JOURNAL OF CATALYSIS 132, 472–489 (1991)

Mechanisms of C–C Bond Formation and Cleavage on Metal Surfaces: Formation of Butenes and Hexenes from Linear and Branched Pentenes over Ru/SiO_2 Catalysts

ELOY RODRIGUEZ, MICHEL LECONTE, AND JEAN-MARIE BASSET

Institut de Recherches sur la Catalyse, Laboratoire Propre du CNRS, Conventionné à l'Université Claude-Bernard, Lyon I, 2, Avenue Albert Einstein, 69626 Villeurbanne Cedex, France

Received March 25, 1991; revised June 28, 1991

Over Ru/SiO_2 catalysts, at temperatures above 100°–150°C and in the presence of hydrogen, linear and branched pentenes (1-pentene, *cis*- and *trans*-2-pentene, 2-methyl-2-butene, 3-methyl-1-butene, and 2-methyl-1-butene) undergo isomerization, hydrogenation, hydrogenolysis, and homologation. The main primary products of these last two reactions of C–C bond cleavage and formation are methane, butenes, and hexenes. At low temperature (100–150°C), the formation of methane is reduced and the major products are C_4 and C_6 olefinic hydrocarbons, which are obtained in roughly comparable amounts. The distribution of the butenes isomers and of the hexenes isomers strongly depends on the structure of the starting pentene (linear or branched, terminal or internal). The results confirm that hydrogenolysis and homologation of a C_5 olefinic hydrocarbon occur at comparable rates and involve: (i) cleavage of mainly a terminal C–C bond of the pentene isomer leading to C_4 and C_1 fragments, (ii) reaction of this C_1 fragment with the starting C_5 to give C_6 hydrocarbons, and (or) (iii) hydrogenation of the C_1 fragment to methane. Two mechanisms, based on concepts of organometallic chemistry, can account for the results (especially for the distribution of the C_4 and C_6 olefinic isomers): (i) a methylene insertion–deinsertion mechanism or (ii) a mechanism that involves formation and decomposition of dimetallacyclic intermediates. Several experimental results seem to be in favor of the last proposed mechanism.

1. INTRODUCTION

A number of reactions, which occur on metal surfaces, involve elementary steps of carbon–carbon bond formation or cleavage. Such reactions are, for example, synthesis of hydrocarbons from CO + H_2, homologation and hydrogenolysis of hydrocarbons, or skeletal isomerization of alkanes.

In the last few years, several studies have suggested that mechanistic relationships could exist between these reactions. Correlations have been established between chain growth in Fischer–Tropsch synthesis and homologation (*1–7*) or hydrogenolysis (*8*) of hydrocarbons, or between hydrogenolysis and isomerization of alkanes (*9–11*).

More recently, in a preliminary study (*12*), it was suggested that hydrogenolysis and homologation of olefins were mechanistically related. This hypothesis was supported by experiments that showed that hydrogenolysis and homologation of pentenes to butenes and hexenes were taking place simultaneously and at the same rate over a Ru/SiO_2 catalyst. This was confirmed by labeling experiments: on a Ru/SiO_2 catalyst, a C_n olefin could undergo a cleavage of mainly a terminal C–C double bond to give (i) a C_{n-1} fragment and (ii) a C_1 fragment that could lead to the formation of methane (at high temperature) or react with the starting C_n olefin to give C_{n+1} hydrocarbons. A detailed analysis of the butene isomers produced from the hydrogenolysis of linear and branched pentenes showed that the distribution of the butenes was strongly dependent on the structure of the starting pentene. Two mechanisms, already proposed for chain growth in Fischer–Tropsch synthesis or ho-

0021-9517/91 $3.00

mologation of light olefins (such as ethylene and propene), were considered to account for the distribution of hydrogenolysis products: (i) a carbene insertion–deinsertion mechanism to (from) a metal-alkyl fragment (*8, 13, 14*) and (ii) a carbene–olefin pathway via dimetallacyclopentane intermediates (*1, 2, 4*).

It is the purpose of this present paper to complete our previous preliminary study (*12*) by reporting, more comprehensively, the main features of the hydrogenolysis–homologation reaction of linear and branched pentenes on a Ru/SiO$_2$ catalyst (i.e., for various pentene isomers, the influence of parameters such as contact time and reaction temperature on (i) the conversion to C_1–C_4, C_6 hydrocarbons and (ii) the distribution of these hydrocarbons). Particularly, one of the main objectives of the work reported here was to achieve a careful analysis of the isomer distribution of the hexenes from each pentene isomer and to explain the distribution of these hexenes in the light of the mechanisms previously proposed.

2. EXPERIMENTAL

2.1. Materials

1-Pentene, 2-pentene (*cis* + *trans*), 3-methyl-1-butene, 2-methyl-2-butene, and 2-methyl-1-butene (Fluka) were used as received. The lower and higher hydrocarbon contents in these pentenes were negligible.

2.2. 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 cluster was then decomposed overnight under flowing H$_2$ at 300°C. The final metal content was 1.0%, and the average particle size determined by conventional transmission electron microscopy was ca. 15 Å.

2.3. Catalytic Reactions

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$_2$ 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. The reagents were a mixture of pentene/H$_2$/argon. Pentene was introduced in a saturator, the temperature of which was stabilized at 0°C, and the flow rate of the olefin was regulated by the flow of argon. Typically, the flow rates of argon and hydrogen were such that the final mixture corresponded to pentene/H$_2$ = 1/1 (molar ratio).

The experiments were carried out according to the following procedure: the catalyst Ru/SiO$_2$ (ca. 200 mg) introduced in the reactor was heated at the reaction temperature under a flow of pure hydrogen; then the mixture pentene/H$_2$/argon was allowed to flow over the catalyst for 10 min before the products of the reaction were analyzed by gas-phase chromatography.

Separation and analysis of the products were carried out with a fid gas-phase chromatograph Intersmat IGC 120 FB. Hydrocarbons from C$_1$ to C$_4$ were separated by employing a $\frac{1}{8}$ in. × 6 m squalane (7%)/alumina column. Hydrocarbons from C$_5$ to C$_7$ were separated employing a set of two columns including a $\frac{1}{8}$ in. × 4.5 m SE 30/Chromosorb column and a $\frac{1}{8}$ in. × 2 m DC 550/Chromosorb column.

3. RESULTS

3.1. General Features of the Reaction Pentene + H$_2$

When a mixture of pentene/H$_2$/argon is allowed to flow over a Ru/SiO$_2$ catalyst, isomerization (*cis–trans* isomerization and double-bond migration), hydrogenation, hydrogenolysis, and homologation of the pentene are observed. These reactions occur regardless of the starting isomer (1-pentene, 2-pentene (*cis* + *trans*), 3-methyl-1-butene, 2-methyl-2-butene, and 2-methyl-1-butene). In the experimental conditions used, skeletal isomerization is not observed.

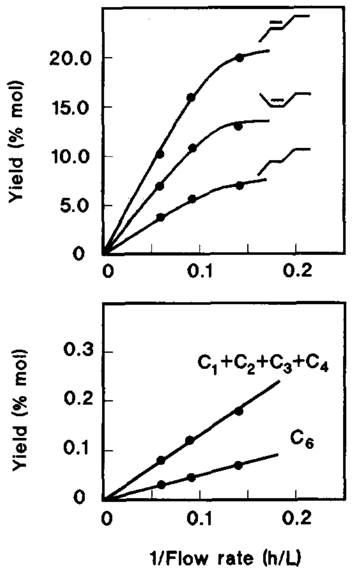


FIG. 1. Influence of contact time on the conversion of 1-pentene to products (2-pentenes, *n*-pentane, C_1–C_4, and C_6 hydrocarbons) in the reaction of 1-pentene and H_2 over Ru/SiO_2. m_{cata} = 200 mg; T = 250°C; 1-pentene/H_2 = 1/1 (mol).

Isomerization and hydrogenation are the preponderant reactions but significant amounts of lower hydrocarbons (from C_1 to C_4) and higher hydrocarbons (C_6 + traces of C_7) are produced (Fig. 1, example of 1-pentene). For hydrogenolysis and homologation, conversions are proportional to contact time. Comparison between 1-pentene, 2-pentene, and 2-methyl-2-butene shows that the formation of C_6 hydrocarbons is disfavored by the presence of substituents on the double bond (Fig. 2). Branched pentenes require higher temperature relative to linear pentenes for achieving the same conversion levels in hydrogenolysis and homologation reactions (Fig. 3). Increasing the reaction temperature causes a significant increase in the conversion to C_1–C_4 hydrocarbons (particularly in the case of branched pentenes).

