JOURNAL OF CATALYSIS 32, 294-303 (1974)

# The Mechanisms of Isomerization and Exchange of Olefins Over Metal Catalysts

## III. Isomerization of Butenes in the Presence of Perdeuteropropene on Iron Films

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Received February 23, 1973

The initial deuterium distributions of the reaction products obtained by isomerization of but-1-enes, *cis*- and *trans*-butenes in the presence of perdeuteropropene on iron films at −37°C are examined in this paper, together with the product distributions obtained by co-isomerization of *cis*-$d_0$- and $d_8$-butenes.

While but-1-ene yields poorly exchanged *cis* and *trans* isomers, best interpreted by assuming an intramolecular hydrogen shift, highly deuterated but-1-enes with a maximum in $d_8$ are obtained from *cis*- and *trans*-butenes. This result can only be explained if two different types of site for double bond migration are present on the surface and if $\alpha$- and $\beta$-olefins are adsorbed on each type of site with very different strengths.

*Cis–trans* isomerization, on the other hand, occurs mostly by a Horiuti–Polanyi mechanism restricted to a single interconversion between mono- and diadsorbed species (formation of the $d_1$ isomer), but also by a direct process which does not involve the breaking or the formation of any C–H bond and leads to $d_0$-butenes.

The results obtained in the co-isomerization experiment confirm these views and suggest moreover that the replacement of the hydrogen atoms of an olefin during the exchange reaction is fast when compared with the mobility of the adsorbed hydrogen or deuterium atoms.

## INTRODUCTION

In this paper, we discuss the deuterium distribution of the exchanged and isomerized olefins obtained from *cis*-butene, *trans*-butene and but-1-ene on iron films in the presence of perdeuteropropene. The co-isomerization of light and heavy *cis*-butenes are also considered.

## EXPERIMENTAL METHODS

The experimental procedures and the analytical methods used in the study of the isomerization and exchange of butenes in the presence of perdeuteropropene have been described in the preceding paper (*1*). This experimental part is restricted to the methods and techniques used for the co-isomerization of $d_0$ and $d_8$ *cis*-butene.

**Preparation of *cis*-$C_4D_8$ (*2*).** Three grams of alumina prepared from aluminum isopropoxide were activated for 24 hr in nitrogen, 24 hr in oxygen at 640°C, and then outgassed at the same temperature until a vacuum of $10^{-5}$ Torr was obtained. A mixture of 2.6 mmole of but-1-ene and 9.4 mmole of deuterium (99.9% of isotopic purity) was admitted to this catalyst in a circulating flow system and reacted for 30 min at 200°C. The materials noncondensable in liquid nitrogen ($H_2$–HD–$D_2$) were then removed and a new dose of deuterium admitted. After 10 similar operations, a mixture of butenes with an isotopic purity of 99.7% (96.8 and 3.2% of $d_8$- and $d_7$-butenes, respectively) was obtained, contaminated by 6% of perdeutero-

