Hydrogenolysis of Cyclohexane over Ir/SiO_2 Catalyst: A Mechanistic Study of Carbon−Carbon Bond Cleavage on Metallic Surfaces

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Abstract: The hydrogenolysis of cyclohexane catalyzed by supported Ir/SiO_2 has been studied to get mechanistic information on the elementary steps of C−C bond cleavage for cyclic saturated hydrocarbons. The reaction was studied under conditions in which no dehydrogenation to benzene occurs. When a mixture of cyclohexane and H_2 flows over a Ir/SiO_2 catalyst at 200 °C and for a H_2/cyclohexane ratio superior to 40, methane, ethane, propane, *n*-butane, *n*-pentane, and *n*-hexane are identified to be primary products. The hydrogenolysis of ethane and *n*-hexane has also been studied to clarify several mechanistic questions. To account for the primary products in the above reactions, a mechanism is proposed in which the key step of the carbon−carbon bond cleavage occurs via concerted electronic transfer in dimetallacyclopentane intermediate. The comparison of product distributions in the hydrogenolysis of cyclohexane and that observed for *n*-hexane led to conclusions about the relative ease of carbon−carbon bond cleavage with respect to surface alkyl isomerization.

Introduction

Investigation on the mechanism of carbon−carbon bond cleavage of cyclic compounds at the surface of metal catalysts is of great fundamental and practical interest.

From a fundamental stand point many important catalytic reactions imply formation or cleavage of carbon−carbon bond: the Fischer−Tropsch synthesis, the hydrogenolysis of hydrocarbons, the dehydrocyclization of hydrocarbons, and the skeletal isomerization of hydrocarbons, to name a few. Some studies, in particular those of Garin, Gault, and Maire,[1−3] Rooney and co-workers,[4] Pettit and co-workers,[5] Basset and co-workers,[6−8] Zaera et al.,[9−11] and Barteau et al.[12,13] suggested mechanistic relationships between different processes implicating carbon−carbon bond cleavage or formation. Many of these reports suggest elementary steps which are related to or even identical with those already found in molecular organometallic chemistry. These analogies are important since they may produce a coherent and unified view of the reactivity of surface organometallic fragments certainly common in heterogeneous catalysis. The understanding of these elementary steps will lead to the better, more rational design of catalysts for a given catalytic reaction.

From an applied point of view, reforming petroleum feedstock leads to the formation of a wide variety of compounds ranging from methane to heavy waxes or tars. LCO (light cycle oil), which is rich in aromatic compounds, is used to produce diesel fuels. The accepted measure of diesel fuel quality is the Cetane Number (CN), which is directly related to the type of molecules that are found in the fuel. Unfortunately, aromatic and polyaromatic compounds have the lowest CN number. Normal paraffins have the highest CN, followed by normal olefins, isoparaffins, and naphthenes. Therefore, saturation of aromatics in diesel fuel and conversion of the resulting compounds to acyclics are the key points in improving the quality of diesel fuel. Indeed, patents claim partial hydrodecyclization of the naphthenes produced after hydrogenation of polycyclic aromatics.[14,15]

Studies of the hydrogenolysis of cycloalkanes have mainly been limited to 3- to 6-member carbocycles. They apparently showed no interesting effects of the cyclic nature of these substrates. Aromatization, rearrangement with dehydrocyclization, and multiple carbon−carbon bond cleavage (that we shall designate later as deep hydrogenolysis) were observed. The selectivity between ring opening and deep hydrogenolysis has

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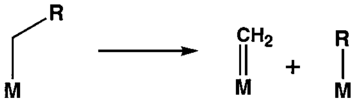
Scheme 1. C−C Bond Cleavage or Formation: Gault Mechanisms

been widely studied for cyclopentane. Hydrogenolysis is selective on Pt and Pd.[10] Turn over frequency (TOF) seemed to depend on particle size for Pt, Rh, and Ni catalysts but not for supported Pd and Ir catalysts.[16−18] Concerning hydrogenolysis of the C_6 ring it has been shown that methylcyclohexane is converted to toluene and ring opening products as well as deeper hydrogenolysis products.[19] The global product distribution depends on the nature of the catalyst. Selectivity with respect to deep hydrogenolysis appears to be dependent on metal particle size whereas the distribution of ring opening products does not seem to exhibit such dependence.

