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ACTIVATION OF SATURATED HYDROCARBONS BY METAL COMPLEXES IN SOLUTION

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A. INTRODUCTION

The development of coordination catalysis, which is a result of the recent advances in inorganic and bioinorganic chemistry, has made it possible to start a new field — homogeneous metal-complex activation of saturated hydrocarbons. After the successful solution of the problem of homogeneous activation of molecular hydrogen [1], activation of olefins [2], aromatics [3, 17], CO [4], O_2 [5] and, finally N_2 [6], the next task is, as Halpern put it in 1968, "to develop a successful approach for activation of C—H bonds, particularly saturated hydrocarbons, this problem being at present one of the most important and challenging in the entire field of homogeneous catalysis" [7].

The complexity of the problem lies in the chemical inertness of alkanes also known as paraffins (from Latin: *parum affinis* without affinity) and their inability to enter into an addition reaction because of their completely saturated state, which accounts for their other name "saturated hydrocarbons". Reactions of alkanes usually involve cleavage of strong covalent C—H or C—C bonds. In this respect, the problem of activation of C—H bonds in paraffins is similar to that of activation of H_2, where cleavage of the strong H—H σ-bond is also required. Activation of H_2 with metal complexes is ensured by intermediate formation of hydride M—H bonds [1] (here and elsewhere M stands for a metal atom or ion in a metal complex). Since the dissociation energy of M—C bonds is only slightly lower than that of M—H bonds [8], activation of alkanes via the formation of M—C compounds is thermodynamically possible. However, comparison of physico-chemical characteristics of alkanes and molecular hydrogen indicates that saturated hydrocarbons are less vulnerable to a chemical attack than H_2. Some values characterizing the reactivity and possibilities of activation of alkanes are given in Table 1, including dissociation energies of the weakest C—H bond, ionization potentials, electron and proton affinities, as well as the kinetic acidity, for hydrocarbons, their derivatives and H_2. Analysis of the tabulated data permits the following conclusions to be drawn as to the reactivity of alkanes:

(1) Any derivatives of saturated hydrocarbons are, as a rule, more reactive than the hydrocarbons themselves. Therefore, it is difficult to stop a reaction at the stage yielding primary products, e.g., monofunctional derivatives (the problem of selectivity with respect to products).

(2) Methane followed by its homologs apparently should be the most inert hydrocarbons, while the reactivity of isoalkanes and cycloalkanes should be

TABLE 1

Physico-chemical characteristics of hydrocarbons and some of their derivatives

Molecule	D(R—H)	kcal mol^{-1}	I.P. (eV)	EA (eV)	PA (eV)	pKa
H_2		104	15.4	−3.6	4.4	25
CH_4		104	12.7		5.3	40
C_2H_6		98	11.5		5.6	42
				$\ll 0$		
C_3H_8	(1)	97	11.1		6.1	
	(2)	94				44
C_6H_{12}		94	9.9			46
C_2H_4		106	10.5	−1.81	6.9	36.5
C_2H_2		120	11.4			25
C_6H_6		109	9.2	−1.10	7.5	37
CH_3OH		92	10.9		7.8	16
CH_3CN		79	12.1		8.1	25
$CH_3CH{=}CH_2$		86	9.7		7.9	35.5
$CH_3C_6H_5$		85	8.8	−1.3	8.1	35

TABLE 2

Types of reactions of saturated hydrocarbons

Homolytic (nonionic) reactions
1 Radical reactions $RH + X\cdot \rightarrow R\cdot + XH$
2 Carbenoid (molecular) reactions $RH + :CH_2 \rightarrow R{-}CH_2{-}H$ $RH + :\underset{\cdot\cdot}{\ddot{O}} \rightarrow ROH$
Heterolytic (ionic) reactions
3 $RH + B^- \rightarrow R^- + HB$
4 $RH + H^+ \rightarrow R^+ + H_2$

higher. Therefore, activation of methane and its nearest homologs should involve the greatest difficulties. On the other hand, in the case of more complex hydrocarbons, a problem arises as to how certain bonds can be selectively acted upon without involving the others (the problem of selectivity with respect to the place of attack).