3.2. Distribution of C_1–C_4 and C_6 Hydrocarbons

In the range of flow rates used, the distribution of C_1–C_4 and C_6 hydrocarbons does not vary significantly with contact time (Fig. 4; example of 1-pentene) but is strongly dependent on the nature of the starting pentene isomer (Fig. 5). Generally speaking, at 250°C, the major products of the hydrogenolysis of pentenes (linear or branched) are methane and C_4 hydrocarbons and smaller amounts (10–20%) of C_2 + C_3 hydrocarbons (with $C_2 \leq C_3$) are produced. Depending on the pentene isomer, the proportion of methane in the products varies from 30 to 65% and increases in the order: 1-pentene < 3-methyl-1-butene < 2-pentene < 2-methyl-1-butene < 2-methyl-2-butene. Conversely, the proportion of C_6 hydrocarbons decreases from 25 to ca. 5% in the order: 1-pentene > 2-pentene > 3-methyl-1-butene > 2-methyl-1-butene > 2-methyl-2-butene (in the case of 1-pentene, traces of C_7 hydrocarbons are formed in measurable amounts). It clearly appears that the greater the substitution of the double bond of the pentene, the higher the fraction of methane produced and the lower the fraction of C_6 hydrocarbons. In the experimental conditions used, olefins are the major products among the C_2–C_4 and C_6 hydrocarbons.

Reaction temperature has a strong effect on the distribution of the C_1–C_4 and C_6 hydrocarbons (Fig. 6). An important decrease of the selectivity for methane is observed when decreasing temperature; simultaneously there is an increase of C_4 and C_6 fractions. In other words, the lower the temperature, the higher the selectivity for an apparent disproportionation of the C_5 olefin to the C_4 and C_6 olefins. This phenomenon occurs regardless of the linear or branched nature of the pentene isomer, but is particularly significant in the case of 1-pentene: at 110°C, the major products of hydrogenolysis–homologation of this isomer are C_4 and C_6 hydrocarbons, with only ca. 5% CH_4 being formed. Unfortunately, for the other pentene isomers, it was not possible to obtain accurate data at temperatures as low as ca. 100°C, due to the low amounts of products formed.

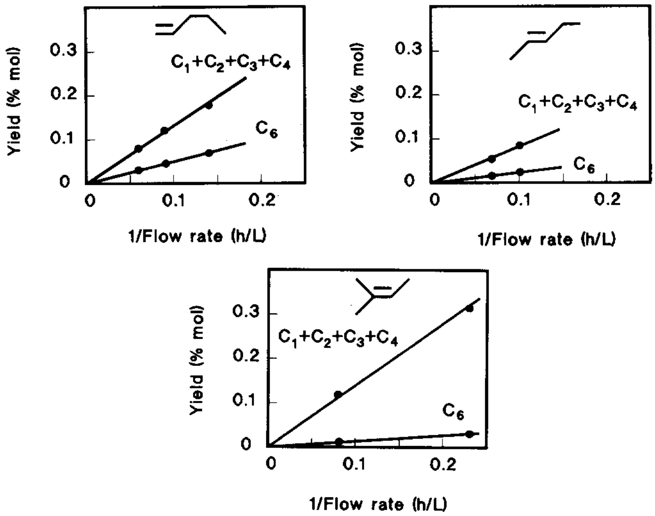


FIG. 2. Influence of contact time on the yield in C_1–C_4 and C_6 hydrocarbons produced in the reaction pentene + H_2 over Ru/SiO_2. m_{cata} = 200 mg; T = 250°C; pentene/H_2 = 1/1 (mol).

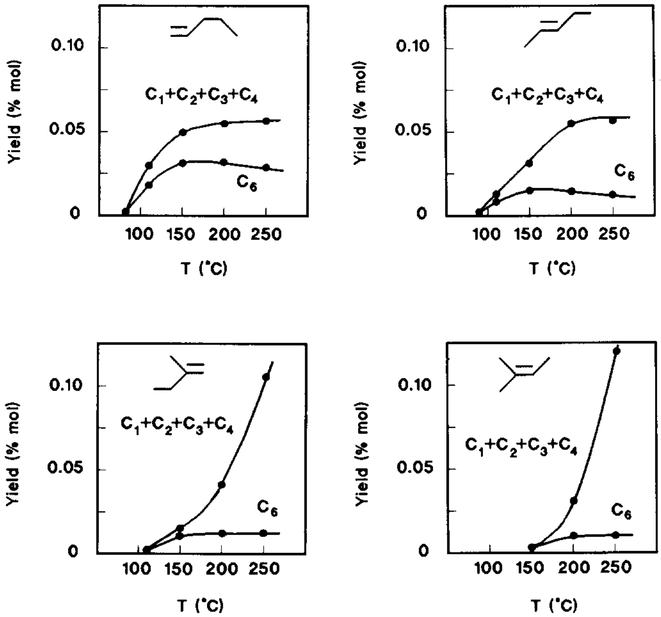


FIG. 3. Influence of reaction temperature on the yield in C_1–C_4 and C_6 hydrocarbons produced in the reaction pentene + H_2 over Ru/SiO_2. m_{cata} = 200 mg; T = 250°C; pentene/H_2 = 1/1 (mol); overall flow rate = 15 liter × h^{-1}.

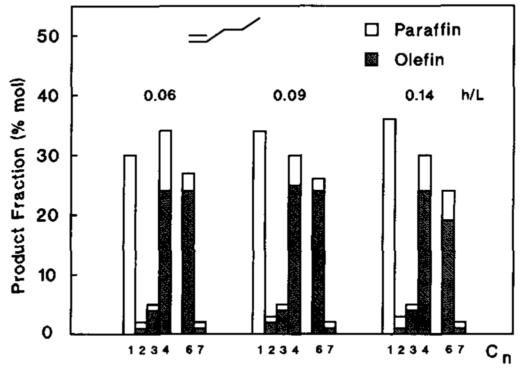


FIG. 4. Influence of contact time on the distribution of C_1–C_4 and C_6 hydrocarbons produced in the reaction 1-pentene + H_2 over Ru/SiO_2. m_{cata} = 200 mg; T = 250°C; 1-pentene/H_2 = 1/1 (mol).

3.3. Distribution of the Butene Isomers Produced from the Hydrogenolysis of Pentenes

The distribution of the butene isomers produced by the hydrogenolysis of the five linear or branched pentenes was determined at various contact times (Fig. 7).

At low contact time, 1-pentene and 2-pentene give roughly the same distribution of butene isomers with 1-butene as the major product, 2-butene in smaller amounts (*cis*-2-butene = *trans*-2-butene), and only traces (< 0.5%) of isobutene. However, it must be noted that the fraction of 2-butene is higher in the case of 2-pentene. For both 1-pentene and 2-pentene, the 2-butene/1-butene ratio and the *trans*/*cis* 2-butene ratio increase with increasing contact time. Secondary reactions of double-bond migration and *cis–trans* isomerization favor, at high contact time, the formation of the thermodynamic products (Table 1) (*15*). Therefore, it is likely that a significant fraction of the 2-butenes produced comes from these secondary reactions and that 1-butene is the main primary C_4 product of the hydrogenolysis of 1-pentene and 2-pentene. Branched C_5 olefins give different results from linear olefins.

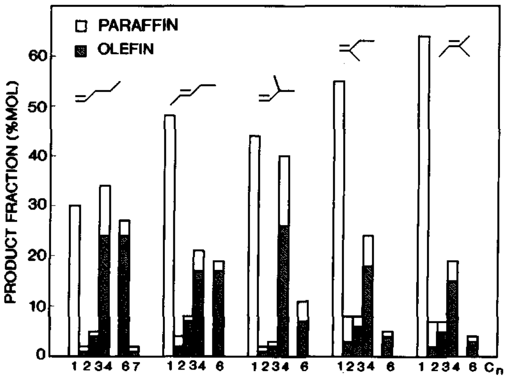


FIG. 5. Influence of the nature of the pentene isomer on the distribution of C_1–C_4 and C_6 hydrocarbons produced in the reaction pentene + H_2 over Ru/SiO_2. m_{cata} = 200 mg; T = 250°C; pentene/H_2 = 1/1 (mol).

