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Mechanism of C-H Activation of Hexane on Platinum

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Summary: Olefinic intermediates are identified as the precursors for the perdeuteration process observed upon single surface interaction of the alkane.

C-H activation of saturated hydrocarbons which represents the key step of such important processes as crude oil refinement, still remains one of the mysterious reactions in organic chemistry. Much attention has been focused lately on C-H activation of alkanes by transition metal complexes[1], isolated metal atoms[2], and theoretical calculations[3]. However, very little is known about the actual mechanism even on heterogeneous surfaces despite considerable efforts in the past.[4]

We have studied the mechanism of C-H activation by H/D exchange experiments with hexane[5] in a gas phase flow apparatus. Two distinctively different catalysts were selected, a 1% Pt on gamma alumina (metal surface area 0.85 m^2/g, dispersion 42%) to represent highly dispersed catalysts (high energy surfaces) and ordinary Pt foil for bulk metal (low energy Pt surfaces). The mechanism of hydrocarbon activation was studied by exchange experiments with deuterium as carrier gas. The substrate/carrier gas ratio was controlled by injection of the substrate via a syringe pump. In order to avoid multiple adsorption, the experiments were carried out at a low overall conversion (<10%) which can be controlled readily by the syringe pump flow.

$$\text{n-}C_6H_{14} \xrightarrow{D_2/Pt} \underset{\leq 10\%}{(\text{n-}C_6H_{13}D_1 + \text{n-}C_6D_{14})} + \underset{\geq 90\%}{nC_6H_{14}}$$

The product was analyzed by GC-MS. In a series of experiments[6] we found, independent of temperature and catalyst, that the dominant isotopic isomers produced were d_1 and d_{14} n-hexane (see table 1, experiment A) indicating either a surface structure insensitive reaction or a reaction catalyzed by the low energy surfaces dominating on the foil (terraces). No evidence for a preferred formation of d_2 or d_3 isomers, which would be indicative for π- or allylic

intermediates, could be detected. This confirms the results of Somorjai et. al. who obtained similar results under ultrahigh vacuum conditions on [1.1.1] Pt (terraces) and [10.8.7] Pt (terraces, steps, and kinks) surfaces with n-hexane.[7] Dominance of d_1 and perdeuterated isomers have also been reported on catalysts other than Pt.[8].

In our experiments we obtained ratios for the d_1/d_{14} isotopic isomers formed ranging between 10 to 0.1. Although we have not been able to control this relative ratio, a clear dependence from the total hydrocarbon exposure of the catalyst has been noted. Since the gross surface structure of the catalysts should not change considerably under our mild reaction conditions the observed change in the d_1/d_{14} ratio is attributed to yet unknown changes in the carbon layers on the catalyst surfaces.

The dominant formation of the d_1 isomer can be interpreted as the formation of surface alkyls by insertion into one C-H bond by the metal surface. Recombination of the alkyl with a surface hydrogen isotope (H or D, whichever happens to be closer to the alkyl) will result in the desorption of the d_1-n-hexane:

figure 1

The formation of the perdeuterated species upon a single surface interaction is more difficult to understand. Based on the above hypothesis that C-H activation is catalyzed by terraces, we suggest a

π-allyl mechanism similar to that proposed by Gault et. al.[9]

figure 2

It is safe to assume that surface alkyls are formed by simple α-insertion. These surface alkyls (1) may desorb to form the observed d_1 isomers, or undergo a second C-H activation to form either a surface alkylidene[10] (2) or an α,β-adsorbed species (3) (π-complex). Whereas the surface alkylidene is a reasonable and likely surface intermediate which does not seem to affect the overall catalytic reaction. The π-complex, however, must suffer severe strain due to surface interactions with its allylic hydrogen atoms (4). Simple calculations based on known Pt-π complexes indicate a distance between 1.3 - 2.8 Å for the allylic hydrogen atoms to a flat Pt surface. This distance is within the bonding range to the metal resulting in a strong reduction of the activation barrier for the allylic position. Rapid formation of an allylic intermediate (4) will follow. Depending on the space available on the surface a rapid multiple C-H insertion process may occur leading to a "naked" carbon chain on the Pt surface which can not explain the formation of d_5-maxima in the deuteration of cyclopentane.[11] Another argument against such a mechanism is the even distribution of less deuterated isomers ranging from d_2-d_{13} observed. More likely is a process in which the allylic species picks up a deuterium atom from the surface to form the π-intermediate 5 followed by another allylic activation and so on. In such a process the hydrocarbon may exchange some or all

its hydrogen atoms by an alternating π-allyl interaction which rapidly migrates back and forth through the molecule. Such a process will be blocked by any quaternary center and is thus in agreement with the early findings of Burwell that perdeuteration occurs preferentially in only one of the carbon chains connected to quaternary centers.[8,12]

