

C-H Activation on Platinum, a Mechanistic Study

Carlito B. Lebrilla and Wilhelm F. Maier*

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. Received September 9, 1985

Abstract: C-H activation on heterogeneous Pt catalysts is found to be most facile at low Pt dispersion and surface structure insensitive at dispersions above 10%. Two distinct processes have been identified which lead to the formation of mono- and polydeuterated products, respectively. The ratio of mono-/polydeuteration processes increases with increasing dispersion. Evidence is provided for the formation of π -intermediates as the initiator of polydeuteration. The most facile mechanism of exchange propagation in a single molecule is through a π -allyl-type interconversion. The deuterium in monodeuterated *n*-hexane is located at the terminal position by high-resolution deuterium NMR. NMR spectroscopy also provides evidence for steric effects which prevent significant H/D exchange at positions close to quaternary centers. C-H activation appears to be sensitive to steric hindrance, the C-H bond energy, and the partial pressure of the substrate.

The lack of understanding of the activation of C-H bonds in alkanes as a fundamental process in catalytic organic chemistry has already stimulated intensive research in many areas of chemistry. The mechanism of C-H activation has been studied intensively on supported catalysts,¹⁻³ with isolated metal atoms,⁴ on defined surfaces,⁵ and by theoretical methods.⁶ The successful activation of alkanes by homogeneous transition-metal complexes⁷ has generated renewed interest in C-H activation. However, with the increasing wealth of information the likelihood of deriving a simple and comprehensive description of this reaction seems further away than ever.

The importance of C-H activation, however, is its key position in the mechanistic interpretation of the many important reactions based on the refinement of saturated hydrocarbons. C-H activation in heterogeneous catalysis, investigated predominantly by isotopic exchange and kinetic studies, was the subject of intensive studies in the 60s and early 70s. Many of the problems connected to C-H activation in heterogeneous catalysis have been identified and reviewed and possible mechanistic pathways have been proposed and discussed.¹⁻³ However, despite the immense effort dedicated to such mechanistic studies little precise insight has been achieved. Gault concluded in 1979 that indeed, "the reaction mechanisms in heterogeneous catalysis are much less understood than in homogeneous catalysis"; and he reasons "a reaction catalyzed heterogeneously is always very complex, on account of the extreme complexity of the solid-gas (or solid-liquid) interface" and "the extreme difficulty of characterizing a reaction intermediate in heterogeneous catalysis".⁸

Probably the most detailed knowledge about C-H activation as well as the most precise thermodynamic parameters have been

obtained in homogeneous chemistry.⁷ Most C-H activation studies in homogeneous chemistry, however, are based on complexes with only one central atom which at most resemble atomically dispersed catalysts. In addition, our lack of precise knowledge about the importance of steric effects induced by the particular choice of ligands, the extreme reaction conditions, the actual role of the nature of the central atom, as well as the lack of mechanistic understanding of alkane activation^{7c} gave us the impression that a direct comparison of the homogeneous and heterogeneous C-H activation is yet premature.

What Is Known About the Mechanism and the Nature of C-H Activation on Heterogeneous Catalysts? H/D exchange studies with ethane on heterogeneous catalysts in 1954 showed a variation in the activation barrier for the exchange reaction from 6 (Ni) to 21 kcal/mol (Pd). In addition the deuterium distribution produced was found to be a function of the catalyst metals. Whereas W, Mo, Ta, and Ni exhibit d_1 maxima with statistical fall-off at the higher deuterated isomers, Pd and Rh show a d_6 maximum. In contrast Zr, Cr, V, and especially Pt show mono- and perdeuterated maxima.⁹ A similar sensitivity to the transition metal was reported in H/D exchange experiments with methane; the activation barriers as well as the exchange pattern were found to change from W, Ta, and Mo with dominant d_1 , to Re, Pd, and Pt with d_1 and d_4 maxima, to Rh and Ni where perdeuterated appears to dominate.¹⁰ Further evidence for this element sensitive nature¹¹ of C-H activation is documented by exchange studies with polymethylcyclopentanes.¹² H/D exchange of 1,1,3,3-tetramethylcyclopentane on Pt produced predominantly d_1 isomers from 0 to 30 °C at low conversion. Rh exhibited a d_2 maximum at lower temperatures which converts into a d_4 maximum at 30 °C. Pd showed equal amounts of d_1 and d_2 ; and Ni at high temperatures produced distinct d_1 and d_4 maxima.¹²

Several review articles¹⁻³ on the mechanism of C-H activation are helpful introductions to the complexity faced in attempting to solve such a challenging problem. Unfortunately, they are also quite confusing due to the lack of molecular data we are accustomed to from homogeneous chemistry. The confusion generated by the information in the various articles, however, cannot be blamed only on the complexity of heterogeneous reactions but also on the fact that most of the data these mechanistic interpretations are based on were derived from studies on Pd and/or a variety of different transition metals under various conditions. In addition, the H/D exchange experiments at that time could only be analyzed by MS which is incapable of locating the exact positions of the deuterium atoms in the exchanged hydrocarbon. Speculation is therefore still the dominant basis of our mechanistic understanding of C-H activation on heterogeneous catalysts. Insufficient at-

(1) Trapnell, B. M. W. In "Catalysis"; Emmet, P. H., Ed.; Reinhold Publishing Corp.: New York, 1955; Vol. III. Taylor, T. I. *Ibid.* 1957; Vol. V. Anderson, J. R. *Rev. Pure Appl. Chem.* 1957, 165. Kemball, C. *Adv. Catal.* 1959, 11, 223. Emmett, P. H. *Catal. Rev.* 1972, 7, 1. Ozaki, A. "Isotopic Studies of Heterogeneous Catalysis"; Academic Press: New York, 1977.

(2) Burwell, R. L., Jr. *Acc. Chem. Res.* 1969, 2, 289.

(3) Clarke, J. K. A.; Rooney, J. J. *Adv. Catal.* 1976, 25, 125.

(4) Remick, R. J.; Asunta, T. A.; Skell, P. S. *J. Am. Chem. Soc.* 1979, 101, 1320. Ozin, G. A.; McIntosh, D. F.; Mitchell, S. A.; Garcia-Prieto, J. *Ibid.* 1981, 103, 1574. Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Ibid.* 1981, 103, 962. Klabunde, K. J.; Tanaka, Y. *J. Am. Chem. Soc.* 1983, 105, 3544.

(5) Davis, S. M.; Somorjai, G. A. *J. Phys. Chem.* 1983, 87, 1545.

(6) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* 1984, 106, 2006. Baetzold, R. C. *J. Am. Chem. Soc.* 1983, 105, 4271.

(7) (a) Parshall, G. W. *Acc. Chem. Res.* 1975, 8, 113. Shilov, A. E.; Shteinman, A. A. *Coord. Chem. Rev.* 1977, 24, 97. Crabtree, R. H.; Demou, P. C.; Eden, D.; Mihelcic, J. M.; Parnell, C. A.; Quirk, J. M.; Morris, G. E. *J. Am. Chem. Soc.* 1982, 104, 6994. Baudry, D.; Ephritikhine, M.; Felkin, H.; Zadrewski, J. *J. Chem. Soc., Chem. Commun.* 1982, 1235. Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* 1983, 105, 7190. Wax, M. J.; Stryker, J. M.; Buchanan, J. M.; Kovac, C. A.; Bergman, R. G. *J. Am. Chem. Soc.* 1984, 106, 1121 and references therein. (b) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* 1985, 106, 1650. (c) Bergman, R. G. *Science* 1984, 902.

(8) Gault, F. G. *Gazz. Chem. Ital.* 1979, 109, 255.

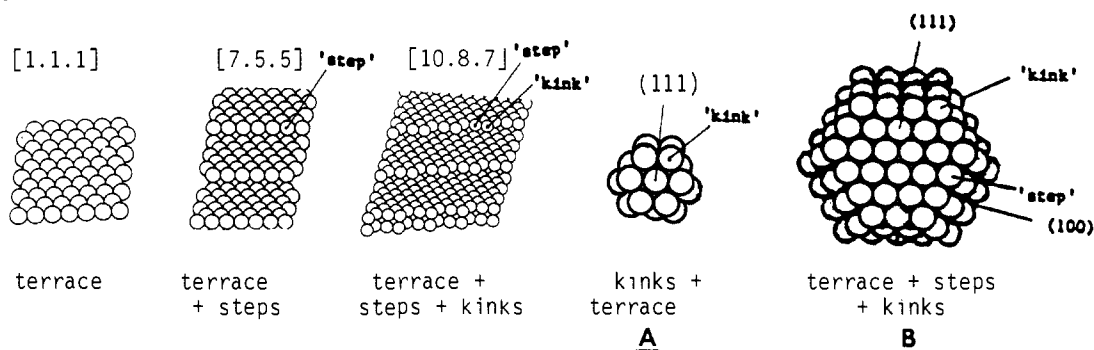
(9) Anderson, J. R.; Kemball, C. *Proc. R. Soc.* 1954, 223, 361.

(10) Frennet, A. *Catal. Rev.-Sci. Eng.* 1974, 10, 37.

(11) Boudart, M.; Aldag, A.; Benson, J. E.; Dougharty, N. A.; Harkins, C. G. *J. Catal.* 1966, 6, 92.

(12) Gault, F. G.; Rooney, J. J.; Kemball, C. *J. Catal.* 1962, 1, 255.

Scheme I. Types of Surface Atoms on Flat Surfaces and on Particles

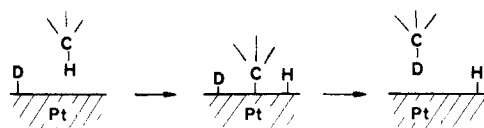


tention has been paid to the stability and shape of the catalyst particles. Especially Pd, which has been the metal of choice in C-H activation studies, has been found to undergo drastic morphological changes even under mild reaction conditions.¹³

Another important aspect of heterogeneously catalyzed reactions is the surface structure sensitivity of C-H activation reactions. This parameter, introduced by Boudart,¹⁴ is determined by the sensitivity of a reaction to the particle size (dispersion) of the catalyst. The basic principle of this approach can be rationalized as follows: there are only few distinctly different sites on a metal surface—*terraces* = (111) surfaces (representing the lowest energy surface of *fcc* solids, every surface atom is surrounded by 9 direct neighbors) and (100) surfaces (eight direct neighbors), *stepped* surfaces which consist of terrace and *step* atoms (seven direct neighbors), and *kinked* surfaces which contain terrace, step, and *kink* atoms (six direct neighbors). Numerous examples of reactions exhibiting sensitivity to surface structures of the single crystal have been published.¹⁴⁻¹⁶ Three examples of typical surfaces are represented in Scheme I.

Exactly the same type of surface atoms are found on metal particles of various sizes (A and B) as indicated in Scheme I. The smaller particle A has few (6) low-energy surface atoms, most of the surface atoms being of the kink and step type. However, on the larger particle B more terrace atoms, some step atoms, and a few kink atoms can be identified. In general, the ratio of kink/terrace atoms decreases with increasing particle size whereas the step atoms, according to a quantitative analysis by Van Hartefeld and Van Montfort, have a maximum concentration at a particle size of 20 Å (corresponding to ~50% dispersion).¹⁷ Dependence of reaction rates as well as deuterium distribution on dispersion in exchange reactions with alkanes will therefore provide direct information about surface structure effects of this reaction.

