

C-H Activation on Rhodium: Reaction Mechanism and the Role of Carbonaceous Residues

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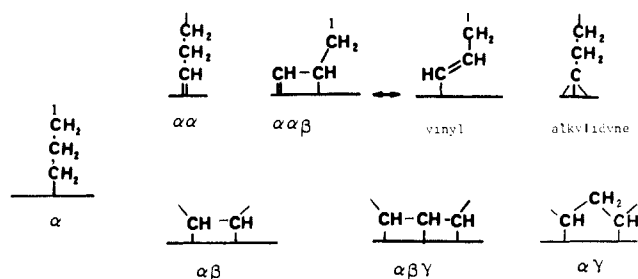
Abstract: Evidence for two C-H activation mechanisms, the oxidative addition of a single C-H bond and the concerted oxidative addition of two adjacent C-H bonds, is presented. The two mechanisms show different sensitivity to surface structure or particle size. While the first process ($E_a \sim 21$ kcal/mol) is insensitive to the hydrocarbon structure, the second process ($E_a \sim 5-9$ kcal/mol) is sensitive to the hydrocarbon structure. C-H activation is found to be 0.6 order in hexane and zero order in deuterium, which is consistent with oxidative addition as the rate-determining step. The d_2 maximum obtained by H/D exchange of linear alkanes on Rh results from surface olefins, as indicated by high-resolution deuterium NMR. Evidence against the participation of carbonaceous residues in the H/D exchange process is presented, indicating that carbonaceous material is not part of the active site. Two types of carbonaceous residues are detected. One forms at lower temperatures and does not interfere with the reaction; the other forms at higher temperatures and acts to poison the catalyst.

Carbon-hydrogen bond (C-H) activation of alkanes, one of the most fundamental reactions in heterogeneous catalysis, has received ongoing attention, and the progress has been reviewed regularly.¹⁻⁶ Due to the complexity of heterogeneous reactions, where intermediates cannot be readily isolated and characterized, many of the unique features of C-H activation remain unsolved and much of the current mechanistic understanding is still based on speculation. Interpretations of C-H activation center around the initial formation of a discrete monoadsorbed surface alkyl (see Scheme I) followed by further dissociation to an α,β -surface intermediate or reductive elimination.^{2,3,6} Interconversion of these two intermediates, the so called α,β -process,⁷ is often considered the basic mechanism for H/D exchange propagation,⁸ although convincing evidence for the alternative π -allyl interconversion mechanism has been obtained.⁹

On most transition-metal catalysts, H/D exchange experiments with linear alkanes yield mono- and/or perdeuterioalkanes as dominant products while Rh¹⁰ and to a lesser extent Ni also exhibit d_2 maxima at lower temperatures.¹¹ Already in the early studies of C-H activation on heterogeneous catalysts Rh had been recognized for its unusual activity and product distribution. Studies with bimetallic Rh-Pt catalysts on silica indicate that Rh is 20-30 times more active for H/D exchange of compounds capable of forming α,β -adsorbed intermediates, while Pt is as effective as Rh with hydrocarbons lacking adjacent C-H bonds.¹² In a H/D exchange study with cyclopentane ²H NMR indicated the presence of predominant *cis*- d_5 on Pt, simple d_1 on Ir, and α,β - d_2 on Rh.⁸ With Pd, Rh, and Ni the distributions provide evidence for direct dissociation of cyclopentane to diadsorbed cyclopentane.⁸ Although this could have been interpreted as evidence for the formation of surface olefins, the alternative α,γ - and α,α -intermediates as precursors of the d_2 products were not dismissed.^{8,13}

Rh film was reported to be more effective than other transition metals for multiple H/D exchange of methane¹⁴ and neopentane,¹⁵

Scheme I. Representation of the Surface Intermediates Discussed in the Text



molecular indicators of the ease of α,α or α,γ activation. Exchange of 1,1,3,3-tetramethylcyclopentane showed a d_4 maximum on Rh at lower temperature than on Pt, leading to the hypothesis that deuteration of both sides of the ring in a single catalyst-hydrocarbon interaction may proceed through surface alkylidenes.¹⁶ However, alternative modes to deuteration of both faces, such as the formation of surface vinyls,⁹ were not considered. d_2/d_6 maxima for the exchange of ethane and d_1/d_4 for methane on Rh were reported by Sarkany et al. on Rh black.¹⁷ They concluded that the dissociation of surface alkyls on Rh into doubly bound surface species proceeds readily, explaining the dominant formation of multiply deuterated isomers. A strong d_6 maximum for cyclohexane on Rh at low temperatures (-48 °C) is indicative of the more facile propagation of H/D exchange through the activation of adjacent carbons relative to the formation of surface alkylidenes,⁷ while d_2/d_{14} maxima, observed for *n*-hexane,^{10,18} point to a subtle difference between linear alkanes and cycloalkanes. Alkylidene intermediates have been detected on Rh single crystals.¹⁹

In a recent study on the H/D exchange of hydrocarbons on Ni catalysts, which also produce a pronounced d_2 maximum, Dessauges and Gäumann discard the α,β -mechanism by statistical arguments and propose two separate processes to explain the two maxima obtained in the products: dissociation of one C-H bond under formation of a surface alkyl and concerted dissociation of two C-H bonds under formation of a surface olefin.^{11a} It is interesting to note that Gault and Kemball already in 1961 made a similar proposal, although then based on the Eley-Rideal-type mechanism.¹⁰ However, in 1971 Kemball emphasizes the inter-

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Table I. Activation Energies of Hydrocarbons on Heterogeneous Rh Catalysts^a

| compound | Rh film | dispersed Rh | Rh/SiO ₂ |
|------------------|-----------|--------------|---------------------|
| methane | 23.6 (1) | 22.5 (17) | 17.6 (12) |
| | 20.0 (48) | | |
| neopentane | 15.5 (15) | 17.0 (17) | |
| ethane | 11.7 (1) | | |
| cyclohexane | 10.4 (7) | | |
| <i>n</i> -hexane | 9.5 (10) | | |

^aThe literature reference is indicated in parentheses.

conversion of α - with α,α - and α,β -adsorbed species on Rh catalysts.⁵ Gault, Rooney, and Kemball in 1962 base their argument of a stepwise α - α,β conversion leading to the d_2 maximum on hindered rotation in the case of higher hydrocarbons relative to ethane, which was backed by a lack of a d_2 maximum in early ethane exchange experiments.¹⁶ This argument, however, became invalid when distinct d_2 and d_6 maxima for ethane exchange were reported on Rh black.¹⁷ There seems to be general agreement that α,β -adsorption is the most facile type of activation. However, convincing evidence for the nature of the precursor to the d_2 product on Rh is still missing. Surface alkylidenes (known to form less readily than α,β -intermediates) and α,γ -diadsorbed intermediates (postulated intermediates in isomerization reactions on Pt)²⁰ are still being considered. Sensitivity of the formation of α,γ -intermediates to C-H bond strength has been obtained in exchange reactions with 2,2-dimethylbutane and 3,3-dimethylpentane on Pt.⁹

In addition to exchange patterns, activation barriers provide information on the mechanism. Some activation barriers compiled from the literature are presented in Table I. With methane, where propagation of exchange through adjacent C-H bonds is not possible, the activation barrier for α,α and higher exchange was determined by Kemball on Rh films to be about 4 kcal higher than the barrier for single α -exchange (20 kcal/mol). Table I clearly shows that the activation energy for pure α -activation is higher than that of molecules where α,β -activation is possible. On Rh the activation energy for the formation of the various isomers in neopentane suggests that α,α - or α,γ -activation has a 5 kcal/mol higher barrier than the simple α -activation.¹⁵ This leads to the following general ordering of the activation barriers: $\alpha,\beta < \alpha < \alpha,\alpha, \alpha,\gamma$.

Most of the data in Table I were obtained on Rh films, which represent bulk Rh metal rather than the more common dispersed Rh catalysts. While the activation barriers of methane on the Rh black and on the dispersed Rh catalyst agree reasonably well, the activation barriers of ethane show notable deviation, indicating that there may be dispersion effects on the activation of molecules capable of forming α,β intermediates. The possible effect of catalyst particle size and surface structure on catalytic processes, which has to be considered in all heterogeneously catalyzed processes, has been discussed elsewhere.^{9,21} A direct link between the results of surface science studies and supported heterogeneous catalysis has been provided recently by Augustine,²² who obtained the same correlation between benzene and *n*-hexane formation from cyclohexane with the relative concentration of chemically determined kink, step, and terrace sites as that reported by Herz et al. on defined single-crystal surfaces.²³

Potential problems with the use of activation barriers as well as exchange patterns for mechanistic interpretation from these data are the lack of knowledge on the surface composition and the interference of carbonaceous materials with the mechanism of C-H activation. The involvement of carbonaceous deposits in the reactions of hydrocarbons on heterogeneous catalysts has been of general concern. Previous studies on carbonaceous layer²⁴⁻²⁹

Table II. Percent Rh by Weight and Dispersion (Exposed Rh/Total Rh) of the Catalysts Used in This Study

| catalyst | % dispersion |
|--|--------------|
| Rh foil | 0 |
| Rh black | 0.3 |
| 25% Rh/Al ₂ O ₃ | 1.2 |
| 11% Rh/Al ₂ O ₃ | 26 |
| 1% Rh/Al ₂ O ₃ | 92 |
| 0.1% Rh/Al ₂ O ₃ | 100 |

formation during reactions in related systems indicate that temperature, hydrogen pressure, and degree of hydrogen precoverage of the catalyst are important variables in determining the amount and type of carbonaceous layer formed. Early observations³⁰⁻³² indicated that ethylene self-hydrogenates on tungsten and iridium and that initial ethane produced upon exposure of W, Ni, Rh, or Fe to ethylene and deuterium was rich in hydrogen.³³ These observations led to the proposal that chemisorbed ethylene might serve as a mediator for the transfer of hydrogen or deuterium atoms to gas-phase ethylene molecules during ethylene hydrogenation.³² In 1979 Hattori and Burwell³⁴ provided evidence that the carbonaceous layer was not involved in hydrocarbon hydrogenations on Pt/silica at -31 °C. However, Zaera et al. and Wieckowski et al.³⁵⁻³⁷ have recently proposed that the carbonaceous layer is directly involved in ethylene hydrogenation on Pt (111) single crystals at 300 K, and they suggest that studies on the role of the carbonaceous layer in other systems would be worthwhile. In contrast, Beebe and Yates³⁸ found that the ethylidyne fragments are bystanders in the reaction on Pd and are never formed to any significant extent if the initial hydrogen-to-hydrocarbon ratio is greater than 1.5. Ethylene hydrogenation is totally unaffected by the presence of as much as 0.25 monolayer coverage of ethylidyne on Pd.³⁸ One hypothesis is that carbonaceous residues may provide sites for desorption of reaction intermediates during catalytic reactions.²⁵

Even less is known about the role of carbonation in C-H activation processes. Inoue et al. concluded from H/D exchange studies with cyclopentane on platinum that the exchange reaction probably proceeds on the surface of the platinum and not upon the carbonaceous residues.²⁸ Carbonaceous material appears to deactivate the catalyst while no effect upon the selectivity of the process could be noted, although a possible activating effect of some initial residue formed in the first few instants of the exposure to the hydrocarbon was not excluded.²⁸ The study, however, could not differentiate between carbonation on the metal and on the support.