Essential for our mechanistic interpretation is the formation of a π-adsorbed intermediate which initiates the perdeuteration by simple steric effects. Any olefinic intermediate, therefore, must be prone to perdeuteration. To prove this hypothesis we passed a mixture of 0.1% trans-4-methyl-2-pentene and 99.9% n-hexane over the platinum foil at 117 °C. The results are summarized in table 1 (experiment B). The 2-methylpentane formed (6) shows only one dominant isotopic isomer, the d_{14}. The product n-hexane, due to the small olefin concentration is unaffected showing the normal d_1/d_{14} pattern. Since the total conversion in this experiment is only 7% the perdeuteration in the 2-methylpentane must have resulted from a single surface interaction supporting our above hypothesis. A control experiment (C) with a mixture of 2-methylpentane and n-hexane showed no preference of the Pt catalyst for 2-methylpentane excluding selective deuteration.

figure 3, table 1

This simple experiment connects two related processes, the C-H activation of hydrocarbons and the hydrogenation of olefins. In experiment D a much larger olefin concentration (3%) was employed and the expected drastic reduction of the perdeuterated species in the n-hexane was observed. This is evidence for the successful competition of the olefin for the active sites catalyzing the perdeuteration which provides further support of the proposed mechanism. In addition we see a drastic change in the deuteration pattern of the 2-methylpentane produced which now displays the dominating d_1,d_2,d_3 pattern observable in olefin deuterations on heterogeneous catalysts.[6,13] This dependence of the deuteration pattern from the olefin concentration suggests that the reductive elimination of the saturated olefin formed in a hydrogenation reaction is facilitated by the presence of excess olefin. This process may be compared with the ligand assisted reductive elimination observed by Yamamoto in homogeneous nickel complexes.[14] It can also explain the general difference in activation barriers for the C-H activation of hydrocarbons of about 20 kcal/mol[15] and the hydrogenation of olefins of only 10 kcal/mol[16] on heterogeneous catalysts.

It has been shown, that the rate determining step in olefin hydrogenation is the reductive elimination of the hydrocarbon[17] and that of the C-H activation is the initial cleavage of the C-H bond (i.e. the dissociative adsorption)[18]. Hydrocarbon adsorption on Pt is an exothermic process[19] indicating, according to the law of microscopic reversibility, that the activation barrier for desorption of a

hydrocarbon should be larger than the activation barrier for adsorption contradicting adsorption as the rate determining step. Since the desorption (reductive elimination) of the product hydrocarbon should be identical processes in olefin hydrogenation and C-H activation the general difference of 10 kcal/mol in the activation barrier for the two processes represents an unresolved conundrum.

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Table: isotopic distribution produced by Pt foil

exp.		conv.	d1	d2	d3	d4	d5	d6	d7	d8	d9	d10	d11	d12	d13	d14
A	n-hexane	4	10	1	2	3	3	3	4	4	5	5	7	8	14	31
B	(.1% olefin)															
	2-methylpentane	-	2	4	5	7	8	10	9	8	5	6	7	8	7	12
	n-hexane	7	23	5	5	4	4	5	5	6	6	6	7	7	7	11
C	2-methylpentane	13	15	6	4	4	4	3	4	3	5	7	12	12	13	7
	n-hexane	14	11	4	3	3	3	2	3	3	4	7	12	17	17	9
D	(3% olefin)															
	2-methylpentane	-	6	35	13	9	7	5	5	5	4	3	3	3	2	2
	n-hexane	16	45	14	8	4	4	3	4	4	4	4	3	2	2	2

figure 3:

