

The Reaction of Deuterium with Olefins on Nickel Catalysts: Evidence for Adsorbed Vinylic Species

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The interaction of deuterium with 1,2-dimethylcyclopentene, 2,3-dimethylcyclopentene, 1-methyl-2-methylenecyclopentane, 1,2-dimethylcyclobutene, 1-methyl-2-methylenecyclobutane, bicyclo[2,2,1]heptene, but-1-ene, and *cis*-but-2-ene was studied from -85 to 50°C on nickel films in a static apparatus and on Ni/pumice in a flow system. Unexpected d_3 and d_4 molecules were obtained in the deuteration of bicyclo[2,2,1]heptene. The position of the double bond in the ring of the other cycloolefins was the main factor governing their behavior: in the deuteration of 1,2-dimethylcycloalkenes, the saturated products, especially the *trans* isomers, were much more exchanged and the percentage of *trans* was lower than when the starting material consisted of the olefins with the double bond in 2,3 or exocyclic positions. The hyperfine distribution, obtained by microwave analysis, of the exchanged d_1 but-1-ene, revealed that the major part of the deuterium was introduced on C_2 ; the *cis*-*trans* isomerization was much faster than the double bond migration with the introduction of zero or one deuterium atom while the isomerized but-1-ene showed a multiple exchange up to d_4 ; in the isomerized d_1 but-1-ene, the deuterium atom was distributed on the three carbon atoms C_1 , C_2 , C_3 . Most of these results clearly show that the classical Horiuti–Polanyi mechanism is not the only one taking part in the reactions. The introduction of other intermediaries, σ -vinylic, σ -vinylic π -olefinic, and σ -vinylic π -allylic species, provides a coherent explanation for all our findings. It is shown that nickel and iron behave in a very similar way.

INTRODUCTION

It has long been known that nickel metal catalyzes the hydrogenation of olefins. The classical Horiuti–Polanyi (HP) mechanism was proposed in 1934 to explain the hydrogenation of ethylene on nickel and since then it has been used quasi-exclusively to explain the hydrogenation of olefins *on nickel*. Many kinetic studies have been made to investigate this mechanism further, but they have led to erratic results, probably due to poor characterization of the catalyst (film, filament, Raney Ni, Nikieselguhr, etc.), the incomplete reduction

of the metallic phase and/or the susceptibility of nickel to poisoning. Isotopic tracer studies with deuterium, using the statistical calculations of Kemball (1) to take into account the deuterium distribution of saturated and unsaturated products, strongly sustained this mechanism in the case of hydrogenation of ethylene.

The HP mechanism was later extended to the hydrogenation of higher olefins on nickel (2). However, if one applied this mechanism to the deuteration of propene, a quasi-equal distribution of deuterium on the three carbon atoms of deuterated propene was to be expected, but Hirota and Hironaka (3), using microwave spectrometry analysis, found that on nickel catalysts the deuterium was localized mainly on the C_2 carbon atom in the exchange reaction between propene and D_2 or D_2O . Thus, considering the unique HP mechanism to be operating in the reaction, Hirota and

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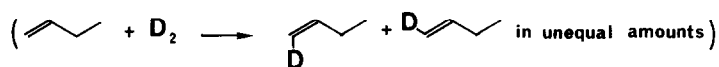
Hironaka had to suppose that the *n*-propyl radical ($M-CH_2-CHD-CH_3$) was much more reactive than the isopropyl radical ($CH_2D-CH_2-CH_3$). In coordination

$$\begin{array}{c} | \\ M \end{array}$$

chemistry, there is no direct proof for such a difference in the reactivity of alkyl radicals.

An alternative explanation is the existence of *alkenyl reactive species*. On iron films, in the exchange reaction between deuterated and nondeuterated olefins, it was clearly demonstrated (4) that the pre-

cursor step in the β -olefin \rightarrow α -olefin double bond migration was vinylic dissociative adsorption. This type of adsorption was confirmed when it was found that but-1-ene, in the presence of perdeuteropropene on iron films, gives rise almost exclusively to the $CH_2=CD-C_2H_5$ molecule (5). More recently Ledoux *et al.* (6) have taken as a proof of σ vinylic reactive species the dissymmetry of deuterium distribution between spectroscopic 1 and 2 positions on carbon 1 of but-1-ene formed in the deuterium exchange reaction of but-1-ene:



On nickel film, in the deuterium exchange reaction of but-1-ene with perdeuteropropene, this dissymmetry was only slightly noticeable and it disappeared when the reaction was carried out in the presence of deuterium at lower temperature.