Cabrol and Oberlin have studied the nature and localization of carbonaceous deposits on Pt/alumina catalysts by transmission electron microscopy.³⁹ They came to the conclusion that carbon deposition takes place randomly on the alumina. No special relationship between carbonation and the Pt particles was detectable, indicating that this type of carbon deposit has insignificant poisoning effect. This was confirmed by Lietz et al., who found

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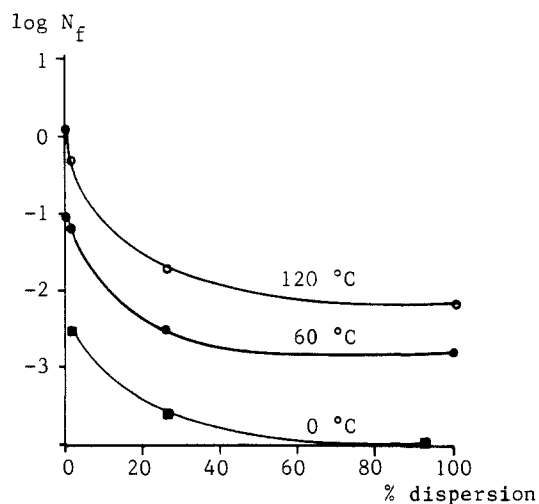


Figure 1. Dispersion sensitivity of *n*-hexane activation on heterogeneous Rh catalysts at 0, 60, and 120 °C.

that the larger fraction of the carbon deposit is located on neutral areas of the alumina and not in the vicinity of the Pt particles.⁴⁰

As this introduction shows, all possible surface intermediates and exchange processes have already been proposed and much information has been collected. However, a comprehensive picture of the mechanism of H/D exchange on Rh is still missing, including its surface structure or catalyst particle size dependence, its dependence on the carbonaceous surface material, and evidence for the nature of the d_2 product as well as its mechanism of formation. These and other aspects of the H/D exchange on heterogeneous Rh catalysts will be addressed in this study. Whenever relevant our results with Rh will be compared and contrasted with those observed on Pt⁹ to illustrate element-specific aspects of heterogeneous C–H activation.

Results and Discussion

Temperature and Dispersion Dependence. H/D exchange of *n*-hexane under gas-phase flow conditions at ambient pressure was chosen as the model reaction. The turnover frequency, N_f [molecules per surface metal atom and second], was determined on five Rh catalysts of different dispersion (Table II). All experiments were carried out at low conversion to ensure single-surface interaction. Figure 1 shows the dispersion dependence at 0, 60, and 120 °C. Independent of dispersion from about 20–100%, the plots show a nearly constant N_f at various temperatures while at very low dispersion a drastic increase is obtained, amplifying the behavior of Pt reported earlier.⁹ The exchange on Rh at 0 °C is dominated by dideuteration and polydeuteration leading to d_2 and d_{14} *n*-hexanes as the product maxima as observed by Gault and Kemball.¹⁰ This is in sharp contrast to the exchange behavior of Pt where d_1 hexane always accounted for 10 to 40% of the deuterated products.⁹ For comparison, *n*-hexane was exchanged at 0 °C on 10% Pt/Al₂O₃ (see Figure 2). No d_1 or d_2 but only polydeuteration is obtained, characterizing a fundamental difference between Rh and Pt catalysts.

Figure 3 shows MS traces of the exchanged *n*-hexane at various Rh dispersions and temperatures. The relative size of the d_2 maximum decreases with increasing temperature and dispersion. At 0 °C, due to the low surface area of the foil and the small amount of Rh on the 0.1% Rh/alumina, exchange on these catalysts could not be determined. A relatively rapid deactivation of the catalyst at 0 °C occurred in the presence and absence of hydrocarbon, which is attributed to the formation of water from trace amounts of oxygen inevitably present in the flow gases and apparatus.^{34,41} At 60 °C the dominant product on all of the catalysts was perdeuteriohexane, with the exception of the foil, which still contains a dominant dideuterio maximum. A weak

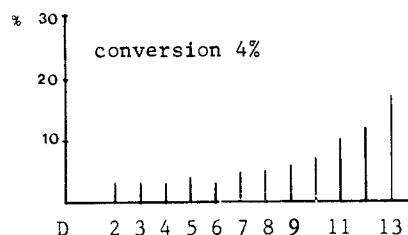


Figure 2. Isotopic exchange pattern of *n*-hexane obtained at 0 °C on a 10% Pt/alumina catalyst.

d_2 maximum is still present on the low-dispersed catalysts at 60 °C, while the two highly dispersed catalysts change to additional d_1 maxima, indicating a dispersion and temperature dependence of the exchange mechanism. At 120 °C the d_2 isomer has disappeared as a maximum on all catalysts. The highly dispersed Rh catalyst shows a pronounced d_1 maximum similar to that of Pt.⁹ The temperature dependence of the d_2 and d_{14} maxima is shown in Figure 4.

At this point it is important to determine whether these maxima are indeed products reflecting the interaction of Rh surface atoms with the hydrocarbons or whether the buildup of a carbonaceous layer is interfering with the product composition.

Carbonaceous Layer. Before the effect of carbonaceous materials on the C–H activation can be established, it is important to be able to correlate the amount of alkane passed over the catalyst with the carbonaceous layer buildup. Correlation of the catalyst activity and the product composition with the amount of carbonaceous material should provide the data necessary to determine the function of surface carbon in the exchange process. An unsupported Rh catalyst (0.3% dispersed Rh black⁴²) was selected for this study to avoid unnecessary complications by carbonaceous buildup on the support and other support effects. To bypass undefined effects due to exposure to air or catalyst transfer, in situ cycling between oxidation, reduction, and hexane H/D exchange was required. The reaction products were continuously monitored by an on-line quadrupole and when desired trapped for GC/MS analysis. The amount of carbon was determined by the area of the ion intensity vs. time curve for the CO₂ signal (M^+ 44) upon oxidation of the catalyst (sensitivity of carbon atoms/surface rhodium atoms (C/R_s) $<10^{-3}$). Unless otherwise mentioned, regardless of the temperature at which the carbonaceous layer was deposited, the catalyst activity was determined with a standardized experiment (30 °C, deuterium flow of 40 mL min⁻¹, 50 μL of hexane, addition rate 8.1 μL min⁻¹) by GC–MS product analysis. To ensure that active reaction intermediates did not contribute to the measured carbonaceous layer, the catalyst was maintained at 80 °C under deuterium or hydrogen for 1 h after exchange was complete and before oxidation, unless otherwise mentioned.

Carbonation at 80 °C. At 80 °C with He as carrier gas a rapid buildup of carbonaceous material is observed, which reaches a C/Rh_s ratio of 1 already after the addition of only 300 μL of *n*-hexane. This carbon layer is almost completely removed by a 1 h hydrogen purge at 80 °C, indicating that such a carbon layer is probably similar to reactive intermediates of the exchange reaction. To obtain information on the carbonaceous deposit not related to reactive intermediates, defined amounts of *n*-hexane were passed over the catalyst under exchange conditions at 80 °C in a stream of hydrogen. Figure 5 shows a fast deposition of 0.04 monolayer followed by a slow buildup of carbonaceous material to a surface coverage of about 0.1 monolayer. Even after the exchange of 30 mL of *n*-hexane at 80 °C (quantitative conversion conditions), which corresponds to a turnover number $>10^4$ molecules/surface atom, only 200 μg of carbonaceous material were formed (0.3 monolayer) and no noticeable drop in activity

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(42) The catalyst had been used extensively through several oxidation, reduction, and H/D exchange cycles. Constant activity for H/D exchange in different experiments after oxidative regeneration indicated that no significant morphology changes were occurring under the conditions of these experiments.

