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# Catalytic Isomerization of Ethylenic Hydrocarbons

## XIV. Effect of Drying and Reaction Temperature on the Isomerization of Deuterated Butenes over Alumina

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By studying the isomerization of ($D_2$-2,3)-*cis*-butene and ($D_6$-1,4)-*cis*-butene on alumina, the relative importance of the reactions with or without exchange of hydrogen between the olefin and the catalyst has been determined, as has the vinylic or allylic nature of the intermediate species. The drying temperature and the sodium content of alumina, as well as the working temperature, have a marked influence on the reactions observed: when alumina is preheated at 500°C, the isomerization without exchange is favored by a rise in the working temperature, whereas the reverse is observed when alumina is preheated at 580°C.

Double-bond shift and *cis–trans* isomerization, with exchange, always occur simultaneously. The characteristics of these reactions, especially the vinylic isotope effect measured for *cis–trans* isomerization, are explained by a carbonium ion mechanism.

On aluminas preheated up to 500°C, the only reaction without exchange observed is *cis–trans* isomerization: a concerted carbanion-like mechanism involving $\sigma$-allylic species is proposed. On alumina preheated at 580°C, the *cis–trans* isomerization without exchange is always accompanied by an intramolecular double-bond shift: these reactions may be explained by a nonconcerted mechanism with additional $\pi$-allylic carbanions as intermediates.

## I. INTRODUCTION

In a recent investigation of butene isomerization on alumina (*1*) it was found that double-bond shift always involved the exchange of an allylic hydrogen of the molecule with the catalyst, whereas *cis–trans* isomerization proceeded along two parallel paths:

The first one involves the exchange of a vinylic hydrogen with the catalyst. This reaction, like the double-bond shift, probably takes place with carbocations as intermediates and is favored at low temperatures.

The second reaction takes place without any exchange of hydrogen. This reaction, which we called "intramolecular," is favored by an increasing temperature.

To account for the latter reaction, two kinds of intermediates have been proposed: carbocations $\sigma$-bonded to Lewis acid sites, and allylic species. Some points have still to be clarified if we are to choose between these two possibilities. Indeed, $\sigma$-bonded carbocations explain the fact that *cis–trans* isomerization is the only reaction without exchange which we have observed. However, these carbocations do not account for the isotope effect of the allylic deuterium during this above reaction, if this effect is a primary one. On the contrary, allylic species account for a primary isotope effect, but they do not explain why an intramolecular double-bond shift does not take place at the same time as *cis–trans* isomerization without exchange.

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In the present work, the effect of drying temperature on the previously used alumina (*1–3*) has been examined. At a reaction temperature of 250°C, the same reactions with and without exchange are observed, but their relative importance depends very much on the drying temperature. At 85°C, the alumina preheated at a high temperature gives an additional intramolecular double-bond shift without exchange of hydrogen with the catalyst. This work allowed us to conclude that *cis–trans* isomerization without exchange always takes place with a primary isotope effect of allylic deuterium. For the purpose of comparison, a pure alumina was prepared by hydrolyzing aluminum isopropylate: on this catalyst, the selectivities are different from those obtained on the first alumina. This may be due to the sodium content of the latter, and is why the pure alumina exchanged by sodium ions has been studied briefly.

The present results are discussed, and reaction mechanisms are proposed.

## II. EXPERIMENTAL METHODS

The preparation of deuterated butenes has already been described (*2*).

The AP alumina is the one previously used (*1–3*), i.e., the activated alumina from Prolabo. It has a specific BET surface area of 165 $m^2/g$ and a sodium content of 0.13 wt%. The AI alumina was prepared by neutral hydrolysis of aluminum isopropylate. It has a specific BET surface area of 215 $m^2/g$, and contains no sodium. This alumina was exchanged by sodium carbonate; the catalyst obtained, which will be called AINa, contains 0.1 wt% Na. These aluminas are predried overnight *in situ* in an atmosphere of dry nitrogen. The drying temperatures were chosen between 300 and 580°C. The catalysts obtained will be called AP-*t*, AI-*t*, and AINa-*t*, where *t* is the drying temperature.