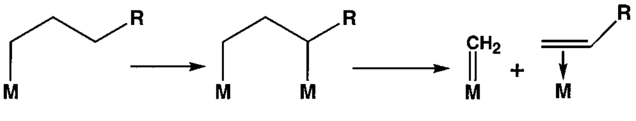
Apparently, there is no clear consensus regarding the elementary steps of carbon−carbon bond cleavage and formation in the literature. Gault and co-workers[3] have observed that distribution of products obtained by hydrogenolysis and isomerization of methylcyclopentane were the same as those obtained with *n*-hexane. He has proposed two competing mechanisms: a selective mechanism implying a $\alpha,\alpha,\beta,\beta$-tetraadsorbed species and a nonselective mechanism implying coordinated olefin and bis-carbene intermediates (Scheme 1).

For the hydrogenolysis of neohexene, Leconte and Basset have proposed two possible mechanisms. The first implies a 1,2 carbon−carbon activation that invokes the deinsertion of a methylidene fragment from a surface metal−alkyl species (Scheme 2). A second mechanism which seems to be more general implies a 1,3 carbon−carbon bond activation in which the key steps are the formation of dimetallacyle by γ-H elimination from a metal−alkyl followed by carbon−carbon bond cleavage via concerted electron transfer[20−25] (Scheme 3).

Scheme 2. C−C Bond Cleavage or Formation: Basset A Mechanism



Scheme 3. C−C Bond Cleavage or Formation: Basset B Mechanism



In the latter case, one should notice that the global mechanism implies only elementary steps already well-known in molecular organometallic chemistry: reductive elimination, α-H elimination, β-H elimination, γ-H elimination, concerted electronic transfer (as in olefin metathesis), carbene insertion into metal−alkyl bonds, and the corresponding reverse reactions.[26]

In this study we chose an iridium catalyst for the hydrogenolysis of cyclohexane because this metal was found in preliminary experiments to be the most selective one for ring opening of bicyclic compounds such as decalin with minimal deep hydrogenolysis, a key parameter for the acquisition of high cetane numbers in diesel fuels.

Experimental Section

Catalyst Preparation and Characterization. The Ir/SiO$_2$ catalysts were prepared by adsorbing Ir(acac)$_3$ (Strem Chemicals 77-1500) from a toluene solution onto silica (Aerosil 200 $m^2 \cdot g^{-1}$ Degussa) that had been pretreated at 520 °C under dry oxygen flow overnight. Solvent was filtered and solid was washed 3 times with cold solvent. The physisorbed iridium was then decomposed into small metal−oxide particles under flowing O_2 at 320 °C. Iridium oxide was then reduced at 320 °C under H_2 flow. The final metal content was 0.97%. The dispersion (*D*) of the sample, estimated from oxygen, carbon monoxide, and hydrogen adsorption, assuming the respective stoichiometries of 1 O/Ir$_s$, 1 CO/Ir$_s$, and 2 H/Ir$_s$, was found to be, on average, about 35%. A more detailed presentation of the synthesis and characterization of our Ir/SiO$_2$ catalysts is discussed elsewhere.[27]

All the catalytic tests were performed with the same batch of catalyst. Before each experiment, the catalyst was treated under H_2 at 320 °C. After such a treatment the activity and selectivity of the catalyst were reliably restored. The amount of catalyst introduced in the reactor was between 20 and 100 mg.

The catalytic tests were performed with a dynamic glass microreactor working at atmospheric pressure. The reactor is a vertical U-tube equipped with a sintered glass on which a thin layer of Ir/SiO$_2$ catalyst was deposited. Temperature was measured by using a thermocouple inserted in the catalytic bed. The reactor was heated with a thermoregulated tubular oven. Gas reactants were introduced through gas lines equipped with a mass flow meter (Brooks 5850TR). Liquid reactants were introduced by means of a HPLC pump or by flowing a gas stream through a saturator. Vaporization was completed by using a heat exchanger.

Hydrogen (Air Liquid C, >99.995% pure), helium (Air Liquid U, >99.95% pure), cyclohexane, hexane, cyclohexene, and 1-hexene (Aldrich) were used without further treatment. The purity of the hydrocarbon reactants was confirmed prior to each experiment by online chromatographic analysis. When trace hydrocarbons were detected in the unreacted starting material, they were taken into account when product analysis was carried out.

