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Mechanisms of Isomerization of Butenes on Supported Iron Catalysts: Comparison with Iron Films

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Isomerization and exchange of butenes in the presence of perdeuteropropene were studied on an iron/pumice catalyst. The results are compared with those obtained previously on iron films. Replacing iron film by iron/pumice produces the following effects: (1) *cis–trans* isomerization of but-2-ene increases relatively to double bond migration; C_1-exchange and isomerization of but-1-ene increases relatively to C_2-exchange. This is interpreted by an increase of the associative Horiuti–Polanyi mechanism relative to the dissociative mechanism. (2) The multiple exchange that accompanies $\beta \rightarrow \alpha$ double-bond migration yields all the deuterated but-1-enes and *cis*-butenes up to d_5 in comparable amounts, while on iron films perdeutero-d_8-but-1-ene is mainly produced. This difference is interpreted by the different roughness of a film deposited at 0°C and supported catalysts treated by hydrogen at 400°C.

INTRODUCTION

Although no conclusive proof has been produced in favor of the associative Horiuti–Polanyi mechanism (*1*), this mechanism has been widely used to interpret the results in most of the papers dealing with the exchange and isomerization of olefins on metals. However, if the product distributions are looked at carefully and the location of the label in the molecules is determined by microwave spectroscopy, the associative mechanism is found to be only one among several competing mechanisms. In the case of the exchange of propene on bulk metals, Hirota and coworkers showed that, besides the associative mechanism, a Farkas dissociative mechanism (*2*) and an allylic mechanism (*3*) also take place on platinum and palladium, respectively (*4, 5*). More recently the mechanism of exchange of but-1-ene was shown to involve the rupture of a vinylic carbon–hydrogen bond on iron and nickel films (*6–8*) and of an allylic carbon–hydrogen bond on palladium films (*9*). In these latter cases the associative mechanism was not found to be of any significance in the exchange reactions. In but-1-ene isomerization, a nonrepetitive Horiuti–Polanyi mechanism that introduces one deuterium atom into the molecule and a direct process without deuterium incorporation account for the formation of the *trans* isomer on all metals (*10*). Lastly, double-bond migration takes place on nickel and palladium films either by an intramolecular 1–3 hydrogen shift or by a multistep allylic mechanism involving several interconversions between π-allylic and π-olefinic species (*9, 11*): the latter mechanism on iron films is assisted by the additional formation of a σ carbon–metal bond (*12*).

The existence of so many competing mechanisms, especially on metal films, is very probably related to surface heterogeneity. In an attempt to correlate the various reaction mechanisms and the structures of the metal surfaces (*13*), all the reactions of olefins were classified into three groups, associated with three different types of sites. Metal atoms of a low coordination number, such as the corner atoms in a crystallite or isolated adatoms, are believed to accommodate three ligands, two ad-

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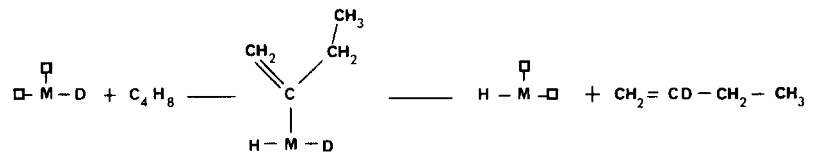
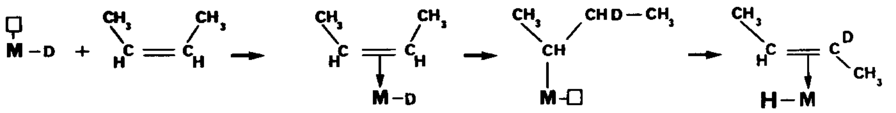
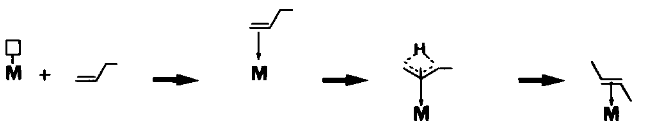
sorbed hydrogen atoms and one adsorbed olefin, and to promote all the reactions involving dissociative adsorption of the vinylic or allylic type.



The associative mechanism, which requires in the precursor state two bonds between metal and adsorbates, would take place on the sites arising at the intersection of two faces with low Miller indices (edge atoms).



Lastly, the more highly coordinated metal atoms (those of the low Miller index faces) would accommodate only one ligand and be responsible for direct *cis–trans* isomerization and intramolecular 1–3 hydrogen shift.



