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Catalytic Isomerization of Olefins on Alumina

II. Catalyst Deactivation and Its Effects on the Mechanism[1]

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The deactivation of an alumina catalyst during double-bond isomerization of 2,3-dimethyl-1-butene has been studied. An "oxygen-containing" surface compound has been suggested as being responsible for the deactivation. The hydrogen transfer during the isomerization changes from predominantly intramolecular to intermolecular during the deactivation. A simple two-site model is proposed to explain the observed phenomena and a cyclic allylic carbanion-like species is suggested as an intermediate for the intermolecular double-bond isomerization at final stable activity. Kinetic isotope effects clearly show that the allylic C–H (or C–D) bond cleavage must be involved in the rate-determining step.

I. INTRODUCTION

A carbanion-like intermediate in the double-bond isomerization of olefins on alumina has been proposed in Part I of this series (*1*), where the reactivity of substituted olefins was investigated. These studies had been carried out on catalysts which had already attained stable activity after an initial deactivation. It has also been stated during the discussion on that paper (*1*) that the hydrogen transfer occurs intermolecularly under such conditions.

Deactivation of alumina catalysts in the initial stages of isomerization reactions have been reported in the past (*2–6*). Various explanations have been given. Thus, Rooney and Pink (*3*) assumed the formation of polymer species or "coke" on Lewis acid sites and Germain (*4*) explained the deactivation by the formation of highly condensed hydrocarbons on the surface. These interpretations were rejected recently by Ghorbel *et al.* (*6*), who refer to the observation of Peri (*7*) that the *cis*-2-butene formed during the 1-butene isomerization is held relatively strongly on the alumina surface. This strongly adsorbed *cis*-2-butene is therefore considered responsible for the initial catalyst deactivation. The reaction temperatures in these studies were always above room temperature, in some cases above 200°C. Hightower and Hall (*8*), when studying the D_2-exchange and isomerization of noncyclic olefins on an η-Al_2O_3 at 25–30°C, reported that there was no polymerization or any appreciable catalyst deactivation observed. Furthermore Hightower and Hall (*8–10*) concluded from their exchange and tracer experiments that, under the experimental conditions used by them (particularly reaction temperature near room temperature), the D_2-exchange and the isomerization were completely independent reactions, and that neither of these reactions involved a significant fraction of the catalyst OH-groups. The conclusion is in line with the observation of Kaneda *et al.*

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(*11*) that no deuterium was incorporated either in the reactant or in the products when 1-butene was reacted over a deuterated alumina surface at 20°C. Large primary kinetic isotope effects and extensive isotopic scrambling occurred when $C_4H_8 + C_4D_8$ mixtures were coisomerized (*9*). Isotopic scrambling was also observed when 1-butene (*12*) or *cis*-2-butene (*13*) was isomerized in the presence of perdeutero-propylene. Ozaki and Kimura (*12*) therefore proposed a proton donor-acceptor mechanism, in which the propylene chemisorbed on Lewis acid sites of the alumina surface was the proton source. Sakurai *et al.* (*13*) concluded that the double-bond isomerization occurred on some protonic sites formed by the adsorption of the olefin molecules and that deuterium scrambling between terminal olefins was an independent process. Hightower and Hall (*9*) have rejected the possibilities that catalyst OH-groups or residue molecules act as sites for butene isomerization, though they state that "it is possible that a small number of active sites has associated OH-groups and that these are responsible for intermolecular mixing or exchange with D_2." In this conflicting situation, again Hightower and Hall (*9*) express the opinion that "the true picture probably is a composite of several mechanisms acting on different sites. Whatever mechanisms are considered, however, they must include C–H (or C–D) bond cleavage in the transition state."

One may expect that the mechanistic details strongly depend on the actual state of the catalyst surface. An initial catalyst deactivation should then not only reduce the catalyst activity but also influence the reaction mechanism. The deactivation of an η-Al_2O_3 during the double-bond shift of 2,3-dimethyl-1-butene as a standard reactant and the chemical nature of the residue molecules formed during deactivation has therefore been studied in the present paper. The effect of the deactivation on the mechanism of the double-bond shift is also investigated.

II. EXPERIMENTAL

1. *Materials.*

Catalyst. The alumina was prepared by hydrolysis of aluminium isopropoxide (Fluka) at 25–30°C and calcination at 700°C in air of the resulting hydroxide. The oxide showed the X-ray powder pattern of the η- or γ-phase, the η-phase being the most probable according to the criteria put forward by Lippens and Steggerda (*41*). The BET-surface area of this oxide was (178 ± 10) m^2/g. Another η-Al_2O_3 was also prepared and mainly used for the spectroscopic work from a bayerite (P. Spence) by calcination at 700°C in air. The BET-surface area of this oxide was (100 ± 10) m^2/g. The catalytic behavior of this material principally resembled that of the η-Al_2O_3 from the isopropoxide; however, it could be handled much more easily in the preparation of ir-transparent plates. Both aluminas were stored in ambient air so that they could readsorb water. The particle size fraction of 0.3–0.4 mm was used for the catalytic studies and good ir-transparent plates have been obtained by pressing the bayerite under a pressure of 1500 N/cm^2 for 3 min and subsequent calcination of the plates. These were then about 0.3 mm thick and had a weight of 17–20 mg/cm^2.