The hydrocarbons produced were routinely analyzed online by gas-phase chromatography on two parallel columns each equipped with automatic injection loops and flame ionization detectors (Delsi D1200). The analysis of C_1−C_4 products was performed on a KCl/Al$_2$O$_3$ column (50 m × 0.32 mm × 5 μm, Chrompack No. 7515) and the analysis of C_5−C_{10} products was simultaneously performed on an HP5 column (30 m × 0.32 mm × 25 μm, 5% methyl silicon gum, ref HP 19091

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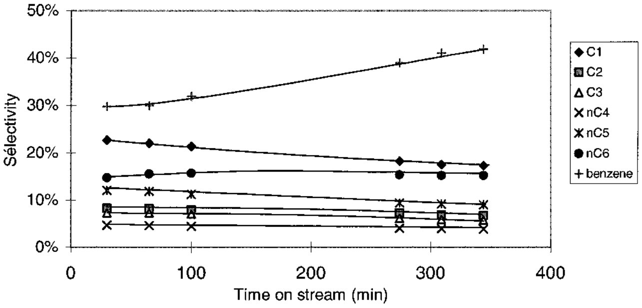

Figure 1. Variation of selectivity in hydrogenolysis of cyclohexane over Ir/SiO_2 with time on stream: $T = 257$ °C, flow $= 11.3\ mL\cdot min^{-1}$, $H_2/HC = 37$, mass of catalyst $= 50$ mg.

J-413). The system was calibrated with standard hydrocarbons. H_2/reactant ratio and hydrocarbons traces were measured prior to any experiment by by-passing the reactor.

The nature of the products was determined by using gas chromatography coupled with a mass spectrometer (HP G1800A and G1704A). Columns as described above were used depending on the products analyzed. It was necessary to obtain more concentrated samples for GC−mass spectral analysis: The reaction gas stream was passed through a trap at 77 K. The trap was then warmed and a gas sample taken via a syringe. Assuming there is no accumulation of products on the catalyst in steady-state conditions, analysis of the outgoing mixture leads to classical conversions and selectivities.

Conversion is expressed as the molar amount of carbon in the products versus the total molar amount of carbon in the outgoing mixture. Space velocity (pph) is expressed as the amount of reactant introduced in the reactor per hour and per gram of catalyst. Contact time, a less conventional term that the authors are more comfortable with, is thus adequately described as the reciprocal of space velocity. Turn-over frequency (TOF) is calculated from the corresponding conversion, molar flow of the hydrocarbon, and quantity of surface iridium. Molar selectivity is expressed as the carbon content of a given product versus the total carbon content of products.

$$\text{conversion (\%)} = \frac{\text{mol of C in product}}{\text{mol of C in reactant} + \text{mol of C in products}} \tag{1}$$

$$\text{space velocity or pph (h}^{-1}\text{)} = \frac{\text{reactant flow (g}\cdot\text{h}^{-1}\text{)}}{\text{mass of catalyst (g)}} \tag{2}$$

$$\text{turn-over frequency (s}^{-1}\text{)} = \frac{\text{molecular flow rate (mol}\cdot\text{s}^{-1}\text{)}}{\text{surface iridium (mol)}} \tag{3}$$

$$\text{molar selectivity for } P_i = \frac{\text{quantity of product } P_i \text{ (mol)}}{\sum \text{quantity of products (mol)}} \tag{4}$$

It was previously verified with the same apparatus that in the case of dehydrogenation of isobutane into isobutene, there is no diffusional limitation for conversion lower than 10% (T.O.F. lower than $40\ s^{-1}$).[28] In this study, when contact time was varied by regulation of gas flow over the same catalyst bed, conversion varied linearly with contact time. Furthermore, when the mass of catalyst was varied from 40 to 122 mg while simultaneously varying gas flow such that space velocity was kept constant, very little change in conversion was observed. Thus one can assume that in these experimental conditions, the reaction was under kinetic control.

With time on stream a slight deactivation of the catalyst and a significant change in selectivity occur (Figure 1). Since the changes of selectivity were very rapid during this initial period, we chose to study the reaction after a stable catalytic regime had been established. Thus we measured reaction products only after 30 min of exposure of the catalyst to the reactant stream. After each measurement, the catalyst was regenerated at 300 °C under H_2 flow for 4 h. It was then allowed to cool to the reaction temperature and maintained at this temperature under hydrogen until the next experiment was carried out. By using this protocol, the catalyst can be used for many runs without variation of activity and selectivity.