Studies investigating this aspect have come to the conclusion that C-H activation is a surface structure insensitive reaction.^{11,18-21} Unfortunately, the few studies related to surface

Scheme II. H/D Exchange of *n*-Alkanes

structure effects cannot be termed reliable from today's point of view. Not only were the reaction conditions applied not strictly comparable (different mass transport limitations), but the range of dispersions investigated was usually very small and never covered the whole range from bulk catalyst metal to highly dispersed materials. Some caution on the interpretation of older surface structure sensitivity studies is called upon by recent reports by Figueras, who found an increase in hydrogenolysis activity with decreasing dispersion²² (compare to the opposite result obtained by Guzzi¹⁹), the report by Boitiaux²³ on the dispersion sensitivity of hydrogenation reactions which are generally considered surface structure insensitive, or the loss of catalytic activity for MCP hydrogenolysis at high dispersion reported by Klabunde.¹⁶ A separate route of surface structure dependence is explored by Augustine, who associates different reaction types to different surface sites.²⁴

In this study we attempt to provide a more comprehensive picture on the mechanism of C-H activation on heterogeneous catalysts. Due to the element sensitive nature of C-H activation we have restricted this mechanistic study to platinum. Platinum was selected for two reasons: (1) Pd and Pt represent probably the most intensively studied catalyst metals. (2) Contrary to Pd,¹³ Pt is a more stable catalyst metal which does not appear to change its particle structure (dispersion) significantly under our mild reaction conditions (although nothing is known about the surface structural changes associated with use and carbonation).

What Is Known About the Mechanism of C-H Activation on Platinum? Monodeuteration as a preferred mode of exchange was reported in all H/D exchange studies with hydrocarbons on platinum. This exchange mode is found with all types of hydrocarbons ranging from methane through linear and cyclic alkanes to polycyclic hydrocarbons like adamantane. The mechanism is interpreted within the framework of the Horiuti-Polanyi mechanism²⁵ as a single C-H insertion of the catalyst surface into one C-H bond under formation of a surface alkyl and a surface hydride followed by reductive elimination of the surface alkyl with a surface deuteride as outlined in Scheme II.

In addition to the monodeuteration process, perdeuteration during single surface interaction was identified as the other dominant process. Maxima due to mono- and perdeuteration have been observed by Anderson⁹ and Guzzi²⁶ with small alkanes. In

(13) Maier, W. F.; Chettle, S. B.; Rai, R. S.; Thomas, G. *J. Am. Chem. Soc.*, in press.

(14) Boudart, M. *Adv. Catal.* **1969**, *20*, 153.

(15) Manogue, W. H.; Katzer, J. R. *J. Catal.* **1974**, *32*, 166. Cusumano, J. A.; Dembrinski, G. W.; Sinfelt, J. H. *J. Catal.* **1968**, *5*, 471. Dorling, T. A.; Moss, R. L. *J. Catal.* **1966**, *5*, 111. Salmeron, M.; Gale, R. J.; Somorjai, G. A. *J. Chem. Phys.* **1979**, *70*, 2807. Yates, D. J. C.; Sinfelt, J. H. *J. Catal.* **1967**, *8*, 348. Davis, A. M.; Somorjai, G. A. *Surf. Sci.* **1980**, *91*, 73. Sinfelt, J. H.; Rohrer, J. C. *J. Phys. Chem.* **1962**, *66*, 1559. Boudart, M.; Aldag, A. W.; Ptak, L. D.; Benson, J. E. *J. Catal.* **1968**, *11*, 35. Blakely, D. W.; Somorjai, G. A. *J. Catal.* **1976**, *42*, 181. Carturan, G.; Facchin, G.; Cocco, G.; Enzo, S.; Navazio, G. *J. Catal.* **1982**, *76*, 405. Zakarina, N. A.; Zakumbaeva, G. D.; Toktabaeva, N. F.; Dyusenbina, B. B.; Lit'yakova, E. N.; Kuanyshev, A. S. *Kinet. Catal.* **1984**, *733*.

(16) Matsuo, K.; Klabunde, K. J. *J. Org. Chem.* **1982**, *47*, 843.

(17) Van Hardevel, R.; Van Montfort, A. *Surf. Sci.* **1966**, *4*, 396.

(18) Anderson, J. R.; MacDonald, R. J. *J. Catal.* **1969**, *13*, 345. Guzzi, L.; Tetenyi, P. *Ann. N.Y. Acad. Sci.* **1973**, *213*, 173.

(19) Guzzi, L.; Gudkov, B. S. *React. Kinet. Catal. Lett.* **1978**, *9*, 343.

(20) Inoue, Y.; Herrmann, J. M.; Schmidt, H.; Burwell, R. L., Jr.; Butt, J. B.; Cohen, J. B. *J. Catal.* **1978**, *53*, 401.

(21) Frennet, A.; Lienard, G.; Degols, L.; Crucq, A. *Bull. Soc. Chim. Belg.* **1979**, *88*, 621.

(22) Del Angel, G.; Coq, B.; Dutartre, R.; Figueras, F. *J. Catal.* **1984**, *87*, 27.

(23) Boitiaux, J. P.; Cosyns, J.; Vasudevan, S. *Appl. Catal.* **1983**, *6*, 41. (24) Augustine, R. L.; Warner, R. W. *J. Catal.* **1983**, *80*, 358. Augustine, R. L.; Wesdyk, R. *Langmuir* **1985**, *1*, 262.

(25) Horiuti, J.; Polanyi, M. *Nature (London)* **1933**, *132*, 819. Horiuti, J.; Polanyi, M. *Trans. Faraday Soc.* **1934**, *30*, 633. See also ref 3.

(26) Guzzi, L.; Sárkány, A.; Tétényi, P. *J. Chem. Soc., Faraday Trans. 1* **1974**, *1971*. Guzzi, L.; Karpiński, Z. *J. Catal.* **1979**, *56*, 438.

1954 Anderson and Kemball found no fundamental difference between the H/D exchange results obtained on films, supported Pt, or bulk Pt in the form of Pt-black, a first vague indication of structure insensitivity.⁹ The predominant formation of mono- and perdeuterated ethane was confirmed on Pt single-crystal surfaces.²⁷ With cyclohexane Guzzi reported the predominant formation of d_1 product at 53 °C and d_1, d_{12} maxima at temperatures above 100 °C on Pt.²⁸ Cyclopentane forms mono- and perdeuteration maxima at temperatures above 100 °C on Pt films.²⁹ On (111) and (10,8,7) Pt single-crystal surfaces, mono- and perdeuteration of *n*-hexane were found to be the dominant processes of H/D exchange.⁵ Mono- and perdeuteration were also obtained with hexane on Pt films.³⁰ Some preference for methyl over methylene exchange in hexane is identified by ¹H NMR.³⁰

Perdeuteration was shown to stop at quaternary positions,³¹ indicating the importance of α -C-H bonds which led to the formulation of π -adsorbed species through which deuteration may propagate. Although there is little doubt about the importance of π -type intermediates, no direct or indirect evidence for their existence as reactive intermediates in polyexchange processes has been provided. However, the nature of surface π -intermediates, still the subject of speculative discussion in 1983,³² has been resolved by a recent NEXAFS study showing a C-C bond distance of 1.49 Å for chemisorbed ethylene on (111) Pt which is evidence for a di- σ -bound (cyclopropyl type) species rather than a weakly bound surface π -complex.³³

The most controversial problem appears to be the mode of propagation of C-H exchange after the formation of π -intermediates. Although some evidence for the π -allyl interconversion has been provided, the peculiar exchange pattern produced on cyclopentane has resulted in on-going discussions.^{2,3,20,28,34} Two peculiar aspects observed on Pd, the formation of a dominant d_5 maximum at lower temperatures followed at higher temperatures (above 100 °C) by a slight maximum at d_8 and a distinct maximum at d_{10} ,^{35,36} have led to extensive discussions about the exchange mechanism involved.³ On Pt and Pt-Au alloys, the d_8 maximum was never obtained. The d_5 maximum dominates only at room temperature; at temperatures above 100 °C mono- and perdeuteration remain the only significant maxima in the product distribution.²⁹ Inoue et al. studied the dispersion dependence of this exchange reaction and came to the conclusion that the turnover from one side to the other side of the ring on low dispersed Pt proceeds predominantly through α, α -alkylidene-type³⁶ intermediates, whereas on highly dispersed Pt the "rollover" mechanism² may dominate.²⁰ No considerable change in turnover frequency with change in dispersion was detected.²⁰ Of interest is the observed formation of 90% d_1 isomer with Pt/TiO₂ under photocatalytic conditions.³⁷ The strongest argument against the importance of α, α -diadsorbed intermediates (surface alkylidenes) as important surface species in the polydeuteration process is the lack of maxima other than d_1 in H/D exchange reactions of methane or neopentane.³⁸

The studies mentioned so far lack characterization of the dominant isotopic isomers produced as well as evidence other than the MS-trace of the product mixture for the involvement of the proposed intermediates. Nonstandardized conditions make a reliable comparison of the exchange results obtained with different hydrocarbons in different publications impossible and allow only

vague statements about the relative importance of the various mechanisms for H/D exchange. Clearly missing is a comprehensive study comparing the different chemical probes for the various mechanisms under identical conditions, which is attempted in this paper. Due to the problems associated with uncontrollable surface structure changes and surface carbonation during the reaction we feel that kinetic studies neglecting these changes cannot add anything new to the many kinetic studies reported in the past. We have therefore restricted our study to a qualitative determination of the structural effects of catalyst and hydrocarbon on C-H activation.

Results and Discussion

1. Surface Structure Sensitivity. Of crucial importance for mechanistic studies of heterogeneously catalyzed reactions is determining the surface structure sensitivity of the reaction of interest. We chose the H/D exchange reaction of hexane as a suitable model reaction and the turnover frequency (reacted molecules per second per surface atom), T_f , as a reliable measure of catalytic activity. The reactions were carried out in a gas-phase flow reactor. A high deuterium/substrate ratio was maintained to reduce dilution of surface deuterium by the exchanged hydrogen. To avoid multiple surface interaction the total conversion of the substrate was kept below 10%. This implies non-equilibrating reaction conditions (large excess of substrate) which make the reaction rate sensitive to the specific reaction conditions in every experiment (mass transport effects). These expected mass transport limitations were indeed readily detected by changes in T_f by a factor between one and two, induced through changes of catalyst bed size (mixing of the catalyst with additional support), hydrocarbon flow rate, and change of the total amount of catalyst (ratio of active metal surface area to amount of substrate over time).

To allow a meaningful comparison under the restrictions indicated we have conducted the experiments under conditions where the imposed mass transport conditions were constant. To achieve this the following conditions were observed: the same support, the same amount and size of catalysts bed (maintained by addition of naked support to the catalysts of higher loading), a similar Pt-surface/substrate ratio, the same substrate addition rate, and a constant substrate/deuterium ratio.