Reagents. 2,3-Dimethyl-1-butene (23DMB1) from Fluka was >98% pure and was used without further purification beyond drying over molecular sieve LINDE 3A. The impurities were saturated low-boiling hydrocarbons only. A mono-deuterated 3-D-23DMB1 was prepared from 3-chloro-2,3-dimethyl-1-butene (obtained by HCl-addition onto 2,3-dimethyl-1,3-butadiene at −25°C and slow distillation of the reaction mixture at 112-115°C (*14*)) by reaction with D_2-gas over a quinoline poisoned Pd/C-catalyst, which was suspended in bis-2-methoxyethylether containing NaOD (*15,16*). The resulting 3-D-23DMB1 had a boiling point of 56°C after distillation in a 75 cm-vigreux column. Its purity was 97% as determined by gas chromatography. The average number of D-atoms per molecule was calculated from the mass spectra to be 1.45. Quantitative NMR (using anisol as a standard) gave a value of 1.43 D-atoms/molecule. 61% of the substance contained a D-atom in the desired C_3-allyl position, whereas in some molecules deuterium was also incorporated in the vinyl position (0.23 D-atoms per molecule) and the 3 methyl groups (0.02 D-atoms per molecule in the methyl group attached to vinyl $C^{(2)}$ and 0.55 D-atoms per molecule in the 2 methyl groups attached to allyl $C^{(3)}$).

The carrier gases helium and hydrogen were all 99% pure and were dried over molecular sieve LINDE 3A at 77 K.

2. *Apparatus and Procedures*

Catalytic studies. A microcatalytic pulse reactor was used in connection with a 4 m dimethylsulfolane/chromosorb W column (4.8 l helium/h, 25°C). The isomeric olefins were completely resolved and were separately trapped at 77 K for mass-spectral analyses, which were carried out on an Atlas MAT type MS 352 instrument. Deuterium distributions were calculated from the parent peaks. The average number $\bar{d}$ of D-atoms per molecule is calculated from Eq. (1)

$$\bar{d} = \sum_i i d_i, \qquad (1)$$

where i is the fraction of molecules containing d_i deuterium atoms.

The catalyst (0.3g) was treated at 300°C in dry helium for 1 h and then cooled down to the standard reaction temperature of 80°C. Longer treatment at 300°C did not appreciably affect the catalytic behavior of the oxide. This procedure corresponds to the one used in our previous work (*1*). Two microliter-pulses were generally injected. The conversion is taken as a measure of the catalyst activity, which is exact only for conversions below 10–20% where the equilibrium reaction can be neglected, and conversion is directly proportional to the first-order rate constant (*1*). For higher conversions this proportionality no longer exists; nevertheless, the conversion is a good measure to characterize qualitatively the initial deactivation of a catalyst.

Kinetic isotope effects have been calculated from the conversions (< 10%) of H- and D-containing 23DMB1. True kinetic isotope effects were calculated from the experimental isotope effects α_{exp} by correction for the deuterium content in the C_3-allyl position of the deuterated reactant according to Eq. (2) (*17*)

$$\alpha = \frac{b' \times \alpha_{\text{exp}}}{1 - a' \times \alpha_{\text{exp}}}, \qquad (2)$$

where $a' = 0.39$ and $b' = 0.61$ are the percentages of the undeuterated and deuterated compound in the reactant 3-D-23DMB1.

Infrared spectroscopic studies. The ir cell used has been described elsewhere (*18*). The alumina wafers were treated for 1 hour at 300°C *in vacuo* ($< 10^{-4}$ mm Hg) and then cooled to the ambient temperature within the ir-transparent part of the cell. This ambient temperature cannot be measured exactly due to the heating effect of the incident ir-beam (light source was a Globar); it should, however, not exceed 80°C (see also Section III.2). All spectra were taken at this "ambient" temperature, while adsorption was carried out at well known temperatures within an independent furnace.

Spectra were measured with a Perkin-Elmer 225 spectrometer. Spectra were recorded with a resolution of 3 cm^{-1} in the range 2800–4000 cm^{-1} and better than 2 cm^{-1} in the range 1000–2800 cm^{-1}, the scan speed being 0.25 cm^{-1}/sec.

Electronic spectra. Electronic spectra were recorded on a Beckman DK2A spectrometer applying the diffuse reflectance technique (*19,20*). The particle size fraction of 0.4–0.5 mm was used in a quartz-cell. The catalyst pretreatment was the same as that of the ir-transparent wafers. Spectra were recorded at room temperature using MgO as a reference, while adsorption could be carried out at any desired temperature when the quartz-cell was attached to the vacuum system in a furnace.

