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The Mechanism of Isomerization and Exchange of Olefins over Metal Catalysts

IV. Reactions of Some C_5, C_6 and C_7 Alkenes in the Presence of Perdeuteropropene on Iron Films

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The exchange and isomerization of pent-1-ene, *cis*-pentene, *cis*-hept-2-ene, *trans*-hept-3-ene, 2-methylbut-2-ene and 2,3-dimethylbut-2-ene have been investigated on iron films in the presence of a large excess of perdeuteropropene.

Further evidence has been given for the occurrence of a direct intramolecular hydrogen shift in double bond migration, and, in *cis–trans* isomerization, for a direct process without the formation or the breaking of any C–H bond.

The classical Horiuti-Polanyi mechanism seems to be restricted to *cis–trans* isomerization and involves only two consecutive steps.

The pronounced maxima for d_8, d_5 and d_4 deutero-isomers in the distributions of but-1-ene, pent-1-ene and 3-methylbut-1-ene obtained from the corresponding alk-2-enes show that the isomerization mechanisms involve a dissociative adsorption at a vinylic carbon atom, accompanied by a complete exchange of all the adjacent primary allylic hydrogen atoms. It is suggested that interconversions between σ–π-binuclear surface complexes are responsible for this process.

INTRODUCTION

In the two previous papers of this series (*1*,*2*), the isomerization of butenes and the exchange of a number of olefins have been studied on iron films in the presence of a large excess of perdeuteropropene. For both exchange and isomerization reactions, α-olefins and β-olefins behave in a very different manner:

1. While the exchange of β-olefins is extremely slow, the simple exchange of α-olefins is very fast and the number of exchangeable hydrogens, determined for various olefins, corresponds to the number of vinylic hydrogen atoms in the molecule (*1*). That the exchange of α-olefins involves dissociative adsorption at a vinylic carbon atom (Farkas mechanism) was recently confirmed by the microwave analysis of the monodeutero- and dideuteromolecules obtained in the exchange of but-1-ene in the presence of perdeuteropropene: the hydrogen atom attached to carbon 2 is by far the most rapidly exchanged, followed by the hydrogen atoms attached to carbon 1, *trans* and then *cis* to the alkyl group (*3*).

2. Further differences were observed between α- and β-olefins for double bond migration. In isomerization and exchange of but-1-ene, the deuterium distribution patterns of the *cis* and *trans* isomers may be deduced from those of the exchanged molecules, by assuming that double bond migration takes place by a simple intramolecular hydrogen shift (mechanism A). On the contrary, the isomerization of *cis*- and *trans*-butenes to but-1-ene is associated with a complete exchange of the molecule (mechanism B).

This difference of behavior between but-

1-ene and but-2-enes in isomerization, which seems to violate the principle of microscopic reversibility, may be explained only if one assumes that mechanisms A and B take place on different sites, and that the strength of adsorption of the α- and β-olefins is different on each type of sites: on sites A, associated with intramolecular double bond shift, α-olefins are more strongly adsorbed than β-olefins; on sites B, associated with the fast exchange of but-1-ene and the isomerization of but-2-enes, β-olefins are more strongly adsorbed than α-olefins (*2*).

Besides exchange and double bond migration, occurring according to mechanisms A and B, *cis-trans* isomerization also takes place, yielding d_0 and d_1 isomers according to two independent mechanisms: a simple nonrepetitive interconversion between 2-alkyl and 2,3-alkene adsorbed species accounts for the d_1 isomer (mechanism C), while the d_0 isomer results from a direct *cis–trans* isomerization which does not involve the formation or the breaking of any C–H bond (mechanism E).[1]

Lastly, a minor mechanism D takes place in double bond migration and *cis–trans* isomerization as well, associated with the exchange of a small number of hydrogen atoms of the molecule.

While the description of mechanisms A, E, C is relatively easy, although the nature of the driving forces (for mechanism E especially) is not clearly understood, very little is known of the two other mechanisms B and D. The first aim of this study was to investigate further the mechanism B involved in the β-olefin → α-olefin isomerization in the presence of perdeuteropropene. Various olefins with different structures, viz, *cis*-pentene, 2-methylbut-2-ene, hept-2-ene, 2,3-dimethylbut-2-ene, were used for this purpose. Second, the double bond migration between two internal positions, which could not be considered previously, was also investigated by using the long-chain olefins hept-2-ene and hept-3-ene as model molecules.