The experiments were performed on fresh samples of catalyst in the microreactor described previously (*1*) and were limited to a maximum of 10 runs of butene. Every run contained about 1 $cm^3$ ($4.5 \times 10^{-5}$ mole) of deuterated reactant. All the catalysts, except AP-500, presented an almost stable activity, and were studied from the first run. AP-500 showed a short deactivation during the first four runs before reaching a stable and reproducible activity; this latter catalyst was studied after deactivation. The activities of the catalysts were compared under conditions where conversion was less than 10%. The absence of isotopic dilution of the hydrogen of the catalyst was verified by including the reactant in a large slug of ethylene or propylene: no change was observed in the isotope distribution in the reaction products.

The isotope distributions reported in the tables were obtained by plotting the amount of each deuterated species in the reaction product against the percent of conversion, and then extrapolating the curves to zero conversion. Each curve required from four to six experiments carried out on different samples of fresh catalyst, except for AI and AINa where only two or three experiments at low conversion were performed. To determine the isotope effects, the deuterated *cis*-butenes were injected between two runs of light *cis*-butene in the same conditions (catalyst weight, carrier gas space velocity). The amount of each isomer produced from the deuterated *cis*-butene was plotted against the amount of the same isomer formed from light *cis*-butene. The isotope effect $k_H/k_D$ is given by the slope of the curve at zero conversion.

The reactions were studied between 50 and 300°C, but more often than not at 85 and 250°C. At temperatures lower than 85°C, the equilibrium amount of 1-butene is too small to allow accurate determination of its initial isotope distribution using our method.

TABLE 1

Isomerization of Butenes on AP Aluminas at 250°C Effect of Drying Temperature

| Catalyst: | AP-300 | AP-400 | AP-500 | AP-580 |
|---|---|---|---|---|
| Relative activities: | 1[a] | 15 | 25 | 220 |
| $S$ 1/$t$: | 0.15 | 0.2 | 0.3 | 1.8 |
| Starting material: ($D_2$-2,3)-*cis*-butene | | | | |
| Products | | | | |
| 1-Butene Isotope distribution | 100% ($D_2$) | 100% ($D_2$) | 100% ($D_2$) | 100% ($D_2$) |
| Isotope effect | 1.0 | 1.0 | 1.0 | 1.0 |
| *trans*-Butene Isotope distribution | 5% ($D_1$)<br>95% ($D_2$) | 10% ($D_1$)<br>90% ($D_2$) | 25% ($D_1$)<br>75% ($D_2$) | 50% ($D_1$)<br>50% ($D_2$) |
| Isotope effect | 1.05 | 1.1 | 1.2 | 1.4 |
| Starting material: ($D_6$-1,4)-*cis*-butene | | | | |
| Products | | | | |
| 1-Butene Isotope distribution | 100% ($D_5$) | 100% ($D_5$) | 100% ($D_5$) | 95% ($D_5$)<br>5% ($D_6$) |
| Isotope effect | 1.8 | 1.6 | 1.8 | 1.6 |
| *trans*-Butene Isotope distribution | 100% ($D_6$) | 100% ($D_6$) | 100% ($D_6$) | 100% ($D_6$) |
| Isotope effect | 2.2 | 1.9 | 1.6 | 1.3 |
| % Reactions with exchange | | | | |
| Double-bond shift | 13 | 16 | 24 | 60 |
| *Cis–trans* isomerization | 4 | 9 | 18 | 19 |
| Total | 17 | 25 | 42 | 79 |
| % Reactions without exchange | | | | |
| Double-bond shift | 0 | 0 | 0 | 4 |
| *Cis–trans* isomerization | 83 | 75 | 58 | 17 |
| Total | 83 | 75 | 58 | 21 |

[a] Reference.

## III. RESULTS

On some catalysts, an exchange reaction independent of isomerization was observed; however, it was always negligible at low conversion. As only extrapolated results were reported, this reaction, which was previously observed (*4*), will not be taken into account.

### *1. Effect of Drying Temperature on AP Alumina at 250°C (Table 1)*

The isomerization activity increases when the drying temperature is raised from 300 to 580°C. The $S$ 1/$t$ ratio of 1-butene to *trans*-butene formed from light *cis*-butene is small on AP-300, AP-400, and AP-500, but reaches 1.8 on AP-580.