It therefore seemed to us that much work needed to be done to conclude firmly regarding the existence of σ -vinylic reactive species on nickel. For this purpose we have studied the hydrogenation of various cycloolefins, the stereochemistry of which was expected to give information on the reaction intermediaries. We have also studied the hydrogenation and related reactions of butenes where it is possible to locate the deuterium atoms by microwave spectroscopy. The latter study was performed with deuterium (and not perdeuteropropene) as tracer agent and on supported nickel catalysts in a wide range of temperatures.

EXPERIMENTAL

Catalysts

Metal films were prepared in a conventional high vacuum system (10^{-6} Torr) by evaporation of specpure nickel (Johnson Matthey) and condensation on Pyrex glass at 0°C .

Ten percent nickel on pumice was prepared according to a procedure described by Covert *et al.* (7). Dried pumice was impregnated with a solution of $Ni(NO_3)_2$, and nickel carbonate was precipitated at room temperature by addition of $(NH_4)_2 CO_3$; after filtration and drying overnight at 100°C , the resulting powder was reduced under a hydrogen flow at 450°C during 1 hr.

A new batch of catalyst was used for each reaction. Before each run the catalyst was treated overnight at 450°C under a hydrogen flow and 90 min under a deuterium flow at the same temperature.

As we were not sure that this procedure resulted in a total reduction of nickel, the reaction of 1-butene with hydrogen was carried out on the powder obtained just before reduction, which was believed to be NiO. No significant conversion of the olefin was observed: 0.05% of isomerization and 0.2% of hydrogenation were detected under experimental conditions where the reduced catalyst gave typically 7% isomerization and 80% hydrogenation. It was also checked that the pumice carrier was completely inactive for these reactions.

The particle size of the metal in the nickel/pumice catalyst, as measured by X-ray diffraction, was approximately 500 \AA .

On the evaporated films we expect that the crystallites were also quite large.

Materials

Pure grade hydrogen and 99.4% deuterium from Air Liquide were dried on molecular sieves at 77 K before use.

Puriss grade but-1-ene was purchased from Fluka.

Bicyclo[2,2,1]heptene, shown below as (VI), was of high purity (>99%) and was purchased from Aldrich. Hydrogenation of this hydrocarbon on Raney nickel at 50°C and 150 atm. gave bicyclo[2,2,1]heptane. The preparation and purification of the other cycloolefins have already been described (8).

Apparatus and Procedure

Static system. The apparatus was connected to an AEI MS2 mass spectrometer. The reaction of the cyclopentenes with deuterium was extremely fast and was completed in a few minutes. Bicyclo[2,2,1]heptene reacted much more slowly and the deuteration could be stopped after a few percent conversion. In all cases a mixture of 50 Torr of deuterium and 5 Torr of olefin was introduced on the freshly prepared film at the desired temperature.

Flow system. The catalytic reaction was carried out in an all-glass grease-free system including a reactor operating under dif-

ferential conditions. A small amount of reactant (a few milligrams) was used for each run and was carried through the reactor at a constant partial pressure (5 Torr) by deuterium gas (755 Torr). The hydrocarbon reaction mixture was collected at 77 K and then analyzed and separated by gas-liquid chromatography. Each olefin isomer was analyzed by *mass spectrometry* and for but-1-ene and in one case for *cis*-butene by *microwave spectroscopy*.

All these analysis procedures are described elsewhere (9). The mass spectrometer used was a Varian Mat-CH7 and the rotational spectrum of butene was recorded on a conventional 50-kHz square-wave Stark spectrometer (University of Nancy) and a Hewlett-Packard 33-kHz spectrometer (University of Strasbourg).

RESULTS

Deuteration of Disubstituted Cycloolefins on Nickel Films

The deuteration of 1,2-dimethylcyclopentene (I), 2,3-dimethylcyclopentene (II), 1-methyl-2-methylenecyclopentane (III), 1,2-dimethylcyclobutene (IV), and 1-methyl-2-methylenecyclobutane (V) has been studied on a nickel film at 0 or -20°C. At these temperatures, the reaction was very fast and the olefin disappeared after 3 or 4 min. No further exchange of the saturated products was observed.

