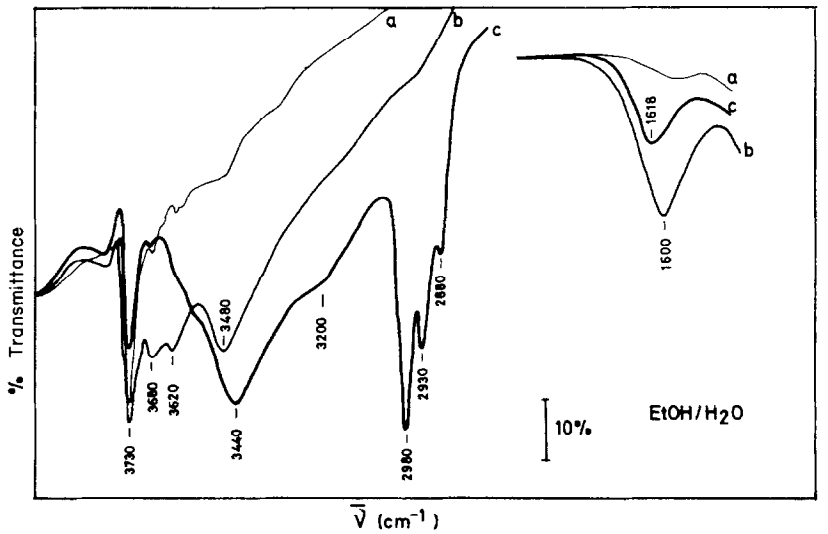


FIG. 6. Infrared spectra for the water displacement experiment: (a) standard surface; (b) covered with 1.80 H_2O nm^{-2}; (c) after equilibration with excess of ethanol.

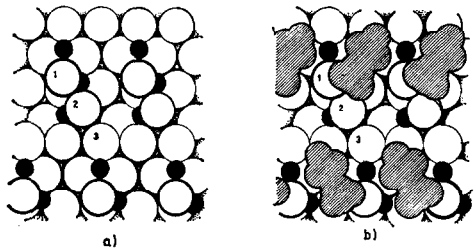


FIG. 7. (a) Plane view of the (111) stoichiometric cleavage plane of anatase (*12*). (b) Adsorption model for ethanol adsorbed on this plane.

tained from these lines fulfill the Arrhenius equation, from which kinetic parameters were calculated (data compiled in Table 2). The values agree fairly well with those previously obtained by TPD method, thereby corroborating the first-order reaction assumed in the TPD calculations. Furthermore, as experiments were carried out under vacuum, diffusion control on the reaction rate can be eliminated.

Displacement of Water by Alcohols

In order to check the possible influence of the decomposition products, particularly water, the desorption of which has been proposed as the controlling step in catalytic dehydration of alcohols by Krylov (*18*), volumetric and ir displacement studies were carried out at room temperature using a standard surface previously covered with ca. 1.8 H_2O nm^{-2}; after recording the ir spectrum, a measured amount of alcohol exceeding the adsorption capacity of the sample was admitted at room temperature and was placed in contact with the hydrated surface, until no changes of pressure were observed. The gas phase and the weakly adsorbed species were condensed at 77°K, and the ir spectrum was recorded again. Meanwhile, the total amount of condensed vapors (water plus alcohol) was measured volumetrically. Figure 6 shows the ir spectra of the anatase surface during these experiments with EtOH, while similar patterns were obtained for the other two alcohols. The amount of alcohol adsorbed in these experiments was evaluated from the absorbances of the ν_{CH} band, with the aid of the absorbance/coverage plots in Fig. 4, while the amount of water remaining at the surface was calculated by subtracting the quantity of nonadsorbed alcohol from the total amount of the condensed vapors. Data obtained in this way for all three alcohols have been summarized in Table 3.