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TABLE 1

ISOMERIZATION OF BUTENES IN THE PRESENCE OF $C_3D_6$ ON IRON FILM AT −37°C

| Reacting hydrocarbons: | But-1-ene | | | | | | *cis*-Butene | | | | | | *trans*-Butene | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_3D_6/C_4H_8$ ratio: | 9 | | | 15.4 | | | 14 | | | 14 | | | 14 | | | 14 | | |
| Isomers: | B-1 | *trans* | *cis* | B-1 | *trans* | *cis* | B-1 | *trans* | *cis* | B-1 | *trans* | *cis* | B-1 | *trans* | *cis* | B-1 | *trans* | *cis* |
| %: | 98.2 | 1 | 0.8 | 98.3 | 1 | 0.7 | 1.8 | 0.95 | 97.3 | 0.6 | 0.4 | 99 | 0.53 | 99.4 | 0.07 | 0.9 | 98.9 | 0.2 |
| $d_0$ | 53.4 | 52.6 | 55.2 | 33.6 | 33 | 38.2 | 2.2 | 25.6 | 99.9 | 1 | 26.4 | 100 | — | 100 | 8.3 | 1.9 | 99.7 | 13.1 |
| $d_1$ | 42.7 | 33.9 | 31.9 | 56.1 | 41.6 | 38.8 | 3.3 | 59.2 | 0.1 | 7.6 | 65.6 | — | 3.2 | — | 77.8 | 1.7 | 0.3 | 81.7 |
| $d_2$ | 3.05 | 9.2 | 8.9 | 8.5 | 15.8 | 15.9 | 7 | 2.2 | — | 15.8 | 1.9 | — | 3.3 | — | 1.8 | 3.3 | — | 1.3 |
| $d_3$ | 2.25 | 2.7 | 2.8 | 1.15 | 5.3 | 5 | 4.5 | 4.1 | — | 11.6 | 1.3 | — | 4.9 | — | 2.3 | 5.4 | — | 1.1 |
| $d_4$ | 0.05 | 1.05 | 0.9 | 0.1 | 2.1 | 1.5 | 2.7 | 3.9 | — | 7.9 | 1.05 | — | 4.7 | — | 2.2 | 5.7 | — | 1 |
| $d_5$ | — | 0.30 | 0.3 | 0.01 | 1 | 0.3 | 0.9 | 1.5 | — | 3.8 | 1.05 | — | 3.7 | — | 2.2 | 3.9 | — | 0.7 |
| $d_6$ | 0.01 | 0.25 | — | — | 0.7 | 0.3 | 1.7 | 0.5 | — | 1.7 | 0.85 | — | 0.6 | — | 2.6 | 0.7 | — | 0.7 |
| $d_7$ | 0.15 | — | — | 0.05 | 0.4 | — | 24 | 1.1 | — | 5.8 | 0.75 | — | 9.3 | — | 0.6 | 11 | — | 0.1 |
| $d_8$ | 0.40 | — | — | 0.50 | 0.1 | — | 53.7 | 1.9 | — | 44.8 | 1.1 | — | 70.3 | — | 2.2 | 66.4 | — | 0.3 |

butanes; this equilibrium mixture of but-1-ene, *cis*- and *trans*-butenes was separated on a dimethylsulfolane column at 0°C. This *cis*-butene thus prepared contained less than 1.5% of *trans*-butene and 0.1% of but-1-ene.

**Experimental procedure.** A mixture of 2.9 Torr of *cis*-$C_4D_8$ and 3.2 Torr of *cis*-$C_4H_8$ was introduced to a reaction vessel of 400 ml on the freshly prepared iron film at −37°C and allowed to react during 5 min at this temperature.

The reaction products were then removed from the reaction vessel, separated by gas chromatography on a DMS column and each product was analyzed for its isotopic content. The purity of each isomer after separation was better than 99% and corrections were made on each mass spectrum to eliminate the contribution of the various impurities.

**Mass spectrometric analysis.** The analyses were performed with 25 eV electrons using an MS2 mass spectrometer. After the usual corrections for the naturally occurring isotopes, the fragmentation calculations were effected on a statistical basis by using the three first fragments of the light and heavy molecules ($C_4H_8$ and $C_4D_8$).

## RESULTS

### *I. Reactions of Butenes in the Presence of $C_3D_6$*

The deuterium distributions of the exchanged and isomerized products obtained from but-1-ene, *cis*- and *trans*-butenes are reported in Table 1; each experiment was repeated twice.

#### *But-1-ene*

Together with the very fast quasi-simple exchange of the molecule, already discussed, a slow isomerization yields *cis*- and *trans*-butenes in approximately equal amounts. The deuterium distributions of each isomer are very similar; they include mainly $d_0$ and $d_1$ (about 85% of the total products) with decreasing amounts of the more highly deuterated molecules.

#### *cis-Butene*

The isomerization of *cis*-butene is about as fast as the isomerization of but-1-ene while its exchange is negligible. The deuterium pattern of the two reaction products, but-1-ene and *trans*-butene, are very different. The but-1-enes distribution may be considered as the sum of two different distributions. The major one, B, characteristic of a multiple exchange, contains mainly $d_7$ and $d_8$. The other one, D, includes all the isomers from $d_0$ to $d_6$ with a maximum at $d_2$. The *trans*-butenes distribution, on the other hand, consists mainly of $d_0$ and $d_1$; only small amounts of the most highly deuterated molecules are present.

#### *trans-Butene*

The behavior of this molecule on an iron film in the presence of $C_3D_6$ is very much the same as the behavior of *cis*-butene: the exchange of the *trans*-butene is negligible. The highly deuterated *but-1-enes* represent more than 75% of the total α-olefins. Distribution D is also present with a slight maximum at $d_3$ or $d_4$. $d_1$-*cis-Butene* and, to a smaller extent, $d_0$, are the major products obtained by *cis–trans* isomerization.

