

## Correlation between Electronic Structure and Reaction Mechanisms. Reactions of Olefins on Transition Metal Films

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Reactions of *n*-butenes have been investigated in the presence of C<sub>3</sub>D<sub>8</sub> on iridium, rhodium, platinum, and chromium films and compared with the reactions on iron, nickel, and palladium films. The mechanisms of the reactions taking place on high-coordinate metal atoms (mainly isomerization) are hardly affected by the nature of the metal. On the contrary, the mechanisms of the reactions using low-coordinate metal atoms as sites (mainly exchange and hydrogenation) depend strongly upon the nature of the metal. It is suggested that the number of *s* electrons in the fundamental state of the metal plays an important role. The nature of the geometric effect on the olefin reactions has been described previously; in the present work a strong electronic effect on these reactions is established.

### INTRODUCTION

An extensive study of the exchange and isomerization of the three *n*-butenes on transition metal films has shown that at least four mechanisms were competing at the surface (1-4). On iron (1, 8) and nickel (2, 3), dissociative vinylic adsorption is responsible for the exchange reaction of the but-1-ene; on palladium (4) the dissociative allylic adsorption can lead to the same exchange reaction and to some of the isomerization of the three *n*-butenes. A combination of these two mechanisms partially accounts for the isomerization on nickel (and iron), but almost all the products of isomerization are obtained via a direct intramolecular shift or via a non-repetitive classical Horiuti-Polanyi (5) mechanism.

To explain this complex set of mechanisms, a model of the surface with different reaction sites has been introduced (6) and applied (7). The atoms of low-Miller-index faces, or sites A, are responsible for the intramolecular shift, a reaction leading to isomerization; the atoms located on the edges of the steps, or sites B, promote the Horiuti-Polanyi mechanism of isomerization; the different dissociative mechanisms

of exchange and isomerization and the hydrogenation occur on the corner atoms or adatoms, sites C.

The first two families of mechanisms taking place on sites A and B will only slightly depend upon the nature of the metal while the dissociative mechanisms using sites C will be greatly affected by the particular metal. This is demonstrated in the following comparative study on iridium, rhodium, platinum, and chromium films.

### EXPERIMENTAL

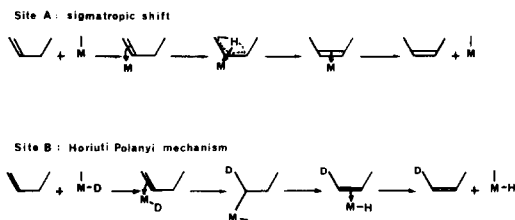
The system used for the experiments and the analytical procedure involving gas-liquid chromatography, mass spectrometry, and microwave spectroscopy have been described previously (2-4). Preparation of films of iron (8), nickel (2), and palladium (4) has already been reported. Platinum films were obtained from a filament made of a 50-cm specpure wire of platinum ( $\phi = 0.12$  mm), tightly wound on a 13-cm tungsten wire ( $\phi = 0.3$  mm). Chromium films were obtained from a 0.5-g chip of pure Cr (Fluka, 99.997%) placed in the centre of a seven-loop coil of specpure tungsten wire ( $\phi = 0.3$  mm), itself connected to two tungsten conductors ( $\phi = 1$  mm). The same

conductors were used for the preparation of rhodium and iridium films; the coil was replaced by a 3-cm rhodium wire ( $\phi = 0.5$  mm) or a 3-cm iridium wire ( $\phi = 0.5$  mm) bound to the two conductors by a splice made with a tungsten wire ( $\phi = 0.2$  mm). All the films were condensed at  $0^\circ\text{C}$ .

### RESULTS

The detailed results obtained on iron, nickel, and palladium films (1-4) will not be reported here; only the main points will appear in the tables of comparison.

The exchange and isomerization of the but-1-ene (B-1) and the *cis*-but-2-ene (*cis*B-2) have been made in the presence of  $\text{C}_3\text{D}_6$  under similar conditions on iridium films; the distribution of the deuterium between the various molecules is given in Table 1.



SCHEME 1. Mechanisms of isomerization reactions on sites A and B.

These results must be compared with the same reaction on Ni films (2, 3). The isomerization reactions are similar for both B-1 and *cis*B-2 leading by intramolecular shift (6) to the  $d_0$  isomer molecules (16.5 to 33.5%), or by the Horiuti-Polanyi mechanism (6) mainly to the  $d_1$  isomer molecules (58.3 to 70.4%) and to the few  $d_2$  and  $d_3$  isomer molecules (Scheme 1).