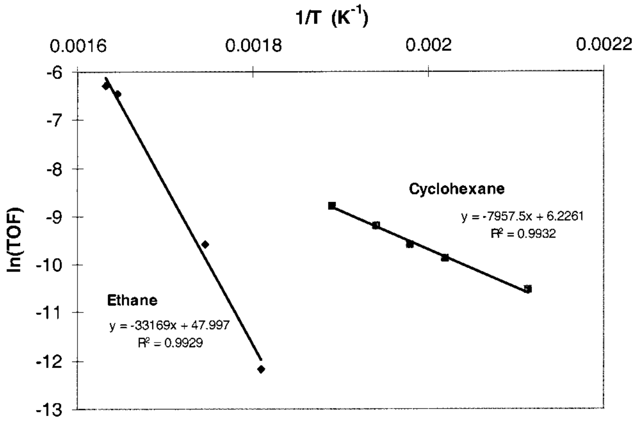

Figure 2. Arrhenius plots of (a) cyclohexane (■) over Ir/SiO_2 − $H_2/cC_6 = 36$, flow $= 11.3\ mL\cdot min^{-1}$, mass of catalyst $= 50$ mg and (b) ethane (◆) over Ir/SiO_2 − $H_2/C_2 = 50$, flow $= 11\ mL\cdot min^{-1}$, mass of catalyst $= 50$ mg.

Results

Hydrogenolysis of Cyclohexane. When a mixture of H_2 and cyclohexane was passed over a Ir/SiO_2 catalyst, depending on the experimental conditions, there is formation of benzene (aromatization), *n*-hexane, (ring opening), or lower alkanes (deep hydrogenolysis). No other products were detected.

A mixture of H_2 and cyclohexane (36/1) was flowed over Ir/SiO_2 catalyst at constant flow ($11.3\ mL\cdot min^{-1}$) at various temperatures. In accordance with thermodynamic calculations, in the range 200−260 °C, the higher the temperature, the higher the conversion. One may notice that conversion is 10 times greater at 260 °C than at 200 °C. A plot of ln(conversion) versus 1/temperature (K^{-1}) (Figure 2) gives an apparent activation energy of 16 $kcal\cdot mol^{-1}\cdot K^{-1}$. This result is consistent with previous reports[29] but one should note that this energy is related to an overall conversion to several pathways: Cyclohexane is transformed into benzene by aromatization or to linear alkanes by hydrogenolysis.

Increasing the temperature leads to a strong increase in the selectivity for benzene, a dramatic decrease in the selectivity for hexane, but no significant change in the selectivity for lower alkanes (Figure 3). The decrease in the selectivity for *n*-hexane was accompanied by an increase in the selectivity for methane: the C_6/C_1 ratio was higher at 200 °C (2.6) than at 260 °C (0.6).

Influence of the H_2/Cyclohexane Ratio. The influence of H_2/cyclohexane ratio has been measured at constant flow (11 $mL\cdot min^{-1}$) and temperature (200 °C). Aromatization leads to the formation of H_2. To disfavor aromatization, a high H_2/HC ratio should be used. If one increases the H_2/HC ratio, higher conversions are obtained. Besides, formation of benzene can be totally suppressed at 200 °C by using a H_2/HC ratio higher than 50: under these conditions, there is no significant variation of selectivity among the hydrogenolysis products.

To eliminate aromatization, one should work at low temperature (typically 200 °C) and use a very high H_2/cyclohexane ratio (typically >50). Therefore, primary products in cyclohexane hydrogenolysis were obtained at 200 °C and with a hydrogen-to-hydrocarbon ratio (H_2/HC) of 70.