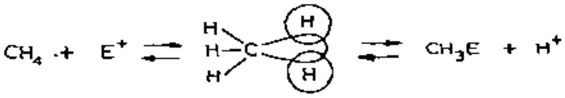
(3) Comparison with H_2 shows that dihydrogen exhibits more pronounced electron-acceptor properties, while hydrocarbons tend to be stronger electron donors. Hence, molecular hydrogen is more liable to enter into reactions with nucleophilic reagents, in particular, with bases and reductants, while methane and its homologs react more easily with electrophiles, namely acids and oxidants. Activation of H_2 in alkaline media and that of CH_4 in superacids are well known.

(4) Alkanes can react readily only with active particles (radicals, ions, carbenes and their analogs (Table 2)); homolytic reactions are more typical of alkanes [9,12] due to their nonpolar nature; in reactions with acids and bases they exhibit amphoteric properties [10].

In recent years, owing to contributions from Olah and Hogeveen, our knowledge of RH activation in highly acidic media, e.g. $HF{-}SbF_5$ or $HSO_3F{-}SbF_5$, has been considerably broadened [11]. Alkanes are activated in these media through coordination between the proton and alkane and intermediate formation of carbonium (CH_5^+-type) and carbenium (CH_3^+-type) cations.

$$CH_4 + H^+ \rightleftarrows CH_5^+ \rightleftarrows CH_3^+ + H_2$$

In superacids, there occur reactions of H—D exchange with D^+ and D_2, protolysis (cleavage of a C—C bond with the proton), nitration and nitrolysis, alkylation and alkylolysis, polycondensation, isomerization, chlorination and chlorolysis, carbonylation, as well as electrochemical oxidation and acetoxylation. All these reactions share a common mechanism including attack by an electrophile (H^+, D^+, R^+, NO_2^+, Hal^+) of the σ-electron pair of the C—H or C—C bond, followed by the emergence of a transition or intermediate state with 5-coordinated carbon and a three-center two-electron bond.



The relative reactivity of alkanes and dihydrogen as well as the selectivity of the attack on C—H bonds are opposite for S_E2 and S_N2 reactions

S_E2 $H_2 < CH_4 < C_2H_6 < C_3H_8$ ... prim < sec < tert [12]

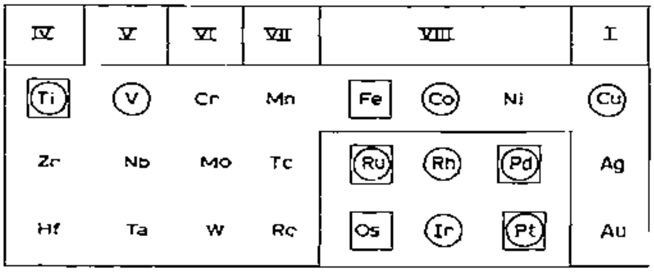
S_N2 $H_2 > CH_4 > C_2H_6 > C_3H_8$ ... prim > sec > tert [13]

This can be explained by the opposite trends in changes of ionization potentials, electron and proton affinities, and kinetic acidities in this series (see Table 1).

In 1969, we demonstrated for the first time the possibility of activating methane and its homologs with Pt(II) and Co(I) complexes in solutions [14]. Since then, we and other investigators have studied the reaction of H—D exchange with alkanes with the participation of Pt(II) and discovered alkane oxidation reactions catalyzed by Pt(II). All these reactions involve intermediate formation of Pt—R. Studies conducted by different scientists have eventually extended the range of metals forming compounds capable of activating alkanes, and the present state of the problem is represented in Fig. 1 which shows that compounds of both platinum and non-platinum transition metals can activate C—H bonds.