If such a correspondence between sites and mechanisms is correct, the reaction mechanisms should change significantly when the structure of the metal surface is changed. Drastic changes have indeed been observed when the roughness of palladium and nickel films was modified either by thermal treatment or by exposure to hydrogen (*14*). The aim of this study was to explore this correspondence further by comparing isomerization and exchange of butenes on iron films and on supported iron catalysts. Supported catalysts and films are expected to have different structures (particle size, roughness, etc.) and should therefore promote different reaction mechanisms. Since the isomerization and exchange of all three butenes have been extensively studied on iron films (*6*, *10*, *12*) we present in this paper, for comparison, only some results obtained on supported iron catalysts.

EXPERIMENTAL

Catalysts

The 10% Fe/pumice catalyst was prepared in a conventional way (*15*) by impregnating the carrier with an aqueous solution of ferric nitrate, calcining it in oxygen at 350°C for 12 hr, and reducing it with hydrogen at 400°C for 20 hr. Before each run the catalyst (1 g) was activated with a flow of hydrogen for 20 hr at 400°C. Deuterium was then introduced at the same temperature for 1 hr to remove the hydrogen (the mass spectrum analysis of the effluent gases gave less than 2% of HD). Lastly, most of the adsorbed deuterium was eliminated with a flow of helium at 100°C for 0.5

hr. This last treatment drastically reduced the extent of deuteration but did not prevent isomerization or C_4H_8–C_3D_6 exchange. It was checked in blank experiments that, up to 200°C, pumice treated in the same way did not catalyze either isomerization of butenes, or exchange.

Materials

The three butenes were from Fluka (puriss grade). Perdeuteropropene obtained from Merck, Sharpe and Dohme had an isotopic purity of 99.1%. Hydrogen and deuterium and U-grade helium (less than 5 ppm of impurity) were dried on a molecular sieve at 77 K.

Apparatus and Procedure

The catalytic reaction was carried out in an all-glass grease-free flow system including a reactor operating under differential conditions. Just after catalyst activation, a mixture of butene (6 Torr) perdeuteropropene (200 Torr) and helium (550 Torr) was passed over the catalyst (1 g) for 20 min. About 4 mg of butenes and 56 mg of propene were used in each run. The constancy of the overall hydrocarbon pressure was checked by using a katharometer inserted in the flow line before the reactor, and repeated analysis by gas–liquid chromatography showed that the hydrocarbon composition remained unchanged throughout the run. The hydrocarbon reaction mixture was collected at 77 K, the perdeuteropropene and the three butenes were separated by glc on a 5-m, $\frac{1}{4}$-in. dimethylsulfolane/firebrick column operated at −35°C, and each molecular species was analyzed by mass spectrometry and in some cases by microwave spectroscopy.

Analysis

Mass spectrometry. The mass spectrometer used was a Varian Mat–CH_7 operating with 70 V electrons to ionize the molecule, a trap current of 300 μA, and a resolution of about 2000. The amounts of the various deuteriomolecules were determined from the parent peaks after the usual corrections for natural isotope and fragmentations, made on a statistical basis and using the fragmentation of both the light (d_0) and the heavy (d_8) butenes (*6*).

Microwave analysis. The rotational spectrum of butene was measured with a 50 kHz square-wave Stark microwave spectrometer. The measurements were made at −60°C using a 5 m absorption cell and field of 1400 V cm^{-1}. The spectra of the d_1 but-1-enes, of some of the d_2 but-1-enes, and of the d_1 but-2-enes have already been described (*16–18*). The notation d_1 or d_2 (mono- or dideuterated species) will be preceded by the number of the carbon atoms of the butene molecule on which the deuterium atoms are attached. In but-1-ene, 1a-d_1 and 1b-d_1 correspond respectively to *trans* and *cis* 1-d_1 but-1-ene as indicated in Fig. 1. The compositions of all monodeutero but-1-enes and of the 1,2-d_2, 2,3-d_2, and 3,3-d_2 species were determined by measuring the intensities of the rotational $4_{14} \rightarrow 3_{13}$ transition for the skew form and checked by using the $4_{13} \rightarrow 3_{12}$ lines of the spectrum for the same transition. For the analysis of the d_1-*cis* but-2-enes, the $9_{18} \rightarrow 9_{27}$ EE transition was generally used.