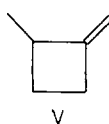
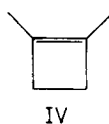
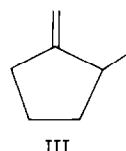
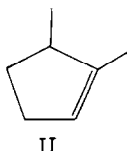
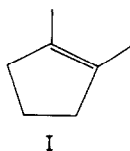


TABLE I

Deuteration of 1,2-Dimethylcyclopentene, 2,3-Dimethylcyclopentene, 1-Methyl-2-methylenecyclopentane, 1,2-Dimethylcyclobutene, and 1-Methyl-2-methylenecyclobutane on Nickel Films at 0°C

Hydrocarbon	1,2-Dimethylcyclopentene (I)		2,3-Dimethylcyclopentene (II)		1-Methyl-2-methylenecyclopentane (III)		1,2-Dimethylcyclobutene (IV)		1-Methyl-2-methylenecyclobutane (V)	
	<i>cis</i> 66.5%	<i>trans</i> 33.5%	<i>cis</i> 29.5%	<i>trans</i> 70.5%	<i>cis</i> 48%	<i>trans</i> 52%	<i>cis</i> 84%	<i>trans</i> 16%	<i>cis</i> 67%	<i>trans</i> 33%
d_0	8.9	3.3	13.5	17.0	10.9	12.5	8.1	3.2	3.2	5.8
d_1	15.9	7.7	21.5	18.4	17.7	15.8	25.8	8.1	21.5	25.2
d_2	20.8	11.7	24.4	28.4	19.3	16.1	36.0	17.1	52.8	51.2
d_3	11.9	14.1	16.9	15.5	14.5	14.3	15.0	19.3	12.3	11.2
d_4	9.8	13.1	10.9	9.8	11.0	12.0	7.9	13.1	7.3	4.3
d_5	8.0	11.9	6.4	5.6	8.1	9.3	4.3	10.8	2.0	1.2
d_6	6.4	9.9	3.4	2.9	5.3	6.8	1.7	8.4	0.8	0.5
d_7	5.1	8.1	1.7	1.5	4.5	4.6	0.5	7.0	0.3	0.2
d_8	4.0	6.4	0.7	0.6	2.8	2.7	0.5	5.0		0.2
d_9	3.1	4.9	0.7	0.3	1.9	1.9	0.2	3.4		0.1
d_{10}	2.4	3.6	0.3	0.1	1.2	1.1	0.1	2.1		
d_{11}	1.7	2.5	0.1	0.05	1.0	1.1		1.4		
d_{12}	1.1	1.6	0.1		1.0	0.7		1.0		
d_{13}	0.7	0.9	0.05		0.8	0.5				
d_{14}	0.3	0.2			0.1	0.5				
$M = \sum_{i=0}^{14} id_i/100$	3.76	4.94	2.47	2.20	3.44	3.42	2.16	4.25	2.10	1.91

The main results obtained in the deuteration of the different olefins at 0°C are given in Table 1. The results at -20°C are not included as they are not significantly different from those at 0°C.

If one first compares the deuterium distributions of the *cis* and *trans* 1,2-dimethylcycloalkanes obtained in the deuteration of the various cycloolefins, some interesting features appear. If the reacting olefin was 1-methyl-2-methylenecyclobutane (V), the saturated molecules were poorly exchanged, with a maximum in d_2 and a decreasing distribution beyond this maximum. The value of the mean deuterium content M was therefore small and no appreciable difference between the distribution of the *cis* and *trans* dimethylcycloalkanes could be noticed. The situation was different with 1,2-dimethylcyclobutene

(IV): in this case the *trans* isomer was much more exchanged than the *cis* one ($M = 4.25$ and 2.16, respectively).

A parallel variation appeared in the cyclopentene series. The deuteration of 2,3-dimethylcyclopentene (II) gave similar distributions for the *cis* and *trans* isomers with a low deuterium content. The same results were given by 1-methyl-2-methylenecyclopentane (III) but it is worth noting that the deuterium content was much higher than in the deuteration of the corresponding 1-methyl-2-methylenecyclobutane (V). 1,2-Dimethylcyclopentene (I) gave highly deuterated cycloalkanes, more deuterated than in the reaction of 1,2-dimethylcyclobutene (IV), and with a large difference between the *cis* and *trans* isomers, as in the deuteration of 1,2-dimethylcyclobutene (IV).