The structure-sensitivity study was conducted with platinum catalysts ranging from bulk metal (Pt-foil) to 80% dispersion on alumina as support. The catalyst dispersion, determined before and after the experiments by hydrogen adsorption,³⁹ was found to be constant on all our catalysts. The T_f was measured after the activity of the fresh catalyst had stabilized. Activity stabilization was usually achieved reliably by passing about 0.5 mL of hydrocarbon per m² of Pt surface over the catalyst under exchange conditions. The hydrocarbon (about 50 μ L) was introduced into the D₂-carrier gas via a syringe pump and collected after the catalyst bed in a cold trap. The product composition was analyzed by computerized GC-MS. The deuterium analysis was corrected for natural abundance of ¹³C, and the isotopic distribution was determined automatically. When this program was written we noted a special sensitivity of the data evaluation at low conversion to correction errors for the abundance of the monodeuterated isomer resulting in an unusually high abundance of the d_1 -isotopic isomers. The problem was overcome by empirical refinement of the correction program to produce the desired zero conversion for undeuterated *n*-hexane which was used routinely as a standard to monitor reliable behavior of the MS analysis. The results of the surface structure sensitivity study are plotted in Figure 1.

For a large range of dispersions (10–80%), which is the range associated to the most significant changes in overall surface structure, a constant activity was observed ($T_f = 5 \times 10^{-4}$ at 390 K). This is in qualitative agreement with the lack of structure sensitivity reported³² and with earlier observations by Guzzi and Sarkany, who reported a turnover frequency of about 3.5–3.7 \times

(27) Zaera, F.; Somorjai, G. A. *J. Phys. Chem.*, in press.

(28) Sárkányi, A.; Guzzi, L.; Tétényi, P. *J. Catal.* **1975**, *39*, 181.

(29) Dessing, R. P.; Ponoc, V. *J. Catal.* **1976**, *44*, 494.

(30) Long, M. A.; Moyes, R. B.; Wells, P. B.; Garnett, J. L. *J. Catal.* **1978**, *52*, 206.

(31) Burwell, R. L., Jr.; Briggs, W. S. *J. Am. Chem. Soc.* **1952**, *74*, 5096.

(32) Eskinazi, V.; Burwell, R. L., Jr. *J. Catal.* **1983**, *79*, 118.

(33) Stöhr, J.; Sette, F.; Johnson, A. *J. Phys. Rev. Lett.* **1984**, *53*, 1684.

(34) Schrage, K.; Burwell, R. L., Jr. *J. Am. Chem. Soc.* **1966**, *88*, 4549, 4555.

(35) Burwell, R. L., Jr.; Tuxworth, R. H. *J. Phys. Chem.* **1956**, *60*, 1043.

(36) Anderson, J. R.; Kemball, C. *Proc. R. Soc.* **1954**, *A226*, 472.

(37) Courbon, H.; Herrmann, J.-M.; Pichat, P. *J. Catal.* **1981**, *72*, 129.

(38) Kemball, C. *Trans. Faraday Soc.* **1954**, *50*, 1344. Rowlinson, H. C.; Burwell, R. L., Jr.; Tuxworth, R. H. *J. Phys. Chem.* **1955**, *59*, 225.

(39) Farrauto, R. J. *AIChE Symp. Ser. No. 143* **1974**, *70*, 9.

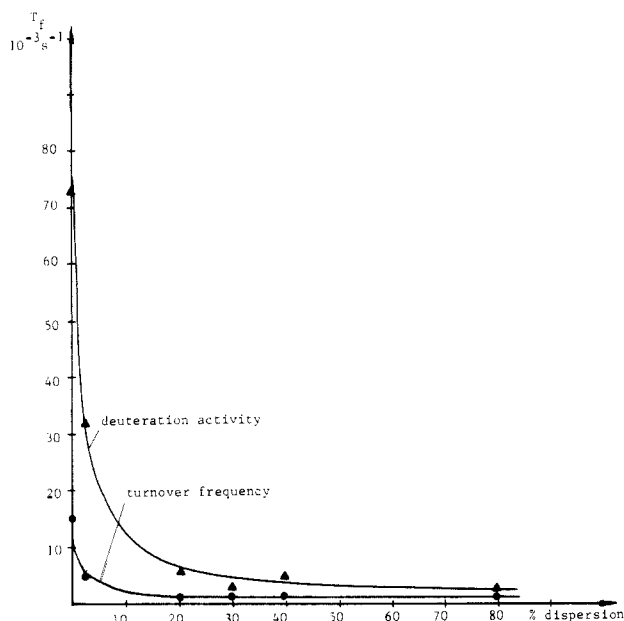


Figure 1. Surface structure sensitivity of hexane activation on heterogeneous Pt catalysts.

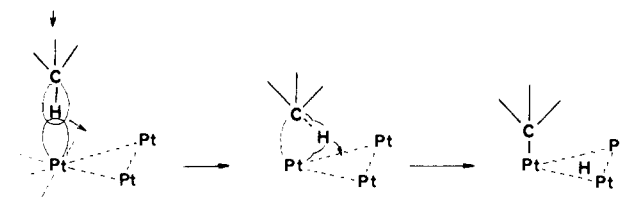
10^{-4} for 1% and 32.5% dispersed Pt/SiO₂ for the exchange of ethane at 95 °C.⁴⁰ However, at lower dispersion a significant increase of the turnover frequency was observed. Both low dispersed catalysts, Pt foil (dispersion ~0%) and 25% Pt/alumina (dispersion 2.5%), were annealed at 900 °C to ensure a smooth metal surface, a procedure believed to increase the relative amount of (111) facets.^{14,41}

These results indicate that the low-energy terraces or planes [(111) and (100) surfaces] represent the most active surface for C-H activation (as suggested already in 1956 by Addy and Bond⁴²). This may be compared to a recent single crystal study by Davis and Somorjai,⁵ who report a slightly higher H/D exchange rate with *n*-hexane on low-energy (111) Pt over the stepped and kinked (10,8,7) Pt single-crystal surface at 573 K. Since the dominant surface on both single crystals is of the (111) type, the lower activity observed with the (10,8,7) crystal may be due to the relative decrease in (111) sites. The higher activity of low-energy terraces for C-H activation may also explain the increase in T_f reported earlier for some catalysts treated at 450 °C.³²

This high activity of low-energy surfaces for C-H activation shows that there is a fundamental difference between the most active heterogeneous site and homogeneous complexes. This difference must be attributed to the electronic difference of bulk metal particles and to the steric constraints a substrate faces on a truly two-dimensional metal surface. Due to the expected steric restrictions, low-energy terraces are not even being considered presently as *the* active sites for C-H activation,³² despite contrary reports from surface studies.^{5,27,43} The following mechanism, modeled on a representative (111) surface atom, is proposed (a more detailed and sophisticated discussion of a similar subject, from which some of our qualitative arguments were extracted, has been presented by Baetzold and Saillard and Hoffmann⁶).

For simple steric reasons the only readily accessible orbital for ligand interactions on a (111) or (100) surface atom is the a_1 hybrid orbital shown in Scheme III. This orbital, which represents the LUMO in 16e ML₅ and many ML₄ transition-metal fragments,⁴⁴ should not gain much stabilization by combination with adjacent orbitals on the surface and should therefore remain unoccupied and available for favorable interaction with the occupied C-H

Scheme III. Proposed Mechanism for C-H Activation on a Flat Metal Surface



σ -orbital. d-Orbital interactions of the d_{xy} -type can be excluded by simple steric arguments, since they would require a side-on approach in order to achieve favorable overlap with the σ^* -orbital of the C-H bond.

We therefore propose that activation on such a surface does not proceed to produce a surface hydride and a surface alkyl but to a surface alkyl and a hydrogen as outlined in Scheme III. There are several factors supporting such a slipping of hydrogen into the hollow between three (111)-surface atoms. The process appears symmetry allowed as long as the two C-H σ electrons remain in the new C-Pt bond. With the descent of the hydrogen atom into the hole electron donating d-orbital interaction with the σ^* -C-H orbital can assist the cleavage process. Furthermore, the hydrogen atom will end up at the position where it has already been located on (111)-Pt surfaces, i.e., on the center between three surface atoms (octahedral face).⁴⁵ That LUMO-type interactions of the catalyst surface are important in catalytic processes is supported by the sensitivity toward poisoning by formally electron-donating "ligands". Especially C-H activation is readily poisoned by the presence of formal electron donors like phosphines,⁴⁶ amines,⁴⁷ or alkaline metals.⁴⁸ Such a hydrogen-slipping activation of C-H bonds may be restricted to low-energy surfaces. On steps or kinks (ML₄ and ML₃ fragment analogues) the conventional carbene-type activation process may be operating.

The next experimental data to be addressed are the isotopic distributions of the exchanged hexanes. Two maxima are observed, d_1 and d_{14} hexane, in agreement with earlier reports on Pt, where mono- and perdeuteration have been reported on supported catalysts as well as on single crystals.^{5,9,26-29} However, monodeuteration did not occur with the fresh Pt-foil (only perdeuteration maximum) and no perdeuteration maxima were produced initially with the fresh dispersed catalysts (only monodeuteration maximum). Only after the catalysts had experienced some initial deactivation, both maxima were obtained on the foil as well as on the less dispersed catalysts (<40%). This indicates not only a sensitivity of the exchange mechanism to carbonation or surface structure changes experienced by the fresh catalysts but also a mechanistic surface structure insensitivity of the principle exchange processes under steady-state conditions. The two deuteration maxima obtained from single surface interactions point to two exchange processes occurring parallel or sequentially on the catalyst surface. Although the combined rate of these two processes (T_f) is insensitive to surface structure changes above 10% dispersion, as outlined before, the relative ratio of mono- and polydeuterated products appears to be sensitive to the catalyst dispersion as shown in Figure 2. This indicates that the polydeuteration is a secondary reaction following the initial chemisorption which governs T_f .

The amount of monodeuteration increases with increasing dispersion and reaches its maximum at higher dispersions (>50%). It is logical to assume that the perdeuteration represents the ultimate product of a propagating exchange process responsible for all higher deuterated products (d_2 - d_{14}). Polydeuteration, which increases with decreasing dispersion (see Figure 4), is therefore favored by low-energy surfaces (terraces). Interestingly, perdeuteration as a distinct maximum was only found at dispersions

(40) Gucci, L.; Sárkány, J. *J. Catal.* **1981**, *68*, 190.

(41) Lyon, H. B.; Somorjai, G. A. *J. Chem. Phys.* **1967**, *46*, 2539. McLean, M.; Mykura, H. *Surf. Sci.* **1966**, *5*, 466.

(42) Addy, J.; Bond, G. C. *Trans. Faraday Soc.* **1957**, *253*, 368, 383, 388.

(43) Somorjai, G. A. "Chemistry in Two Dimensions"; Cornell University Press: Ithaca, 1981.

(44) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

(45) Conrad, H.; Ertl, G.; Latta, E. E. *Surf. Sci.* **1974**, *41*, 435.

(46) Maxted, E. B. *Adv. Catal.* **1951**, *3*, 129.

(47) De Aguirre, I.; Duque, B. In "Catalysis"; Delmon, B., Jannes, G., Eds.; Elsevier Scientific Publishing Company: New York, 1975.

(48) Zaera, F.; Somorjai, G. A. *J. Catal.* **1983**, *84*, 375.