RESULTS

Reactions of But-1-ene

But-1-ene was reacted over Fe/pumice at 50 and 100°C in the presence of perdeuteropropene. The results are reported in Tables 1 and 2. Although each run was made under similar experimental conditions, the activities and also the product distributions were rather irreproducible. The major changes were found for the ratios between the exchange and isomerization rates, the extent

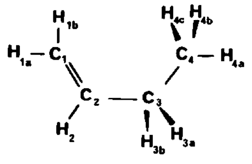


FIG. 1. Notation of atoms in but-1-ene.

TABLE 1

Exchange and Isomerization of But-1-ene at 50°C

Run		1			2			3			4	
Isomerization α_i (%)		1.75			22.9			24.9			43.1	
trans/cis		1.2			1.45			1.55			1.45	
Exchange α_e (%)		40.9			40.7			93.1			71.3	
Exchange/Isomerization α_e/α_i		25			2.5			6.7			2.8	
Products	1-B	*trans*	*cis*	1-B	*trans*	*cis*	1-B	*trans*	*cis*	1-B	*trans*	*cis*
Composition (%)	98.25	0.95	0.8	76.0	14.3	9.7	65.1	21.1	13.8	50.0	29.7	20.3
d_0	59.1	41.0	43.3	59.3	52.6	56.7	6.9	9.2	8.5	28.7	23.6	29.6
d_1	37.5	43.6	42.0	26.4	16.9	16.7	39.2	25.0	26.1	21.0	20.0	21.9
d_2	3.2	13.8	13.1	10.3	11.3	10.2	34.1	33.0	35.0	19.9	16.2	15.0
d_3	0.2	1.6	1.5	3.9	8.8	7.9	19.3	22.0	21.3	28.5	17.4	14.8
d_4	—	—	0.1	0.06	8.6	7.7	0.3	10.0	8.7	1.0	16.5	15.1
d_5	—	—	—	—	1.7	0.7	0.2	0.8	0.4	0.9	5.7	3.0
d_6	—	—	—	—	0.06	0.08	—	—	—	—	0.3	0.3
d_7	—	—	—	—	—	—	—	—	—	—	0.2	0.2
d_8	—	—	—	—	—	—	—	—	—	—	0.1	0.1
$M = \Sigma\, idi$	44.5	75.9	73.5	57	109	95.7	167	200.5	196.5	120	203	175.6
Hyperfine distribution of but-1-enes (obtained by microwave spectroscopy)												
1a-d_1		2 ± 2			10 ± 1						17 ± 3	
1b-d_1		2 ± 2			10 ± 1						17 ± 3	
2-d_1		96 ± 1			81 ± 3						65 ± 3	
3-d_1, 4-d_1		0			0						0	

TABLE 2

Exchange and Isomerization of But-1-ene at 100°C

Run	5	6		
Isomerization (%)	15.1	35		
trans/cis	—	1.15		
Exchange (%)	51.4	50		
Exchange/isomerization	4.05	2.9		
Products	1-B	1-B	*trans*	*cis*
Composition (%)	84.8	65.0	18.5	16.5
d_0	48.6	50.0	10.7	15.8
d_1	42.6	26.1	16.0	25.0
d_2	7.9	9.8	14.7	22.0
d_3	0.8	4.6	11.5	13.5
d_4	0.1	2.2	10.4	8.5
d_5	—	1.9	9.7	4.8
d_6	—	1.8	8.8	3.5
d_7	—	1.6	9.2	3.1
d_8	—	—	9.0	3.8
$M = \Sigma\, idi$	61.1	99.8	359.1	240.2
Hyperfine distribution of but-1-enes (MW)				
1a-d_1	8 ± 3	10 ± 3		
1b-d_1	8 ± 3	6 ± 3		
2-d_1	80 ± 1	80 ± 1		
3-d_1, 4-d_1	4 ± 2	0		

of multiple exchange (i.e., the amounts of d_2 and d_3 but-1-enes, relative to d_1), and the percentages of 1-d_1 species in the hyperfine distribution of the d_1 but-1-enes. In contrast, the *cis/trans* ratio remained practically constant, around 1.4, and the 2-d_1 species was always predominant among the d_1 exchange products. Moreover, in all experiments 1a-d_1 and 1b-d_1 but-1-enes, on the one hand, and 1a,2-d_2 and 1b,2-d_2 but-1-enes, on the other hand, were obtained in equal amounts.

Runs 1 and 2, with the same percentages of unexchanged but-1-ene, allow a more precise comparison to be made. In run 2, there was a much higher conversion to isomers, larger amounts of d_2 and d_3 but-1-enes relative to d_1, and larger amounts of 1-d_1 molecules in the hyperfine distribution of the d_1 but-1-enes. The interrelation between the amount of 1-d_1 species and the extent of isomerization is further confirmed in run 4.

