ACTIVATION OF ALKANES BY TRANSITION METAL COMPLEXES

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Abstract - The data are presented for catalytic H-D exchange of alkanes with protic solvents and some other reactions of alkanes in the presence of transition metal complexes, particularly Pt(II). In Pt(II) chloride solutions the activity of Pt-containing species towards alkanes is in the order \( \text{S}_2\text{PtCl}_2 > \text{S}_2\text{PtCl}_3 > \text{PtCl}_4 \) (S—solvent). Ligands with properties of soft bases (CN\(^-\), CNS\(^-\), PPh\(_3\) etc.) decrease the rate of H-D exchange. There is a strong evidence that alkyl derivatives and carbene complexes are the intermediates in reactions of alkanes catalyzed by Pt(II). The first step of the reaction is likely to be an oxidative addition

\[
\text{RH} + \text{Pt(II)} \rightarrow \text{R}<\text{H}> \text{Pt(IV)}
\]

INTRODUCTION

Activation of C-C or C-H bonds in alkanes by transition metal complexes is, as J. Halpern put it in 1968 (1), one of the most important and challenging problems in the entire field of homogeneous catalysis.

Creation of new selective catalytic processes of alkanes as a substitute for poorly selective radical chain reactions is particularly important now since the shortage of traditional sources of alkanes such as oil and natural gas is becoming a real problem.

The well known inertness of alkanes is reflected in their other names such as "paraffins" (from Latin: parum affinis - without affinity), and "saturated hydrocarbons" (from their inability to enter any addition reactions). However in respect of cleavage of strong covalent C-H bonds the problem looks similar to that of H-H bond activation in molecular hydrogen which was successfully solved in coordination catalysis.

Activation of \( \text{H}_2 \) by metal complexes is known to involve oxidative addition as a primary step in a number of catalytic systems:

\[
\text{M} + \text{H}_2 \rightarrow \text{M}<\text{H}>
\]

(\( \text{M} \) — here and further is a metal atom or ion in a metal complex).

If a similar reaction takes place in case of alkanes:

\[
\text{M} + \text{RH} \rightarrow \text{M}<\text{R}>
\]

it could give rise to consequent reactions, the simplest being H-D exchange with solvent's exchangeable deuterium provided the alkyl hydride formed has acidic properties:

\[
\text{M}<\text{H} > \rightarrow \text{M} - \text{R}^- + \text{H}^+
\]

Another possibility is the isotope exchange of RH with D\(_2\) if reversible decomposition of trihydride \( \text{MH}_3 \) occurs in the presence of hydrocarbon and deuterium

\[
\text{MH}_3 \rightarrow \text{H}_2 + \text{MH}
\]

\[
\text{MH} + \text{D}_2 \rightarrow \text{MHD}_2 \rightarrow \text{MD} + \text{HD}
\]

\[
\text{MD} + \text{RH} \rightarrow \text{M}<\text{R} > \rightarrow \text{RD} + \text{MH} \quad \text{etc.}
\]
Proceeding from the above assumed mechanisms we observed in 1969 the isotope exchange between alkanes and $D_2O + CH_3CO_2D$ in the presence of Pt(II) and also between alkanes and $D_2$ in the presence of $(Ph_3P)_2CoH_2$ (2).

Afterwards other platinum as well as non-platinum metal complexes were found by several groups of workers to be active towards alkanes, and some other reactions of alkanes catalyzed by metal complexes were discovered besides isotope exchange.

It should be noted that though the first observation of C–H bond activation in alkanes in the presence of metal complexes in solution was made in 1969, other reactions involving C–H activation by transition metals had been known before which may now be compared with homogeneous activation of alkanes, e.g.,

i. heterogeneous activation of alkanes at metal surface

ii. homogeneous activation of C–H bond in aromatic compounds and some molecules with "activated" C–H bond

iii. intramolecular insertion of metal in ligands with aliphatic and aromatic C–H bonds in some coordination compounds ("cyclometallation reaction")

**H–D EXCHANGE**

When methane and ethane are heated to 100°C in sealed ampoules containing solutions of $K_2PtCl_4$ in $D_2O - CH_3COOD$ mixture deuteration of the alkanes molecules is observed (2). In the absence of a catalyst this reaction is known to be possible only at about 1000°C, i.e., at temperatures of alkane pyrolysis.

