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Homologation and Hydrogenolysis of Linear and Branched Butenes and Butanes on Ru/SiO_2 Catalysts

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In order to investigate the possible mechanism(s) by which C–C bonds are cleaved or are formed on metallic surfaces, the reactions of linear and branched butenes and butanes over Ru/SiO_2 catalysts are studied. At temperatures above 50–100°C and in the presence of hydrogen, 1-butene, *cis*-2-butene, *trans*-2-butene, or isobutene simultaneously undergo isomerization (*cis-trans* isomerization or double-bond migration), hydrogenation, hydrogenolysis, and homologation reactions. In the same conditions, *n*-butane and isobutane only undergo hydrogenolysis. The influence of the structure of the starting hydrocarbon, contact time, reaction temperature, and hydrogen/hydrocarbon ratio on conversions and selectivities has been examined. Mechanisms for these reactions of hydrocarbons over metallic surfaces in the presence of hydrogen are envisaged using the known concepts of molecular chemistry: the results suggest that metal-alkyl species are key intermediates. Concerning hydrogenolysis and homologation of butenes, it appears that these two reactions occur at comparable rates, which suggests that they are mechanistically related. These reactions involve: (i) the formation of C_3 and C_1 (probably methylene) fragments from a C_4 olefin and (ii) the reaction of the C_1 fragments with the starting olefin to give C_5 hydrocarbons, in competition with the hydrogenation of these C_1 fragments leading to methane. Two simple mechanisms can explain the simultaneous and reversible nature of these two reactions of C–C bond cleavage and formation: (i) the insertion–deinsertion of a metallocarbene into (or from) a metal-alkyl species and (ii) the formation–rearrangement of a dimetallacyclopentane intermediate.

1. INTRODUCTION

Metallic surfaces of group VIII transition metals are known to cleave C–C bonds of alkanes and alkenes or to make C–C bonds from alkenes or CO/H_2. It is of great interest to determine, at a molecular level, the mechanism of C–C bond cleavage as well as C–C bond formation; in this respect, a particular question of interest in our laboratory is to investigate if a mechanistic relationship exists between C–C bond cleavage and C–C bond formation.

About 10 years ago, it was shown that, over highly dispersed metallic catalysts Fe/MgO, SiO_2, or Al_2O_3, CO + H_2 could be converted to C_1–C_5 hydrocarbons with high selectivities in propene and very small selectivities in ethylene (*1, 2*). In order to explain these results, it was suggested that ethylene was a primary product of the Fischer–Tropsch synthesis, which was able to react rapidly with a surface C_1 fragment to give propene selectively. This hypothesis was supported by experiments that showed that, on the same catalysts but in the absence of CO, ethylene could give, besides methane and ethane, higher hydrocarbons with a high selectivity in propene (*3*). These results suggested that the mechanism of chain growth in Fischer–Tropsch synthesis could involve intermediates and elementary steps the same as those of the reaction which led from a C_n to a C_{n+1} olefin. These observations were in agreement with the pioneer work by Eidus on cobalt catalysts (*4*), and with other studies dealing with the reactions of olefins over Fischer–Tropsch catalysts (*5–13*).

In further studies it was shown that, over

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Fischer–Tropsch catalysts such as Fe/SiO_2, Ru/SiO_2, and Os/SiO_2, a C_3H_6/H_2 mixture gave not only propane but also lower and higher olefinic and saturated hydrocarbons (*14, 15*). This "hydrogenolysis–homologation" reaction showed a number of similarities with hydrocarbon synthesis starting from CO/H_2. In both reactions, which occurred on the same catalysts and at the same temperatures, (i) the hydrocarbon distribution depended on the metal (the chain growth was favored in the order: Os < Ru < Fe), (ii) high temperatures reduced chain growth, (iii) at low conversions, the hydrocarbon distribution did not vary with contact time, and (iv) at low contact time, terminal olefins were the major products. Moreover, for a given metal and at a given temperature, the isobutene/*n*-butene ratios extrapolated at zero conversion were found to be identical in $CO + H_2$ reaction and in $C_3H_6 + H_2$ reaction (*14*).

All these observations favored the hypothesis that the same mechanism of carbon–carbon bond formation would be involved for chain growth in both Fischer–Tropsch synthesis and olefin homologation. In agreement with other studies (*16–20*), it was confirmed that, at least on Fe, Ru, and Os/SiO_2 catalysts, C–C bond formation did not require the presence of molecular CO, but more probably involved partially hydrogenated C_1 fragments (possibly methylene fragments) obtained from either $CO + H_2$, $C_nH_{2n} + H_2$, or $CH_2N_2 + H_2$ (*21*).

On the other hand, Pettit and co-workers (*22*) found a relationship between the mechanism of chain growth in Fischer–Tropsch synthesis and the mechanism of hydrogenolysis of saturated and unsaturated hydrocarbons. It was also suggested by Rooney and co-workers (*23*) that alkane homologation and Fischer–Tropsch synthesis could obey the same mechanism of C–C bond formation. Garin *et al.* (*24–26*) demonstrated by labeling experiments that the mechanisms of hydrogenolysis and isomerization of alkanes on metals could involve common intermediates. Obviously, the idea progressively arose that, over metal surfaces, a number of reactions involving elementary steps of C–C bond formation or cleavage could be related by a simple and probably unique mechanism (Scheme 1).

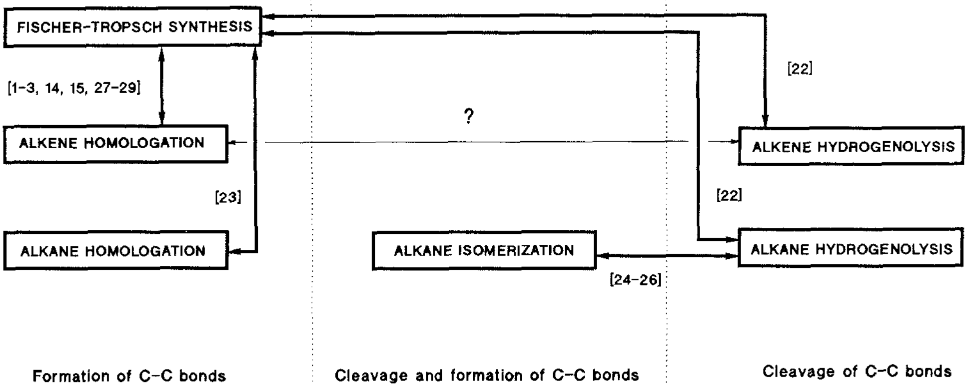
However, although mechanistical relationships were shown to occur between Fischer–Tropsch synthesis and homologation (*1–3, 14, 15, 27–29*) or between Fischer–Tropsch synthesis and hydrogenolysis (22), it was essential to explore hydrocarbon homologation in relation with hydrocarbon hydrogenolysis. In this respect, we report here a detailed study of the hydrogenolysis–homologation reaction of linear and branched butenes and butanes on a Ru/SiO_2 catalyst.

2. EXPERIMENTAL PART

2.1. *Apparatus Used for Catalytic Tests*

The catalytic tests were carried out in a dynamic glass microreactor working at atmospheric pressure. The reactor was a vertical U-tube equipped with a sintered glass on which a thin layer of Ru/SiO_2 catalyst was deposited. The reactor was introduced into a cylindrical oven equipped with a thermostat. The temperature of the catalytic bed was measured by a thermocouple. Three gas lines (hydrogen, argon, hydrocarbon), equipped with various valves and manometers, allowed the preparation of well-determined gas mixtures.

The hydrogen (Air Liquide C, >99.995% pure) and the argon (Air Liquide U) were purified by flowing through a deoxo-catalyst (BASF R-3-11) and 5-Å molecular sieves to eliminate any trace of oxygen and water. The deoxo-catalyst and the molecular sieves were regularly regenerated. The butenes and butanes (Air Liquide N20, >99% pure) were used without prior treatment. The purity of hydrogen, butenes, and butanes was controlled by chromatographic analysis: the percentage of methane in the hydrogen and the percentage of lower and higher hydrocarbons in each butene or butane must be negligible.



SCHEME. 1. Mechanistic relationships (demonstrated or suggested) between reactions occuring over metal surfaces.

2.2. *Analysis of the Products*

The hydrocarbons produced in the reaction were analyzed with an on-line gas-phase chromatograph equipped with a flame ionization detector (Intersmat IGC 120 FB). The separation of the C_1–C_4 hydrocarbons was performed on a 0.22 cm i.d. × 6 m stainless-steel column packed with squalane (7%) on alumina. The system was calibrated with standard hydrocarbon mixtures (Alltech). The separation of C_5 hydrocarbons was performed on a 0.22 cm i.d. × 7.5 m stainless-steel column packed with SE 30 (10%) on Chromosorb P-AW. For C_5, the standardizations were realized with binary hydrocarbon mixtures (Fluka products).

2.3 *Catalyst*

The Ru/SiO$_2$ catalyst was prepared by adsorbing $Ru_3(CO)_{12}$ (Johnson Matthey) from a hexane solution onto silica (Aerosil 200 Degussa) that had been pretreated at 500°C under 10^{-4} Torr for 16 h. The grafted cluster $((\mu\text{-H})(\mu\text{-OSi}\leqslant)Ru_3(CO)_{10}$ (*30*) was then decomposed into small metal particles under flowing H_2 at 300°C. The final metal content was 1%, and the average particle size, determined by electron microscopy, was ca. 15 Å.

All the catalytic tests were performed using the same batch of catalyst. The Ru/SiO$_2$ catalyst was treated under H_2 at 250°C between each experiment, allowing thus the conservation of the activity and selectivity for all our studies. Electron microscopy analyses conducted after several months of utilization of the same sample showed that there was neither an increase in average particle size nor any significant variation of the dispersion of the metallic phase on the silica surface.

In most of our experiments, the amount of catalyst introduced into the reactor was 100 mg, corresponding to a volume of ca. 0.5 cm^3.

3. RESULTS

3.1. *General Features of the Reaction Butenes + H_2*

When a butene/H_2 mixture (1/1) is allowed to flow over a Ru/SiO$_2$ catalyst (at 250°C and under atmospheric pressure), reactions of isomerization, hydrogenation, hydrogenolysis (formation of lower hydrocarbons), and homologation (formation of higher hydrocarbons) are observed. In Figs. 1 to 4, the variations of conversion as a function of the contact time (or, more precisely, as a function of the inverse of flow rate for a given amount of catalyst) are represented for each butene isomer and each reaction. The various butene isomers exhibit similar behavior. The main reactions are *cis-trans* isomerization and double-bond

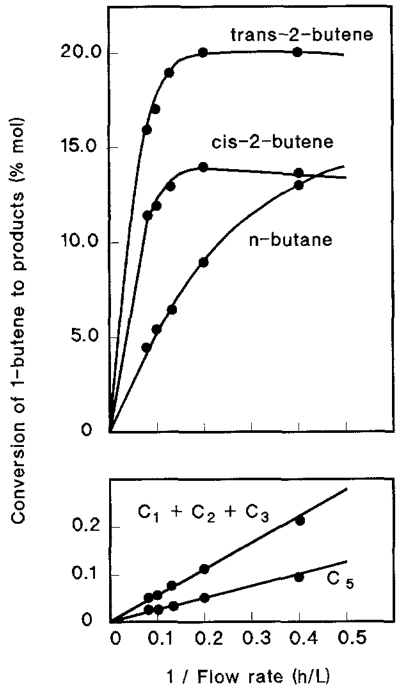


FIG. 1. Influence of contact time on the conversion of 1-butene to products in the reaction of 1-butene and H_2 over Ru/SiO_2. m_{cata} = 100 mg; T = 250°C; 1-butene/H_2/Argon = 1/1/3 (mol).

migration (for linear butenes), and hydrogenation, without any skeletal isomerization.