The variations in the *cis-trans* distribu-

TABLE 2

Deuteration of 1,2-Dimethylcyclopentene (I) and 2,3-Dimethylcyclopentene (II) on Supported Nickel Catalyst at 25°C

Hydrocarbon	1,2-Dimethylcyclopentene (I)			2,3-Dimethylcyclopentene (II)		
Conversion	8.1			3.1		
	<i>cis</i> %	<i>trans</i> %	Olefin	<i>trans</i> %	<i>cis</i> %	Olefin
	75.5	24.5		61.2	38.8	
d_0	9.8	1.0	97.78	8.1	12.2	98.24
d_1	10.1	2.6	1.20	17.8	12.4	1.55
d_2	27.3	11.6	0.58	36.8	27.4	0.21
d_3	15.9	30.4	0.30	15.3	20.7	
d_4	12.9	19.7	0.14	9.9	14.2	
d_5	11.5	16.6		6.2	5.7	
d_6	4.6	8.5		2.4	2.0	
d_7	2.1	4.4		1.3	1.8	
d_8	1.4	1.9		0.6	1.1	
d_9	0.9	0.8		0.3	0.6	
d_{10}	0.9	0.7		0.3	0.4	
d_{11}	0.9	0.5		0.2	0.4	
d_{12}	0.5	0.5		0.2	0.4	
d_{13}	0.5	0.5		0.2	0.4	
d_{14}	0.5	0.5		0.4	0.4	
$M = \sum_{i=0}^{14} id_i/100$	3.21	4.16	1.68	2.54	2.77	1.12

tions were also very important. The deuteration of 1,2-dimethylcyclopentene (I), 1-methyl-2-methylenecyclopentane (III), and 2,3-dimethylcyclopentene (II) gave 33.5, 52, and 70.5% of *trans* 1,2-dimethylcyclopentane, respectively. A significant feature of these experiments is that the percentages of *trans* isomer vary in a parallel way in the cyclobutene series: 16% of *trans* 1,2-dimethylcyclobutane was obtained in the deuteration of 1,2-dimethylcyclobutene (IV) and up to 30% if the reacting olefin was 1-methyl-2-methylenecyclobutane (V). However, we must point out that the percentage of the *trans* isomer was much lower than in the case of the corresponding olefin with a five-membered ring. This is related to the higher M values which we observed in the cyclopentane series as pointed out above.

Deuteration of Distributed Cycloolefins on a Supported Nickel Catalyst

The deuteration on nickel films was so fast that it was impossible to see whether any double-bond shift occurred and to check whether the deuterium and *cis-trans* distributions at high conversion were substantially different from the corresponding distributions at low conversion. Several experiments were therefore carried out in a flow system using 10% nickel/pumice catalyst (much lower activity) and the reaction was stopped after a few percent of the olefin had been converted into saturated hydrocarbons.

The reaction of 1,2-dimethylcyclopentene (I) and 2,3-dimethylcyclopentene (II) with deuterium was studied at 25°C and the results are given in Table 2. It is clear that

TABLE 3

Deuteration of Bicyclo[2,2,1]heptene (VI) on Nickel Films: Distribution of Bicyclo[2,2,1]heptane

Temperature (°C)	0	0	0	0
P_{D_2} (Torr)	120	60	30	15
d_0	10.4	8.7	3.7	4.1
d_1	15.2	6.6	25.7	20.4
d_2	57.1	61.8	39.1	47.5
d_3	11.7	17.1	26.0	23.2
d_4	5.6	5.6	5.4	4.7
d_5	0.5	0.5	0.5	0.5
$M = \sum_{i=0}^5 id_i/100$	1.86	2.04	2.14	2.04

no substantial differences appeared with the figures which were obtained on films and presented in Table 1, although the M values were somewhat higher on films, this probably being due to their greater reactivity: the deuterium distributions of the *cis* and *trans* 1,2-dimethylcyclopentanes were similar and up to 61.2% of the *trans* isomer was obtained when the reacting olefin was 2,3-dimethylcyclopentene (II) while the *trans* was only 24.5% and was much more exchanged in the case of 1,2-dimethylcyclopentene (I).

It is interesting that experiments at high conversion on supported catalysts gave the same results as reactions at high conversion on films and at low conversion on supported catalysts: 25.5% of *trans* 1,2-dimethylcyclopentane was obtained from 1,2-dimethylcyclopentene (I) at 70% of conversion and 67.8% from 2,3-dimethylcyclopentene (II) at 95% of conversion.

An important point is that we have never detected any trace of isomerized olefin in the gas chromatographic analysis of the reaction products. As can be seen in Table 2, the reacting olefins are poorly exchanged.

Deuteration of Bicyclo[2,2,1]heptene on Nickel Films

The deuteration of bicyclo[2,2,1]heptene (VI) on nickel films was substantially

slower than the reaction of the disubstituted cycloolefins which are mentioned above. However, only 4 or 5 min were necessary for half of the olefin to disappear and, if we have been able to calculate initial distributions, the figures obtained in this way are not very accurate. This is the reason why the distributions given in Table 3 have been determined after 30 sec of reaction, which corresponds in all cases to a conversion of about 10%.

