

## Correlation between Surface Structure and Reaction Mechanisms: Reactions of Olefins on Nickel and Palladium Films

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Reactions of *cis*-but-2-ene have been investigated in the presence of  $C_2D_6$  or  $D_2$  on nickel and palladium films treated in different ways. Condensing the films at 470°C instead of 0°C reduces drastically the extent of exchange and the formation of highly deuteriated isomers. Treatments by hydrogen at 0°C of the palladium films condensed at 470°C restore almost entirely the properties of the unsintered films. It is suggested that some specific sites of low coordination number, such as corners or isolated adatoms, are responsible for all the reactions involving dissociative adsorption, and that the defects are erased by thermal treatment and reconstructed by exposure to hydrogen via hydride formation.

### INTRODUCTION

A recent reinvestigation of the exchange and isomerization of butenes on metal films has shown that several mechanisms were competing to give these reactions (1-4). Exchange of but-1-ene on iron and nickel takes place almost exclusively by dissociative adsorption on a vinylic carbon atom (5) (oxidative addition) while on palladium it involves mainly the rupture of an allylic carbon-hydrogen bond (4). *cis-trans* isomerization takes place essentially by a Horiuti-Polanyi mechanism (6) (*cis* ligand insertion) forming mainly the monodeuterioisomer, or by a direct process without incorporation of deuterium. A third mechanism involving also repeated interconversions between  $\pi$ -allylic and  $\pi$ -olefinic species provides extensively exchanged molecules. Double-bond migration proceeds by three mechanisms: sigmatropic hydrogen shift, Horiuti-Polanyi mechanism, and  $\pi$ -allylic mechanism.

In order to account for the complexity of the reactions of olefins on metals, a model was proposed with three different types of sites on the surface, classified according to their coordination number (7). *Sites A*, the atoms of low Miller index faces, are believed to form only one bond with an adsorbate (hydrogen adatom or  $\pi$ -adsorbed olefin): sigmatropic hydrogen shift and direct *cis-trans* isomerization may occur on sites A (Fig. 1a). Simultaneous adsorption of one hydrogen atom and of an unsaturated molecule would take place on surface atoms of *type B*, located on the edges of the steps in a metal crystallite: sites B are required for the Horiuti-Polanyi associative mechanism (Fig. 1b). Lastly *sites C* are atoms with low coordination number such as isolated adatoms on a rough surface or corner atoms of high Miller index unstable surfaces. These sites may accommodate two adsorbed hydrogen atoms and one adsorbed olefin at least and would promote all the reactions involving

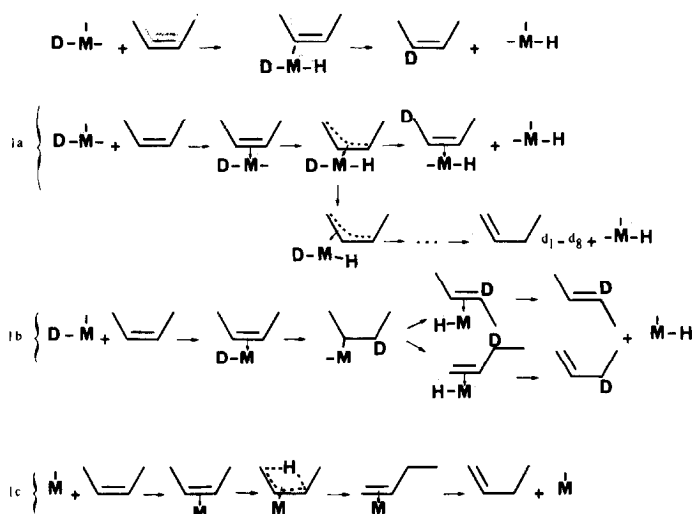


FIG. 1. Mechanisms of exchange and isomerization.

dissociative adsorption, i.e., exchange of the vinylic and allylic type and isomerization with extensive deuterium incorporation (Fig. 1c). Since one may reasonably assume that film reconstruction affects the face and edge atoms of the crystallites much less than the defects such as corners and adatoms, one expects that any treatment modifying the roughness of the film should change the relative contributions of the various mechanisms drastically. Two examples of such changes in reaction mechanism are given in this paper. The first one was observed when condensing nickel or palladium films at high temperature and the second one arises from the reconstruction of a palladium surface by hydrogen pretreatment.