The isomerization reactions are quite fast since even at low contact time a ca. 20% conversion of each linear butene into its two other linear isomers is observed. For this reaction, the conversion increases rapidly with increasing contact time, reaches a maximum, then decreases for higher contact times (this last phenomenon reflects the secondary hydrogenation of isomerized olefins).

The rate of hydrogenation is lower than that of isomerization. At the lowest contact time used, the conversion into butane is ca. 5% and comparable among the different isomers. At low conversion range, the conversion of butenes to butane increases roughly linearly with contact time.

In the presence of hydrogen, the various butene isomers give simultaneously lower (C_1, C_2, C_3) and higher (C_5) hydrocarbons. The conversions for hydrogenolysis and homologation reactions, although low in the range of contact times studied, are significant and increase linearly with increasing contact time. The simultaneity of these two reactions of C–C bond formation and cleavage supports the idea that they are mechanistically related. Therefore, we found it interesting to investigate those two reactions in parallel.

3.2. Formation of C_1, C_2, C_3, and C_5 Hydrocarbons from Butene/H_2 Mixtures

3.2.1. Conversion into C_1, C_2, C_3, and C_5 hydrocarbons. Generally speaking, the conversions increase roughly linearly with increasing $P_{H_2}/P_{C_4H_8}$ ratio (Fig. 5). In the absence of hydrogen, there is neither hydrogenolysis nor homologation of the butenes.

In the 50 to 250°C range, the conversion

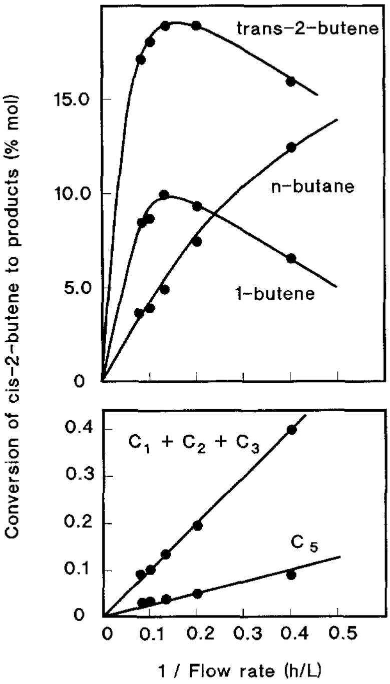


FIG. 2. Influence of contact time on the conversion of *cis*-2-butene to products in the reaction of *cis*-2-butene and H_2 over Ru/SiO_2. m_{cata} = 100 mg; T = 250°C; *cis*-2-butene/H_2/Argon = 1/1/3 (mol).

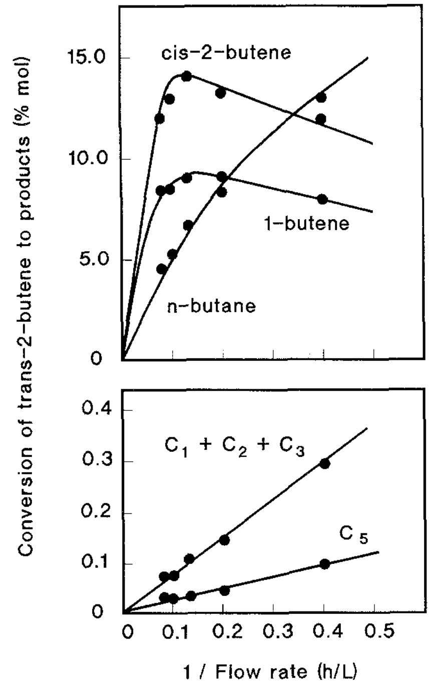


FIG. 3. Influence of contact time on the conversion of *trans*-2-butene to products in the reaction of *trans*-2-butene and H_2 over Ru/SiO_2. m_{cata} = 100 mg T = 250°C; *trans*-2-butene/H_2/Argon = 1/1/3 (mol).

of butenes to lower hydrocarbons and, to a lesser extent, to higher hydrocarbons increases with increasing temperature (Fig. 6). Nevertheless, there are significant differences depending on the butene isomer.

In the case of 1-butene, measurable amounts of lower and higher hydrocarbons are produced at temperatures as low as 50°C. The amount of these hydrocarbons increases markedly up to ca. 100°C, then increases moderately for higher temperatures. The conversion to C_5 hydrocarbons appears relatively constant between 100 and 250°C.

For *cis*- and *trans*-2-butenes, lower and higher hydrocarbons are formed only above 110°C; the conversions to C_1–C_3 hydrocarbons increase with temperature to reach, at 250°C, values two times greater than those obtained for 1-butene. The conversion to C_5 hydrocarbons increases moderately with temperature.

In the case of isobutene, an exponential increase in the amount of C_1–C_3 hydrocarbons is observed with increasing temperature. At 250°C, the conversion to C_1–C_3 is ca. two times greater than that obtained for the 2-butenes. However, the conversion to C_5 hydrocarbons remains very low and does not vary with temperature.

To summarize, when the reaction temperature increases, hydrogenolysis is favored with respect to homologation, and this tendency follows the order: isobutene > 2-butenes > 1-butene.

3.2.2. Distribution of the C_1, C_2, C_3, and C_5 hydrocarbons. For a given isomer, there is only a little variation in this distribution when increasing contact time (Fig. 7). However, the distribution depends upon the butene isomer used as substrate. In particular, depending on the structure of the olefin, there is a kind of inverse relationship be-

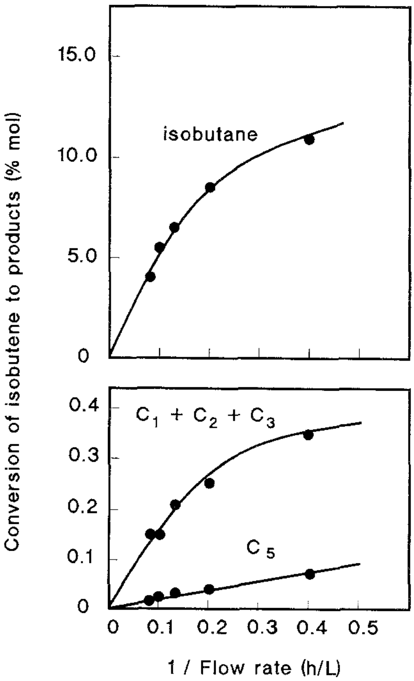


FIG. 4. Influence of contact time on the conversion of isobutene to products in the reaction of isobutene and H_2 over Ru/SO_2. m_{cata} = 100 mg; T = 250°C; isobutene/H_2/Argon = 1/1/3 (mol).

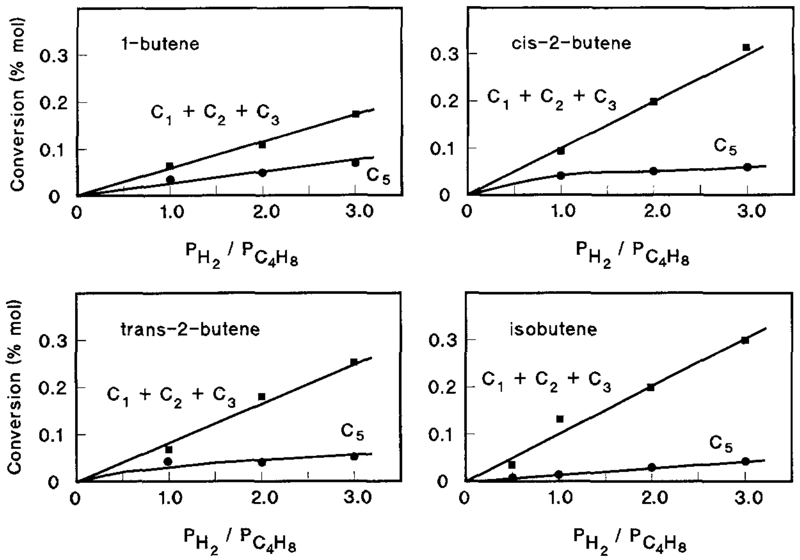


FIG. 5. Influence of $P_{H_2}/P_{C_4H_8}$ ratio on the conversion of butenes to C_1–C_3 and C_5 hydrocarbons. m_{cata} = 100 mg; T = 250°C; overall flow rate = 12 liter × h^{-1}.

tween the selectivity for methane and the selectivity for pentenes. Thus, the selectivity for methane increases from 20 to 50% in the order: 1-butene < *trans*-2-butene < *cis*-2-butene < isobutene. At the same time, selectivity toward C_5 hydrocarbons drops from 35 to 10% in the order: 1-butene > *trans*-2-butene > *cis*-2-butene > isobutene. These observations are discussed later but already suggest that the hydrogenation of a

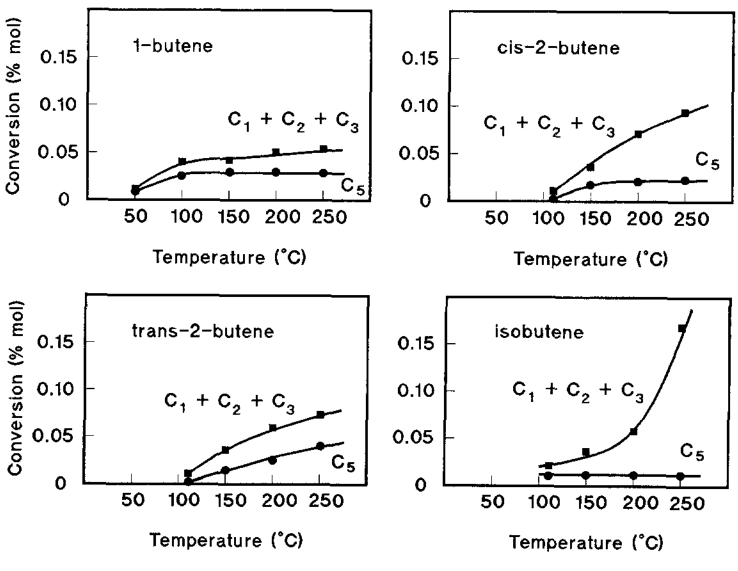


FIG. 6. Influence of reaction temperature on the conversion of butenes to C_1–C_3 and C_5 hydrocarbons. m_{cata} = 100 mg; butene/H_2/argon = 1/1/3 (mol); overall flow rate = 12 liter × h^{-1}.