TABLE 3

Adsorbed Species on Anatase Surface after Partial Displacement of Water by Alcohols at Room Temperature

Alcohol	Adsorbed alcohol (molecules nm^{-2})	Adsorbed water (molecules nm^{-2})
EtOH	2.00	1.00
2-PrOH	1.60	1.40
t-BuOH	1.30	1.40

TABLE 4

Catalytic Flow Reactor Kinetic Parameters of Alcohol Dehydration on an Anatase Surface

Alcohol	Activation energy (kJ mol^{-1})	Frequency factor (molecules m^{-2} s^{-1})
EtOH	79.4 ± 2	1.1×10^{22}
2-PrOH	91.5 ± 2	1.4×10^{26}
t-BuOH	56.4 ± 2	1.4×10^{23}

As shown in Fig. 6, adsorption of the alcohols on a water-covered surface disturbs the ir spectrum of the adsorbed water. For all three alcohols, the intensity of the bands at 3680 and 3620 cm^{-1} noticeably decreases, while the broad band at 3480 cm^{-1} broadens and moves to 3440 cm^{-1} with a shoulder at 3200 cm^{-1}, the sharp bands of ν_{CH} now appearing in the spectra. In the bending region of water, the intensity of the original band at 1600 cm^{-1} decreases in the order EtOH > 2-PrOH > t-BuOH, while it becomes asymmetric and displaced

toward higher wavenumbers (1618, 1613, and 1608 cm^{-1} for EtOH, 2-PrOH and t-BuOH, respectively). These two facts confirm that alcohols displace water from their adsorption centers, though the extension of this displacement depends on the alcohol itself.

Catalytic Dehydration of the Alcohols

Catalytic decomposition of the three alcohols under pseudo-zero-order conditions (fully covered surface) gave olefin and water exclusively, except for EtOH, where traces of butenes and ether could be detected again, though always in a percentage lower than 3% of the olefin. Arrhenius plots for all three alcohols gave the kinetic parameters compiled in Table 4.

By comparing the activation energy for the catalytic dehydration with those activation energies previously obtained for the thermal decomposition of the adsorbed phase from TPD or ir data, good agreement was observed. This agreement suggests that, under the above conditions, the catalytic process involves the adsorbed species that must decompose in a manner very similar to that in the TPD or ir experiments, suggesting that the role of alcohol in the gas phase during the catalytic process was only to dislodge the water molecules produced during the reaction from their adsorption sites and, thus, close the catalytic cycle.

DISCUSSION

Adsorption

The adsorption capacity of the anatase surface pretreated under the standard conditions used in this work [almost completely dehydroxylated (*16*)] depends on the type of alcohol, decreasing with the length of the hydrocarbon chain. The values for "irreversible adsorption" are rather low for all three alcohols, as can be shown by calculation of the cross section of each alcohol from its density in the liquid state (*14*), and, therefore, the adsorbed molecules should be rather sparsely distributed over the surface, so we may conclude that specific interactions occur between the alcohol molecules and surface sites.

In the case of EtOH, the "irreversible adsorption" was 2.25 EtOH nm^{-2}, not far from the value reported for water (*12*), which suggests that the same type of centers should be involved in the adsorption of both species. However, infrared spectroscopy was found to be more sensitive for discriminating between different types of adsorptions. Thus, Fig. 4 clearly suggests that, for EtOH and water, adsorption occurs in the same way, only up to a coverage of ca. 2 molecules nm^{-2}, while, for higher coverages, new forms of adsorption appear. The amount of more tightly adsorbed ethanol, 2 EtOH nm^{-2}, agrees with the number of more exposed Ti^{IV} ions on the anatase surface (1.9 Ti^{IV} nm^{-2}), as calculated from the surface model shown in Fig. 7a and previously proposed for this oxide (*12*). This fact clearly suggests that adsorption must take place with the ethanol acting as a bridging ligand between two neighboring Ti^{IV} ions, filling the coordinative unsaturation of these ions, as shown in Fig. 7b. However, TPD experiments illustrated in Fig. 5 indicate that ca. 50% of this adsorbed ethanol is easily removed from the surface without decomposition, indicating that half of the adsorbed molecules should be more weakly bonded than the remaining 1 EtOH nm^{-2} that decomposes upon heating to give mainly olefin. This seems to suggest that the sixfold coordination attained by the Ti^{IV} ions at the surface with two bridging alcohol molecules, as shown in Fig. 7b, is rather unstable, and desorption of 1 EtOH nm^{-2} occurs giving a surface with Ti^{IV} ions in an average fivefold coordination, resulting from alternate elimination of the alcohol molecules (Fig. 7b). Similar behavior had been reported previously by us (*16*) for

the desorption of 50% of the "irreversible adsorbed" water from this anatase sample.