The deuterium distributions of the three butenes are reported in full detail in Table 1, together with the *M* values defined by Eq. (1):

$$M = \sum_{i=1}^{8} idi. \tag{1}$$

While in the experiments made at 50°C the *M* values for the *cis* and the *trans* isomer were the same and exceeded the *M* values for the but-1-ene by less than 100, in run 6 made at 100°C *M* was larger for the *trans* than for the *cis*, and for the *cis* than for the but-1-ene. Noticeable also in the experiments made at 50°C are the breaks after d_3 in the deuterium distributions of the exchanged but-1-enes and after d_4 in the distribution of the *cis* and the *trans* isomers. In run 6 made at 100°C, these breaks no longer existed, and the deuterium distributions of both exchanged and isomerized molecules extended up to d_8. Simultaneously, small but definite amounts of 3-d_1 species appeared in the hyperfine distribution of the exchanged but-1-enes.

In run 4, the d_1 *cis*-butene was analyzed by microwave spectroscopy: the deuterium lay predominantly on carbon 1.

Reactions of cis-Butene

cis-Butene was reacted over Fe/pumice at 50°C in the presence of C_3D_6. The results of two runs made at low and high conversions are reported in Table 3, together with the results of one run made at −37°C on iron film (*10*). Exchange of *cis*-butene took place on the supported catalyst and not on the film. It was faster than double-bond migration and led to a characteristic decreasing deuterium distribution with two "plateaus," at d_3–d_5 and d_6–d_8. Microwave spectroscopy showed that most of the d_1 *cis*-butene (over 90%) consisted of the 2-d_1 species.

On supported catalyst but not on films the *trans* but-2-enes were the major reaction products. They included mostly d_1 and d_0, with a d_1/d_0 ratio around 2, and also

TABLE 3

Isomerization and Exchange of *cis*-Butene at 50°C

	Ref. (*10*)			Run 7, this work			Run 8, this work		
Catalyst		Fe Film			Fe/pumice			Fe/pumice	
T(°C)		−37			50			50	
Isomerization (%)		2.7			29.9			57.1	
Exchange (%)		0.1			11.1			43.8	
Products	*cis*	*trans*	1-B	*cis*	*trans*	1-B	*cis*	*trans*	1-B
Composition (%)	97.3	0.95	1.8	70.6	24.4	5.0	42.9	53.5	3.5
d_0	99.9	26.5	2.2	89.9	23.8	8.8	56.2	27.4	13.1
d_1	0.1	59.2	3.3	2.9	51.2	22.0	23.9	55.5	18.4
d_2	—	2.2	7.0	2.1	5.7	26.8	13.7	11.7	18.6
d_3	—	4.1	4.5	1.2	4.2	20.0	2.8	2.2	17.9
d_4	—	3.9	2.7	1.3	4.6	14.2	1.9	1.6	20.5
d_5	—	1.5	0.9	1.3	5.0	5.2	1.4	1.5	9.3
d_6	—	0.5	1.7	0.5	1.8	1.4	0.06	0.06	1.0
d_7	—	1.1	24.0	0.4	2.1	0.6	0.04	0.04	0.7
d_8	—	1.9	53.7	0.4	1.6	1.0	0.04	0.05	0.5
$M = \Sigma\, i d_i$				31.4	160	239	74.8	93.7	262

Hyperfine distribution of but-1-ene (MW)	
1-d_1	21 ± 2
2-d_1	33 ± 2
3-d_1	45 + 5
4-d_1	0
1,2-d_2	23.5 ± 4
2,3-d_2	70 ± 4
3,3-d_2	9 ± 2

small amounts (20–25%) of more highly deuterated molecules. The "plateaus" at d_3–d_5 and d_6–d_8 in the deuterium distributions of the *trans* isomer are obviously related to the ones that appear in the deuterium pattern of the exchanged *cis* butene.

The deuterium distribution of the but-1-enes obtained on Fe/pumice by double-bond migration was very different from the ones obtained on iron films. It included mostly the less deuterated molecules, with a pronounced break after d_5. By using microwave spectroscopy, a complete analysis of the d_1 species and a partial analysis of some of the d_2 species (1a,2-d_2/1b,2-d_2/2,3-d_2/3,3-d_2) was achieved in run 8 made at the higher conversion.

DISCUSSION

Reactions of But-1-ene

Exchange. Three reaction mechanisms may be proposed for the exchange of but-1-ene on metals.