All experiments have been carried out at 0°C. The olefin pressure in the system being maintained at a fixed value of 5 Torr, the deuterium pressure was varied between the large limits of 30 to 120 Torr. We always found a maximum value for d_2 bicyclo[2,2,1]heptane but significant amounts of d_3 and d_4 , up to 31% of the total reaction products, were also obtained. There was a tendency for the sum ($d_3 + d_4$) to decrease with increasing hydrogen pressure. No appreciable quantities of molecules more exchanged than d_4 were present in the distribution.

We have also studied the exchange of bicyclo[2,2,1]heptane in similar conditions (0°C and $P = 60$ Torr). The only molecules present in the distribution after 30 sec of reaction (~10% conversion) were d_1 (78.4%) and d_2 (21.6%). Clearly no further exchange proceeded beyond d_2 . This was already observed by Burwell *et al.* on palladium (10).

Reactions of Butenes with Deuterium

The isomerization, hydrogenation, and exchange of but-1-ene with deuterium were studied at -85, -37, 0, 23, and 50°C on 10% Ni/pumice and the same reactions from *cis*-butene were studied at 24°C. The results are given in Tables 4 and 5 which include the mass spectrum distribution of the different olefins together with the microwave localization of the deuterium atom in the d_1 but-1-ene exchanged and isomerized molecules.

Although no kinetic studies were made on these catalysts, it can be seen from Table 4 that at temperatures lower than 50°C

TABLE 4
 Deuterium-But-1-ene Reactions on Ni Supported on Pumice

Temperature (°C)	50	23	23	0	-37	-85
Weight (ω) (mg)	100	100	100	150	200	800
Butene flow rate (F) ($\mu\text{l}/\text{min}$)	6.5	1.2	1.5	1	0.5	1.2
$\alpha_c^d(\alpha_c \times F/\omega)$	47.4 (3.09)	47.6 (0.57)	2 (0.03)	60.2 (0.40)	32.3 (0.08)	1.6 (2.4×10^{-3})
$\alpha_c^t(\alpha_c \times F/\omega)$	18.5 (1.20)	51.3 (0.62)	2.5 (0.04)	43.4 (0.29)	41.6 (0.10)	14.1 (0.021)
$\alpha_{\text{H}}^d(\alpha_{\text{H}} \times F/\omega)$	29.5 (1.92)	86 (1.03)	62.2 (0.93)	90.5 (0.60)	88.7 (0.22)	15.9 (0.024)
Products	<i>trans</i>	<i>cis</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>cis</i>
Composition of olefins	52.6	19.1	16.8	39.8	21.5	98.4
d_0	81.5	45.3	49.0	39.8	67.7	1-B
d_1	13.3	29.5	28.9	56.6	58.4	86.0
d_2	3.2	14.7	13.0	33.6	32.8	13.6
d_3	1.0	6.4	5.6	6.7	6.2	0.4
d_4	0.5	2.6	7.2	1.9	1.6	
d_5	1.0	0.9	4.5	0.7	0.5	
d_6	0.3	0.3	3.3	0.3	0.3	
d_7	0.2	1.6	1.1	0.5	0.1	
d_8		0.9	0.5	0.3	0.2	
$M = \sum_{i=0}^8 id_i/100$	0.25	0.97	0.87	1.36	1.42	0.14
$\phi = \sum_{i=1}^8 id_i/100$	1.3	1.77	1.70	1.31	1.3	1
(with $\sum_{i=1}^8 d_i = 100$)						
Hyperfine distribution of - d_1 but-1-ene	52 ± 4 22 ± 1 26 ± 2	76 ± 1 13 ± 1 11 ± 1	80 ± 1 12 ± 2 8 ± 1	88 ± 2 6 ± 2 6 ± 2	96 ± 1 2 ± 1	
- d_1 cis-butene	51 ± 5 49 ± 5					

 $\alpha_{\text{H}}^d = \text{butane/butane} + \sum \text{butenes}; \alpha_i = \text{but-2-enes}/\sum \text{butenes}; \alpha_c = \sum_{i=1}^8 d_i \text{ but-1-ene.}$