According to the above conclusion, the tight adsorption for 2-PrOH and t-BuOH corresponds to ca. 1 molecule nm^{-2}, the same as for ethanol, but, with these two alcohols, the maximum coordination number (6) for the surface Ti^{IV} ions could not be completely attained by saturation with alcohol vapor (only 1.6 and 1.3 molecules nm^{-2}, respectively). The situation seems to be rather similar to that existing in titanium alcoholates, $Ti(OR)_4$, in which differences in coordination from 6 to 4 occur with increasing complexity of the alkyl group, so that $Ti(OMe)_4$ and $Ti(OEt)_4$ have hexacoordinated Ti^{IV} ions with bridging alkoxide groups, while $Ti(O\ t\text{-}Bu)_4$ is a monomeric liquid in which the Ti^{IV} ions have a fourfold coordination (*19*). Therefore, adsorption of alcohols up to 1 *R*OH nm^{-2} leads to a half-covered surface in which each Ti^{IV}, originally in a fourfold coordination, will accept a fifth bridging ligand at alternated Ti^{IV} pairs. A further adsorption on this surface must accomplish the sixfold coordination of the cations, but inductive as well as steric effects of the highly nucleophilic and bulky ligands may limit this second state for 2-PrOH and t-BuOH but not for EtOH or water.

Provided that the total number of molecules, even in the case of EtOH, is rather small compared with the density of the liquid alcohol or the respective alcoholates, we may conclude that electronic saturation should be the more important factor in determining the coordination number after saturative adsorption, now that, as shown in Fig. 7b, all three alcohols can be easily packed on the surface, thus discarding steric effects. In summary, the increasing donor capacity of the alcohol molecules with the size and branching of the alkyl group may lead to a saturation of the Ti^{IV} charge that produces a leveling off of the adsorption capacity in agreement with the well-known electroneutrality principle of Pauling.

The broad band at 3480 cm^{-1} suggests that the coordinative adsorption occurs mainly in a nondissociative way, the hydrogen of the alcohol group being involved in H bonding to neighboring O^{2-} ions at the surface, as previously proposed by Jackson and Parfitt (*7*). In addition to the main nondissociative adsorption of the alcohols, two possibilities exist for the small dissociative adsorption that occurs simultaneously:

(a)

$$ROH \rightarrow RO^-_{ad} + H^+$$
$$H^+ + O^{2-}_{sf} \rightarrow OH^-_{ad}$$

(b)

$$ROH \rightarrow R^+ + OH^-_{ad}$$
$$R^+ + O^{2-}_{sf} \rightarrow RO^-_{ad}$$

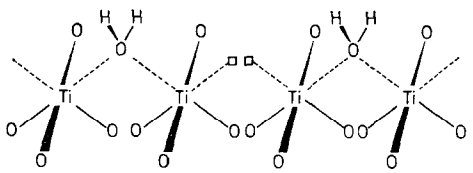
where (ad = adsorbed and sf = surface).

Form (a) should be more likely for EtOH and leads to the rise of the band at 3620 cm^{-1} that, according to our previous model for the surface, corresponds to residual OH groups in some of the positions labeled **3** in Fig. 7a. Mechanism (b) should increase in importance for 2-PrOH and t-BuOH due to the inductive effect of their alkyl chains. The new OH groups should be packed between oxygen atoms labeled **2** in that figure, outside the coordination sphere of the more exposed Ti^{IV} ions, giving rise to the band at 3680 cm^{-1}. Highly nucleophilic oxygens, labeled **1**, may now participate in the second step of alcoholate formation through mechanism (b); this leads to a fourfold coordination of some of the surface Ti^{IV} ions, even after adsorption of the alcohols. This may also contribute to the more rapid decrease of the 3730 cm^{-1} OH band in the cases of 2-PrOH and t-BuOH adsorption, due to highly basic OH groups in some of the positions labeled **1** in Fig. 7a.