Reactions with exchange of a deuterium atom between the molecule and the catalyst and reactions without exchange are observed on all AP catalysts. The percentages of these reactions are reported in the last lines of Table 1. They are calculated from the $S$ 1/$t$ ratio and the percentages of exchanged or unexchanged species in the products of the reaction, without taking into account the isotope effects. A more elaborate calculation taking into consideration the isotope effects yields similar results, but requires additional assumptions. The values obtained show that all the reactions with exchange are favored by an increase in the drying temperature. The selectivity of these reactions, given by the ratio of double-bond shift with exchange to *cis*–

TABLE 2

Isomerization of Butenes on AP-580 Effect of Reaction Temperature

| Reaction temp (°C): | 85 | 135 | 200 | 250 |
|---|---|---|---|---|
| $S$ 1/$t$: | 0.2 | 0.4 | 1.4 | 1.8 |
| Starting material: ($D_2$-2,3)-*cis*-butene | | | | |
| Products | | | | |
| 1-Butene Isotope distribution | 100% ($D_2$) | 100% ($D_2$) | 100% ($D_2$) | 100% ($D_2$) |
| Isotope effect | 1.0 | 1.0 | 1.0 | 1.0 |
| *trans*-Butene Isotope distribution | 100% ($D_2$) | 15% ($D_1$)<br>85% ($D_2$) | 40% ($D_1$)<br>60% ($D_2$) | 50% ($D_1$)<br>50% ($D_2$) |
| Isotope effect | 1.0 | 1.1 | 1.3 | 1.4 |
| Starting material: ($D_6$-1,4)-*cis*-butene | | | | |
| Products | | | | |
| 1-Butene Isotope distribution | 100% ($D_6$) | 62% ($D_5$)<br>38% ($D_6$) | 90% ($D_5$)<br>10% ($D_6$) | 95% ($D_5$)<br>5% ($D_6$) |
| Isotope effect | 3.0 | 2.4 | 1.8 | 1.6 |
| *trans*-Butene Isotope distribution | 100% ($D_6$) | 100% ($D_6$) | 100% ($D_6$) | 100% ($D_6$) |
| Isotope effect | 3.0 | 2.0 | 1.5 | 1.3 |
| % Reactions with exchange | | | | |
| Double-bond shift | 0 | 17 | 52 | 60 |
| *Cis–trans* isomerization | 0 | 11 | 17 | 19 |
| Total | 0 | 28 | 69 | 79 |
| % Reactions without exchange | | | | |
| Double-bond shift | 17 | 11 | 6 | 4 |
| *Cis–trans* isomerization | 83 | 61 | 25 | 17 |
| Total | 100 | 72 | 31 | 21 |

*trans* isomerization with exchange, shows no important modifications. *Cis–trans* isomerization is the only reaction without exchange observed on AP-300, AP-400 and AP-500, but on AP-580 double-bond shift also takes place without exchange.

The isotope effect measured for *cis–trans* isomerization of ($D_2$-2,3)-*cis*-butene increases with the rise in the drying temperature, as does the percentage of *cis–trans* isomerization with exchange. On the other hand, the isotope effect measured for *cis–trans* isomerization of ($D_6$-1,4)-*cis*-butene decreases. ($D_2$-2,3)-*cis*-butene gives only ($D_2$)-1-butene without an isotope effect; the isotope effect of allylic deuterium for double-bond shift is approximately constant.

### *2. Effect of Reaction Temperature on AP Aluminas*

*AP-500.* At all the temperatures studied in the 175–300°C range, ($D_6$-1,4)-*cis*-butene yields ($D_5$)-1-butene and ($D_6$)-*trans*-butene. The isotope effect measured for double-bond shift normally decreases from 2 to 1.5 as the reaction temperature increases from 175 to 300°C. On the other hand, there is a slight increase in the isotope effect of the allylic deuterium for *cis–trans* isomerization (from 1.5 to 1.65). The results obtained in isomerization of ($D_2$-2,3)-*cis*-butene have been previously reported (*1*): *cis–trans* isomerization without exchange is favored by an increase of temperature.

