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# The Mechanism of Double-Bond Isomerization of Olefins on Solid Acids

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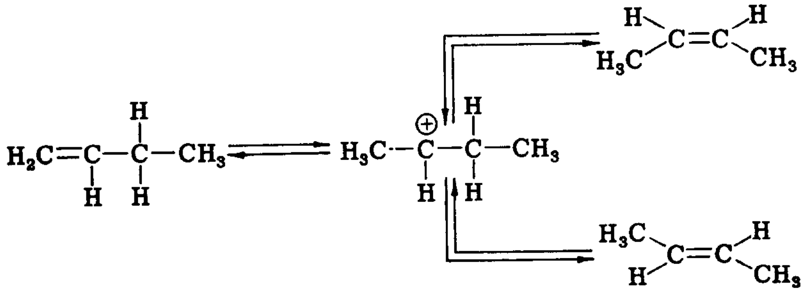
The double-bond and *cis-trans* isomerizations of *n*-butenes, *n*-pentenes, and *n*-hexenes on a series of solid acids at 150°C have been studied by means of microreactor-GLC techniques. Various acidic catalysts were found to display different selectivities with respect to double-bond shift and *cis-trans* isomerization. Upon double-bond shift, *cis*-olefins normally are formed in preference over their *trans*-isomers, an exception being the preferred formation of *trans*-2-hexene from *cis*-3-hexene. In those reactions where *cis*-olefins are preferentially formed, *trans*-olefins are also formed as true primary products of double-bond shift. It is concluded that double-bond shift largely occurs by way of a concerted reaction.

## INTRODUCTION

The simplest acid-catalyzed hydrocarbon reactions in the aliphatic series are the double-bond and *cis-trans* isomerizations of olefins, during which the hydrocarbon skeleton remains unchanged. As to the detailed mechanism of the former reaction several suggestions have been put forward, viz.: (a) Addition of a proton to a carbon atom adjacent to the double bond, followed by the shift of a hydride ion or a proton in the carbonium ion and return of a proton to the catalyst (1,2); (b) addition of a proton to a carbon atom adjacent to the double bond and subsequent release of a proton from a $\beta$-carbon atom (3,4); and (c) a "switch mechanism" in which the two processes mentioned under (b) occur simultaneously (5).

As it is likely that *cis-trans* isomerization proceeds via a carbonium ion, the first two mechanisms would imply that the same carbonium ion is an intermediate in both *cis-trans* and double-bond isomerization. In the case of the *n*-butenes, the second mechanism can be represented as shown in Scheme 1. It has been elaborated by Haag and Pines (4), who proposed that the interconversions between the carbonium ion and the olefins proceed via intermediate $\pi$-complexes.

Upon acid-catalyzed isomerization of 1-butene, the *cis*-isomer of 2-butene is formed predominantly. This phenomenon



SCHEME 1

was already mentioned by Voge and May (6) in 1946 and has also been the subject of recent investigations by Haag and Pines (4), by Lucchesi *et al.* (7), and by Foster and Cvetanovic (8). According to Haag and Pines, the *cis*- and *trans*-isomers of 2-butene are formed simultaneously from 1-butene; the preferred formation of the *cis*-isomer is then explained on the basis of a supposedly higher stability of the $\pi$-complex with the *cis*-isomer. Lucchesi *et al.*, however, concluded that a direct reaction from 1-butene to *trans*-2-butene does not take place, but that *trans*-2-butene is formed according to the reaction sequence

$$\text{1-butene} \rightleftarrows \textit{cis}\text{-2-butene} \rightleftarrows \textit{trans}\text{-2-butene} \quad (1)$$

This paper describes a study of the isomerizations of *n*-butenes, *n*-pentenes, and *n*-hexenes, catalyzed by silica-alumina, silica-magnesia, silicotungstic acid, and $\gamma$-alumina, which permitted distinguishing the three mechanisms mentioned. It was further possible to ascertain whether *cis*-2-butene is an essential intermediate in the formation of *trans*-2-butene from 1-butene.

The investigations were carried out mainly by the microreactor pulse technique introduced by Kokes *et al.* (9).

## EXPERIMENTAL METHOD

Unless stated otherwise the reactions were carried out at 150°C.