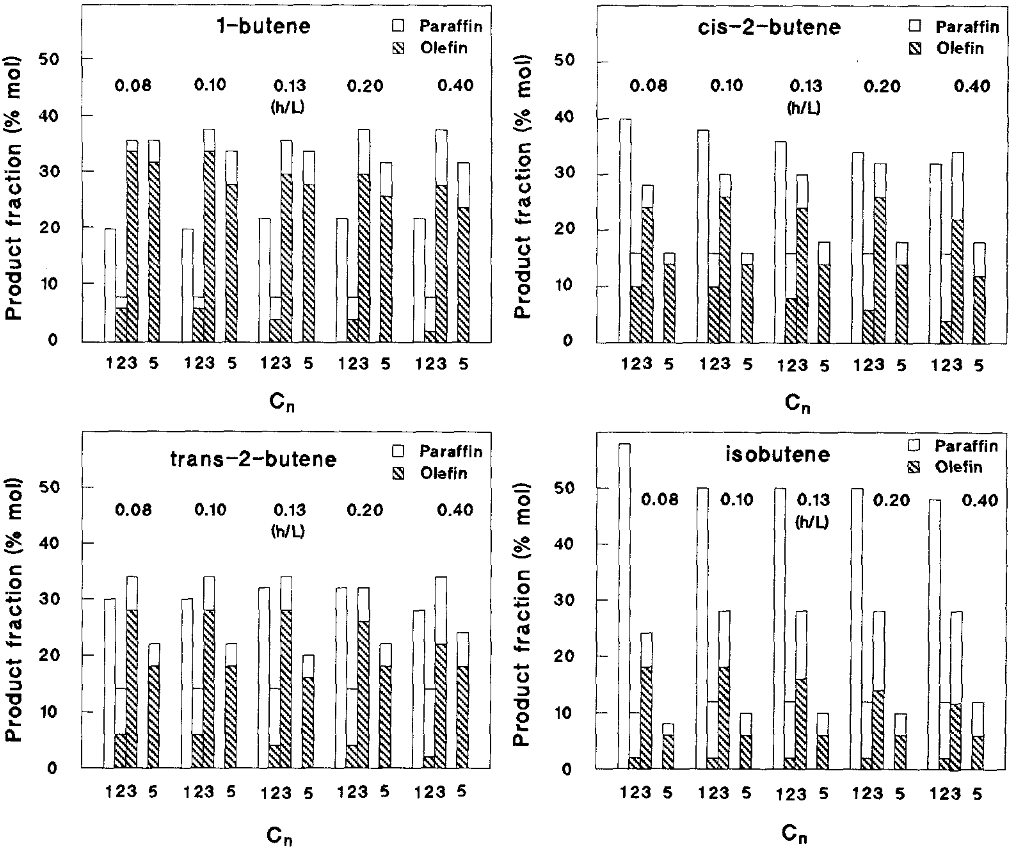


FIG. 7. Influence of contact time (inverse of flow rate) on the distribution of C_1, C_2, C_3, and C_5 hydrocarbons produced in the reaction of butene and H_2 over Ru/SiO$_2$. m_{cata} = 100 mg; T = 250°C; butene/H_2/Argon = 1/1/3 (mol).

surface C_1 fragment competes with its incorporation to the starting olefin.

For a given butene isomer, the paraffin/olefin ratio in C_2, C_3, and C_5 hydrocarbons increases with contact time: the major primary products are methane and C_2, C_3, and C_5 olefins, which are further hydrogenated into paraffins (Fig. 7).

For each butene isomer, the proportion of methane decreases with decreasing reaction temperature, whereas an increased amount of C_3 and C_5 hydrocarbons is observed (Fig. 8). As discussed later, the hydrogenation of the surface C_1 fragment (which competes with its incorporation to the starting olefin), is not easily achieved at low temperature.

Except for the case of 1-butene, the $P_{H_2}/P_{C_4H_8}$ ratio has little influence on the distribution of products (Fig. 9). For 1-butene, increasing the partial pressure of hydrogen causes an increase in methane selectivity and a decrease in C_5 selectivity. The distributions obtained from 1-butene under a high partial pressure of hydrogen are similar to those obtained from *cis*- and *trans*-2-butene. These distribution changes occurring when the partial pressure of hydrogen increases, are likely due to a faster isomerization of 1-butene to 2-butenes, probably via a metal-alkyl intermediate.

Likewise, paraffin content in the C_2, C_3, and C_5 hydrocarbons increases with $P_{H_2}/P_{C_4H_8}$ ratio.

3.2.3. Distribution of the pentene iso-

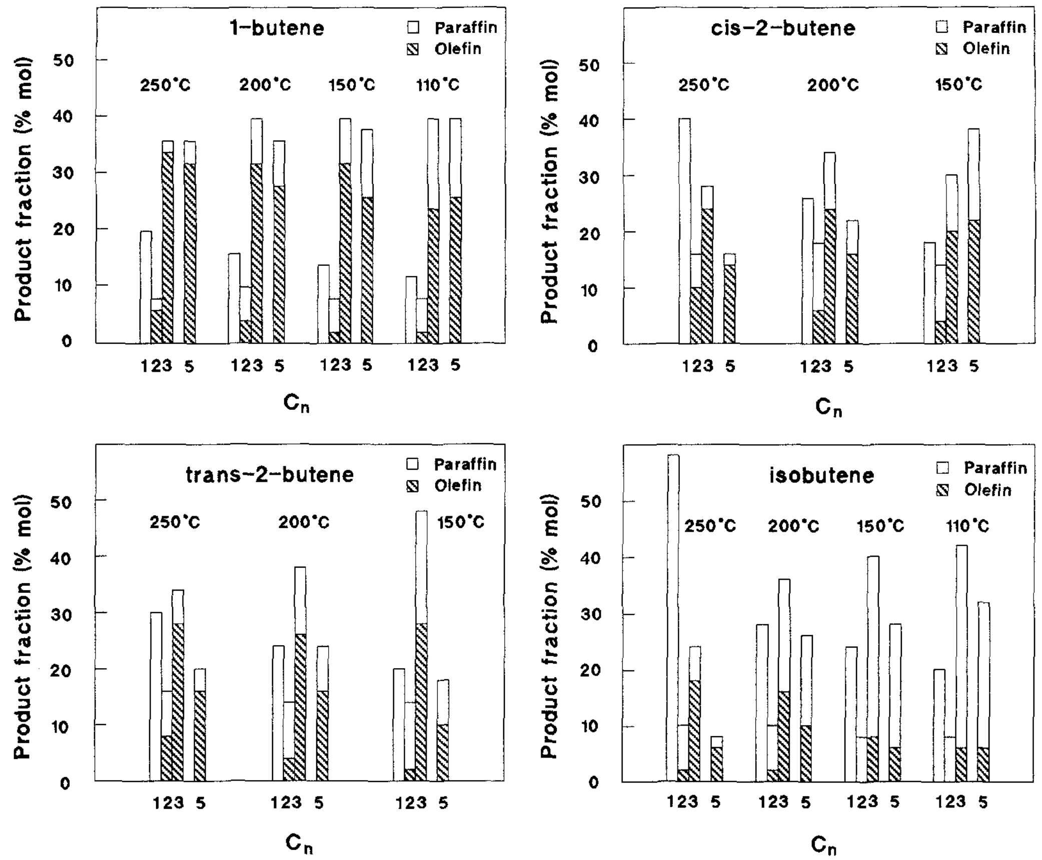


FIG. 8. Influence of reaction temperature on the distribution of C_1, C_2, C_3, and C_5 hydrocarbons produced in the reaction of butene and H_2 over Ru/SiO_2. m_{cata} = 100 mg; butene/H_2/argon = 1/1/3 (mol); overall flow rate: 12 liter × h^{-1}.

mers. The distribution of the pentene isomers obtained by homologation does not vary significantly when starting from 1-butene, *cis*-, or *trans*-2-butene (Fig. 10). At low contact time, the major products are 1-pentene, *cis*-2-pentene, and *trans*-2-pentene. The selectivity for 1-pentene decreases with increasing contact time, while the selectivities for *cis*- and *trans*-2-pentene increase and tend toward thermodynamic equilibrium (*31*). This suggests that 1-pentene is a primary product of linear butene homologation and that a part of the 2-pentenes might come from a secondary isomerization reaction of 1-pentene (the experimental data does not allow us to determine whether the 2-pentenes are primary products or not). A significant amount (ca. 10%) of branched pentenes also forms: 2-methyl-2-butene and 2-methyl-1-butene. The selectivity in 2-methyl-2-butene slowly increases with increasing contact time, while the selectivity in 2-methyl-1-butene decreases. Formation of 3-methyl-1-butene is not observed.

Homologation of isobutene gives only the three branched pentenes. The selectivity for 3-methyl-1-butene is high at low conversion, then decreases with increasing contact time, while selectivities for 2-methyl-2-butene and 2-methyl-1-butene increase. At high contact time, the selectivities are close to the thermodynamic equilibrium values (*31*). These results suggest that 3-methyl-1-bu-

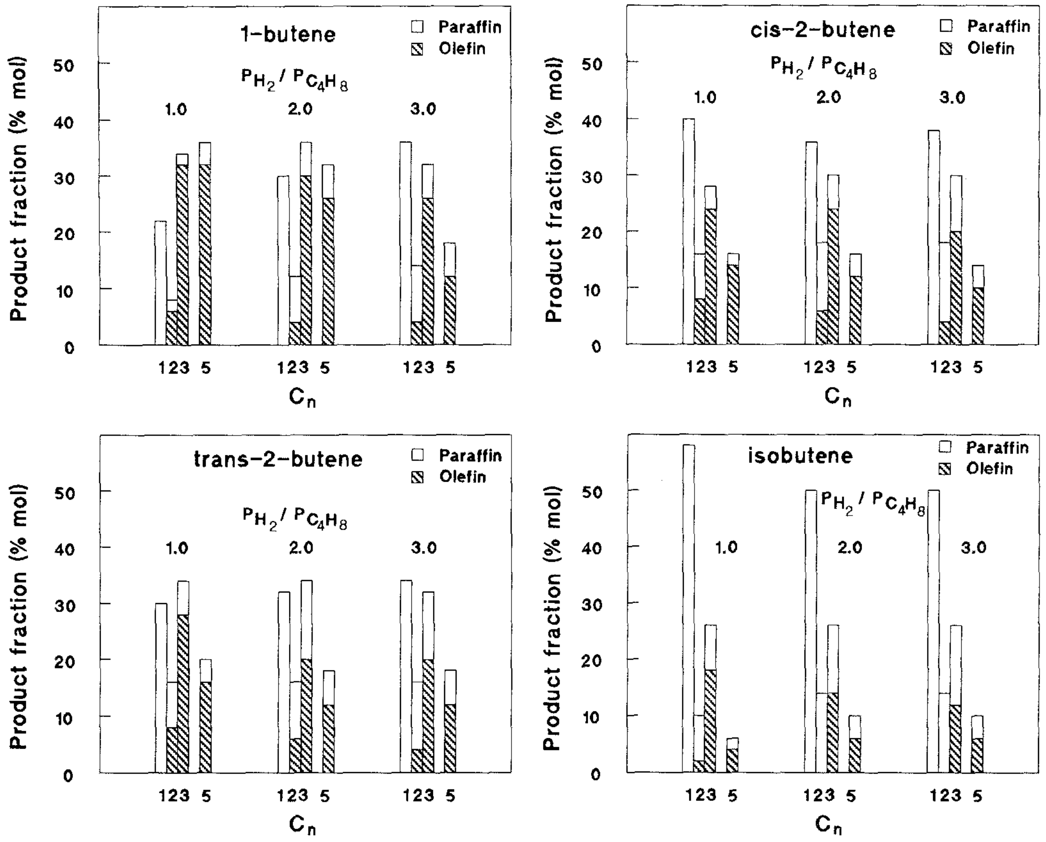


FIG. 9. Influence of $P_{H_2}/P_{C_4H_8}$ ratio on the distribution of C_1, C_2, C_3, and C_5 hydrocarbons produced in the reaction of butene and H_2 over Ru/SiO$_2$. m_{cata} = 100 mg; T = 250°C; overall flow rate = 12 liter × h^{-1}.

tene is the primary product of homologation of isobutene and that the two other branched isomers are mainly produced by secondary isomerization reactions.