### *II. Co-isomerization of cis-Butenes $d_0$ and $d_8$*

The deuterium distributions of the various isomers are reported in Table 2. While

TABLE 2
CO-ISOMERIZATION OF *cis*-BUTENES $d_0$ AND $d_8$ ON IRON FILM AT −37°C

| Isomers: | B-1 | *trans* | *cis* |
|---|---|---|---|
| %: | 0.6 | 3.7 | 95.7 |
| $d_0$ | 28.7 | 47 | 51.9 |
| $d_1$ | 26.2 | 14.9 | — |
| $d_2$ | 10.8 | 0.75 | — |
| $d_3$ | 4.0 | 0.20 | — |
| $d_4$ | 3.0 | 0.10 | — |
| $d_5$ | 5.3 | 0.45 | — |
| $d_6$ | 8.4 | 1.30 | — |
| $d_7$ | 9 | 18 | 1.5 |
| $d_8$ | 4.6 | 17.3 | 46.5 |

*cis*-butene consists only of the reacting species, the *trans*-butenes include mainly $d_0$ and $d_1$, $d_7$ and $d_8$ with the approximate ratios $d_0/d_1 = 3$ and $d_7/d_8 = 1$. The but-1-ene distributions are obviously divided into two parts: one includes the light molecules $d_0$, $d_1$, $d_2$, and in the other, less important, the highly deuterated isomers from $d_5$ to $d_8$ are present.

## DISCUSSION

Three reactions take place simultaneously when butenes and $C_3D_6$ are contacted with an iron film: exchange of the reacting olefins, double bond shift and *cis–trans* isomerization.

Exchange has already been discussed (*1*). It is much faster for an $\alpha$-olefin than for a $\beta$-olefin (the rates differ at least by two orders of magnitude); the exchange of olefins is a "simple" one and involves only the breaking of vinylic carbon–hydrogen bonds (*1*).

The present discussion is mainly devoted to the two other reactions occurring, namely, double bond shift and *cis–trans* isomerization.

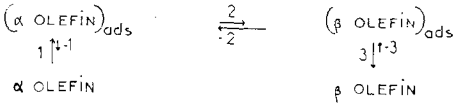
### *Double Bond Migration*

For this reaction, as for exchange, the but-1-ene and the but-2-enes react in entirely different ways. While the *cis*- and *trans*-butenes obtained from but-1-ene are very poorly exchanged, *cis*- and *trans*-butenes yield mostly the perdeutero but-1-ene ($d_8$).

The very large amounts of $d_0$-but-2-enes obtained *in the isomerization of but-1-ene* strongly suggests that the reaction proceeds mostly *by a simple intramolecular hydrogen shift* (Reaction A). Since the exchange of the but-1-ene is very fast in comparison with its isomerization, the readsorption of the adsorbed molecules has to be considered and part of the $d_1$- and $d_2$-but-2-enes can also be explained by the same process (Appendix 1).

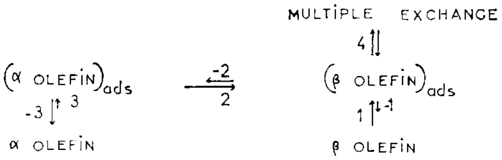
*In the isomerization of cis- and trans-butenes,* on the other hand, the $d_0$-but-1-ene which is expected by the reverse of Reaction A is formed only in minor amount. Double bond shift in this case *is accompanied by an almost complete exchange* of all the hydrogen atoms so that $d_7$- and $d_8$-but-1-enes represent more than 80% of the reaction products (Reaction B).

The existence of two different isomerization reactions, A and B for the $\alpha$- and $\beta$-olefins, which seems to violate the principle of microscopic reversibility, can only be explained if one assumes that two types of sites A and B are present on the catalyst surface and that the strengths of adsorption for $\alpha$- and $\beta$-olefins are very different on each type of site.



SCHEME A

*On sites A,* the but-1-ene would be much more strongly adsorbed than the but-2-enes and therefore the direct intramolecular shift associated with these sites would be restricted to the $\alpha$-olefins (Scheme A). Hilaire and Gault (*4*) proposed that $\pi$-olefinic species were the precursor for this reaction and Smith and Swoap (*6*) suggested as a possible transition state an intermediate involving a bridged hydrogen atom between two carbon atoms in the $\alpha$–$\gamma$ position (*6*).