TABLE 1

Exchange and Isomerization of *n*-Butenes on Iridium Films in the Presence of  $\text{C}_3\text{D}_6$

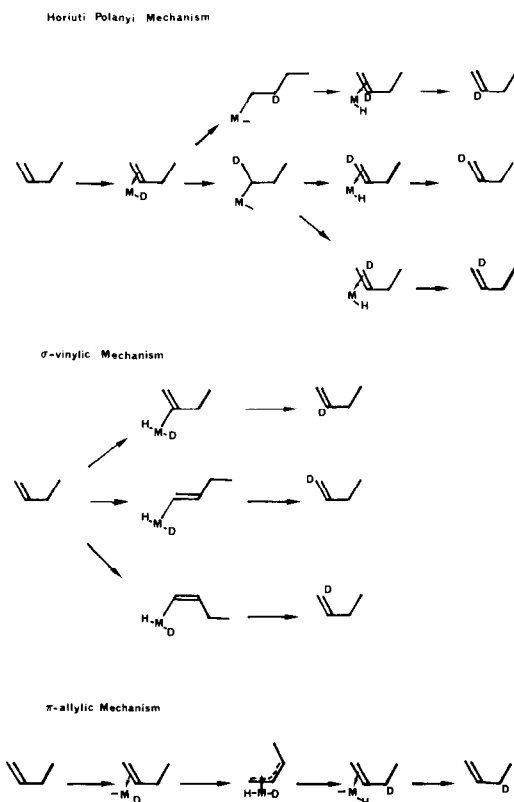
| Starting products:              | B-1                                   |                  |                | <i>cis</i> B-2                            |                  |                |
|---------------------------------|---------------------------------------|------------------|----------------|-------------------------------------------|------------------|----------------|
| Reaction time and temp.:        | 12 min $0^\circ\text{C}$              |                  |                | 5 min $33^\circ\text{C}$                  |                  |                |
| Pressure (t = Torr):            | 11t B-1 + 146t $\text{C}_3\text{D}_6$ |                  |                | 12.5t B-1 + 135.5t $\text{C}_3\text{D}_6$ |                  |                |
| Film weight (mg):               | 5.8                                   |                  |                | 4.2                                       |                  |                |
| Product:                        | B-1 <sup>a</sup>                      | <i>trans</i> B-2 | <i>cis</i> B-2 | B-1                                       | <i>trans</i> B-2 | <i>cis</i> B-2 |
| Conversion (%):                 | 93.9                                  | 3.4              | 2.3            | 1.5                                       | 3.2              | 95.3           |
|                                 | Composition (%)                       |                  |                |                                           |                  |                |
| Mass spec.                      |                                       |                  |                |                                           |                  |                |
| $d_0$                           | 86.5                                  | 33.5             | 25.8           | 16.5                                      | 28.0             | 99.4           |
| $d_1$                           | 12.1 <sub>5</sub>                     | 58.3             | 64.6           | 65.2                                      | 70.4             | 0.2            |
| $d_2$                           | 1.2                                   | 7.2              | 8.2            | 12.9                                      | 1.4              | 0.3            |
| $d_3$                           | 0.1                                   | 0.8              | 1.1            | 2.1                                       | 0.2              | $\epsilon$     |
| $d_4$                           | —                                     | 0.2              | 0.3            | 0.6                                       | —                | —              |
| $d_5$                           | —                                     | —                | —              | 0.2                                       | —                | —              |
| $d_6$                           | —                                     | —                | —              | 0.0                                       | —                | —              |
| $d_7$                           | —                                     | —                | —              | 0.2                                       | —                | —              |
| $d_8$                           | —                                     | —                | —              | 2.4                                       | —                | —              |
| Microwave                       |                                       |                  |                |                                           |                  |                |
| B1-1 $d_1$                      | 38                                    |                  |                |                                           |                  |                |
| B1-2 $d_1$                      | 18                                    |                  |                |                                           |                  |                |
| B1-3 $d_1$                      | 44                                    |                  |                |                                           |                  |                |
| Other B1- $d_1$                 | 0                                     |                  |                |                                           |                  |                |
| B1-(1-2) $d_2$                  | n.d.                                  |                  |                |                                           |                  |                |
| B1-(1-3) $d_2$                  | $\epsilon$                            |                  |                |                                           |                  |                |
| B1-(2-3) $d_2$                  | n.d.                                  |                  |                |                                           |                  |                |
| <i>cis</i> B2-(1 + 2 + 3) $d_1$ |                                       |                  | 100            |                                           |                  |                |
| <i>cis</i> B2-4 $d_1$           |                                       |                  | 0              |                                           |                  |                |

<sup>a</sup> 0.4% of butane is observed. n.d.: Not detected.