#### EXPERIMENTAL

The static system used for the experiments, as well as the analytical procedure involving gas liquid chromatography and mass spectrometry, have been described previously (1, 4).

Three types of films have been prepared by condensation on glass of metal vapor obtained by heating a speckure nickel wire ( $\varnothing$  0.5 mm, 13 cm) or a filament made of a 30-cm speckure wire of palladium ( $\varnothing$  0.2

mm) tightly wound on a 15-cm tungsten wire ( $\varnothing$  0.3 mm).

Films I were obtained after outgassing the filaments by depositing the metal on the reaction vessel at 0°C. The pressure during film evaporation was in the range of  $10^{-6}$  to  $10^{-7}$  Torr. Films II were prepared as films I, but the glass support was heated at 470°C during evaporation. Films III were deposited on the glass vessel at 470°C and cooled down to room temperature; hydrogen was admitted then for 2 min at a pressure of 60 Torr in the case of nickel, or 400 Torr in the case of palladium, and pumped off. Film IV was deposited at 470°C and a first dose of hydrogen (90 Torr) was introduced at 470°C for 3 min. After cooling, the hydrogen was pumped away, a new dose (60 Torr) was admitted at 0°C for 2 min, and evacuated. Film IV was investigated because the preparation of this film simulates better than films I, II, or III the preparation of supported palladium catalysts.

#### RESULTS AND INTERPRETATION

The exchange and isomerization of *cis*-but-2-ene have been performed in the presence of  $C_3D_6$  under similar conditions on three types of nickel films I, II, and

TABLE 1

Exchange and Isomerization of *cis*-but-2-ene on Nickel Films in the Presence of Perdeuteriopropene

Catalysts Reaction time Temp. (°C)	Film I			Film II			Film III		
	10 min	30 sec	0.5°C	23 min	26°C		20 min	28°C	
Pressures in Torr	2.4 ( <i>cis</i> B2) + 32.4 (C <sub>3</sub> D <sub>6</sub> )			2 ( <i>cis</i> B2) + 42.2 (C <sub>3</sub> D <sub>6</sub> )			2.4 ( <i>cis</i> B2) + 35.2 (C <sub>3</sub> D <sub>6</sub> )		
Film weights (mg)	16			21.6			18.6		
Products	<i>cis</i> B2	<i>trans</i> B2	B1	<i>cis</i> B2	<i>trans</i> B2	B1	<i>cis</i> B2	<i>trans</i> B2	B1
Composition (%)	97.3	1.1	1.6	98.1	0.7	1.2	98.9	0.6	0.5
d <sub>0</sub>	94.3	14.8	5.4	99.5	49.15	49.5	99.92	29.6	37.7
d <sub>1</sub>	2.9	46.1	9.5	0.35	41.35	21.75	0.08	67.7	35.0
d <sub>2</sub>	0.9	4.9	12.6	0.1	2.3	7.3	—	0.7	11.7
d <sub>3</sub>	0.4	3.8	12.4	—	1.3	3.6	—	0.5	4.2
d <sub>4</sub>	0.3	4.0	11.7	—	1.1	3.1	—	0.4	2.4
d <sub>5</sub>	0.2	4.5	10.2	—	1.2	3.0	—	0.3	2.2
d <sub>6</sub>	0.2	5.8	9.5	—	1.6	3.7	—	0.3	2.6
d <sub>8</sub>	0.75	8.9	15.55	—	0.8	4.0	—	0.1	1.7
Conversion on sites C <sup>a</sup>	5.6	0.4	1.15	0.4	0.05	0.25	0.08	0.01	0.08

<sup>a</sup> For isomers: percentage of products · ( $\sum_3^8 d_i$ ); exchanged molecules: ( $\sum_1^8 d_i$ ) · percentage of reactant.