*AP-580* (Table 2). The $S$ 1/$t$ ratio in-

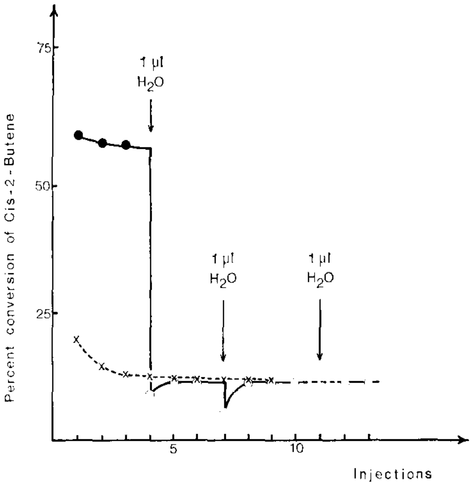

FIG. 1. Effect of water on the activity of AP-580. 0.3 g AP-580 at 85°C (●) and 250°C (○); 0.3 g AP-500 at 250°C (×).

creases from 0.2 to 1.8 when the reaction temperature is raised from 85 to 250°C.

At 85°C it appears that both *cis–trans* isomerization and double-bond shift occur entirely without any exchange of hydrogen between the reactant and the catalyst. On the other hand at 250°C there are only 21% of reactions without exchange and 79% with exchange. Consequently, reactions with exchange are favored by an increase in temperature, which is the contrary to what is observed with AP-500. Finally, an increase in reaction temperature causes a decrease in the allylic deuterium isotope effect for *cis–trans* isomerization and double-bond shift, and simultaneously produces a vinylic deuterium isotope effect for *cis–trans* isomerization.

### *3. Effect of Water on AP Alumina*

The addition of 1.0 µl water to a sample of AP-300, AP-400 or AP-500 at 250°C, prior to a *cis*-butene run, brings about a decrease in activity of 1.5 without changing either the $S$ $1/t$ ratio, or the isotope distribution in the products. After a further run, the catalyst recovered its normal activity.

When adding 1.0 µl water to a sample of AP-580 at 85°C, the catalyst loses all its activity. If the reaction temperature is then raised to 250°C, the catalyst possesses an activity which is the same as that of AP-500 at this temperature (Fig. 1). When injecting deuterated butenes on the damped catalyst at 250°C, the products obtained have the same isotope distribution as those resulting from isomerization on AP-500 at the same temperature. As for AP-500, additional amounts of water do not bring about any more changes in activity and in selectivity. Water produces the same effects when added to AP-580 at 250°C.

### *4. Comparison between AP and AI Aluminas (Table 3).*

*Aluminas predried at 300°C.* AP-300 and AI-300 catalyse the same reactions: *cis–trans* isomerization and double-bond shift with exchange, and *cis–trans* isomerization without exchange. However, the reactions with exchange are much more important on AI-300 than on AP-300.

We obtain a lower $S$ $1/t$ ratio and a lower percentage of reactions with exchange with sodium treatment: AINa-300 is intermediate between AI-300 and AP-300.

*Aluminas predried at 580°C.* AI-580 was less active than AP-580, whereas AI-300 was more active than AP-300. On AI-580, *cis–trans* isomerization and particularly double-bond shift involve a partial hydrogen exchange, whereas no exchange was observed on AP-580.

The effect of the sodium treatment on the $S$ $1/t$ ratio and on the percentage of reactions with exchange is identical to the one observed on AI-300: the behavior of AINa-580 is more like that of AP-580 than that of AI-580.

*Effect of water on AI Aluminas.* Water, which had no effect on AP-300, has no effect either when added to AI-300. By adding water to a sample of AI-580 at 85°C, it becomes inactive, as does AP-580.