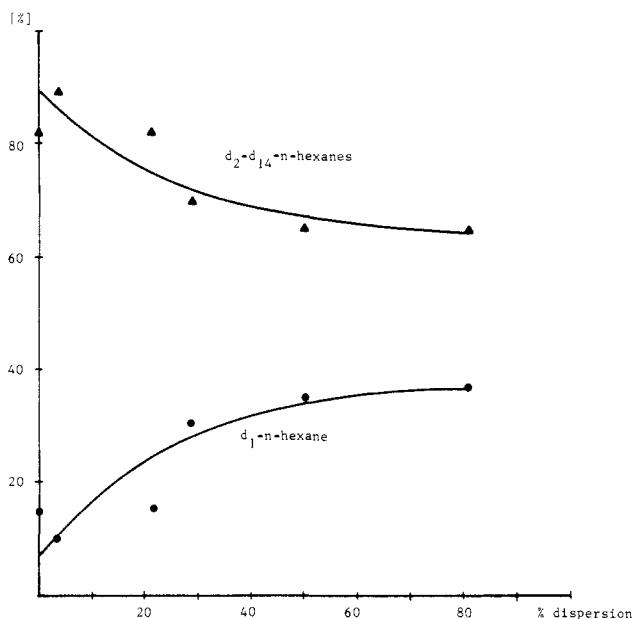


Figure 2. Surface structure sensitivity of mono- and polydeuteration of *n*-hexane on heterogeneous Pt catalysts.

below 40%. The dispersion range where monodeuteration dominates (>20%) corresponds to the range where the turnover frequency remains unchanged.

2. Monodeuteration. The mechanism of monodeuteration appears to be the activation of a single C–H bond under formation of a surface alkyl and a surface hydrogen atom followed by desorption of the monodeuterated alkane under reductive elimination of the surface alkyl with a surface deuterium atom.¹⁻³ However, for a better understanding of monodeuteration we also need to know (1) why some molecules incorporate only one deuterium while others undergo polydeuteration and (2) whether monodeuteration is position specific (for example, guided by C–H bond energies or steric effects) or a random process occurring throughout the molecule.

It is interesting that the relative amount of monodeuterated hexane formed in all our many exchange experiments with *n*-hexane never exceeded 45% of the total exchanged *n*-hexane and thus appears to correlate with the 43% of terminal C–H bonds available in *n*-hexane. We were curious to see whether there is any general correlation between the relative amount of *d*₁ isomer formed and the ratio of terminal and internal C–H bonds. Therefore, exchange experiments were carried out on *n*-pentane, *n*-hexane, and *n*-heptane under identical reaction conditions.

Indeed, as shown in Figure 3, a surprising correlation of the amount of monodeuteration and the percentage of terminal C–H bonds in linear hydrocarbons was found, indicating that the deuterium in the *d*₁ isomer should be located primarily at the terminal methyl position. This implies that polydeuteration is predominantly initiated by activation of the secondary C–H positions.

High-resolution deuterium NMR of the exchanged products was used to identify the position of the deuterium in the monodeuterated hexane. Unfortunately, separation of the monodeuterated from the higher deuterated isomers is not possible and the low conversion and small amount of sample made the analysis difficult. In addition, the larger deuterium content of the higher deuterated isomers tends to mask the deuterium signal of monodeuterated isomers in cases of unselective distribution of the deuterium atom.

Spectrum A in Scheme IV shows the chemical shift of deuterium in the three positions of *n*-hexane (natural abundance spectrum). Spectra B–E represent different samples of exchanged *n*-hexanes where the percentage of deuterium corresponding to the monodeuterated hexane in the isotopic mixture increases from 3% over 6% to 16% and 17%. Clearly, the only significant change observable in the four spectra is the increase of a signal super-

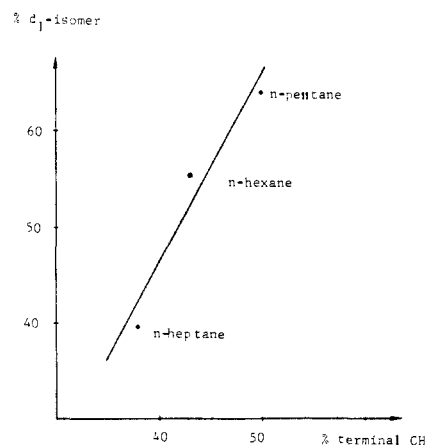
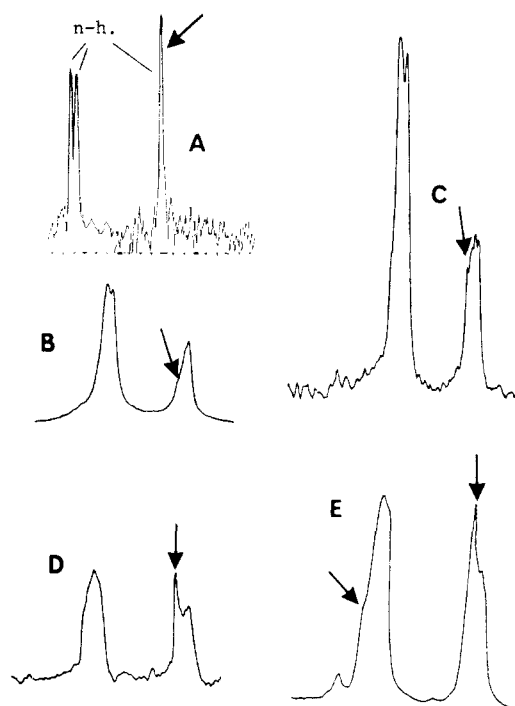


Figure 3. Correlation of monodeuterated product with the amount of terminal C–H positions (116 °C, 1% Pt/alumina).

Scheme IV. ²H NMR Spectra (76.7 MHz)



A, natural abundance of *n*-hexane with cyclohexane;
B, mixture of exchanged *n*-hexanes with 3% ²H;
C, mixture of exchanged *n*-hexanes with 6% ²H;
D, mixture of exchanged *n*-hexanes with 16% *n*-exchange-*d*₁;
E, mixture of exchanged *n*-hexanes with 17% *n*-hexane-*d*₁

imposable with the terminal deuterium position in *n*-hexane (as confirmed by a mixed spectrum run with independently synthesized *n*-hexane-1-*d*₁). Since we expect a sharp deuterium signal from a monodeuterated hydrocarbon, the above spectra serve as evidence that monodeuteration is predominantly a terminal exchange process. However, a small shoulder, superimposable with deuterium at the 2-position of *n*-hexane (marked by arrow) in the 17% sample, can be identified. This indicates that some secondary monodeuteration may have formed. Deuteration at the 3-position cannot be identified due to signal position which, at 0.025 ppm upfield of the 2-position, is hidden under the bulk of the methylene signals. There is no reason to expect that this position should contain more deuterium than the 2-position. Since the relative amount of monodeuteration increases with increasing dispersion, we conclude that the higher dispersed catalysts (more higher energy surface atoms) are either less selective toward the bond energy of the C–H bond to be activated or propagation of deuteration of a terminal surface alkyl is less facile on highly dispersed catalysts.

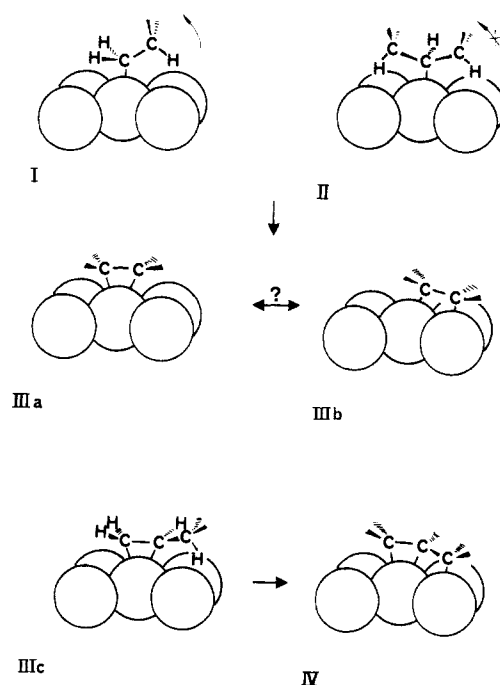
Table I. H/D Exchange Competition Experiment with *n*-Hexane (A), *cis*-4-Methyl-2-pentene (B), and 2-Methylpentane (C)

| experiment | 1 | 2 | | 3 | 4 | | 5 | | 6 | | 7 | | 8 | 9 | |
|----------------|------|------|------|------|------|------|------|----|------|------|------|----|------|--------|----|
| catalyst | foil | foil | | foil | foil | | foil | | foil | | foil | | foil | 10% Pt | |
| temp, °C | 270 | 250 | | 250 | 270 | | 250 | | 270 | | 270 | | 270 | 170 | |
| hydrocarbons | A | B | A | A | B | A | C | A | B | A | B | A | B | B | A |
| composition, % | 100 | 0.1 | 99.9 | 100 | 0.1 | 99.9 | 40 | 60 | 1.3 | 98.7 | 10 | 90 | 100 | 3 | 97 |
| conversion, % | 4 | | 8 | 8 | | 30 | 13 | 14 | 100 | 8 | 100 | 0 | 100 | 100 | 16 |
| d_1 | 10 | 2 | 23 | 21 | 1 | 17 | 15 | 11 | 4 | 23 | 2 | | 6 | 6 | 45 |
| d_2 | 1 | 4 | 5 | 5 | 7 | 6 | 6 | 4 | 11 | 6 | 6 | | 11 | 35 | 14 |
| d_3 | 2 | 5 | 5 | 5 | 2 | 5 | 4 | 4 | 8 | 4 | 7 | | 12 | 13 | 7 |
| d_4 | 3 | 7 | 4 | 4 | 14 | 2 | 4 | 3 | 7 | 4 | 8 | | 12 | 9 | 4 |
| d_5 | 3 | 8 | 4 | 4 | 1 | 3 | 4 | 3 | 7 | 4 | 9 | | 12 | 7 | 4 |
| d_6 | 3 | 10 | 5 | 5 | 4 | 5 | 3 | 3 | 9 | 3 | 8 | | 11 | 5 | 3 |
| d_7 | 4 | 9 | 5 | 5 | 4 | 6 | 4 | 3 | 9 | 5 | 7 | | 8 | 5 | 4 |
| d_8 | 4 | 8 | 6 | 5 | 4 | 6 | 3 | 3 | 8 | 5 | 6 | | 7 | 5 | 4 |
| d_9 | 5 | 5 | 6 | 6 | 4 | 7 | 5 | 5 | 6 | 5 | 6 | | 6 | 4 | 4 |
| d_{10} | 5 | 6 | 6 | 6 | 4 | 8 | 7 | 7 | 5 | 6 | 7 | | 5 | 3 | 4 |
| d_{11} | 7 | 7 | 7 | 7 | 12 | 8 | 12 | 12 | 5 | 6 | 8 | | 4 | 3 | 3 |
| d_{12} | 8 | 8 | 7 | 7 | 13 | 8 | 12 | 17 | 7 | 6 | 9 | | 4 | 2 | 2 |
| d_{13} | 14 | 7 | 7 | 8 | 12 | 8 | 13 | 17 | 6 | 8 | 9 | | 2 | 2 | 2 |
| d_{14} | 31 | 12 | 11 | 13 | 18 | 11 | 7 | 9 | 9 | 15 | 9 | | 1 | 2 | 3 |

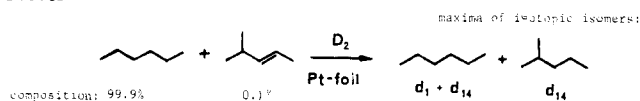
3. Polydeuteration. The association of monodeuteration with activation of the terminal C-H bonds implies that polydeuteration is initiated by activation of the secondary C-H positions. Aside from unknown electronic effects on C-H activations, steric interactions are likely to play an important role in surface reactions. The surface structure sensitivity study outlined above has indicated that terraces lead to higher T_f for C-H activation and promote the propagation of deuteration more than higher energy sites (steps or kinks). The following steric arguments will therefore be based on a (111) surface structure as a valid model for low-energy surfaces (all arguments used would equally well apply to a 100 surface). An obvious difference of secondary to primary surface alkyls is the increase of steric interaction with the β -hydrogens in the secondary surface alkyl as shown in Scheme V. In the primary alkyl I the Pt-C-C angle can readily increase above 109° to the expense of decreased Pt-C-H angles, a strain reducing deformation which is not possible to that extent in the secondary surface alkyl II.

