JOURNAL OF CATALYSIS **152**, 306–312 (1995)

Hydrogenolysis and Homologation of 3,3-Dimethyl-1-butene on Ru/SiO₂ Catalyst: Implications for the Mechanism of Carbon–Carbon Bond Formation and Cleavage on Metal Surfaces

Jamil Toyir, Michel Leconte,[1] Gerald P. Niccolai, and Jean-Marie Basset[2]

Laboratoire de Chimie Organométallique de Surface, UMR CNRS-CPE 9986, 43 Bd. du 11 Novembre 1918, 69616 Villeurbanne, France

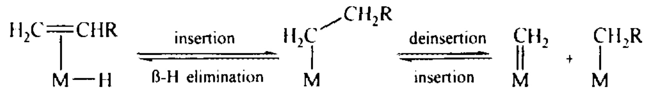
Received March 30, 1994; revised November 22, 1994

The reactions of 3,3-dimethyl-1-butene (neohexene) with hydrogen in the presence of zero-valent ruthenium metal particles supported on silica are reported. The predominant reaction is the hydrogenation of neohexene to neohexane. Simultaneous but slower homologation and hydrogenolysis reactions are reported. The homologation and hydrogenolysis reactions run at approximately equal rates, suggesting a mechanistic link between the two processes. The relative quantities of C_1–C_5 and C_7 products and the variation of these quantities with respect to varying temperature, neohexene/hydrogen ratio, and contact time are reported. The distribution of the primary products, neopentane, isobutene, and methane for hydrogenolysis and 2,2-dimethyl pentane, 2,2,3-trimethyl butane, and 4,4-dimethyl-1-pentene for homologation is discussed in terms of current thought on the mechanism of homologation and hydrogenolysis of alkanes. The most likely and strongly indicated mechanism for the hydrogenolysis of neohexene involves the deinsertion of a methylidene fragment from a ruthenium–neohexyl intermediate which is also an intermediate in the hydrogenation of neohexene. The distribution of C_7 homologation products does not allow one to distinguish between a simple insertion mechanism and a mechanism passing through a metallacyclic intermediate. © 1995 Academic Press, Inc.

INTRODUCTION

The hydrogenolysis of saturated hydrocarbons over heterogeneous transition metal catalysts converts alkanes in the presence of H_2 to lower chain hydrocarbons including methane (1–5). Interestingly, when olefins are hydrogenolyzed on the same catalysts, one observes not only the shorter chain olefinic and saturated hydrocarbons, including methane, but also longer chain hydrocarbons (6, 7). The latter reaction is called the homologation of olefins (7, 8). It has been suggested by Osterloh *et al.* (5) that the hydrogenolysis of hydrocarbons is mechanistically related to the Fischer–Tropsch synthesis in terms of carbon–carbon bond formation and cleavage. Evidence was also given for a mechanistic similarity between paraffin and olefin homologation and the Fischer–Tropsch synthesis (8). We have presented evidence that olefin hydrogenolysis to lower olefins is mechanistically related to the homologation of the same olefin to higher hydrocarbons. Significantly, when the temperature is low enough (e.g., 100°C for Ru/SiO₂ catalyst) the rate of homologation of 1-pentene to hexenes and hexanes can be very close to the rate of hydrogenolysis to butenes and butane (9). Similar results have been obtained more recently using linear and branched butenes showing that the relationship between carbon–carbon bond formation and carbon–carbon bond cleavage is not coincidental (10–12).

Two simple mechanisms based on known elementary steps of organometallic chemistry (13–16) can explain the simultaneous and reversible nature of carbon–carbon bond formation and cleavage: These are (A) the insertion (deinsertion) of a metallo-carbene into the metal–carbon bond of a metal–alkyl species and (B) the formation–rearrangement of a metallacyclic intermediate. Although several results concerning the product distribution in the hydrogenolysis of several isomers of penetenes suggest that mechanism B is more probable than mechanism A for that particular olefin, no clear evidence was given to distinguish unambiguously between these two mechanisms (13, 17). The proposal of mechanism A requires that the metal alkyl resulting from the insertion of the olefin into the metal–hydride bond has a CH_2 group in the α-position of the alkyl chain allowing deinsertion of a metal–methylidene fragment and also a β-hydrogen to achieve a β-hydride elimination to give olefin (Scheme 1).



