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The Mechanisms of Isomerization and Exchange of Olefins Over Metal Catalysts

II. Exchange of Olefins in the Presence of Perdeuteropropene on Iron Films

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The exchange of α-olefins (ethylene, propene, but-1-ene and pent-1-ene) and of β-olefins (*cis*-butene and *cis*-pentene) has been studied on iron films at −37 and 0°C in the presence of an excess of perdeuteropropene or perdeuteroethylene. While the exchange of the α-olefins is very fast, about 20 times faster than their isomerization, the exchange of the β-olefins may be considered as negligible.

Whereas the exchange of the simplest molecules, ethylene propylene, may be considered as a simple exchange of all four and three vinylic hydrogens, respectively, in the case of but-1-ene and pent-1-ene the internal and terminal vinylic hydrogens seem to be differentiated and a multiple exchange takes place.

INTRODUCTION

In the preceding paper (*1*) it has been shown that replacing deuterium by perdeuteropropene in tracer experiments allowed us to study the mechanisms of isomerization and exchange of olefins without interference of deuteration reactions. This new method applied to the reactions of dimethylcyclopentenes on palladium showed that exchange proceeds mainly via an olefin dissociatively adsorbed at an allylic position and that double bond migration consists of an intramolecular hydrogen shift.

It seemed interesting to us to use the same technique in order to study the isomerization and exchange reactions of olefins on other metals. Iron films were first chosen as catalyst, on account of the very large differences between iron and palladium in electronic structure as well as in catalytic behavior (*2, 3*). Acyclic olefins have also been preferred because *cis–trans* isomerization represents for these molecules an additional reaction path.

In order to clarify the presentation of the results and the discussions of the various mechanisms, this study of the catalytic reactions of olefins on iron films will be divided into three sections. The present paper deals with exchange. Double bond migration and *cis–trans* isomerization of butenes will be considered next. Finally, several more complicated molecules will be studied in order to determine the nature of the various reaction mechanisms.

EXPERIMENTAL METHODS

Materials and Catalysts

Iron films with an approximate weight of 10 mg have been prepared by evaporation under high vacuum (10^{-6} Torr) of a specpure wire obtained from Johnson & Matthey.

Ethylene, but-1-ene, *cis* and *trans* butenes, pent-1-ene of high purity grade (better than 99.9%) were obtained from Fluka. *cis*-Pentene with a purity of 97.5% was prepared from a mixture of *cis* and *trans* pentenes by semipreparative gas chromatography on a 5 m ¼ in. dimethylsulfolane column at 25°C. Perdeuteropropene was obtained from Merck Sharpe and Dohme. It contained 5.3% of C_3D_5H.

Apparatus and Procedure

The same apparatus and experiment procedures have been used as in Part I (*1*). The mixture in the reaction vessel contained 3 Torr of the reacting olefin. Unless otherwise specified, the pressure of C_3D_6 (or of C_2D_4 in the C_2D_4/C_3H_6 system) was adjusted so that the ratio between the deuterium and the hydrogen atoms was 9.4 in all experiments. Similarly the exchange of C_3D_6 (first part of Table 2) was performed in the presence of an excess of d_0-but-1-ene and the partial pressures of both olefins were such that the ratio H/D in this case was equal to 9.8.

After reaction and before mass spectrometric analysis the various molecules were separated by gas chromatography over a DMS column at 0°C, or over a silica column at 25°C in the case of the C_2H_4/C_3D_6 system.

Mass Spectrometric Analysis

Parent peaks were used for the analysis after the usual corrections for natural isotopes and fragmentation.

The fragmentation corrections for the various deuteromolecules were made on a statistical basis by using the fragmentation pattern of the light and heavy molecules. In the case of pentenes on account of the very small $m - 1$ ion the C–H and C–D fragmentations were assumed to be identical.

The energy of the ionizing electrons was 15 eV for propene and 25 eV for all other molecules.