These two mechanisms involve, as a first step, the formation of a  $\pi$ -olefinic species on sites A and B, respectively. A more complex mechanism taking place on sites C, and probably similar to those observed on Ni (3), gives the slight maximum at  $d_8$  in the B-1 obtained from the *cis*B-2. The difference between the exchange reactions of the B-1 and the *cis*B-2 is similar to those on Ni and Fe (1, 2, 3, 8). The exchange of *cis*B-2 is very weak (exch./isom. = 0.12), while the exchange of B-1 is 20 times more important (exch./isom. = 2.3). Three mechanisms can lead to the exchange of the B-1 (see Scheme 2).

The best tool for choosing among these three ways is microwave analysis of the exchanged  $d_1$  and  $d_2$  B-1 molecules.

**Criterion 1.** The label on carbon atom 3 (spectroscopic positions 4 and 5) is only obtained by the  $\pi$ -allylic process.



SCHEME 2. Possible mechanisms of exchange of but-1-ene.

**Criterion 2.** The Horiuti–Polanyi mechanism gives an equivalent amount of deuterium on spectroscopic positions 1 and 2 on carbon atom 1. Corollary: a dissymmetry between these two positions involves the  $\sigma$ -vinylic process (3).

**Criterion 3.** If one assumes (see Rh part) that the  $d_2$ -exchanged molecules are the result of two consecutive adsorptions by the  $\sigma$ -vinylic process or by a repetitive Horiuti–Polanyi process, these two mechanisms must lead, respectively, to a different or an equal amount of molecules B1-(1-3) $d_2$  and B1-(2-3) $d_2$  (3).

If one applies these three criteria to the exchanged B-1 on Ir, no  $\pi$ -allylic process is involved because B1-4 $d_1$  and 5 $d_1$  = 0 and all the exchange, as on Ni, is obtained from the  $\sigma$ -vinylic process because B1-1 $d_1$  = 38 > B1-2 $d_2$  = 18 and B1-(1-3) $d_2$  > B1-(2-3) $d_2$ .

The distribution of the deuterium in the molecules obtained by reaction of the three *n*-butenes on Rh films is given in Table 2. Isomerization reactions involved on this metal are similar to those observed on Ir, i.e., mainly  $d_0$  and  $d_1$  molecules obtained, respectively, by intramolecular shift and Horiuti–Polanyi mechanism. As on Ni (3), microwave analysis of the B1- $d_1$  molecules obtained from the *cis*B-2 shows a strong  $\sigma$ -vinylic readsorption of the  $d_0$  molecules obtained by the intramolecular shift mechanism (39%).

The exchange of the *cis*B-2 is still very weak in comparison to the B-1 reaction (exch./isom. = 0.25 and 4.6) but is more significant than that on Ir. Microwave analysis of the exchanged *cis*B2- $d_1$  shows that the deuterium is wholly located on carbon atom 2. Such a label could be obtained in one step only by the dissociative vinylic process (see Scheme 3).

In the microwave analysis of the exchanged B1- $d_1$ , the 2% of B1-4 $d_1$  + B1-5 $d_1$  exhibits the  $\pi$ -allylic process (criterion 1), already observed only on Pd films (4). The analysis of the B1- $d_2$  justifies the assumption in criterion 3 that the  $d_2$  molecules are

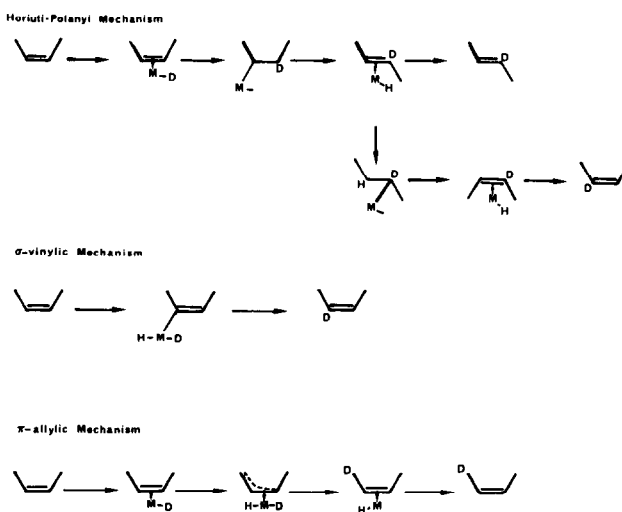
TABLE 2

Exchange and Isomerization of *n*-Butenes on Rhodium Films in the Presence of C<sub>3</sub>D<sub>6</sub>