III. RESULTS AND DISCUSSION

1. *Catalyst Deactivation*

At temperatures above 80°C a strong catalyst deactivation occurred, so that the catalyst activity decreased rapidly for successive 2 µl-pulses of the reactant 23DMB1. An example is shown in Fig. 1 for a standard reaction temperature of 80°C, where the conversions and the irreversibly adsorbed amounts are plotted versus the total injected volume of reactant. The conversion drops from a value near 80% for the first pulse to only a few percent for the thirteenth and subsequent pulses. This low conversion represents a final stable activity after the deactivation has been completed, which is the case when a total of 2.3×10^{13} molecules/cm^2 have been retained on the catalyst surface (Fig. 1, left abscissa). The number of molecules retained on the surface has been calculated from the difference between the volume injected and the volume which is eluted from the microcatalytic reactor. Thus, irreversibly adsorbed molecules are accumulated on the surface during the deactivation process (full points in Fig. 1) and the final horizontal part of the curve at a level of 2.3×10^{13}molecules/cm^2 indicates the saturation of the respective "sites" and gives an estimate of their number. As the deactivation proceeds during the accumulation of irreversibly adsorbed material on the catalyst surface and both processes seem to terminate simultaneously, the deactivation should be due to poisoning of "active sites" by the irreversibly retained reactant or product molecules. It seems unlikely that the deactivation could result from the impurities (<2%) of the reactant olefin, since these consisted of saturated hydrocarbons only. Furthermore, the peak size of the impurities in the gas chromatogram remains constant during the deactivation procedure, while the 1-olefin peak increases in size for successive pulses. The total number of irre-

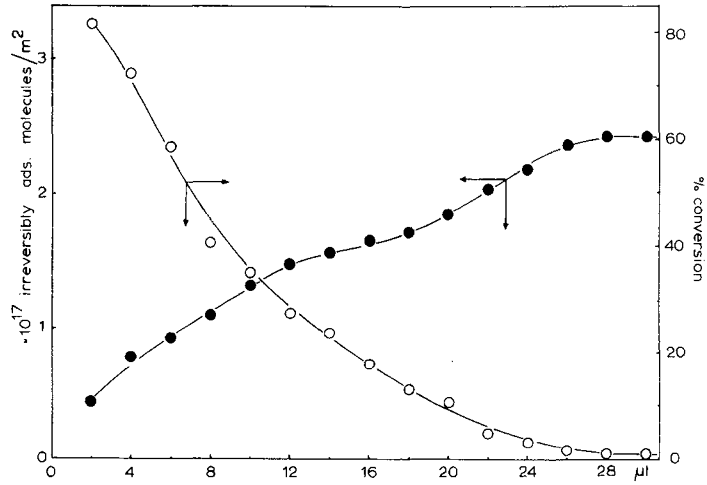


FIG. 1. Conversion and number of irreversibly adsorbed molecules vs total amount of reactant 23DMB1 injected in 2 µl-pulses.

versibly retained molecules (see above) is higher by an order of magnitude than the total number of impurity molecules injected during the deactivation process. This is additional evidence for the fact, that the strongly held material is due to an irreversible adsorption of either the reactant 1-olefin or the product 2-olefin. Any information about the chemical nature of this strongly held material should consequently characterize the nature and properties of the "active sites."

2. *Chemical Nature of Strongly Adsorbed Molecules*

ir-Spectroscopy was applied to study the chemical nature of the adsorbed molecules. Adsorption was carried out in the cell volume at the saturation pressure of the olefin at room temperature (~200 mm Hg). Figure 2 shows the background of the alumina wafer and the spectrum of adsorbed 23DMB1 in the presence of the vapor in the region between 1200–1800 cm^{-1}. This spectrum has been recorded after adsorption at ambient temperature with the sample in the infrared transparent part of the cell and during illumination by the infrared beam. The bands of symmetric and asymmetric CH_3-deformation modes at 1375 and 1450 cm^{-1} are clearly seen; furthermore, the band of the C=C stretching mode is recognized at 1638 cm^{-1}. The other spectral regions also resemble very nearly the spectra of 23DMB1; particularly is the band of the methylene, C–H stretching mode at 3080 cm^{-1} observed. Adsorption is completely reversible under these conditions as shown by the absence of characteristic bands after desorption at ambient temperature.