EXPERIMENTAL METHODS

Apparatus and Procedure

The apparatus and experimental procedures have been described previously (*1,2*). In each experiment, the partial pressure of the light olefin in the reaction vessel (400 ml) was 3 Torr and the pressure of perdeuteropropene was adjusted so that the D/H ratio was 9.4 as in the butene isomerization experiments.

Products

Pent-1-ene, *trans*-hept-3-ene, 2,3-dimethylbut-2-ene and 2-methylbut-2-ene were obtained from Fluka (puriss or purum grade). Their purity, determined by gas–liquid chromatography, was always higher than 99.9%. *Cis*-Pent-2-ene was prepared with 97.5% purity (2.5% *trans*) from a mixture of pentenes enriched in the *cis* isomer. Similarly 92.4% pure *cis*-hept-2-ene (7.6% *trans*) was obtained from a mixture of hept-2-enes.

Gas Chromatographic Analysis and Separation

The analysis of the reaction mixture and the separation of the isomers before mass spectrometric analysis were effected in most cases on a 5 m × 1/4 in. column of firebrick impregnated with 30% of dimethylsulfolane. Such a column does not allow the separation of hept-1-ene and *trans*-hept-3-ene. For the C_7 hydrocarbon mixtures the analysis was then effected on two columns in series: one (2.5 m) impregnated with dimethylsulfolane, the second (5 m) impregnated with glutaronitrile propene carbonate. This double column could be used for analytical but not preparative purposes.

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[1] Direct evidence for this direct *cis-trans* isomerization was given in a study of the co-isomerization of *cis*-butenes d_0 and d_8 on iron films (*3,4*).

Mass Spectrometric Analysis

The analysis of each molecule was effected after gas chromatographic separation by using an AEI MS2 mass spectrometer operating with 25 V electrons. The amounts of the various deuteromolecules were determined from the parent peaks after the usual corrections for natural isotopes and fragmentations, made on a statistical basis. Three fragments were taken into account at masses M—1, M—2 and M—3, and since these fragments represent less than 1, 3, 5 and 7% of the parent peaks in the case of heptenes, dimethylbutenes, pentenes and methylbutenes, respectively, the C–H and C–D fragmentations were assumed to be equal.

RESULTS

A. Isomerization and Exchange of Pentenes

The deuterium distributions of the exchanged and isomerized molecules obtained from pent-1-ene and *cis*-pentene are reported in Table 1.

Pent-1-ene

The very fast *exchange* of pent-1-ene has already been studied and discussed extensively in a previous paper of this series (*1*). It involves mostly three hydrogen atoms and the initial distributions include d_1, d_2 and d_3 in decreasing amounts.

As already observed in the case of but-1-ene, the deuterium pattern of *isomerized* molecules parallels closely the deuterium pattern of the exchanged pent-1-ene. One may also notice that the *trans*/*cis* ratio is higher than unity.

Cis-*Pentene*

The main reaction of *cis*-pentene on an iron film at −37°C is *cis–trans* isomerization. The amounts of *trans*-pentene are approximately 10 and 6 times larger than the amounts of pent-1-enes and *cis*-deuteropentenes, respectively. More than 90% of the *trans*-pentene consists of d_0 and d_1 in the ratio 1:2 which confirms the results obtained in the case of *cis*-butene. The exchanged molecules include mainly d_1 and d_2 in decreasing amounts.

TABLE 1

EXCHANGE AND ISOMERIZATION OF *n*-PENTENES OVER IRON FILMS AT −37°C

Reacting hydrocarbons:	Pent-1-ene			Pent-2-ene							
C_3D_6/C_5H_{10} ratio:	18			18				18			
Isomers:	Pent-1	*trans*	*cis*	Pent-1	*trans*	*cis*		Pent-1	*trans*	*cis*	
%	92.8	4.9	2.3	2	21.8	76.1		2.3	23.3	74.4	
d_0	25.8	31.0	30.3	1.2	30.4		94.8	0.5	27.5	93.1	
d_1	46.2	38.1	38.8	1.9	61.1	71.1	3.7	1.6	61.7	4.7	67.4
d_2	21.4	20.1	20.6	4.3	3.3	14.5	0.8	4.4	3.4	1.1	15.4
d_3	5.7	7.8	7.8	8.5	1.1	4.1	0.2	8.7	1.3	0.3	4.4
d_4	0.8	2.4	2.0	25.6	1.5	4.5	0.2	25.5	1.9	0.4	5.5
d_5	0.1	0.5	0.4	45.3	1.8	4.7	0.2	44.1	2.6	0.4	6.7
d_6	—	0.1	0.1	9.4	0.5	1.1	0.1	8.8	0.7	ϵ	0.6
d_7	—	—	—	1.1	0.1			3	0.3	—	
d_8	—	—	—	0.5	0.2			1.2	0.2	—	
d_9	—	—	—	1.4	—			1.1	0.1		
d_{10}	—	—	—	0.8	—			1.1	0.1		