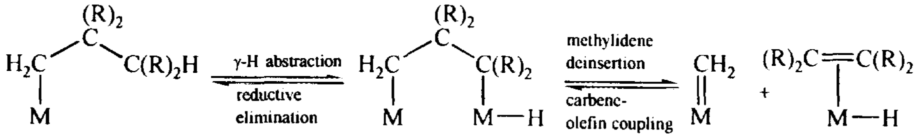
SCHEME 1. Hydrogenolysis by mechanism A.

---

[1] Deceased, August 10, 1993.

[2] To whom correspondence should be addressed.

0021-9517/95 $6.00



SCHEME 2. Hydrogenolysis by mechanism B.

The proposed mechanism B requires that there is a hydrogen atom at the γ-position of the alkyl chain resulting from the olefin insertion of the olefin into the metal–hydride bond (Scheme 2).

A simple verification of the occurrence of mechanism A would be to study the hydrogenolysis of an olefin which, after semi-hydrogenation, could not undergo γ-hydrogen activation leading to a metallacyclic intermediate. We therefore decided to study the hydrogenolysis of neohexene (3,3-dimethyl-1-butene) which can lead to neopentane only by a deinsertion of a methylidene fragment and not by metallacyclic intermediate (Scheme 3).

We present here the results concerning the hydrogenolysis and the homologation of neohexene in the presence of hydrogen over a Ru/SiO$_2$ catalyst.

METHODS

The catalytic tests were carried out in a glass dynamic microreactor 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 placed in a cylindrical oven equipped with a thermostat. The temperature of the catalyst bed was measured with a thermocouple. The reactor was placed in line with a gas source capable of producing neohexene/hydrogen/argon mixtures of known composition.

The use of neohexene, a liquid at room temperature, implies the use of a saturator in the argon channel. The neohexene was introduced to the saturator at 0°C. The flow of neohexene is regulated by regulating the flow of argon. The partial pressure of neohexene at 0°C was determined independently.

The catalytic tests were performed as follows: (a) a stable temperature was established in the reactor under a flow of pure hydrogen, (b) the reactant mixture (neohexene/hydrogen/argon) was allowed to flow through the catalyst for 5 min,[3] and (c) the product gas stream was sampled and analyzed by gas chromatography.

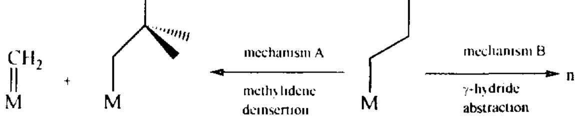
The Ru/SiO$_2$ catalyst was treated under hydrogen at 250°C for 2 h after each experiment, thus allowing the conservation of the activity and selectivity for all of the studies. Electronic microscopy analyses (STEM–EDX) conducted after the same sample was used for several months showed that there was no significant variation of the metallic phase (i.e., distribution of particle size, composition, etc.) on the silica surface (6, 7, 11).

The hydrogen (Air Liquide C, > 99.995% pure) and the argon (Air Liquide U) were passed through a deoxo-catalyst (BASF R-3-11) and 5 Å molecular seives to eliminate any trace of oxygen or water. The deoxo-catalyst and molecular sieves were regularly regenerated.

The purities of neohexene (Fluka, > 99.5% pure), hydrogen, and argon were verified by gas chromatography. The methane impurity in the hydrogen was negligible. There was 2-methyl-2-butene present as an impurity in the neohexene gas, some of which is transformed to methyl butane during the reaction. The total amount of this branched C$_5$ hydrocarbon present in the product stream is less than the amount of 2-methyl-2-butene impurity in the neohexene and is five times less abundant than neopentane formed by the reaction.