| Starting products:       | B-1                   |                  |                | <i>trans</i> B-2  |                  |                | <i>cis</i> B-2        |                  |                |
|--------------------------|-----------------------|------------------|----------------|-------------------|------------------|----------------|-----------------------|------------------|----------------|
| Reaction time and temp.: | 10 min 20°C           |                  |                | 10 min 20°C       |                  |                | 10 min 20°C           |                  |                |
| Pressure (t = Torr):     | 12.5t B + 149.5t pro. |                  |                | 13t B + 148t pro. |                  |                | 13.5t B + 144.5t pro. |                  |                |
| Film weight (mg):        | 3.7                   |                  |                | 3.1               |                  |                | 2.7                   |                  |                |
| Product:                 | B-1                   | <i>trans</i> B-2 | <i>cis</i> B-2 | B-1               | <i>trans</i> B-2 | <i>cis</i> B-2 | B-1                   | <i>trans</i> B-2 | <i>cis</i> B-2 |
| Conversion (%):          | 93.0                  | 3.0              | 4.0            | 1.0               | 97.8             | 1.2            | 2.15                  | 3.9              | 93.95          |

|                                             | Composition (%)      |                   |      |      |                   |      |      |      |                   |  |
|---------------------------------------------|----------------------|-------------------|------|------|-------------------|------|------|------|-------------------|--|
| Mass spec.                                  |                      |                   |      |      |                   |      |      |      |                   |  |
| <i>d</i> <sub>0</sub>                       | 66.8 <sub>5</sub>    | 46.6              | 58.3 | 31.3 | 98.2 <sub>4</sub> | 38.9 | 14.9 | 20.6 | 98.4 <sub>7</sub> |  |
| <i>d</i> <sub>1</sub>                       | 25.3                 | 29.5 <sub>5</sub> | 21.9 | 22.8 | 1.3 <sub>5</sub>  | 52.9 | 26.4 | 70.8 | 0.9 <sub>8</sub>  |  |
| <i>d</i> <sub>2</sub>                       | 6.1                  | 12.0              | 9.7  | 17.9 | 0.1 <sub>7</sub>  | 2.5  | 22.9 | 3.0  | 0.2 <sub>4</sub>  |  |
| <i>d</i> <sub>3</sub>                       | 1.1 <sub>5</sub>     | 5.5               | 4.5  | 13.1 | 0.0 <sub>8</sub>  | 1.3  | 16.3 | 1.6  | 0.0 <sub>9</sub>  |  |
| <i>d</i> <sub>4</sub>                       | 0.3                  | 2.8               | 2.4  | 6.3  | 0.0 <sub>5</sub>  | 0.8  | 9.4  | 1.2  | 0.0 <sub>6</sub>  |  |
| <i>d</i> <sub>5</sub>                       | 0.2                  | 1.8               | 1.5  | 2.3  | 0.0 <sub>3</sub>  | 0.6  | 2.7  | 0.8  | 0.0 <sub>5</sub>  |  |
| <i>d</i> <sub>6</sub>                       | 0.1                  | 1.1               | 1.0  | 1.6  | 0.0 <sub>4</sub>  | 0.4  | 2.0  | 0.6  | 0.0 <sub>4</sub>  |  |
| <i>d</i> <sub>7</sub>                       | 0.0 <sub>5</sub>     | 0.1 <sub>5</sub>  | 0.1  | 2.1  | 0.0 <sub>2</sub>  | 0.6  | 2.5  | 0.7  | 0.0 <sub>3</sub>  |  |
| <i>d</i> <sub>8</sub>                       | 0.0 <sub>2</sub>     | 0.1 <sub>5</sub>  | 0.1  | 2.1  | 0.0 <sub>2</sub>  | 0.9  | 2.8  | 0.6  | 0.0 <sub>3</sub>  |  |
| Microwave                                   |                      |                   |      |      |                   |      |      |      |                   |  |
| B1-1 <i>d</i> <sub>1</sub>                  | 36                   |                   |      |      |                   |      | 14   |      |                   |  |
| B1-2 <i>d</i> <sub>1</sub>                  | 29                   |                   |      |      |                   |      | 7    |      |                   |  |
| B1-3 <i>d</i> <sub>1</sub>                  | 33                   |                   |      |      |                   |      | 19   |      |                   |  |
| B1-(4 + 5) <i>d</i> <sub>1</sub>            | 2                    |                   |      |      |                   |      | 61   |      |                   |  |
| Other B1- <i>d</i> <sub>1</sub>             | 0                    |                   |      |      |                   |      | 0    |      |                   |  |
| B1-(1-2) <i>d</i> <sub>2</sub>              | 33 (33) <sup>a</sup> |                   |      |      |                   |      |      |      |                   |  |
| B1-(1-3) <i>d</i> <sub>2</sub>              | 41 (37) <sup>a</sup> |                   |      |      |                   |      |      |      |                   |  |
| B1-(2-3) <i>d</i> <sub>2</sub>              | 26 (30) <sup>a</sup> |                   |      |      |                   |      |      |      |                   |  |
| <i>cis</i> B2-(1+2+3) <i>d</i> <sub>1</sub> |                      |                   | 100  |      |                   |      |      |      | 0                 |  |
| <i>cis</i> B2-4 <i>d</i> <sub>1</sub>       |                      |                   | 0    |      |                   |      |      |      | 100               |  |

<sup>a</sup> Calculated values are in parentheses.SCHEME 3. Possible mechanisms of exchange of *cis*-but-2-ene.

the product of two consecutive adsorptions through the  $\sigma$ -vinylic process. If one calculates the theoretical values of the B1- $d_2$  species from the observed B1- $d_1$  species, one obtains the following values: B1-(1-2) $d_2$  = 33% (measured: 33%), B1-(1-3) $d_2$  = 37% (measured: 41%), and B1-(2-3) $d_2$  = 30% (measured: 26%). These values fit correctly considering the absolute error on measured data of  $\pm 2\%$ .