Consequently, α,β -activation will occur more readily in the secondary surface alkyls. The resulting α,β -adsorbed intermediate III, however, will suffer severe strain due to the surface interaction with its allylic hydrogen atoms (if present), as illustrated in IIIc. Although nothing is known about the exact position of olefinic intermediates during H/D exchange (IIIa may very well be in equilibrium with IIIb or IIIb may be the prominent form), we have chosen IIIa as a representative model structure because its repulsive surface interactions should be smaller than in the bridging IIIb. Simple estimates based on the geometry of known Pt- π complexes⁴⁹ indicate a distance of 1.3–1.8 Å for the allylic hydrogen in IIIc to the Pt surface. Such a distance is within bonding range to the metal which must result in a strong reduction of the activation barrier for chemisorption. Rapid formation of an allylic intermediate from the π -intermediate is therefore likely. Polydeuteration may now proceed rapidly by addition of one deuterium atom to the first carbon of the allylic intermediate IV under formation of the shifted π -intermediate of type IIIb, activation to a shifted allyl intermediate, and so on. In such a π -allyl interconversion sequence, where the site of chemisorption zips rapidly back and forth through the molecule, the exchange process can be interrupted at any stage by formation of a surface alkyl followed by reductive elimination. Such interruption can account for the even distribution of partly deuterated products. Naturally, multiply chemisorbed intermediates like $\alpha,\beta,\gamma,\delta$ -species and so on may also form during the process depending on the molecule and the particular surface condition. However, the ability of π -allyl interconversion appears to be a prerequisite for efficient multiple exchange upon single surface interaction on Pt surfaces. Although indirect evidence for the π -allyl-type process has been

Scheme V. Surface Intermediates Initiating the Polydeuteration Process



Scheme VI. Olefin Competition Experiment To Demonstrate the Precursor Nature of Chemisorbed Olefins in the Polydeuteration Process



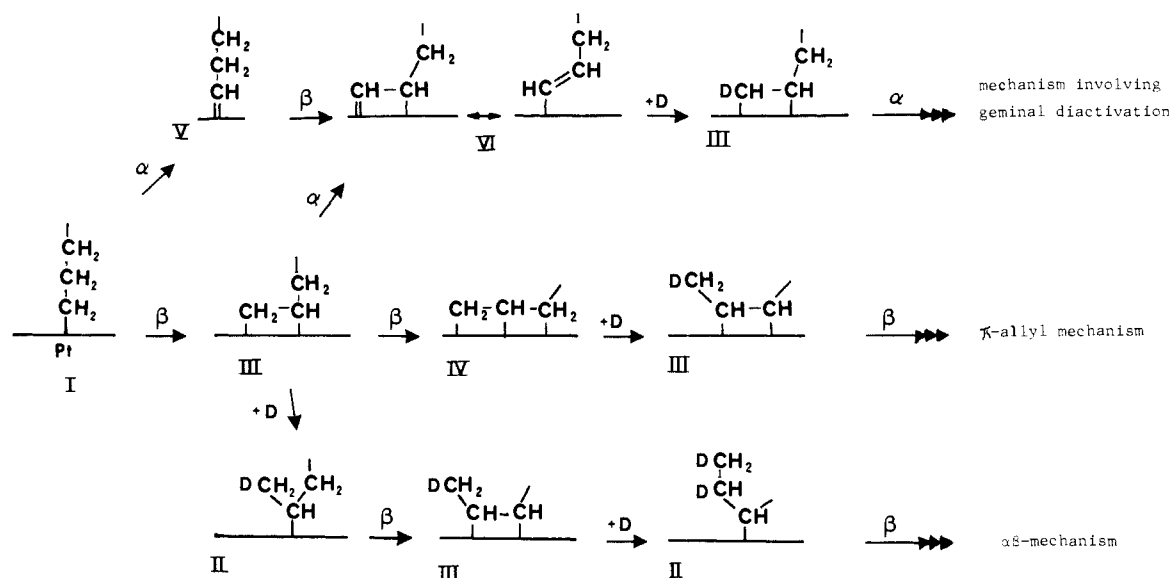
provided,⁵⁰ most of the work has been performed on Pd.

If the above mechanistic scheme is correct, then any olefinic intermediate formed during the exchange process should be more prone to perdeuteration than a saturated hydrocarbon, a hypothesis which may be tested by passing a mixture of an olefin and an alkane over the catalyst. The unknown crucial to make such an experiment work is the steady-state concentration of the olefinic intermediate. In accord with above mechanistic considerations we assumed this concentration to be very small and designed the experiment with an olefin concentration above the reliable detection limit of our instrument. A mixture of 0.1% *trans*-4-methyl-2-pentene and 99.9% *n*-hexane was passed over the Pt-foil at 270 °C and the product was analyzed by GC-MS. Pt-foil was

(49) Benedetti, E.; Corradini, P.; Pedone, C. *J. Organomet. Chem.* **1969**, *18*, 203.

(50) Rooney, J. J. *J. Catal.* **1963**, *2*, 53.

Scheme VII. Propagation Modes of Deuteration



used because of its pronounced tendency to favor polydeuteration. The results are summarized in Table I. Experiment 1 shows the pure *n*-hexane deuteration pattern prior to the competition experiments. The 2-methylpentane formed in the competition experiments (experiments 2, 4, and 6) showed only one dominant isotopic isomer, the perdeuterated d_{14} . The *n*-hexane, due to the small olefin concentration, is unaffected, showing the normal d_1 - d_{14} pattern.

Since the total conversion in these experiments is below 10%, the perdeuteration in the 2-methylpentane must have resulted from a single surface interaction supporting the above hypothesis. Control experiment 5 with a mixture of 2-methylpentane and *n*-hexane shows no preference of the catalyst for 2-methylpentane deuteration excluding selective deuteration as a possible cause for the product composition in experiments 2, 4, and 6. Due to the low surface area of our Pt-foil and the flow conditions we have not been able to obtain a reliable conversion of the *n*-hexane at higher olefin concentrations. In agreement with earlier reports by Burwell on the partial pressure dependence of deuteration with 1-hexene,³⁵ we observe a clear decrease in multiple exchange in the olefin with increasing partial pressure of the latter. As shown in experiment 7 the deuteration pattern in the olefin obtained from an olefin concentration of 10% is already identical with the deuteration pattern obtained in pure olefins (experiment 8). Experiment 9, although on a supported catalyst, shows that at higher olefin concentration (3%) the polydeuteration of the alkene is already suppressed ("normal" olefin deuteration pattern) but so is the polydeuteration of the *n*-hexane indicating that the perturbation of the exchange reaction with added olefin has clearly surpassed the steady-state concentration of an olefinic intermediate.

The above experiments are especially remarkable since they directly connect two important processes in heterogeneous catalysis, the hydrogenation and the C-H activation. The lack of extensive polydeuteration in the *n*-hexane at higher olefin concentration is further evidence for the successful competition of the olefin for the active sites catalyzing polydeuteration. In addition, a change in the deuteration pattern of the 2-methylpentane changes from a d_{14} maximum to a d_1, d_2, d_3 pattern common for the hydrogenation of olefins on Pt is observed.⁵¹ Indeed, no further change in the deuteration pattern is observed when the olefin concentration is increased to 100%. This dependence of the deuteration pattern on the olefin concentration can be explained by two alternative or complementary mechanisms:

1. The reductive elimination of the surface alkyl formed during the hydrogenation process⁸ is assisted or facilitated by the presence of excess olefin. Such a process may be compared to the ligand assisted reductive elimination observed by Yamamoto in homogeneous Ni complexes.⁵²

2. The olefin, due to its lack of activation barrier for chemisorption and its tendency to form multilayers on Pt,^{53,54} occupies the metal surface area so densely that multiple exchange is prevented by simple surface crowding effects. This explanation not only allows the formation of the few higher deuterated products but it also explains the efficient incorporation of exchanged hydrogen atoms responsible for the relatively large amount of d_1 product generally observed in olefin deuterations.

Such an analysis raises a carefully avoided conundrum in hydrocarbon catalysis, the origin of the difference in activation barrier for olefin hydrogenation (typically around 10 kcal/mol)⁵⁵ and C-H activation of alkanes (around 20 kcal/mol).^{27,40} The rate-determining step in olefin hydrogenation has been identified as the reductive elimination of the final alkane (hydrogen addition to the semihydrogenated intermediate).⁵⁶ It is also well established that the chemisorption of alkanes as well as that of alkenes are exothermic processes⁵⁴ which make the activation barrier for alkane desorption automatically higher than the adsorption barrier. This suggests that the rate-determining steps in alkene hydrogenation and alkane activation are identical which is contradicted by the experimental data. However, this conundrum is resolved if mechanism 1 and/or 2 is operating and the reductive elimination of alkanes is more facile in the presence of olefins. This interesting side aspect, however, is not of primary importance for the present study of the mechanism of C-H activation and deserves a separate investigation.

After having shown that chemisorbed olefins are important intermediates in the H/D exchange process, the next problem addressed is the preferred route of propagation of the H/D exchange from the stage of a chemisorbed olefin. Three principally different activation modes (outlined in Scheme VII) have to be considered: π -allylic activation with formation of an α,β,γ -adsorbed intermediate (type IV), geminal activation leading to some

(52) Yamamoto, T.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1971**, *93*, 3350.

(53) Weinberg, W. H.; Deans, H. A.; Merrill, R. P. *Surf. Sci.* **1974**, *41*, 312.

(54) Palfi, S.; Lisowski, W.; Smutek, M.; Cerny, S. *J. Catal.* **1984**, *88*, 300.

(55) Schlatter, J. C.; Boudart, M. *J. Catal.* **1972**, *24*, 482. Dorling, T. A.; Eastlake, M. J.; Moss, R. L. *J. Catal.* **1969**, *14*, 23. Farkas, A.; Farkas, L. *J. Am. Chem. Soc.* **1938**, *60*, 22.

(56) Hirota, K.; Hironaka, Y. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2638. Hirota, K.; Hironaka, Y. *J. Catal.* **1965**, *4*, 602. Burwell, R. L., Jr. *Catal. Rev.* **1972**, *7*, 25.