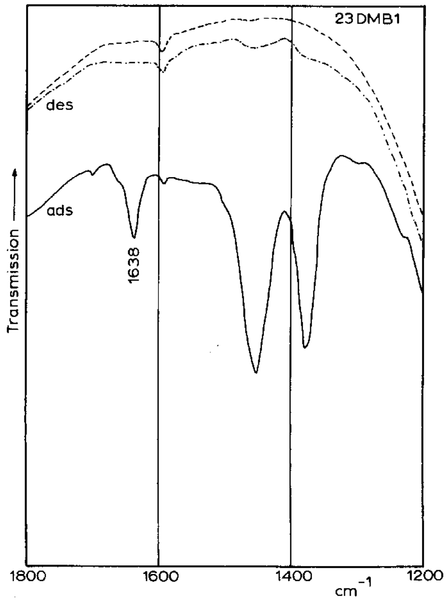


FIG. 2. ir-Spectra of 23DMB1 absorbed on η-Al_2O_3 (300°C): (---) background; (—) ads: approx. 200 mmHg 23DMB1 at "ambient" temperature; (-·-·-) des: after desorption (30 min) at "ambient" temperature.

It should also be noted that the background spectrum did not show any band (except a small impurity band near 1590 cm^{-1}) besides the surface OH stretching bands. Particularly molecular water should be absent after the pretreatment procedure at 300°C as evidenced by the absence of the H_2O-deformation band around 1630 cm^{-1}.

Adsorption is no longer reversible if the adsorption temperature exceeds 80°C and the spectra of the irreversibly retained molecules do not resemble that of the olefin. Figure 3 shows a series of spectra of the irreversibly adsorbed material, which were obtained at "ambient" temperature after adsorption and desorption at increasingly higher temperatures. Most striking changes are observed in the region between 1550 and 1700 cm^{-1}. At 87°C a new band at 1675 cm^{-1} is developed besides a less intensive band at 1640 cm^{-1}.

The band of the methylene CH stretching mode at 3080 cm^{-1} has vanished simultaneously with the appearance of the band at 1675 cm^{-1}. The intensity ratio of the 1675 and 1640 cm^{-1} bands changes with increasing temperature. At 175°C the band at 1640 cm^{-1} becomes the dominant band and at 200°C the band at 1675 cm^{-1} has completely vanished. As the temperature is fur-

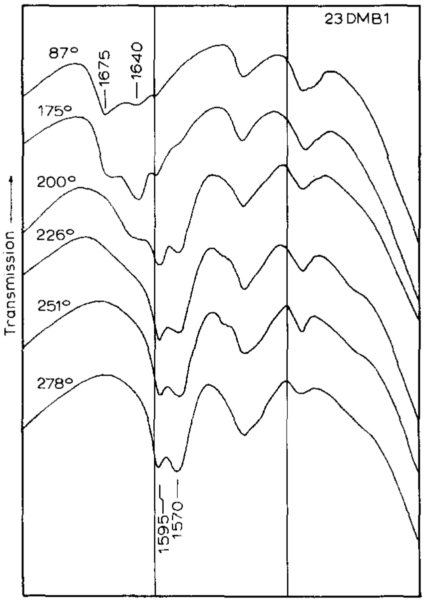


FIG. 3. ir-Spectra of irreversibly retained material after desorption of 23DMB1 at the indicated temperatures.

ther increased, the band at 1640 cm^{-1} is also replaced and a band at 1595 cm^{-1} and a pair of bands at 1570 and 1470 cm^{-1} develops. (The latter band partly obscures the asymmetric CH_3-deformation band at 1450 cm^{-1}). The interpretation of these various bands is given below.

Band at 1675 cm^{-1}. This band is dominant at the lower adsorption–desorption temperatures. The band of the methylene CH-stretching mode vanishes when the band at 1675 cm^{-1} develops. Double bond isomerization occurs already at temperatures of 80°C, so that 2,3-dimethyl-2-butene (23DMB2) is present in the gas phase and could be responsible for the formation of strongly held species. The disappearance of the band of the methylene CH stretching mode would be compatible with this assumption, since 23DMB2 has no methylene hydrogens. This symmetric olefin possesses an inversion center and the C=C stretching vibration is therefore infrared inactive, but gives rise to a Raman band at 1680 cm^{-1} (*21*) in the free molecule. This band might become active in the infrared in an adsorbed molecule, due to a loss of symmetry under the action of an asymmetric surface field. The band observed at 1675 cm^{-1} for the strongly held molecules when 23DMB1 is adsorbed could then be assigned as the C=C stretching vibration of strongly held 23DMB2. Such an interpretation of the irreversibly adsorbed species (and the resulting deactivation) would be identical to that put forward recently by Ghorbel *et al.* (*6*). The direct adsorption of 23DMB2 was therefore studied. Figure 4 shows that the C=C stretching vibration is indeed activated in the adsorbed molecule (band at 1640 cm^{-1}); however, the adsorption of 23DMB2 is reversible even at temperatures above 100°C. The bands observed on adsorption and desorption of 23DMB1 at 87°C can therefore not be assigned as characteristic bands of a strongly held 2-olefin.