A further comparison can be made between the changes observed in the intensities of the OH stretching bands with increasing coverages of water and those

observed in the case of the alcohols (Fig. 4). Previous studies (*12*) suggest that adsorption of water should occur at an early stage as a bridging ligand filling half of the coordination positions of the fourfold-coordinated Ti^{IV} ions at the surface, according to:

SCHEME 1



This water gives a TPD peak at 270°C and a broad ir band centered at 3480 cm^{-1}, as shown in Figs. 4 and 7, respectively. Further adsorption up to 2 H_2O nm^{-2} displaces the TPD peak to 220°C, and, together with the band at 3480 cm^{-1}, bands at 3620 and 3680 cm^{-1} appear with the same wavenumber as the isolated OH groups remaining on the outgassed anatase surfaces. Higher coverages lead to a new type of adsorption characterized by a TPD peak at 125°C (Fig. 5), together with a displacement of the bending mode of the water from 1600 to 1610 cm^{-1}, which has been explained (*12*) by assuming that, under these conditions, the adsorbed molecules are subjected to an asymmetric field, probably involving some hydrogen bonding with a mainly electrostatic interaction.

As can be observed in Fig. 6, the bands at 3680 and 3620 cm^{-1} in the water-covered sample are immediately removed after adsorption of alcohol, suggesting that this water is easily displaced by the alcohol molecules from the gas phase. Volumetric and ir data confirm this fact, though some water remains on the surface, which gives with the alcohol a total coverage of 2.7–3.0 molecules nm^{-2}. This residual nondisplaced water gives a very asymmetric bending mode displaced toward higher wavenumbers, the shift of the band depending upon the alcohol. A comparison of the fully hydrated anatase surface holding ca. 3 H_2O nm^{-2} and the surface resulting from the displacement of water by ethanol (2 EtOH nm^{-2} plus 1 H_2O nm^{-2}) shows that an important difference between the ir spectra of both surfaces occurs in the 1600-cm^{-1} region. While in the hydrated surface the third water molecule only slightly displaces its bending mode from 1600 to 1610 cm^{-1}, in the case of adsorbed ethanol this band is asymmetric and appears at 1618 cm^{-1}, suggesting a situation different from that of the water remaining in this surface. Indeed, the low reversible adsorption of water on a surface holding 2 EtOH nm^{-2} (Fig. 1, isotherm c of HOH) suggests that EtOH does not completely displace water, which partially remains at the coordination sphere of the Ti^{IV} ions. Therefore, during displacement experiments, EtOH molecules in the gas phase must attack the bridging water ligands, producing almost complete displacement of these molecules from the coordination sphere of the surface Ti^{IV} ions; a small amount of this water can remain on the coordination positions of the cations, together with the alcohol, giving rise to the band at 1618 cm^{-1}, characteristic of a high electron density on these water molecules held by fully coordinated Ti^{IV} ions. It should be emphasized that the existence of bridging ligands and/or free coordination positions around the cations should be of paramount importance in facilitating and promoting the nucleophilic attack of the alcohol molecules.

In the cases of 2-PrOH and t-BuOH, the situation seems to be somewhat different. Only 1.6 and 1.3 molecules nm^{-2} of these alcohols are retained on the water-covered surface, the same values as for the ir "irreversible adsorptions" on a standard sample, while some water remains adsorbed, completing a 2.7–3.0 molecules nm^{-2} coverage. Then, 2-PrOH and t-BuOH can be adsorbed by opening alternating

water bridging ligands on the coordination sphere of the Ti^{IV} and displacing half of the water molecules, as with EtOH. However, when alcohol adsorbs according to scheme (b), the coordination number around the exposed Ti^{IV} should not increase, and the water molecules will remain on the surface, generally in their original positions. Whatever the situation, it can be expected that the bending mode of water does not become displaced too far from its original position at 1600 cm^{-1}, as actually observed for these two alcohols.

Decomposition

The first point to be emphasized is the absence of ethers as decomposition products; traces of diethyl ether were observed only in the case of ethanol, in the same range of temperature as observed in TPD evolution of ethylene. This fact suggests that, on anatase, monomolecular dehydration of the alcohols is produced more easily than is the dimolecular process. This behavior is rather different from that observed by Knözinger (*20*) in the case of alumina catalysts, where formation of ethers has been related to the existence of well-defined alcoholate species upon adsorption of normal aliphatic alcohols. On the other hand, traces of butenes were also detected together with ethylene in all decomposition experiments with EtOH, suggesting a Ziegler–Natta oligomerization process, probably involving alkyl–titanium species formed on the surface during decomposition of alcohol, as will be discussed in a forthcoming paper.