In later studies a homogeneous exchange catalyzed by platinum (II) salts was observed for a whole series of simple alkanes including also iso-alkanes and cyclo-alkanes, the latter being particularly reactive (3). The isotope exchange may serve as an effective way of deuterated alkanes preparation. Substituted derivatives of alkanes (halo-alkyls, alcohols, acids etc.) are also capable to H–D exchange with a solvent, which is often facilitated in the substituent's presence. However, in the case of some of these compounds the exchange is complicated by side processes such as oxidation, hydrolysis etc. Ethylene does not exchange its hydrogen atoms with solvent's protons in platinum (II) solutions, while at the same time it inhibits exchange in alkanes probably due to the formation of strong $\pi$-complexes with Pt(II) (4).

Alkanes of the $RC(CH_2)_n-CH=CH_2$ type, containing a quaternary carbon atom in the vicinity of the double bond, exchange their hydrogen atoms in the presence of platinum salts in the alkyl part of the molecule and almost exclusively in C5 (5)

\[
\begin{align*}
H - PtCl_2 & \rightarrow CH_2CH_2CH(CH_3)_2CH_3 \\
& \rightarrow CH_2CH_2CH(CH_3)_n-CH=CH_2
\end{align*}
\]

Investigation into selectivity of the attack of Pt(II) on C–H bond in alkanes revealed importance of steric hindrances, which is even more pronounced than that of C–H bond energy changes. Thus the ratio of selectivity of primary, secondary and tertiary C–H bonds was found to be 1: 1: 0, e.g., for isobutane 9 atoms out of 10 turned out to be exchangeable, the tertiary C–H bond being unaffected.

In 1973 Garnett found that Na$_2$IrCl$_4$ can catalyze H–D exchange of alkanes with $CH_3COOD - D_2O$ (6). Recently RhCl$_3$ was found to be able to catalyze similar exchange as well (7) Ir(I) and Rh(I) isoelectronic with Pt(II) (d$^9$) were assumed to be active in the isotope exchange, Pt(II) being the most active out of the three.

Some isotope exchange in the presence of non-platinum metal complexes besides $(Ph_3P)_2CoH_2$ mentioned above has been also studied. Activation of methane to H–D exchange in the presence of Ziegler catalysis based on Ti and V was reported in (8), and in recent work ( $\pi$-CoH$_2$)$_2V$ was found to catalyze isotope exchange of methane and ethylene (9).

In 1977 Cu(II) in water solution was found to be the first non-platinum metal catalyzing H–D exchange of alkanes with protic solvent (10).
Transition metal compounds have been often used to initiate radical chain reactions of hydrocarbons, e.g., oxidation by molecular oxygen, the role of initiator being to form free radicals.

At present, however, there is some evidence for possibility of catalytic transformations of alkanes directly in coordination sphere of complexes(II). Thus in the presence of Pt(II) complexes Pt(IV) is reduced by alkanes including methane and ethane in aqueous solutions at 100-120°C to Pt(II), the latter being the catalyst (12). The main products of alkanes transformation are chlorohydrocarbons, whereas alcohols, esters and some other compounds are the by-products. Benzene is the main product in the case of cyclohexane. (Table 1) Kinetic results show that chlorohydrocarbons are intermediates for other products including benzene.