### *Pulse Experiments*

Glass or quartz microreactors were used. They contained 20–100 mg of catalyst, the void space being filled with glass beads or quartz chips. Pulses amounted to about 1 mg of olefin. Hydrogen was used as carrier gas at a flow rate of 2–5 liters/hr. Generally the hydrogen was dried over silica gel; for the experiments where the influence of the water content of the catalyst was studied, the hydrogen was dried over molecular sieves (Linde 4A) and activated alumina. Catalysts were rewetted by exposing them for 3–10 min to hydrogen that had passed through a water saturator at room temperature.

### *Flow Experiments*

In the flow experiments a sampling system was connected to the end of the microreactor. As under flow conditions most of the catalysts were rapidly deactivated, flow periods were restricted to 3 min at the end of which samples were taken. Flow experiments of long duration were made with alumina only.

### *Catalysts*

Fresh silica-alumina (e.g., Ketjen MS3-A fluid catalyst steamed at 500°C) was so active that under the conditions used complete equilibrium was reached between all isomers of the same skeletal structure. Hence, in order to obtain low conversions, partially deactivated silica-alumina catalysts were used. Deactivation was achieved in various ways: by passing large pulses of octenes over the catalyst at 275°C (deposition of polymers); by poisoning with increasing amounts of alkali; by heat treatment at 850°C; and by steam treatment at 720°C.

One of the silicotungstic acid (STA) catalysts was prepared by impregnating pure silica (Aerosil) with 5 wt % of STA. Another STA catalyst consisted of 1 wt % of STA on Hyflo, a support with wide pores and low surface area. The former catalyst was also gradually deactivated by passing octene over it at 275°C. $\gamma$-Alumina was prepared by neutral aqueous hydrolysis of aluminum isopropylate followed by calcination of the hydroxide at 500°C. Silica-magnesia was a commercial fluid catalyst.

### *Olefins*

The olefins used were either Research Grade from Phillips Petroleum Co. or pure American Petroleum Institute samples.

### *Analytical Procedure*

Butenes were separated on a 19-m dimethyl sulfoxide column at 25°C (30 wt % on Sil-O-Cel, 50–80 mesh) (10). Pentenes were analyzed on a 10-m dimethylsulfolane column at 20°C (23 wt % on Sil-O-Cel, 30–50 mesh).

The linear hexenes were analyzed on an

11-m di-$n$-propyl phthalate column at 30°C (25 wt % on Sil-O-Cel, 50–80 mesh); *cis*-3-hexene and *trans*-3-hexene were not resolved on this column.

A calibrated flame-ionization detector was used throughout.

## Results

### *Isomerization of n-Butenes on Silica-Alumina, Silica-Magnesia, and Silicotungstic Acid*

The results of experiments in which pulses of each of the $n$-butenes were passed over silica-alumina and silicotungstic acid are given in Figs. 1–3.

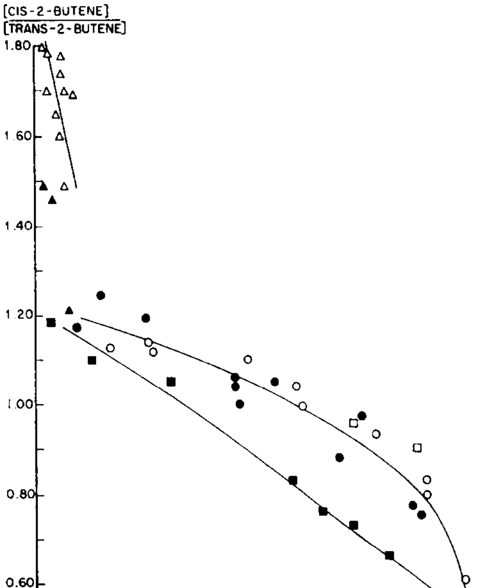


FIG. 1. Ratio of products formed upon isomerization of 1-butene at 150°C. KEY: (○) silica-alumina, progressively deactivated by coke deposition; (●) silica-alumina plus Li, Na, K, or Ba; (□) silica-alumina, steam or heat treated; (■) silicotungstic acid on Aerosil; (△) silicotungstic acid on Hyflo; (▲) sulfuric acid on Hyflo.