(1) The associative mechanism (Horiuti–Polanyi (*1*)): after the hydrogenation step giving *n*-butyl and *sec*-butyl intermediates, the following dehydrogenation step leads to 2-d_1 and 1-d_1 but-1-ene species, respectively. If, as is generally assumed, several consecutive alkyl–alkene reversals occur before desorption, multideuterated species are initially produced.

(2) The allylic mechanism (*3*): this produces the 3-d_1 but-1-ene or, if a multistep mechanism with several interconversions between π-allylic and π-olefinic species occurs before the desorption, multideuterated species labeled on all four carbon atoms are produced.

(3) The vinylic-type dissociative mechanism (Farkas (*2*)): this involves the rupture of one of the three vinylic carbon–hydrogen bonds. Contrary to the Horiuti–Polanyi

mechanism, the Farkas mechanism is expected to produce, besides 2-d_1 but-1-ene, la-d_1 and lb-d_1 but-1-enes in unequal amounts.

In the reactions of but-1-ene on iron at 50°C, the pronounced break in the deuterium distribution of the but-1-enes after d_3 and the absence of deuterium on carbon 3 in the d_1 but-1-enes suggest that only the vinylic hydrogens were exchanged in this molecule. The allylic mechanism and the repetitive associative mechanism must therefore be discarded. Two mechanisms are left to account for the observed distribution, namely, the vinylic-type dissociative mechanism and the nonrepetitive associative mechanism.

Although most of the exchange results in the literature have been interpreted by means of the Horiuti–Polanyi mechanism, some evidence has recently been given in favor of the vinylic-type dissociative mechanism. On iron films, for instance (*6*, *7*), exchange of the internal vinylic hydrogen atom widely predominates (more than 99% of the d_1 but-1-ene is labeled on carbon 2) and la,2-d_2 and lb,2-d_2 but-1-enes are obtained in unequal amounts (65/35) by consecutive reactions. It was therefore proposed that all three vinylic hydrogens in but-1-ene are exchanged according to a Farkas dissociative mechanism. Since on Fe/pumice, 2-d_1 but-1-ene is the major exchange product, we consider that on the supported catalyst also this species is obtained mostly by a dissociative mechanism. In contrast, la-d_1 and lb-d_1 but-1-ene, obtained in *equal amounts* on supported iron catalysts, is thought to be formed by alkyl–alkene reversal and *not* by a dissociative mechanism, which is characterized by an unequal amount of la- and lb-d_1 (*5*).

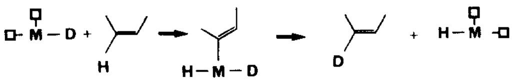
The existence of two exchange mechanisms, associative and dissociative, which produce 1-d_1 and 2-d_1 but-1-enes, respectively, and which probably have different sensitivities to poisoning and catalyst pretreatment, could account for the great irreproducibility of the 1-d_1/2-d_1 ratio. Carbonaceous residues and carbides which are known to form easily on iron catalysts could be a selective poison of reactive sites where a dissociative type mechanism takes place.

But-1-ene → but-2-ene isomerization. On iron films, most of the *cis* and *trans* isomers were obtained without deuterium incorporation, by a direct sigmatropic 1–3 hydrogen shift (*10*). On the supported iron catalysts at 50°C, the *M* values were larger for the but-2-enes than for the exchanged but-1-enes, and a break after d_4 in the deuterium pattern of the isomers corresponds to the break after d_3 in the distribution of the exchanged molecules. Therefore, besides the intramolecular hydrogen shift, an additional reaction takes place, in which one deuterium atom is introduced on carbon 1, according to the microwave analysis of the d_1-*cis* butenes. This additional reaction could proceed either by an allylic or by an associative mechanism. Because of the close parallelism between the amounts of 1-d_1 but-1-enes and the extent of isomerization, we believe that the nonrepetitive Horiuti–Polanyi mechanism and *not* the allylic mechanism is responsible for this additional isomerization reaction.

In the experiments made at 100°C, the breaks in the deuterium distribution of both the isomerized and the exchanged molecules disappeared and highly deuterated species were obtained. These results suggest the occurrence of a repetitive process which might be allylic, since small but definite amounts of 3-d_1 but-1-ene are obtained.