### Table 1. Products of Oxidation of Hydrocarbons in Aqueous Solution of H₂PtCl₆ — Na₂PtCl₄

<table>
<thead>
<tr>
<th>No.</th>
<th>Alkane</th>
<th>t°C/time(h)</th>
<th>Products (relative yield, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methane, 50atm</td>
<td>120/4</td>
<td>Methyl chloride</td>
</tr>
<tr>
<td>2</td>
<td>Ethane, 20atm</td>
<td>120/4</td>
<td>Ethyl chloride</td>
</tr>
<tr>
<td>3</td>
<td>Propane, 6atm</td>
<td>120/4</td>
<td>n-C₃H₇Cl (75), iso-C₃H₇Cl (25)</td>
</tr>
<tr>
<td>4</td>
<td>Pentane</td>
<td>120/0.25</td>
<td>n-C₅H₁₁Cl (56), sec-C₅H₁₁Cl (44)</td>
</tr>
<tr>
<td>5</td>
<td>Isopentane</td>
<td>120/0.25</td>
<td>prim-C₅H₁₁Cl (78), sec-C₅H₁₁Cl (22)</td>
</tr>
<tr>
<td>6</td>
<td>Hexane</td>
<td>110/5</td>
<td>n-C₆H₁₃Cl (40), n-C₆H₁₃OCOCP₃ (30, 5), C₄H₉COCH₃ (23, 9), sec-C₆H₁₂OCOCF₃, sec-O₆H₁₁Cl (1, 4)</td>
</tr>
<tr>
<td>7</td>
<td>Cyclohexane</td>
<td>110/5</td>
<td>C₆H₆ (77, 6), C₆H₅Cl (11), C₆H₁₁Cl (5, 4), C₆H₁₁OCOCF₃ (5), cyclohexanone, traces of alcohol and dichloride</td>
</tr>
<tr>
<td>8</td>
<td>Methyl cyclohexane</td>
<td>110/5</td>
<td>Toluene (61, 6), n-chlorotoluene (11, 2), CH₃C₆H₁₀Cl (9, 1), CH₃C₆H₁₀OCOCP₃ (8, 2), C₆H₁₁CH₂Cl (4, 1), ketone (4, 1)</td>
</tr>
<tr>
<td>9</td>
<td>Decalin</td>
<td>110/5</td>
<td>Naphthalene</td>
</tr>
</tbody>
</table>

Note. Experiments (1-5)—in H₂O, 0.5M Pt(IV), 0.05M Pt(II); (6-9)—in 8.7M CF₃COOH, 0.18M Pt(IV), 0.02M Pt(II).

The selectivity of the reaction is similar to H–D exchange and distinctly different from that of radical chain reactions, e.g., chlorination. Thus the yield if n-C₃H₇Cl is considerably higher than of iso-C₃H₇Cl again indicating importance of steric factors.

Though Pd(II) complexes do not catalyze H–D exchange of alkanes with the solvent, solutions of PdSO₄ in sulfuric acid were shown (13) to absorb alkanes at 90°C. The reaction is accompanied by formation of SO₂ and palladium metal. Presumably olefines are formed first which are then subject to fast reaction of sulfonation, oxidation and dehydrogenation. Benzene and benzene sulfonic acid are formed in the case of cyclohexane. As distinct from Pt(II) catalyzed reaction "normal" order of selectivity of attacking C–H bonds (tert>sec>prim) was found for palladium induced oxidation.

It was found later (4) that alkanes (n-hexane and cyclohexane) reduce Pd(II) trifluoroacetate at 90°C in trifluoroacetate acid to Pd(0). The stoichiometry for cyclohexane is

\[
3 \text{Pd(CF}_3\text{CO}_2\text{)}_2 + C_6\text{H}_{12} \rightarrow 3 \text{Pd(0)} + C_6\text{H}_6 + 6 \text{CF}_3\text{CO}_2\text{H}
\]
Chloride complexes of Ru(IV) substantially accelerate the oxidation of alkanes in aqueous solutions of chromic acid, alkyl chlorides being the primary products of alkanes transformation (15). Alkyl chlorides were found to be also formed in solution of Cu(II) chlorides, which undergo reduction to Cu(I) (10). Activation of alkanes by Cu(II) complexes to oxidation as well as to H-D exchange with the solvent is of particular interest since its mechanism may be similar to alkanes activation by certain monooxygenases in bacteria. It was found recently (16) that the enzyme isolated from methane oxidizing bacteria Methylosinus trichoporum contain copper.