Corresponding experiments with silica-magnesia yielded results very similar to those for silica-alumina. In these figures the ratio of the products formed is plotted against per cent conversion to equilibrium

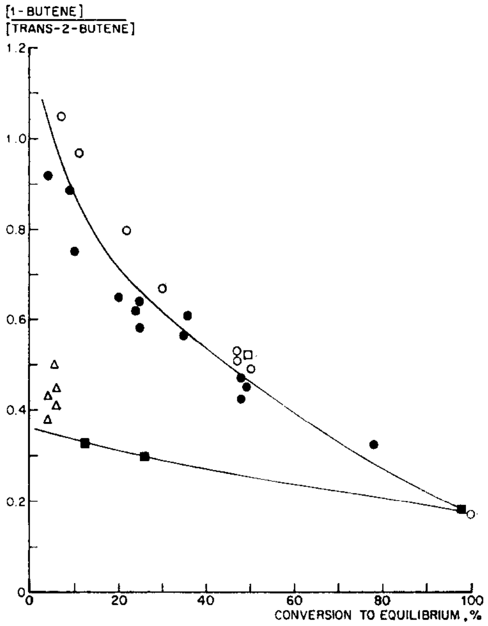


FIG. 2. Ratio of products formed upon isomerization of *cis*-2-butene at 150°C. KEY: (○) silica-alumina, progressively deactivated by coke deposition; (●) silica-alumina plus Li, Na, K, or Ba; (□) silica-alumina, steam or heat treated; (■) silicotungstic acid on Aerosil; (△) silicotungstic acid on Hyflo.

of the starting material which is defined as follows:

$$\% \text{ conversion to equilibrium} = 100 \cdot (1-x)/(1-x_e)$$

where $x$ is the mole fraction of starting material in the effluent, and $x_e$ is the equilibrium mole fraction of the starting material, both with respect to total linear butenes.*

The relative rates of all six reactions occurring in the $n$-butene system were determined at low conversions by passing alternate pulses of each of the components over the catalyst. The values are given in Table 1; for both catalysts the rate of the reaction 1-butene → *cis*-2-butene has been arbitrarily taken as unity.

From Figs. 1–3 it appears that the behavior of the silica-alumina catalysts is

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* At 150°C, $x_e$ is 0.10, 0.30, and 0.60 for 1-butene, *cis*-2-butene, and *trans*-2-butene, respectively.

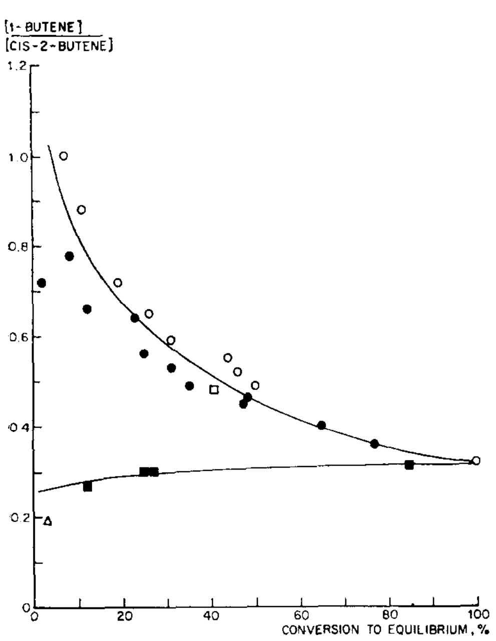


FIG. 3. Ratio of products formed upon isomerization of *trans*-2-butene at 150°C. KEY: (○) silica-alumina, progressively deactivated by coke deposition; (●) silica-alumina plus Li, Na, K, or Ba; (□) silica-alumina, steam or heat treated; (■) silicotungstic acid on Aerosil; (△) silicotungstic acid on Hyflo.

independent of the method of deactivation. Figure 1 shows that isomerization of 1-butene on all catalysts leads to mixtures of 2-butenes in which the *cis*-isomer is present in excess, not only with respect to the *cis*/*trans* equilibrium ratio but also in an absolute sense. As was expected, the *cis*/*trans* ratio at low conversions could be increased by using a macroporous catalyst of low activity (compare STA on Hyflo with STA on Aerosil).

TABLE 1

RELATIVE RATES OF THE REACTIONS IN THE *n*-BUTENE SERIES

| Reaction | Catalyst: Silica-alumina | Catalyst: Silicotungstic acid on Aerosil |
|---|---|---|
| 1-B → *c*-2-B | *1.00* | *1.00* |
| 1-B → *t*-2-B | 0.88 | 0.89 |
| *c*-2-B → 1-B | 0.29 | 0.35 |
| *c*-2-B → *t*-2-B | 0.29 | 0.93 |
| *t*-2-B → 1-B | 0.17 | 0.16 |
| *t*-2-B → *c*-2-B | 0.19 | 0.55 |

Apart from the observation that the *cis*-isomer of 2-butene is more readily formed than the *trans*-isomer, it is seen from the results that silica-alumina strongly differs from silicotungstic acid in that it clearly favors double-bond shift over *cis-trans* isomerization.