TABLE 1

Equilibrium Concentrations of the Butenes at 250°C (According to Ref. (*15*))

Isomer	1-Butene	*c*-2-Butene	*t*-2-Butene	Isobutene
Mole fraction	0.07	0.17	0.26	0.50

Both 2-methyl-2-butene and 3-methyl-1-butene lead to the formation of isobutene as the major product (65–70%), with 20–25% of 2-butene (*cis* and *trans*) and only a very small amount of 1-butene. At low contact time, 2-butene/1-butene ratio is slightly higher in the case of 3-methyl-1-butene (4.0 vs 2.1). With increasing contact time, neither isobutene/*n*-butenes nor 2-butene/1-butene ratios vary significantly.

In contrast to the previously mentioned isomers, 2-methyl-1-butene gives, at low contact time, linear butenes as the major products (ca. 80%), with roughly comparable amounts of 1-butene and 2-butene (*cis* and *trans*). 2-Butene/1-butene ratio increases with increasing contact time due to secondary double-bond migration. The fraction of isobutene slightly increases with increasing contact time: this is a surprising result since we have never observed any reaction of skeletal isomerization in our experimental conditions. A possible explanation is that at high contact time, a nonnegligi-

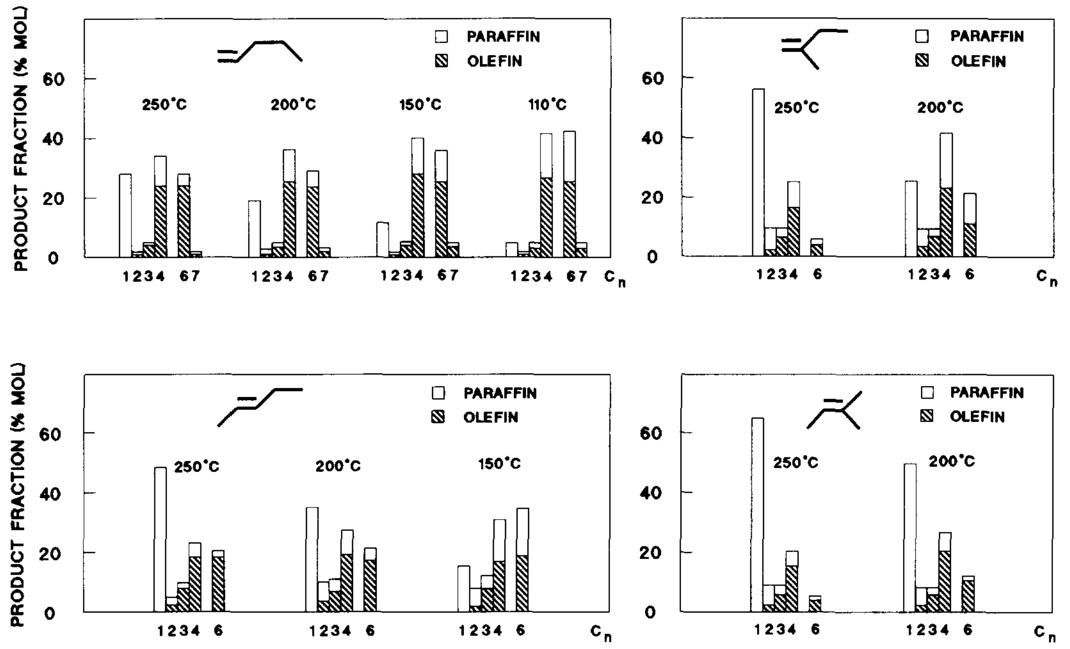


FIG. 6. Influence of reaction temperature on the distribution of C_1–C_4 and C_6 hydrocarbons produced in the reaction pentene + H_2 over Ru/SiO_2. m_{cata} = 200 mg; T = 250°C; pentene/H_2 = 1/1 (mol); overall flow rate = 15 liter × h^{-1}.

ble fraction of starting 2-methyl-1-butene is converted into 2-methyl-2-butene (the most thermodynamically stable isomer), the hydrogenolysis of which mainly leads to isobutene.

To summarize, 1-butene, 2-butene (*cis* and *trans*) and isobutene are primary C_4 products in the hydrogenolysis of 2-methyl-1-butene (although a fraction of 2-butene likely comes from isomerization of 1-butene, the 2-butene/1-butene ratio obtained at low contact time is too high to assume that 2-butene is only a secondary product).

In conclusion, the structure of the butenes strongly depends on the structure of the starting pentene isomer, which supports the hypothesis that the C_4 fragments are directly formed from the starting C_5 skeleton and not by recombination of C_1, C_2, or C_3 surface fragments. The regioselectivity of the hydrogenolysis is governed by the skeleton of the starting olefin, and, in some cases, by the position of the double bond in this skeleton.

3.4. Distribution of the Hexene Isomers Produced by the Homologation of Pentenes

Five pentene isomers have been tested: 1-pentene, 2-pentene (*cis* + *trans*), 2-methyl-2-butene, 3-methyl-1-butene, and 2-methyl-1-butene (Fig. 8). The influence of contact time on the distribution of the hexene isomers was studied in the case of the three first C_5 isomers.

At any contact time, the homologation of 1-pentene only leads to the formation of linear hexenes. At low contact time, 1-hexene is the major product (ca. 80%). The other hexenes produced are *cis*- and *trans*-2-hexenes, which are formed, in part, by a secondary isomerization reaction of 1-hexene, since the 2-hexene/1-hexene ratio increases with increasing contact time.

2-Pentene (*cis* + *trans*) gives different results from 1-pentene: at any contact time, the formation of linear hexenes is not observed. At low contact time, 90% of the

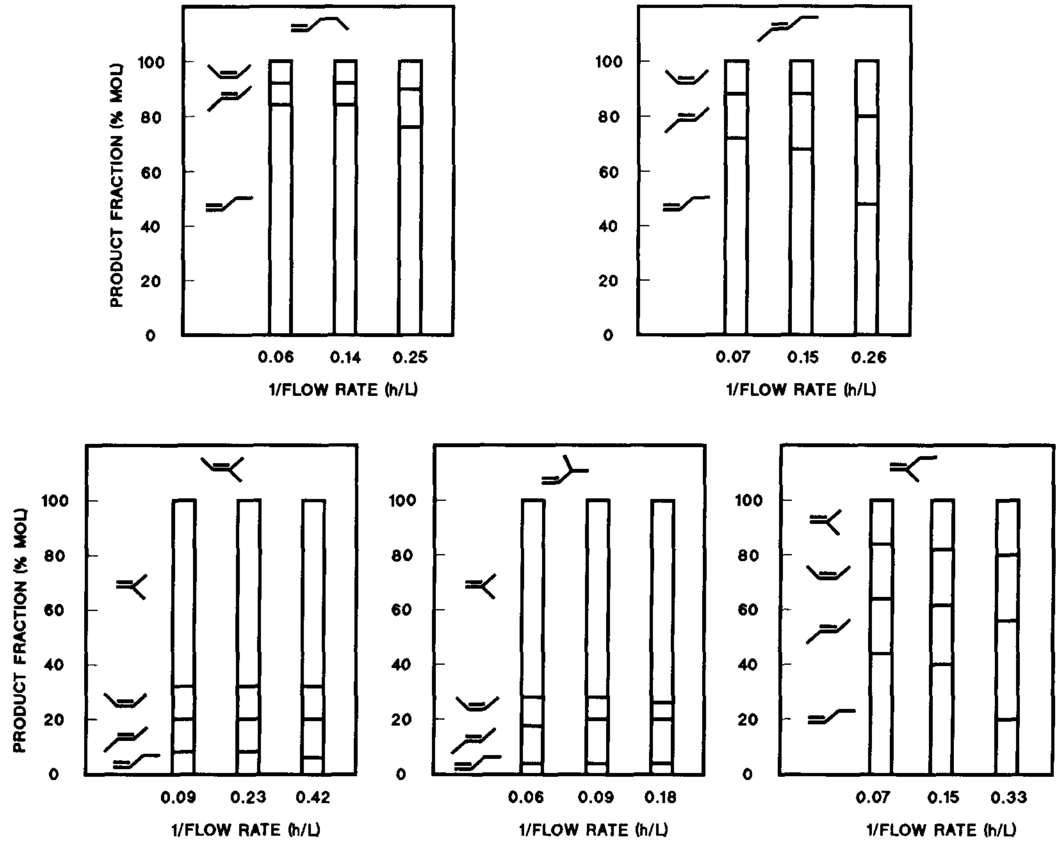


FIG. 7. Influence of contact time on the distribution of the butene isomers produced from the hydrogenolysis of various pentenes over Ru/SiO$_2$. m_{cata} = 200 mg; T = 250°C; pentene/H$_2$ = 1/1 (mol).

hexenes produced are 2-methyl-1-pentene and 2-methyl-2-pentene. Lower amounts of *cis*- and *trans*-3-methyl-2-pentene also form; with increasing contact time, the proportions of these two isomers increase to reach values close to thermodynamic equilibrium (Table 2) (*15*).