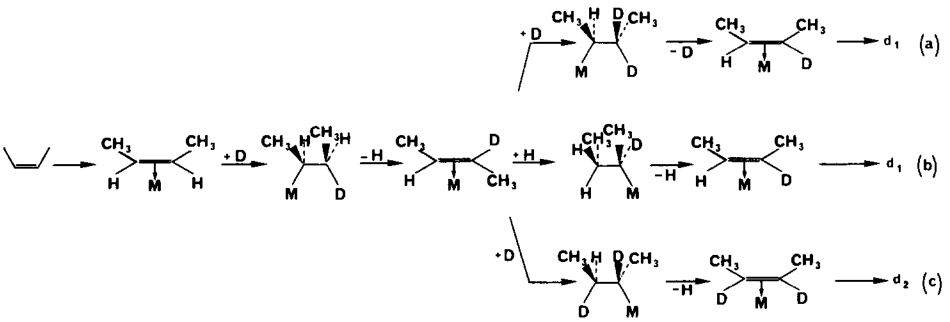
Reactions of cis But-2-ene

Exchange. The most striking difference between the experiments made on films and on supported catalysts is that *cis* but-2-ene is rapidly exchanged over Fe/pumice and *not* on Fe films (*10*). The location of the deuterium on carbon 2 in the d_1 *cis*-butene could be explained either by a dissociative mechanism of the Farkas type (Scheme 1):



SCHEME 1

or by an associative mechanism (Scheme 2):

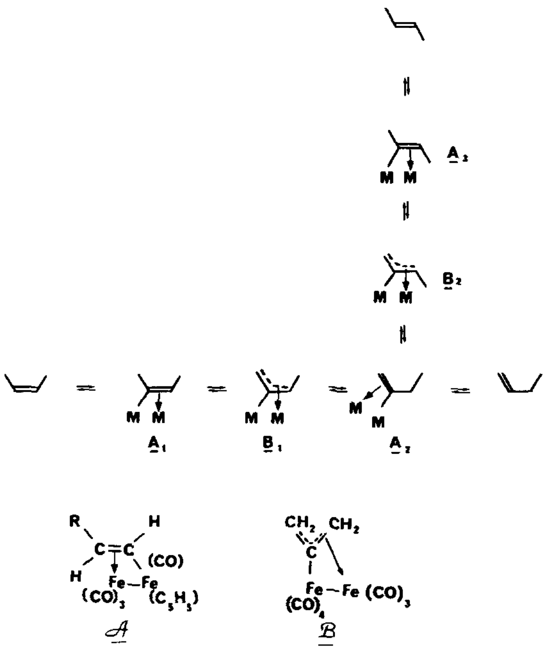


SCHEME 2

In the latter case, however, two consecutive steps are required to form the 2-d_1-*cis* but-2-ene, involving either the addition of an adsorbed hydrogen atom to the *trans* π-olefinic species (reaction 2b) or the elimination of a deuterium atom from an adsorbed dideuterio alkyl radical (reaction 2a). Since isotopic dilution was rather low under our experimental conditions and since the rupture of a carbon–hydrogen bond is easier than the rupture of a carbon–deuterium bond, one would expect reactions 2a and 2b to be less important than reaction 2c and d_2-*cis* but-2-ene to be obtained in much larger amounts than d_1-*cis* but-2-ene. Just the reverse, however, is observed: d_1/d_2 is larger than unity, which shows that exchange of *cis* butene does not take place according to an associative Horiuti–Polanyi mechanism, but rather according to a *vinylic-type dissociative mechanism.*

On the other hand, the shape of the deuterium distribution pattern of the *cis* but-2-ene, especially the break after d_5, strongly suggests that a multiple exchange of the allylic type, extending to just one half of the molecule, is superimposed on the vinylic type of exchange.

It is therefore tempting to explain the exchange of *cis* butenes on supported iron by a mechanism similar to the one that explains $\beta \rightarrow \alpha$ double-bond migration on iron films (*12*). Several interconversions between two diadsorbed species, σ-vinylic π-olefinic (*A*) and σ-vinylic π-allylic (*B*) (Scheme 3) which are similar to the well-known stable iron complexes, $\mathcal{A}$ and $\mathcal{B}$, respectively (*19–23*), could explain the deuterium distribution of the exchanged *cis* but-2-enes on supported iron catalysts with the break at d_5, and also, on account of the free rotation around the C_2–C_3 bond in species A_2, the similar deuterium distribution of the d_2–d_5 *trans* isomers.



SCHEME 3

cis–trans isomerization. The two major products in this reaction are the d_0 and the d_1 *trans* butenes. While the 2-d_1 monodeutero molecule is easily accounted for by a simple nonrepetitive Horiuti–Polanyi mechanism (Scheme 2), the mechanisms for the direct process, yielding d_0-*trans* butene, involve weakening of the C_2–C_3 bond and free rotation either by partial displacement of one of the methylic hydrogens (*13*) or by a charge transfer from the adsorbed olefin to the metal (*9*).