A six-way valve was used to divert the product stream into an injection loop linked to a gas chromatograph. The gas chromatograph was equipped with a flame ionization detector (Delsi DI 200). Separation of products was accomplished under isothermal conditions on a fused silica capillary column (Chrompack PLOT Al$_2$O$_3$/KCl, 50 m, ϕ = 0.32 mm). Product identities were confirmed by co-injections of pure products and other possible hydrocarbon products. Quantitative measurements were obtained by preparation of several standard hydrocarbon mixtures to give the necessary calibration curves.

The Ru/SiO$_2$ catalyst was prepared by adsorbing Ru$_3$(CO)$_{12}$ (Johnson Matthey) from hexane solution onto silica (Aerosil 200, Degussa) which had been pretreated at 500°C under vacuum (10^{-4} Torr) for 16 h. It has been established that, during this chemisorption process,



SCHEME 3

---

[3] We have determined that the catalytic activity of Ru/SiO$_2$ decreases during the first 5 min of time on stream. The activity is stable thereafter.

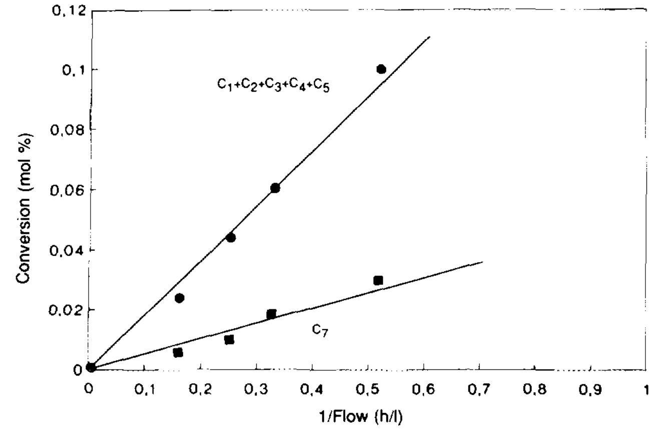


FIG. 1. Transformation vs contact time (T = 200°C, $P(H_2)/P$(neohexene) = 1/1; t = 5 min; m_{cata} = 200 mg).

$Ru_3(CO)_{12}$ reacts with surface silanol groups to give a grafted species $(\mu\text{-H})(\mu\text{-OSi}\equiv)Ru_3(CO)_{10}$ (18). The grafted cluster was then decomposed into metal particles under flowing hydrogen at 300°C. The final metal content was 1% and the average particle size determined by electron microscopy was found to be 20 Å.

Hydrogenolysis and homologation are in fact secondary reactions under the reaction conditions described. Hydrogenation is by far the dominant reaction. The high rate of this reaction prevented us from determining with precision the conversion of neohexene to neohexane (saturation of chromatographic column); one can nevertheless estimate that hydrogenation is about 40 times faster than hydrogenolysis.

RESULTS

General Features of the Reaction between Neohexene and Hydrogen

Neohexene undergoes simultaneous hydrogenation, hydrogenolysis, and homologation processes in the presence of hydrogen and a Ru/SiO_2 catalyst at temperatures above 100°C.

The hydrogenolysis of neohexene produced neopentane, methane, isobutene, and isobutane. C_2 and C_3 olefinic and saturated hydrocarbons were also produced in much smaller amounts.

The homologation of neohexene proceeded at about the same rate as hydrogenolysis. The only products that could be quantified were 2,2-dimethyl pentane and 2,2,3-trimethyl butane (in a ratio of 10 : 1). 4,4-Dimethyl-1-pentene was detected in amounts too small to be accurately quantified.

The conversion of neohexene to hydrogenolysis as well as homologation products was found to be proportional to the contact time (Fig. 1) and to increase with temperature (Fig. 2).

We were able to confirm the formation of 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene at 100°C (in a proportion five times less than homologation products). This result indicates an initial skeletal isomerization of neohexene. At low temperature skeletal rearrangement products were not among the primary products.