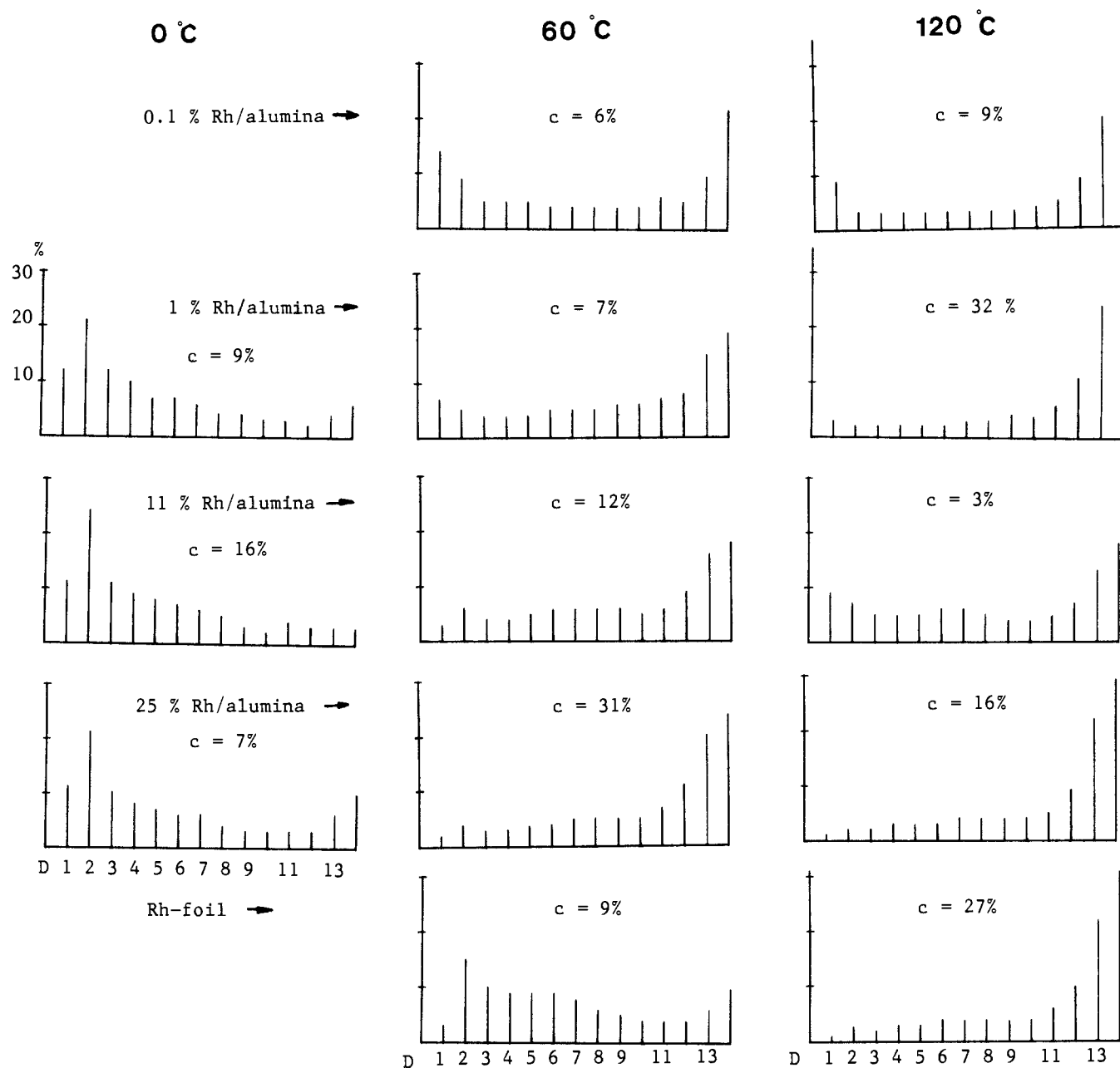


Figure 3. Isotopic exchange patterns obtained on differently dispersed Rh catalysts at 0, 60, and 120 °C showing the effect of dispersion and temperature on the isotopic distribution in *n*-hexane. Total conversion is indicated with *c*.

was detectable. The activity and exchange pattern after increasing amounts of hydrocarbon conversion (see Figure 6) were determined during this 30-mL-exchange experiment. Neither activity nor exchange pattern of the *n*-hexane is affected by the buildup of the carbon layer at 80 °C.

This experiment was repeated with 2 mL of *n*-hexane, and after disappearance of the physically adsorbed hexane the products of a 6-h hydrogen purge were trapped with liquid nitrogen and analyzed by GC-MS. The only product present was *n*-hexane with less than 1% of smaller hydrocarbons. The removable carbonaceous deposit at 80 °C therefore consists of unbroken C₆ carbon chains, supporting the results of Inoue et al. on supported Pt catalysts.²⁸ Since this removable carbonaceous deposit cannot belong to the reactive intermediates of the fast H/D-exchange process but maintains its C₆ carbon chain, it must be a more strongly adsorbed surface intermediate. Since surface alkylidynes are known to form readily on Rh surfaces and their rate of formation and removal is rather slow ($N_f 10^{-3}$ at 310 K)³⁷ compared to the N_f for H/D exchange, surface alkylidynes most likely represent this removable carbonaceous deposit. The conditions we have chosen ensure that the measured carbon layer does not

contain any active H/D-exchange intermediates, since the inverse of the turnover frequency for exchange at 80 °C suggests that the residence time of these species is less than 2.5 s. Even with a site being composed of ten or more surface atoms this amounts to an actual residence time much shorter than the 1 h hydrogen purge applied.

Carbonation at 400 °C. To determine the effect of strongly bound carbonaceous material, *n*-hexane was H/D exchanged at 400 °C. At this temperature hydrogenolysis is found to compete significantly with simple exchange reactions. The rapid buildup of the carbonaceous material at 400 °C correlates with the drop in activity and is proportional to the amount of reacted hydrocarbon (Figure 7). Complete deactivation is already achieved after only 4 mL of reacted *n*-hexane (turnover 10³). However, despite this fast drop in activity at 400 °C, the selectivity, as determined by the exchange pattern, remains unchanged. This indicates that the carbonaceous material produced at 400 °C is deactivating and thus significantly different than that formed at 80 °C. The initial activity of such deactivated Rh is completely restored by oxidation, indicating a lack of structural or morphological changes of the Rh during the carbonation process.

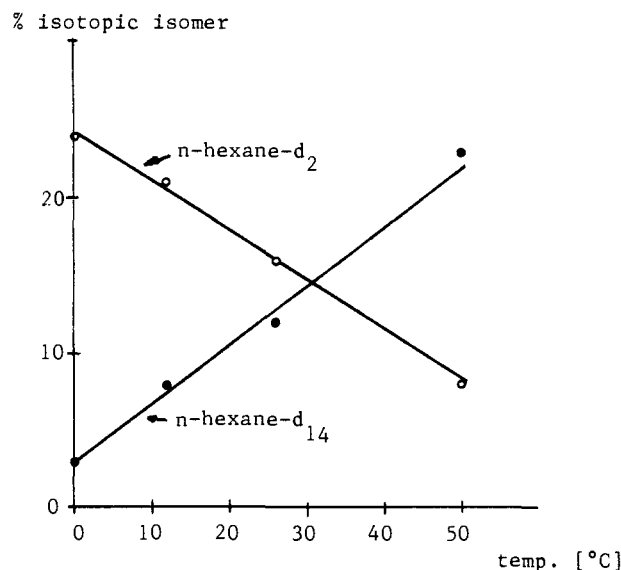


Figure 4. Change in relative intensity of the d_2 and d_{14} maxima of exchanged n -hexane with temperature on the 11% Rh/alumina catalyst.

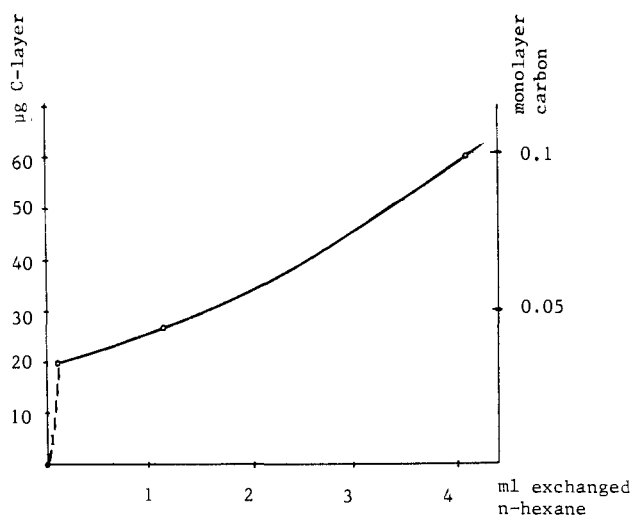


Figure 5. Buildup of carbonaceous material on Rh black with the amount of H/D-exchanged n -hexane at 80 °C.

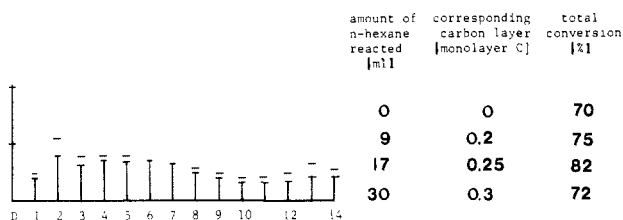


Figure 6. Isotopic exchange pattern and activity for n -hexane H/D exchange after increasing carbonation, expressed in mL of exchanged n -hexane, on Rh black. The range of fluctuations of the isotopic exchange patterns is indicated.

Comparison of 80 and 400 °C Results. The slow buildup of a carbonaceous layer at 80 °C and the lack of significant irreversible carbonation at this temperature are consistent with previous studies,^{25,27} where much higher temperatures were required for considerable buildup of a carbonaceous layer. It is significant that a C/Rh_s ratio of 0.17 formed at 400 °C deactivated the catalyst by 81% with no change in selectivity while a ratio of 0.3 formed at 80 °C caused no change in activity nor selectivity. Our results are in agreement with the observation by Inoue et al. on supported Pt catalysts²⁸ and support the conclusions by van Meerten et al. from their study on Ni²⁷ that three types of surface carbonaceous species are formed: (1) the reaction intermediates;

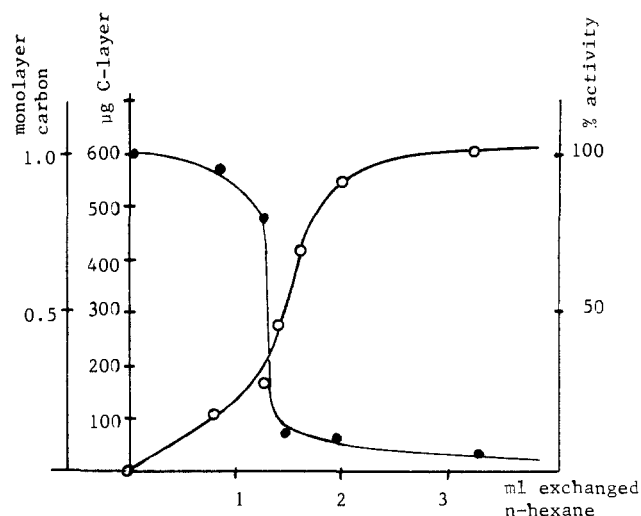


Figure 7. Buildup of carbonaceous material on Rh black with the amount of H/D-exchanged n -hexane at 400 °C: (○) buildup of carbonaceous layer (left scale); (●) decrease in activity as determined by standardized conversion experiments (right scale).