Much more interesting is the distribution of the pent-1-enes; the deuterium pattern increases continuously from C_5H_{10} to $C_5H_5D_5$ and, after a definite break at d_5, includes only d_6 in significant amounts. It is worthwhile to outline that a similar pattern (maximum in d_5 followed by a smaller d_6 and negligible perdeuteromolecules) is also found to a minor extent in the distribution of *cis*-pentene and *trans*-pentene together with the major distribution.

B. Isomerization and Exchange of Heptenes

The exchange and isomerization of *cis*-hept-2-ene and *trans*-hept-3-ene have been studied at 0°C on iron films. The deuterium distributions of the various molecules are given in Tables 2 and 3.

Cis-*Hept-2-ene*

The main reaction is again *cis–trans* isomerization. The amounts of *trans*-hept-2-enes are 5, 16, and 3 times larger than the amounts of hept-3-enes, hept-1-enes and exchanged *cis*-hept-2-enes, respectively. The distribution of *trans*-hept-2-enes is very much the same as that of *trans*-pentenes obtained by isomerization of *cis*-pentene: d_0 and d_1 in a 1:2 ratio constitute 80% of the molecules. Another part of the distribution (B) includes d_2, d_3, d_4 and d_5 in approximately equal amounts. Only 1% of the total *trans*-hept-2-enes contains more than six deuterium atoms. It is interesting to note that the same distribution B d_2 to d_5 is obtained in the exchanged *cis*-hept-2-ene together with the major reaction product d_1.

Although *trans*-hept-3-ene and hept-1-ene were not separated before mass spectrometric analysis, the deuterium distributions of the *trans* 1-heptene and of the *cis*-hept-3-ene fractions are very similar. No definite break appears in the deuterium distribution which consists of d_0, d_1 and d_2 (75-80% of the products), a plateau at d_3, d_4, d_5 and decreasing amounts of d_6, d_7, etc.

Trans-*Hept-3-ene*

cis-Hept-3-enes, hept-2-enes and exchanged *trans*-hept-3-enes are formed in similar amounts. The hept-1-enes could not be analyzed. The distribution of *cis*- and *trans*-hept-2-enes consists of three different parts: there is a light isomer region extending from d_0 to d_3, which is very dif-

TABLE 2
EXCHANGE AND ISOMERIZATION OF *cis*-HEPT-2-ENE OVER IRON FILMS AT 0°C

Isomers:	*trans*-hept-3	Hept-1	*cis*-Hept-3	*trans*-Hept-2	*cis*-Hept-2	
%:	4.4	1.6	0.6	25.2	68.1	
d_0	26.8		22.5	24.7	87.9	
d_1	34.6		35.8	55.2	5.9	48.4
d_2	14.6		13.6	5.7	2	16.7
d_3	7		6.2	3.8	1.1	9.2
d_4	7.1		6.4	5.2	1.6	13
d_5	5.2		5.8	4.0	1.2	10.3
d_6	2.3		3	0.8	0.2	1.7
d_7	0.9		1.9	0.3	ε	0.4
d_8	0.4		1	0.1	ε	0.3
d_9	0.4		1.1	0.1		
d_{10}	0.3		0.8	ε		
d_{11}	0.1		0.6	ε		
d_{12}	0.1		0.6	ε		
d_{13}	0.1		0.5	ε		
d_{14}	0.1		0.2	ε		