The following characteristics of the curves in Figs. 2 and 3 are consistent with these points:

1. Isomerization of *cis*-2-butene on silicotungstic acid leads to a product in which the 1-butene/*trans*-2-butene ratio is considerably higher than the corresponding equilibrium ratio, whereas upon isomerization of *trans*-2-butene the 1-butene/*cis*-2-butene ratio is lower than the equilibrium ratio.
2. With silica-alumina, the 1-butene/*trans*-2-butene and the 1-butene/*cis*-2-butene ratios are both higher than the corresponding equilibrium ratios, the difference being greater in the former case.

To ascertain whether the results obtained in the pulse experiments could be regarded as representative of the behavior of the catalyst–olefin systems, we performed some flow experiments with silica-alumina and silica-magnesia as catalysts. Although conversions were much lower than under pulse conditions, product ratios at given conversions were the same as before.

The influence of the water content of the catalyst on activity and selectivity was studied for heat-treated and steam-treated silica-alumina and for silica-magnesia. The catalysts were alternately dried at 475°C and rewetted at 150°C before passing the feeds over them. The selectivity (*cis-trans* isomerization versus double-bond shift) was not affected by the water content. The activity varied somewhat, depending on the catalyst and on whether flow or pulse experiments were done.

### *Isomerization of n-Pentenes on Silica-Alumina and Silicotungstic Acid*

Figures 4 and 5 show the results of pulse experiments with *n*-pentenes. The main characteristics are the same as observed

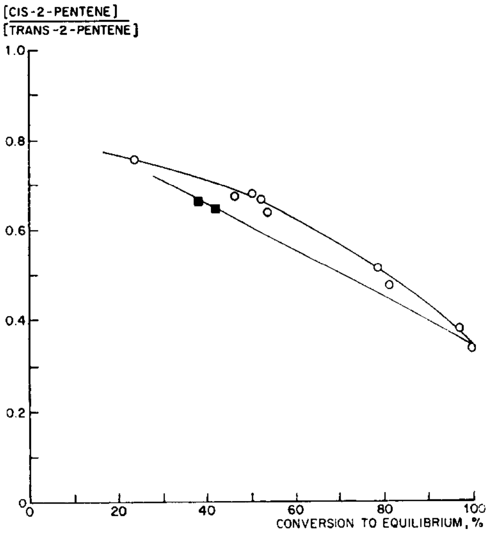


FIG. 4. Ratio of products formed upon isomerization of 1-pentene at 150°C. KEY: (○) silica-alumina, progressively deactivated by coke deposition; (■) silicotungstic acid on Aerosil.

with the butenes, the deviations that occur being inherent in the differences between butenes and pentenes.

With silica-alumina, the 1-pentene/*trans*-2-pentene and the 1-pentene/*cis*-2-pentene ratios at low conversions deviated less from the respective equilibrium ratios than the corresponding ratios did in the case of the butenes. This is because 2-pentene cannot be distinguished from 3-pentene. Consequently, the reactions

$$\textit{cis}\text{-2-pentene} \leftrightarrows \textit{trans}\text{-3-pentene} \qquad (2a)$$

$$\textit{trans}\text{-2-pentene} \rightleftarrows \textit{cis}\text{-3-pentene} \qquad (2b)$$

are counted as *cis-trans* isomerizations although they are in fact double-bond shifts. Since on silica-alumina double-bond shift proceeds more rapidly than true *cis-trans* isomerization (cf. preceding section), reactions (2a) and (2b) contribute largely to the observed *cis-trans* isomerization. In the case of silicotungstic acid, however, reactions (2a) and (2b) play but a minor part.

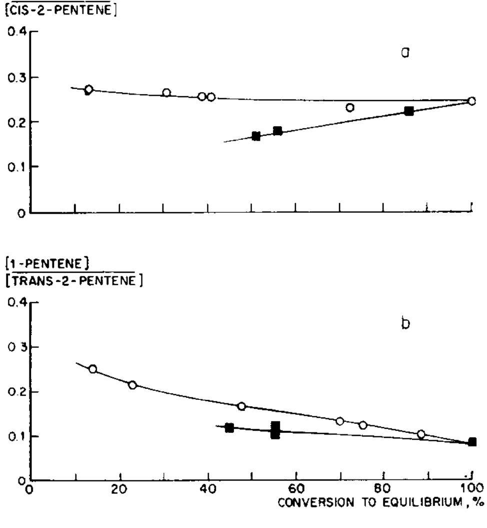


FIG. 5. Ratio of products formed upon isomerization of (a) *trans*-2-pentene and (b) *cis*-2-pentene at 150°C. KEY: (○) silica-alumina, progressively deactivated by coke deposition; (■) silicotungstic acid on Aerosil.