III. The distributions of the isomers and of the deuterio-molecules are reported in Table 1.

While the thermal treatment of films II and III strongly decreases the exchange of *cis*-but-2-ene by a factor of 10 at least, the extent of isomerization is reduced only by two or less. The deuterium distributions of the isomers, however, are very different on the film deposited at 0°C and on those condensed at 470°C. Maxima at d<sub>8</sub> are obtained for both isomers on film I, which completely disappear on films II and III. The *trans* isomer includes 34.2% of d<sub>3</sub>-d<sub>8</sub> species when obtained on film I, and 7.2 and 1.5% when obtained on films II and III, respectively. Similarly, ca. 70% of the but-1-enes formed on films II and III consists of d<sub>0</sub> and d<sub>1</sub> molecules and only 15% on film I.

If one assumes that both exchange of *cis*-but-2-ene and formation of d<sub>3</sub>-d<sub>8</sub> isomers take place by dissociative adsorption and involve type-C sites, the percentage of the products involving these sites drops from 86% on films I to 33 and 14% on films II and III, respectively.

The reactions of *cis*-but-2-ene on the palladium films of types I, II, III, and IV have been investigated at 0°C in the presence of C<sub>3</sub>D<sub>6</sub> and the product distributions are reported in Table 2. As on nickel, the thermal treatment of film II drastically decreases the exchange reaction by a factor of 20, and also the formation of the highly deuteriated isomers. The *trans*-but-2-ene includes 12% of d<sub>3</sub>-d<sub>8</sub> molecules on film II, as opposed to 39% on film I, and the deuterium content of the but-1-ene is 4.3 atoms per molecule on film I as opposed to 2.5 on film II.

Unlike the nickel films, the palladium film III condensed at 470°C and exposed to hydrogen at 0°C behaves very much like the film I deposited at 0°C for the extent of exchange (17.1%), the percentage of d<sub>3</sub>-d<sub>8</sub> *trans*-but-2-enes (31.6%) and the deuterium content of the but-1-ene (3.6). Repeated exposure to hydrogen (film IV) increases the percentage of exchange and the incorporation of deuterium in the isomers even more.

Since it was shown previously (4) that exchange and formation of deuterioisomers

TABLE 2

Exchange and Isomerization of *cis*-but-2-ene on Palladium Films in the Presence of Perdeuteriopropane

Catalysts Reaction Temp. time (°C)	Film I			Film II			Film III			Film IV		
	5 min	0°C		10 min	0°C		10 min	0°C		10 min	0°C	
Pressures in Torr	2.8 ( <i>cis</i> B2) + 34.6 (C <sub>3</sub> D <sub>6</sub> )			2.7 ( <i>cis</i> B2) + 44.4 (C <sub>3</sub> D <sub>6</sub> )			2.8 ( <i>cis</i> B2) + 38.6 (C <sub>3</sub> D <sub>6</sub> )			2.7 ( <i>cis</i> B2) + 37.6 (C <sub>3</sub> D <sub>6</sub> )		
Film weights (mg)	26.8			43.5			86.9			40.3		
Products	<i>cis</i> B2	<i>trans</i> B2	B1	<i>cis</i> B2	<i>trans</i> B2	B1	<i>cis</i> B2	<i>trans</i> B2	B1	<i>cis</i> B2	<i>trans</i> B2	B1
Composition (%)	93.4	2.0	4.6	97.9	1.1	1.0	90.2	3.2	6.1	78.5	8.5	12.1
d <sub>0</sub>	86.7	24.6	1.7	99.5	27.8	11.0	82.9	23.0	2.1	63.2	22.5	1.9
d <sub>1</sub>	7.0	31.0	8.1	0.5	56.6	34.3	9.8	34.9	10.5	18.2	26.3	8.0
d <sub>2</sub>	2.0	5.3	12.8	—	3.2	16.3	3.0	10.7	22.8	7.7	13.4	21.9
d <sub>3</sub>	1.3	4.1	14.0	—	2.5	8.0	1.6	6.0	18.0	4.2	9.4	19.4
d <sub>4</sub>	1.0	5.2	13.6	—	2.6	8.7	1.0	6.3	14.4	2.7	8.6	16.2
d <sub>5</sub>	0.8	8.2	15.9	—	3.3	9.2	0.8	6.9	13.1	2.0	8.6	13.7
d <sub>6</sub>	0.8	11.1	16.6	—	2.4	7.4	0.6	6.8	10.2	1.3	7.0	10.5
d <sub>7</sub>	0.3	8.3	13.3	—	1.2	4.2	0.2	4.5	6.9	0.5	3.6	6.5
d <sub>8</sub>	0.1	2.1	3.4	—	0.4	0.9	0.1	1.1	2.0	0.1	0.7	2.0
Conversion on sites C	12.4	0.8	3.5	0.5	0.15	0.4	15.4	1.0	3.9	28.9	3.2	8.25

d<sub>3</sub>-d<sub>8</sub> were related to dissociative adsorption, the percentage of the products involving type-C sites may be estimated and equals 86% on film I, 39% on film II, and 82 and 81% on films III and IV.