TABLE 3

Isomerization of Butenes on AI, AINa, and AP Aluminas

| Catalyst: | AI-300 | AINa-300 | AP-300 | AI-580 | AINa-580 | AP-580 |
|---|---|---|---|---|---|---|
| Reaction temp (°C): | 250 | 250 | 250 | 85 | 85 | 85 |
| Relative activities: | 50 | 10 | 1[a] | 0.1 | 0.07 | 1[a] |
| $S$ 1/$t$: | 2.0 | 1.2 | 0.15 | 0.7 | 0.3 | 0.2 |
| Starting material ($D_2$-2,3)-*cis*-butene | | | | | | |
| Products | | | | | | |
| 1-Butene Isotope distribution | 100% ($D_2$) | 100% ($D_2$) | 100% ($D_2$) | 100% ($D_2$) | 100% ($D_2$) | 100% ($D_2$) |
| Isotope effect | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| *trans*-Butene Isotope distribution | 40% ($D_1$)<br>60% ($D_2$) | 20% ($D_1$)<br>80% ($D_2$) | 5% ($D_1$)<br>95% ($D_2$) | 5% ($D_1$)<br>95% ($D_2$) | 100% ($D_2$) | 100% ($D_2$) |
| Isotope effect | 1.4 | 1.2 | 1.05 | 1.1 | 1.0 | 1.0 |
| Starting material: ($D_6$-1,4)-*cis*-butene | | | | | | |
| Products | | | | | | |
| 1-Butene Isotope distribution | 100% ($D_5$) | 100% ($D_5$) | 100% ($D_5$) | 50% ($D_5$)<br>50% ($D_6$) | 25% ($D_5$)<br>75% ($D_6$) | 100% ($D_6$) |
| Isotope effect | 1.6 | 1.6 | 1.8 | 1.8 | 3.2 | 3.0 |
| *trans*-Butene Isotope distribution | 100% ($D_6$) | 100% ($D_6$) | 100% ($D_6$) | 100% ($D_6$) | 100% ($D_6$) | 100% ($D_6$) |
| Isotope effect | 1.2 | 1.7 | 2.2 | 2.3 | 3.4 | 3.0 |
| % Reactions with exchange | | | | | | |
| Double-bond shift | 67 | 55 | 13 | 21 | 6 | 0 |
| *Cis–trans* isomerization | 13 | 9 | 4 | 3 | 0 | 0 |
| total | 80 | 64 | 17 | 24 | 6 | 0 |
| % Reactions without exchange | | | | | | |
| Double-bond shift | 0 | 0 | 0 | 20 | 17 | 17 |
| *Cis–trans* isomerization | 20 | 36 | 83 | 56 | 77 | 83 |
| Total | 20 | 36 | 83 | 76 | 94 | 100 |

[a] Reference.

## IV. DISCUSSION

The behavior of alumina is very sensitive to drying and to reaction temperature, as well as to the amount of sodium introduced either during the preparation of the catalyst or by exchange of a pure alumina. This sensitivity might explain the divergences found in the literature (*5*). Indeed, the reaction temperatures are often different, varying from 20 to 300°C (*6–11*) and even reaching 500°C (*12*), as are the pretreatment conditions and the origin of the catalyst. Moreover, the deactivation state of the catalyst may strongly affect the selectivity of the reactions (*9*). This deactivation state may differ with the type of reactor used: with a static reactor (*5, 6, 13*) deactivation is not generally taken into account, as it sometimes is with a flux reactor (*10*); with a pulse reactor (*9, 13*) initial activity is generally taken into consideration.

With all our catalysts we can observe reactions with exchange of hydrogen between the olefin and the catalyst, and reactions without exchange. The former need to have the participation of protonic sites on the catalyst or at least hydrogen-containing sites, but those sites which are active for isomerization without exchange can, on the other hand, be considered nonprotonic.

### 1. *Comparison between Aluminas; Effect of Sodium Content*

The behavior of AP and AI aluminas is rather different (Table 3): the $S$ 1/$t$ ratio is higher and the reactions with exchange are more important on AI than on AP alumina. The relative activities of these aluminas depend upon the drying temperature: AI-300 is more active than AP-300, AP-580 more than AI-580. However, the AI and AP aluminas change with the variation of the drying temperature in a similar manner, and the water effect is only noticeable after pretreatment at a high temperature.

Experiments carried out at 50°C show that the specific activities of AP-580 and AI-580 are similar to those measured by others (*7*). Moreover, the results obtained in the isomerization of deuterated butenes on AI-580 at 85°C are similar to those obtained by Hightower and Hall (*13*) in coisomerization of ($D_0$) and ($D_8$)-*cis*-butenes: double-bond shift partly involves deuterium exchange, like *cis–trans* isomerization at a lower level, these reactions occurring with an important isotope effect. On the other hand, AP-580 only catalyzes reactions without any exchange at 85°C.