2-Methyl-2-butene gives only (in measurable amounts) two homologation products: 2,3-dimethyl-1-butene, which is the major product at low conversion, and 2,3-dimethyl-2-butene. The selectivity for the internal isomer, which is thermodynamically favored at 250°C (Table 2) (*15*), increases with increasing contact time.

At low contact time, homologation of 3-methyl-1-butene leads, with a high selectivity (ca. 85%), to the formation of 4-methyl-1-pentene. Three other isomers are produced in minor amounts: 4-methyl-2-pentene, 2-methyl-2-pentene, and 2,3-dimethyl-1-butene.

Finally, 2-methyl-1-butene gives a major amount of 3-methyl-1-pentene (ca. 65%). The other products are 2-ethyl-1-butene and 3-methyl-2-pentene (*cis* and *trans*), which form in comparable amounts.

The most meaningful results can be summarized as follows:

—Generally speaking, the hexene isomers produced at low contact time are not the thermodynamic ones (this confirms that the products observed are actually the primary products of pentene homologation).

—1-Pentene gives only linear hexenes.

—2-Pentene gives only branched hexenes.

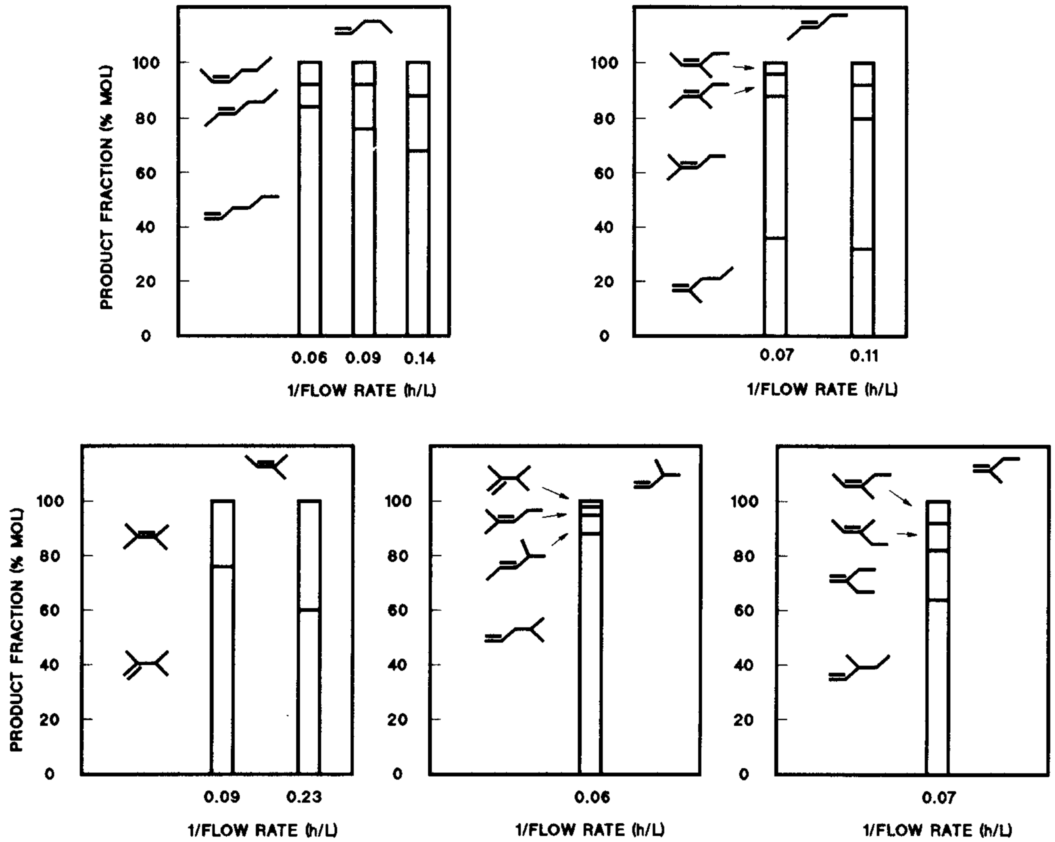


FIG. 8. Distribution of the hexene isomers produced from the homologation of various pentenes over Ru/SiO$_2$. m_{cata} = 200 mg; T = 250°C; pentene/H$_2$ = 1/1 (mol).

—Each methyl-butene leads to specific branched hexenes.

It thus appears clearly that the structure of the homologation products is strictly governed by the structure of the starting pentene isomer, including the position of the double bond. These results confirm that the homologous C_6 olefin is actually produced via addition of a C_1 fragment to the C_5 starting olefin (or to a C_5 surface fragment coming from the starting olefin).

4. DISCUSSION

Two types of mechanism of C–C bond cleavage and formation can be considered for these reactions of hydrogenolysis and homologation of linear and branched pentenes (these mechanisms are directly deduced from known reaction pathways of molecular organometallic chemistry):

(i) Mechanism **A**, in which chain decrease (or growth) is achieved via the deinsertion (or insertion) of a methylene fragment from (or into) a surface metal-alkyl species.

(ii) Mechanism **B**, where the chain decrease (or growth) involves the formation and decomposition of dimetallacyclic intermediates.

In the following parts of this discussion, these two mechanisms are considered to describe the formation, from the various pentene isomers, of C_1–C_4 and C_6 hydrocarbons.

TABLE 2

Equilibrium Concentrations of the Hexenes at 250°C (According to Ref. (*15*))

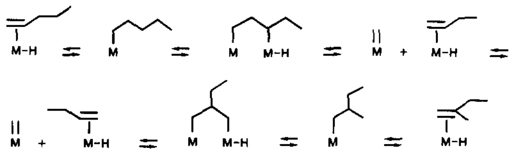
Isomer	1-Hexene	*c*-2-Hexene	*t*-2-Hexene	*c*-3-Hexene	*t*-3-Hexene
Mole fraction	0.005	0.025	0.04	0.01	0.02
Isomer	2-Me-1-pentene	3-Me-1-pentene	4-Me-1-pentene	2-Me-2-pentene	
Mole fraction	0.10	<0.005	0.01	0.23	
Isomer	*c*-3-Me-2-pentene	*t*-3-Me-2-pentene	*c*-4-Me-2-pentene	*t*-4-Me-2-pentene	
Mole fraction	0.13	0.18	0.03	0.04	
Isomer	2-Et-1-butene	2,3-di-Me-1-butene	3,3-di-Me-1-butene	2,3-di-Me-2-butene	
Mole fraction	0.035	0.055	0.005	0.085	

4.1. Possible Mechanisms for the Cleavage of C–C Bonds during the Hydrogenolysis of Pentenes

In mechanism **A**, C–C bond cleavage is achieved via deinsertion of a methylene from a C_5 surface metal-alkyl species, itself formed by insertion of π-coordinated pentene into a *M*–H bond. The new C_4 metal-alkyl group formed after deinsertion of methylene may undergo a β-H abstraction to give butenes, may be hydrogenated to butane, or may undergo a new deinsertion reaction to give C_3, then C_2, hydrocarbons. The methylene surface fragments can be hydrogenated to methane or can react with the starting C_5 metal-alkyl species to give higher hydrocarbon homologues.

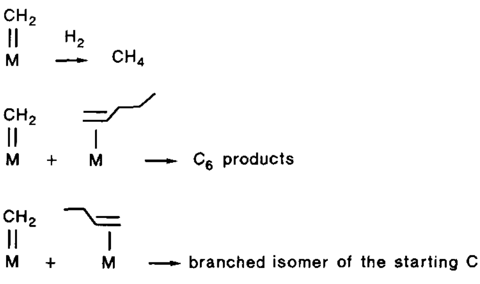
In mechanism **B**, the first step is also the formation of a surface C_5 metal-alkyl species resulting from the insertion of π-coordinated pentene into a *M*–H bond. Then, this species can undergo a γ-H elimination, which leads to a dimetallacyclic intermediate. This dimetallacycle can then rearrange, via a metathesis-like process, to give a metallocarbene fragment and a C_4-coordinated olefin.