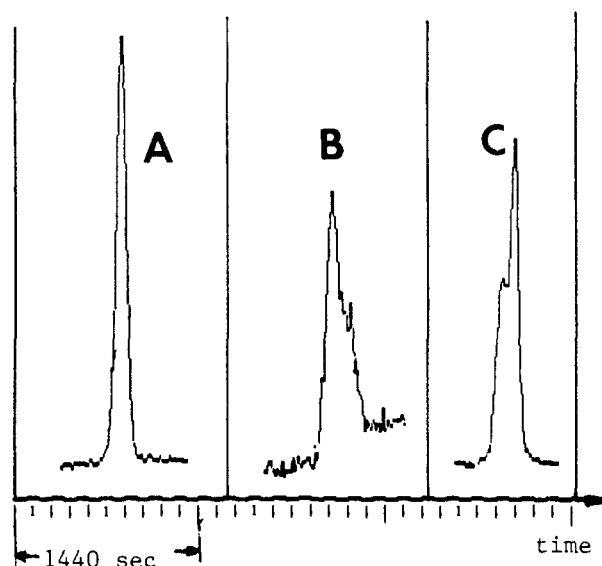


Figure 8. Shape of the CO_2 peaks obtained upon temperature programmed oxidation of the carbonaceous material formed during exchange of n -hexane on Rh black. 800 μL (A) and 30 mL (B) of n -hexane at 80 °C and 2 mL of n -hexane at 400 °C (C). The vertical scales of the three peaks are different, but the horizontal time scale and the heating rate are identical. Time scale indicates peak width only.

(2) a form which is more slowly removable under the reaction conditions and does not deactivate the catalyst, most likely surface alkylidynes; and (3) a more strongly adsorbed form which blocks active sites and can only be removed by oxidation at elevated temperatures (graphitic carbon?).

In addition to the difference in deactivation behavior between the carbon layer formed at 80 °C vs. 400 °C the MS trace of CO_2 upon temperature programmed oxidation of the catalyst for three representative experiments (Figure 8) supports the distinction between the 2nd and 3rd carbon layer form. Peak A (symmetrical and sharp) was that obtained after exchange of 800 μL at 80 °C; peak B (shoulder at higher temperature) after exchange of 30 mL at 80 °C, and peak C (shoulder at lower temperature) after 2 mL at 400 °C clearly pointing to two different forms of carbon.

Is the Initial Carbon Layer Active in H/D Exchange? The rapid buildup of only about 0.1 monolayer of carbonaceous material on the catalyst at the beginning of an experiment does not rule out that this surface carbon is part of the active site of the catalytic process. Although the number of surface sites for hydrogen activation is known from the hydrogen adsorption measurements,

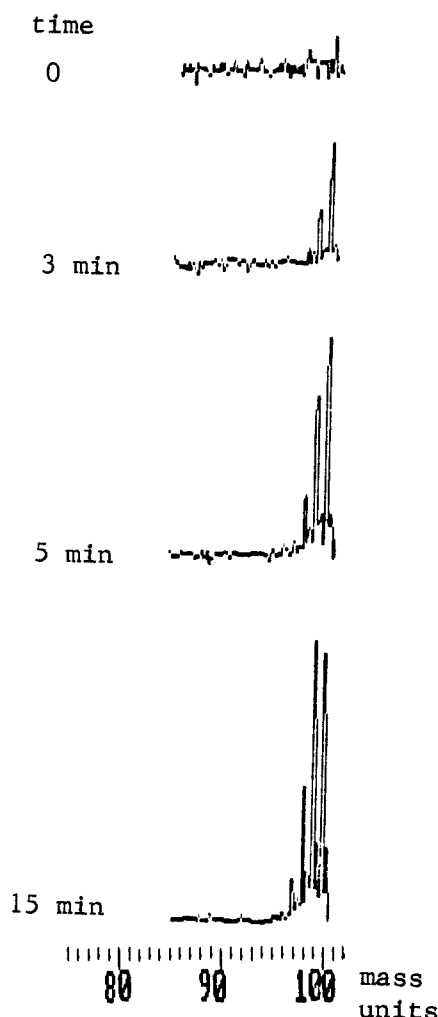


Figure 9. MS trace of the initial product composition from H/D exchange of *n*-hexane on freshly oxidized and reduced Rh black monitored over a short period of time showing *n*-hexane-*d*₁₄ as the first product and the increase of some hydrogen dilution with time.

these are not necessarily identical in number or shape with the active sites for H/D exchange of *n*-hexane. In fact, the 81% deactivation caused by a C/Rh_s ratio of 0.17 suggests that the number of active sites for C-H activation might be lower than that determined from the hydrogen adsorption data. Simple steric considerations imply that it is impossible that all surface atoms are active sites for *n*-hexane activation at the same time. Such considerations are supported by surface science studies, where the formation of ordered overlayer structures (a benzene molecule covers 8 Rh atoms on a (111) surface⁴³) has been well established.⁴⁴

In order to test for the catalytic activity of the initial carbon layer, the initial products of a *n*-hexane pulse under H/D exchange conditions on freshly oxidized and reduced (deuterium) Rh black catalyst were monitored with the on-line quadrupole. If the carbonaceous layer is formed before exchange can occur, then initial hydrogen dilution should result in the formation of some lower deuterated *n*-hexanes as the first product. Dilution of the surface deuterium with hydrogen from the reacting hydrocarbon is a commonly observed phenomenon in H/D exchange experiments.² However, as shown in Figure 9, the first detectable product desorbing from the catalyst is pure *n*-hexane-*d*₁₄ while hydrogen dilution only shows later, when (Figure 9) the initial *d*₁₄ maximum slowly changes to a *d*₁₃ maximum.

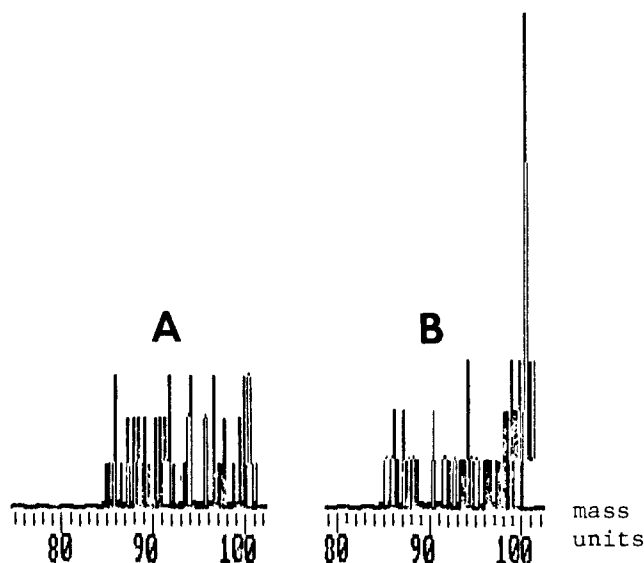


Figure 10. MS trace of the product formed after a 0.04- μ L pulse of *n*-hexane with deuterium as carrier gas on fresh Rh black (A is the background spectrum).

Table III. ²H NMR Chemical Shifts (ppm) of Mono and Geminal Dideuteriohexanes Relative to Me₄Si-*d*₁₂

| no. of D atoms | carbon | | |
|----------------|--------|------|------|
| | 1 | 2 | 3 |
| 1 | 0.91 | 1.32 | 1.29 |
| 2 | 0.89 | 1.30 | 1.27 |

In a second experiment, 0.04 μ L of *n*-hexane was injected in the stream of deuterium to fresh Rh black at 80 °C under perdeuteration conditions. Such a small amount of hexane, even if totally dissociated, can only produce a maximum of 0.037 mono-layer of carbon. However, not only was the *n*-hexane not consumed, but it was completely exchanged (see the clean *d*₁₄ maximum in Figure 10). Catalyst oxidation immediately after the experiment showed no detectable carbonation, indicating that the carbon layer formed was smaller than 10⁻³ monolayer. Such a small concentration of sites, however, is unlikely to be responsible for the complete conversion of these 0.04 μ L of *n*-hexane to perdeuterio *n*-hexane which rules out any participation of surface carbon in the active sites for C-H activation.

The Nature of the Dideuteriohexane Product. With the exception of the exchange products formed on the highly dispersed Rh catalyst at 60 and 120 °C no *d*₁ product maxima were observed (see Figure 3). Note that the hexane product from the 0 °C hexane exchange (Figure 3) contains about as much *d*₁ hexane as the hexene deuteration product (vide infra Table IV), which suggests that most of the *d*₁ product from hexane exchange might be an artifact due to unavoidable hydrogen dilution, as must be the case for the hexene deuteration product *d*₁.

The large abundance of the dideuterio product at low temperatures points to the relative importance of its precursor as an intermediate during the exchange reaction. High-resolution proton-decoupled ²H NMR spectroscopy (76.8 MHz) was used to determine the nature of the *d*₂ isomer resulting from *n*-hexane exchange. Deuterium isotope effects on chemical shifts through two and three bonds are well-known and can be used to distinguish between α - α , α - β , and dideuterio hexanes with separated deuterium atoms like α - γ or α - δ .¹³ Deuterium spectra are shown in Figure 11. The natural abundance peak of the cyclohexane used as the NMR solvent is visible in these spectra and served as a convenient internal standard (marked S). Chemical shifts are reported relative to Me₄Si-*d*₁₂. Spectrum A, the natural abundance spectrum of *n*-hexane, shows the chemical shift of the three monodeuterio *n*-hexanes. Since the isotope shift from a dideuterio α - γ interaction of 0.001 ppm is negligible,¹³ these also represent the chemical shifts expected for α - γ dideuterio hexanes.

(43) Van Hove, M. A.; Lin, R.; Somorjai, G. A. *Phys. Rev. Lett.* **1983**, *51* (9), 778.