Factors Influencing Product Distribution

1. Temperature of reaction. The temperature of the reaction has a determining influence on the distribution of the products of hydrogenolysis (Fig. 3).

When the temperature is raised between 100 and 250°C, the selectivity for methane increases from 20 to 75%. Simultaneously, the selectivity for neopentane decreases from 45 to 15% and the selectivity for the homologation products decreases from 30 to 10%. The selectivity for C_4 hydrocarbons passes through a maximum around 200°C. One may remark that the ratio C_4/C_5 increases as one increases the temperature. Increasing temperature also favors the formation of isobutene as opposed to isobutane.

2. Contact time. The contact time has little effect on the carbon number distribution (Fig. 4), which confirms that the cleavage and formation of carbon–carbon bonds are simultaneous and rapid reactions on the surface.

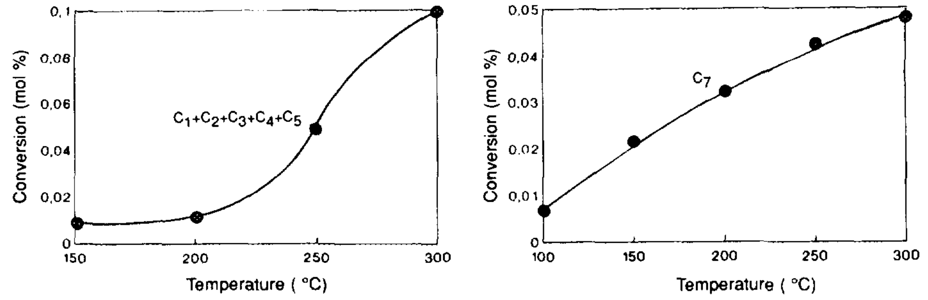


FIG. 2. Transformation vs temperature (flow rate = 1.9 liter/h, $P(H_2)/P$(neohexene) = 1/1; t = 5 min; m_{cata} = 200 mg).

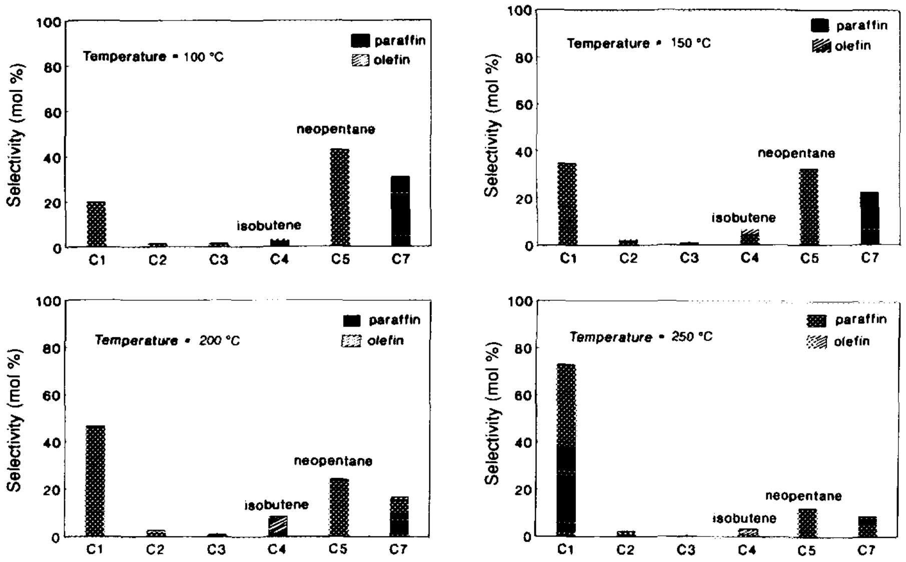


FIG. 3. Influence of temperature on the homologation and hydrogenolysis of neohexene (flow rate = 1.9 liter/h; $P(H_2)/P$(neohexene) = 1/1; t = 5 min; m_{cata} = 200 mg).

There is a slight reduction of selectivity for methane and a slight increase in the selectivity for iso-C_4 as the contact time is increased.