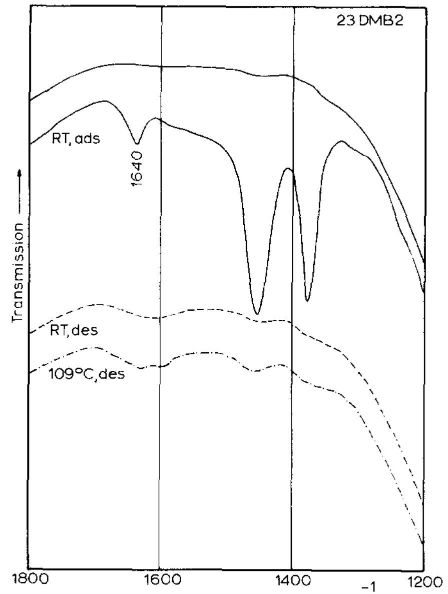


FIG. 4. ir-Spectra of 23DMB2 absorbed on η-Al_2O_3 (300°C): (—) background; (—) RT, ads: approx. 100 mm Hg 23DMB2 at "ambient" temperature; (---) RT des: after desorption (30 min) at "ambient" temperature; (-.-.-) 109°C, des: after adsorption of approx. 100 mm Hg 23DMB2 and desorption at 109°C.

Alternatively, the band at 1675 cm^{-1} of the irreversibly retained species from 23DMB1 adsorption might be assigned as a carbonyl band. This interpretation is compatible with the disappearance of the methylene CH stretching bands and suggests the oxidation of the terminal olefin to form an "oxygen-containing" surface compound. Completely analogous behavior has been observed for other terminal olefins such as 1-hexene and 3,3-dimethyl-1-butene (*31*). The exact molecular structure of the postulated "oxygen-containing" surface compound is not known, it might, however, tentatively be assigned as an aldehyde- or ketone-like species; the aldehyde-like species should be preferable since its formation only requires a 1,2-hydrogen shift, whereas the formation of a ketone-like species would need a methyl migration. However the C–H stretching band of aldehydes near 2700 cm^{-1} could not be observed. This might be due to its low intensity and the low surface concentration of the "oxygen-containing" surface compound.

Various experimental results have been obtained which are in favor of the above interpretation. The strongly held species which is obtained on adsorption of 23DMB1 at 80°C gives rise to a uv-absorption in the diffuse reflectance spectrum at 266 nm. This band is located in the region where aldehydes and ketones usually absorb (*22*) and a very intense uv-absorption is in fact observed at 285 nm on adsorption of 2-hexanone on η-Al_2O_3. Furthermore, as shown in Fig. 5, the carbonyl band of 2-hexanone adsorbed on η-Al_2O_3 at "ambient" temperature appears at 1668 cm^{-1} which is very close to the wavenumber of the proposed "oxygen-containing" surface compound. Spectroscopic evidence seems therefore to be completely compatible with this surface species.

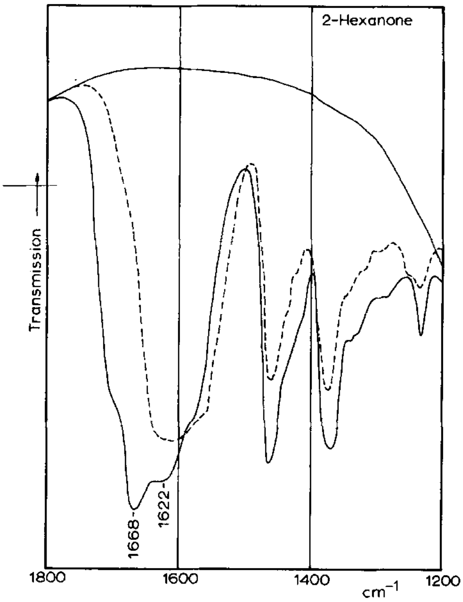


FIG. 5. ir-Spectra of 2-hexanone adsorbed on η-Al_2O_3 (300°C): (—) approx. 7 mm Hg 2-hexanone at "ambient" temperature; (---) after desorption (30 min) at "ambient" temperature.

The "oxygen-containing" surface compound can also be displaced from the surface by water vapor. A displacement reaction has been carried out at 80°C within the infrared cell, after the dominant formation of the band at 1675 cm^{-1} had been checked. The gas phase was then trapped at liquid nitrogen temperature after the displacement procedure and an analysis was carried out by mass-spectroscopy. Figure 6 compares the parent peaks of the mass spectrum of 23DMB1, which had not been in contact with an alumina surface, with those of the displaced material. The most striking result besides minor changes near the parent mass 84 of the olefin is the appearance of mass 100 (=84 + 16). This should be the parent mass of the "oxygen-containing" surface compound, the more so as the relative intensities of the peaks 16(=m_O) and 29(=m_{CHO}) are also increased as compared to the mass-spectrum of the olefin. The result of this displacement experiment seems therefore to represent strong evidence for the formation of an "oxygen-containing" surface species on adsorption of terminal olefins at temperatures above 80°C.