### *Isomerization of n-Hexenes on Silica-Alumina and Silicotungstic Acid*

In addition to the interconversions between 1-hexene and *cis*- and *trans*-2-hexene, which showed similar patterns as obtained with the butenes and pentenes, two aspects were studied with the hexenes, viz.: (a) the influence of the steric configuration of the starting material on the *cis/trans* ratio of the products formed in the reaction

$$\textit{cis}\text{-3-hexene} \rightarrow \textit{cis} + \textit{trans}\text{-2-hexene} \qquad (3a)$$

$$\textit{trans}\text{-3-hexene} \rightarrow \textit{cis} + \textit{trans}\text{-2-hexene} \qquad (3b)$$

(b) the shift of the double bond over a greater distance along the carbon chain,

$$\text{1-hexene} \rightleftarrows \text{2-hexenes} \rightleftarrows \text{3-hexenes} \qquad (4)$$

It appeared that the *cis/trans* ratio of the products strongly depended on the configuration of the starting material. The *cis/trans* ratio of the 2-hexenes was 0.9 when they were formed from 1-hexene or from *trans*-3-hexene and about 0.2 when they were formed from *cis*-3-hexene; these values, obtained at 25–35% conversions, may be compared to the equilibrium ratio 0.4.

As to reaction (4), upon isomerization of 1-hexene, the 2-hexenes were initially formed in large excess over the 3-hexenes (Table 2). Apparently the 3-hexenes are formed by a consecutive reaction.

TABLE 2
Ratio of 2-Hexenes to 3-Hexenes Formed from Isomerization of 1-Hexene

| Catalyst | 1-Hexene converted, % | $(c + t)$-2-hexenes/ $(c + t)$-3-hexenes |
|---|---|---|
| Silica-alumina | 95[a] | 3 |
| Silica-alumina | 88 | 3 |
| Silica-alumina | 79 | 4 |
| Silica-alumina | 78 | 4 |
| Silica-alumina | 75 | 3 |
| Silica-alumina | 59 | 5 |
| $\gamma$-Alumina | 47 | 8 |
| Silicotungstic acid | 39 | 7 |
| Silicotungstic acid | 5 | 11.5 |

[a] Nearly complete equilibration.

## *Isomerization of n-Butenes on γ-Alumina*

In contrast with silica-alumina and silica-magnesia, both the activity and the selectivity of alumina with respect to *n*-butene isomerization depended strongly on the water content of the catalyst. On rewetted alumina, double-bond shift was rapid in comparison with *cis-trans* isomerization; for example, the 1-butene/*trans*-2-butene ratio at low conversions of *cis*-2-butene was about unity. When alumina was heated beforehand in dry hydrogen at 475°C the rates of both reactions increased, the relative increase in the activity for *cis-trans* isomerization, however, being about fifty times that for double-bond shift. Consequently, the catalyst dried at 475°C favored *cis-trans* isomerization to such an extent that the ratio 1-butene/*trans*-2-butene was as low as 0.01–0.02. Upon more drastic dehydration (at 700°C) there was a further increase in activity, this time especially for the double-bond isomerization. As a result the very dry catalyst again favored double-bond isomerization.

A similar change in selectivity occurred when a continuous flow of *cis*-2-butene was led over alumina dried at 475°C. Figure 6 gives the variation with time of the amounts of 1-butene and *trans*-2-butene in the effluent stream. Whereas the activity for double-bond isomerization at first dropped sharply and subsequently, after 20–30 min, became constant, that for *cis-trans* isomerization decreased gradually. In this experiment the feed was pretreated with maleic anhydride and anhydrous magnesia. When the maleic-anhydride treatment was omitted (removal of traces 1,3-butadiene?) activity decline was more rapid and the amount of *trans*-2-butene formed fell below that of 1-butene after 60 min.