Table 3 reports three experiments made in the presence of deuterium at -82°C on nickel film I and palladium films I and II. The observed reactions are always very fast and extensive deuteriogenation occurs, especially on palladium film I. Notice on

nickel film I the very small amount of but-1-ene present in the reaction mixture, most probably due to the very fast deuteration of this molecule, and also the low deuterium content of the isomers, as compared with the one observed in the presence of C<sub>3</sub>D<sub>6</sub>. Interesting also is the comparison between the two experiments made on palladium films of type II, in the presence of C<sub>3</sub>D<sub>6</sub> and in the presence of D<sub>2</sub>. In the latter case, a very fast exchange of *cis*-

TABLE 3

Exchange and Isomerization in the Presence of Deuterium

Catalysts Reactions	Nickel film I <i>cis</i> -but-2-ene + D <sub>2</sub>				Palladium film I <i>trans</i> B2 + D <sub>2</sub>		Palladium film II <i>cis</i> -but-2-ene + D <sub>2</sub>			
	4 min	-82°C			3 min	-84°C	2 min 30 sec	-84°C		
Reaction Temp. time (°C)	2.5 ( <i>cis</i> B2) + 36.3 (D <sub>2</sub> )			2.6 ( <i>cis</i> B2) + 50.6 (D <sub>2</sub> )		3 ( <i>cis</i> B2) + 29.7 (D <sub>2</sub> )				
Pressures in Torr	20.4			47.8		9.8				
Film weights (mg)	<i>cis</i> B2	<i>trans</i> B2	B1	Butane	<i>trans</i> B2	Butane	<i>cis</i> B2	<i>trans</i> B2	B1	Butane
Products	35.7	46.6	0.1	17.6	0	100	33.0	50.4	5.5	11.1
Composition (%)	73.65	43.8	35.5	3.7	—	2.4	40.0	6.3	5.4	0.0
d <sub>0</sub>	11.9	31.7	23.7	11.65	—	2.3	10.2	19.1	11.5	3.1
d <sub>1</sub>	6.0	9.55	17.7	22.2	—	4.3	9.8	12.6	15.7	8.7
d <sub>2</sub>	3.4	5.9	10.5	22.2	—	2.9	8.4	11.7	16.0	10.2
d <sub>3</sub>	2.3	3.9	6.3	17.1	—	3.0	7.6	11.1	14.9	11.0
d <sub>4</sub>	1.3	2.55	3.1	11.0	—	4.4	7.3	11.2	13.3	11.6
d <sub>5</sub>	0.8	1.5	1.75	6.3	—	4.8	7.1	11.7	10.9	12.1
d <sub>6</sub>	0.4	0.8	0.9	3.4	—	6.5	6.1	10.6	8.3	13.0
d <sub>7</sub>	0.2	0.3	0.5	1.6	—	13.2	3.2	5.7	4.0	13.8
d <sub>8</sub>	—	—	—	0.75	—	27.7	—	—	—	11.0
d <sub>9</sub>	—	—	—	0.2	—	28.4	—	—	—	5.4
d <sub>10</sub>	—	—	—	—	—	—	—	—	—	—
Conversion on sites C	9.4	7.0	0.02	17.6	0	100	19.8	31.25	3.7	11.1

but-2-ene and an extensive deuterium incorporation in the isomers take place.

### DISCUSSION

Great changes in the product distributions and deuterium patterns of the isomers are observed in the experiments made on nickel or palladium in the presence of  $C_3D_6$  when films I condensed at  $0^\circ C$  are replaced by films II condensed at  $470^\circ C$ . On films II exchange and isomerization with extensive deuterium incorporation are drastically decreased, while isomerizations with introduction of one or zero deuterium atoms in the molecule are hardly affected. These results may easily be explained if one assumes that the former reactions occur on corner atoms or adatoms (sites C) while the latter take place on edge and face atoms (sites B and A).