TABLE 5

Deuterium/*cis*-2-Butene Reactions on Ni Supported on Pumice at 24°C

Weight (ω) (mg)	100		
Butene flow rate (F) (μ l/min)	0.65		
$\alpha_i^a(\alpha_i \times F/\omega)$	16	(0.10)	
$\alpha_e^a(\alpha_e \times F/\omega)$	2.9	(0.019)	
$\alpha_h^a(\alpha_h \times F/\omega)$	56.3	(0.37)	
Products	1-B	<i>trans</i>	<i>cis</i>
Composition of olefins			
d_0	0.9	15.1	84.0
d_1	24.7	49.3	97.1
d_2	30.0	39.3	1.6
d_3	22.4	6.3	0.8
d_4	13.4	2.8	0.3
d_5	7.9	1.4	0.1
d_6	0.9	0.6	
d_7	0.7	0.2	
d_8			
$M = \sum_{i=0}^8 id_i/100$	1.54	0.70	0.045
$\phi = \sum_{i=1}^8 id_i/100$	2.05	1.38	1.55
(with $\sum_{i=1}^8 d_i = 100$)			
Hyperfine distribution of d_1 but-1-ene			

^a α_h = butane/butane + Σ butenes; α_i = but-1-ene + *trans*-butene/ Σ butenes; $\alpha_e = \sum_{i=1}^8 d_i$ *cis*-butene.

the activity for hydrogenation was larger than for isomerization ($\alpha_h > \alpha_i$). This is characteristic of nickel as compared, for example, with palladium (11).

Very striking results were obtained from the hyperfine distribution of exchanged d_1 but-1-ene analyzed by microwave spectroscopy. At all temperatures the deuterium atom was localized mostly on C_2 . This result is completely different from that which happened on palladium (11) where

the deuterium atom of the exchanged d_1 but-1-ene was mainly attached to the C_1 carbon atom. Another interesting point is that the amount of d_1 on C_2 regularly decreased with increasing temperature: the percentage of deuterium atom on C_1 varied from $4 \pm 2\%$ at -85°C to $52 \pm 4\%$ at 50°C .

No deuterium was found on C_3 . This is a significant point since it means that no read-sorption of but-2-ene isomers had to be considered even when the isomerization conversion was large: in Table 5 we give the localization of the deuterium atom d_1 in the but-1-ene resulting from the isomerization of *cis*-but-2-ene at 24°C . It can be seen that the deuterium atom was largely ($56 \pm 8\%$) localized on C_3 .

In the but-2-ene reactions, it can be noticed that the *cis*-*trans* isomerization ran much faster than the double bond migration with the introduction of mainly zero or one deuterium atom while the isomerized but-1-ene showed a multiple exchange restricted to the first moiety of the distribution d_0 - d_4 ; the equal distribution of the deuterium atom on C_1 and C_2 shows that this distribution is not obscured by a consecutive exchange of but-1-ene d_0 which would lead to a $2-d_1/1-d_1$ but-1-ene ratio equal to 4 as was obtained in the but-1-ene exchange reaction.

DISCUSSION

The Horiuti-Polanyi (HP) mechanism is based on interconversions between mono-adsorbed and $\alpha\beta$ -diadsorbed species linked to the metal atoms by σ bonds. It involves *cis*-addition and provides a good explanation for the deuterium distribution of saturated products, centered around a maximum in d_2 ; in the particular case of the hydrogenation of disubstituted cycloolefins, *cis* isomers are expected. In butene reactions a common mechanism for exchange, double bond migration and *cis*-*trans* isomerization is predicted so that a good correlation between the distributions of the reaction products is expected. It is

quite clear that our results on the deuteration of disubstituted cycloolefins and butenes are much more complicated than a simple HP mechanism would foresee. We shall discuss the cycloolefins and butenes separately.

Cycloolefins

A HP mechanism would not explain the high percentage of *trans* 1,2-dimethylcyclopentane obtained in the C₅ ring series, especially with the 2,3-dimethylcyclopentene. It cannot account for the large differences observed in the distribution of the *cis* ($M = 3.8$) and *trans* ($M = 5$) 1,2-dimethylcyclopentanes obtained from the 1,2-dimethylcyclopentene. It also fails to give a correct interpretation of the parallel evolution of the percentages of *trans* isomer and the mean deuterium atom number in the C₅ and C₄ ring series; although the 2,3-dimethylcyclobutene was not available, it turns out that both values vary as a function of the position of the double bond in the ring. The *trans* percentages and $1/M$ values vary in the order: $2.3 > \text{exo} > 1.2$.