3.3. *Hydrogenolysis and Homologation of n-Butane and Isobutane*

In order to complete the results obtained in the hydrogenolysis–homologation of butenes, we have studied the reaction of butanes with hydrogen on the same Ru/SiO$_2$ catalyst and in the same experimental conditions.

When a C_4H_{10}/H_2 (C_4H_{10} = *n*-butane or isobutane) mixture is allowed to flow over Ru/SiO$_2$ (at 250°C and under atmospheric pressure) the formation of methane, ethane, propane, and traces of propene is observed. In contrast to the case of butenes, only traces of C_5 hydrocarbons are produced (*n*-pentane and methyl-butane in the case of *n*-butane). For butanes, the conversions to higher hydrocarbons are ca. 100 times less than those obtained in the reaction of butenes with hydrogen.

Skeletal isomerization was not observed in our experimental conditions.

3.3.1. Conversion of n-butane and isobutane to C_1–C_3 hydrocarbons. The conversions of *n*-butane and isobutane to C_1–C_3 hydrocarbons are proportional to contact time (Fig. 11). A comparison with the butene/H$_2$ reaction shows that the hydrogenolysis of *n*-butane is 50 times faster than that of 1-bu-

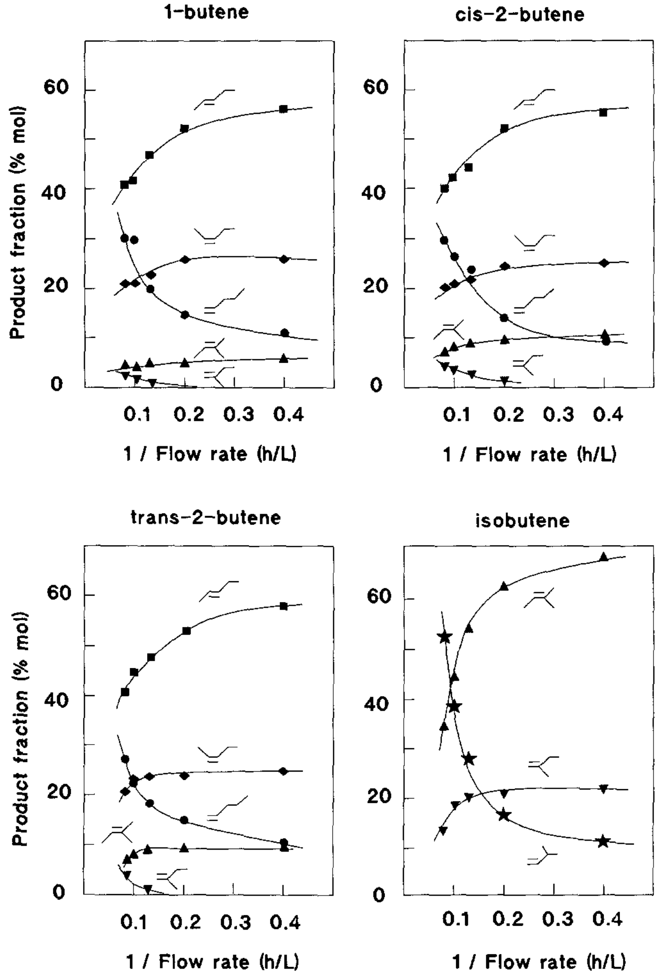


FIG. 10. Influence of contact time on the distribution of pentene isomers produced in the reaction of butene and H_2 over Ru/SiO_2. m_{cata} = 100 mg; T = 250°C; butene/H_2/Argon = 1/1/3 (mol).

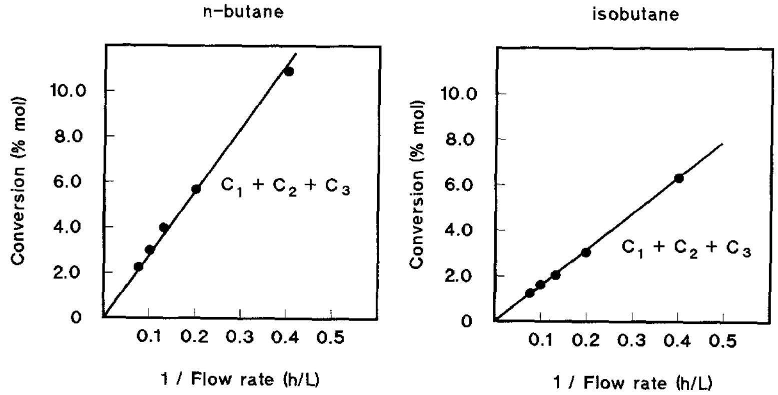


FIG. 11. Influence of contact time on the conversion of butane to C_1–C_3 hydrocarbons in the reaction of butane and H_2 over Ru/SiO_2. m_{cata} = 100 mg; T = 250°C; butane/H_2/Argon = 1/1/3 (mol).

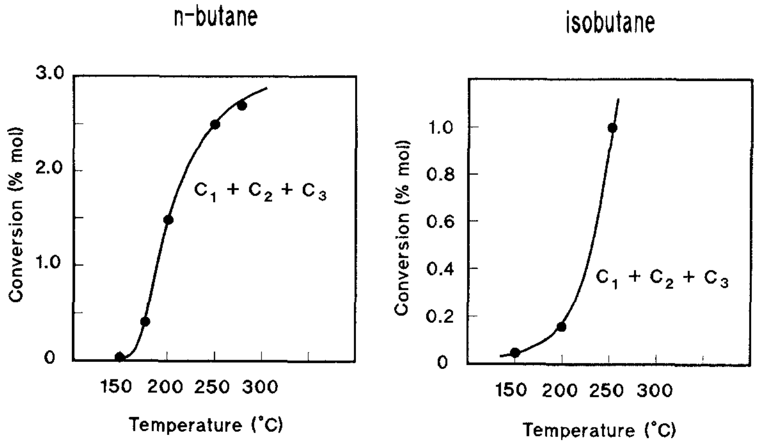


FIG. 12. Influence of reaction temperature on the conversion of butane to C$_1$–C$_3$ hydrocarbons in the reaction of butane and H$_2$ over Ru/SiO$_2$. m_{cata} = 100 mg; butane/H$_2$/Argon = 1/1/3 (mol); overall flow rate = 12 liter × h^{-1}.

tene; likewise, the hydrogenolysis of isobutane is 10 times faster than that of isobutene.

Figure 12 illustrates the effect of the reaction temperature on the hydrogenolysis of *n*-butane or isobutane. Measurable amounts of C$_1$–C$_3$ hydrocarbons are formed at 150°C and above. The conversion increases with increasing temperature. This increase is exponential in the case of isobutane, while for *n*-butane it seems to reach a plateau above 275°C (note that the conversions are not in the same range for *n*-butane and isobutane: between 150 and 250°C, the conversion of *n*-butane varies from 0.1 to 2.5%, whereas the conversion of isobutane varies from 0.02% to 1%).

The conversions of *n*-butane and isobutane to C$_1$–C$_3$ hydrocarbons increase linearly with increasing $P_{H_2}/P_{C_4H_{10}}$ ratio (Fig. 13). Only a negligible amount of hydrogenolysis products forms in the absence of hydrogen.

3.3.2. Distribution of the C_1, C_2, and C_3 hydrocarbons. As in the case of butenes, with increasing contact time there is only a slight variation in the distribution of lower hydrocarbons produced in the hydrogenolysis of *n*-butane or isobutane (Fig. 14). Methane is the major product at 250°C (ca. 75% for *n*-butane and ca. 90% for isobutane).

For both *n*-butane and isobutane, with de-

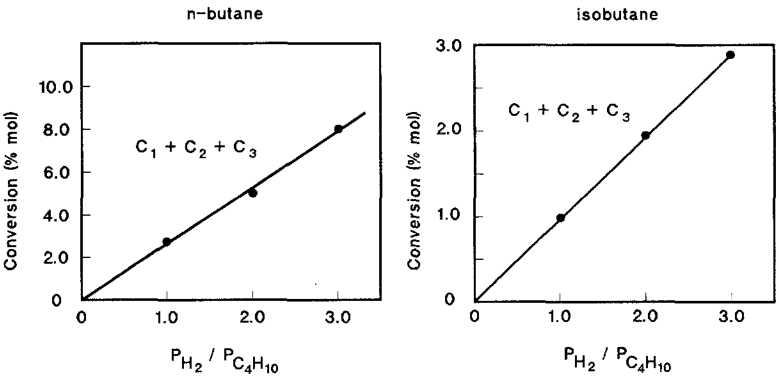


FIG. 13. Influence of $P_{H_2}/P_{C_4H_{10}}$ ratio on the conversion of butane to C$_1$–C$_3$ hydrocarbons in the reaction of butane and H$_2$ over Ru/SiO$_2$. m_{cata} = 100 mg; T = 250°C; overall flow rate = 12 liter × h^{-1}.

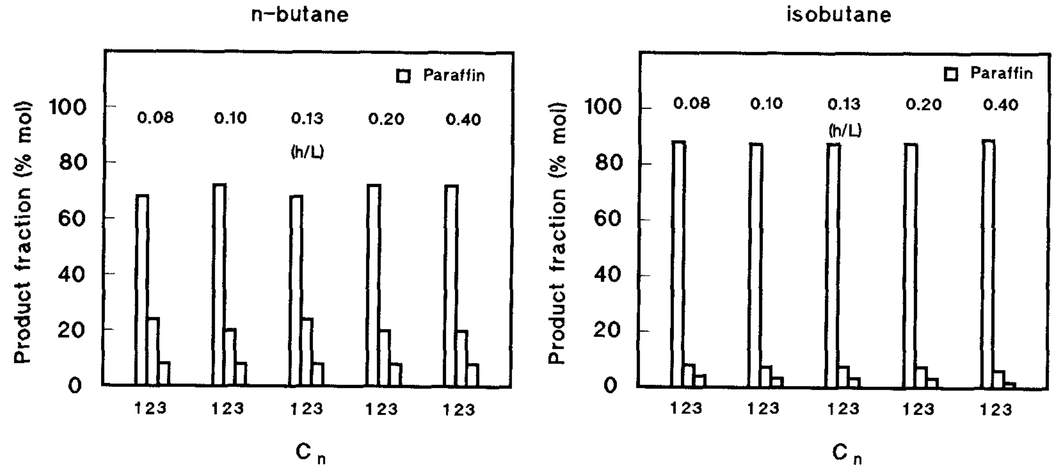


FIG. 14. Influence of contact time on the distribution of C_1, C_2, C_3 hydrocarbons produced in the reaction of butane and H_2 over Ru/SiO_2. m_{cata} = 100 mg; T = 250°C; butane/H_2/Argon = 1/1/3 (mol).

creasing reaction temperature, the selectivity to methane decreases to the benefit of ethane and propane (Fig. 15) (similar results were obtained with butenes). At 150°C–175°C, for isobutane as well as for *n*-butane, the selectivity to methane is lower than the selectivity to ethane.