TABLE 3

EXCHANGE AND ISOMERIZATION OF *trans*-HEPT-3-ENE OVER IRON FILMS AT 0°C

Isomers:	*trans*-Hept-3		*cis*-Hept-3	*trans*-Hept-2	*cis*-Hept-2	*trans*-Hept-3		*cis*-Hept-3	*trans*-Hept-2	*cis*-Hept-2
%:	76.5		9.1	11.8	2.6	80		8.85	8.85	2.3
d_0	79.9		18.3	12.3	4.5	86.3		7.7	12.6	3
d_1	12	60.2	57.3	34.7	28	8.6	62.8	67.7	38.2	31.7
d_2	5.2	25.7	14.7	20.4	27.4	3.4	24.5	15.6	19.2	26.7
d_3	1.6	7.7	3.9	10.7	12.7	1.0	7.3	3.8	9.7	11
d_4	0.5	2.6	1.3	5.9	7	0.3	2.6	1.3	5.3	6.3
d_5	0.3	1.4	0.9	6.3	8.1	0.2	1.3	0.8	5.6	7.3
d_6	0.2	1.1	1.0	5.6	7.6	0.1	0.9	0.7	5.3	7.4
d_7	0.1	0.6	0.7	2.2	2.6	ϵ	0.4	0.6	2.3	3.2
d_8	ϵ	0.3	0.4	0.8	0.8	ϵ	0.2	0.4	0.8	1.1
d_9	ϵ	0.1	0.4	0.5	0.7			0.4	0.4	0.8
d_{10}	ϵ	0.1	0.3	0.2	0.3			0.2	0.2	0.4
d_{11}	ϵ	ϵ	0.2	0.1	ϵ			0.2	0.2	0.4
d_{12}	ϵ	ϵ	0.2	0.1	ϵ			0.2	0.1	0.3
d_{13}	ϵ	ϵ	0.2	0.1	ϵ			0.2	0.1	0.3
d_{14}	ϵ	ϵ	0.1	0.1	ϵ			0.2	0.1	0.1

ferent for the *cis* and *trans* isomers, a plateau including d_4, d_5 and d_6, and a steeply decreasing distribution (d_7 to d_{14}) which represents only 4% of the total molecules and which is identical in both isomers. Concerning the first region, much smaller amounts of d_0 are present in the *cis* than in the *trans*-hept-2-ene. Moreover, the ratio d_1/d_2 is different in both isomers.

The deuterium patterns for *cis*- and *trans*-hept-3-enes are very different from the ones described above. The exchange distribution pattern obtained by isomerization consists of d_0, d_1 (the major molecules) and decreasing amounts of the more deuterated molecules. No break at all is observed in these two distributions.

C. 2-Methylbut-2-ene and 2,3-Dimethylbut-2-ene

These substituted molecules do not react at temperatures lower than 100°C.

TABLE 4

EXCHANGE AND ISOMERIZATION OF 2,3-DIMETHYLBUT-2-ENE AND 2-METHYLBUT-2-ENE OVER IRON FILM AT 100°C

Reacting hydrocarbons:	2,3-Dimethylbut-2-ene		2-Methylbut-2-ene			
Isomers:	2,3-dimethyl but.-1	2,3-dimethyl but.-2	3-methyl but.-1	2-methyl but.-1	2-methyl but.-2	
%:	3.8	96.2	0.5	2.7	96.8	
d_0	61.1	99.6	24.1	54.1	98.5	
d_1	24.4	0.4	21.8	34	1.0	71.1
d_2	6.2		14.5	6.3	0.2	11.3
d_3	2.3		15.2	2.3	0.1	6.3
d_4	1.2		21.4	1.1	0.1	7.6
d_5	0.9		0.9	0.7	ϵ	1.8
d_6	0.8		1.2	0.5	ϵ	1.9
d_7	0.3		0.9	0.2		
d_8	0.5			0.1		
d_9	0.5			0.2		
d_{10}	0.3			0.5		
d_{11}	0.6					
d_{12}	0.9					

The product distributions of the isomers and exchanged molecules obtained at 100°C from 2-dimethylbut-2-ene and 2,3-dimethylbut-2-ene are given in Table 4.

The exchange of 2,3-dimethylbut-2-ene is negligible and the deuterium distribution of its isomer, the 2,3-dimethylbut-1-ene, is decreasing and consists mainly of d_0 (61%) and d_1 (24.4%).

In contrast, exchange and isomerization of 2-methylbut-2-ene occur at a comparable rate. In the exchange of this molecule, d_1 represents the main reaction product. After a steep decrease in the deuterium pattern a slight maximum at d_4 and a definite break between d_4 and d_5 are observed. About 90% of 2-methylbut-1-ene, the major isomer formed from 2-methylbut-2-ene, consists of d_0 and d_1. After a strong break after d_1, the distribution decreases rapidly. On the other hand, the deuterium distribution of the minor isomer, the 3-methylbut-1-ene, is entirely different. Five molecules d_0 to d_4 are formed in approximately equal amounts and a definite break is observed after d_4: the d_5 to d_{10} molecules represent only 3% of the total molecules.