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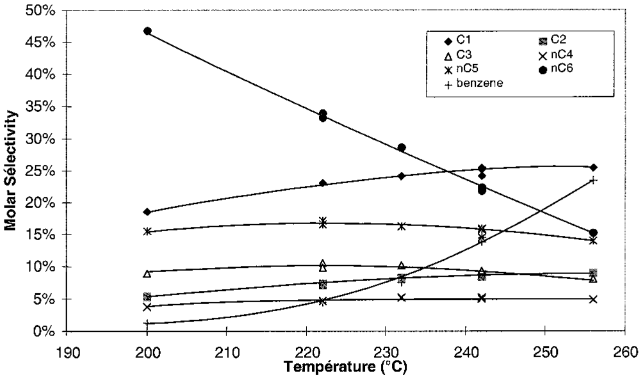


Figure 3. Influence of temperature on molar selectivity of products from cyclohexane hydrogenolysis over Ir/SiO$_2$ − H$_2$/cC$_6$ = 36, flow = 11.3 mL·min^{-1}, mass of catalyst = 50 mg.

Table 1. Distribution of C$_1$ to C$_5$ Products in the Hydrogenolysis of Cyclohexane or *n*-Hexane over Ir/SiO$_2$ (Temperature = 200 °C, H$_2$/HC = 50)[a]

			molar selectivities (%)					
entry		temp (°C)	C1	C2	C3	*n*-C4	*n*-C5	*n*-C$_6$
1	ethane	280	100					
2	*n*-hexane	200	9	18	47	16	9	
3	cyclohexane	200	15	4	12	6	13	50
4	cyclohexane[a]	200	30	8	24	12	26	

[a] C$_1$−C$_5$ selectivities normalized to 100%.

Influence of Space Velocity on the Primary Products. At 200 °C and for a H$_2$/cyclohexane ratio of 70, aromatization does not occur. The only products formed were *n*-hexane, *n*-pentane, *n*-butane, propane, ethane, and methane. Increasing space velocity time leads to a reduction of conversion as has already been discussed but no significant change in selectivity occurs. None of the selectivities dropped to zero when extrapolated to infinite space velocity: all these products are primary ones. Molar selectivities at infinite space velocity are summarized in Table 1, entry 3. Of course, C$_1$ to C$_5$ products cannot be obtained by the cleavage of only one carbon−carbon bond. One must therefore assume that there is on the surface of the working catalyst a fast equilibrium between several alkyl species, some of them giving lower alkanes. Relative molar selectivities among these multiple bond hydrogenolysis products (i.e. C$_1$−C$_5$ selectivities normalized to 100%) are listed in Table 1, entry 4.

Hydrogenolysis of *n*-Hexane. When a mixture of H$_2$ and hexane (50/1) was allowed to flow over a Ir/SiO$_2$ catalyst at 200 °C, hydrogenolysis is observed. Methane, ethane, propane, *n*-butane, and *n*-pentane were the only observed products. Increasing space velocity has no significant influence on the selectivity. Extrapolation of the selectivity to infinite space velocity (zero contact time) results in positive values for all of the products observed as tabulated in Table 1, entry 2. Thus, propane is the major product, the other alkanes are all technically primary products.

Hydrogenolysis of Ethane. When a mixture of H$_2$ and ethane (50/1) is passed over a Ir/SiO$_2$ catalyst at temperatures up to 270 °C (total flow = 11 mL·min^{-1}), no hydrogenolysis, that is, formation of methane, was observed. At higher temperatures, hydrogenolysis of ethane was observed, and from an Arrhenius plot of our experimental data (Figure 2) an apparent activation energy of 66 kcal·mol^{-1}·K^{-1}, much higher than the (very imperfect) energy measured for the disappearance of cyclohexane. Thus we consider that carbon−carbon bond activation of ethane is due to some fundamentally different type of reaction.

Discussion

During the first few minutes of exposure of the catalyst to the reactant mixture very sharp changes in the catalysts activity and selectivity were observed. At very short exposure times, conversions were relatively high and deep hydrogenolysis was favored at the expense, notably, of dehydrogenation. It can be suggested that during this time benzene formed remains at the surface, poisoning very active hydrogenolysis sites. After this short period a somewhat stabler regime is established marked by slight changes in selectivity in which gradually the aromatization reaction wins out over hydrogenolysis. The stable regime obtained after 30 min on stream was chosen for this study. A regeneration protocol was developed which provided highly reproducible results for the same catalyst bed over dozens of experiments.