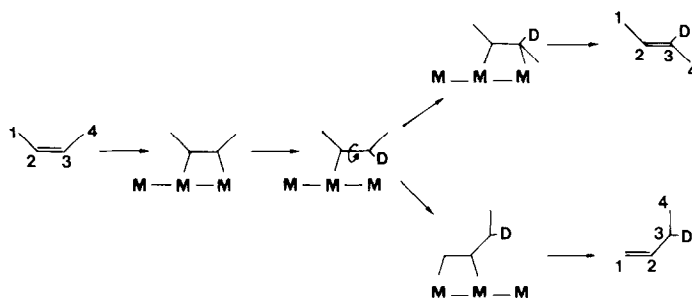
A HP mechanism would also hardly explain the formation of d_3 and d_4 bicyclo[2,2,1]heptanes from bicyclo[2,2,1]heptene. On a nickel film at 0°C up to 31% of $d_3 + d_4$ could be obtained. This is quite different from what was observed on palladium: in one experiment on a palladium film at 0°C, negligible amounts of d_3 and d_4 molecules were detected and the distribution was the following (the conversion was approximately 10%)

d_0	d_1	d_2	d_3	d_4
0.0	2.5	94.2	2.6	0.6

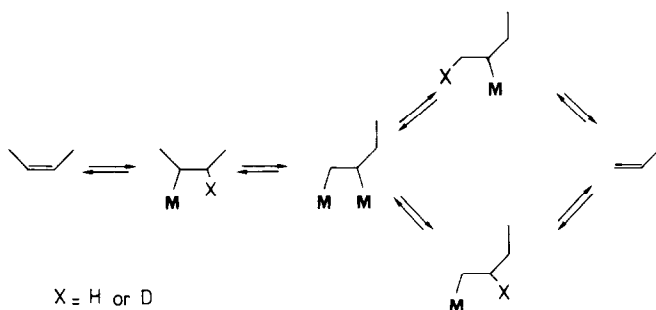
A similar result was found by Kung and Burwell (12) on Pd/SiO₂ at 20°C. A simple HP model could explain the formation of d_3 and d_4 molecules only if one imagines that the hydrogen atoms in bridgehead positions can be exchanged. However, such a process is highly improbable (13) and if it really occurred it should happen on palladium rather than on nickel since the displacement of a carbon-carbon double bond is much easier on the former metal (11).

Butenes

A nonrepetitive HP mechanism can account for the *cis-trans* isomerization with introduction of one deuterium atom and also for a part of the double bond migration because in the but-2-ene \rightarrow but-1-ene reaction, 56% of deuterium atoms in d_1 but-1-ene are located on C₃ (Scheme 1). However, but-1-ene provided from but-2-ene and but-2-ene provided from but-1-ene show a distribution spread from d_0 to d_4, d_5 so that two deuterium atoms ($\phi \approx 2$) are introduced on the average in each deuterated molecule during the double bond migration. To account for such a distribution by a HP mechanism we would have to suppose several interconversions between mono- and diradicals before desorption. As has been seen, such a multistep process did not exist during the *cis-trans* isomerization which included the same intermediaries. For this reason we think that *an additional*



SCHEME 1.



SCHEME 2.

double bond migration mechanism has to be envisaged. It is also clear that exchange and double bond migration did not involve the same intermediaries as a HP mechanism would predict. This latter mechanism would lead to the same deuterium distribution on C₁ and C₂ in the exchanged and isomerized 1-*d*₁ but-1-ene produced from but-1-ene *d*₀ and from but-2-ene, respectively (Scheme 2).

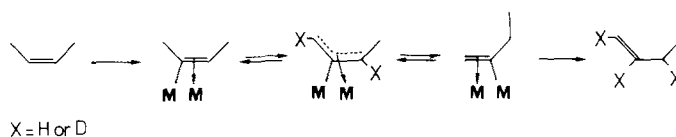
From all this evidence, we think it quite clear that the HP mechanism is not the only one taking part in the reactions of olefins with deuterium on nickel. Other mechanisms, with possibly new species, must be postulated besides those involving the classical mono- and $\alpha\beta$ -diadsorbed molecules.

An α -vinylic intermediary, already introduced by Farkas and Farkas (14), was proposed by Erkelens *et al.* (15) to explain the deuteration of bicyclo[2,2,1]heptene on iron films where up to 23% of *d*₃ and *d*₄ molecules was found at 88°C (only 7% at 0°C) and at total conversion. Such a species might explain our results with the same molecule. In particular, if one imagines a competition between such a dissociative species and a half-hydrogenated radical, the latter will be favored by an increase of the deuterium pressure. This is in good agreement with our experiments since we found a decrease from 28 to ~17% of the sum *d*₃ + *d*₄ when the deuterium pressure was varied from 15 to 120 Torr. However, it would not give a correct account for the large variations in the deuteration of the

other cycloolefins. A supplementary mechanism is certainly involved. We believe that this mechanism proceeds via an $\alpha\alpha\beta$ -triadsorbed intermediate which can be viewed as a σ -vinylic π -olefinic species. This species could permit attack by deuterium atoms on both sides of the ring.