SCHEME B

*On sites B,* $\beta$-olefins are much more strongly adsorbed than $\alpha$-olefins. As a first consequence of this, when the reacting molecule is the *cis*- or the *trans*-but-2-ene, repeated exchange and isomerization to but-1-ene takes place much faster than desorption of the adsorbed $\beta$-olefin, so that perdeuterobut-1-ene is the major reaction product (Scheme B). Conversely, the residence time for an adsorbed $\alpha$-olefin on the surface is expected to be very small, so that the only possible reaction is a simple exchange of the molecule. This latter reaction does indeed exist on iron films, and was shown to take place with the dissociation of vinylic C–H bonds (*1*).

It is therefore tempting to correlate the B-type sites with a dissociative adsorption of the olefins at a vinylic carbon atom. When the adsorbed molecule is weakly held to the surface ($\alpha$-olefin), only a fast *simple* exchange takes place. When the adsorbed molecule is strongly bonded to the surface ($\beta$-olefin), *extensive* exchange and double bond shift occur. It is interesting to note that extensive exchange of but-1-enes which proceeds to a very small, but significant, extent can be explained similarly by assuming two consecutive isomerizations before desorption (successions of steps 3, 2, 4, $-2$, $-3$ in Scheme B).

In conclusion, the double bond migration occurs mostly by two processes A and B, i.e., direct intramolecular hydrogen shift and isomerization assisted by the formation of a vinylic carbon–metal bond. Further confirmation and developments of this theory will be developed in a later paper.

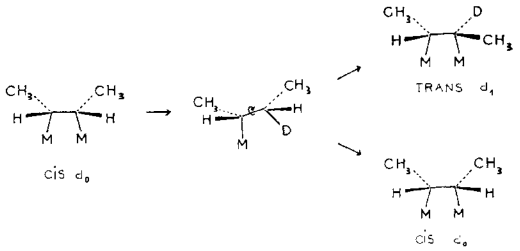
It should be pointed out, however, that processes A and B do not represent *all* the possible isomerization paths. In the isomerization of but-1-ene, 20–30% of the but-2-enes, containing 1 to 5 deuterium atoms, cannot be accounted for by an intramolecular double bond shift and similarly part of the but-1-ene distribution in the isomerization of *cis*- or *trans*-butenes include molecules with a small number of deuterium atoms (1 to 5) and a maximum in $d_3$. We shall not try to discuss for the moment the isomerization mechanism D associated with these distributions.

## *Cis–trans Isomerization*

### *Co-isomerization of $d_0$- and $d_8$-cis-Butenes*

ene yields mainly the $d_0$ and $d_1$ isomers.

The formation of $d_1$ is very easily explained by a simple Horiuti–Polanyi mechanism, namely, adsorption of the olefin, addition of a deuterium atom to form the half-hydrogenated state, free rotation around the $C_2$–$C_3$ bond, dehydrogenation and desorption of the olefin (Scheme C). The same mechanism accounts also for the fact that neither *cis*- nor *trans*-butene is exchanged during the reaction. When *cis*-butene, for example, is formed from *cis*-butene, after the succession of steps described in Scheme C, the same deuterium atom which has been added to the adsorbed olefin is taken off in the dehydrogenation step. The large break in the product distribution after $d_1$ suggests that the Horiuti–Polanyi process takes place only once for each reacting adsorbed molecule; in other words, the desorption of an adsorbed olefin is much faster than its rehydrogenation to the half-hydrogenated intermediate. It is worthwhile to point out also at this stage that the Horiuti–Polanyi mechanism seems to be restricted to the *cis–trans* isomerization. The amounts of $d_1$-*but*-1-ene and more generally of light but-1-enes are very small in the isomerization of *cis*- or *trans*-butene. This result implies: (i) that the picture of several contiguous metal atoms allowing the propagation of exchange to more than two carbon atoms in a chain cannot be considered in the case of an iron catalyst, and (ii) that the free rotation along the $\sigma$ carbon–metal bond is very slow in comparison with the free rotation around the carbon–carbon bond in the half-hydrogenated state.



SCHEME C

The most interesting feature in the *cis–trans* isomerization of butenes is the formation of very large amounts of $d_0$ isomer. This $d_0$-butene could be obtained either on account of a very high isotopic dilution on the surface or as the result of an independent process, i.e., *a direct cis–trans isomerization,* which would not involve any break or formation of a carbon hydrogen bond.