The ratio isobutene/isobutane tends to increase as the contact time is shortened, and at the shortest contact time studied, the olefin is the sole C_4 product detected. This suggests that isobutane is due, at least in part, to a secondary reaction, the hydrogenation of isobutene.

DISCUSSION

On Ru/SiO$_2$ catalyst in the presence of hydrogen, neohexene undergoes a main pathway reaction of hydrogenation to neohexane. This is a logical result which leads us to assume a reaction mechanism of the formation of a metal–neohexenyl intermediate followed by a reductive elimination of neohexane (Scheme 4).

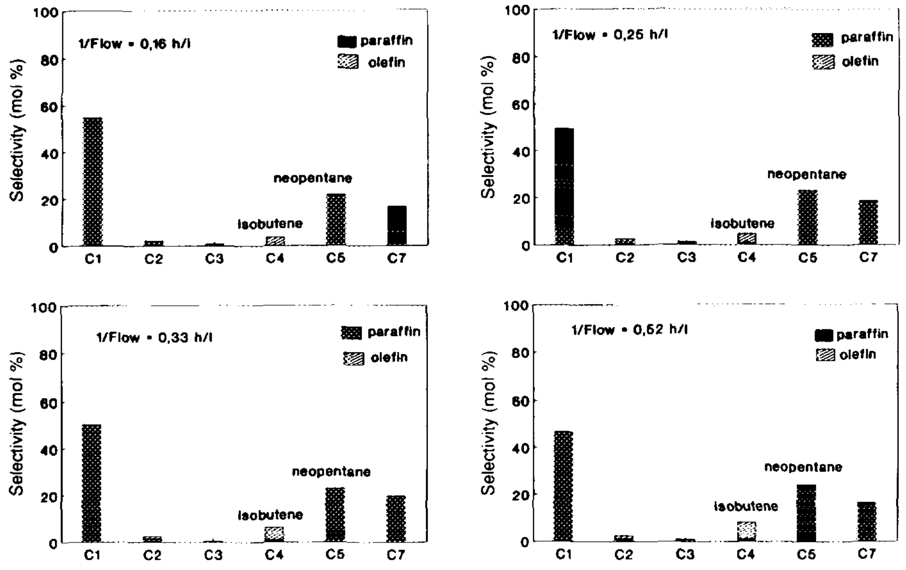
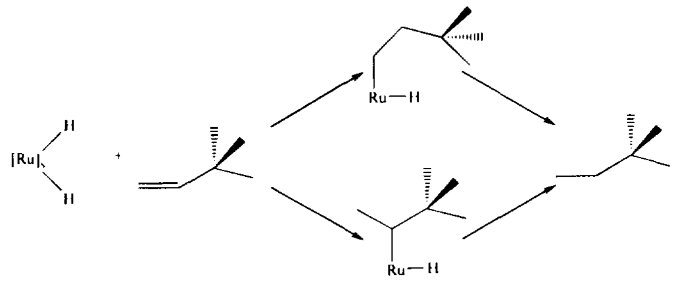


FIG. 4. Influence of contact time on the homologation and hydrogenolysis of neohexene (T = 200°C; $P(H_2)/P$(neohexene) = 1/1; t= 5 min; m_{cata} = 200 mg).