The values of the $S\ 1/t$ ratio and of the percentage of the reactions with exchange are lowered by the sodium exchange of AI alumina. The neutralizing of protonic sites by sodium ions (*8*, *14*) may quite well explain this modification. Moreover, the sodium exchange has a greater effect on the activity of AI-300, which is essentially active in the reactions with exchange which need the participation of protonic sites, than on the activity of AI-580 which results mainly from nonprotonic sites.

Though other factors might have an effect on the selectivity of aluminas, the different sodium contents of AP and AI aluminas may explain the differences observed. The results obtained with AP alumina are discussed below. The similarity in the changes of AP and of AI aluminas with varying drying temperature allows us to believe that the conclusions of this discussion may be extended to AI alumina.

### *2. Nature of Intermediate Species*

The isomerization of selectively deuterated butenes allows us to determine the relative importances of the reactions with and without exchange of hydrogen between the olefin and the catalyst. By measuring the isotope effects it is possible to find the accurate position of the C–H bond-breaking, and hence to determine the vinylic or allylic nature of the intermediate species, especially for *cis–trans* isomerization.

*Isomerization without exchange.* On AP aluminas preheated between 300 and 500°C, only *cis–trans* isomerization occurs without any exchange (Table 1). The isotope effects arising in this reaction are difficult to assess, because this reaction always competes with *cis–trans* isomerization with exchange. However, the percentage of *cis–trans* isomerization without exchange and the isotope effect for allylic deuterium show similar changes with varying drying temperature. Moreover, on AP-500 at 300°C (*1*) and on AP-300 and AP-400 at 250°C, where *cis–trans* isomerization without exchange prevails, the isotope effect measured for allylic deuterium is greater than the primary one found for double-bond migration with exchange. On the other hand, no important vinylic deuterium isotope effect is detected. Therefore *cis–trans* isomerization without exchange takes place with a primary isotope effect for allylic deuterium.

Over AP-580 at 85°C, both *cis–trans* isomerization and double-bond shift occur without exchange. No vinylic deuterium isotope effect is detected, but both reactions give rise to the same large, therefore primary, isotope effect for allylic deuterium. The ratio of the double-bond shift without exchange to the *cis–trans* isomerization without exchange (Table 2) is 0.2 in the 85–250°C range. Consequently these two reactions have the same apparent activation energy: they probably occur through the same intermediate.

On AP aluminas, all the reactions without exchange involve an allylic C–H bond-breaking during the rate-determining step. Thus, it would appear that allylic species do intervene, but these intermediates, which allow both double-bond shift and *cis–trans* isomerization over AP-580, give only *cis–trans* isomerization on the other AP catalysts.

*Isomerization with exchange. Cis–trans* isomerization and double-bond shift with exchange always occur simultaneously.

Double-bond shift involves an allylic deuterium isotope effect varying from 1.6 to 1.8 on all AP catalysts at 250°C. No vinylic deuterium isotope effect is detected.

Since *cis–trans* isomerization without exchange gives rise only to an allylic deuterium isotope effect (cf. preceding paragraph) the isotope effect for vinylic deuterium is related only to *cis–trans* isomerization with exchange. Then the percentage of reactions with exchange allows us to calculate (*1*) the vinylic deuterium isotope effect just for the *cis–trans* isomerization with exchange. Values from 1.8 to 2.0 are obtained on all AP catalysts at 250°C.

On all these catalysts the reactions with exchange involve an allylic C–H bond-breaking for double-bond shift and a vinylic one for *cis–trans* isomerization during the rate-determining step. These results are consistent with the single-adsorbed carbonium ion mechanism proposed earlier (*3*). Other mechanisms, such as the allylic carbanion mechanism (*9, 15*) or the push–pull mechanism (*16*), which might quite well explain the double-bond shift, cannot account for the *cis–trans* isomerization with exchange of a vinylic hydrogen atom. Let us assume that the reactions with exchange occur through the same intermediates, then the carbonium ion mechanism is quite probable.