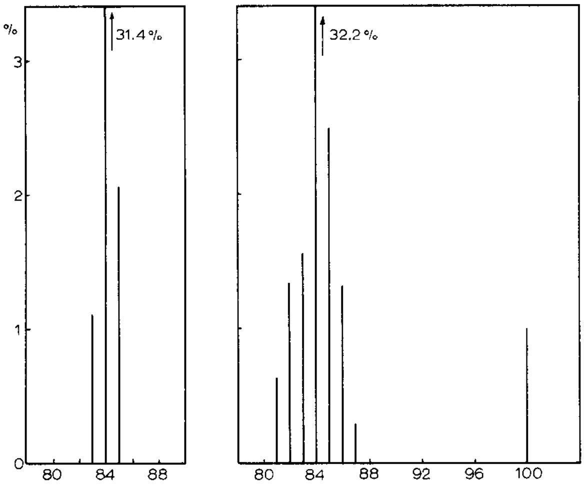


FIG. 6. Mass spectra of 23DMB1 (left) and of the material displaced by water vapor (right).

It should also be noted that the ambient temperature of the alumina wafer in the infrared beam should be less than 80°C (see Section II.2), since the surface reactions observed at this temperature did not occur when adsorption was carried out with the wafer in the infrared transparent part of the cell and heated only by the infrared beam.

Bands at 1640 and 1595 cm^{-1}. These bands are developed at increasing temperatures between 100 and 230°C, while the band at 1675 cm^{-1} of the "oxygen-containing" compound disappears. Since this species is not merely desorbed, it should undergo surface reactions, the products of which give rise to the infrared bands at 1640 and 1595 cm^{-1}. uv-Absorption of this material occurs around 360 nm and the mass-spectrum of the thermally desorbed material contains masses as high as 280. As alumina is known to be a catalyst for condensation reactions of ketones and aldehydes (*23*), one may suggest condensation reactions of the initially formed "oxygen-containing" surface compounds to occur at sufficiently high temperatures. The high masses of the thermally desorbed material, the low wavenumbers of the infrared bands (*24*) and the position of the electronic absorption band at long wavelength (*25*) are in agreement with this interpretation, if the surface condensation products contain conjugated C=O and C=C bonds. Furthermore, bands at 1622 and below 1600 cm^{-1} develop on adsorption of 2-hexanone at "ambient" temperature, as shown in Fig. 5. These absorptions around 1600 cm^{-1} are retained even after desorption of the physically adsorbed ketone and they may therefore indicate products of such condensation reactions. These reactions will certainly occur only at higher temperatures on surfaces where the "oxygen-containing" compound has been formed on olefin adsorption. In this case the surface concentrations are very low and some surface migration is necessary for condensation reactions to occur.

It is interesting to note that Webb (*26*) attributed a band at 330 nm, which was observed on adsorption of 1-butene on silica–alumina, to a polymeric carbonium-ion and a band at 425 nm to "coke." Leftin *et al.* (*27*) in a similar study ascribed a band at 310 nm to a butenyl carbonium ion and a band at 380 nm to "coke." One may speculate on the grounds of the present results that the absorptions near 300 nm belong to "oxygen-containing" compounds and those near 400 nm to condensation products of these.

Band pair at 1570 and 1470 cm^{-1}. The formation of this band pair is accompanied by the appearance of hydrogen in the gas phase at temperatures above 175°C. These bands are usually assigned as the asymmetric and symmetric stretching vibrations of carboxylate structures, which have been observed many times on alumina surfaces (*28,29,40*) on adsorption of a variety of organic molecules. Thus, Lafer *et al.* (*30*) reported the formation of carbonate and carboxylate structures on adsorption of propylene on alumina above 250°C. The band pair at 1570 and 1470 cm^{-1}, which is thermally most stable, is therefore assigned to surface carboxylates also in the present case.

Finally, it is noteworthy that a qualitatively analogous behavior on adsorption of olefins is observed on alumina surfaces which had been treated at temperatures higher than 300°C (*31*). These results will be discussed in a forthcoming contribution which will deal with the influence of the catalyst activation temperature on its isomerization activity.

3. *Catalytic Studies*

Deuterium loss from 3-D-23DMB1. Mass spectroscopic analyses have been made of the unreacted 3-D-23DMB1 and of the 2-olefin formed on isomerization. Some typical data are summarized in Table 1. The deuterium loss from the unreacted terminal olefin amounted to only a few percent in all cases. The product 2-olefin, however, lost varying average numbers of D-atoms depending on the number of pulses, i.e., on the degree of catalyst deactivation. Thus, the 2-olefin lost only 0.05 D-atoms per molecule on isomerization in the first pulse at 80°C (conversion 83%). With increasing deactivation the deuterium loss was increased, reaching 0.27 D-atoms in the tenth pulse. These values correspond to 8 and 44% D-loss, respectively, if the average number of D atoms lost is compared with the value of 0.61 D-atoms in C_3-allyl position in the reactant. The deuterium loss on isomerization increases with further use of the catalyst and on successively increasing the reaction temperature from 80 to 140°C. Finally, the deuterium loss amounts to 0.44–0.48 D-atoms per isomerized molecule on the average between 100 and 140°C. This deuterium loss is equivalent to 72–80% of the 0.61 D-atoms in C_3-allyl position of the reactant. As this reaction was carried out on a hydroxyl-containing surface, deuterium loss on isomerization is equivalent to an intermolecular hydrogen transfer with the participation of surface hydroxyl groups.