Since the dissociative adsorption of an $\alpha$-olefin ($C_3D_6$) is much easier than the dissociative adsorption of a $\beta$-olefin (*cis*- or *trans*-butene), as exemplified by the exchange experiments, the D/H ratio in the hydrogen deuterium pool on the surface is certainly much higher than the one in the gas phase (equal to 9.4 according to the relative pressures of $C_3D_6$ and light butene). One may therefore consider that most of the $d_0$ isomer formed is due to a *direct cis–trans isomerization process.*

Also in favor of this hypothesis is the fact that $d_0$ is more important among the *trans*-butenes formed from *cis*-butene than among the *cis*-butenes formed from *trans*-butene. A very simple explanation may be given for this fact. Let us suppose two processes for *cis–trans* isomerization: one, C, involving adsorbed olefins and a Horiuti–Polanyi mechanism; the other, E, similar to the *cis–trans* isomerization occurring in the gas phase via a triplet transition state and therefore involving molecules which are very slightly adsorbed or even in the gas phase

$$(cis)_{\text{ads}} \underset{k_{-\mathrm{C}}}{\overset{k_{\mathrm{C}}}{\rightleftharpoons}} (trans)_{\text{ads}}, \qquad \text{(C)}$$

$$cis \underset{k_{-\mathrm{E}}}{\overset{k_{\mathrm{E}}}{\rightleftharpoons}} trans. \qquad \text{(E)}$$

The energy levels of *cis*- and *trans*-butenes are very different and $k_{\mathrm{E}}/k_{-\mathrm{E}} \gg 1$ (3 at 25°C). On the other hand it is known that olefin adsorption stabilizes the *cis* configuration so that $k_{\mathrm{C}}/k_{-\mathrm{C}}$ is expected to be smaller or equal to 1. If $(d_0/d_1)_{cis}$ and $(d_0/d_1)_{trans}$ are the ratios between the light and monodeutero isomers obtained from *trans*- and *cis*-butenes, respectively, the expression,

$$\rho = \left(\frac{d_0}{d_1}\right)_{cis} \bigg/ \left(\frac{d_0}{d_1}\right)_{trans} = \left(\frac{k_{-\mathrm{E}}}{k_{-\mathrm{C}}}\right) \bigg/ \left(\frac{k_{\mathrm{E}}}{k_{\mathrm{C}}}\right) = \left(\frac{k_{\mathrm{C}}}{k_{-\mathrm{C}}}\right) \bigg/ \left(\frac{k_{\mathrm{E}}}{k_{-\mathrm{E}}}\right),$$

should be much smaller than unity, which is effectively observed.

Both mechanisms C and E, the Horiuti–Polanyi mechanism and direct *cis–trans* isomerization, explain most of the reaction products. The $d_0$ and $d_1$ molecules indeed represent 85 to 95% of the total isomers. Besides $d_0$ and $d_1$, however, the deuterium distributions of the *cis–trans* isomerization products include, in very small amounts, molecules with a small number of deuterium atoms (maximum at $d_2$ or $d_3$) and perdeuteromolecules. These parts of the distribution correspond closely to the molecules formed in double bond shift by mechanisms D and B,* respectively. It seems likely that these mechanisms take place also, but to a very small extent, in the *cis–trans* isomerization process.

### *Co-isomerization of $d_0$- and $d_8$-cis-Butenes*

The study of this reaction confirms the previous deductions and gives useful additional indications concerning the reaction mechanisms.

### *Double Bond Shift*

The distributions of the deutero but-1-enes obtained in this reaction afford information concerning the mobility of the adsorbed hydrogen and deuterium atoms on the surface. If the adsorbed hydrogens were entirely mobile on the catalyst, one would expect that the surface hydrogen and deuterium concentrations would remain constant throughout the reaction. These concentrations would depend upon the relative adsorption and reaction rates of the light and heavy *cis*-butenes. Since most of the but-1-ene obtained from the *cis*-butene is entirely exchanged, one would expect then *both* $d_0$- and $d_8$-*cis*-butene yielding the same statistical distribution as corresponds to the surface hydrogen–deuterium pool.