### 3. *Comparison of Active Sites of AP Aluminas*

To discuss the strength of the active sites, we shall assume that the smaller the activation energy of a reaction, the more the sites activate the molecule, and the stronger the sites. Over AP-500, the lower the temperature, the more favored the reactions with exchange (*1*); the activation energy for these reactions is consequently smaller than the activation energy for the reactions without exchange, and therefore the protonic sites are stronger than the nonprotonic ones. On the contrary, over AP-580 the reactions with exchange are favored by an increasing temperature: the protonic sites are weaker than the nonprotonic ones. Finally, water which has no effect on AP-500, causes an irreversible reduction in the activity of the protonic and nonprotonic sites of AP-580. This kind of water poisoning on alumina pretreated at a high temperature has been already mentioned (*17*).

These results will be discussed using the model proposed by Peri (*18*) for the surface of alumina. According to Peri, the oxide defects generated by dehydration can account for the catalytic activity of alumina. However, besides these Lewis acid sites, oxide ions are believed to play an important role in catalysis (*19*). The higher the preheating temperature, the larger the number of oxide vacancies, and the stronger the corresponding Lewis acid sites. So, it is quite normal that the sites of AP-580 should prove stronger than those of other AP catalysts. Moreover, if it is assumed that the oxide vacancies proposed by Peri are catalytically active for the reactions without exchange, it is easy to understand that AP-580 is active for this reaction at low temperatures, whereas the other catalysts are active only at high temperatures.

Peri also indicated (*18*) that, when dehydrating alumina, some hydroxyl ions remain on the surface. Their acidity increases with their isolation which, one may consider, becomes more pronounced with the rise in the predrying temperature, and hence their acidity is reinforced. Protonic sites of AP-580 should then be more acid than those of other AP catalysts. This would explain why, at 250°C, these sites are more and more active when passing from AP-300 to AP-580, although the total

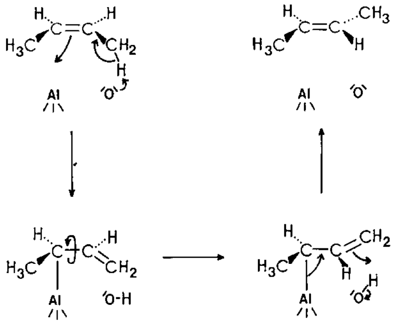

FIG. 2. Isomerization without exchange of *cis*-butene into *trans*-butene on AP-300, AP-400, and AP-500: concerted mechanism.

number of hydroxyl ions must necessarily be less on AP-580.

This model also offers an explanation for the effect of water on AP-580 and other catalysts. On the latter, the weak Lewis acid sites responsible for isomerization without exchange are not easily attacked by water. However, on AP-580, the strong Lewis acid sites can easily be destroyed by water. Moreover, adsorption of water on anionic defects of AP-580 annihilates the strongest protonic sites by suppressing their isolation.

### *4. Mechanism of the Isomerization without Exchange*

On AP-300, AP-400, and AP-500, *cis–trans* isomerization is the only reaction without exchange observed. To account for this isomerization we have previously proposed (*20*) the reaction scheme in Fig. 2. The active sites are supposed to be exposed aluminum ions, weakly acid, associated with neighboring oxide ions which are weakly basic because of the proximity of the anionic vacancy. The acidic and basic functions would be too weak to act separately. Isomerization would occur in a concerted way, with simultaneous intervention of both functions: the removal of an allylic proton by the oxide ion would take place with the concomitant formation of a $\sigma$-bond between the butene molecule and the aluminum ion. Similarly, the reverse reaction, the breaking of the $\sigma$-bond and the returning of the proton to the molecule, would only take place by the same concerted process. This would preclude the formation of 1-butene from 2-butene. This statement might be compared to the argument advanced by Flockart *et al.* (*21*) who consider that the sites active in *n*-propane exchange over alumina are insufficiently strong to bring about the formation of radicals but are capable of inducing a Lewis type acid–base reaction.