RESULTS

1. *Ethylene*

The four hydrogen atoms of ethylene are very rapidly exchanged at −37°C in the presence of a large excess of perdeuteropropene. Two typical distributions obtained after 3 and 15 min of reaction are given in Table 1, together with the statistical distributions calculated with two selected values of the deuterium content $x = D/(H + D)$ of the molecules.

TABLE 1
EXCHANGE OF C_2H_4 IN THE PRESENCE OF C_3D_6 ON IRON FILM AT −37°C

	Observed after 3 min of reaction	Statistical distribution	Observed after 15 min of reaction	Statistical distribution
d_0	11.6	2.5	—	0.03
d_1	16.4	15.3	0.63	0.76
d_2	30	34.6	6.2	7.7
d_3	29.7	34.6	34	34.3
d_4	12.3	13	59.2	57.3

On account of the very large background corrections at mass $m/e = 28$, the determination of the $C_2H_4^+$ ion is very inaccurate, which explains the disagreement between the calculated and observed values for d_0-ethylene. The agreement for the d_1, d_2, d_3, d_4 molecules shows that all the hydrogens of ethylene are exchanged by a simple exchange process (*4*).

2. *Propene*

Heavy propene was exchanged in the presence of a large excess of d_0-but-1-ene at −37°C. The exchange was followed continuously by mass spectrometry, so that several analyses of the deuteropropenes could be made at various reaction times: these are reported in Table 2 together with the values of $\rho = x_1^2/x_0x_2$ when the determination of x_2 was accurate enough.

The distribution at 0.5 and 1.8 min may be considered as initial distributions and show a simple exchange process. The observed value of 3 for ρ corresponds exactly to the one which one might expect if a simple exchange takes place involving three deuterium atoms of the molecule, all equivalent ($\rho = (C_3^1)^2/C_3^0C_3^3$). These results are confirmed by an experiment performed at 0°C in order to obtain larger amounts of perdeuteromolecules. The definite break in the product distribution after d_3 shows again that only three deuterium in C_3D_6 are exchangeable.

It should be noted, however, that the

TABLE 2

Exchange of C_3D_6 in Presence of C_4H_8 and Exchange of C_3H_6 in the Presence of C_2D_4 on Iron Film[a]

	Temp (°C)	t (min)	x_0	x_1	x_2	x_3	x_4	ρ
C_3D_6/C_4H_8	−37	0	94.7	5.3				
		0.5	93.5	6.5				
		1.8	91	9				
		4.5	83.5	16	0.5			
		26	51.5	38.8	9.7			3
		90	36.2	44.6	17.6	1.6		3.1
		180	28.3	44.7	22.8	4.2		3.1
	0	260	14.5	37.9	34.5	11.2	<2	2.9
C_3H_6/C_2D_4	−37	6	84.7	14.8	0.2	0.2		11.8
		10	76.8	22.2	0.7	0.3		9

[a] When the reacting mixture consists of C_3D_6 and C_4H_8, x_0, x_1, x_2, . . . are equal to d_6, d_5, d_4, ... When the reacting mixture consists of C_3H_6 and C_2D_4, x_0, x_1, x_2, . . . are equal to d_0, d_1, d_2, ...

equivalence of the three exchangeable deuterium atoms is not always observed. In a slow experiment effected at −37°C with C_3H_6 in the presence of a large excess of C_2D_4 contaminated by traces of an unknown material (appearing at mass 46), the observed distributions with a high ρ ratio seem to indicate that one hydrogen is more easily exchanged than the others.

3. *Butenes*

The contact reactions of but-1-ene, *cis* and *trans* butenes in the presence of C_3D_6 have been studied at −37°C. The product distributions analyzed after 2 or 3 min of reaction are reported in Table 3 together with the extent of double bond shift.