The results of the reactions of B-1 and *cis*-B-2 on Pt films are reported in Table 3. The isomerization reactions still exhibit the same features as on the other metals ( $d_0$  and  $d_1$  molecules mainly). The evolution of the exchange reaction already observed on Rh is here more accentuated. The exchanges of *cis*-B-2 and B-1 are now equivalent (exch./isom. = 2.7 and 2.5). The *cis*-B-2 exchanges exclusively through the vinylic process (*cis*-B2-4 $d_1$  = 100%), while in the

B-1, the allylic process (B1-4 $d_1$  and B1-5 $d_1$  = 16%) is strongly increasing.

Table 4 shows two reactions of the B-1 on Cr films, one at low conversion (1.3% of isomerization), one at higher conversion (59.3% of isomerization). The first reaction presents the classical patterns of isomerization (mainly  $d_0$  and  $d_1$  molecules) accompanied by a pure  $\sigma$ -vinylic process of exchange. The second reaction has been retained to illustrate the exchangeability of the three vinylic hydrogen atoms, as is shown by the strong break after B1- $d_3$  (1, 8). Finally, the calculated values of the B1- $d_2$  molecules fit correctly with the observed ones.

#### DISCUSSION

Data concerning the exchange reactions of B-1 and *cis*-B-2 on the seven studied

TABLE 3  
Exchange and Isomerization of *n*-Butenes on Platinum Films in the Presence of C<sub>3</sub>D<sub>8</sub>

| Starting products:           | B-1                                              |                   |                 | <i>cis</i> -B-2                                |                   |                   |
|------------------------------|--------------------------------------------------|-------------------|-----------------|------------------------------------------------|-------------------|-------------------|
| Reaction time and temp.:     | 10 min 87°C                                      |                   |                 | 5 min 90°C                                     |                   |                   |
| Pressure (t = Torr):         | 12.5t B-1 + 155.5t C <sub>3</sub> D <sub>8</sub> |                   |                 | 13.5t B-1 + 166t C <sub>3</sub> D <sub>8</sub> |                   |                   |
| Film weight (mg):            | 41                                               |                   |                 | 7.3                                            |                   |                   |
| Product:                     | B-1                                              | <i>trans</i> -B-2 | <i>cis</i> -B-2 | B-1                                            | <i>trans</i> -B-2 | <i>cis</i> -B-2   |
| Conversion (%):              | 93.7                                             | 3.1               | 3.2             | 0.2                                            | 0.7               | 99.1              |
|                              | Composition (%)                                  |                   |                 |                                                |                   |                   |
| Mass spec.                   |                                                  |                   |                 |                                                |                   |                   |
| $d_0$                        | 84.3 <sub>5</sub>                                | 42.4              | 38.5            | 19.2 <sub>5</sub>                              | 26.8              | 97.7 <sub>6</sub> |
| $d_1$                        | 12.3                                             | 39.5              | 39.6            | 30.3                                           | 52.2              | 1.6 <sub>8</sub>  |
| $d_2$                        | 2.1                                              | 8.9               | 10.8            | 15.0                                           | 5.5               | 0.3 <sub>6</sub>  |
| $d_3$                        | 0.6                                              | 3.8               | 4.4             | 8.6                                            | 3.2               | 0.0 <sub>6</sub>  |
| $d_4$                        | 0.3                                              | 2.4               | 2.8             | 6.3                                            | 2.7               | 0.0 <sub>4</sub>  |
| $d_5$                        | 0.2                                              | 1.6               | 1.9             | 5.1                                            | 2.5 <sub>5</sub>  | 0.0 <sub>3</sub>  |
| $d_6$                        | 0.1                                              | 0.9               | 1.2             | 4.8                                            | 2.5 <sub>4</sub>  | 0.0 <sub>3</sub>  |
| $d_7$                        | 0.0 <sub>3</sub>                                 | 0.4               | 0.6             | 5.2 <sub>4</sub>                               | 2.5 <sub>2</sub>  | 0.0 <sub>3</sub>  |
| $d_8$                        | —                                                | 0.1               | 0.2             | 5.5                                            | 2.0               | 0.0 <sub>2</sub>  |
| Microwave                    |                                                  |                   |                 |                                                |                   |                   |
| B1-1 $d_1$                   | 44.2                                             |                   |                 |                                                |                   |                   |
| B1-2 $d_1$                   | 12.2                                             |                   |                 |                                                |                   |                   |
| B1-3 $d_1$                   | 27.5                                             |                   |                 |                                                |                   |                   |
| B1-(4+5) $d_1$               | 16.1                                             |                   |                 |                                                |                   |                   |
| Other B1- $d_1$              | 0                                                |                   |                 |                                                |                   |                   |
| <i>cis</i> -B2-(1+2+3) $d_1$ |                                                  |                   | 100             |                                                |                   | 0                 |
| <i>cis</i> -B2-4 $d_1$       |                                                  |                   | 0               |                                                |                   | 100               |