DISCUSSION

Double Bond Migration from a β to an α Position

a. Type B Mechanism

The deuterium distributions of the isomers obtained from *cis*-pentene, 2-methylbut-2-ene, 2,3-dimethylbut-2-ene (this work) and but-2-enes (*2*) give a complete picture of the type B isomerization associated with a multiple exchange of the molecules. The results are summarized in Table 5. From the distributions of but-1-ene and pent-1-ene, it is clear that all the *vinylic and primary* allylic hydrogen atoms of these molecules are involved in the multiple exchange which accompanies the double bond migration in mechanism B.

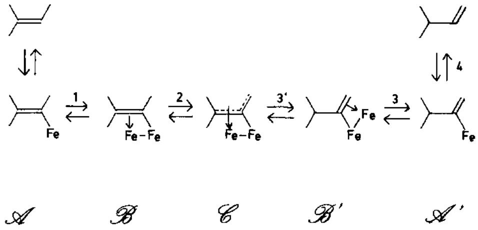
TABLE 5

DEUTERIUM DISTRIBUTION PATTERNS IN VARIOUS ISOMERIZATION REACTIONS: CHARACTERISTIC MAXIMA

Isomerization		Distribution feature
of	to	
cis-Butene	But-1-ene	Maximum in d_8
cis-Pentene	Pent-1-ene	Maximum in d_5
2-Methylbut-2-ene	3-Methylbut-1-ene	Maximum in d_4
2-Methylbut-2-ene	2-Methylbut-1-ene	No maximum at all
2,3-Dimethylbut-2-ene	2,3-Dimethylbut-1-ene	No maximum at all

Moreover, the absence of multiple exchange during the isomerization of 2,3-dimethylbut-2-ene, the definite break after d_4 in the distribution of the 3-methylbut-1-enes and the absence of highly exchanged 2-methylbut-1-ene during the isomerization of 2-methylbut-2-ene suggest that the multiple exchange characteristic of most of the $\beta \rightarrow \alpha$ isomerizations requires the rupture of a vinylic carbon hydrogen bond.

In the case of the *isomerization of 2 methylbut-2-ene into 3-methylbut-1-ene*, it is therefore tempting to explain the exchange of a maximum of four hydrogen atoms by rapid interconversions between σ-vinyl-π-olefinic complexes $\mathscr{B}$ and σ-vinyl-π-allylic complexes $\mathscr{C}$ (Scheme 1). The very fast desorption step 4 is also the main reaction involved in the exchange of the α-olefin. This point was clearly demonstrated by locating the deuterium atom in the d_1 molecules obtained from but-1-ene by simple exchange (*3*):

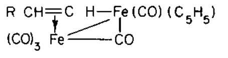


SCHEME 1. Species $\mathscr{B}'$ are not compulsory.

Concerning the alleged species in Scheme 1, it is worthwhile to outline that iron is well known to form stable σ-vinylic organometallic complexes (5). The adsorbed intermediates $\mathscr{B}$ and $\mathscr{C}$, as well as the σ-vinylic precursor $\mathscr{A}$ have their counterparts in iron coordination chemistry: for example the following complexes I to III have been isolated (*6*,*7*) and their structures determined by X-ray crystallography (*8*,*9*):

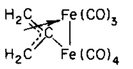
$RCH{=}CHFe(CO)_2(C_5H_5)$

I



II

$R = H, Ph, CH_3CO$ [Ref. (6)]



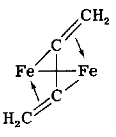
III [Ref. (7)]

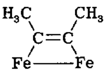
The metal–metal distances in complexes II and III, 2.55 and 2.65 Å, respectively, correspond to a definite iron–iron bond. They approach closely the shortest distance between two metal atoms in the pure metal (2.50 Å), which reinforces the idea that binuclear complexes such as $\mathscr{B}$ and $\mathscr{C}$ may be formed on the surface.

Scheme 1 as such may also explain the isomerization of pent-2-enes into pent-1-enes. However, a sharp maxmium in d_5 is observed in the deuterium distribution pattern of pent-1-ene obtained from *cis*-pentene, instead of a plateau from d_0 to d_4 in the distribution of 3-methylbut-1-ene obtained from 2-methylbut-2-ene. We believe that this difference, as well as the difference of ca. 100°C between the temperatures required to obtain a similar rate for both isomerizations, may be explained by a strong steric hindrance of the methyl group in 2-methylbut-1-ene, which does not exist in *cis*-pentene. As a result of this steric effect, the surface reactions in the isomerization of 2-methylbut-2-ene are slowed down and their rates become comparable with the desorption rates. On the contrary, in the case of pent-2-ene isomerization, the interconversions between the surface complexes are much faster than the desorption steps, which explain the pronounced maximum at d_5 in the pent-1-ene distribution.