Finally, at 250°C, the $P_{H_2}/P_{C_4H_{10}}$ ratio does not greatly influence the C_1–C_3 distribution (Fig. 16).

4. DISCUSSION

In the presence of hydrogen and over a Ru/SiO_2 catalyst, the various butene isomers undergo simultaneous reactions of isomerization (*cis-trans* isomerization and double-bond migration), hydrogenation, hydrogenolysis (formation of lower hydrocarbons), and homologation (formation of higher hydrocarbons). In the same conditions, butane isomers undergo only hydrogenolysis.

In this discussion, we try to explain the experimental results by means of reaction paths deduced from the elementary steps already demonstrated in organometallic chemistry.

We consider that a surface metal-alkyl species is the key intermediate in all these reactions of isomerization, hydrogenation, hydrogenolysis, and homologation of alkenes or alkanes in the presence of a metallic surface covered with hydrogen. Some important reaction pathways starting from (or leading to) metal alkyls are summarized in Scheme 2.

1. By *β-H elimination*, a metal-*n*-alkyl species gives an α-olefin which can reinsert into a *M*–H bond to give a secondary metal alkyl (a new β-H elimination will lead to the internal isomers). These steps are fully reversible, so that any olefin will give any kind of metal alkyl by olefin insertion into the metal-hydride bonds (*32*).

2. By *reductive elimination*, a metal-*n*-alkyl species will give a *n*-alkane. The reverse reaction will be the oxidative addition of the C–H bond of the alkane (*32*).

3. By *α-H elimination*, a metal-*n*-alkyl species will give a metallocarbene. The reverse reaction will hydrogenate the metallocarbene to the metal-alkyl species (*32*).

4. By *γ-H elimination*, a C–H bond of the alkyl group in γ position will be activated and will give a dimetallacyclopentane (or a metallacyclobutane). This type of reaction has been observed for the decomposition of neopentyl complexes of platinum (*33*), nickel or palladium (*34*), and in the synthesis of rhodium and ruthenium metallacyclic

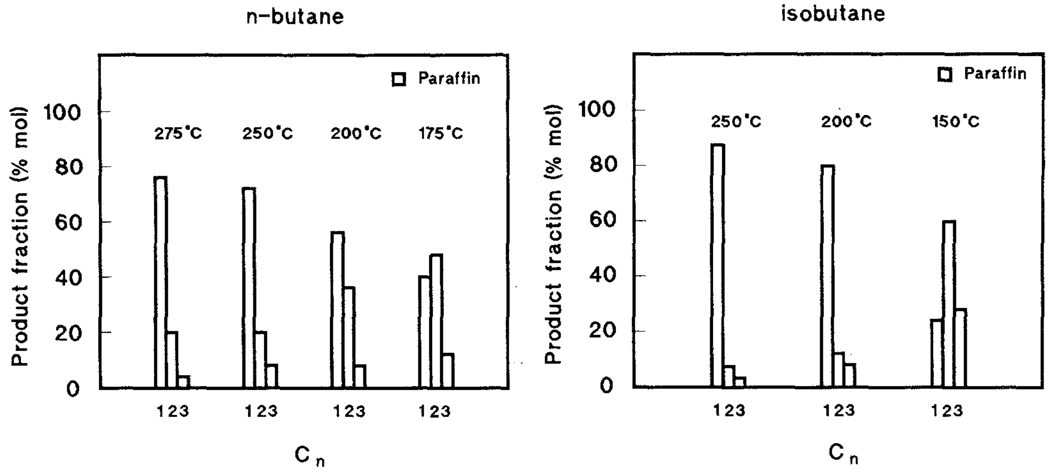


FIG. 15. Influence of reaction temperature on the distribution of C_1, C_2, C_3 hydrocarbons produced in the reaction of butane and H_2 over Ru/SiO_2. m_{cata} = 100 mg; butane/H_2/Argon = 1/1/3 (mol); overall flow rate = 12 liter × h^{-1}.

complexes (*35*). The reverse reaction will transform, by *M*–C bond hydrogenolysis, the metallacycle to a metal-alkyl species.

5. The *dimetallacyclopentane* (or the metallacyclobutane) can also lead, via a *concerted electron transfer,* to a metallocarbene and an olefin. The reverse reaction (considered as a carbene attack to a coordinated olefin) will lead to the (di)metallacycle. This type of reaction has homogeneous precedents with iron (*36*), osmium (*37*), cobalt (*38*), and ruthenium (*39*) complexes.

6. Finally, a *metal alkyl can deinsert a carbene fragment* (e.g., methylene) and give a metal alkyl with one carbon less. A mechanism of this type was proposed by Pettit and co-workers (*22*) to account for the hydrocarbon distribution obtained in hydrogenolysis reactions of *n*-octane and 1-octene on sup-

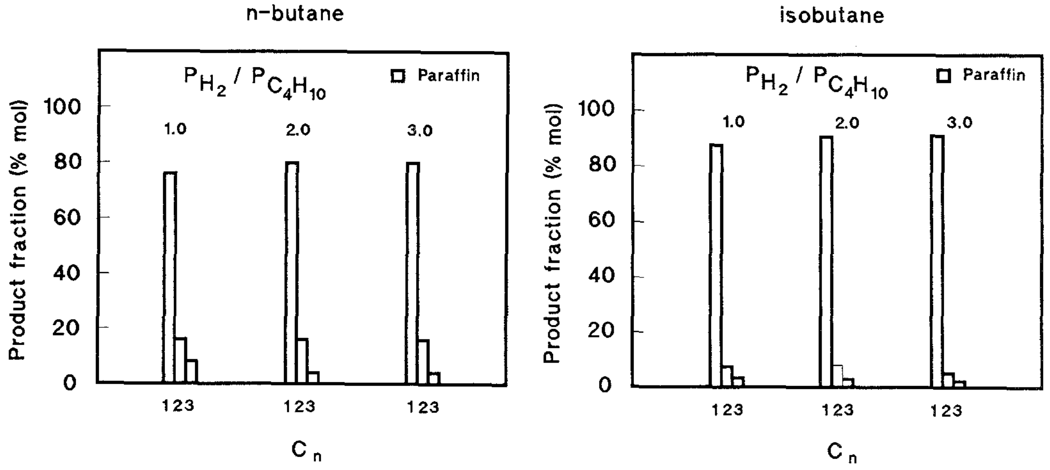
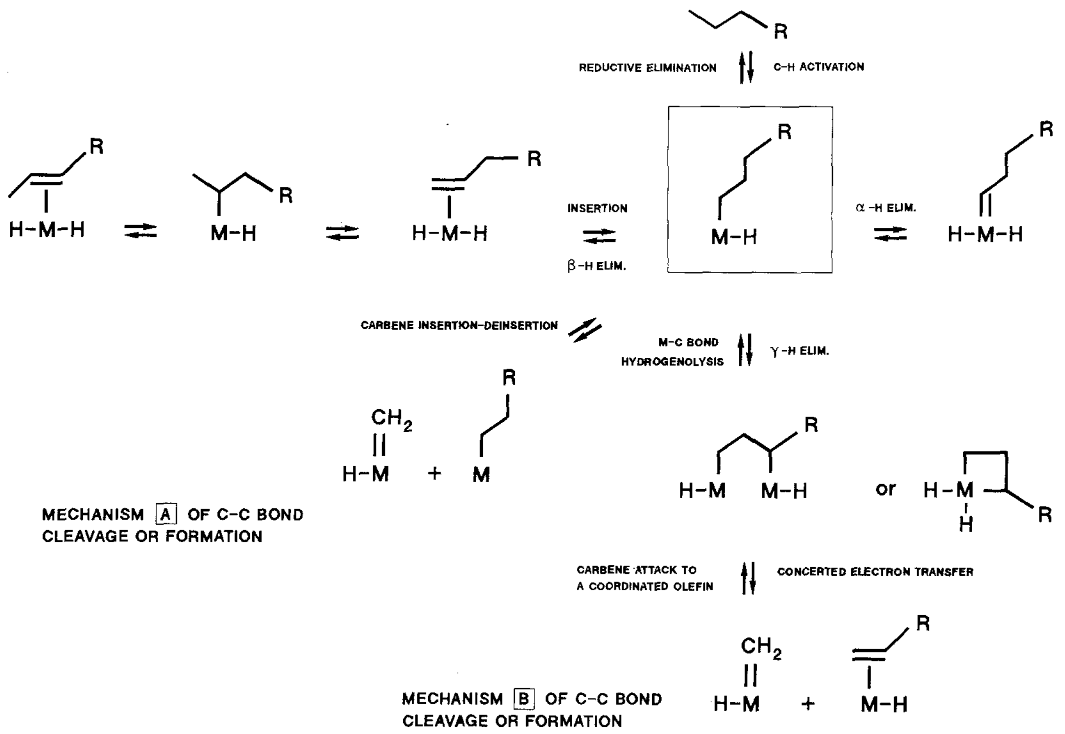


FIG. 16. Influence of $P_{H_2}/P_{C_4H_{10}}$ on the distribution of C_1, C_2, C_3 hydrocarbons produced in the reaction of butane and H_2 over Ru/SiO_2. m_{cata} = 100 mg; T = 250°C; overall flow rate = 12 liter × h^{-1}.



SCHEME. 2. The various elementary steps starting from (or leading to) a metal-alkyl species.

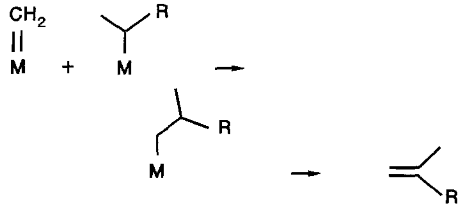
ported ruthenium, cobalt, and nickel catalysts. The reverse reaction will be the insertion of a methylene fragment into a metal-alkyl species, a pathway which has been reported in organometallic chemistry of some complexes of Ni, Ta, Ir, W, Rh, Ru, or Os (*40–45*).

The only elementary steps that lead to C–C bond formation or cleavage are the last two. They are both reversible, which means that the same elementary steps can lead to C–C bond formation of C–C bond cleavage. One important difference between the two mechanisms must be underlined:

—in mechanism A, the formation of a C–C bond implies the insertion of a carbene (methylene) into a "saturated" metal-alkyl fragment;

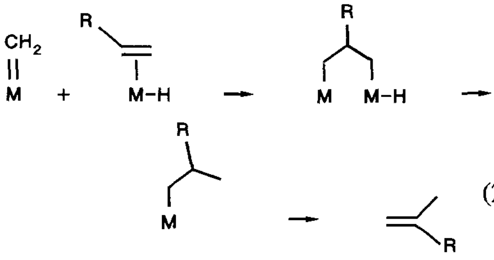
—in mechanism B, the formation of a C–C bond involves the reaction of the same carbene (methylene) into a "unsaturated" olefin.

Both mechanisms account for the formation of branched isomers. For mechanism A, the formation of a branched hydrocarbon results from the carbene insertion into a secondary metal alkyl:



(1)

For mechanism B, branching is due to the attack of the carbene into the substituted carbon of the double bond:



(2)

The elementary steps shown in Scheme 2

are sufficient to explain the simultaneous occurence of olefin isomerization, hydrogenation, homologation, and hydrogenolysis. They also explain alkane homologation and hydrogenolysis.