The results are entirely different. The observed but-1-ene distribution may be considered as the combination of two statistical distributions including, respectively, the lighter and the heavier deutero-but-1-enes. The values of $d_1^2/d_0d_2$ (2.21) and of $d_7^2/d_6d_8$ (2.10) are in fair agree-

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* The participation of sites B in *cis–trans* isomerization will be further discussed in a later paper.

ment indeed with the expected statistical value.

$$\frac{(C_8{}^1)^2}{C_8{}^0C_8{}^2} = \frac{(C_8{}^7)^2}{C_8{}^6C_8{}^8} = 2.28.$$

A reasonable interpretation of the but-1-ene deuterium distributions could therefore be as follows: the *cis*-$C_4H_8$ would exchange all their hydrogen atoms with a hydrogen–deuterium pool considerably enriched in the light isotope ($H/H + D = 0.89$), while the *cis*-$C_4D_8$ would exchange all their deuterium atoms with a "heavy" mixture of adsorbed hydrogen and deuterium atoms ($H/H + D = 0.205$). That would mean:

1. That the average hydrogen–deuterium pool on the surface is highly perturbed by the adsorption and exchange of an olefin.
2. That the mobility of an adsorbed hydrogen is slow when compared with the replacement of the hydrogen atoms of an olefin during the exchange reaction.

The question then arises as to why this "local" isotopic dilution (depending upon the nature, light or heavy, of the molecule adsorbed) is observed in the co-isomerization of $d_0$- and $d_8$-*cis*-butenes and *not* in the isomerization of *cis*-butene-$d_0$ in the presence of $C_3D_6$, where the perdeuterobut-1-ene is always the major product. To answer this question, one should keep in mind the very large difference between the exchange rates of $\alpha$- and $\beta$-olefins: this difference expresses the large difference between the rates of desorption for the dissociatively adsorbed $\alpha$- and $\beta$-olefins. In the isomerization experiments, $C_3D_6$ replaces very quickly, by repeated adsorption and desorption, the hydrogen atoms present on the surface by deuterium atoms, and an extensive exchange may take place. In the co-isomerization experiments, the desorption of a dissociatively adsorbed *cis*-butene is very slow, so that a molecule of *cis*-butene-$d_0$, for example, can only replace its hydrogen atoms by its own hydrogens and the hydrogens (or deuteriums) of the molecules adsorbed in the immediate vicinity, when there are any. The result of this process, of course, is a local surface hydrogen–deuterium pool very rich in hydrogen in the proximity of an adsorbed $d_0$ molecule and very rich in deuterium in the proximity of an adsorbed $d_8$-butene.

If this interpretation is correct, the ratio

$$\sum_{i=0}^{4} d_i \Big/ \sum_{j=5}^{8} d_j$$

is a good measure of the isotopic effect for the isomerization of *cis*-butene to but-1-ene. This ratio, 3.0, very high for a secondary isotopic effect, but much lower than the maximum regular primary isotopic effect, as calculated by using statistical mechanic considerations (*5*), strongly suggests that the rate determining step in the double bond migration involves a transition state where the C–H bond is strongly weakened, but not completely broken.

That is indeed what is expected if an intramolecular hydrogen shift is the rate determining step in isomerization.

We believe then that on iron catalysts the double bond migration occurs on sites B as on site A by an intramolecular hydrogen shift. While the distributions of the deuterobut-2-enes obtained from the but-1-enes allowed us to detect this type of rearrangement, such a mechanism could not be detected from the but-1-enes distributions obtained in the isomerization of but-2-enes, on account of the very fast extensive exchange of the adsorbed olefins.

### *Cis–trans Isomerization*

It is shown in this section that the deuterium distribution of the *trans*-butene obtained by co-isomerization of *cis*-$d_0$ and $d_8$-butenes cannot be explained by a simple Horiuti–Polanyi mechanism and that an additional process, namely, direct *cis–trans* isomerization, must be assumed to interpret the results.

The Horiuti–Polanyi mechanism involves two steps, viz., hydrogenation of an adsorbed olefin to form a half-hydrogenated state (step a), and dehydrogenation of the alkyl radical to restore the adsorbed olefin (step b).

One may *first* suppose that step a is rate determining. Let us assume:

1. That the probability of rupturing a

C–H or a C–D bond in the alkyl radical is the same and does not depend upon the hydrogen and deuterium content of this radical.

2. That the surface concentrations of the hydrogen and deuterium, (H) and (D), reacting with the olefins in step a are the same for a light and for a heavy molecule.

The first assumption may be easily justified: since step a and not step b is rate determining, neither a primary nor a secondary isotopic effect should be observed for step b. The second assumption implies that the Horiuti–Polanyi mechanism takes place on special sites C and that the *associative* adsorption of butenes-$d_0$ or -$d_8$ on these sites do not influence at all the relative rates of *dissociative* adsorption of light and heavy molecules, which is quite reasonable.