(44) Koestner, R. J.; Van Hove, M. A.; Somorjai, G. A. *J. Phys. Chem.* **1983**, *87*, 203.

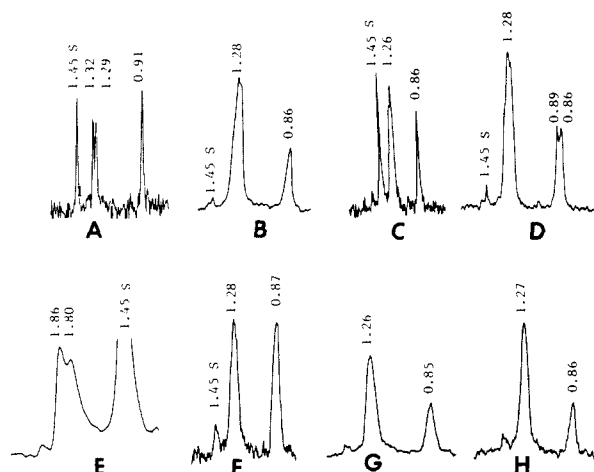


Figure 11. 76.8-MHz deuterium spectra of hydrocarbons in cyclohexane as solvent. The chemical shift relative to $\text{Me}_6\text{Si}-d_{12}$ is given in ppm on top of each peak; the natural abundance peak of the cyclohexane solvent (1.45 ppm, used as internal standard) is marked with S. A, *n*-hexane natural abundance spectrum; B, H/D exchange product of *n*-hexane on 11% Rh/alumina at 0 °C; C, H/D exchange product of *n*-hexane on 11% Rh/alumina at -18 °C; D, same as B spiked with 8% of 1,1-dideuterio-*n*-hexane; E, H/D exchange product of adamantane on 1% Rh/alumina at 80 °C; F, *n*-hexane formed by deuteration of 1-hexene on 11% Rh/alumina at 0 °C; G, *n*-hexane formed by deuteration of 2-hexene on 11% Rh/alumina at 0 °C; H, *n*-hexane formed by deuteration of 3-hexene on 11% Rh/alumina at 0 °C.

Table IV. Product Distributions, Chemical Shifts, and Integration Ratios Corresponding to ^2H NMR Spectra in Figure 11

| isomer | spectrum | | | | |
|---------------------------------------|----------|------|------|------|------|
| | B | C | F | G | H |
| d_1 | 18 | 14 | 19 | 16 | 16 |
| d_2 | 26 | 32 | 36 | 23 | 22 |
| d_3 | 14 | 10 | 18 | 16 | 14 |
| d_4 | 10 | 8 | 10 | 13 | 11 |
| d_5 | 7 | 7 | 5 | 10 | 9 |
| d_6 | 5 | 8 | 3 | 7 | 8 |
| d_7 | 4 | 5 | 2 | 5 | 7 |
| d_8 | 3 | 3 | 1 | 3 | 5 |
| d_9 | 2 | 2 | 1 | 2 | 3 |
| d_{10} | 2 | 1 | 1 | 2 | 2 |
| d_{11} | 2 | 2 | 1 | 1 | 2 |
| d_{12} | 2 | 2 | 1 | 1 | 1 |
| d_{13} | 2 | 2 | 1 | 1 | 1 |
| d_{14} | 1 | 3 | 0 | 0 | 1 |
| δ methylene | 1.28 | 1.26 | 1.28 | 1.26 | 1.27 |
| δ methyl | 0.86 | 0.86 | 0.87 | 0.85 | 0.86 |
| methylene- <i>d</i> /methyl- <i>d</i> | 3.1 | 2.1 | 1.1 | 2.2 | 3.2 |

The three geminal dideuterio hexanes were synthesized individually. Table III summarizes the chemical shifts of all mono and geminal dideuterio *n*-hexanes. For each of the three dideuterio *n*-hexanes, the resonance is shifted upfield by 0.02 ppm relative to the monodeuterio hexanes in agreement with the expected isotope effect on chemical shifts.¹³

The deuterium spectrum of a typical product mixture resulting from *n*-hexane exchange at 0 °C is shown along with that resulting from exchange at -18 °C (see Figure 11, spectra B and C). The isotopic distributions associated with spectra B and C are listed in Table IV.

Although the resolution of the methylene deuterium was rather poor in the product mixture (B and C), the presence of 26% and 30% d_2 product does allow a qualitative analysis. The presence of significant amounts of C-1 and C-2 mono and geminal dideuterio hexanes can be easily ruled out by the lack of signals, since these should be present at least as shoulders if not as distinct maxima in the spectra. This is demonstrated by spiking the product spectrum sample B with 8% of the synthetic sample of 1,1-dideuteriohexane (spectrum D) which shows that the chemical shift of the geminal d_2 hexane is well removed from the main

Table V. Product Distributions Obtained from H/D Exchange of Adamantane (aa) and 2,2,3,3-Tetramethylbutane (tmb) on 1% Rh/Alumina and Rh foil

| catalyst | 1% Rh | 1% Rh | Rh foil | Rh foil |
|----------------------------|-------|-------|---------|---------|
| hydrocarbon | aa | tmb | aa | tmb |
| % conversion | 7 | 4 | 10 | 3 |
| temp, °C | 74 | 109 | 101 | 208 |
| % d_1 isomer | 84 | 84 | 87 | 73 |
| % d_2 isomer | 14 | 10 | 12 | 13 |
| % d_3 isomer | 2 | 6 | 1 | 11 |
| % d_4 isomer | 0 | 0 | 0 | 3 |
| % d_5 and higher isomers | 0 | 0 | 0 | 0 |

portion of the methyl group signal. The 2,2-dideuteriohexane as well as the 1- and 2-monodeuterio hexanes are also well removed from the maxima in spectra B and C (see Table III). Thus the *n*-hexane- d_2 cannot be of the α - γ , 1,1, or 2,2 type. Hence, although the 3,3- d_2 product would lie in the center of the broad methylene signal, its presence can be ruled out by the lack of the expected sharp peak at 1.27 ppm. Furthermore, since there is no evidence for the formation of geminal dideuterio products at positions 1 and 2, the selective formation of such an isotopic isomer at position 3 is unlikely.

Since all other possibilities have been ruled out, these results suggest that the dideuteriohexane product results from the α - β diadsorbed intermediates identical with chemisorbed hexenes. Further support for α - β intermediates was obtained by the exchange of tetramethylbutane and adamantane (see Table V). If alkylidene intermediates accounted for the d_2 product then d_2 products should be especially prominent with these hydrocarbons since other competing processes such as α - β and π -allyl formation are impossible due to structural considerations. Tetramethylbutane, which cannot form α - β intermediates, indeed produces only d_1 exchange products ruling out geminal exchange propagation. It might be argued that the high bond energy of the exclusively terminal C-H bonds in tetramethylbutane may falsify the results. Adamantane, which has methylene hydrogens as well as β -hydrogens, was therefore also exchanged. Adamantane, due to the rigid skeleton, cannot form an unstrained olefin (orthogonal π -bond),⁴⁵ but the alkylidene formation should proceed readily. The exclusive formation of adamantane- d_1 , quite similar to that obtained by Schrage and Burwell with adamantane exchange on Pt,⁴⁶ is additional evidence against surface alkylidenes as direct precursors to the d_2 products. The ^2H NMR (spectrum E in Figure 11) spectrum of this adamantane- d_1 indicates that both positions in adamantane are exchanged with little selectivity.

Hexene Deuteration. Hexane H/D exchange and hexene deuteration should be closely linked, since they appear to share common surface intermediates. We therefore subjected 1-, 2-, and 3-hexenes to H/D exchange conditions on 11% Rh/alumina at 0 °C. The isotopic distributions and ^2H NMR spectra (Table IV and Figure 11, spectra F, G, and H) of the three hexenes are remarkably similar to those obtained from *n*-hexane H/D exchange. In addition, the chemical shifts and spectra integration results obtained from the hexane exchange products are characteristic of those obtained from hexenes. Integration of the 0 °C hexane exchange ^2H NMR spectrum (B) indicates that activation of methylene C-H bonds is favored over methyl C-H bonds at this temperature since the methylene to methyl deuterium content ratio of 3.1:1 at 0 °C and 2.1:1 at -18 °C (C) is considerably higher than the statistical value of 1.3. The hexene deuteration results suggest that at 0 °C, in addition to the α , β dideuteration of the olefinic double bond, π -allyl activation to the terminal carbon must occur to a large extent since both 2- and 3-hexene deuteration products (G and H) contain significant amounts of deuterium in the methyl position (2.2:1 and 3.2:1, respectively). In contrast, the methylene to methyl deuterium content ratio of 1.1 resulting from 1-hexene deuteration (F) is close to the value of 1.0 expected in the absence of migration away

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(46) Schrage, K.; Burwell, R. L., Jr. *J. Am. Chem. Soc.* **1966**, *88*, 4555.

Table VI. Product Distribution of H/D Exchange of *n*-Pentane, *n*-Octane, and 1-Octene Obtained on 11% Rh/Alumina at 0 °C

| isomer | <i>n</i> -pentane ^a | <i>n</i> -octane ^b | 1-octene ^c |
|------------------------|--------------------------------|-------------------------------|-----------------------|
| <i>d</i> ₁ | 5 | 7 | 12 |
| <i>d</i> ₂ | 24 | 32 | 30 |
| <i>d</i> ₃ | 11 | 13 | 18 |
| <i>d</i> ₄ | 9 | 11 | 14 |
| <i>d</i> ₅ | 9 | 8 | 7 |
| <i>d</i> ₆ | 9 | 7 | 5 |
| <i>d</i> ₇ | 8 | 8 | 3 |
| <i>d</i> ₈ | 4 | 7 | 2 |
| <i>d</i> ₉ | 4 | 5 | 1 |
| <i>d</i> ₁₀ | 4 | 3 | 1 |
| <i>d</i> ₁₁ | 5 | 0 | 1 |
| <i>d</i> ₁₂ | 8 | 0 | 1 |
| <i>d</i> ₁₃ | | 0 | 1 |
| <i>d</i> ₁₄ | | 0 | 1 |
| <i>d</i> ₁₅ | | 0 | 1 |
| <i>d</i> ₁₆ | | 0 | 0 |
| <i>d</i> ₁₇ | | 0 | 1 |
| <i>d</i> ₁₈ | | 0 | 2 |

^a 3% conversion. ^b 2% conversion. ^c 100% conversion.

from the terminus. The integrations and chemical shifts of spectra B and C, and G and H seem to suggest that the α,β -activation in *n*-hexane is located at carbons 2 and 3, producing predominantly 2- and 3-hexenes as initial surface intermediates.