Activation of alkanes is now becoming a steadily advancing and highly promising field of metal—complex catalysis [15—18]. At present, it looks well-timed to summarize and evaluate the published data and draw a comparison between these data and heterogeneous activation of alkanes on the surface of metals and oxides. We hope that our review will give impetus to further research in this field which is still in its infancy. The major part of this review will be devoted to the activation of alkanes with complexes of platinum group metals which have been especially studied so far.

In the last sections of this review, we shall consider as yet scant results relating to activation with non-platinum metals. It is in this field that we should expect the most important progess for the future.



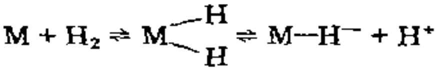
IV	V	VI	VII	VIII			I
Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
Hf	Ta	W	Re	Os	Ir	Pt	Au

Fig. 1. Activation of C-H bonds with complexes of transition metals: activation of alkanes is encircled; intramolecular activation of the alkyl fragment of the ligand is in squares.

B. ACTIVATION OF SATURATED HYDROCARBONS WITH COMPOUNDS OF PLATINUM GROUP METALS

(i) Activation of C—H bonds

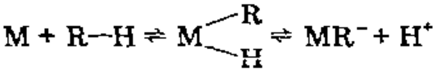
The starting point in the studies that have for the first time led to the observation of hydrocarbon activation in solutions of metal complexes was the above-mentioned analogy with activation of H_2. It is well known that hydrogen can be activated by way of oxidative addition to a metal with the formation of dihydrides which are capable of acid-like dissociation in polar media.



$$M + H_2 \rightleftharpoons M\genfrac{}{}{0pt}{}{\diagup H}{\diagdown H} \rightleftharpoons M\text{—}H^- + H^+$$

The cleavage of the covalent bond and a change in the hybridization of the metal atom are compensated by a gain in energy associated with the formation of two M—H bonds or an M—H⁻ bond and a solvated proton. Since the strength of an M—C bond is only slightly lower than that of an M—H bond, a similar process may also, in principle, take place in the case of alkanes.

When saturated hydrocarbons interact with compounds of transition metals in an oxidative addition reaction, one can expect a further exchange with the solvent protons in protic media in the case of acidic dissociation of the alkyl hydride.



$$M + R\text{—}H \rightleftharpoons M\genfrac{}{}{0pt}{}{\diagup R}{\diagdown H} \rightleftharpoons MR^- + H^+$$

In a solvent containing exchangeable deuterium, an isotope exchange must occur, serving as an indicator of the hydrocarbon-to-metal complex interaction.

In fact, when methane and ethane were heated (to 100° C) in sealed ampoules containing solutions of K_2PtCl_4 in D_2O—CH_3COOD mixture, deuteration of the molecules of these saturated hydrocarbons was observed [14]. Thus, under relatively mild conditions, the following reaction takes place.

$$CH_4 + D_2O \rightarrow CH_3D + HDO$$

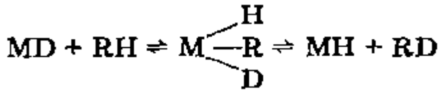
In the absence of a catalyst, this reaction is known to be possible only at a temperature of about 1,000° C, i.e. at the methane pyrolysis temperature.

A similar result was obtained when an exchange between alkanes and molecular deuterium was studied during catalysis of $(PPh_3)_3CoH_3$. This compound is capable of reversible decomposition with elimination of dihydrogen, therefore it catalyzes the exchange between H_2 and D_2.

$$MH_3 \rightleftharpoons MH + H_2 \qquad MH + D_2 \rightleftharpoons MHD_2$$

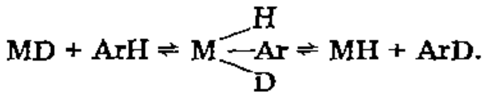
$$MHD_2 \rightleftharpoons MD + HD, \qquad \text{etc.}$$

A similar mechanism is probably involved in the case of alkanes.



$$\mathrm{MD + RH \rightleftharpoons M}\begin{array}{l}\diagup\mathrm{H}\\ \text{—}\mathrm{R}\\ \diagdown\mathrm{D}\end{array}\mathrm{\rightleftharpoons MH + RD}$$

When methane and deuterium were in prolonged contact with a benzene solution of tris-triphenylphosphine cobalt trihydride at room temperature, formation of small amounts of monodeuteromethane was observed, its content gradually increasing with time [14]. A relatively small degree of exchange in methane is, in this case, probably due to the instability of the starting complex which irreversibly decomposes in the course of time and, as was shown later [21], to a faster competitive entry of deuterium into benzene following the same mechanism.