To study the hydrogenolysis reaction unambiguously it was desirable to suppress the dehydrogenation reaction. According to thermodynamics, carbon−carbon bond cleavage would not be strongly influenced by either reaction temperature or H$_2$/HC ratio whereas aromatization would be strongly affected, the equilibrium yield of benzene from cyclohexane ranging from lower than 5% (at 190 °C and a H$_2$/HC ratio of 30) to more than 95% (at 230 °C and H$_2$/HC = 1). Thus, the lower the temperature and the higher the H$_2$/HC ratio, the less benzene we would expect. By working at 200 °C and a H$_2$/HC ratio of 50, the dehydrogenation to benzene is reduced below the limit of detection while maintaining the hydrogenolysis reaction at sufficient conversion to detect the products. Working at a H$_2$/HC ratio of 36 the activation energy for the hydrogenolysis of cyclohexane was determined to be 16 kcal·mol^{-1} (Figure 2).

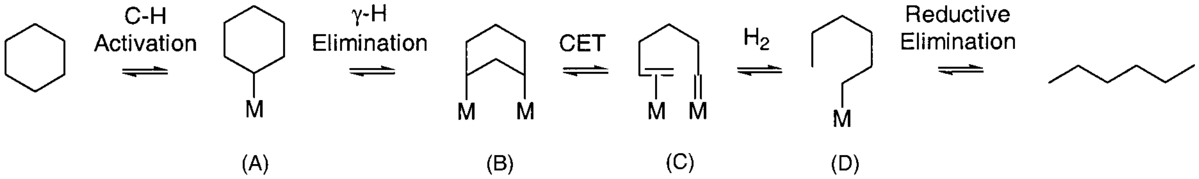
Having established conditions suitable to selective hydrogenolysis, it was necessary to determine whether reaction products reflected kinetic products and that the selectivities were not due to mass transfer limits, that is that conversion was inversely correlated to space velocity. First, reactant flow flux through the catalytic bed was varied to produce contact times (1/pph) between 1.5 and 4.2 mg·min·mL^{-1} and it was observed that conversion was directly proportional to contact time. The longest contact time (lowest space velocity) was then reproduced at several reactant gas flow rates (thus different catalyst masses) and no important variation of conversion was observed.

That is, for the least volatile substrate studied, it was verified that conversion varied inversely with space velocity and that conversion did not vary when the same space velocity was produced at various debit/catalyst mass combinations. The direct study of catalyst partical size was not undertaken for this case, but the catalyst was supported on a nonmicroporous silica and the experiment was performed with the same support, apparatus, and conditions (but a different metal and reactant) for another study.[28] For the lighter reactants (*n*-hexane and ethane) we did verify the inverse relation between conversion and space velocity, a lesser but significant level of verification of kinetic control of product distribution.