The complete exchange of all the hydrogen atoms *during the isomerization of cis- or trans-butene into but-1-ene* may also be explained by interconversions between species $\mathscr{B}$ and $\mathscr{C}$, provided that an additional species be introduced allowing the multiple exchange to propagate from one half to the other half of the molecule. This species could be either a di-σ-vinylic adsorbed species $\mathscr{D}$ or a di-σ-vinylic-di-π-olefinic adsorbed species $\mathscr{D}'$:

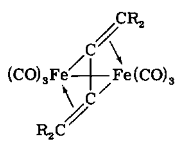
$\mathscr{D}'$



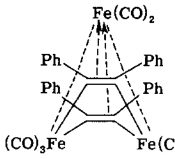


$\mathscr{D}$

A stable organometallic complex of iron with the same structure as $\mathscr{D}'$ has been isolated recently (*10*), and the same bonding as in the di-σ-vinylic adsorbed species $\mathscr{D}$ does exist in some complicated trinuclear complexes (*11*):

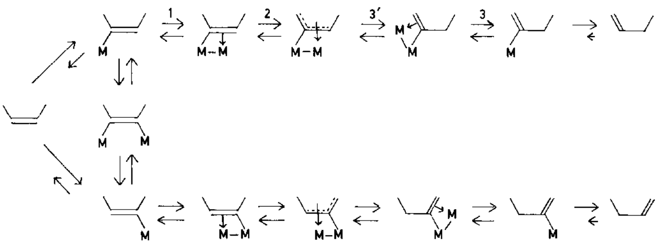


R = H Ph [(Ref. (*10*)]

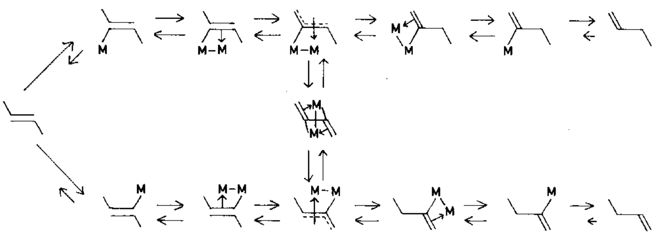


[Ref. (*11*)]

Both mechanisms represented in Scheme 2 and 2′ are therefore able to explain the isomerization of but-2-enes, but it should be pointed out that a transoid form of adsorbed butadiene is required to achieve species $\mathscr{D}'$, while the di-σ-adsorbed butene $\mathscr{D}$ is necessarily *cis*. Since both *cis*- and *trans*-butenes yield d_8 -but-1-ene, the change of configuration by the reversal of steps 3 (or 3′) must therefore be possible, whatever the mechanism might be:



SCHEME 2



SCHEME 2′

b. *Other Mechanisms*

Beside mechanism B, two other mechanisms operate for the double bond shift from a β to an α position. The simple intramolecular shift (type A) which does not occur when the reaction takes place at low temperature, i.e., in the case of linear olefins, represents more than 50% of the isomerization products of 2,3-dimethylbut-2-enes and 2-methylbut-2-enes at 100°C. It is noticeable that this intramolecular rearrangement is not very important when a more facile route such as type B isomerization is possible: very little d_0-pent-1-ene or but-1-ene is formed from pent-2-ene and but-2-ene.

Another mechanism is associated with the decreasing distribution from d_1 to d_5 of 2,3-dimethylbut-1-enes and 2-methylbut-1-enes. This mechanism, which occurs only at high temperature, may be pictured either as a Horiuti-Polanyi process or as an allylic type mechanism involving the removal and addition of a hydrogen or deuterium atom. While the strong break after d_1 in the distribution of 2-methylbut-1-ene is in favor of the allylic mechanism, the continuous decrease of the deuterium pattern in 2,3-dimethylbut-1-enes would seem to indicate that a Horiuti-Polanyi mechanism is involved. More information is then required in order to choose between the two possibilities.

Cis–trans Isomerization

The *trans* isomer represents 80 and 70% of the total reaction products of *cis*-pentene and *cis*-hept-2-ene in the presence of perdeuteropropene. Similarly 85% of the products obtained from a mixture of *cis*-butenes-d_0 and d_8 consist of *trans*-butenes [co-isomerization (*2*)]. *Cis-trans* isomerization is therefore the main reaction occurring on iron catalysts.