One may expect indeed that sintering a metal film or condensing it at high temperature would reduce drastically the number of defects of types C. A number of similar sintering effects have been described in the literature: for example, variation of thermoelectric force connected with decrease of catalytic activity was observed when annealing nickel, platinum, and palladium filaments (8, 9), and these effects were explained by the disappearance of lattice point defects. On the contrary, the number of edge and face atoms in a crystallite (sites B and A) should not be affected as much, if one assumes that stepped surfaces of nickel and palladium are stable in a wide range of temperature, as Blakely and Somorjai showed for many platinum stepped surfaces (10).

When  $C_3D_6$  is replaced by  $D_2$  on palladium films of type II, exchange of *cis*-but-2-ene takes place and appreciable amounts of  $d_3$ - $d_8$  isomers are observed as on films of type I. These results suggest that some reconstruction of the surface with appearance of defects might occur when exposing a sintered film to hydrogen. The experiments

on films III and IV were made to verify this assumption.

The behaviors of nickel and palladium films of type III are very different. Nickel films of type III behave very much like nickel films of type II, except for a slight deactivation for all reactions. Such poisoning of nickel films by exposure to hydrogen has already been described for many reactions (11-13). On the other hand, exposing a sintered palladium film to hydrogen increases its activity for the exchange reaction and for the formation of highly deuteriated isomers. Everything indeed happens as if these defects (sites C) which had been suppressed when condensing the film at high temperature were reconstructed in the presence of hydrogen.

Surface reconstruction induced by hydrogen adsorption has been observed in this laboratory in the case of platinum stepped surfaces (14). In our experiments, the effect of hydrogen seems much deeper since defects with very low coordination number (sites C) seem to be built up by hydrogen treatment. The occurrence of this effect in the case of palladium and *not* in the case of nickel could be related to the possibility of forming a palladium hydride. Recent investigations have shown the limits of stability of the nickel (13) and of the palladium hydrides (15, 16). Under our experimental conditions, palladium hydride is stable and nickel hydride is *not* stable. One could therefore suggest that the formation of defects during the preparation of films III and IV arises from the destruction of the palladium hydride which has been formed during the exposure of the film to hydrogen. Indeed, the formation of the  $\alpha$  and  $\beta$  phases during the hydrogen treatment, by causing an increase of the lattice distances, could induce a rupture of the large crystallites into smaller ones, as observed in the case of palladium sponge (15) with a larger number of lattice point defects; these defects would remain when

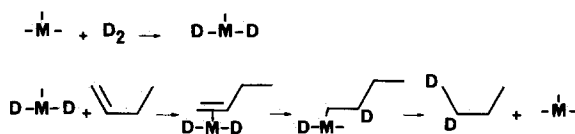


FIG. 2. Mechanism of hydrogenation.

the alloy structure is destroyed by pumping the hydrogen.

Reconstruction of the surface induced by hydrogen treatment could also explain the difference between nickel and palladium films for the deuterogenation reaction. Although the difference of activity between palladium and nickel films of type I is not very large for exchange and isomerization of *cis*-but-2-ene in the presence of  $\text{C}_3\text{D}_6$  at  $0^\circ\text{C}$ , in the presence of deuterium at  $-82^\circ\text{C}$ , the deuteration rate on palladium is considerably greater than on nickel: only saturated hydrocarbons, extensively exchanged, are obtained on palladium, while on nickel the butanes, poorly exchanged, represent only one-fourth of the reaction products. Since *n*-butane does not exchange hydrogen with deuterium on palladium film at  $-82^\circ\text{C}$ , the deuterium incorporation occurs during the deuteration process and not by a consecutive exchange of *n*-butane. These results are easily accounted for if one assumes (i) that the number of sites C are increased in the presence of  $\text{D}_2$  on Pd film and not on Ni film and (ii) that these sites C are responsible for the hydrogenation reaction as they are for dissociative adsorption and multiple exchange (Fig. 2).

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