(51) Mints-Eya, V.; Hilaire, L.; Choplin, A.; Touroude, R.; Gault, F. G. *J. Catal.* **1983**, *82*, 267. Zaera, F.; Somorjai, G. A. *J. Am. Chem. Soc.* **1984**, *106*, 2288.

Table II. Deuteration of 1- and 2-Hexene-*t* on Pt

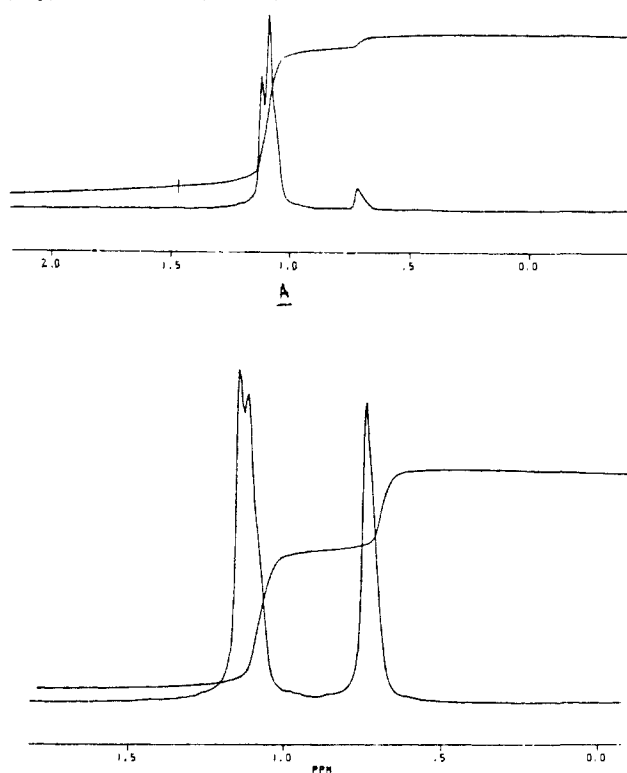
| experiment | 1 | 2 | 3 | 4 |
|-----------------------------------|----------|----|--------------------|----|
| olefins | 1-hexene | | 2-hexene- <i>t</i> | |
| catalysts | 1% | 1% | 1% | 5% |
| Pt/Al ₂ O ₃ | | | | |
| temp, °C | 25 | 25 | 116 | 25 |
| <i>d</i> ₁ | 25 | 23 | 18 | 21 |
| <i>d</i> ₂ | 28 | 35 | 24 | 28 |
| <i>d</i> ₃ | 19 | 19 | 16 | 19 |
| <i>d</i> ₄ | 10 | 11 | 11 | 12 |
| <i>d</i> ₅ | 5 | 6 | 7 | 8 |
| <i>d</i> ₆ | 3 | 3 | 6 | 5 |
| <i>d</i> ₇ | 2 | 2 | 5 | 3 |
| <i>d</i> ₈ | 1 | 1 | 5 | 2 |
| <i>d</i> ₉ | 1 | 1 | 3 | 1 |
| <i>d</i> ₁₀ | 1 | 0 | 2 | 1 |
| <i>d</i> ₁₁ | 0 | 0 | 1 | 0 |
| <i>d</i> ₁₂ | 0 | 0 | 1 | 0 |
| <i>d</i> ₁₃ | 0 | 0 | 0 | 0 |
| <i>d</i> ₁₄ | 0 | 0 | 0 | 0 |

kind of an α,α,β -product (chemisorbed vinylic intermediate) as postulated in cyclopentane activation,⁵⁷ on single crystal surfaces^{58,59} or in the deuteration of olefins on Ni catalysts⁵¹ (types V and VI), and the continuing interconversion of surface alkyls I and II and π -intermediates III ($\alpha\beta$ process¹).

The fact that the *d*₁ maximum is usually larger than the per-deuteration maximum is already evidence against the $\alpha\beta$ mechanism since any of the intermediate surface alkyls formed should have the same probability to desorb as the surface alkyl leading to a *d*₁ isomer. Furthermore, it would require the formation of distinct secondary surface alkyls (II) which, according to the higher steric repulsion sketched in Scheme V, should desorb more readily than the primary surface alkyls.

As test molecules able to differentiate between the other two processes we chose the deuteration of 1- and *trans*-2-hexene. Since both olefins incorporate more than two D atoms per molecule, during the deuteration process the location of the excess deuterium by high-resolution ²H NMR should indicate the preferred direction of propagation. Such an approach is based on the assumption that after hydrogenation the two original olefinic positions will each be occupied by deuterium atoms and the exchanged ¹H atoms are incorporated randomly rather than at preferred positions (*d*₁ and *d*₃ isomers). Since there is no indication for rapid intramolecular hydrogen scrambling in olefins on Pt surfaces⁶⁰ nor any indication for a bimolecular process leading to a selective hydrogen transfer, both assumptions seem reasonable.

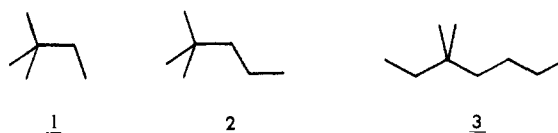
The deuteration experiments were carried out at 25 °C on the 1% Pt on alumina which, due to its intermediate dispersion, is probably more representative of Pt than the extreme dispersions. The results are summarized in Table II. To test for dispersion and temperature effects *trans*-2-hexene was also hydrogenated at 116 °C (experiment 3) and at 25 °C on the less dispersed 5% Pt/alumina. Aside from the slight increase of higher deuterated isomers (experiment 3) no effect was noted. Scheme VIII illustrates the deuterium distribution obtained by integration of the deuterium spectra (experiments 1 and 2 from Table II). Deuteration of 1-hexene resulted in the formation of *n*-hexane with an average deuterium content of 2.75 D/molecule. Assuming that 2 deuterium atoms are located at the position of the initial double bond, the missing 0.75 D is found exclusively in the methylene region, indicating a lack of vinyl or geminal exchange. This points to a strong preference for the π -allyl mechanism over any mechanism involving geminal activation. However, it may be argued that the difference in bond energy between the secondary and the primary position is responsible for the excess activation at the secondary C-H positions in which case a lack of terminal activation in the deuteration of *trans*-2-hexene would be predicted.

Scheme VIII. ²H NMR of Deuteration Product from 2-Hexene-*t* (Top) and 1-Hexene (Bottom)Table III. Product Distribution for H/D Exchange of Hydrocarbons over 5% Pt/Alumina at 116 °C^a

| hydrocarbon fragment | A | B | C | C | C |
|---------------------------|-----|------|----------------|---------------------|---------------------|
| | | | M ⁺ | M ⁺ - 57 | M ⁺ - 29 |
| conversion, % | 3.7 | 18.3 | 55.3 | 49.1 | 59.2 |
| <i>d</i> ₁ | 48 | 41 | 20 | 35 | 18 |
| <i>d</i> ₂ | 21 | 14 | 15 | 22 | 11 |
| <i>d</i> ₃ | 14 | 11 | 6 | 16 | 7 |
| <i>d</i> ₄ | 9 | 6 | 4 | 11 | 5 |
| <i>d</i> ₅ | 5 | 7 | 2 | 8 | 6 |
| <i>d</i> ₆ | 2 | 10 | 1 | 5 | 8 |
| <i>d</i> ₇ | 0 | 10 | 7 | 2 | 12 |
| <i>d</i> ₈ | 0 | 3 | 16 | 1 | 13 |
| <i>d</i> ₉ | 0 | 1 | 21 | 1 | 12 |
| <i>d</i> ₁₀ | 0 | 0 | 6 | 0 | 4 |
| <i>d</i> ₁₁ | 0 | 0 | 1 | 0 | 3 |
| <i>d</i> ₁₂₋₁₆ | 0 | 0 | 0 | 0 | 0 |

^aA = 2,2-dimethylbutane, B = 2,2-dimethylpentane, C = 3,3-dimethylheptane.

The product obtained from deuteration of *trans*-2-hexene contained 2.68 D/molecule. With one D each on the 2 and 3 positions, 0.2 D is located on the terminal methyl position and the remaining 0.48 D on the methylene positions. This indicates little selectivity toward the bond energy of the primary vs. the secondary C-H bond in the allylic activation process confirming the preference of allylic over geminal or vinylic propagation modes of the H/D exchange process.



To probe the generality of the above conclusions about the importance of the π -allyl mechanism over all other modes of propagation as well as to get information on the effect of structural changes on the H/D exchange mechanism, a variety of structurally different hydrocarbons were selected for comparative exchange studies. In the initial study we compare the deuteration of the

(57) Burwell, R. L., Jr.; Shim, B. K. C.; Rowlinson, H. C. *J. Am. Chem. Soc.* **1957**, *79*, 5142.

(58) Demuth, J. E. *Surf. Sci.* **1980**, *93*, L82.






(59) Salmeron, M.; Somorjai, G. A. *J. Phys. Chem.* **1982**, *86*, 341.

Table IV. Deuteration Competition Experiment with *n*-Alkanes and Cycloalkanes at 116 °C on 25% Pt/Alumina

| compd | T_f^a | D_n^b | C^c | d_1 | d_2 | d_3 | d_4 | d_5 | d_6 | d_7 | d_8 | d_9 | d_{10} | d_{11} | d_{12} | d_{13} | d_{14} | d_{15} | d_{16} |
|--|---------|---------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|----------|----------|----------|----------|----------|----------|----------|
| <i>n</i> -C ₅ H ₁₂ | 1 | 5.6 | 5 | 10 | 10 | 9 | 8 | 10 | 11 | 12 | 10 | 6 | 6 | 5 | 2 | | | | |
| <i>c</i> -C ₅ H ₁₀ | 3 | 5.4 | 16 | 15 | 3 | 6 | 16 | 17 | 7 | 7 | 9 | 12 | 8 | | | | | | |
| <i>n</i> -C ₆ H ₁₄ | 5 | 7.0 | 22 | 7 | 8 | 7 | 7 | 7 | 8 | 9 | 10 | 10 | 9 | 7 | 6 | 4 | 2 | | |
| <i>c</i> -C ₆ H ₁₂ | 7 | 3.8 | 34 | 27 | 15 | 13 | 12 | 10 | 7 | 4 | 3 | 3 | 2 | 2 | 1 | | | | |
| <i>n</i> -C ₇ H ₁₆ | 14 | 8.5 | 62 | 8 | 5 | 5 | 5 | 5 | 6 | 6 | 7 | 8 | 9 | 9 | 8 | 7 | 6 | 4 | 2 |
| <i>c</i> -C ₇ H ₁₄ | 17 | 10.4 | 77 | 1 | 1 | 2 | 2 | 4 | 10 | 10 | 5 | 4 | 6 | 9 | 14 | 19 | 12 | | |

^a Turnover frequency [10^{-3} mol site⁻¹ s⁻¹]. ^b Average deuterium content per molecule. ^c Conversion [%].