This conclusion only holds if the observed deuterium loss only occurs from the allylic position, though the deutero-olefin used contained deuterium in different positions. Unfortunately, the quantities of the reacted 2-olefin which can be trapped are much too low for NMR analy-

TABLE 1

Deuterium Loss on Isomerization of 3-D-23DMB 1

Exp. no.	Pulse no.	T(°C)	x(%)	$\Sigma_i\ id_i$ 1-ene	$\Sigma_i\ id_i$ 2-ene	D-loss per molecule	% intermolecular mechanism
I	1	80	83	1.55	1.39	0.05	8
	10	80	5	1.40	1.17	0.27	44
	11	100	15	1.43	1.10	0.34	56
	12	120	32	1.44	1.00	0.44	72
II	8	100	7	1.43	0.97	0.47	77
	19	140	16	1.33	0.97	0.47	77

sis. However, the average number of D-atoms in the unreacted 1-olefin remains practically unchanged and equals that of the reactant itself (see Table 1). Therefore, under the experimental conditions used, deuterium exchange does not occur. One may thus assume that only the allylic hydrogen or deuterium which is directly involved in the H-transfer during the isomerization can interchange with surface hydroxyls.

The assumption of final intermolecular H-transfer is also confirmed by the fact that an appreciable deuterium uptake occurs during isomerization of undeuterated 23DMB1 on a deuterated surface (*33*). Furthermore, the D_2-exchange experiments were in favor of an intermolecular mechanism under conditions when the catalyst deactivation was completed and stable final activity had been attained (*32,33*). In conclusion, the hydrogen shift during the double-bond isomerization seems to occur intramolecularly on a fresh catalyst, but predominantly intermolecularly with participation of surface hydroxyls on a deactivated catalyst.

Kinetic isotope effects. Kinetic isotope effects have been determined on the deactivated catalyst under conditions of the final activity using undeuterated 23DMB1 and 3-D-23DMB1 as reactants. The true primary kinetic isotope effects have been calculated according to Eq. (2). The two olefins were injected alternately and only those conversions obtained after injection of a total number of ten 2 μl-pulses have been used for the calculations. Arrhenius plots for the two olefins and the mean values of the true isotope effects as a function of the temperature are shown in Fig. 7. The difference in the activation energies for the deuterated and undeuterated olefin is found to be (1.7 ± 0.5) kcal/mole. This value compares quite well with the difference in the zero point energies of C–D and C–H bonds, which was shown to be 1.5 kcal/mole (*34*). This fact and the kinetic isotope effects which were found to be between 1.6 and 2.6 in the temperature range of 130 and 100°C strongly suggest that the rupture of an allylic C–D or C–H bond is involved in the rate-determining step of the double-bond isomerization.

IV. CONCLUSIONS

An "oxygen-containing" surface compound has been proposed to be responsible for the catalyst deactivation. The exact

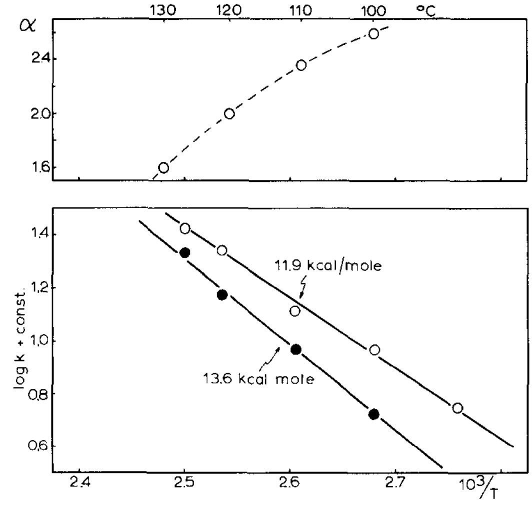
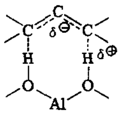


FIG. 7. Kinetic isotope effects (upper part) and Arrhenius-plots (lower part) for the double-bond shift of 23DMB1 and 3-D-23DMB1 on η-Al_2O_3 (300°C).