Such a species can only be formed if a C-H bond in a vinylic position is broken. Since the carbon atoms of the double bond in 1,2-dimethylcyclopentene (I) and 1,2-dimethylcyclobutene (IV) are not bonded to any hydrogen atom, an $\alpha\alpha\beta$ species cannot be formed with these molecules. This means that only a small quantity of *trans* 1,2-dimethylcycloalkane can be expected, as indeed is observed. On the other hand, the formation of an $\alpha\alpha\beta$ species is possible with the other olefins and the *trans* isomers are found in larger quantities.

Concerning the deuterium distribution, we have pointed out that the *trans* 1,2-dimethylcyclopentane obtained in the deuteration of 1,2-dimethylcyclopentene (I) is much more exchanged than the *cis* isomer. This might reveal a small participation of the rollover species (16, 17), responsible for multiple exchange, the formation of which is less favored on nickel than on palladium (18) but cannot be totally excluded. When the $\alpha\alpha\beta$ species can be formed (II and III), most of the *trans* 1,2-dimethylcyclopentane will be obtained via this intermediary and no extensive exchange will occur. On the contrary, if no participation of the $\alpha\alpha\beta$ species is possible, the *trans* iso-



SCHEME 3.

mer will be due to the rollover mechanism species and will be extensively exchanged.

The participation of such α and $\alpha\beta$ species on nickel can explain the results obtained in the reactions of butenes. As a matter of fact the quasi-exclusive exchange observed on C₂ in the but-1-ene molecule at low temperature would be well explained by the formation of a secondary vinylic species which will be more reactive than the primary ones, the latter becoming exchangeable at higher temperature.



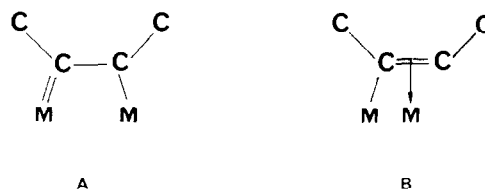
Such an explanation for the exchange reaction will be preferred to a HP mechanism where it would be necessary to assume different rates for the formation of normal and iso half-hydrogenated states. Moreover, if one considers that these α -vinylic species (secondary \gg primary) are the precursors of $\alpha\beta$ species, the reason why the *trans* dimethylcyclopentane is formed in higher amounts from 2,3-dimethylcyclopentene than from 1-methyl-1-2-methylenecyclopentane becomes quite clear.

On the other hand, for the double bond migration mechanism, it is tempting to use the same mechanism which was introduced on iron (4). This mechanism includes the existence of σ -vinylic π -allylic species, besides σ -vinylic π -olefinic species. The interconversions between such species in addition to a high isotopic dilution of adsorbed hydrogen and deuterium atoms permit one to explain the introduction of a deuterium atom in one step on C₁ and C₂ in but-1-ene during the double bond migration from but-2-ene (Scheme 3)

CONCLUSION

We have emphasized in this paper the complexity of the reactions occurring when an olefin, cyclic or linear, interacts with deuterium on nickel catalysts. We have shown that all our results can be explained by a coherent set of mechanisms only if vinylic species are introduced in addition to the classical Horiuti-Polanyi process. An α -vinylic species would be responsible for the exchange reaction and, when another nickel atom is available, an interconversion between this α -vinylic species and a σ -vinylic π -olefinic species would lead to deuteration. In the case of butenes, the interconversion between two σ -vinylic π -olefinic species via a σ -vinylic π -allylic species would lead to the double bond migration.

It is interesting to underline the similarity of the results given by nickel and iron: there is the same deuterium hyperfine distribution for exchanged *d*₁ but-1-ene, similar behavior in the isomerization reaction, and the same deuterium distribution in the reaction of bicyclo[2,2,1]heptene. Formally the $\alpha\beta$ species may be represented in two ways, either as an alkylidene complex (A) as proposed by Kung and Burwell (12) or as a σ -vinylic π -olefinic intermediary (B) already described by Touroude and Gault (4); the latter type of iron complex is well known in coordination chemistry (19).



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