TABLE 4  
Exchange and Isomerization of But-1-ene on Chromium Films in the Presence of C<sub>3</sub>D<sub>6</sub>

| Starting product:               | B-1                                            |                   | B-1                                              |                      |
|---------------------------------|------------------------------------------------|-------------------|--------------------------------------------------|----------------------|
| Reaction time and temp.:        | 4 min -26°C                                    |                   | 4 min 20°C                                       |                      |
| Pressure (t = Torr):            | 13.5t B-1 + 134t C <sub>3</sub> D <sub>6</sub> |                   | 13.5t B-1 + 147.5t C <sub>3</sub> D <sub>6</sub> |                      |
| Film weight (mg):               | 5.7                                            |                   | 4                                                |                      |
| Product:                        | B-1                                            | <i>trans</i> B-2  | <i>cis</i> B-2                                   | B-1 <sup>a</sup>     |
| Conversion (%):                 | 98.7                                           | 0.75              | 0.55                                             | 40.7                 |
|                                 | Composition (%)                                |                   |                                                  |                      |
| Mass spec.                      |                                                |                   |                                                  |                      |
| <i>d</i> <sub>0</sub>           | 80.4 <sub>1</sub>                              | 54.3 <sub>5</sub> | 57.3                                             | 18.8                 |
| <i>d</i> <sub>1</sub>           | 17.3 <sub>9</sub>                              | 34.3 <sub>5</sub> | 32.4                                             | 3.2                  |
| <i>d</i> <sub>2</sub>           | 2.0 <sub>1</sub>                               | 8.0               | 7.5                                              | 20.75                |
| <i>d</i> <sub>3</sub>           | 0.1 <sub>8</sub>                               | 2.3               | 2.0                                              | 52.2                 |
| <i>d</i> <sub>4</sub>           | 0.0 <sub>1</sub>                               | 0.8               | 0.7                                              | 2.25                 |
| <i>d</i> <sub>5</sub>           | —                                              | 0.1               | 0.1                                              | 0.9                  |
| <i>d</i> <sub>6</sub>           | —                                              | 0.0 <sub>5</sub>  | 0.0 <sub>5</sub>                                 | 0.8                  |
| <i>d</i> <sub>7</sub>           | —                                              | —                 | —                                                | 0.7                  |
| <i>d</i> <sub>8</sub>           | —                                              | —                 | —                                                | 0.4                  |
| Microwave                       |                                                |                   |                                                  |                      |
| B1-1 <i>d</i> <sub>1</sub>      | 26                                             |                   |                                                  |                      |
| B1-2 <i>d</i> <sub>1</sub>      | 15                                             |                   |                                                  |                      |
| B1-3 <i>d</i> <sub>1</sub>      | 59                                             |                   |                                                  |                      |
| Other B1- <i>d</i> <sub>1</sub> | 0                                              |                   |                                                  |                      |
| B1-(1-2) <i>d</i> <sub>2</sub>  | <i>b</i>                                       |                   |                                                  | 19 (14) <sup>c</sup> |
| B1-(1-3) <i>d</i> <sub>2</sub>  | 69 (64) <sup>c</sup>                           |                   |                                                  | 46 (54) <sup>c</sup> |
| B1-(2-3) <i>d</i> <sub>2</sub>  | 31 (36) <sup>c</sup>                           |                   |                                                  | 35 (32) <sup>c</sup> |

<sup>a</sup> 34.5% *trans*B-2, 24.2% *cis*B-2, 0.8% butane.

<sup>b</sup> Not detected because of technical problems.

<sup>c</sup> Calculated values are in parenthesis.

metals: Fe, Ni, Cr, Ir, Rh, Pt, and Pd, are reported in Table 5.