Exchange of Other Alkanes and Olefins. To confirm that the *d*₂ maxima and their relation to olefinic intermediates are not unique to *n*-hexane, we studied the product distribution for *n*-pentane, *n*-octane, and 1-octene deuteration at 0 °C on the 11% Rh/alumina catalyst. As shown in Table VI, the isotopic distribution is not affected by the different methylene/methyl ratios supporting the general importance of olefinic intermediates on Rh.

On Pt it was found that the perdeuteration process occurs mainly through π -allyl or higher π -adsorbed interconversions.⁹ Although it is likely that Rh, with its strong tendency to form α,β adsorbed intermediates, will also prefer this mode of deuteration propagation, some additional evidence supporting this hypothesis had to be obtained. The H/D exchange pattern at low conversion was obtained for 2,2-dimethylbutane and 2,2-dimethylpentane (see Table VII). Exchange conditions were chosen where *n*-hexane produces mainly a strong perdeuteration maximum to emphasize polydeuteration conditions. As shown in Table VII, the 2,2-dimethylbutane, incapable of forming allylic intermediates, does not form the *d*₃ maximum expected for complete exchange in the ethyl side chain, while the 2,2-dimethylpentane, capable of π -allyl intermediates, clearly shows the expected perdeuteration to *d*₇ in the propyl side chain. The relative conversions as well as the product distributions indicate that there is a significant difference in the activation of these two hydrocarbons, most likely for steric reasons. The polydeuteration maximum in the exchanged 2,2-dimethylpentane clearly supports the importance of the π -allyl interconversion for exchange propagation. In fact, comparison with the patterns obtained for Pt indicates that the π -allyl argument applies to the Rh more strongly.

Dependence of Exchange Rate on Hexane and Deuterium Pressure. Applying a large excess of deuterium to hexane (>100:1), a 0.61 ± 0.06 and 0.02 ± 0.2 order dependence on hexane and deuterium, respectively, was obtained. The *n*-hexane order was determined from 6 points over a pressure range of 1.1–6.4 Torr at a D₂ pressure of 1 atm and the deuterium dependence from 4 points over a pressure range from 208 to 760 Torr with a *n*-hexane pressure of 1 Torr. These results can be compared to those obtained by Anderson and Kemball for ethane⁴⁷ and propane⁴⁸ exchange on Rh films, where the orders in alkane were 0.8 and 0.5, respectively, and the orders in deuterium were –0.7 and –0.8, respectively, and to ethane and deuterium orders

of 1.2 and –0.55 obtained on Pt (111) single crystals.⁴⁹ The ratio of deuterium to alkane was higher in our study. With a large excess of deuterium it is not surprising to find a zero-order dependence on deuterium pressure. Such positive order in alkane and zero to negative order in deuterium are most consistent with the oxidative addition of alkane as the rate-determining step. This conclusion seems convincing considering that the reaction is occurring on a surface saturated with deuterium, which, as expressed in negative orders, can successfully block active sites for C–H activation.

Activation Energies for Exchange. The next question addresses the nature of the initial C–H activation step at low temperatures. The lack of *d*₁ maxima suggests that there may be no significant amount of surface alkyls formed on rhodium but only π , allyl, or higher coordinated intermediates responsible for the bulk of the exchanged products. This, however, would require that there is either a concerted activation process operating, where two adjacent C–H bonds are activated simultaneously, as suggested by Dessauges and Gäumann for exchange on nickel,^{11a} or a concerted C–H activation process in which the second C–H bond is activated with little or no activation barrier. To test this hypothesis, the activation barriers for H/D exchange of selected hydrocarbons were determined on two catalysts of extreme dispersion, the 1% Rh/alumina and the Rh foil. The 1% Rh catalyst with a dispersion of over 90% (average particle size <10 Å) can be considered to have exclusively high energy surface sites (kinks) while the surface of the Rh foil can be considered to consist mainly of terrace atoms of the (111) and (100) type. To distinguish between different activation processes, the activation barrier for H/D exchange was determined for *n*-hexane and *n*-octane, both capable of α,β -intermediates, adamantane, which has secondary and tertiary C–H bonds as well as hydrogens on all adjacent carbons but is incapable of the formation of stable olefins due to its rigid cage structure, and 2,2,3,3-tetramethylbutane, which has only primary C–H bonds and has no hydrogens on adjacent carbons.

Arrhenius plots for the H/D exchange of *n*-hexane, *n*-octane, 2,2,3,3-tetramethylbutane, and adamantane on 1% Rh/alumina and Rh foil are shown in Figures 12 and 13 (see also Table VIII). These data were obtained by monitoring the conversion as a function of temperature on a given catalyst sample during a continuous experiment. The activation barrier was obtained by the Arrhenius data in the form $E_{act} = -(R) \ln(\text{conv}_a/\text{conv}_b)/(1/T_a - 1/T_b)$. This allowed the determination of the activation barrier even when the exact addition rate of hydrocarbon was not accurately known, provided that conditions at the various temperatures were identical with respect to hydrocarbon addition rates etc. during a given experiment. This method was desirable since adamantane (melting point 205 °C) cannot be added conveniently at a known rate to the gas-phase hydrogen stream. Adamantane and 2,2,3,3-tetramethylbutane were evaporated by heating in the stream of deuterium at 30 °C. Hexane and octane were added via syringe pump.

On the 1% Rh catalyst, which does not produce distinct *d*₂ maxima at the temperatures studied, the activation energies for all four hydrocarbons were determined to 20–25 kcal/mol^{–1} (see Figure 12). Considering the range of C–H bond energies (isolated terminal, primary, secondary, and tertiary C–H bonds are represented) and structures this suggests that C–H activation on small Rh particles is a stepwise process which is rather insensitive to the nature of the C–H bond to be activated. This appears to be in contrast to previous studies, where differences in activation energy were attributed to differences in C–H bond energies.⁵⁰

On the foil, however, the activation energies for exchange of the molecules capable of facile olefin formation, *n*-hexane and *n*-octane, are considerably lower at 5 and 9 kcal/mol^{–1}, while the activation barrier for adamantane and 2,2,3,3-tetramethylbutane exchange remains near 20 kcal/mol^{–1}.⁵¹ This is direct evidence

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(48) Kemball, C. *Proc. R. Soc.* **1954**, *223*, 376.

(49) Zaera, F.; Somorjai, G. A. *J. Phys. Chem.* **1985**, *89*, 3211.

(50) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Reidel: Dordrecht, 1984; p 191.

Table VII. Isotopic Exchange Patterns Obtained at 70 °C on 11% Rh/Alumina under Identical Conditions (Pt Data from ref 9)

| compound | catalyst | conversion, % | d_1 | d_2 | d_3 | d_4 | d_5 | d_6 | d_7 | d_8 |
|----------------------|----------|---------------|-------|-------|-------|-------|-------|-------|-------|-------|
| 2,2-DMB ^a | Rh | 4 | 17 | 23 | 31 | 15 | 12 | 1 | 0 | 0 |
| | Pt | 3 | 54 | 17 | 18 | 6 | 3 | 2 | 0 | 0 |
| 2,2-DMP ^b | Rh | 23 | 9 | 12 | 6 | 10 | 18 | 19 | 28 | 0 |
| | Pt | 12 | 48 | 10 | 7 | 8 | 9 | 9 | 8 | 0 |

^a2,2-DMB = 2,2-dimethylbutane. ^b2,2-DMP = 2,2-dimethylpentane.

Table VIII. Activation Energies for H/D Exchange of Various Hydrocarbons on 1% Rh/Alumina and Rh Foil

| hydrocarbon | catalyst | activation energy (kcal/mol) |
|---------------------------|---------------|------------------------------|
| <i>n</i> -hexane | 1% Rh/alumina | 20 |
| | Rh foil | 5 |
| adamantane | 1% Rh/alumina | 21 |
| | Rh foil | 18 |
| 2,2,3,3-tetramethylbutane | 1% Rh/alumina | 21 |
| | Rh foil | 22 |
| <i>n</i> -octane | 1% Rh/alumina | 25 |
| | Rh foil | 9 |

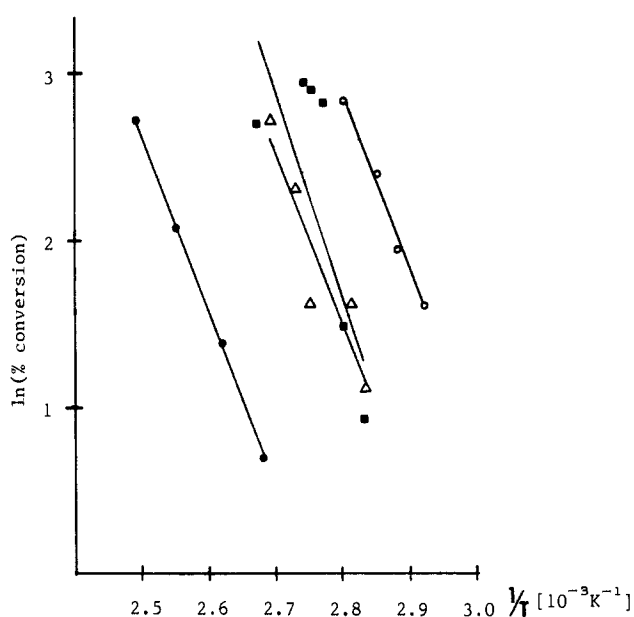


Figure 12. Arrhenius plots for the H/D exchange of the hydrocarbons indicated on 1% Rh/alumina: ●, 2,2,3,3-tetramethylbutane ($E_a = 21$ kcal/mol); Δ, *n*-hexane ($E_a = 20$ kcal/mol); ■, *n*-octane ($E_a = 25$ kcal/mol); ○, adamantane ($E_a = 21$ kcal/mol).

for a concerted α,β -activation process of linear alkanes on the Rh foil (terrace surfaces). The high activation barrier for adamantane, where β -hydrogens are present but cannot be activated as readily for the formation of olefinic intermediates, especially emphasizes the presence of a concerted process in the linear alkanes. Further qualitative support for this hypothesis is provided by the d_2 maxima produced on Rh foil with the linear alkanes in the temperature range studied, while tetramethylbutane and adamantane only exhibit the d_1 maximum. Scheme II illustrates the mechanism suggested for a concerted activation of adjacent C-H bonds, in which the two hydrogens simultaneously slip into the two surface holes while the olefin formed interacts initially as a π -complex with this surface atom. It can be argued that such a synchronous process is unlikely for simple entropic reasons, but the basic mechanism would not be affected if the two C-H bonds are not activated simultaneously but in a sequential manner as long as there is no additional barrier and the adjacent C-H bond is able to contribute enough surface bonding to cause the observed re-

(51) No evidence for mass transfer or diffusion effects was obtained. The activation energies are consistent with those obtained under a variety of conditions, including much lower temperatures (vide infra).