Table 2 summarises the metals, which in their complexes are able to activate aliphatic C-H bond in free alkanes (circles) and in ligands bound to metal in complexes (squares).

### TABLE 2. Metals Activating Alkanes

<table>
<thead>
<tr>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
<th>VIII</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
<td>Fe</td>
<td>Co</td>
</tr>
<tr>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
<td>Rh</td>
</tr>
<tr>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Au</td>
</tr>
</tbody>
</table>

It is seen that there are now a number of metals in their complexes able to C-H bond activation, and one can expect that the list will continue to grow.

**MECHANISM OF ALKANES ACTIVATION**

**a. The Nature of Active Centre**

The mechanism of alkanes activation by various transition metal complexes is by no means certain and probably not the same for different systems. The most detailed mechanistic information has been obtained from the investigations of H-D exchange with the solvent and oxidation of alkanes in the presence of Pt(II) complexes (17-25).

The reaction of H-D exchange at 80-120°C is about 30 times as fast in 50% deuterated acetic acid as in D2O. Thus is indicative of a specific solvation of the active particle with acetic acid molecule, probably with formation of a weak chelate complex of PtCl2

\[
\text{Cl}_2\text{Pt}<\text{D}^{-}\text{O}^{-}<\text{C}^{-}\text{CH}_3
\]

H-D exchange is of the first order with respect to hydrocarbon concentration, the reaction rate being virtually independent on ionic strength and the acidity in the range of 0.2 to 1.0M.

The order of the reaction with respect to a chloride ion changes from 0 to -1 as the concentration of Cl⁻ increases (Fig.1)

![Figure 1](image-url)
Investigation of the dependence of the rate on Cl⁻ concentration shows (17,18,21) that $S_2PtCl_2$ are the most active species in platinum(II) chloride solution in equilibrium with $SPtCl_3^-$ and $PtCl_4^{2-}$ (S-solvent molecule). The line in Fig. 1 corresponds to the formula

$$k = \frac{k_1 + k_2[Cl^-] + k_3[k_12]}{1 + k_2[Cl^-] + k_3[k_12]} \frac{[PtCl_2]}{0}$$

where $k_1$, $k_2$, and $k_3$ are the rate constants for $S_2PtCl_2$, $SPtCl_3^-$ and $PtCl_4^{2-}$ respectively, $K_{12} = K_1K_2$, and $K_1$ and $K_2$ are equilibrium constants for reactions

$PtCl_4^{2-} \rightleftharpoons SPtCl_3^- + Cl^-$

$SPtCl_3^- \rightleftharpoons S_2PtCl_2 + Cl^-$

respectively.

For cyclohexane at 100°C

$k_1 : k_2 : k_3 = 100 : 14 : 0.6$

From the temperature dependence of $k_1$ in the range from 81 to 112°C it follows that

$$k_1 = 2.5 \times 10^8 \exp \left( -18.2 \frac{200}{R} \right) \text{M}^{-1} \text{sec}^{-1}$$

To elucidate the nature of activation of alkanes the effect of ligands was studied (21) on the rate of H-D exchange catalyzed in $PtLCl$ (L = H₂O, Cl⁻, NO₂, DMSO, NH₃, Py) and $PtCl_2L_2$ (L = H₂O, Cl⁻, Br⁻, I⁻, NO₂, CN⁻, Ph₃P). As can be seen from Table 3 the exchange rate constant changes by three orders of magnitude depending on ligands decreasing towards more basic as well as softer (more polarizable) ligands with a growing tendency for double bonding.