4.1. Isomerization and Hydrogenation of Butenes

Let us consider isomerization and hydrogenation reactions in the light of the proposed mechanisms of Scheme 2. The two reactions are parallel but the rate of isomerization appears to be higher than that of hydrogenation. This experimental fact can be explained if one assumes that β-H elimination from the metal-alkyl species to the isomerized olefin is faster than the reductive elimination of the same metal-alkyl species leading to the alkane.

4.2. Hydrogenolysis and Homologation Reactions of Butenes

It is important to recall here the main features of these two parallel reactions.

In addition to the preponderant isomerization and hydrogenation reactions, the various butene isomers undergo reactions of cleavage and formation of C–C bonds at temperatures above 50–100°C. The conversions are low but nevertheless significant. They have the same order of magnitude for each of the four butene isomers and are proportional to contact time (only in the range of low conversions for the case of isobutene). The major products formed at 250°C are methane and the C_3 and C_5 hydrocarbons. A nonnegligible proportion of C_2 hydrocarbons also forms, as well as traces of C_6 hydrocarbons.

The results suggest that on a Ru/SiO_2 catalyst and in the presence of hydrogen, a C_4 olefin can undergo cleavage of a terminal C–C bond, which leads to the formation of C_1 and C_3 surface fragments. The C_3 fragments give propene and propane, while C_1 fragments can be either hydrogenated to methane or can react with butene to produce C_5 hydrocarbons. Such a hypothesis has already been checked by labeling experiments in the case of 1-pentene homologation and hydrogenolysis over Ru/SiO_2 (*46*). The presence of ethylene and ethane can be explained by the formation of C_2 fragments formed via a possible cleavage: $C_4 \rightarrow C_2 + C_2$ or via degradation of C_3 fragments: $C_3 \rightarrow C_1 + C_2$.

The fact that the product distribution varies only slightly with contact time can be explained easily if one assumes that, for a given olefin and a given range of temperature, the rate of hydrogenolysis is, in a first approximation, comparable to that of homologation. If the rate of C–C bond cleavage were much larger than that of C–C bond formation, one should observe a much higher amount of hydrogenolysis products at high contact time. In other words, the rate of addition of a C_1 fragment to a C_n fragment is comparable to the rate of elimination of a C_1 fragment from a C_n fragment. However, a deeper analysis of the data suggests a more complex situation.

First, methane formation, which results from the hydrogenation of the C_1 fragment, competes with C–C bond formation so that the amount of homologation products is usually less important than the amount of hydrogenolysis products. Interestingly, there are temperature ranges where methane formation can be significantly reduced, e.g., at 110°C starting from 1-butene or isobutene (Fig. 8), and then the rate of homologation tends to be close to that of hydrogenolysis.

Second, the structure of the olefin has some effect on the respective rates of hydrogenolysis and homologation. For example, for 1-butene the amount of C_5 hydrocarbons is close to that of C_3 hydrocarbons (Figs. 7 and 8), whereas for isobutene, the amount of C_5 hydrocarbons is lower than that of C_3 hydrocarbons. Besides, for isobutene, the amount of methane is always larger than that observed for the other isomers. Steric effects occur during homologation of sterically hindered olefins and the competing reaction of C_1 hydrogenation becomes preponderant.

So far, we have always considered the product distribution by the C_n number, without considering whether or not the hydrocarbons are olefinic or saturated. The effect of contact time on the olefin/paraffin ratio (Fig. 7) clearly shows that olefins are primary products both in hydrogenolysis and homologation. Regarding the alkanes produced in both reactions, their percentage is low at short contact time. The accuracy of our experimental data is not sufficient to conclude that they are not primary products. Nevertheless, if they are primary products, the high olefin/paraffin ratio at low contact time suggests, as previously mentioned, that the β-H elimination leading to olefins is favored with respect to the reductive elimination leading to paraffin.

Two simple mechanisms for C–C bond cleavage and formation (deduced from Scheme 2) explain the simultaneous occurrence of hydrogenolysis and homologation of butenes:

(i) mechanism A, where the chain decrease (or growth) is achieved via the deinsertion (or insertion) of a metallocarbene fragment from (or into) a surface metal-alkyl species;

(ii) mechanism B, where the chain decrease (or growth) requires the formation of dimetallacyclic intermediates.

In the following parts of this discussion, these two mechanisms are considered to describe the formation of C_1–C_3 and C_5 hydrocarbons from each butene isomer.

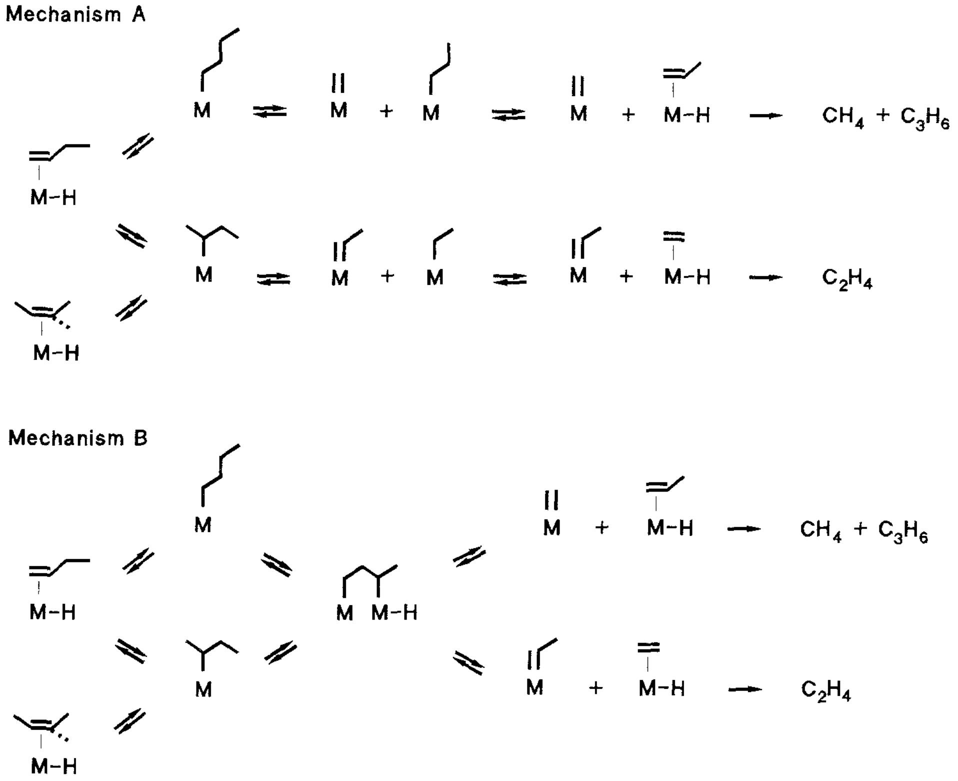
4.2.1. Possible mechanisms for the cleavage of C–C bonds during hydrogenolysis of butenes (Schemes 3 and 4). In mechanism A, C–C bond cleavage is achieved via deinsertion of a metallocarbene (or a μ-methylene) from a surface metal-butyl species, itself formed by insertion of π-coordinated butene into a M–H bond. The new metal-propyl group, formed after deinsertion of a carbene undergoes a β-H abstraction to give propene, is hydrogenated into propane, or undergoes a new deinsertion to give C_2 hydrocarbons. The metallocarbene (or μ-methylene) surface fragments can be hydrogenated into methane or can react with the C_4 alkyl species to give the higher hydrocarbon homologues.

In mechanism B, the first step also is the formation of a surface metal-butyl species resulting from the insertion of π-coordinated butene into a M–H bond. This species then undergoes a γ-H elimination which leads to a dimetallacyclic intermediate. The dimetallacyclic intermediate will then rearrange, via a metathesis-like mechanism, leading to a metallocarbene and a coordinated C_3 olefin.

Mechanisms A or B can satisfactorily explain the formation of C_1 and C_3 hydrocarbons from each of the butene isomers. It must be noted, however, that in the case of mechanism A, the formation of C_1 and C_3 hydrocarbons from the 2-butenes requires prior isomerization into 1-butene. This isomerization is not necessary in mechanism B.

The direct formation of C_2 hydrocarbons from linear butenes can be explained by mechanism B using one of the possible ways of decomposition of the dimetallacycles that leads to the formation of an ethylidene species and coordinated ethylene. In mechanism A, it must be assumed that it is possible to deinsert a metal-ethylidene species from a metal-alkyl species, which has no equivalent in organometallic chemistry. Nevertheless, it cannot be excluded that a fraction, if not all, of the C_2 fragments results from the hydrogenolysis of the initially formed C_3 fragments. This is probably true for isobutene where neither mechanism A nor mechanism B can account for a direct reaction $C_4 \rightarrow C_2 + C_2$.

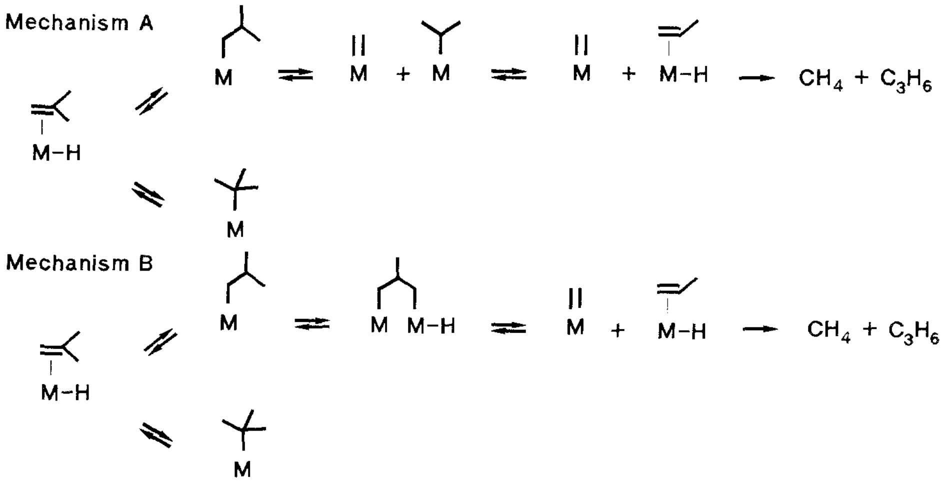
4.2.2. Possible mechanisms for the formation of C–C bonds during the homologation of butenes (Schemes 5 and 6). In mechanism A, the chain length is increased via insertion of a surface metallocarbene (or μ-methylene) species into a metal-butyl bond. The homologous metal-pentyl species thus formed can undergo a β-H abstraction, which leads to a terminal C_5 olefin, or it can be hydrogenated to pentane. If the C_5 terminal olefin initially formed is reinserted into a M–H bond, a secondary metal-pentyl species is obtained which will give internal C_5 olefins. The formation of branched C_5