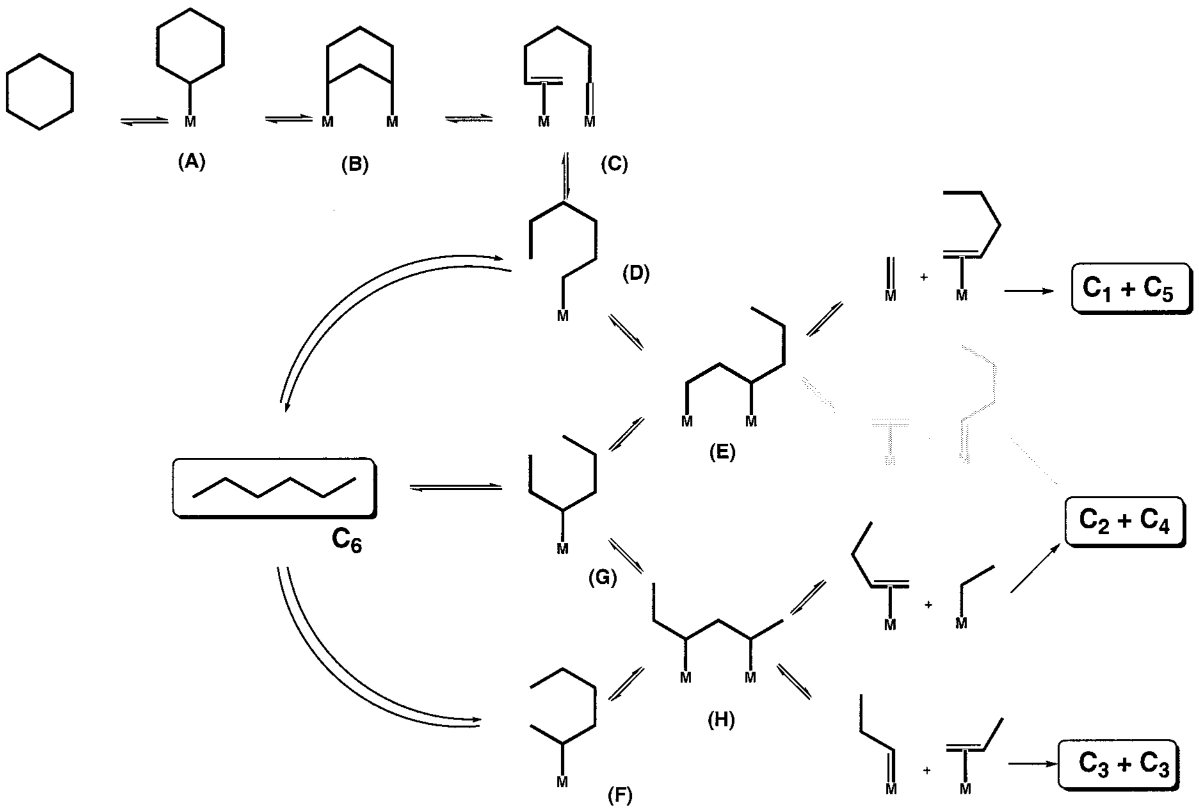
Thus one can determine the primary products of the reaction, from which mechanistic conclusions can be drawn. There was little variation of product selectivities over the range of space velocity studied. The major product of the reaction was *n*-hexane (~50%) followed by methane (15%), *n*-pentane (13%), propane (11%), and ethane and *n*-butane (5% each). If one extrapolates the selectivity of each of the products to infinite space velocity we find that all of the linear hydrocarbons C$_1$ to C$_6$ are primary products in approximately the proportions listed above.

Hexane is unique among these products in that it is the product of one and only one carbon−carbon bond cleavage

Scheme 4. Proposed Mechanism for Formation of *n*-Hexane from Cyclohexane



Scheme 5. Proposed Mechanism for C−C Bond Cleavage of Cyclohexane



reaction. The other products can only be produced by a second carbon−carbon cleavage. If one assumes that all products are the product of only one or two bond cleavage reactions, methane and pentane are *coproduced* as are ethane and *n*-butane and thus these products should have equivalent selectivities. This is very nearly the case but clearly some three carbon−carbon bond hydrogenolysis is taking place. It is very clear, however, that this hydrogenolysis is not taking place by stepwise C_6 to C_5 to C_4 etc. hydrogenolysis, *a very important observation.*

To study more carefully the hydrogenolysis of the unique product, *n*-hexane, to lower products, conditions were established in which the hydrogenolysis could be studied under kinetic control. Again product selectivities were only very slightly affected by space velocity and the primary products were propane (47%), ethane (18%), *n*-butane (16%), methane (9%), and *n*-pentane (9%). Again, note that at infinite space velocity, ethane and butane selectivities are very close and *n*-pentane and methane selectivities are equivalent.

One last observation important to the mechanistic discussion is that ethane does not undergo hydrogenolysis to methane at temperatures up to 270 °C. The full range of temperatures studied for this reaction allow the estimation of the activation energy for ethane hydrogenolysis at 66 kcal·mol^{-1} (Figure 2) and thus suggest that some other mechanism or carbon−carbon cleavage produces this hydrogenolysis. Given this observation and the unusual selectivities observed for cyclohexane and *n*-hexane hydrogenolysis, mechanisms implying 1,2 carbon activation such as Gault's mechanisms and the methylidene deinsertion mechanism are discarded (Schemes 1 and 2).

The metallacyclic mechanism of carbon−carbon bond cleavage (Scheme 3) does however fully account for our observations. An illustration of this mechanism for the production of *n*-hexane from cyclohexane is given in Scheme 4. Initial carbon−hydrogen bond activation produces a surface cyclohexyl fragment **A**, which then undergoes a second carbon−hydrogen bond activation at the γ-position to give the key dimetallacyclopentane intermediate **B**. In a step taken from the olefin metathesis reaction, concerted electron transfer (a 2 + 2 decyclization) leads to a noncyclic hydrocarbyl surface fragment, **C**, precisely a carbene ligand chelated via a terminal olefinic function. Hydrogenation of the carbon−carbon double bond and hydrogenolysis of the metal carbon double bond lead through a surface *n*-hexyl fragment **D** to the *n*-hexane product.