Theoretically, mechanism **B**, which involves dimetallacyclic intermediates, should lead, in addition to hydrogenolysis and homologation products, to a skeletal isomerization of the starting olefin (*9–11*). For example, in the case of 1-pentene, the following sequence of elementary steps could occur:



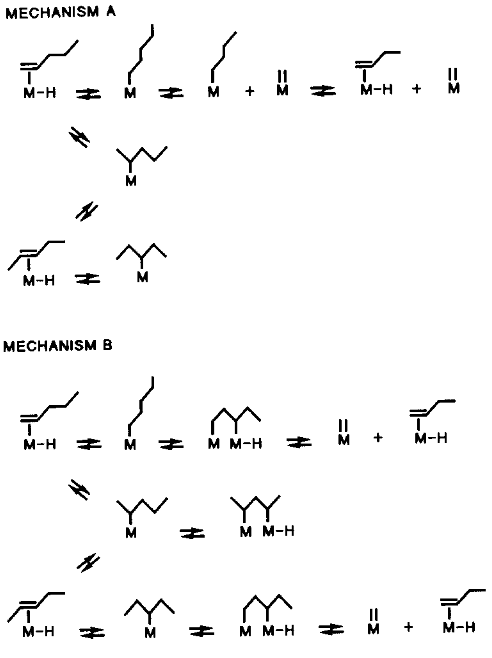
(1)

The fact that we have never observed, over Ru/SiO_2 catalyst and in the experimental conditions used, any skeletal isomerization of the starting olefin can be related to the various possible reactions of the first formed metallocarbene with the various species present on the surface. In fact, there are at least three possible reactions:



(2)

It is likely that the yields in the products obtained by the two first reactions are significantly higher than the yield in the product of the third reaction, due to the highest concentration of adsorbed hydrogen and pentene on the surface as compared to the concentration of 1-butene. If the concentration of adsorbed 1-butene is lower than the concentration of 1-pentene by a factor of



SCHEME 1. Possible mechanisms for the formation of 1-butene starting from 1-pentene or 2-pentene (*cis* + *trans*).

100 (as suggested by the yields obtained for hydrogenolysis products), then we can assume that the yields in skeletal isomers of the starting pentene will be 100 times lower than the yields in homologation products, which can explain that products of skeletal isomerization were not detected.

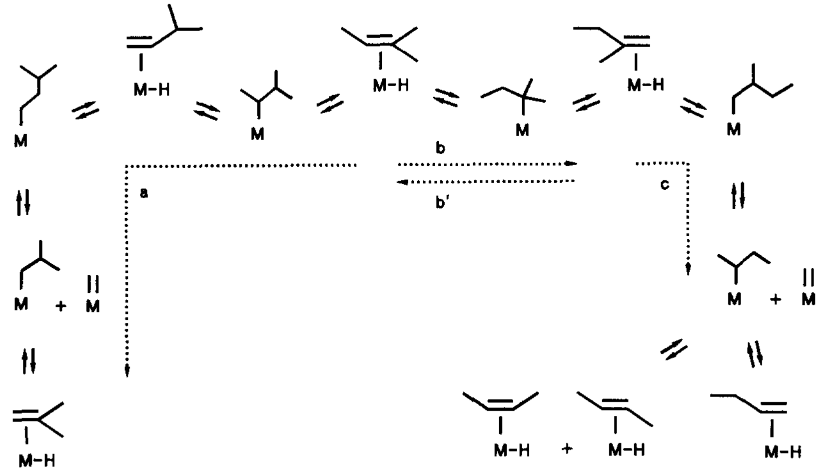
Mechanism **A**, as well as mechanism **B**, accounts for the preferential formation of 1-butene from the hydrogenolysis of 1-pentene or 2-pentene (Scheme 1). *However, in the hypothesis of mechanism* **A**, *formation of* C_1 *and* C_4 *fragments from 2-pentene requires a first step of isomerization of 2-pentene to 1-pentene.* This isomerization is not necessary in the hypothesis of mechanism **B**. On the other hand, in mechanism **B**, the direct formation of C_3 and C_2 fragments from 2-pentene or 1-pentene can be easily envisaged, due to the possible formation of a dimetallacyclic intermediate with two tertiary carbons in 1,3 positions; in mechanism **A**, such a direct reaction involves the deinsertion of ethylidene or propylidene fragments from secondary metal-alkyl species, a reaction path that has no molecular analogue in coordination chemistry.

The two different mechanisms **A** and **B** account for the formation of the butene isomers from branched pentenes.

Let us consider first the hypothesis of mechanism **A** (Scheme 2). When starting from 3-methyl-1-butene or 2-methyl-2-butene, the formation of isobutene in major amounts can be explained if we suppose that the formation of tertiary metal-alkyl species is more difficult than the formation of primary or secondary metal-alkyl species. The reaction path **a** would be favored with respect to the reaction path **b** + **c**. In a similar manner, the formation of linear butenes in major amounts starting from 2-methyl-1-butene could be explained by the reaction pathway **c**, favored with respect to the reaction pathway **b**′ + **a**. *However, it seems difficult to explain, in the light of mechanism* **A**, *that the ratios 2-butene/1-butene are significantly higher in the case of 3-methyl-1-butene or 2-methyl-2-butene than in the case of 2-methyl-1-butene (4.0 and 2.1 vs 0.8).*

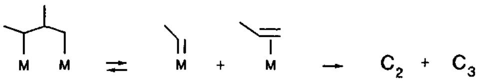
Let us consider now the hypothesis of mechanism **B** (Scheme 3). The formation of isobutene in major amounts when starting from 3-methyl-1-butene and 2-methyl-2-butene and the preferential formation of linear butenes from 2-methyl-1-butene can be explained on the same basis as in mechanism **A**. *But the variation of the ratio 2-butene/1-butene with the nature of the* C_5 *isomer is now easily accounted for by the simultaneous occurrence of two reaction paths leading to 2-butene* (**e** *and* **g**): *with 2-methyl-1-butene, the ratio 2-butene/1-butene close to unity is explained by the major and equiprobable reaction paths* **g** *and* **h** *and with 3-methyl-1-butene and 2-methyl-2-butene, the higher ratios 2-butene/1-butene are explained by the possibility of another reaction path* (**e**) *leading to 2-butene.*

Hydrogenolysis of 2-methyl-2-butene and 2-methyl-1-butene leads to the formation of



SCHEME 2. Possible mechanism for the formation of butenes starting from methyl-butenes (mechanism **A**).

C_2 and C_3 hydrocarbons in rather significant amounts ($C_2 + C_3 = 15\%$ with $C_2 \approx C_3$). This result suggest the possibility of a cleavage reaction $C_5 \rightarrow C_3 + C_2$. Mechanism **B** can account for this reaction, via one of the two decomposition modes of the dimetallacyclic intermediates involved in the reaction paths **e** and **g** (Scheme 3):



(3)

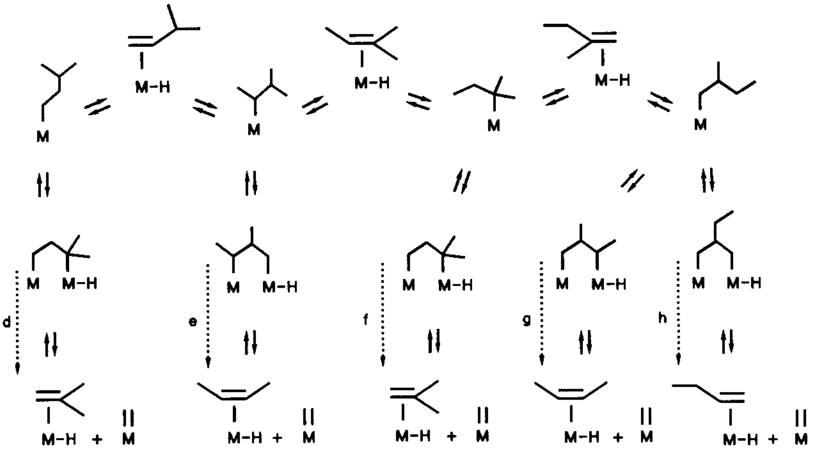
With mechanism **A**, one must assume the possibility of deinsertion reactions of ethylidene or propylidene fragments from secondary and tertiary metal-alkyl species, which we cannot easily consider.