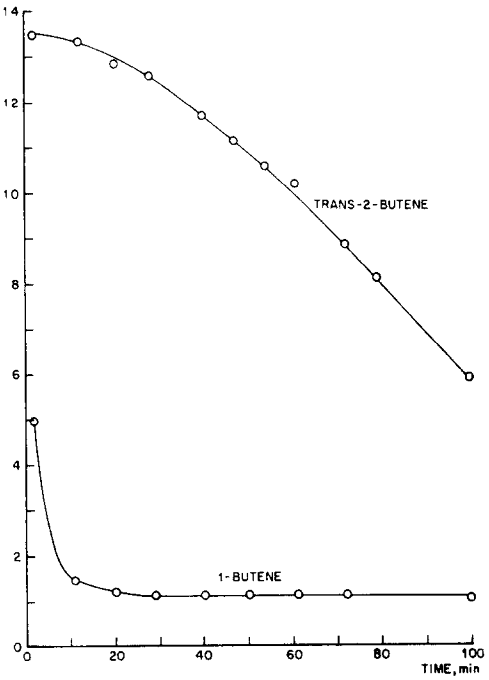


Fig. 6. Isomerization of *cis*-2-butene over alumina at 150°C. Change of activity with time. (Ordinate shows concentration of products in effluent, in mole per cent.)

## *Energy and Entropy of Activation*

1-Butene treated with maleic anhydride and magnesia was isomerized on dry alumina in a flow experiment until the activity became constant (after 30 min, compare the reversed reaction, Fig. 6). The temperature was then raised to 160°, 175°, and 200°C, and the conversions to *cis*-2-butene were determined. From the plot of log $k$ against $1/T$ (Fig. 7), a value of $12.5 \pm 0.4$ kcal/mole is found for the activation energy. From the reaction rate, expressed in molecules reacted per site per second, and the activation energy, the activation entropy can be estimated by means of the

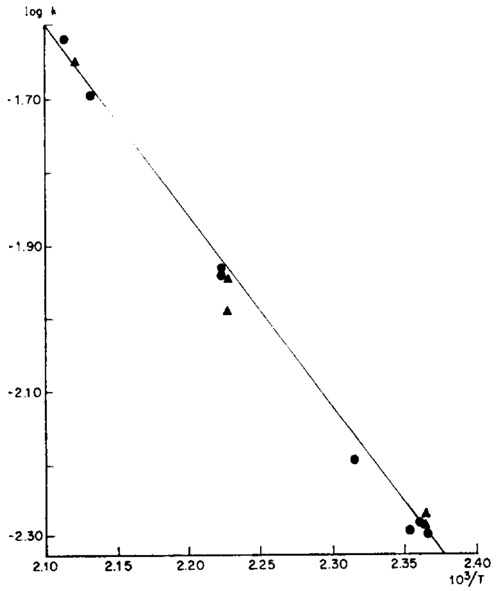


FIG. 7. Reaction 1-butene → *cis*-2-butene over γ-alumina. Temperature dependence of reaction rate $k$ (in mmoles $\sec^{-1}$ $g^{-1}$) at atmospheric pressure.

theory of absolute reaction rates (11, 12). If a value of $10^{20}$ active sites per gram of catalyst (13, 14) is inserted in the equation, the activation entropy turns out to be about −40 cal/mole deg.

## DISCUSSION

It is remarkable that in the closely related reactions, double-bond shift and *cis-trans* isomerization, appreciable catalyst-dependent selectivity is still found. One would not expect such a selectivity on basis of a mechanism in which both reactions proceed via the same intermediate. If we take the conversion of *cis*-2-butene as an example, there is no obvious reason why the ratio of the rates at which 1-butene and *trans*-2-butene are formed from the common carbonium ion should vary from catalyst to catalyst. Especially the selective poisoning of alumina as shown in Fig. 6 indicates that the catalyst surface must meet different requirements for the two reactions. Another salient feature of the present work is that the *cis/trans* ratio of the olefins formed upon double-bond shift appears to depend on the configuration of the starting material. It will be shown in the following that neither observation is compatible with a mechanism involving the same carbonium-ion intermediate in both types of isomerization, but that the assumption of a concerted reaction for double-bond shift is completely consistent with the experimental results. Before going further into this question, a few remarks on the rate-determining step, on the preferred formation of *cis*-olefins, and on the question of direct formation of *trans*-isomers will be made.