A striking difference is observed between

TABLE 3

Exchange and Isomerization of Butenes in the Presence of C_3D_6 on Iron Film at −37°C

Reacting hydrocarbon:	But-1-ene		*trans*-Butene		*cis*-Butene	
C_3D_6/C_4H_8 ratio:	9	15.4	14	14	14	14
Contact time (min):	2	3	3	8	2	4
Isomerization (%):	*trans* 1	1	*cis* 0.07	0.15	*trans* 0.95	0.4
	cis 0.8	0.7	1 0.53	0.92	1 1.8	0.6
Exchange (%)	46.6	66.4	0	0.3	0.1	0
d_0	53.4	33.6	100	99.7	99.9	100
d_1	42.7	56.1		0.3	0.1	
d_2	3.05	8.5				
d_3	0.25	1.13				
d_4	0.03	0.09				
d_5	—	0.02				
d_6	0.02	—				
d_7	0.15	0.06				
d_8	0.40	0.50				

the behavior of α- and β-olefins. *Cis* and *trans* butenes are virtually not exchanged, while a very fast reaction is observed with but-1-ene. The distribution obtained for this compound shows that the exchange reaction is most probably a simple exchange process and moreover that *one* hydrogen is much more reactive than the others, as already observed in the "abnormal" reaction of propene.

4. *Pentenes*

The deuterium distributions of the exchanged molecules obtained from the pentenes at -37°C after 5 or 6 min of reaction (Table 4) confirm the preceding results. Although some of the pent-2-enes result from a double bond shift, the amounts of exchanged β-olefins are very small when compared with the amounts of isomerized products. On the other hand, the exchange of pent-1-ene is about as fast as the exchange of but-1-ene.

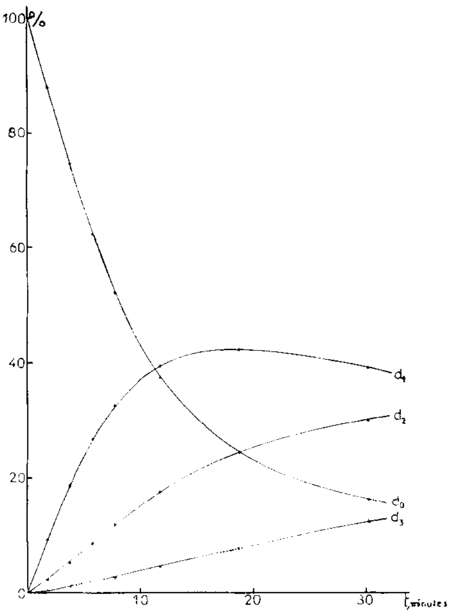


FIG. 1. Exchange of pent-1-ene in the presence of perdeuteropropene on iron film at -37°C.

In order to determine the initial distribution and the number of exchangeable hydrogens, the reaction of pent-1-ene in the presence of C_3D_6 at -37°C was followed mass spectrometrically (Fig. 1). Some of the distributions are given in Table 5 with the distribution calculated on a statistical basis with two selected values of deuterium content $x = D/(H + D)$ of the molecule. It is obvious from Fig. 1 and from the first distribution reported that a *multiple exchange* takes place in this case. The break after d_3 in the distribution obtained after 50 min of reaction shows again that three hydrogen

TABLE 4
EXCHANGE AND ISOMERIZATION OF PENTENES IN THE PRESENCE OF C_3D_6 ON IRON FILM AT -37°C

Reacting hydrocarbon:	Pent-1-ene		*cis*-Pentene	
C_3D_6/C_5H_{10} ratio:	18		18	18
Contact time (min):	5.30		6	7
Isomerization (%):	*trans* 4.9 *cis* 2.3		*trans* 21.3 1 2	22.7 2.3
Exchange (%)	74.2	Calculated distribution	5.2	6.9
d_0	25.8	25.8	94.8	93.1
d_1	46.2	46.2	3.7	4.66
d_2	21.4	18	0.76	1.06
d_3	5.7	3	0.21	0.30
d_5	0.75		0.24	0.38
d_5	0.12		0.24	0.46
d_6	0.03		0.05	0.04
d_7–d_{10}	—		—	—