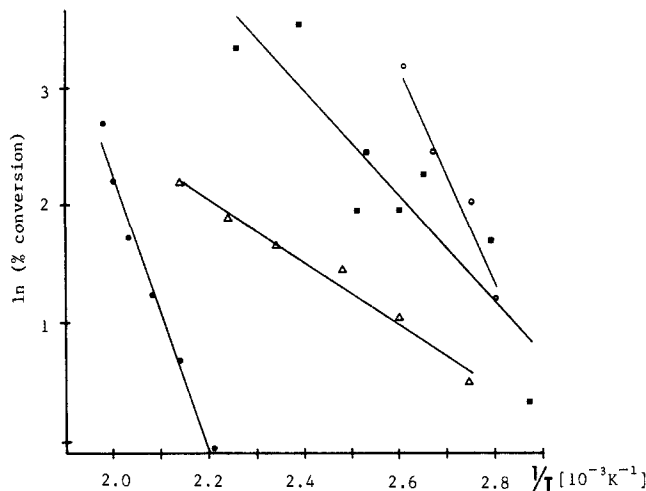
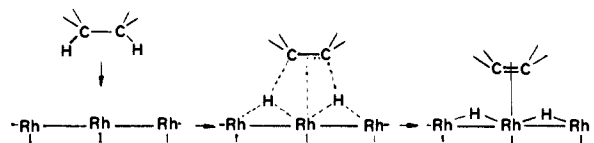


Figure 13. Arrhenius plots for the H/D exchange of the hydrocarbons indicated on Rh foil: ●, 2,2,3,3-tetramethylbutane ($E_a = 22$ kcal/mol); Δ, *n*-hexane ($E_a = 5$ kcal/mol); ■, *n*-octane ($E_a = 9$ kcal/mol); ○, adamantane ($E_a = 18$ kcal/mol).

Scheme II. Schematic Representation of the Concerted Activation of Adjacent C-H Bonds under Formation of a Surface Olefin (α,β -Intermediate)



duction of the activation energy relative to isolated C-H bonds.

Although this mechanism occurring on the Rh foil appears unprecedented, two phenomena in homogeneous chemistry, β -elimination⁵² and agostic interactions,⁵³ seem particularly relevant. Such a concerted mechanism may be widespread in heterogeneous catalysis. For example, it may contribute to some extent on other metals, where its detection might be prevented as a result of other competing processes, such as facile allylic activation.

More important than the evidence for a concerted C-H activation process under formation of surface alkenes is the surface structure sensitivity of this process. Our results suggest that on Rh terraces a second mechanism with a lower activation barrier is operating which clearly discriminates between hydrocarbons able to form surface olefins and those which are not. This means that there are two mechanisms for C-H activation on Rh, the activation of a single C-H bond and a concerted process involving simultaneous activation of two adjacent C-H bonds. While the first process, which occurs predominantly on dispersed Rh particles, is independent of hydrocarbon structure, the second process dominates on terrace surfaces and requires a hydrocarbon structure capable of facile formation of surface olefins. The first process appears to be similar to the C-H activation mechanism identified on Pt.⁹ This is also supported by the d_1 maximum obtained with *n*-hexane exchange on the 1% Rh catalyst at higher temperatures,

(52) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 1120.

(53) (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) Cracknell, R. B.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1984**, 326.

which is very similar to the exchange pattern obtained with Pt.⁹

An Arrhenius plot of the d_{3-14} products from *n*-hexane exchange on Rh foil yields an activation barrier of 6 kcal/mol (1 kcal/mol higher than the overall activation barrier), indicating that the loss of the d_2 maximum at higher temperatures results from the rather small 1 kcal/mol barrier from π to allylic activation. In contrast, no such barrier exists for Pt.⁵⁴

The difference in activation barriers and exchange patterns obtained for *n*-hexane on Rh foil and dispersed Rh suggested a strong preference of Rh terraces for the generation of olefinic intermediates (see above). To see whether such a preference is also reflected in the activation barriers for olefin hydrogenations, we attempted to determine the activation barriers for 1-hexene hydrogenation under gas phase flow conditions in the temperature range between 20 and 120 °C. However, the activation barriers determined for 1-hexene on Rh foil as well as on the 1% Rh/alumina were found to be zero at these conditions; the reaction was zero order in hexene and 0.9 order in hydrogen with a turnover frequency of 250 molecules per surface site and second. Zero order in olefin concentration has been reported also by Bond et al.⁵⁵ Zero activation barriers either indicate mass transport effects or (since those are unlikely in reactions on solid metal foils in the absence of support) the activation of hydrogen as the rate-determining step which is more consistent with the observed 0.9 order in hydrogen. Hydrogen activation as rate-determining step has been detected in H/D exchange studies on Pt single crystals.⁵⁶ That such data do not necessarily contradict previous studies was shown by Beebe and Yates, who reported in recent studies on the hydrogenation of ethylene on Pd reaction rates which decrease with increasing temperature (negative activation barrier) and concluded "The observed decrease in reaction rate with temperature has prevented us from obtaining a meaningful activation energy. It suggests that the equilibrium surface concentration of reactant species...decreases as temperature increases, leading to lower rates."³⁸ This result suggests that in the presence of a large excess of olefins the rate-limiting step for olefin hydrogenation is not the reductive elimination but hydrogen chemisorption.

Conclusion

C-H activation is catalyzed directly by the metal surface. Evidence against the participation of carbonaceous material in the active site has been obtained. The only way carbon layers can participate in this C-H activation is if product compositions and reaction rates on such overlayers are indistinguishable from those on the Rh surface.

C-H activation of alkanes on heterogeneous Rh catalysts is initiated by two different mechanisms. Mechanism one, the simple oxidative addition of a single C-H bond, is favored on dispersed Rh particles, hydrocarbon structure insensitive, and has an activation barrier of about 21 kcal/mol. The concerted oxidative addition of two adjacent C-H bonds under formation of a surface olefin (activation barrier 5-9 kcal/mol) dominates on terrace surfaces and requires hydrocarbon structures capable of olefin formation. The d_2 maximum, formed from surface olefins, decreases with increasing dispersion and temperature.

Because of the apparent involvement of surface olefins in the C-H activation of alkanes on Pt we had pointed in a previous paper to an apparent discrepancy.⁹ Although H/D exchange and olefin hydrogenation are believed to occur through the same rate-determining step (reductive elimination of a surface alkyl), they show drastically different rates and activation barriers. After this study the solution to the problem appears obvious. The two processes must occur with different rate-determining steps, since the rates and activation barriers for the two processes are quite different. Since *n*-hexane initially forms a surface olefin, the rate-determining step in H/D exchange must be the oxidative addition of *n*-hexane. The different order dependences of these processes support this

hypothesis. C-H activation is near first order in hydrocarbon and close to zero order in hydrogen. Apparently the catalyst under C-H activation conditions has a lower surface coverage of chemisorbed hydrocarbons while surface hydrogen is present in abundance. Olefins, on the other hand, do not have an activation barrier for chemisorption and their high surface affinity is responsible for a drastic change in reaction orders—generally zero to negative order in alkene and positive order in hydrogen, indicating that either reductive elimination or H₂ activation is rate determining. We are presently engaged in the determination of surface concentrations and thermochemistry of olefins and hydrocarbons on Rh under exchange conditions to finally clarify the difference between olefin hydrogenation and alkane H/D exchange.

Experimental Section

General. All hydrocarbons (analytical grade) were screened for purity by GC/MS and used as obtained. Deuterium gas was generated by electrolysis of 99.9% deuterium oxide in a General Electric Model 15EHG3B1 hydrogen generator. House oxygen was passed through alumina and potassium hydroxide. In addition, all gases were passed through 4 Å molecular sieves. Gas flows were monitored with Matheson 8141 and 8143 mass flow detectors. Exchange products were analyzed either with a Hewlett Packard 5970A mass selective detector interfaced with a HP 5790A GC containing a 50 m cross-linked methyl silicone column and controlled by a HP 59970A Workstation or a Dycor Model M200M quadrupole mass spectrometer with electron multiplier. In all cases appropriate ions were monitored and corrected for natural heavy isotope abundance contributions. M - 1 fragmentation contributions were found to be negligible, except with adamantane where the correction was not necessary due to low conversion and the d_1 maximum. Low conversions were maintained to minimize multiple interactions between the catalyst and substrate. In addition, a large excess of deuterium to hydrocarbon was used. The reduction pretreatment temperatures were high enough to fully reduce the catalyst as confirmed by on line MS analysis of the water produced during temperature-programmed reduction from room temperature to 400 °C. ¹H NMR spectra were obtained on the UCB 200 MHz spectrometer. ²H NMR spectra were obtained at 76.8 MHz on a Bruker AM-500 spectrometer. Broadband proton decoupling was used to simplify the ²H spectra.