Concerning the *cis–trans* isomerization of the *trans* isomers, the reaction rate, r_{tc}, of the *trans* is expected to be much smaller than the reaction rate, r_{ct}, of the *cis*, since $r_{tc}/r_{ct} = (cis/trans)_{equil}$. Indeed *cis*-hept-3-ene represents only 30% of the total products formed from *trans*-heptene.

In any isomerization experiment of linear olefins, d_0 and d_1, in the approximate ratio 1 : 2, represent more than 85% of the deuteromolecules and in the co-isomerization experiment 97% of the product consists of d_0, d_1, d_7, d_8. The two mechanisms E and C, viz, direct *cis–trans* isomerization and the nonrepetitive Horiuti-Polanyi process, already discussed (*2*), represent therefore the major reaction routes for normal olefins on iron films. In the case of methyl-substituted olefins, the results of *cis-trans* isomerization would be 2,3-dimethylbut-2-ene-d_0 or 2-methylbut-2-ene-d_0 and d_1. Only the latter molecule can be detected and is one of the major reaction products obtained from 2-methylbut-2-ene.

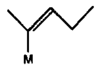
Exchange

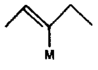
It was noted previously that the exchange of *cis*- and *trans*-butene was negligible (*1*) on iron film at −37°C. In the case of pent-2-ene and *cis*-hept-2-ene, on the other hand, exchange represents 13 to 17% of the total reactions. While part of the exchanged *cis*-pentenes may be considered as resulting from a double bond migration, that is not true for the *cis*-hept-2-ene. Therefore, one may state that the lengthening of the chain in the β-olefins $CH_3—CH{=}CHR$ increases the exchange rate considerably, i.e., decreases the strength of olefin adsorption. An explanation for this could be a decrease of the stabilizing effect of the substituent R on the adsorbed molecule when a methyl is replaced by a larger alkyl group.

A second point of interest is the product distribution of the exchanged molecules, very much the same for *cis*-pentene and *cis*-hept-2-ene. A fast decrease from d_1 to d_3 is followed by a plateau up to d_5, after which a definite break appears in the distribution. Such a deuterium pattern cannot be considered as the result of a single mechanism but rather of two independent mechanisms occurring simultaneously: one corresponds to a continuously decreasing distribution from d_1 and the other one is associated with a deuterium distribution similar to the one observed in the pent-1-ene isomer. These mechanisms, therefore, should probably be identified with the mechanism B, already discussed, which explains the double bond migration from a β to an α position.

We suggest that they correspond to the two possible vinylic precursors which may be formed from a β-olefin: $\mathscr{A}_1$ leading to a multiple exchange up to d_5 and $\mathscr{A}_2$ leading to a quasi-simple exchange.

$\mathscr{A}_1$





$\mathscr{A}_2$

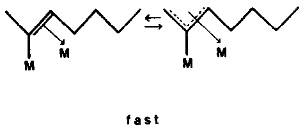
Concerning the multiple exchange, it is noticeable that the distributions of the d_2–d_5 exchanged molecules is very much the same as the distributions of the d_2–d_5 molecules appearing in the *trans* isomer. Moreover, these *cis* and *trans* molecules are obtained in approximately equal amounts, namely, 5 and 9% of the total reaction products of *cis*-pentene and *cis*-hept-2-ene, respectively. We believe then that most of the d_2–d_5 molecules obtained in *both cis* and *trans* isomers are formed on the same sites B associated with the dissociative adsorption of the olefins and the extensive exchange of all the vinylic and primary allylic hydrogen. If so, a fast *cis–trans* isomerization should take place on sites B before desorption, as was already assumed in Schemes 2 and 2′.

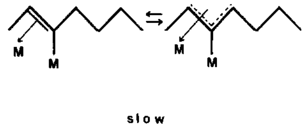
In order to support this assertion, that part of exchange and *cis–trans* isomerization takes place on sites B, it is useful to examine carefully the deuterium distributions of some other molecules. As expected, d_2-d_8-*trans*-butenes and d_2-d_4-2-methylbut-2-enes are formed. They represent, respectively, 3 and 8% of the total reaction products. On the other hand, hept-3-enes do not contain any primary allylic hydrogen. For these molecules mechanism B would be restricted therefore to the exchange of the two vinylic hydrogen atoms and neither pronounced maxima, nor definite breaks are expected in *cis* or *trans* deuterium distributions. Effectively, only a decreasing distribution with a slightly prominent d_2 is observed in the deuterium pattern of *trans*-hept-3-ene.