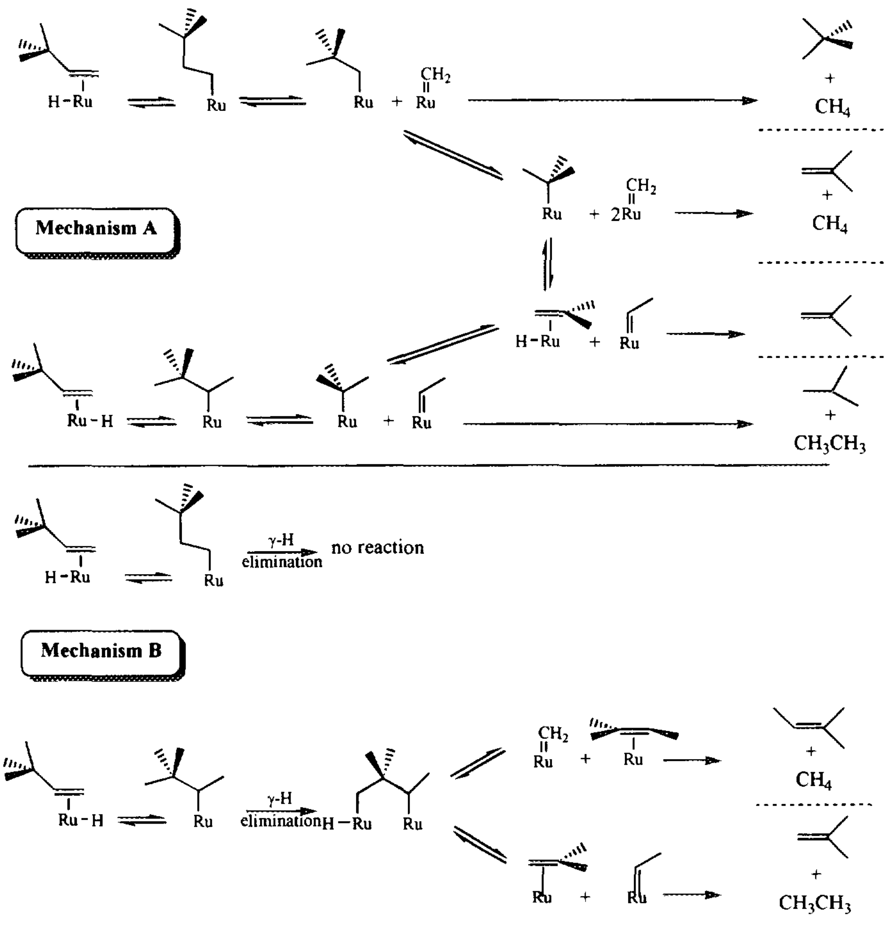
SCHEME 4. The insertion of neohexene into a ruthenium–hydride bond.

In parallel to this main pathway, two different reactions occur as already observed with various pentenes and butenes (13, 19). Hydrogenolysis to lower hydrocarbons and homologation to higher hydrocarbons occur simultaneously and at about the same rate. Let us examine the product distribution of these two reactions at low contact time and try to explain the product distribution in the light of mechanisms A and (or) B.

Hydrogenolysis Reactions of Neohexene

The main hydrocarbons formed by the hydrogenolysis of neohexene are neopentane (a "neopentyl olefin" is not possible), isobutene, isobutane, and methane. The formation of neopentane and methane can be explained only by a mechanism in which the carbon–carbon cleavage step is the deinsertion of a methylene fragment from a Ru–neopentyl moiety (Scheme 5, mechanism A). *Mechanism B is not possible because the γ-carbon in the alkyl chain bears no hydrogen atom.* No significant formation of 2-methyl-2-butene was observed, which suggests that there is no or very little hydrogenolysis of neohexene by a mechanism of type B (Scheme 5). However, it must be noted that the obtaining of 2-methyl-2-butene by mechanisms B required first a step of formation of a secondary alkyl fragment, a reaction which may be strongly disfavored with respect to the formation of a primary alkyl fragment.

The formation of isobutene does not allow for distinction between mechanisms A and B because both mechanisms produce this product (Scheme 5). Mechanism A