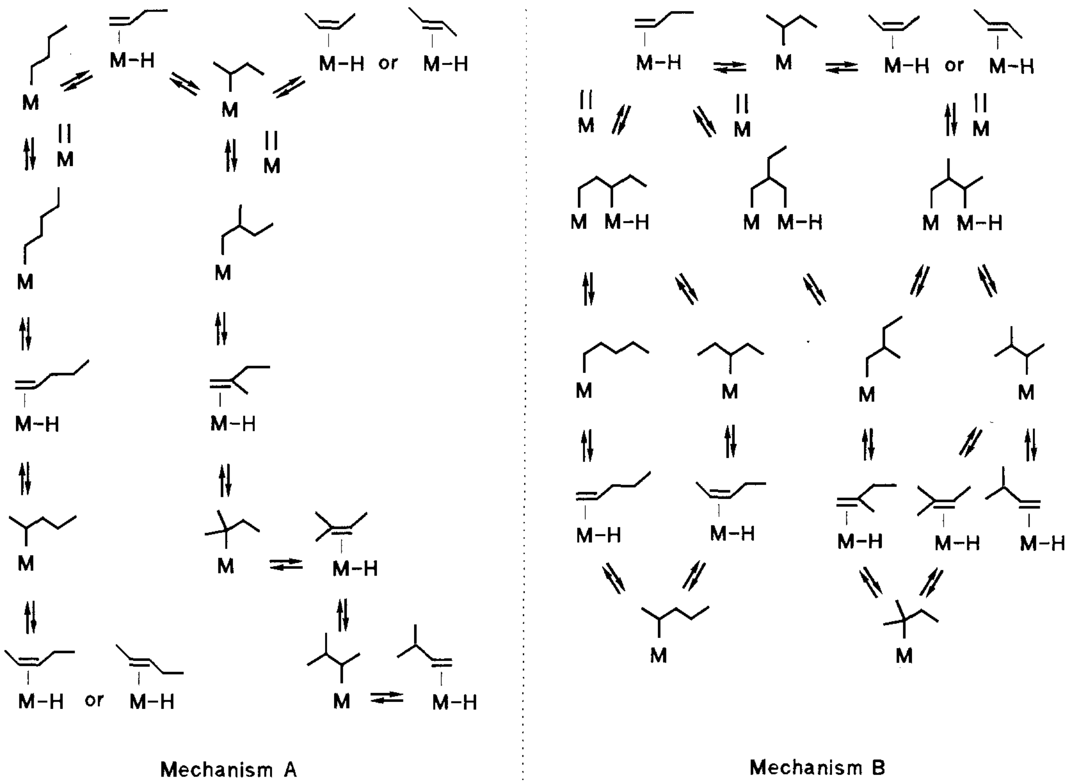
SCHEME. 3. Possible mechanisms for hydrogenolysis of 1-butene and 2-butene (*cis* or *trans*).

olefins is due to the insertion of a metallocarbene into a secondary metal-butyl species.

In mechanism B, the chain growth involves the reaction of a surface metallocarbene (or μ-methylene) with the coordinated C_4 olefin to give a dimetallacyclopentane intermediate. This intermediate can then undergo hydrogenolysis of one of its *M*–C bonds to give either a primary metal-pentyl species which leads (via β-H abstraction) to



SCHEME. 4. Possible mechanisms for hydrogenolysis of isobutene.



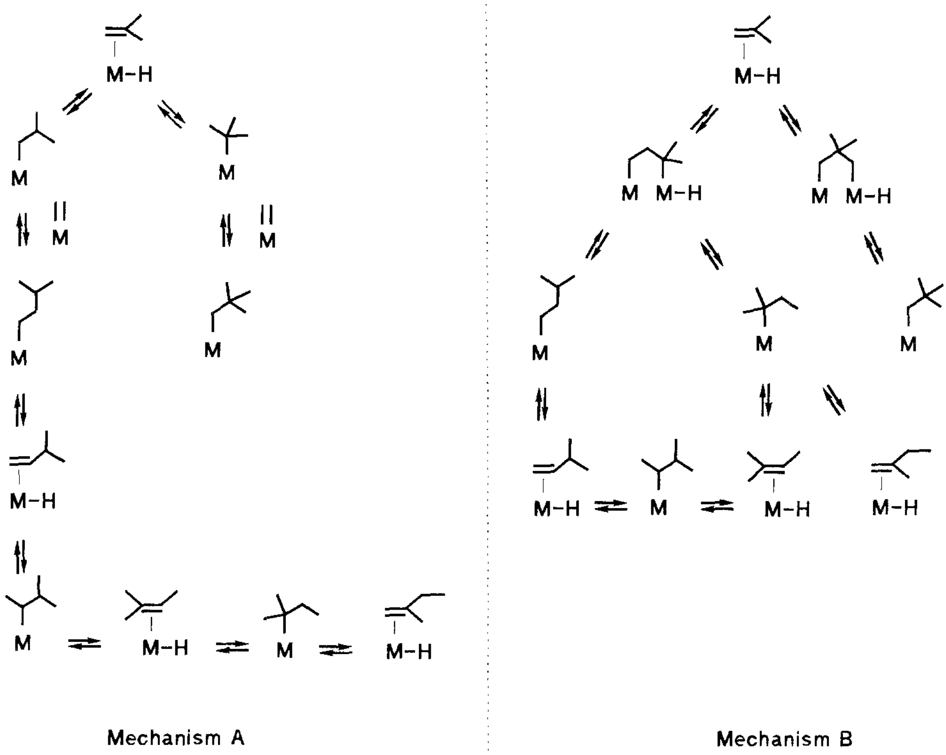
SCHEME. 5. Possible mechanisms for homologation of 1-butene and *cis*- or *trans*-2-butene.

a terminal C_5 olefin, or a secondary metal-pentyl species leading to internal C_5 olefins. Branched C_5 olefins are formed via the reaction of metallocarbene on the most highly substituted carbon of the C_4 coordinated olefin.

A mechanistic scheme for the formation of C–C bonds, similar to the one proposed here, has been envisaged for the homologation of paraffins on metal films (*23, 47*). This mechanism involves metallacyclobutane intermediates. The formation of dimetallacyclopentane intermediates appears to be more plausible, because of the steric restrictions imposed by the surface. Moreover, dimetallacyclopentanes of iron (*36*), osmium (*37*), cobalt (*38*), and ruthenium (*39*) are known or have been previously proposed as intermediates; these species can be obtained by reaction of μ-methylene species with ethylene and they partially decompose to give propene.

A comparison of the distribution of pentene isomers formed during the homologation of linear butenes shows that 1-butene, *cis*-2-butene, and *trans*-2-butene give almost identical results with, notably, a high selectivity (ca. 90%) for linear pentenes (Fig. 10). Huang and Ekerdt (*48*) obtained similar results on Ru/SiO_2 catalysts.

If the hypotehsis of mechanism A is considered (Scheme 5), the results suggest that for any linear butene isomer initially introduced, the respective concentrations in primary and secondary butyl species are the same on the catalyst's surface. (Note that the 2-butene ↔ 1-butene isomerization is a very fast reaction and that at lower contact times, ca. 10% of *cis*-2-butene or *trans*-2-butene is already converted into 1-bu-



SCHEME. 6. Possible mechanisms for homologation of isobutene.

tene.) The high selectivity for linear pentenes can be explained by a high concentration of primary metal-alkyl species and(or) by an insertion of a carbene into a primary alkyl species easier than that into a secondary alkyl species. Among the linear pentenes, 1-pentene is a primary product which rapidly isomerizes into *cis*- and *trans*-2-pentenes (thermodymanically more stable). The experimental results agree with this hypothesis, even though it cannot be determined whether or not 2-pentenes are formed at zero conversion. For C_5 branched olefins, the primary product formed after insertion of metallocarbene into the secondary C_4 alkyl species is 2-methyl-1-butene, which rapidly isomerizes into the more thermodynamically stable 2-methyl-2-butene.

If we consider mechanism B (Scheme 5), the high selectivity for linear pentenes suggests a high concentration in π-adsorbed 1-butene species and (or) a reaction of metallocarbene that is faster on the unsubstituted olefinic carbon of 1-butene than on the substituted carbons of 2-butene. When the dimetallacyclopentane intermediate formed by reaction of metallocarbene with 1-butene decomposes, either 1-pentene or 2-pentene forms. The formation of 1-pentene is kinetically favored due to the release of the steric constraints by hydrogenolysis of the most hindered *M*–C bond of the dimetallacycle. Branched pentenes are the result of the reaction of metallocarbene on the most highly substituted olefinic carbon of 1-butene, or the result of metallocarbene reacting on 2-butene. The decomposition of the dimetallacyclopentane thus formed can give the three branched pentenes. The formation of 2-methyl-1-butene is slightly favored, at low conversion, due to release of steric constraints. The formation of 3-methyl-1-butene has not been experimentally observed, probably due to its low thermodynamic stability.

For isobutene, since it is not isomerized, the formation of pentene homologues is also easily explained (Scheme 6). Only branched pentenes are formed with a high selectivity for 3-methyl-1-butene (even though this isomer is not thermodynamically favored).

In mechanism A, the insertion of isobutene into a *M*–H bond can give a primary metal-butyl or a tertiary metal-butyl species. Insertion of the metallocarbene (coming from the hydrogenolysis of isobutene) into a primary metal-butyl species allows the formation of a C_5 metal-alkyl intermediate which gives, via β-H abstraction, 3-methyl-1-butene. This isomer can then isomerize into 2-methyl-2-butene and 2-methyl-1-butene (at 250°C, the thermodynamic equilibrium of 3-methyl-1-butene/2-methyl-2-butene/2-methyl-1-butene is 2/70/28 (*31*)). When a metallocarbene inserts into a tertiary metal-alkyl species, a branched C_5 metal alkyl without hydrogen in β-position is formed; consequently, this step cannot give an olefin.

In the hypothesis of mechanism B, the reaction of a metallocarbene on the least substituted olefinic carbon of isobutene gives a dimetallacyclopentane intermediate. Hydrogenolysis of the most hindered *M*–C bond of this metallacycle preferentially gives 3-methyl-1-butene. Although less probable, hydrogenolysis of the least hindered *M–C* bond of the metallacycle should lead to 2-methyl-2-butene and 2-methyl-1-butene, even at low conversion. Unfortunately, it is not possible to ascertain whether or not these olefins are primary products. The reaction of metallocarbene on the most substituted carbon of isobutene would give a dimetallacyclopentane, which does not possess a β-hydrogen, and no olefinic product can be obtained.