Table V. Deuteration Pattern of Hydrocarbons Produced by H/D Exchange at 116 °C on 25% Pt/Alumina

| compd | T_f^a | D_n^b | C^c | d_1 | d_2 | d_3 | d_4 | d_5 | d_6 | d_7 | d_8-d_{14} |
|---|---------|---------|-------|-------|-------|-------|-------|-------|-------|-------|--------------|
|  | 7 | 1.0 | 7 | 95 | 5 | | | | | | |
|  | 6 | 1.7 | 3 | 54 | 17 | 18 | 6 | 3 | 2 | | |
|  | 26 | 2.9 | 12 | 48 | 10 | 7 | 8 | 9 | 9 | 8 | |
|  | 39 | 2.3 | 17 | 36 | 21 | 25 | 11 | 5 | 1 | | |
|  | 28 | 5.0 | 12 | 28 | 2 | 3 | 8 | 21 | 5 | 5 | 26 |
| <i>n</i> -hexane | 44 | 7.4 | 15 | 11 | 6 | 5 | 5 | 6 | 6 | 7 | 54 |

^{a-c} See footnotes for Table IV.

three hydrocarbons listed in Table III.

The deuteration pattern reveals a clear d_1 maximum for the 2,2-dimethylbutane (1) with a statistical fall-off at higher deuteration. Compound 2, where π -allyl formation is possible, shows a d_1 maximum together with a maximum shared by d_6 and d_7 , indicating allylic activation (for clean allylic activation a d_6 maximum would be expected).³ Compound 3, however, which contains internal competition of π against allylic propagation, has clear maxima at d_1 and d_9 , indicating clean polydeuteration of the *n*-butyl group. A deuteration minimum at d_5 can be taken as evidence against significant polydeuteration in the ethyl side chain. Despite the high conversion this deuterium distribution could be confirmed by the fragment ions obtained at 16-eV ionization potential. The $M - 29$ peak appears to contain the d_9 maximum, whereas the $M - 57$ peak exhibits only the d_1 maximum with statistical falloff to higher deuteration. The lack of significant deuterium scrambling in MS fragmentation studies has already been demonstrated.³²

Aside from the difference in the deuterium distribution produced in these hydrocarbons on Pt, differences in turnover frequency obtained under identical conditions were also observed. This led us to a brief investigation of the factors governing T_f of hydrocarbons in gas-phase flow conditions. Since all our results so far were in agreement with α -activation as the initiating activation mode of all exchange processes, it was of interest to determine whether T_f is sensitive only to the kinetic energy of the hydrocarbon molecule in the gas phase or also to the bond energy of the C-H bond to be activated. The results are summarized in Table IV. The dependence on the kinetic energy of the turnover frequency is obvious from Figure 4 in which the T_f of *n*- and cyclopentane through heptane are plotted against the boiling point of the six hydrocarbons (thick dots). The data were obtained in a single competition experiment to assure identical conditions. A relatively constant increase of T_f with decreasing kinetic energy is observed, indicating little effect of the primary C-H bonds present only in the *n*-alkanes. The scattering of the points may be attributed to structural and entropic differences of linear over cyclic alkanes. The reliability of this trend is confirmed by the good match of two independent T_f s obtained for cyclopentane and *n*-hexane under different conditions in different experiments at the same temperature (thin points). All other points in Figure 4 were obtained with branched hydrocarbons under the same reaction conditions (see Table V). Whereas the three compounds with one quaternary carbon show a clearly reduced T_f relative to the unbranched

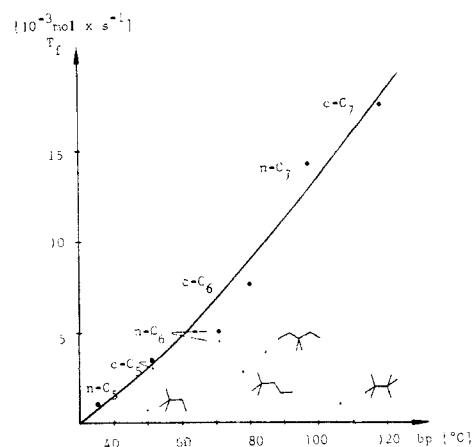


Figure 4. T_f correlation with boiling point of structurally similar and dissimilar hydrocarbons (25% Pt/alumina, 116 °C): (●) competition experiment of *n*- and -C₅-C₇ alkanes; (•) individual experiments.

Table VI. Deuterium Distribution in Alkanes Exchanged at 116 °C on 1% Pt/Alumina Determined by ²H NMR

| | position | | |
|---------------------|----------|----|----|
| | 3 | 4 | 5 |
| 2,2-dimethylbutane | 33 | 68 | |
| 2,2-dimethylpentane | 13 | 34 | 53 |
| 3,3-dimethylpentane | | 43 | 57 |

alkanes, the tetramethylbutane, lacking any secondary C-H, shows a very pronounced reduction in T_f . This can readily be attributed to the higher C-H bond energy of isolated methyl groups (100 kcal/mol) apparently fewer of which get activated upon collision with the catalyst surface. The lack of apparent differentiation between the secondary C-H activation (bond energy around 95 kcal/mol) and terminal methyl C-H (bond energy 98 kcal/mol) may be attributed to a higher steric hindrance of secondary surface alkyls relative to primary surface alkyls (see Scheme V) which may just counterbalance the ease of secondary activation. On the basis of these data, the presence of secondary C-H groups appears more important for C-H activation than partial pressure.

Lack of considerable polydeuteration or even d_2 exchange in tetramethylbutane is evidence against the formation of surface

Table VII. Temperature Dependence of the Deuteration of Cyclopentane and 2,2-Dimethylbutane Produced by H/D Exchange on 5% Pt/Alumina

| temp, °C | conv, % | d_1 | d_2 | d_3 | d_4 | d_5 | d_6 | d_7 | d_8 | d_9 | d_{10} |
|--------------------|---------|-------|-------|-------|-------|-------|-------|-------|-------|-------|----------|
| 2,2-Dimethylbutane | | | | | | | | | | | |
| 116 | 4 | 48 | 21 | 14 | 9 | 5 | 2 | | | | |
| 150 | 7 | 47 | 15 | 14 | 10 | 10 | 2 | | | | |
| 175 | 4 | 40 | 18 | 17 | 12 | 10 | 2 | | | | |
| 200 | 18 | 40 | 16 | 15 | 12 | 13 | 4 | | | | |
| Cyclopentane | | | | | | | | | | | |
| 116 | 18 | 18 | 3 | 4 | 11 | 22 | 8 | 6 | 8 | 10 | 10 |
| 150 | 4 | 20 | 2 | 2 | 3 | 4 | 2 | 3 | 8 | 21 | 36 |

alkylidenes (structure V in Scheme VII) as important intermediates in the propagation of C-H activation.

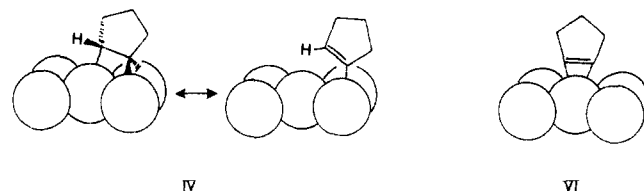
High-resolution ^2H NMR of the isomers 1, 2, and 4 reveal another aspect of these exchange experiments (see Table VI). Not only is most of the deuterium located at the terminal position confirming earlier investigations.³⁰ However, the internal CH_2 group in 2 bears less deuterium than expected from the large amounts of higher deuterated isomers formed, indicating lack of allylic activation. Clearly, allylic propagation is hindered α to quaternary centers which points to a high sensitivity of C-H activation to steric effects confirming earlier results.^{12,32}

The two isomers 2,2-dimethylpentane and 3,3-dimethylpentane, which have a small T_f difference clearly guided by kinetic energy (see Figure 4), were expected to show a difference in deuterium content according to the lack of the 3,3-isomer to undergo π -allyl propagation. However, we find only a marginally higher deuterium content in the isomer 2 which is able to undergo allylic activation (confirmed by a direct competition experiment). ^2H NMR (Table VI) shows that the 3,3-dimethylpentane has even more deuterium at the CH_2 group connected to the quaternary carbon than the 2,2-dimethylpentane. Together with the considerable formation of isotopic isomers containing more than 5 deuterium atoms this indicates α,γ - or 1,3-activation as an important propagation mode for polydeuteration. The lower deuterium content of the 3,3- relative to the 2,2-dimethylpentane together with the obvious lack of 1,3-activation in 3,3-dimethylheptane (see above) points to 1,3-activation as an alternative propagation mode in cases where π -allyl propagation is not possible. The lack of considerable 1,3-activation in 2,2-dimethylbutane as well as in neopentane³⁸ can be explained by the lack of a second CH_2 group α to the quaternary center.

Another aspect derived from the ^2H spectrum of the exchanged 2,2-dimethylpentane is the considerable decrease in the deuterium content going from the terminal methyl position to the CH_2 group connected to the quaternary carbon. This decrease must be attributed to some sensitivity of the π -allyl propagation to steric hindrance which supports our above hypothesis that steric hindrance is a significant factor in the mechanism of C-H activation.

The next major question addressed is the mode of deuteration propagation in the cases where allylic activation is not possible or hindered.

The experiment with 2,2-dimethylbutane and more so with 3,3-dimethylpentane indicate moderately efficient propagation of deuteration in the ethyl groups. The deuterium NMR in both cases shows an excess of deuterium at the terminal position on the order of or greater than 2:1. The next most simple mechanism that fits such a propagation, excluding α,α and α,β on reasons outlined earlier, is a α,α,β -type intermediate⁵⁸ (type VI in Scheme IV, compare also Scheme IX). Some evidence for such an intermediate as a preferred surface species has been obtained indirectly in the reaction of olefins on nickel catalysts⁵¹ and on Pt (111) surfaces.⁶¹ Successive deuteration of the terminal position through repetitive α,β and α,α,β adsorption appears likely.

Scheme IX. Most Likely Surface Intermediates Responsible for the Propagation of H/D Exchange to the Other Side of Cyclic Hydrocarbons

An unusual feature in the collection of compounds studied is the d_5 maximum of cyclopentane, indicating a barrier for exchange propagation to the other side of the five-membered ring which is less pronounced as d_6 in cyclohexane and d_7 in cycloheptane (see Table IV). A similar trend can be found in the cyclohexane and cyclopentane exchange on Pd.⁵⁷ The same α,α,β -mechanism (type VI) must be postulated for the propagation of the deuteration to the other side of the carbocyclic alkanes since π -allyl propagation is unlikely due to steric constraints involved. For cyclopentane, however, even the α,α,β -type propagation should be much less favorable than in cyclohexane since the rigid structure cyclopentane should be less able to accommodate a symmetrical α,α,β -surface intermediate (see Scheme IX). Due to the lack of any d_8 maximum on Pt, the "rollover mechanism"² as an important contribution to the exchange of cyclopentane must be excluded. Even α,α -activation should not be more likely than in any other hydrocarbon, and the $\alpha\beta$ mechanism cannot propagate to the other side of cyclopentane due to the unlikely *trans*-cyclopentene involved.