Double Bond Migration Between Two Internal Positions

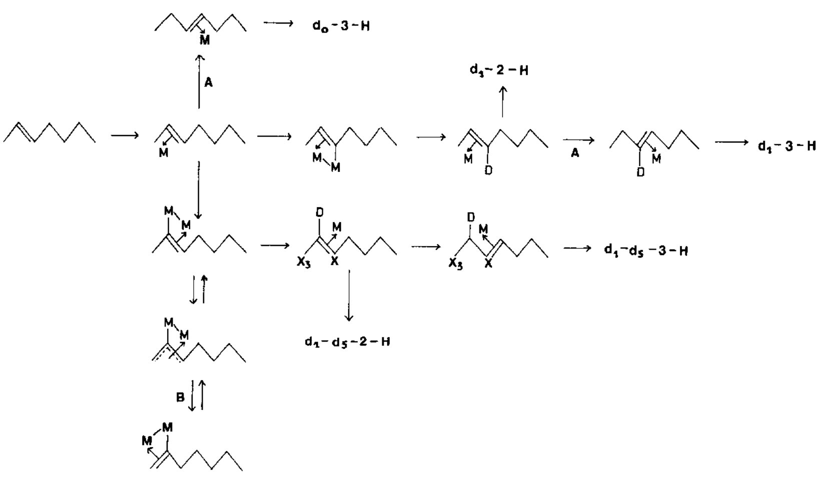
In the present work, two such reactions have been considered, namely, the isomerization of *cis*-hept-2-ene to *cis*- or *trans*-hept-3-ene and the isomerization of *trans*-hept-3-ene to *cis*- or *trans*-hept-2-ene. The deuterium distribution patterns of the hept-2-ene (2-H) obtained from hept-3-ene (3-H) and of the hept-3-ene obtained from hept-2-ene present many common features: there is a definite d_0 followed by decreasing amounts of d_1 to d_3, a plateau extending up to d_5 (2-H → 3-H) or up to d_6 (3-H → 2-H) and decreasing amounts of the more highly deuterated molecules. It is worthwhile to mention that the hept-2-enes obtained by exchange consist also of decreasing amounts of d_1, d_2 and a plateau at d_3–d_5.

The similarity in the d_2–d_5 regions between the deuterium distribution patterns of the 3-H isomers and of the 2-H exchanged molecules on the one hand, and the presence of d_0 isomers among the reaction products on the other hand, suggests that both type B isomerization (involving σ-vinylic binuclear complexes) and type A isomerization (intramolecular double bond shift) are involved. If one assumes that interconversions between σ-vinyl-π-olefinic species and *terminal* σ-vinyl-π-allylic species are fast in regard to desorption, while interconversions between σ-vinyl-π-olefinic species and *internal* σ-vinyl-π-allylic species are slow, one may account for the particularities of the deuterium distribution of the isomers and the exchanged products:





As an example, the various elementary steps for the surface reactions of hept-2-ene are described in Scheme 3:



SCHEME 3

CONCLUSION

The results presented in this paper and the preceding ones (*1,2*) show that several exchange and isomerization mechanisms compete on iron film catalysts. Apparently these mechanisms differ mostly in the nature and the strength of the olefin adsorption. An associative adsorption, when not interconnected with more complicated species, determines either a simple hydrogen intramolecular shift (mechanism A) or a direct *cis–trans* isomerization (mechanism E). When related to a half-hydrogenated state (mechanism C) the associative adsorption leads also to *cis–trans* isomerization. On the other hand, dissociative vinylic adsorption may form either the loosely bonded species which are involved in the simple exchange of α-olefin or strongly held intermediaries responsible for the double bond migration from a β to an α position (mechanism B).

This complexity of the reaction mechanisms on iron suggests a wide heterogeneity of the surface. Although the exact nature of the sites is not yet completely clarified, comparison with homogeneous catalysis and coordination chemistry strongly suggests that the *cis–trans* isomerization involves one single metal atom, while the isomerization of β- to α-olefins requires two. For this latter reaction, indeed, direct evidence (microwave analysis of exchanged but-1-enes) and indirect evidence (deuterium distributions of isomerized olefins) have been given of the participation of binuclear surface complexes, whose structures are similar to the ones of the stable σ-π-diiron organometallic complexes.

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