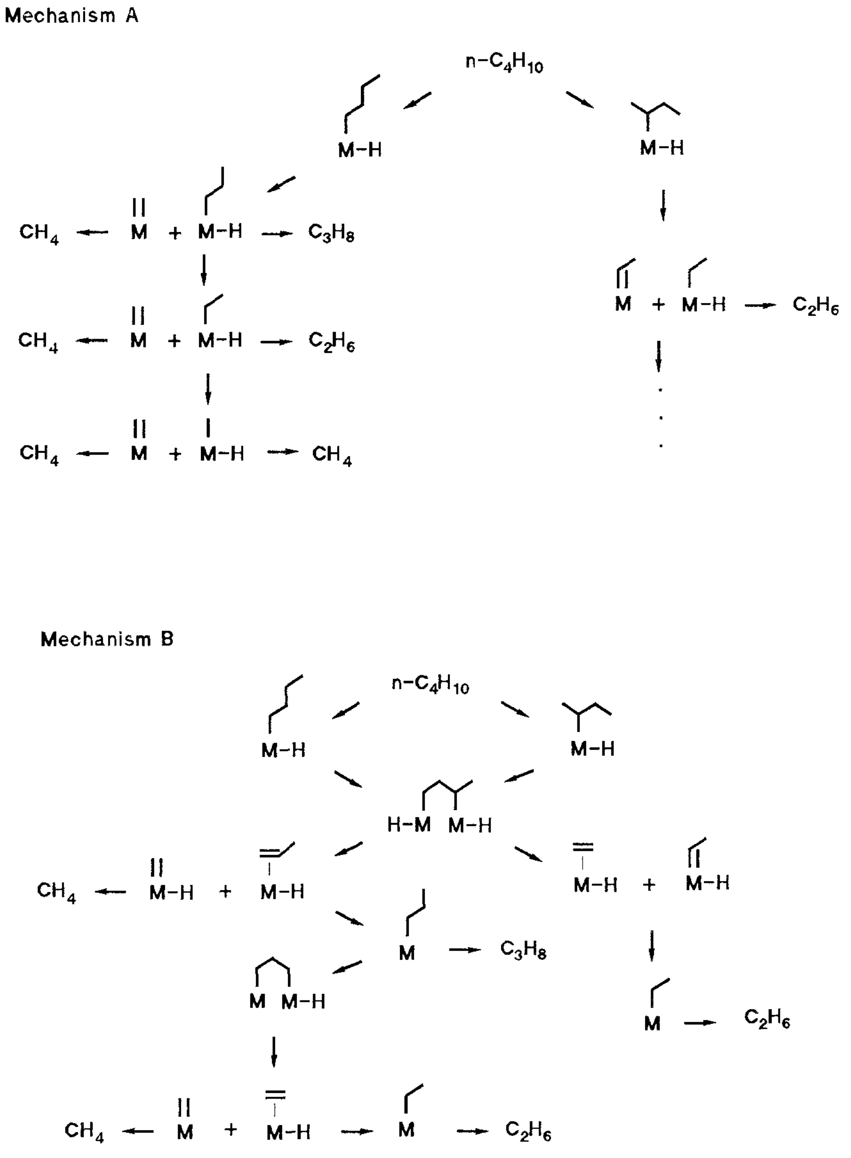
4.3. Hydrogenolysis Reactions of n-Butane and Isobutane (Schemes 7 and 8)

In the presence of hydrogen and over Ru/SiO_2 catalysts, isobutane and *n*-butane undergo hydrogenolysis reactions with conversions respectively 10 to 50 times greater than isobutene and the linear butenes. On the other hand, the formation of significant amounts of higher hydrocarbons is not observed in the experimental conditions used. The distribution of hydrogenolysis products (which are only saturated hydrocarbons except for traces of propene) is independent of the contact time but varies in function of the reaction temperature. Low temperatures favor the formation of ethane and propane at the expense of methane. Also, it is observed that for the same reaction temperature, the selectivity for methane is higher and the selectivity for ethane is lower for isobutane hydrogenolysis than for *n*-butane hydrogenolysis.

As in the case of butenes, two mechanisms for hydrogenolysis can be envisaged: one involving deinsertion of metallocarbene fragments, and a second involving the formation and decomposition of dimetallacyclopentane intermediates. These possible mechanisms of C–C bond cleavage in the hydrogenolysis of *n*-butane and isobutane are illustrated in Schemes 7 and 8 and require some comments.

First, it appears that mechanism B involves π-adsorbed olefin intermediates, for both *n*-butane hydrogenolysis and isobutane hydrogenolysis. This is also the case of mechanism A for isobutane hydrogenolysis. As previously mentioned, traces of propene are actually found during the hydrogenolysis of *n*-butane as well as during isobutane hydrogenolysis.

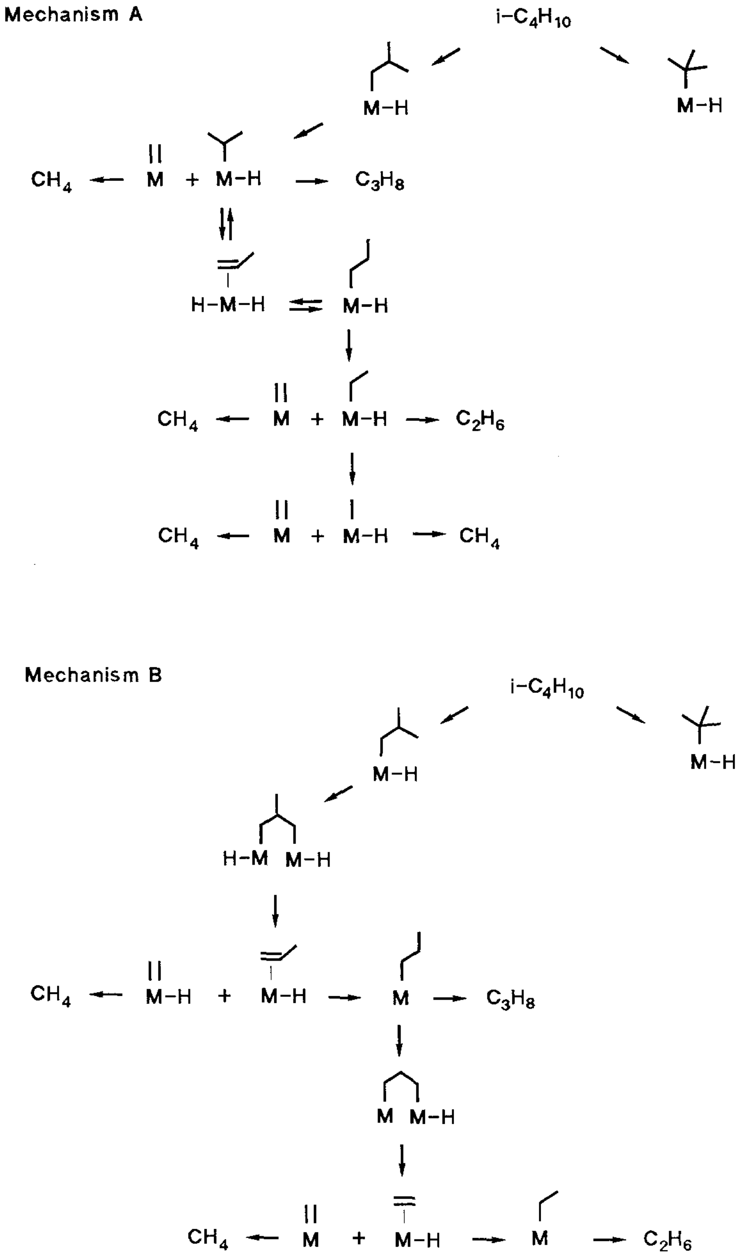
Second, according to mechanism B, the ethane produced during the hydrogenolysis of *n*-butane can be the result of two different reaction paths, either $C_4 \rightarrow C_2 + C_2$, or $C_3 \rightarrow C_2 + C_1$. In isobutane hydrogenolysis, ethane can be produced only by hydrogenolysis of the C_3 fragment. This explains why formation of ethane from *n*-butane is higher than that from isobutane, at a given temperature. This difference between *n*-butane and isobutane can be explained by mechanism A only if one admits, for *n*-butane, the possi-



SCHEME. 7. Possible mechanisms for hydrogenolysis of *n*-butane.

bility of a deinsertion of a metal-ethylidene species from a secondary metal-alkyl intermediate (an unlikely hypothesis). It is also possible that the reaction $C_3 \rightarrow C_2 + C_1$ is more difficult in the case of isobutane than in the case of *n*-butane since in the first case the formation of a π-adsorbed propene intermediate seems to be required.

A significant difference between the two mechanisms A and B lies in the step of hydrogenolysis of the C_2 fragments into two C_1 fragments. It is reasonable to think that this step actually occurs, at least at temperatures of 250°C and above, given the high proportion of methane produced (if this step did not exist, the amount of methane should stay less than or equal to the sum: propane + 2 × ethane). While mechanism A



SCHEME. 8. Possible mechanisms for hydrogenolysis of isobutane.

easily accounts for the formation of methane from a metal-ethyl species, mechanism B, which requires a step of γ-H abstraction to form a dimetallacyclopentane, obviously cannot be applied to this reaction. It is therefore necessary to postulate a different intermediate such as a dimetallacyclobutane, as previously proposed for the hydrogenolysis of ethane (*49*), the reverse reaction being the well-known coupling of two methylenes

(*50*), which is an easy process on metal surfaces (*21*).

Finally, a significant experimental result that requires interpretation is the absence of homologation of butanes in our experimental conditions. This result may mean that during the reaction of alkanes with hydrogen, the rate of the hydrogenation of the formed metallocarbene fragments is greatly higher than their rate of reaction with the starting hydrocarbon. Another interpretation, which does not exclude the first one, is that homologation of hydrocarbons actually occurs via reaction of metallocarbene with a *π-coordinated olefin* (a major species in the case of butenes) and not by insertion of a metallocarbene into the *M*–C bond of a metal-alkyl intermediate (a major species in the case of butanes).

5. CONCLUSION

The purpose of this work was to investigate the possible mechanism(s) by which C–C bonds are cleaved or are formed on a metallic surface using the known concepts of molecular chemistry. In this respect, homologation and hydrogenolysis of alkenes are useful test reactions since they occur simultaneously with similar rates and with specific regioselectivity in the C–C bond formation and C–C bond cleavage. Information on such regioselectivities is of considerable importance when trying to elucidate a mechanism. So far, ethylene (*51*), propene (*15*), and pentene (preliminary results) (*46*) have been investigated as starting materials. For the first time, we have investigated in detail the regioselectivity both in hydrogenolysis and homologation as a function of the structure of the starting butene (1-butene, *cis-* and *trans*-2-butene, and isobutene).

The results obtained not only confirm the simultaneous occurence of hydrogenation, isomerization, hydrogenolysis, and homologation, but they also indicate that the last two reactions occur with comparable rates, which suggests that they are mechanistically related.

The ensemble of results concerning hydrocarbon distribution confirm previous labeling experiments (*46*) indicating that a C$_1$ fragment (probably a metallocarbene or μ-methylene) resulting from the C$_4$ olefin reacts with this olefin to give a C$_5$ olefin.

At high temperature, the selectivities for C$_3$ and C$_5$ hydrocarbons decreases to the benefit of methane which can become the major product: at high temperature, the C$_1$ fragment appears to be hydrogenated into methane more easily than inserted into the C$_4$ olefin or the C$_4$ fragment.

The C$_1$–C$_5$ distribution particularly depends on the structure of the starting olefin (position and crowding of the double bond). This result suggests that a key step of the mechanism is situated at the double bond whose presence appears necessary for the formation of C–C bonds.

This hypothesis is corroborated by the following experimental facts:

(i) in our experimental conditions, homologation of butanes does not occur, while hydrogenolysis of butanes is clearly more rapid than hydrogenolysis of butenes;

(ii) the distribution of the different C$_5$ isomers depends upon the nature of the starting olefin. For example, isobutene gives exclusively branched pentenes. This indicates that the formation of higher hydrocarbons implies the addition of a C$_1$ fragment on the unchanged skeleton of the starting olefin and not a random association of C$_1$ fragments.

Two simple mechanisms can explain the simultaneous and reversible nature of the two reactions of C–C bond cleavage and formation:

(i) the insertion–deinsertion of a metallocarbene into (or from) a metal-alkyl species;

(ii) the formation–rearrangement of a dimetallacyclopentane intermediate.

The intermediates involved in those mechanisms seem to be common to a wide variety of reactions of hydrocarbons that occur on metallic surfaces.

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