According to the reaction stoichiometry,

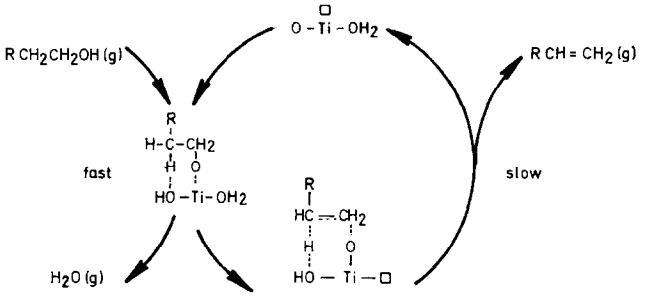
$$\text{Alcohol} \rightarrow \text{olefin} + \text{water},$$

about 1 H_2O nm^{-2} should be produced in TPD experiments with all three alcohols. This water should give a TPD peak at 270°C in the case of a free standard surface (shown by dashed lines in Fig. 5); this temperature is lower than that for decomposition of EtOH itself. Therefore, upon decomposition of this alcohol in the range 300–350°C, water must be immediately desorbed from the surface. For 2-PrOH, the decomposition temperature coincides with that for desorption of 1 H_2O nm^{-2} from a standard surface, indicating that both alcohol decomposition and desorption of the water formed in the reaction must occur simultaneously. However, in the case of t-BuOH, the olefin isobutene emerges early in the TPD scanning, giving a peak at 180°C, followed by the water in a well-differentiated peak at 250°C, a temperature that is slightly lower than that for desorption of 1 H_2O nm^{-2} from the standard surface. It is noteworthy that the activation energy for water desorption (33 kJ mol^{-1}) was lower here than for the evolution of the olefin. Thus, the high temperature of water evolution must be ascribed to an entropy effect rather than to enthalpy differences. Desorption would require an important loss of entropy of the adsorbed water molecules that should be considered as forming a mobile phase on the surface, under the decomposition conditions.

If no other factors influence the rate of decomposition, desorption of water from the active centers should be the controlling step, at least in the dehydration of t-BuOH. However, displacement experiments illustrate very clearly the importance of the dislodging capacity of the alcohol molecules from the gas phase in removing from the surface the water molecules produced during the reaction. By comparing Fig. 5 with the ir spectra in Fig. 6 we may conclude that the nucleophilic attack of the alcohol molecules in the gas phase on the Ti^{IV} which holds the adsorbed water is of paramount importance in deciding the con-

trolling step of the catalytic cycle:

SCHEME II



The existence of vacancies in the coordination sphere of these Ti^{IV} ions plays an important role in this displacement process. Thus, if the nucleophilicity of the t-BuOH molecules weakens the strength of the bond of the adsorbed water, making the displacement easier than the decomposition of the alcohol itself, the whole process will also be controlled here by the surface reaction step in the presence of this alcohol in the gas phase. Indeed, this latter condition might not be required in the cases of 2-PrOH and EtOH, since water desorption and alcohol decomposition occur at the same temperature and, so, the produced water should immediately leave the surface.

The results for catalytic dehydration of the three alcohols, in fair agreement with those for TPD decomposition of the adsorbed phase, support the above conclusion. Moreover, the ir spectra indicate that, after decomposition of the adsorbed phase, the surface completely recovers its original state, thus allowing a new catalytic cycle. This is actually the only condition required for TPD kinetic data to be comparative with those directly obtained under catalytic steady-state conditions. Contrary to Knözinger's view (*9*), in the above circumstances, the study of the decomposition of the adsorbed phase really may provide conclusions on the catalytic dehydration mechanism, and kinetic parameters for the catalytic reaction can be drawn from the thermal decomposition studies of the adsorbed phase.

By dividing the values of the rate constants in Table 4 by the preexponential factors of the Arrhenius equation in Table 1 or 2, the number of active sites under catalytic conditions can be estimated as 10^{14}–10^{15} cm^{-2}. This seems reasonable under the experimental conditions used in the flow reactor, with a pressure of alcohol on the catalyst giving a fully covered surface (pseudo-zero order). This leads to the conclusion that the low values for the frequency factors given in Table 1, compared with those predicted by transition-state theory should be ascribed to an entropy effect. A simple calculation (*21*) indicates that the decrease of ca. 30 e.u. observed with these alcohols may be due to the loss of the translational and rotational freedom of the adsorbed molecules on the surface when they form the transition state leading to the reaction products, thus suggesting a transition state with a two-point interaction as in an E_2 mechanism.

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