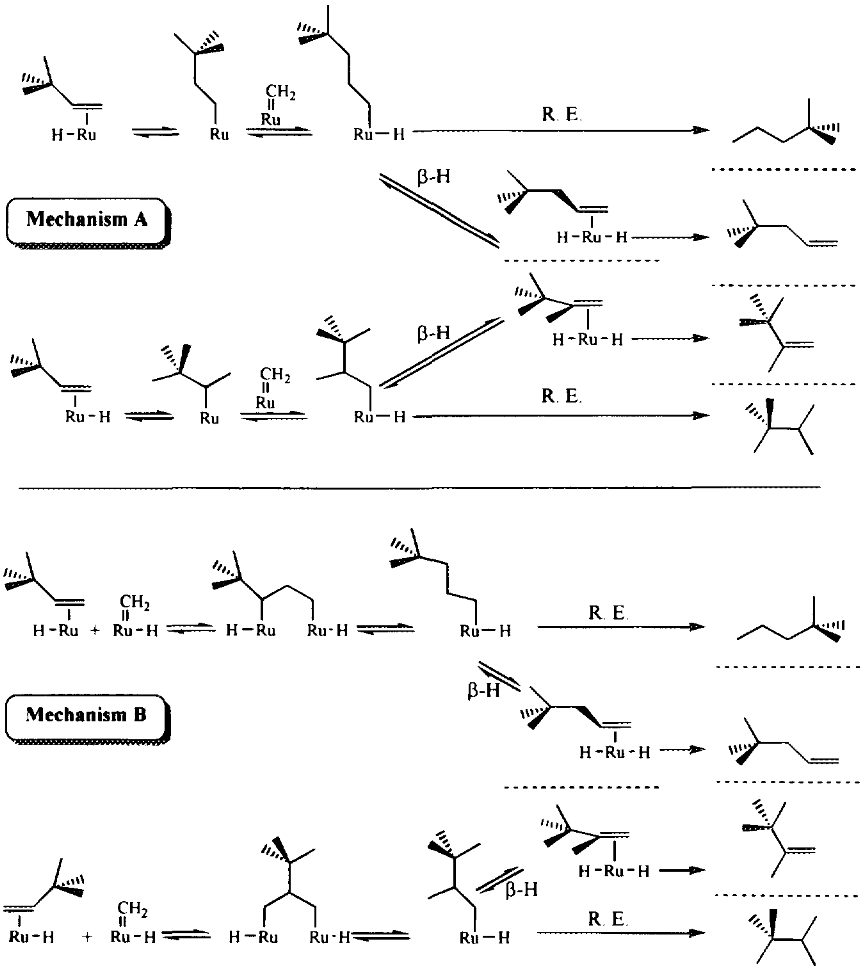
SCHEME 5. Possible mechanisms for the hydrogenolysis of neohexene.

can lead to this product by two routes. The most consistent explanation is that isobutene is formed by the deinsertion of a methylidene fragment from the ruthenium–neopentyl intermediate in parallel with the reductive elimination of the neopentyl ligand to produce neopentane. Another route to isobutene within mechanism A is the deinsertion of an ethylidene fragment from a secondary alkyl intermediate, an uncommon process in the organometallic literature. Mechanism B can lead to isobutene, again via a secondary alkyl intermediate (Scheme 5, bottom). This seems unreasonable considering (1) the lack of C$_2$ products formed (mechanism B produces ruthenium–ethylidene fragments together in equimolar quantities with ruthenium–isobutyl fragments, thus one would expect ethane and/or ethylene in comparable amounts with isobutene) and (2) the total absence of 2-methyl-2-butene as a product, which would be expected from the intermediate metallacycle. Thus, the most reasonable route to isobutene (Scheme 5) is the extension of mechanism A for formation of neopentane.

Homologation Reactions of Neohexene

The principal products of the homologation of neohexene are 2,2-dimethyl pentane and 2,2,3-trimethyl butane. The formation of these C$_7$ hydrocarbons can be explained equally well by mechanisms A and B. The preference for the formation of 2,2-dimethyl pentane is neatly explained either by the preferential formation of a primary alkyl from the insertion of neohexene into a M–H bond or the favorable insertion of a methylene into such a primary alkyl ligand (Scheme 6, mechanism A) or by steric factors favoring the formation of a metallacycle in which the carbon–carbon bond is formed between the methylidene fragment and the unsubstituted olefinic carbon of neohexene (Scheme 6, mechanism B). (Recall that the methylidene fragments are primary products in the hydrogenolysis of neohexene.)