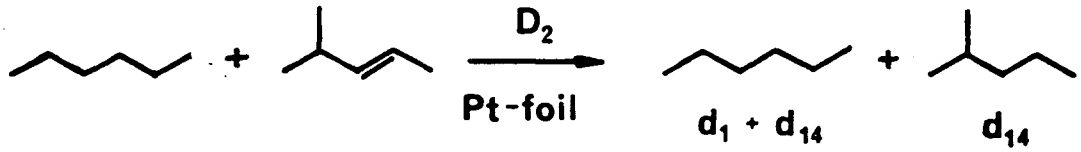


figure 1:

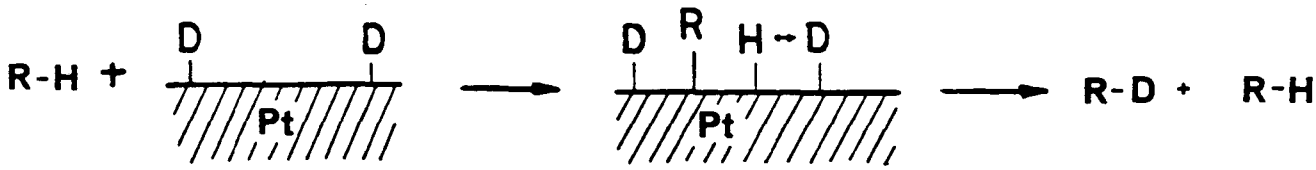
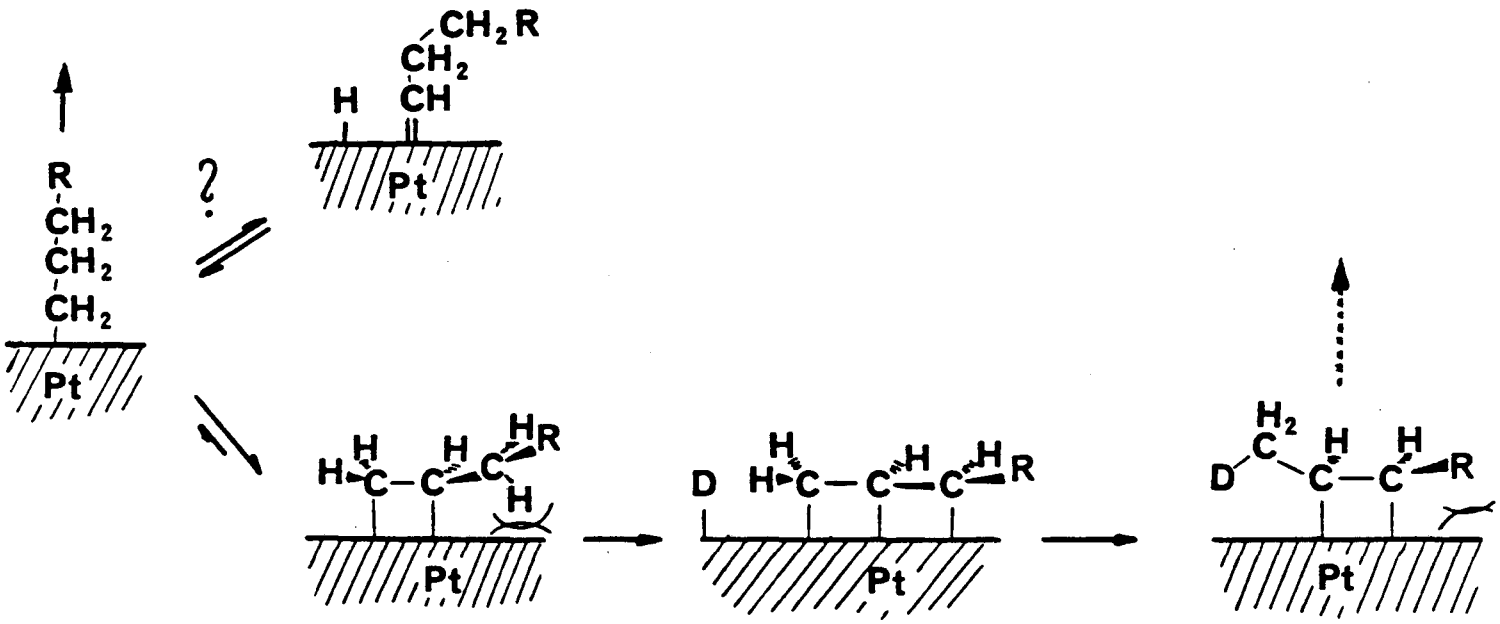


figure 2:



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