TABLE 5
EXCHANGE OF PENT-1-ENE IN THE PRESENCE OF C_3D_6 ON IRON FILM AT −37°C

	Observed after 2 min of reaction	Statistical distribution (x = 0.034)	Observed after 50 min of reaction	Statistical distribution (x = 0.47)
d_0	88	88	12	12
d_1	9.3	9.3	31.9	31.9
d_2	2.3	0.33	34.5	28.3
d_3	0.4		18.6	8.7
d_4	—		2.5	
d_5	—		0.5	
d_6–d_{10}	—		—	

atoms are more readily exchanged than the seven others. On account of the multiple exchange taking place, it is difficult to decide about the equivalence or the nonequivalence of the exchangeable hydrogens. However, if one assumes a similar difference in reactivity between the hydrogens as that observed in the case of but-1-ene, and takes into account the multiple exchange estimated from the initial distribution in Table 5, it is possible to restore approximately a distribution not very different from the one which is effectively observed (third row of Table 4).

DISCUSSION

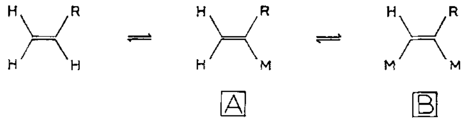
Vinylic Dissociative Adsorption

All the results presented in this work show that *only* the vinylic hydrogens are involved in the exchange of acyclic α-olefins on iron catalysts. Four hydrogen atoms are exchanged in the case of ethylene and three for any of the monosubstituted ethylenes considered (C_3H_6, C_4H_8, C_5H_{10}).

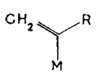
This important result shows once more the specificity of the metal in the catalytic reactions. On palladium it was shown that dissociatively adsorbed olefin at an *allylic* position was responsible for the exchange process (*1*). On iron the allylic type of adsorption does not seem to play an important role, at least as far as the α-olefins are concerned, while the *vinylic* C–H bonds are broken very easily.

Two other matters are also subject to discussion. In ethylene and propene, it seems that all the vinylic hydrogens are equivalent for the exchange reaction and a simple exchange takes place. When the length of the alkyl substituent increases from methyl (in propene) to *n*-propyl (in pent-1-ene) the multiple exchange is increased and the differentiation of one vinylic hydrogen atom becomes more pronounced.

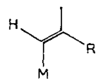
The first feature implies a longer residence time of the dissociatively adsorbed species on the surface which makes possible the formation of diadsorbed species B. Interconversion between monoadsorbed species A and diadsorbed species B accompanied by direct *cis–trans* isomerization which is described in the next paper (*5*) explains the multiple exchange.



Although the localization of the deuterium could not be made in the exchanged but-1-ene and pent-1-ene molecules, we suggest that the vinylic hydrogen atom which is more rapidly exchanged than the other two is the internal vinylic hydrogen atom. That would imply that species A is more favored than species A′ on the metal surface.



A



A′

It is worthwhile to outline that propene 2-d_1 was found to be much more favored than any other species in the exchange of propene with deuterium and deuterium oxide on a nickel catalyst (*6*). It would be interesting to compare with our method the properties of nickel and iron in the exchange reaction and work in this direction is in progress in our laboratory.

Differences in Exchange Rates Between α- and β-Olefins

The second main result in this work concerns the difference between the rates of exchange of α- and β-olefins. These rates differ by two to three orders of magnitude. Two different explanations may be provided for this observation:

1. The rate of adsorption of β-olefins is much smaller than the rate of adsorption of α-olefins.
2. Adsorbed β-olefins are indeed formed, but more strongly held on the surface than α-olefin, which would mean that the carbon–metal bond is much stronger in an adsorbed β-olefin than in an α-olefin.

Although the results presented here are not sufficient to choose between the two hypotheses, the fact that the exchange of α-olefin is a simple exchange or a quasi-simple exchange and not a multiple exchange is in favor of the second hypothesis. We show in Ref. (*5*) that the study of the double bond shift strengthens this view.

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