The results reported in lines 6, 7, 8, and 9 demonstrate the existence of a  $\sigma$ -vinylic process if we apply criteria 2 and 3, as previously defined. The nature of this  $\sigma$ -vinylic exchange is examined in lines 1 and 2. From Fe to Cr, the position on carbon atom 2 is more exchanged than the positions on carbon atom 1 (line 2: C<sub>1</sub>/C<sub>2</sub> < 1), whilst from Ir to Pd C<sub>1</sub>/C<sub>2</sub> > 1. Line 3 shows the contribution of the  $\pi$ -allylic process, absent on Fe, Ni, Cr, and Ir and increasing from Rh to Pd.

It is possible to classify the different reactions of  $\sigma$ -vinylic and  $\pi$ -allylic exchange of B-1 on iron as shown in Scheme 4.

At low conversion the only apparent product is the exchanged B1-*d*<sub>1</sub> on carbon

atom 2. The activation energies for the dissociative adsorption on carbon atom 1 and for the  $\pi$ -allylic process are very high and the rate of the corresponding reactions are very slow. (Although a steric effect can explain easily the different reactivity of the two hydrogen atoms on carbon 1, the high reactivity of the hydrogen atom on carbon atom 2 is less clear; a different acidity of these protons could possibly account for this experimental result.)

For the nickel, a downward shift of the activation free energy levels of the dissociative adsorption and therefore a decrease of the free energy of desorption will allow the exchange on carbon atom 1. We can imagine a constant shift from iron to palladium (4) which will explain the observed results for the vinylic exchange and the appear-

TABLE 5

The Exchange Reactions on the Seven Studied Metals

|   |                                                           | Metal |          |     |            |            |            |                         |
|---|-----------------------------------------------------------|-------|----------|-----|------------|------------|------------|-------------------------|
|   |                                                           | Fe    | Ni       | Cr  | Ir         | Rh         | Pt         | Pd                      |
| 1 | % of exchange on C2 in B-1. $\sigma$ -vinylic process     | 100   | 86       | 59  | 44         | 33         | 27         | 7                       |
| 2 | exch. on C1/exch. on C2 in B-1. $\sigma$ -vinylic process | 0     | 0.16     | 0.7 | 1.3        | 2.0        | 2.1        | 13.1                    |
| 3 | % of exchange on C3 in B-1. $\pi$ -allylic process        | 0     | 0        | 0   | 0          | 2          | 16         | 60                      |
| 4 | exch./isom. of <i>cis</i> B-2                             | 0     | <i>a</i> | —   | 0.12       | 0.25       | 2.7        | 2                       |
| 5 | Nature of the exchange of the <i>cis</i> B-2              | —     | —        | —   | —          | 100% vinyl | 100% vinyl | 70% vinyl;<br>30% allyl |
| 6 | % of exchange on C1 in B-1 on position 1 <sup>b</sup>     | 0     | 10       | 26  | 38         | 36         | 44         | 71                      |
| 7 | % of exchange on C1 in B-1 on position 2                  | 0     | 4        | 15  | 18         | 29         | 12         | 22                      |
| 8 | % of exchange in B-1 on the position 1-3 $d_2$            | 66    | 65       | 69  | $\epsilon$ | 62         | —          | —                       |
| 9 | % of exchange in B-1 on the position 2-3 $d_2$            | 33    | 35       | 31  | 0          | 38         | —          | —                       |

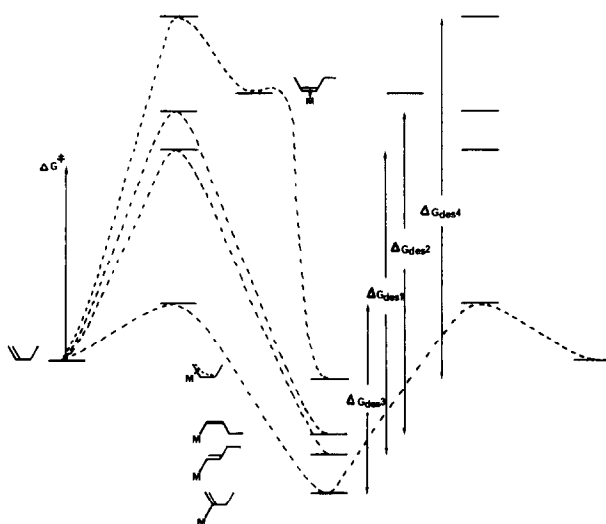
<sup>a</sup> No reproducible value because of the high sensitivity to poisons (Ref. (3)).

<sup>b</sup> 40% of vinylic exchange of B-1 on Pd has been extended to 100%.