Let us now call $k$ and $k\alpha$ the rate constants for step a in the half hydrogenation of *cis*-butene-$d_0$ and -$d_8$, respectively, and use (*cis*-$d_0$) and (*cis*-$d_8$) to describe the surface concentrations of these molecules. The initial distribution of $d_0$-, $d_1$-, $d_7$- and $d_8$-*trans*-butenes, $D_0$, $D_1$, $D_7$ and $D_8$ will be

$$D_0 = \tfrac{1}{2}k(\mathrm{H})\ (cis\text{-}d_0),$$
$$D_1 = \tfrac{1}{2}k\alpha(\mathrm{D})\ (cis\text{-}d_0),$$
$$D_7 = \tfrac{1}{2}k(\mathrm{H})\ (cis\text{-}d_8),$$
$$D_8 = \tfrac{1}{2}k\alpha(\mathrm{D})\ (cis\text{-}d_8).$$

Therefore

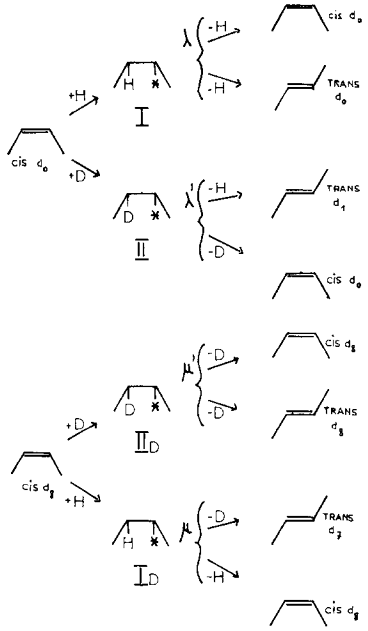
$$\frac{D_0}{D_1} = \frac{D_7}{D_8} = \frac{1}{\alpha}\frac{(\mathrm{H})}{(\mathrm{D})}.$$

*According to a second hypothesis,* step b could be rate determining. Call $\lambda$, $\lambda'$, $\mu$, $\mu'$ the overall rates of dehydrogenation of the alkyl radicals I, II, $\mathrm{I_D}$, $\mathrm{II_D}$, respectively (Scheme C') and $\alpha'$ the ratio between the probabilities of rupturing a C–D and a C–H bond. If any secondary isotopic effect is neglected, the following relationships are verified:

$$\frac{\lambda'}{\lambda} = \frac{1+\alpha'}{2};\quad \frac{\mu}{\mu'} = \frac{1+\alpha'}{2\alpha'};\quad \lambda' = \mu,$$

and the initial distribution $D_0$, $D_1$, $D_7$, $D_8$ may be expressed as follows:

$$D_0 = \frac{\lambda}{2}\,(\mathrm{I}) \qquad D_7 = \mu\frac{\alpha'}{1+\alpha'}\,(\mathrm{I_D}),$$
$$D_1 = \frac{\lambda'}{1+\alpha'}\,(\mathrm{II}) \qquad D_8 = \frac{\mu'}{2}\,(\mathrm{II_D}).$$



SCHEME C'

One may assume that the ratio between $d_0$-alkyl and $d_1$-alkyl radicals, (I)/(II), equals the ratio between $d_7$-alkyl and $d_8$-alkyl radicals, $(\mathrm{I_D})/(\mathrm{II_D})$. If it is assumed that no isotopic effect takes place in step a (formation of alkyl radicals), this assumption is identical to the one previously made, where $d_0$-and $d_8$-*cis*-butenes were supposed to react with the same hydrogen–deuterium pool on the surface. As a consequence of this:

$$(\mathrm{I_D})/(\mathrm{II_D}) = (\mathrm{I})/(\mathrm{II}) = (\mathrm{H})/(\mathrm{D}),$$

whence

$$\frac{D_0}{D_1} = \frac{D_7}{D_8} = \frac{(\mathrm{H})}{(\mathrm{D})}.$$

It is noticeable that the observed ratio $D_0/D_1$ is three times larger than the ratio $D_7/D_8$, while according to either hypothesis, one should observe the equality of

$D_0/D_1$ and $D_7/D_8$. This result can only be explained *if a direct cis–trans isomerization takes place.*

## GENERAL DISCUSSION

The main results of this study are:

1. The existence of two different types of sites A and B for the adsorption of butenes on iron.
2. The existence of direct double bond shift and *cis–trans* isomerization processes.

While the but-2-enes are generally found to be more strongly held than but-1-ene on catalysts and it is the case indeed on sites B, the results show definitely the existence on iron of another type of sites A associated with a direct double bond shift where but-1-ene and not but-2-enes are sufficiently held to undergo a reaction.