### *Rate-Determining Step*

Desorption of the products does not form the rate-determining step in the isomerization reactions. As with isomerization of 1-hexene at low conversions the 2-hexenes are formed in large excess over the 3-hexenes (Table 2), desorption of the 2-hexenes is obviously faster than isomerization of adsorbed 2-hexenes to adsorbed 3-hexenes. This result is in agreement with the negative entropy of activation for the isomerization of the butenes on alumina reported in the foregoing. In view of this either the adsorption of the olefin must be rate determining or the rate-determining step must be preceded by a $\text{olefin}_{\text{gas}} \rightleftarrows \text{olefin}_{\text{ads}}$ equilibrium that lies to the left-hand side.

Recently Peri (15) reported that in the isomerization of butene on deuterated alumina about 250 molecules are isomerized for each deuteroxyl group exchanged. Probably this results from the fact that only part of the deuteroxyl groups are catalytically active and that the deuterium in these active groups is rapidly depleted; subsequent isomerization on these sites will then occur without further exchange. This seems to agree with our results. The absolute value of the activation entropy calculated on the assumption that all hydroxyl groups are active sites is 40 eu, which is larger than one would expect from known values of the entropies of condensation and freezing. This may indicate that the number of active sites is actually lower than the number of surface hydroxyl groups. In this connection it is interesting to note that we have found that 1-butene formed in the isomerization of *cis*-2-

butene on deuterated silica contains almost exclusively the monodeuterated species.

### *Preferential Formation of cis-Isomers*

Apart from one exception to be discussed later preferential formation of *cis*-isomers was found in all cases. The phenomenon is explained by Haag and Pines (4) by assuming that the intermediate $\pi$-complex between catalyst proton and olefin is more stable for the *cis*-isomer than for the *trans*-isomer. This assumption is based on the fact that *cis*-olefins give more stable $\pi$-complexes with $Ag^+$ (16) and Pt(II) (17) than *trans*-olefins do. However, as yet no experimental proof has been furnished of *cis*-isomers giving the more stable $\pi$-complexes with proton donors. In fact, preliminary measurements of the solubilities of hydrogen chloride in *cis*- and *trans*-2-butene at —78°C did not reveal any differences. This matter therefore deserves still further attention.

A related question is whether upon double-bond shift *trans*-olefins are exclusively formed via their corresponding *cis*-isomers, as has been stated by Lucchesi *et al.* (7), or whether they are also formed as true primary products. According to our results *trans*-isomers, indeed, can be formed as true primary products. This follows directly from the fact that the *cis/trans* ratio of the 2-hexenes formed from *cis*-3-hexene is lower than the thermodynamic equilibrium ratio. Direct formation of *trans*-isomers is not restricted to this particular case. As isomerization of *trans*-2-butene on silica-alumina results in an olefin mixture in which the 1-butene/*cis*-2-butene ratio exceeds the equilibrium ratio considerably (Fig. 3), *cis*-2-butene cannot be an essential intermediate in the interconversion of 1-butene and *trans*-2-butene.

### *Mechanism of Double-Bond Shift*

The mechanism of double-bond shift proposed by Whitmore (3) and extended by Haag and Pines (4) involves a carbonium ion that is a common intermediate in both double-bond shift and *cis-trans* isomerization [Eq. (1)]. This mechanism fails to explain the main observations of the present investigation, namely, the catalyst-dependent selectivity and the influence of the configuration of the starting material on the *cis/trans* ratio of the olefins formed.

We have to take into account that the intermediate carbonium ion can have various conformations and that the configuration (*cis* or *trans*) of the olefin formed will be determined by the conformation of the carbonium ion at the moment of proton transfer to the catalyst. Now two possibilities have to be considered, i.e., either that all conformations of the carbonium ion are in rapidly established equilibrium, as has been tacitly assumed by Haag and Pines, or that the rate of conformational change is comparable to, or slower than, proton release.

The former possibility can be excluded on the basis of two observations. First, the *cis/trans* ratio of the 2-hexenes formed from the 3-hexenes depends on the configuration of the latter. Second, the relative speed of *cis-trans* isomerization with respect to the reactions in which double-bond shift is involved is three times as high for silicotungstic acid as for silica-alumina (Table 1). Even much greater differences are observed when dry and rewetted $\gamma$-alumina are compared or upon deactivation of $\gamma$-alumina during the flow experiments shown in Fig. 6. This change of selectivity would have to be explained by the assumption that the relative rates of the interconversions of 1-butene and the carbonium ion and of the 2-butenes and the carbonium ion depend on the catalyst. There is, however, no plausible reason for such an assumption. The possibility that geometric factors are involved ($\alpha$-olefin versus $\beta$-olefin) can be excluded as the same phenomenon is observed with the relative rates of the reactions *cis*-2-pentene $\rightleftarrows$ *trans*-2-pentene and 2-pentenes $\rightleftarrows$ "3"-pentenes.