structure of this compound is not clear, though an aldehyde-like species seems to be most probable. The reaction mechanism of this surface reaction is also unknown. Chemisorbed oxygen species have been suggested to be necessary for redox-reactions of aromatic hydrocarbons to occur on alumina (*35*). One may speculate that such oxygen species might also be responsible for the formation of the "oxygen-containing" compound. On the other hand, French and Somorjai (*36*) have shown by LEED experiments on the (0001)-face of α-Al_2O_3 that this surface layer was oxygen deficient and a chemical composition of Al_2O was proposed, which then must contain monovalent aluminum ions. A surface reduction with H_2 was also shown to occur with γ- and η-Al_2O_3 by Weller and Montagna (*37*). A non-stoichiometric alumina was produced with a reduced surface layer. These results seem to show that a surface reduction of aluminas may occur under certain conditions and one may therefore speculate that an analogous process, which involves certain surface sites of particular configurations, leads to the "oxygen-containing" surface compound on reactions with terminal olefins. The distribution of aluminium ions between tetrahedral and octahedral sites in the surface layer may also be of importance with respect to the observed phenomena.

A consistent picture of the present observations can be drawn if two types of chemically different sites are postulated to exist on the surface, though such a description is certainly oversimplified. Sites of the first type, type A, should be characterized by a high specific activity for the double-bond shift; they should not contain reactive hydrogen and these sites must therefore catalyze an intramolecular hydrogen shift. Type A sites must furthermore possess oxidizing properties which lead to the formation of the "oxygen-containing" compound. This species then poisons the type A sites and eliminates them as active sites for the double-bond shift. The number of these sites can be estimated to be about $2.3 \times 10^{13}/cm^2$ and corresponds to the number of "oxygen-containing" surface species formed on the η-Al_2O_3 surface after thermal treatment at 300°C. Sites of the second type, type B, exhibit no oxidizing properties at the reaction temperatures under study; they are therefore not eliminated by self-poisoning and remain active after the deactivation process. The type B-sites are described as developing comparably low specific activity and as having reactive hydrogen available. At conditions of final stable activity the double-bond shift therefore occurs with an intermolecular hydrogen-shift under participation of surface hydroxyls.

The type B-sites are the ones on which the previously proposed (*1*) allylic carbanion-like intermediate of the double-bond isomerization should be formed. The nature of the type B-sites may be specified to be made up by a basic oxygen ion, an acidic part (incompletely coordinated aluminium ion) and a hydroxyl group. These three elements must be arranged in a suitable configuration and they must exhibit favorable relative acidic and basic properties, so that a cyclic allylic carbanion-like species may be formed from an olefin:



The carbanion character in this intermediate is not fully developed; the H-addition to $C^{(1)}$ and allyl H-abstraction must be concerted (*1*), but the loosening of the allyl $C^{(3)}$-H bond is assumed to be relatively more in progress than the formation of the new $C^{(1)}$-H bond. Allylic carbanions have been detected by infrared spectroscopy and shown to be intermediates in the double-bond isomerization on ZnO by

Kokes and Dent (*38*), who already proposed an analogous mechanism for alumina. The present spectroscopic studies did not show any evidence for the existence of such intermediate species, though they are in accord with all other experimental observations, particularly with the reactivity of substituted olefins (*1*), with the kinetic isotope effects and with the D-loss experiments. It must therefore be concluded that the surface concentration and/or the lifetime of this intermediate is too low for its detection in the infrared or electronic spectra.

The kinetic isotope effects of 1.6–2.6 in the covered temperature range clearly show that the allyl C–H (or C–D) bond cleavage must be involved in the rate-determining step of the double-bond shift and this conclusion is in agreement with the previously observed Taft correlations (*1*). Guisnet *et al.* (*39*) recently reported a kinetic isotope effect of 2.0 for the double-bond shift on alumina at 250°C. This value was compared with a value of 2.9 for the double-bond shift on a silica-alumina at 85°C and it was concluded from the proximity of the two values that a carbonium-ion intermediate was the most probable in both cases. However, the two values are not very close since kinetic isotope effects are temperature dependent. The two values are therefore not comparable. Instead, assuming a difference of the zero point energies for C–D and C–H bonds of 1.5 kcal/mole (*34*), one calculates a value of 3.9 for a temperature of 85°C from the value of 2.0 reported for 250°C on alumina. This value is appreciably higher than that obtained for silica-alumina by Guisnet *et al.* (*39*). One may therefore conclude that those isotope effects do at least not exclude an allylic carbanion-like intermediate on alumina.

The described simple model of a catalyst surface containing the type A and B sites readily explains the fact that Hightower and Hall (*8–10*) did not observe any deactivation and that the double-bond shift was an intramolecular process under their conditions. These authors worked around 30°C. As shown by our present spectroscopic studies, the "oxygen-containing" surface compound is still not formed at a detectable level at such low temperatures. The type A-sites therefore remain active and because of their postulated high specific activity, they will dominate the mechanism. An intramolecular hydrogen transfer has been observed at the initial stages also in the present work.

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