4.2. Possible Mechanisms for the Formation of C–C Bonds during the Homologation of Pentenes

In the hypothesis of mechanism **A**, the chain growth is achieved via the insertion of a methylene fragment (coming from the hydrogenolysis of the starting pentene) into a C_5 metal-alkyl species (obtained by insertion of π-coordinated pentene into a M–H bond). The C_6 metal-alkyl species can undergo a β-H elimination to give a C_6 terminal olefin or can be reductively eliminated to hexane. The terminal hexene formed as a primary product can be reinserted into a M–H bond to give a secondary metal-alkyl species, which will lead to internal hexenes. The formation of branched hexenes (with a doubly substituted olefinic carbon) can be explained by possible insertion of a methylene fragment into a secondary C_5 metal-alkyl species.

In the hypothesis of mechanism **B**, chain growth occurs via reaction of a surface methylene fragment with the double bond of coordinated pentene to give a dimetallacyclopentane intermediate. This intermediate can then undergo the hydrogenolysis of a M–C bond to give either a primary metal-alkyl species leading (after β-H elimination) to a terminal C_6 olefin or a secondary metal-alkyl species leading to internal C_6 olefins. The formation of branched olefins can be explained by the reaction of the metallocarbene on the more substituted olefinic carbon of the starting C_5 olefin.

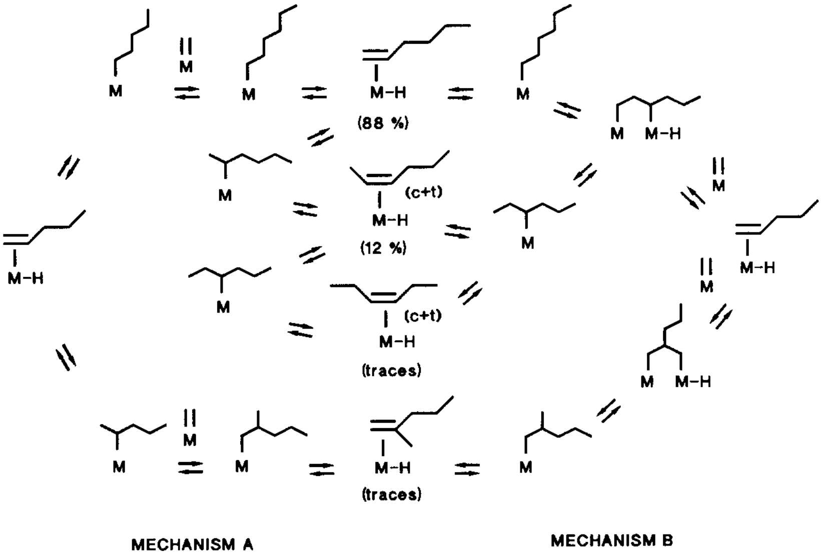
Experimentally, the homologation of 1-pentene only leads to linear hexenes, with 1-hexene as the major primary product (>85%). According to mechanism **A**



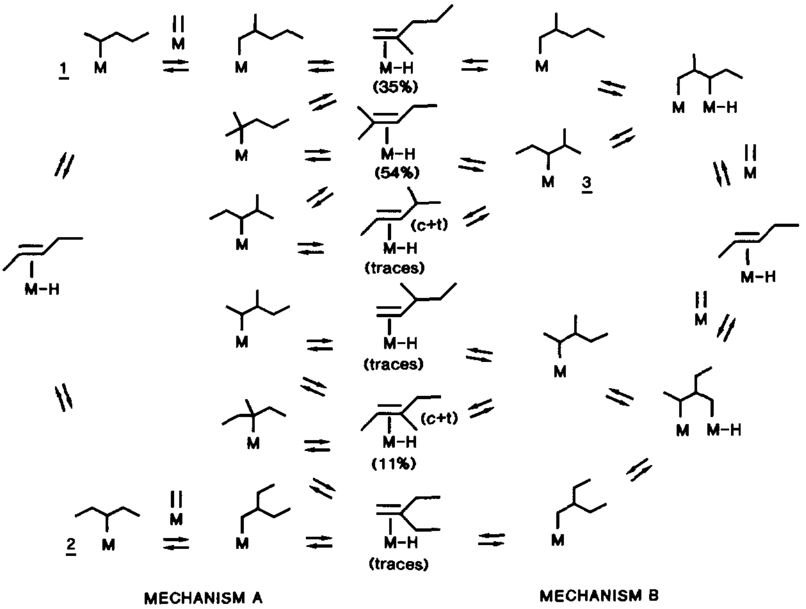
SCHEME 3. Possible mechanism for the formation of butenes starting from methyl-butenes (mechanism **B**).

(Scheme 4), these results can be explained by the highly favored formation of an *n*-alkyl species and (or) by an easier insertion reaction of a methylene fragment into a primary metal-alkyl bond, with respect to the insertion into a secondary metal-alkyl bond. Via β-H elimination, the *n*-C$_6$-alkyl species will give 1-hexene as the primary product. *Trans*- and *cis*-2-hexenes, thermodynamically favored, would be produced by secondary isomerization reaction of 1-hexene (unfortunately, due to too low conversions, it was not possible to verify whether or not 2-hexene is actually formed at very low contact time).

In the light of mechanism **B** (Scheme 4), the selective formation of linear hexenes reflects a highly favored reaction of the metal-



SCHEME 4. Possible mechanisms for the homologation of 1-pentene.

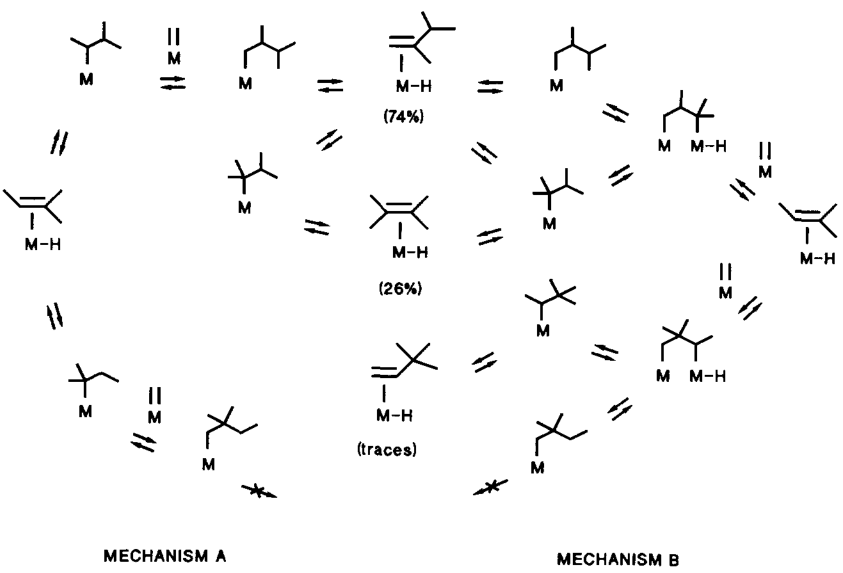


SCHEME 5. Possible mechanisms for the homologation of 2-pentene (*cis* + *trans*).

locarbene on the unsubstituted olefinic carbon of the starting 1-pentene (with respect to the reaction on the substituted olefinic carbon). Hydrogenolysis of a *M*–C bond of the dimetallacyclopentane thus formed can lead to 1-hexene, but also to 2-hexenes and 3-hexenes. The selective formation of 1-hexene (>85%) is easily explained by a preferential hydrogenolysis, due to release of steric constraints, of the more crowded metal–carbon bond of the dimetallacyclopentane. The unfavored hydrogenolysis of the less substituted *M*–C bond gives a secondary metal-alkyl species that can lead to 2-hexenes or 3-hexenes. The reason why formation of 2-hexenes is experimentally favored with respect to the formation of 3-hexenes is not clear, but may be related to the higher thermodynamic stability of 2-hexenes with respect to 3-hexenes (Table 2) (*15*).