The possibility of a double bond migration by hydrogen intramolecular shift, first envisaged by Smith and Swoap (*6*) for the reactions of cyclohexene on palladium, received a good support with the study of the reaction of dimethylcyclopentenes on palladium films in the presence of deuterium (*4*) or perdeuteropropene (*3*). The interesting feature with but-1-ene on iron, unlike palladium, is that the intramolecular double bond shift does not take place on the same sites as the exchange, so that direct evidence can be provided for this reaction.

The existence of a direct process for the *cis–trans* isomerization of butenes is also a new concept, at least in metal catalysis. Good evidence for a direct *cis–trans* isomerization of butenes has been provided independently on a magnesium oxide catalyst (*7*) and on calcium films (*8*). The proof for this mechanism relied upon the almost complete absence of deuterium in the isomers obtained either by co-isomerization of *cis*-butene-$d_0$ and -$d_8$ (*7, 8*) or by isomerization of *cis*-butene in the presence of $C_3D_6$.

On transition metals, on the other hand, the direct process does not seem to be the only, or even the major, route for *cis–trans* isomerization. It is therefore difficult to demonstrate the existence of this reaction unambiguously. However, Yasuda and Hirota (*9*), recalculating the data obtained by Flanagan and Rabinovitch in the isomerization of $C_2H_2D_2$ on nickel, concluded that a direct *cis–trans* isomerization process should be included in the reaction mechanism. In the present study we believe that the presence of very large amounts of $d_0$ isomers obtained among the reaction products represent a very good proof for a direct *cis–trans* isomerization process on iron: indeed, this metal seems to be a good catalyst among the transition metals for this particular reaction.

## APPENDIX

The amounts of $d_1$-but-2-enes obtained by an intramolecular hydrogen shift (mechanism A) may be easily calculated if one assumes that the exchange of but-1-ene is simple and that both exchange and isomerization follow first order kinetics ($k$ and $k'$ being the rate constants). As a first approximation, only one hydrogen atom is exchanged in but-1-ene. Let us call $\lambda$ the deuterium content of this molecule at time *t*.

$$\left.\begin{array}{l} d_0 = 1 - \lambda \\ d_1 = \lambda \end{array}\right\}. \qquad (1)$$

The variation of $\lambda$ may be obtained from the following equation,

$$\frac{d(d_0)}{dt} = k[-\mu d_0 + (1 - \mu)d_1], \qquad (2)$$

where $\mu$ represents the constant surface concentration of deuterium. From Eqs. (1) and (2) one may deduce Eqs. (3) and (4).

$$\frac{d\lambda}{dt} = k(\mu - \lambda), \qquad (3)$$

whence

$$\lambda = \mu(1 - e^{-kt}). \qquad (4)$$

Let us consider now the direct isomerization process: the conversion being small, the reverse reactions may be neglected and

$$\delta_0 = \int_0^t k'[1 - \mu(1 - e^{-kt})]dt,$$

$$\delta_1 = \int_0^t k'\mu(1 - e^{-kt})dt,$$

$\delta_0$ and $\delta_1$ represent the amounts of *cis* (or *trans*)-butenes with zero or one deuterium atom, respectively,

$$\frac{d_0}{d_1} = \frac{1 - \mu(1 - e^{-kt})}{\mu(1 - e^{-kt})}, \qquad (5)$$

and

$$\frac{\delta_0}{\delta_1} = \frac{kt[(1 - \mu)/\mu] + 1 - e^{-kt}}{kt - (1 - e^{-kt})}. \qquad (6)$$

$\mu$ may be estimated from the relative amounts of perdeuteropropene and -butene, by assuming that the adsorption equilibrium constant for the dissociative adsorption is the same for both molecules and by neglecting any isotopic effect. It is therefore possible to deduce $kt$ from Eq. (5) and to calculate $\delta_0/\delta_1$. The values for $\delta_0/\delta_1$, 0.34 and 0.59 in Expts. 1 and 2, show that 58.5 and 57.7% of the total $d_1$-cis-butenes, and 52.4 and 46.5% of the total $d_1$-*trans*-butenes are obtained by a direct intramolecular shift.

If one assumes an isotopic effect of 3 for the dissociative adsorption of light and heavy olefins, these values will be only slightly raised to 59.5 and 60.5% in the *cis*-butene, and 53.5 and 49.0 in the *trans*-butene.

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