<table>
<thead>
<tr>
<th>No.</th>
<th>Complex</th>
<th>Time (hrs)</th>
<th>$\sum d_i %$</th>
<th>$k_1 \times 10^3$ (1 mol⁻¹ sec⁻¹)</th>
<th>$M = \frac{\sum d_i}{\sum d_i}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PtCl₂S₂</td>
<td>2</td>
<td>0.230</td>
<td>7.42</td>
<td>1.93</td>
</tr>
<tr>
<td>2</td>
<td>KPtcCl₃S</td>
<td>2</td>
<td>0.154</td>
<td>4.97</td>
<td>1.74</td>
</tr>
<tr>
<td>3</td>
<td>K₂PtCl₄</td>
<td>1.66</td>
<td>0.333</td>
<td>2.78</td>
<td>1.75</td>
</tr>
<tr>
<td>4</td>
<td>K₂Pt(NO₂)Cl₃</td>
<td>7</td>
<td>0.185</td>
<td>0.366</td>
<td>1.52</td>
</tr>
<tr>
<td>5</td>
<td>KPt(NH₃)Cl₃</td>
<td>2.5</td>
<td>0.140</td>
<td>0.777</td>
<td>1.65</td>
</tr>
<tr>
<td>6</td>
<td>KPt(py)Cl₃</td>
<td>12</td>
<td>0.0268</td>
<td>0.025</td>
<td>1.46</td>
</tr>
<tr>
<td>7</td>
<td>KPt(DMSO)Cl₃</td>
<td>12.5</td>
<td>0.0549</td>
<td>0.056</td>
<td>1.60</td>
</tr>
<tr>
<td>8</td>
<td>Pt(DMSO)Cl(NO₃)</td>
<td>4</td>
<td>0.0242</td>
<td>0.083</td>
<td>1.62</td>
</tr>
<tr>
<td>9</td>
<td>K₂Pt(NO₂)Cl₄</td>
<td>7</td>
<td>0.0584</td>
<td>0.115</td>
<td>1.41</td>
</tr>
<tr>
<td>10</td>
<td>Pt(PPh₃)Cl₂</td>
<td>16.5</td>
<td>0.0078</td>
<td>0.007</td>
<td>1.34</td>
</tr>
<tr>
<td>11</td>
<td>Pt(acac)₂</td>
<td>7.5</td>
<td>0.0511</td>
<td>0.094</td>
<td>1.57</td>
</tr>
<tr>
<td>12*</td>
<td>Pt(CP₃COO)₂</td>
<td>0.3</td>
<td>0.0158</td>
<td>0.732</td>
<td>1.34</td>
</tr>
</tbody>
</table>

*Experiment carried out in CP₃COOD at 91°C

The rate changes in parallel with a multiplicity factor M (average number of D atoms entering an alkane molecule during its contact with Pt(II) complex). All the ligands tested can be arranged as to their effect on the rate of deuterium exchange of cyclohexane in the following order

$CN \approx CNS < Ph < DMSO \approx py < NO₂ < I < Br < NH₃<OH < H₂O \approx F \approx SO₄$
TABLE 4. Distributions of d—methanes formed in methylation Pt(II) by CH₃HgBr and direct H-D exchange of CH₄ and D₂O

<table>
<thead>
<tr>
<th>Conditions</th>
<th>D=∑d₁</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂PtCl₄ : HgCl₂ : DCI= 0.915</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>1:1:3; PCH₄ = 760torr 100°C; 9 hours</td>
<td>0.650 0.251 0.07350.0296</td>
<td></td>
</tr>
<tr>
<td>K₂PtCl₄ : CH₃HgBr : DCI= 35.0</td>
<td>1.49</td>
<td></td>
</tr>
<tr>
<td>1:1:3; 100°C; 0.3 hour</td>
<td>0.630 0.268 0.0815 0.0212</td>
<td></td>
</tr>
</tbody>
</table>

The distribution of deuteroalkanes formed in multiple exchange does not depend on the time at the initial stages of the reaction. Thus all the deuterated species are formed in parallel as a result of a single elementary reaction of an alkane molecule with Pt(II) centre (17,18).