Theoretically, both mechanisms could undergo β-hydride elimination from the C$_7$ alkyl species to produce primarily 4,4-dimethyl-1-pentene and, to a lesser extent,



SCHEME 6. Possible mechanisms for the homologation of neohexene (R. E., reductive elimination; β-H, β-H elimination).

2,3,3-trimethyl-1-butene. Experimentally, only trace quantities of 4,4-dimethyl-1-pentene could be detected. This result suggests that *under our experimental conditions* the reductive elimination of C_7 alkyl species is strongly favored over β-hydride elimination.

CONCLUSIONS

Silica-supported ruthenium catalyzes the hydrogenation, homologation, and hydrogenolysis of neohexene in the presence of hydrogen at temperatures above 100°C. The principal reaction is the hydrogenation. The principal products of hydrogenolysis, neopentane and methane, suggest that the carbon–carbon cleavage process is the deinsertion of a methylidene fragment from a primary alkyl–metal surface species.

The homologation of neohexene happens simultaneously and at about the same rate as hydrogenolysis. This suggests that the two reactions are linked mechanistically as previous studies have suggested (10). The homologation may be the result of the insertion of surface methylidene into metal–carbon bonds or coupling of surface methylidene with coordinated olefin.

An obvious mechanistic link between hydrogenolysis and homologation would be that the carbon–carbon bond cleavage of neohexene produces a C_5 fragment (hydrogenated to neopentane) and a surface metal–methylidene species which can be hydrogenated to methane or may in turn react with second coordinated neohexene in a carbon–carbon bond forming reaction to product C_7 hydrocarbons.

REFERENCES

1. Sinfelt, J. H., *Adv. Catal.* **23,** 91 (1973).
2. Garin, F., and Gault, F. G., *J. Am. Chem. Soc.* **97,** 4466 (1975).
3. Leclercq, G., Leclercq, L., and Maurel, R. *J. Catal.* **50,** 87 (1977).
4. Rooney, J. J., *J. Catal.* **58,** 334 (1979).
5. Osterloh, W. T., Cornell, M. E., and Pettit, R., *J. Am. Chem. Soc.* **104,** 3759 (1982).
6. Leconte, M., Theolier, A., and Basset, J.-M., *J. Mol. Catal.* **28,** 217 (1985).
7. Leconte, M., Theolier, A., Rojas, D., and Basset, J.-M., *J. Am. Chem. Soc.* **106,** 1141 (1984).
8. O'Donohoe, C., Clarke, J. K. A., and Rooney, J. J., *J. Chem. Soc. Faraday Trans. 1* **76,** 345 (1980).
9. Rodriguez, E., Leconte, M., Basset, J.-M., Tanaka, K., and Tanaka, K.-I., *J. Am. Chem. Soc.* **101,** 275 (1988).
10. Rodriguez, E., Leconte, M., and Basset, J.-M., *J. Catal.* **131,** 457 (1991).
11. Jordan, D. S., and Bell, A. T., *J. Catal.* **107,** 338 (1987).
12. Jordan, D. S., and Bell, A. T., *J. Catal.* **108,** 63 (1987).
13. Leconte, M., *J. Mol. Catal.* **86,** 205 (1994).
14. Jenks, C. J., Bent, B. E., Bernstein, N., and Zaera, F., *J. Am. Chem. Soc.* **115,** 308 (1993).
15. Zaera, F., *Acc. Chem. Res.* **25,** 260 (1992).
16. Zaera, F., *J. Mol. Catal.* **86,** 221 (1994).
17. Rodriguez, E., Ph.D. dissertation, Université Claude Bernard, Lyon 1, Villeurbanne, France, 1988.
18. Theolier, A., Choplin, A., D'Ornelas, L., Basset, J.-M., Zanderighi, G. M., Ugo, R., Psaro, R., and Sourisseau, C. *Polyhedron* **2,** 119 (1983).
19. Rodriguez, E., Leconte, M., and Basset, J.-M., *J. Catal.* **132,** 472 (1991).