This leads us to propose another possible reaction path for the deuteration propagation to the other side of cyclopentane, the formation of a surface-cyclopentene (type VI, Scheme IX). Such an intermediate should be favored by the rigid structure of cyclopentane. The stability of cyclic alkyne complexes is well-known in organometallic chemistry.⁶² Alkyne complexes are actually being used to stabilize unstable cyclic alkynes like cyclohexyne.⁶³ The stronger affinity of alkynes relative to olefins to metal surfaces⁵⁴ has found valuable synthetic application in the selective hydrogenation of alkynes to *cis*-olefins.⁶⁴ The relation of surface alkynes to transition-metal complexes is expressed by the similarity of the C-C bond length found to be 1.3 Å on (111) surfaces⁶⁵ and 1.32 Å in organometallic complexes of Pt.⁶⁶ Such a proposed cyclopentene intermediate may form by dehydrogenation from the π -intermediates during the π -allyl propagation on one side of the ring. Precedence for such processes is found in the facile loss of hydrogen from chemisorbed olefins which occurs readily on defined Pt surfaces. In thermal desorption experiments it was found that chemisorbed ethylene loses hydrogen at 300 K after which the remaining surface species show the identical desorption behavior as chemisorbed acetylene.⁵⁸ However, although VI seems

(60) Lebrilla, C. B.; Maier, W. F., unpublished results from experiments with the Pt catalyst analogue to the intramolecular scrambling proof obtained for Ni, see: Lebrilla, C. B.; Maier, W. F. *Tetrahedron Lett.* **1982**, 49, 2875.

(61) Koestner, R. J.; Frost, J. C.; Stair, P. C.; Van Hove, M. A.; Somorjai, G. A. *Surf. Sci.* **1982**, 116, 85.

(62) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, 1980.

(63) Robertson, G. B.; Whimp, P. O. *J. Organomet. Chem.* **1971**, 32, C69.

(64) Marvell, E. N.; Li, T. *Synthesis* **1973**, 457.

(65) Kesmodel, L. L.; Baetzold, R. C.; Somorjai, G. A. *Surf. Sci.* **1977**, 66, 299.

to be a likely intermediate for cyclopentane, we cannot differentiate between IV and VI.

Type IV and type VI intermediates belong to the geminal diactivation pathway of H/D exchange propagation defined in Scheme VII, and according to earlier conclusions this pathway should have a higher activation barrier than the facile π -allyl propagation. Indeed, as outlined in Table VII, at higher temperatures a d_5 maximum is obtained in 2,2-dimethylbutane, indicating perdeuteration of the ethyl group, and the d_5 maximum in cyclopentane disappears at 150 °C, giving way to more pronounced polydeuteration. That this change in deuteration pattern in both compounds occurs in the same temperature range may be taken as indication for a common transition structure (VI) toward perdeuteration.

4. Conclusion. Hydrocarbon activation on Pt is catalyzed by all surfaces. The most active surface sites are terraces or planes which prevent any meaningful direct comparison with C-H activation processes characterized on homogeneous complexes.^{7b} C-H activation on heterogeneous surfaces is achieved by insertion into a single C-H bond. Terminal methyl groups and secondary C-H bonds are more readily activated than isolated methyl groups. Terminal surface alkyls tend to desorb more readily under formation of monodeuterated alkane than secondary surface alkyls which tend to undergo additional C-H activation. Polydeuteration is a secondary process initiated by the formation of an α,β -intermediate from a surface alkyl. Propagation of the deuteration is most facile by a π -allyl-type interconversion process. Propagation of deuteration over a quaternary carbon in a 1,3-activation is restricted to a lack of the more facile π -allyl activation and the presence of secondary C-H bonds on both sides of the quaternary carbon. If π -allyl as well as facile 1,3-activation are excluded by the structure of the alkane, then α,α,β -intermediates are proposed to represent the next most favorable mode of deuteration propagation. No evidence for surface alkylidenes nor the $\alpha\beta$ -process as important parts of the mechanism of C-H activation on platinum has been obtained.

Experimental Section

Deuterium was generated from 99.9% D₂O by a hydrogen generator from General Electric. All hydrocarbons, with the exception of the three described in detail below, and the starting materials for the syntheses are commercially available in high purity. An Aerograph GC with a SE30 on 60/80W column (10 ft \times 1/16 in.) was used for preparative GC. A Hewlett Packard 5790A/5970A GC/MS system equipped with a 59970A workstation and a 50-m capillary column (Ultra No. 1 cross-linked methyl silicone from HP) was used to analyze the product mixture for composition and deuterium content. The deuterium content determined by MS analysis was corrected for ¹³C natural abundance. Due to differences in retention times of the deuterated isomers (at 30 °C the retention time of *n*-hexane-*d*₀ and *n*-hexane-*d*₁₄ differed by about 5 s) a special technique for abundance determination had to be used. The abundance of each isomer was determined by monitoring the parent ion of each mass (*d*₀-*d*₁₄) continuously by selected ion mass spectroscopy (SIMS). Proton-decoupled deuterium NMR spectra were recorded on a Bruker AM-500 instrument. Commercially available catalysts used: 1% Pt/Alumina (Aesar, -300 mesh), 5% Pt/Alumina (Aldrich), and 16 cm² of Pt-foil (0.025-mm thickness). The supported catalysts were used directly. The foil was cut into little pieces and initially treated with oxygen at 700 °C for 7 h and reduced under D₂ at 400 °C for 2 h prior to its use.

The Pt-surface areas of the catalysts were determined in a static vacuum system by selective hydrogen adsorption.³⁹ The catalyst was reduced under H₂ and evacuated overnight under reduced pressure (10⁻⁶ torr at 250 °C). The surface area determination was performed at room temperature with H₂ as the adsorbing gas. The pressure in the apparatus was monitored with a Datametric Barocel Pressure Sensor with a range of 0-1000 torr. The dead volume of the apparatus was determined with He to about 30 cm³.

Synthesis of Selectively Deuterated Hydrocarbons and 3,3-Dimethylheptane. 1-Deuteriohexane.⁶⁷ The Grignard compound formed under

nitrogen from 1-bromohexane (5.050 g, 0.0300 mol) and magnesium (0.970 g, 0.0400 mol) in 20 mL of anhydrous ether (10 mL) was quenched slowly at 0 °C with D₂O. Purification of the product *n*-hexane by preparative GC resulted in *n*-hexane-1-*d*₁ of 98% purity (MS). ²H NMR (rel to Me₄Si): 6.47 ppm.

2-Deuteriohexane.^{67,68} Commercially available 1-hexane (12.850 g, 0.156 mol) was converted to 2-bromohexane by stirring with 50% aqueous HBr (50.0 g, 0.312 mol) with NaBr and ZnBr (ca. 5 g each) at 60 °C for 3 h. The product mixture was extracted with ether and concentrated. The resulting crude bromide was converted to the Grignard, quenched with D₂O, and purified as before. The mass spectra showed again 98%+ monodeuterated *n*-hexane. ²H NMR: s, 6.02 ppm.

3,3-Dimethylheptane.⁶⁹ Dimethylzinc was prepared as described⁷⁰ and converted to dimethylheptane by the method of Reetz et al. (crude yield 70%).⁷¹ Purification of the product was achieved by preparative GC. The product was identified by its MS spectrum M - 15 peak (*m/e* 113), M - 29 (*m/e* 99), and M - 57 (*m/e* 71).

Catalyst Preparation. Preparation of 0.1% Pt/Al₂O₃ (High Dispersion Catalyst). Hydrogen hexachloroplatinate(IV) hydrate (0.0145 g, 3.538 \times 10⁻⁵ mol) was dissolved in deionized water (1.4 mL, from pore volume titration of 5.0 g of alumina). The solution was added dropwise with stirring to dry alumina (Alfa, 60 mesh, 5.007 g). The mixture was dried in an oven for 1 h at 100 °C. The unreduced catalyst was then placed in a flow tube and flushed with hydrogen gas at room temperature for a few minutes. In the hydrogen stream the catalyst was reduced: 3 h at 150 °C; 2 h at 200 °C; 2 h at 250 °C; 2 h at 300 °C; 1 h at 350 °C; and finally 1 h at 400 °C.

Preparation of 0.1% (Intermediate Dispersion), 1%, and 10% Pt/Al₂O₃. All three catalysts were prepared in a similar manner. For the 0.1% catalyst hydrogen hexachloroplatinate(IV) hydrate (0.0125 g, 3.050 \times 10⁻⁵ mol) was dissolved in 10 mL of deionized water. The solution was poured into the alumina (5.1245 g) and stirred, and the water was evaporated. The product was dried in the oven, placed in a flow tube, and reduced as before.

Preparation of 25% Pt/Al₂O₃ (Low Dispersion). Hydrogen hexachloroplatinate (0.5106 g, 1.246 \times 10⁻³ mol) was dissolved in deionized water (10 mL) and added to alumina (0.5123 g). The mixture was stirred, the water evaporated as before, and the unreduced catalyst air dried in an oven at 100 °C for 1 h. It was then placed in a flow tube and reduced at 50 °C for 1 h under hydrogen. After the initial reduction it was then reduced as before. After the reduction, the catalyst was oxidized at 700 °C for 9 h.

Conditions and Apparatus for H/D Exchange

The gas flow was monitored by a mass flow detector (Matheson) before and after the catalyst which is heated by a constant temperature oven. A constant reaction temperature was maintained with an Omega Model 148 controller. At the beginning of each experiment the catalyst was reduced for 15-30 min at 400 °C. After the reduction, the oven was set to the desired temperature and allowed to cool. The substrate (20-40 μ L in a 100- μ L syringe) was injected via syringe pump through a septum into the carrier gas at a constant rate (usually 12.6 to 1.3 μ L/h corresponding to a deuterium gas to hydrocarbon ratio of at least 240). The tube around the injection region is heated (ca. 90 °C) to ensure instant vaporization of the hydrocarbon from the injection needle. After passing the catalyst bed the product was collected in a liquid nitrogen trap and analyzed.

Acknowledgment. This work was supported by NSF Grant No. CHE-8400993. C.B.L. thanks the University of California for a U.C. fellowship. We thank Prof. Somorjai for preprints and Prof. Michaels for discussions about mass transport problems.

Registry No. H₂, 1333-74-0; Pt, 7440-06-4; *n*-C₆H₁₄, 110-54-3; *n*-C₅H₁₂, 109-66-0; *c*-C₆H₁₂, 110-82-7; *n*-C₇H₁₆, 142-82-5; *c*-C₇H₁₄, 291-64-5; *cis*-4-methyl-2-pentene, 691-38-3; 2-methylpentane, 107-83-5; 1-hexene, 592-41-6; 2-hexene, 592-43-8; 2,2-dimethylbutane, 75-83-2; 2,2-dimethylpentane, 590-35-2; 3,3-dimethylheptane, 4032-86-4; 3,3-dimethylpentane, 562-49-2; 2,2,3,3-tetramethylbutane, 594-82-1.

(68) Doyle, P. M.; McOskar, C. C.; West, C. T. *J. Org. Chem.* **1976**, *41*, 1393.

(69) Noller, C. R. *J. Am. Chem. Soc.* **1929**, *51*, 594.

(70) Krug, R. C.; Tang, P. J. C. *J. Am. Chem. Soc.* **1954**, *76*, 2262.

(71) Reetz, M. T.; Westermann, J.; Steinbach, R. *J. Chem. Soc., Chem. Commun.* **1981**, 237.

(66) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1976**, *14*, 246.

(67) Avanesoff, M.; Gäumann, T. *Helv. Chim. Acta* **1971**, *54*, 995.