The formation, at low contact time, of branched hexenes starting from 2-pentene (*cis* + *trans*) can be easily explained by both mechanisms **A** or **B** (Scheme 5). In fact, neither mechanism **A** nor mechanism **B** could account for the formation of linear hexenes starting from an internal pentene. The insertion of the C_1 fragment occurs either at the double bond or in a species directly obtained from that particular double bond. 2-Methyl-1-pentene and 2-methyl-2-pentene are thus the major products from the homologation of 2-pentene. Their formation can be explained by both mechanisms but more easily by mechanism **B**.

If we consider mechanism **A**, formation of these two compounds means that the metal-alkyl 1 (Scheme 5) is favored (with respect to the formation of the metal-alkyl 2) and (or) that the insertion of the methylene fragment into 1 is easier (with respect to the methylene insertion into 2). Then, according to mechanism **A**, the major product would be 2-methyl-1-pentene. The fact that 2-methyl-2-pentene is also produced in significant amount can only be explained by a secondary isomerization reaction of the terminal olefin to the more stable internal olefin. The other possible reaction pathway (via 2) should lead to 2-ethyl-1-butene as a primary product. Since this isomer is not



SCHEME 6. Possible mechanisms for the homologation of 2-methyl-2-butene.

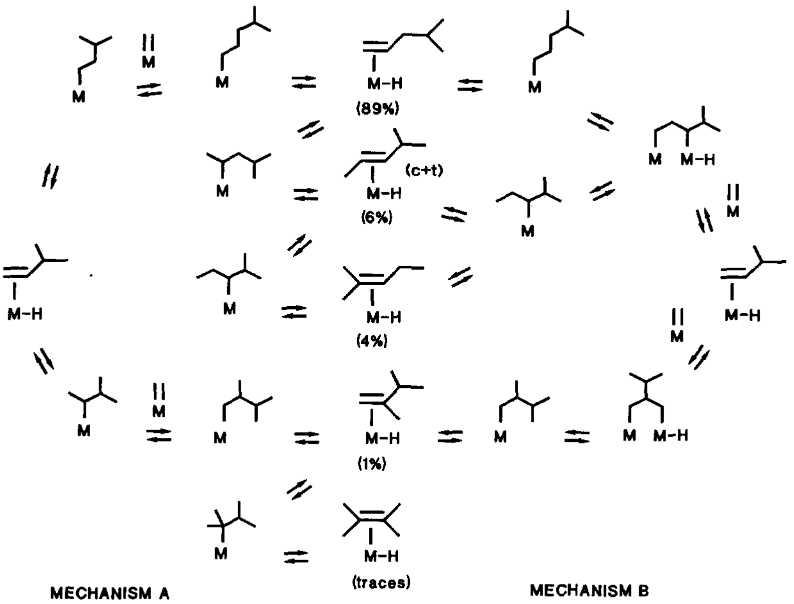
observed, a fast secondary isomerization leading to *cis*- and *trans*-3-methyl-2-pentene, which are highly favored by thermodynamics (Table 2) (*15*), must be invoked.

If we consider mechanism **B** (Scheme 5), the formation of 2-methyl-1-pentene and 2-methyl-2-pentene suggests a preferential reaction of the methylene on the less crowded olefinic carbon of π-coordinated 2-pentene. The dimetallacyclic intermediate thus formed can decompose in two ways leading either to 2-methyl-1-pentene or to 2-methyl-2-pentene effectively observed in comparable amounts. Theoretically, according to mechanism **B**, 4-methyl-2-pentene (*cis* and *trans*) could also be formed. These isomers are not observed but it is possible that β-H elimination from tertiary carbon of the species 3 (Scheme 5) is favored with respect to the elimination from secondary carbon; in addition, 4-methyl-2-pentenes are very disfavored by thermodynamics. The reaction of metallocarbene on the more crowded olefinic carbon of 2-pentene can lead to the formation of 3-methyl-2-pentene (*cis* and *trans*), which is actually produced.

Let us consider now the case of 2-methyl-2-butene, which gives only two homologation products: 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene. Both mechanisms (**A** and **B**) can account for the formation of these two products (Scheme 6).

In the hypothesis of mechanism **A**, the insertion of 2-methyl-2-butene into a *M*–H bond can lead to the formation of a secondary metal-alkyl species. The insertion of a methylene fragment leads to the homologue C_6 metal-alkyl, which gives (via β-H elimination) 2,3-dimethyl-1-butene as the primary product. 2,3-Dimethyl-2-butene, slightly favored by thermodynamics (Table 2), can only be formed via secondary isomerization of the terminal olefin. The insertion of 2-methyl-2-butene into a *M*–H bond can also lead to the formation of a tertiary metal-alkyl species. However, after insertion of the methylene fragment, an homologue metal-alkyl species with no hydrogen in β position would be obtained. Therefore, this reaction pathway could not lead to the formation of C_6 olefins.

In the hypothesis of mechanism **B**, the results suggest, as in the previous case, that



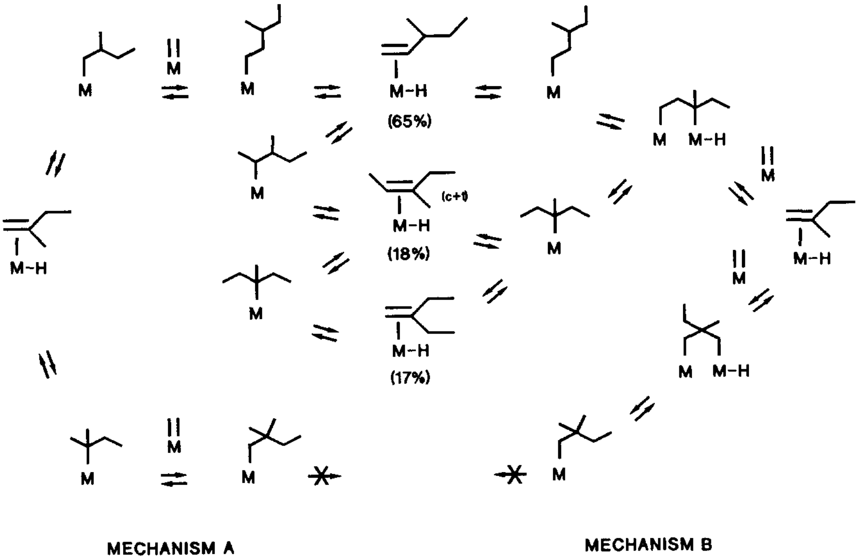
SCHEME 7. Possible mechanisms for the homologation of 3-methyl-1-butene.

the methylene fragment can only react on the less hindered side of the olefin. The dimetallacycle formed may undergo hydrogenolysis of its crowded metal–carbon bond (formation of 2,3-dimethyl-1-butene in a major amount). Hydrogenolysis of the less crowded *M*–C bond of the dimetallacyclic intermediate will give 2,3-dimethyl-2-butene.

Homologation of 3-methyl-1-butene leads to the formation of 4-methyl-1-pentene with a very high selectivity (ca. 90%). According to mechanism **A** (Scheme 7), this result suggests that the formation of a primary metal-alkyl species is very favored with respect to the formation of a secondary metal-alkyl species (and/or that the insertion of a carbene fragment into the primary metal-alkyl is favored with respect to the insertion into the secondary metal-alkyl). Via the methylene insertion reaction, a metal-C_6-alkyl species, which actually leads to 4-methyl-1-pentene as the major primary product, is obtained. The formation of minor amounts of 4-methyl-2-pentene and 2-methyl-2-pentene can only be explained by secondary isomerization reactions. The other possible reaction pathway (via methylene insertion into a secondary metal-alkyl species) appears to be very difficult and could explain why 2,3-dimethyl-1-butene is formed in very low amounts.

In the hypothesis of mechanism **B** (Scheme 7), the high selectivity in favor of 4-methyl-1-pentene is explained again by a strongly favored reaction of the methylene fragment on the unsubstituted olefinic carbon of 3-methyl-1-butene and by the preferential hydrogenolysis of the most crowded *M*–C bond of the dimetallacyclopentane intermediate. 4-Methyl-2-pentene and 2-methyl-2-pentene can also be formed in minor amounts after hydrogenolysis of the less crowded *M*–C bond of the dimetallacycle. Reaction of the methylene fragment on the substituted olefinic carbon of 3-methyl-1-butene is probably difficult, which explains the very low proportion of 2,3-dimethyl-1-butene.