Double-Bond Migration

The double-bond migration mechanism in but-2-ene to but-1-ene isomerization has to account for the but-1-ene distribution in run 8. Four mechanisms for double-bond migration have been proposed so far: an intramolecular hydrogen shift (M_1) which takes place without deuterium incorporation (*24*), a nonrepetitive alkyl–alkene reversal (M_2) or a one-step π-allylic mechanism (M_3), which *both introduce on deuterium on carbon 3,* and the multistep allylic mechanism (M_4) described in Scheme 3, leading to multiply exchanged molecules.

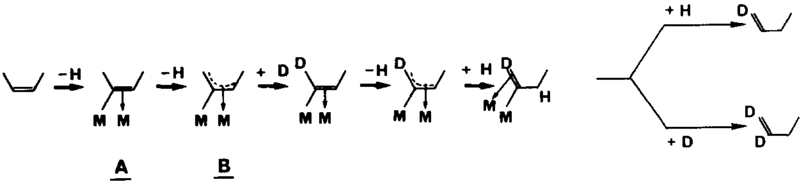
As the distribution is made at high conversion, one has to consider the possibility of consecutive reactions. *cis–trans* isomerization and exchange of but-1-ene, which are much faster than double-bond migration, could occur respectively before and after the double-bond migration and obscure the initial distribution by introducing a deuterium atom on carbon 2 or 3 or both as was discussed before. Two consecutive double bond migrations do not have to be considered because no deuterium atom is introduced on carbon 4.

None of the more simple mechanisms of double-bond migration (M_1, M_2, or M_3), even taking account of consecutive reactions, explain the formation of 1,2-d_2 molecules or the substantial amount of 1-d_1.

Moreover, the difficulty of introducing

deuterium on carbon 1 when forming but-1-ene according to mechanisms M_1, M_2, or M_3 makes it hard to understand the break after d_5: a break after d_3 should be observed instead. Mechanisms M_1, M_2, and M_3 therefore have to be ruled out.

On the other hand, the more complex, multistep allylic mechanism, M_4, would account for the formation of the 1-d_1 and 1,2-d_2 species, if one assumes (a) that adsorbed hydrogen atoms as well as adsorbed deuterium atoms are involved in the various hydrogenation steps (Scheme 4) and (b) that olefin desorption has a similar rate to that of the interconverting between species A and B.



SCHEME 4

Moreover, since all the deuterospecies from d_0 and d_5 are expected to form initially, mechanism M_4, by envisaging consecutive reactions, also easily accounts for the break at d_5 which is observed in the initial deuterium distribution.

The multistep allylic mechanism, then, explains qualitatively the major features of the but-1-ene distributions. The involvement of adsorbed hydrogen atoms, which accounts for the 1-d_1 species, can hardly be explained by assuming simple isotopic dilution; in run 8, less than one deuterium atom on the average was introduced per molecule, whereas the initial C_3D_6 over C_4H_8 ratio was 14. We suggest, therefore, that some of the hydrogen atoms released by the various dehydrogenation steps have no time to be replaced by deuterium before they are involved again in a hydrogenation step.

General Discussion

Iron films and supported iron catalysts differ in two respects.

(1) In the change from films to supported catalysts, there is a significant increase of all reactions occurring according to an associative Horiuti–Polanyi mechanism (*cis–trans* isomerization, C_1 exchange, and isomerization of but-1-ene) relative to the ones involving dissociative adsorption (C_2 exchange of but-1-ene, $\beta \rightarrow \alpha$ double-bond migration).