For methane the phenomenon may be explained assuming reversible formation of a complex of methylene with platinum Pt—CH₀ alongside with methyl platinum compound. The distribution of deuterohydrocarbons can be calculated by the stationary state method from the scheme:

\[
\begin{align*}
\text{CH₄} & \xrightarrow{k₁} \text{CH₃D} \\
\text{Pt—CH₃} & \xrightarrow{k₂} \text{CH₂D₂} \\
\text{Pt—CHD} & \xrightarrow{k₃} \text{Pt=CH₀} \\
\text{Pt=CD₂} & \xrightarrow{k₄} \text{CD₄}
\end{align*}
\]

The part of each deutermethane present in the mixture \( \alpha_i = d_i / \sum d_i \) may be calculated from the factor \( p=k_1/k_0 \). The calculation of the distribution (i.e., values \( \alpha_i \) ) of deuterohydrocarbons for the exchange of methane and ethane in CH₃CO-D-D₀ (1:1) indicates that this scheme adequately represents the experimental results. For ethane and other alkanes the multiple exchange can be explained assuming ethylene and olefines intermediates forming \( \pi \)-complexes with Pt(II) (23). However, experiments with ethane exchange in water solution revealed (24) an unusual stepped distribution including two groups \( \alpha_i, \alpha_i, \alpha_i \) and \( \alpha_i, \alpha_i \), the distribution in each of these groups being ascending (Fig. 3).

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![Figure 3. Distribution of deuteroalkanes in products of H-D exchange. CH₃CH₂CH₂- and (CH₃)₂CH- the distribution in alkanes formed in hydrolysis of corresponding RHgBr. Open lines for C₆H₆ corresponds to a distribution constructed using the 1:1 selectivity ratio for prim.:sec. C—H bonds.](image-url)
Activation of alkanes by transition metal complexes

It may be noted that the order is opposite to that of trans-effect of ligands in substitution reactions in square Pt(II) complexes.

Decrease of activity with the increase of basic properties of ligands indicates that acceptor properties of Pt(II) are important in reaction with alkane molecule which behaves as a donor.

The support for this conclusion was found in a study of the dependence of exchange rate on the nature of substituents in methane and ethane derivatives (20). It turned out that two-parameter Taft equation holds (Fig. 2)

$$\log \frac{k}{k_0} = \sigma^* \cdot \varepsilon^* + n \psi$$

The value of $\sigma^*$ (-1.4) corresponds to moderate electron accepting properties of Pt(II) with respect of hydrocarbon molecule. In addition to the polar parameter $\varepsilon^*$ the reaction rate depends on resonance term $n \psi$. $\psi$ characterizes the conjugation of the $\alpha$-substituent in transition state, $n$—being equal to the number of substituents capable of such a conjugation.

The effect of $\pi$-accepting ligands (inverse trans-effect) apparently correlates with changes in Pt-R and Pt-H bond energies.

According to the assumed mechanism of oxidative addition, alkyl derivatives of Pt(IV) and Pt(II) have to be formed as intermediates in both H-D exchange and oxidation of alkanes catalyzed by Pt(II):

$$\text{Cl}_2\text{Pt} + \text{RH} \rightleftharpoons \text{Cl}_2\text{Pt}^\text{IV}_R \rightleftharpoons \text{ClPt}R + \text{H}^+ + \text{Cl}^-$$

Although the isolation of alkylated intermediates has been so far difficult some evidence for such intermediates was obtained from comparison of distribution of deuterated alkanes obtained in H-D exchange and those formed in reaction of PtCl$_2$ with RHgBr where primary alkylation of Pt is very likely (22). It was mentioned already that polydeuterated alkanes are formed together with monodeuterated alkanes as a result of multiple exchange. The nature of this will be discussed later but independently of its mechanism the distribution of isotope substituted alkanes can be used as a "fingerprint" indicating the source of alkanes formed in the exchange.

In interaction of K$_2$PtCl$_4$ with organomercuric compounds in D$_2$O deuteroalkanes are formed showing the multiple exchange pattern similar to that for alkanes exchange.