On AP-580 both double-bond shift and *cis–trans* isomerization occur without exchange. The sites operative in these reactions would be of the type strong Lewis acid–weak Lewis base. The first step of the reaction would be the $\pi$-adsorption of the butene on the Lewis acid site (a, Fig. 3). An allylic proton would then be readily removed by the adjacent oxide ion to form a $\pi$-allylic carbanion (b) adsorbed on the Lewis site. This species would allow both double-bond shift and *cis–trans* isomerization by changing, respectively, into $\pi$-complexes (a′) or $\sigma$-allylic species (c), according

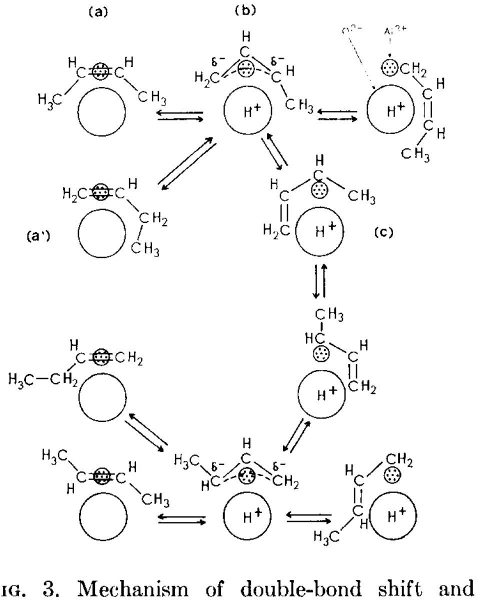

FIG. 3. Mechanism of double-bond shift and *cis–trans* isomerization without exchange on AP-580.

to the model proposed by Dent and Kokes (*22*) for the isomerization on ZnO.

The main difference between the two mechanisms of isomerization without exchange resides in our assumption that the $\pi$-allylic species (e.g., b, Fig. 4) which we suppose are formed on AP-580, would not exist on the other AP catalysts. The change from the $\sigma$-allylic species (c) to the $\sigma$-allylic species (d) would be prohibited on AP-300, AP-400, and AP-500, so that 1-butene, which could only be formed through the $\sigma$-allylic species (d), would not be produced. The formation of the $\pi$-allylic species would only be possible if the Lewis acid sites were strong enough (as on AP-580) for the bond between the site and the adsorbed molecule to be practically ionic, and for a conjugated carbanion to be produced. On AP-300, AP-400, and AP-500, where the Lewis acid sites are assumed to be weak, the C–Al bond would be rather covalent and therefore localized, which would make the double-bond migration impossible.

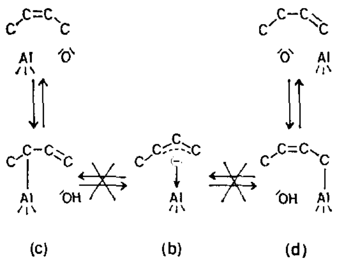

FIG. 4. Consequence of the non-interconversion between $\sigma$- and $\pi$-allylic species on AP-300, AP-400, and AP-500.

## CONCLUSION

The present work has enabled us to show the dependence of selectivity not only on the drying temperature and on the sodium content of alumina, but also on the reaction temperature, which is the more important fact. On these parameters depends the relative importance of the reactions with or without exchange of hydrogen between the olefin and the catalyst. The sites which are active for the reactions with exchange are considered as typically Brønsted acids: these reactions would occur with carbocations as intermediates. The sites which are active for the reactions without exchange are considered as Lewis acid–base pair sites: when they are strong, they catalyze both the double-bond shift and the *cis–trans* isomerization; when they are weak, they catalyze only *cis–trans* isomerization.

All this would explain the divergences found in the literature about the behavior of alumina, most of the investigations having probably been carried out on different catalysts. The isomerization of selectively deuterated molecules, as well as the co-isomerization of a light olefin with a perdeuterated one (*13*), allows us to detect reactions with or without exchange of hydrogen between the olefin and the catalyst. However, the use of selectively deuterated butenes is most suitable in determining the position of the C–H bond-breaking, which is of little interest in double-bond shift but essential in *cis–trans* isomerization. In particular, while only vinylic intermediates have been proposed (*23–25*) up to now for the *cis–trans* isomerization unaccompanied by a double-bond shift, we were able to conclude that this reaction was occurring through allylic intermediates.

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