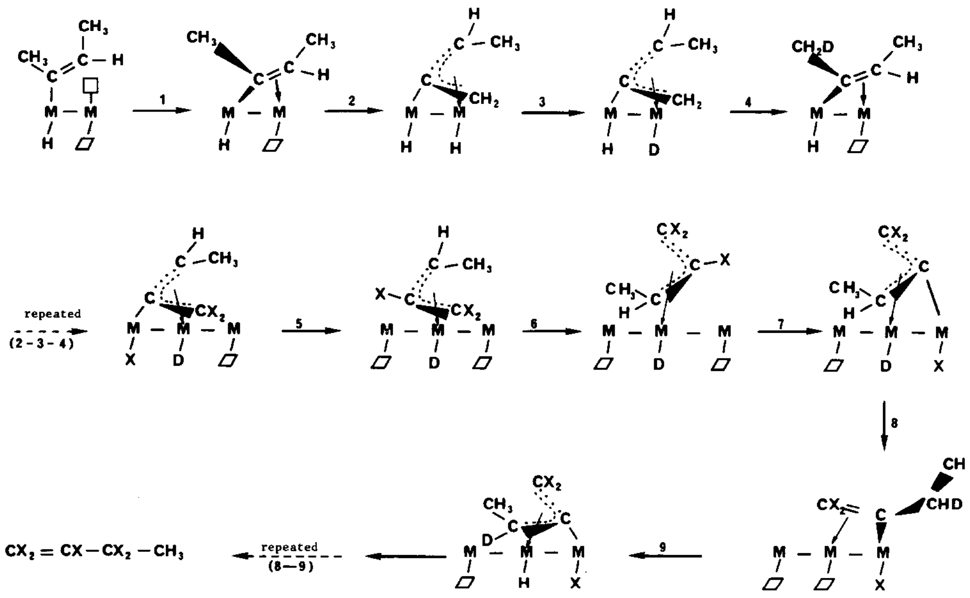
(2) On iron films, the multiple exchange which accompanies $\beta \rightarrow \alpha$ double-bond migration propagates to all four atoms of the molecule, producing mainly the perdeutero d_8 but-1-ene. On iron/pumice, it involves only three carbon atoms and yields all the d_1–d_5 but-1-enes *and cis* butenes in comparable amounts.

The reaction temperatures, −37°C on films and +50°C on supported catalysts, could account for some of the above differences. On nickel/pumice, in a series of exchange experiments made at various temperatures (−85 to +100°C) in the presence of deuterium, a progressive increase of 1-d_1 but-1-ene relative to 2-d_1 has been observed with increasing temperature, and a similar trend has also been noticed on cobalt/pumice catalysts (*25*). However, on iron/pumice at 50–100°C, the variations of the 1-d_1/2-d_1 ratios due to irreproducibility are much larger than those which might arise from temperature change. On the other hand, if one extrapolates to iron the results obtained on nickel with 1-d_1/2-d_1

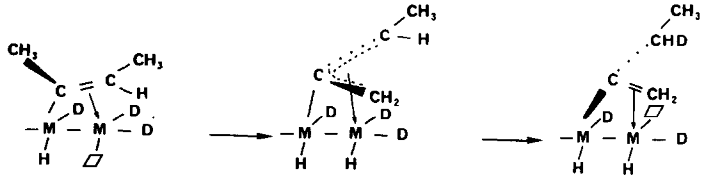
varying from 0.15 at −35°C to 0.30 at 20°C (*25*), the observed variation of 1-d_1/2-d_1 ratios, from 0 on iron films to 0.5 on iron/pumice, is far beyond the expected one.

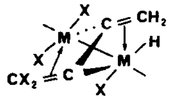
A more satisfactory and general explanation would rest on differences in surface structure: one would expect that in supported iron catalysts the severe pretreatment at 400°C by smoothing the surface would substantially decrease the number of sites of low coordination number relative to edge and face atoms. According to the theory of Ledoux (*13*), this change of surface topography would result in a significant decrease of C_2 exchange of but-1-ene relative to C_1 exchange and *cis–trans* isomerization, which is actually observed.

The differences between iron films and supported catalysts for but-2-ene exchange and but-2-ene → but-1-ene isomerization could be explained in a similar way. If one assumes, for instance, that on supported catalysts the two interconverting species *A* and *B* in mechanism M_4 are bonded to edge atoms (Scheme 5), deuterium would be introduced on carbon 1 only after adsorbed hydrogen had been replaced by a deuterium atom (step 3), while exchange at carbon 3 and double-bond migration would require, in addition, rupture of the vinylic carbon–metal bond (step 5) and rotation of the π-allylic moiety (step 6). During all these processes, desorption may occur, and that would explain the characteristic deuterium distributions of both *cis* butenes and but-1-ene, which imply participation of adsorbed hydrogen atoms, and a fairly high desorption probability. On iron *films*, however, the presence of doublets or multiplets of surface atoms of low coordination number, with at least two hydrogen or deuterium atoms attached to each metal atom, would facilitate the replacement of adsorbed hydrogen by deuterium atoms. Rupture of a σ-carbon–metal bond is no longer required for adding a deuterium atom on carbon 3, and the formation of species such as *C* would allow the exchange to propagate to all four carbon atoms in the molecule.



SCHEME 5





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