Rhodium foil, 99.9% pure, 0.025 mm, was used as received. All other catalysts were prepared as indicated. In catalytic experiments the catalyst was either unused or regenerated by high-temperature oxidation, unless a different treatment is specified. The alumina was high purity neutral—60 mesh.

Preparation of Rh on Alumina Catalysts. The procedure for the preparation of the 1% catalyst is representative. Rhodium chloride trihydrate (0.1554 g) was dissolved in a minimum amount of deionized water. With frequent vigorous shaking, this solution was added dropwise to the alumina (6.00 g) until persistent clumping was observed and then dried at 95 °C. This pore saturation-drying cycle was repeated until all of the rhodium chloride solution was deposited on the alumina. The catalyst was then activated in a steady flow of hydrogen for 45 min at 150 °C and then for 8 h at 200 °C. In preparation of the 0.1% catalyst, the minimum amount of water required to dissolve the rhodium chloride trihydrate was less than that required to saturate the alumina being used. In this case the solution was prepared with enough water to saturate the pores. The low dispersed 25% rhodium catalyst was reduced following the above procedure, oxidized at 700 °C for 30 min, reduced with hydrogen at 200 °C for 30 min, and annealed in helium at 1000 °C for 30 min.

Dispersion Determination. The catalyst surface area was determined by the standard hydrogen chemisorption method.⁵⁷ Samples were evacuated to 1 mTorr at 100 °C. At 100 °C, 200 Torr of hydrogen was introduced and after 30 min the sample was evacuated to less than 10 mTorr. Once again, 200 Torr of hydrogen was added and the sample holder was evacuated as above, and the catalyst was allowed to reduce for several hours at 100 °C under 200 Torr of hydrogen. After 4 h at 1 mTorr and 100 °C the sample was ready for hydrogen chemisorption measurements. At room temperature, several adsorption points were taken ranging from 40 to 250 Torr of hydrogen. Extrapolation to zero pressure, assuming a stoichiometry of one hydrogen atom per active site, provided the total number of surface atoms. From these data and the total Rh content of the catalyst the dispersion was determined.

Exchange Reactions above Room Temperature. For exchange reactions above room temperature the catalyst was heated in a vertical flow

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reactor tube (i.d. 6 mm) by a resistive tube oven regulated by an Omega Model 149 temperature controller. The catalyst was activated for 4 h under a steady stream of deuterium at 120 °C or at reaction temperature, if it exceeded 120 °C. The temperature was then set to the desired level and allowed to equilibrate. The substrate was added via syringe pump into the gas flow. The product was trapped at -198 °C and dissolved in an appropriate solvent for GC/MS and/or ^2H NMR analysis. In addition, the product was continuously monitored by on-line MS before the cold trap. To assure constant conditions⁹ the catalyst bed size was kept constant by addition of alumina. Unless otherwise indicated, standard conditions were used in all exchange reactions. These conditions consisted of a deuterium flow of 20 mL min⁻¹ and a hydrocarbon addition rate of 1.1 μL min⁻¹.

Low-Temperature Exchange Reactions. A U-tube reactor was used for reactions below room temperature to allow sequential heating and cooling with oil and cold baths for catalyst activation and reaction. The catalyst was reduced at 120 °C for 1 h under a stream of deuterium and then cooled and equilibrated to reaction temperature. Substrate addition and analysis proceeded in an analogous manner to the high-temperature procedure.

Carbonaceous Layer Studies. The Rh black (1.75 g) was mixed with about 1 g of sand to provide mechanical support. Appropriate blank runs were performed on a sand sample without Rh. In these studies, the freshly oxidized catalyst was reduced with deuterium for 1 h at 200 °C and then set to the desired temperature. For the 80 °C experiments the deuterium flow and hexane addition rates were 10 mL min⁻¹ and 0.5 mL h⁻¹, respectively. 20 mL min⁻¹ and 1.0 mL h⁻¹ respectively were used for the 400 °C experiments. In both cases, the catalyst activity was determined under the following standard conditions: the catalyst was cooled to 30 °C and 50 μL of *n*-hexane (addition rate 8.1 μL min⁻¹) were exchanged with a deuterium flow of 40 mL min⁻¹; the product was analyzed by GC-MS. The catalyst was then heated to 80 °C and left under a stream of deuterium for 1 h to remove weakly adsorbed carbonaceous deposits. The catalyst was then cooled to room temperature, purged briefly with He, and then heated to 400 °C over a period of 8 min under a 15 mL min⁻¹ oxygen flow. The oxidation was monitored by on-line MS. The quantitative determination of the carbon was obtained by integration of the intensity vs. time curve for CO₂. Immediately after the oxidation of the catalyst was complete, a known amount of *n*-hexane was injected into the oxygen flow at 400 °C and its oxidation product CO₂, formed on the catalyst, was monitored to provide a calibration for the quantification of the CO₂. Increase of the oxidation temperature to 650 °C did not produce any additional CO₂ formation, indicating that the 400 °C oxidation was sufficient. Similar analysis of hexane injections showed that less than 10⁻⁶ g of carbon could be detected by this procedure. Control experiments showed that the conversion to CO₂ was complete in all oxidation procedures.

Synthesis of Geminal Dideuteriohexanes. Similar procedures were employed for the synthesis of 1,1-, 2,2-, and 3,3-dideuteriohexanes, starting from hexanal, 2-hexanone, and 3-hexanone, respectively. The synthesis of the 1,1 case is representative.

1-Deuterio-1-hexanol (1). To 30 mL of ether containing LiAlD₄ (0.44 g, 10.5 mmol) was added a solution of freshly distilled hexanal (3.8 g, 38 mmol) in 3 mL of ether at a rate sufficient to maintain reflux. After addition was complete, reflux was maintained for 45 min. The mixture was cooled with an ice bath and quenched with 10 mL of water. Cold 10% sulfuric acid (20 mL) was added, and the aqueous layer was extracted with two 25-mL ether fractions. The combined ether fractions were washed with water and saturated NaHCO₃ and dried (MgSO₄). Removal of ether by simple distillation afforded 3.4 g (87%) of the alcohol **1**: ^1H NMR (CDCl₃) δ 3.6 (br m, 1 H), 1.4 (br m, 8 H), 0.8

(br s, 3 H); mass spectrum, *m/z* (rel intensity) 86 (1), 85 (13), 70 (81), 56 (100), 55 (99), 44 (51), 41 (68).

1-Deuteriohexyl Tosylate (2). To an ice bath cooled solution of 60 mL of pyridine and **1** (3.4 g, 33 mmol) was added tosyl chloride (12.6 g, 66 mmol). The mixture immediately darkened and began to precipitate pyridinium hydrochloride. After sitting at 0 °C for 18 h, the mixture was poured onto 300 g of ice water. The product was extracted with two 50-mL ether fractions. The combined ether portions were washed with 20% HCl and then with water. After drying (K₂CO₃/Na₂SO₄), rotary evaporation yielded 7.5 g (89%) of the tosylate **2**: ^1H NMR (CDCl₃) δ 7.7 (m, 2 H), 7.4 (m, 2 H), 4.0 (m, 1 H), 2.3 (s, 3 H), 1.6 (m, 2 H), 1.2 (br m, 6 H), 0.8 (t, 3 H).

1-Bromo-1-deuteriohexane (3). To 200 mL of acetone (freshly distilled from K₂CO₃) was added **2** (7.5 g, 29 mmol) and anhydrous lithium bromide (7 g, 80 mmol). After refluxing for 3.5 h, the precipitate was removed by filtration, and most of the acetone was removed by rotary evaporation. The remaining mixture was extracted with 75 mL of ether. The ether layer was washed with saturated aqueous NaCl and water and dried with MgSO₄. Simple distillation afforded 2.3 g (48%) of the bromide **3**: ^1H NMR (CDCl₃) δ 3.4 (m, 1 H), 1.8 (m, 2 H), 1.3 (m, 6 H), 0.8 (t, 3 H); mass spectrum, *m/z* (rel intensity) 167 (1), 165 (1), 138 (43), 136 (45), 86 (45), 56 (65), 44 (73), 43 (100), 42 (44), 41 (65).

1,1-Dideuteriohexane (4). The bromide **3** (0.70 g, 4.2 mmol) was added to 0.7 mL of ether (distilled from LiAlH₄). A flask containing Mg turnings (0.16 g, 6.7 mmol) in 1.4 mL of ether was charged with 0.3 mL of the bromide solution. After initiation of the reaction, the remaining bromide solution was added at a rate sufficient to maintain reflux. After addition was complete the mixture was refluxed for an additional 20 min, cooled in an ice bath, and quenched by slow addition of deuterium oxide. The ether layer was separated and the dideuteriohexane **4** was isolated by preparative GC. GC/MS yield of **4** was ca. 90%, with the major side products being 1-deuteriohexane (9%) and a small amount of *n*-hexane.

Determination of Activation Energies. The catalyst sample was maintained at the required temperature, which was continuously monitored. During a single experiment, the conversion (fraction of molecules which incorporate deuterium) was monitored over a range of temperatures. While *n*-hexane and *n*-octane were conveniently added via syringe pump, addition of tetramethylbutane and adamantane at a known rate was more difficult due to their relatively low volatility. These hydrocarbons were evaporated at 30 °C into the deuterium stream in front of the catalyst and oven. Furthermore, since this temperature was lower than that of the catalyst sample, the varying of temperature of the catalyst region had no effect on the flux of alkane molecules during the entire set of experiments on a given catalyst sample. Deuterium flow rates were constant at 15 mL/min. While this method allowed accurate determination of activation energies, frequency factors are not determined since relative rather than absolute rates are used. Reaction orders were determined by varying the relative amount of hydrogen/deuterium or hexane, while holding the other constant. Helium was introduced as a third gas to maintain a total pressure of 1 atm.

Activation energies for hydrogenation of 1-hexene were measured with an alkene addition rate of 1.1 μL /min and a hydrogen flow rate of 15 mL/min over a temperature range of 20 to 130 °C. Because of the high rate of this reaction, unused tubing and glass were employed (used glassware was found to efficiently catalyze the hydrogenation).

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