The expansion of this mechanism to a second carbon−carbon bond cleavage appears more complicated but is conceptually equivalent (Scheme 5). The surface *n*-hexyl fragment **D** now can follow several different pathways. Either it undergoes reductive elimination to *n*-hexane and β-hydride elimination to coordinated 1-hexene, or it follows the direct route to a second carbon−carbon bond cleavage, which is γ-carbon−hydrogen bond activation to the metallacyclic intermediate **E**. A second metallacyclic intermediate **H** can be formed by a number of routes illustrated in Scheme 3, and lower alkane products are formed from one of these two metallacyclic intermediates. In principle, intermediate **E** can lead either to *n*-pentane and methane or to ethane and *n*-butane, but we have previously suggested that the product leading to the surface methylidene fragment is strongly favored (that is, the pentane/methane route). This suggestion is reinforced by our observations herein, vida infra. Intermediate **H** can undergo concerted electron transfer to surface alkylidene and olefin by two routes leading to either ethane and *n*-butane or to 2 equiv of propane.

Given this mechanism it is clear why ethane does not undergo hydrogenolysis under mild conditions: it is not possible to form the necessary dimetallacyclopentane intermediate. Furthermore, the grouping of products (same selectivities for pentane and methane, butane and ethane) is also implied by the mechanism.

The comparison of the results for *n*-hexane with those for cyclohexane is particularly interesting. Entry 4 of Table 1 lists the selectivity of the C_1-C_5 products of cyclohexane hydrogenolysis normalized to 100% to allow the comparison between the two-bond hydrogenolysis products from cyclohexane with the one-bond hydrogenolysis products from *n*-hexane. Two important mechanistic hypotheses can be drawn from these comparisons: first that ethane and butane are formed only via intermediate **H** and second that lower hydrogenolysis products in the hydrogenolysis of cyclohexane necessarily have passed through the *n*-hexyl surface intermediate **D**.

Assuming for the moment that intermediate **E** leads only to methane and pentane and thus that all of the ethane and *n*-butane formed are due to intermediate **H**, we would expect that the ratio between propane selectivity and ethane/butane selectivity should be the same, as they are formed in parallel from the same intermediate **H**. While the change from cyclohexane to *n*-hexane as reactant has produced a large change in the relative importance of the methane/*n*-pentane coproducts with respect to other products, the ratio of propane to the ethane/butane couple is very close (46/30 or 1.5 for *n*-hexane, 24/20 or 1.2 for cyclohexane). This invariability in the face of the very large change in methane/*n*-pentane selectivity (20% for *n*-hexane, 56% for cyclohexane) seems to indicate that the formation of ethane/*n*-butane is independent of the formation of methane/*n*-pentane, that is that intermediate **E** does not lead to ethane/*n*-butane formation.

Finally, the substrate-dependent change in selectivity for the methane/*n*-pentane couple just cited (20% for *n*-hexane, 56% for cyclohexane) is not surprising when one notices that the C_1 to C_5 products in the case of cyclohexane hydrogenolysis *must* enter the second carbon−carbon bond cleavage scheme through the *n*-hexyl surface intermediate **D** whereas in the case of *n*-hexane hydrogenolysis, the initial carbon−hydrogen bond activation step can lead to any of three alkyl surface intermediates (**D**, **G**, and **F**) before arriving at the key metallacyclic intermediates **E** and **H**. Our results would seem to suggest that the isomerization of the surface alkyl fragments interconverting **D**, **G**, and **F** is slow with respect to the second carbon−hydrogen bond activation step and subsequent carbon−carbon bond cleavage.

Further studies of the hydrogenolysis of cyclic alkanes over Ir/SiO$_2$ catalysts will include alkyl substituent effects and eventually bicyclic systems.

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Supporting Information Available: A schematic diagram of the dynamic microreactor and figures and tables describing the transient behavior of the catalyst, regeneration of the catalyst, the effect of hydrogen/hydrocarbon ration on the reaction, the verification of the kinetic regime, and the determination of primary products (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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