Homologation of 2-methyl-1-butene leads mainly to 3-methyl-1-pentene. According to mechanism **A** (Scheme 8), the insertion of



SCHEME 8. Possible mechanisms for the homologation of 2-methyl-1-butene.

2-methyl-1-butene into a M–H bond can give either a primary metal-alkyl species or a tertiary metal-alkyl species. Insertion of a methylene fragment into the first species leads to a metal-C$_6$-alkyl that will give 3-methyl-1-pentene as the main primary product. Significant amounts of 3-methyl-2-pentene (*cis* and *trans*) and 2-ethyl-1-butene are also formed. These products, more thermodynamically stable than 3-methyl-1-pentene, can only be obtained after secondary isomerization reactions. The other possible reaction pathway cannot give olefinic homologation products (no β-H available).

Mechanism **B** also accounts for the distributions obtained (Scheme 8). The reaction of a methylene fragment on the unsubstituted olefinic carbon of 2-methyl-1-butene leads to the formation of a dimetallacyclic intermediate that will give, via hydrogenolysis of the most crowded M–C bond, 3-methyl-1-pentene as the major primary product. 3-Methyl-2-pentene and 2-ethyl-1-butene also can be formed as primary products, via hydrogenolysis of the less crowded M–C bond of the dimetallacycle. The reaction pathway that involves the reaction of a carbene fragment on the substituted olefinic carbon of 2-methyl-1-butene leads to a dimetallacyclopentane that cannot give C$_6$ olefins.

5. CONCLUSION

As previously and preliminarily reported (*12*), over Ru/SiO$_2$ catalysts, in presence of hydrogen, homologation (formation of C$_6$ hydrocarbons) and hydrogenolysis (formation of C$_1$–C$_4$ hydrocarbons) of linear and branched pentenes occur between 100 and 250°C. These two reactions occur simultaneously and, in a first approximation, at comparable rates, which suggests that they are mechanistically related in terms of formation and decomposition of common surface intermediates. Previous labeling experments (*12*) have shown that hydrogenolysis occurs by stepwise deinsertion of a C$_1$ fragment, which reinserts into the starting olefin to give homologation products. (The rates for hydrogenolysis and homologation are actually comparable at low temperature and for linear pentenes. In the other situations, i.e., at high temperature and/or for branched pentenes (when steric effects may occur) the rate of hydrogenation of the C_1 fragment to methane becomes preponderant as compared to the rate of addition of this C_1 fragment to the C_5 fragment; nevertheless the difference of rates between hydrogenolysis and homologation are less than an order of magnitude).

The experimental data reported here show that the structure of the starting pentene (linear or branched, terminal or internal) strongly governs not only the distribution of C_1–C_4 hydrocarbons, as previously observed (*12*), but also the conversion to C_6 hydrocarbons and the structure of the C_6 olefinic isomers. In particular, the three methyl-butenes, although they can be interconverted by migration of the double bond, clearly give completely different distributions of C_4 and C_6 olefins.

Two possible mechanisms of chain decrease or growth, which were already envisaged in our previous preliminary study (*12*), can account for these distributions. These two mechanisms are close to each other: they involve methylene fragments that can react either with a metal-alkyl species or with a π-coordinated olefin (it is known that these two intermediates are in equilibrium via an insertion–β-H elimination process). However, these two mechanisms can be distinguished. In one case, a unique elementary step of methylene insertion–deinsertion into (from) a metal-alkyl bond can account for C–C bonds formation or cleavage. In the other case, the dimetallacyclic intermediate, which is involved both in the formation and in the cleavage of C–C bonds, can be formed via two reaction pathways: (i) methylene + olefin reaction or (ii) γ-H elimination from a metal-alkyl species.

The two proposed mechanisms present a clear understanding of the mode of C–C bond formation and cleavage:

—They clearly show that the product distribution at zero conversion depends primarily on the position of the double bond, which is the key parameter of these reactions.

—They explain quite well why hydrogenolysis and homologation occur at the same rate, especially at low temperature, and why hydrogenolysis and methane formation become predominant at high temperature.

—They explain quite well why olefins are primary products of all these reactions since, in both mechanisms, a metal-alkyl species is an intermediate.

—They explain quite well why the number of hexenes isomers observed in the homologation of each pentene isomer is rather limited (2 to 4), whereas the total possible number of isomers can be as high as 17.

If the occurrence of one of these two mechanisms is very likely, then it is more difficult to make a definite choice between them.

The mechanism **A** seems nevertheless less likely for the following reasons. In several cases, the distribution of the homologation products of the various isomers of pentene obtained at low contact time cannot be explained unless one assumes a *fast secondary isomerization* of the terminal olefin into the internal one (e.g., 2-hexene in the homologation of 1-pentene, 2-methyl-2-pentene in the homologation of 2-pentene, 2,3-dimethyl-2-butene in the homologation of 2-methyl-2-butene, and 3-methyl-2-pentene in the homologation of 2-methyl-1-butene). Similarly, the distribution of the various isomers of the butenes in the hydrogenolysis of the various pentenes isomers are not easily explained by mechanism **A** unless secondary isomerization is invoked, which should depend on the nature of the starting pentene isomer. Moreover, one must recall that, according to mechanism **A**, *hydrogenolysis of internal pentenes (linear or branched) to butenes requires a first isomerization step of these internal pentenes to the terminal ones.* Finally, mechanism **A**, if it occurred, would also imply that insertion of a methylene into a secondary alkyl group is much less likely than that into a primary alkyl. This hypothesis cannot be estimated as valid or not valid.

Regarding mechanism **B**, it seems to be the preferred one for the following reasons. It explains most of the primary products without introducing the necessary concept of secondary reactions occurring even at low contact time. The only hypothesis required is the fact that a methylene fragment will attack selectively the olefin on its less hindered side and that the dimetallacyclopentane will selectively undergo hydrogenolysis on the bulkiest part of the cycle. This is a reasonable assumption in the field of metallacycles.

In conclusion, the results presented here can be considered as a supplementary proof that, at least for certain metals, formation of C–C bond and cleavage of C–C bond can be rationalized on the basis of simple mechanistic pathways based on molecular chemistry. These mechanisms are probably valid for chain growth in Fischer–Tropsch synthesis, olefin homologation, and hydrogenolysis, as well as for alkane homologation and hydrogenolysis.

ACKNOWLEDGMENT

Eloy Rodriguez thanks the foundation Gran Mariscal de Ayacucho (Venezuela) for financial support.

REFERENCES

1. O'Donohoe, C., Clarke, J. K. A., and Rooney, J. J., *J. Chem. Soc. Faraday Trans. 1* **76,** 345 (1980).
2. Hugues, F., Besson, B., and Basset, J. M., *J. Chem. Soc., Chem. Commun.,* 719 (1980).
3. Leconte, M., Théolier, A., Rojas, D., and Basset, J. M., *J. Am. Chem. Soc.* **106,** 1141 (1984).
4. Leconte, M., Théolier, A., and Basset, J. M., *J. Mol. Catal.* **28,** 217 (1985).
5. Jordan, D. S., and Bell, A. T., *J. Phys. Chem.* **90,** 4797 (1986); and references therein.
6. Jordan, D. S., and Bell, A. T., *J. Catal.* **107,** 338 (1987).
7. Jordan, D. S., and Bell, A. T., *J. Catal.* **108,** 63 (1987).
8. Osterloh, W. T., Cornell, M. E., and Pettit, R., *J. Am. Chem. Soc.* **104,** 3759 (1982).
9. Garin, F., and Gault, F. G., *J. Am. Chem. Soc.* **97,** 4466 (1975).
10. Garin, F., Gault, F. G., and Maire, G., *Nouv. J. Chim.* **5,** 553 (1981).
11. Garin, F., Maire, G., and Gault, F. G., *Nouv. J. Chim.* **5,** 563 (1981).
12. Rodriguez, E., Leconte, M., Basset, J. M., Tanaka, K., and Tanaka, K. I., *J. Am. Chem. Soc.* **110,** 275 (1988).
13. Biloen, P., Helle, J. N., and Sachtler, W. M. H., *J. Catal.* **58,** 95 (1979).
14. Brady, R. C., III, and Pettit, R., *J. Am. Chem. Soc.* **102,** 6181 (1980).
15. Kilpatrick, J. E., Prosen, E. J., Pitzer, K. S., and Rossini, F. D., *J. Res. Nat. Bur. Standards* **36,** 559 (1946).