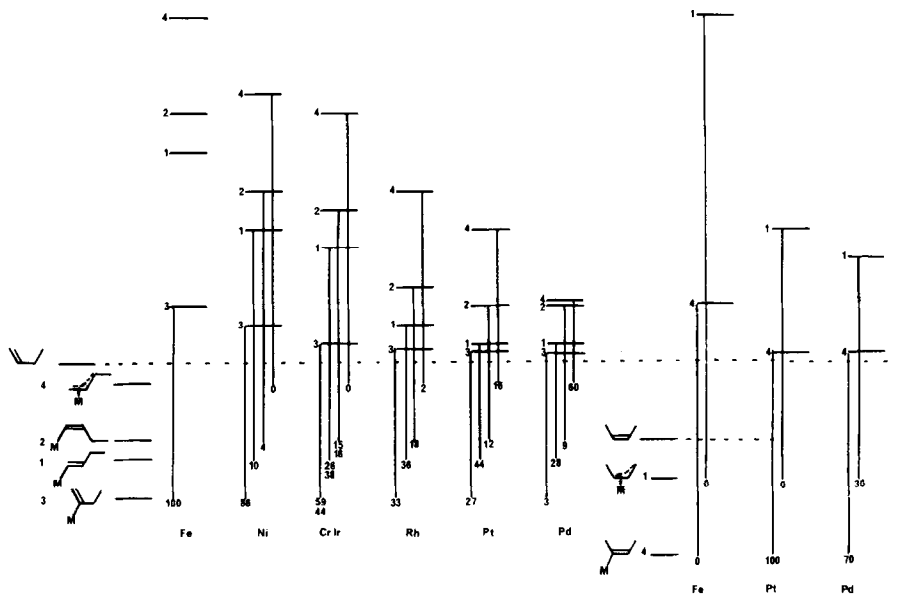
ance of the allylic process (Scheme 5). Scheme 5 is a simplified form of Scheme 4 (Fe) applied to the seven metals.

The rate of the four different reactions of exchange depends directly upon the free

energy of desorption which is approximately represented in Scheme 5 for the seven metals. such a scheme explains the decrease of the exchange on carbon atom 2 (line 1, Table 5), the dissymmetry of the



SCHEME 4. Diagram of free energy for the exchange reactions on Fe.



SCHEME 5. Energy of desorption on different metals.

exchange between carbon atoms 1 and 2 (line 2), the preeminence of the *trans* position on carbon atom 1 when going from Fe to Pd (lines 6 and 7), and the appearance of the  $\pi$ -allylic mechanism (line 3). As *cis*-B-2 is thermodynamically more stable than B-1, the corresponding initial level is lower (or the activation free energy is higher). This fact explains the results reported in lines 4 and 5. The vinylic exchange of the *cis*-B-2 is negligible on Fe and Ni, appears on Ir, and becomes important on Pt and Pd.

If we divide the seven metals into three families according to their number of *s* electrons in the fundamental state from 2 to 0 (9), and if inside each family we classify them according to their atomic number, we obtain the following order: Fe  $3d^64s^2$ , Ni  $3d^84s^2$ , Ir  $5d^76s^2$  || Cr  $3d^54s^1$ , Rh  $4d^85s^1$ , Pt  $5d^96s^1$  || Pd  $4d^{10}5s^0$ .

If the electronic configuration of the metal atoms in C site position (very poor coordination) approaches the fundamental state, the free-doublet  $s^2$  will repel the approaching molecule with its carbon-carbon double bond, rich in electrons, and will increase the activation energy from Pd to

Fe. The mean diameter of the *s* shell decreases when passing from Fe to Ni and Ir and from Cr to Pt because of the charge increase in the nucleus.

In addition, in the case of Pd the formation of the  $\pi$ -olefinic species is favoured largely by an extra stabilizing effect. The filled  $\pi$  orbital of the carbon-carbon double bond has good symmetry for the empty  $5s$  orbital of the metal and the filled  $d_{xy}$  (or  $d_{xz}$  or  $d_{yz}$ ) orbital of the metal has the right symmetry for the back-donation into the empty  $\pi$  antibonding orbital of the olefin.

#### CONCLUSION

The first step of all the reactions (for the most part isomerization) taking place on sites A and B is the  $\pi$ -olefinic adsorption (Scheme 1). However, there is no "s effect" on these reactions (i.e., these reactions are hardly affected when changing the metal) because for a metal atom in site A or B configuration, with a high coordination, the surrounding metal atom neighbours will give a more metallic character (delocalisa-



tion of the valence band) and diminish strongly the  $s$  character.

We can formulate the following rules:

1. All the reactions of olefins which we studied are geometric sensitive (6). The associative isomerizations, by intramolecular shift or Horiuti–Polanyi mechanism, take place, respectively, on the A and B sites. The  $\sigma$ -vinylic and  $\pi$ -allylic dissociative exchange and the  $\pi$ -allylic pure or assisted isomerization take place on the C sites of low coordination.

2. These last C reactions are very electronic sensitive and depend upon the number of  $s$  electrons in the fundamental state of the isolated metal atom concerned.

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