Tabulated below are the distributions of deuteroalkanes in the reaction of CH$_3$HgBr with K$_2$PtCl$_4$ and in direct H-D exchange of CH$_4$ catalyzed by K$_2$PtCl$_4$ under identical conditions.

Close agreement of both distributions is a convincing evidence for the formation of alkyl compounds of platinum in homogeneous activation of alkanes.

Kinetic results for chlorination of alkanes and their derivatives by Pt(IV) catalyzed by Pt(II) show that this reaction involves the same intermediates as for H-D exchange, thus alkylated Pt compounds are also formed in catalyzed chlorination and other oxidation reactions (26-29).
The pattern of stepped distribution suggests that the exchange takes place first in one methyl group of ethane, and then, after the molecule turns round, in the other. Obviously such a distribution is inconsistent with the \( \sigma \)-complex alone as an intermediate and can be explained if the reaction of ethane similarly to that in methane involves intermediate formation of complexes with carbene.

\[
\text{Pt(II)} + \text{C}_6\text{H}_6 \xrightarrow{k_1} \text{Pt} - \text{C}_2\text{H}_5 \xrightarrow{k_2} \text{Pt} \xrightarrow{k_3} \text{Pt} \leftrightarrow \text{CH}_2 \text{CH}_3
\]

The "turning round" might be performed via \( \sigma \)-complex, this reaction being slower than carbene complex formation. The ratio of rate constants \( k_3/k_4 \) apparently depends on medium composition and is responsible for the shape of exchange pattern.

For higher alkanes stepped distribution was also observed (Fig. 3). Analysis of products mass-spectra suggests cyclic intermediates formation alongside with carbene- and \( \sigma \)-complexes as most plausible explanation for the distribution (25).

\[
\text{RH} + \text{Pt}^2+ \xrightarrow{k_1} \text{PtR}^+ + \text{H}^+
\]

It should be noted that formation of alkyl hydrides was directly observed in some cases of intramolecular cleavage of C-H bond in ligands bound to transition metal, the reaction bearing much similarity with behaviour of free alkanes.

The dependence of the reaction rate on Pt(II) concentration also agrees with intermediate alkyl hydride formation rather than with direct substitution of H by Pt.

The transition state of the \( \text{Pt(II)} + \text{RH} \) reaction seems to be similar to that of the reaction of insertion of a singlet carbene (e.g., \( \text{CH}_2 \)) in C-H bond.

\[
\text{CH}_2 + \text{CH}_4 \rightarrow \text{C}_2\text{H}_6
\]

Calculation of potential energy surface made by Hoffmann (30) by means of extended Hückel method as well as by Dewar (31) by means of MINDO/2 method show that the insertion is a concert reaction with \( \text{CH}_2 \) attacking \( \text{CH}_4 \), first almost along C-H axis similarly to H atom abstraction by free radicals. The final stage of the reaction is close to free \( \text{CH}_3 \) radicals recombination in radical pair formed.
Similarly the first step of alkanes activation by square Pt(II) complexes can be visualized as alkane approaching Pt atom along its p-orbital, followed by H atom abstraction forming Pt(III) in a radical pair with alkyl radical R. The process terminates in a recombination of R and Pt(III) to form an octahedral alkyl hydride of Pt(IV). Multiple exchange of alkanes reveals a tendency of Pt(II) to covalent double bonding which is an indication of "carbenoid" properties. The transition state agrees with the order of reactivity of complexes with various ligands (note that multiple exchange factor changes in parallel with exchange rate constant) and also with the effect of substituents (stabilization by R in radical pair by conjugation in ligands).

There is a growing experimental evidence of covalent C-H bond interaction of organic ligands with metal atoms in coordination compounds forming some kind of "soft" hydrogen bonding indicative of low potential barrier for C-H interaction.

Thus C-H bond activation by transition metal complexes is a general phenomenon and form a new and a very promising field of homogeneous catalysis. One may expect an important development for the future with new catalytic processes including those for alkanes.

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