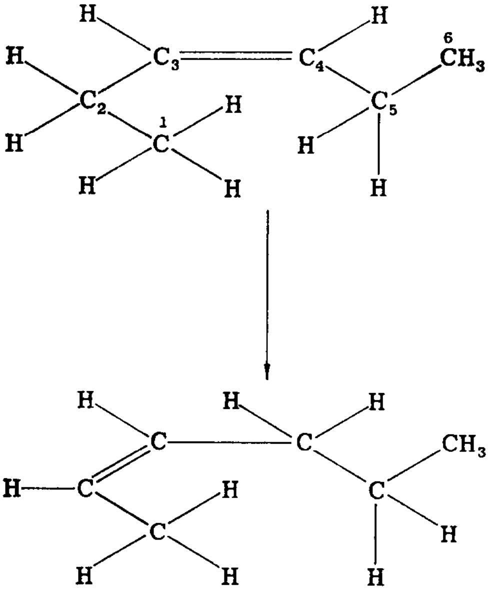
The second possibility, i.e., that the conformational change is relatively slow, would imply that selectivity of the catalyst arises from the relative rates of conformational change and of proton release to the catalyst, respectively. This possibility must also be rejected, however. For even in those cases where conformational change is rapid, that is, where *cis-trans* isomerization is rapid, one has to expect that the ratio in which, for instance, 1-butene and *trans*-2-butene are formed from *cis*-2-butene will be between unity and the thermodynamic equilibrium ratio of the compounds formed. The low 1-butene/*trans*-2-butene ratio found with silicotungstic acid and the very low corresponding values found in many cases with γ-alumina cannot be explained in this way. It may be noted in this connection that inclusion of π-complex type intermediates in the reaction scheme would tend to *raise* the expected 1-butene/*trans*-2-butene ratio.

Consequently, we conclude that a mechanism in which both double-bond shift and *cis-trans* isomerization proceed via the same carbonium ion(s) must be rejected.

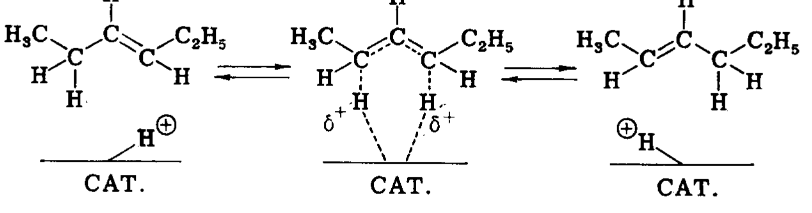
A concerted mechanism for double-bond shift as suggested by Turkevich and Smith (5), who referred to it as a "switch mechanism," is consistent with our results. It not only may explain the phenomenon of selectivity (*cis-trans* vs. double-bond isomerization), but also gives a straightforward explanation for the anomalously low *cis/trans* ratio of the 2-hexenes formed from *cis*-3-hexene. The concerted reaction can be represented as shown in Scheme 2. (Here the catalyst cat-H$^+$ lies *below* the plane of the three central carbon atoms.) The ease with which the concerted reaction occurs will be determined by the capability of the catalyst of simultaneously donating and accepting a proton.

Catalyst selectivity arises from the competition between the two reactions: one being the complete proton transfer to form a carbonium ion and the other, the concerted reaction. The former reaction leads to *cis-trans* isomerization and, to a minor extent, to double-bond shift, whereas the latter gives double-bond shift only.

The anomalous *cis/trans* ratio for the 2-hexenes when formed from *cis*-3-hexene is the result of steric factors. In the conversion of 3-hexenes to 2-hexenes all carbon atoms $C_1$—$C_5$ have to lie in a plane during the critical stage of the reaction when the bonds between $C_3$ and $C_4$ and between $C_2$ and $C_3$ have a partial double-bond character. In the case of the reaction *cis*-3-hexene → *cis*-2-hexene this is energetically unfavorable because of the steric hindrance between the hydrogen atoms at $C_1$ and $C_5$:



No such repulsion occurs in the reactions *cis*-3-hexene → *trans*-2-hexene and *trans*-3-hexene → *cis* or *trans*-2-hexene. In



SCHEME 2

the latter case the normal preference for formation of *cis*-isomers is found.

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