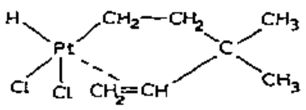
$$\mathrm{MD + ArH \rightleftharpoons M}\begin{array}{l}\diagup\mathrm{H}\\ \text{—}\mathrm{Ar}\\ \diagdown\mathrm{D}\end{array}\mathrm{\rightleftharpoons MH + ArD.}$$

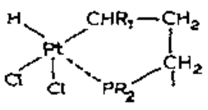
The higher rate of the reaction with benzene is probably due to the ability of the aromatic ring to form complexes with transition metal compounds and also to higher strength of the M—C bond in metal aryls.

In later studies, a homogeneous exchange catalyzed by platinum salts was observed for a whole series of simple alkanes (C_1—C_6) including normal and iso-alkanes [19], for n-decane [21], for such cycloalkanes as cyclobutane [20], cyclopentane and cyclohexane [19], adamantane, norbornane, protoadamantane [21], and for alkyl benzenes [22]. It was shown that the exchange rate grows with the length of the alkane chain and drops with higher degree of branching. The exchange rate is especially high in the case of cycloalkanes. This reaction may serve as an effective preparative method of obtaining deuteroalkanes.

Most substituted derivatives of methane and ethane [23] as well as higher alkanes [24] are capable, just as hydrocarbons themselves, of deuterium exchange with a solvent under similar conditions. However, in the case of some of these compounds, the exchange is complicated by side processes (oxidation, formation of complexes with Pt(II) via substitution, hydrolysis, etc.).

Ethylene does not exchange its hydrogen atoms with solvent protons in platinum(II) solutions, while at the same time it inhibits exchange in alkanes, probably due to the formation of strong π-complexes with Pt(II) [25]. Alkenes of the $RC(CH_3)_2$—$CH=CH_2$ 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 the position C_5 [26]. Evidently, this is the result of the chelate effect after π-complex formation.





A similar chelate effect is also observed during catalysis by Pt(II) of the H—D exchange at the saturated carbon atom in trialkyl phosphines where the exchange proceeds almost exclusively at position 3 of the hydrocarbon chain [27].

Thus, the reaction of exchange with solvent protons, catalyzed by salts of Pt(II), is common for sp^3 hybridized C—H bonds in various compounds.

It should be noted that well before the first studies of paraffins, a similar H—D exchange was revealed in aromatic molecules [28]. Garnett, who discovered these reactions, attributed them to the ability of aromatic molecules to form π-complexes with Pt(II) [29]. Later studies into the isotope exchange of hydrogen in alkyl benzenes, with the same homogeneous platinum catalysts, have shown that the exchange proceeds at comparable rates with both aromatic and alkyl C—H bonds [30]. Evidently, the exchange in an aromatic and aliphatic C—H bond involves a common mechanism for which the interaction of the active center with the C—H bond is essential, while the formation of π-complexes (in the case of aromatic systems) is not. This is also corroborated by the fact that benzene and toluene practically do not hinder exchange in alkanes.

Although oxidation of alkanes with salts of Pd(II) has been found (see Section D), attempts to reveal a Pd(II)-catalyzed exchange of alkanes have failed, probably as a consequence of faster Pd—R oxidation reactions [94]. It is known [31] that Pd(II) catalyzes oxidation reactions better than any other metal of the platinum family owing to Pd(II) → Pd(0) conversion. At the same time, an isotope exchange between benzene and deuterium is known, catalyzed by complexes of Pd(II) [32].

In 1973, Garnett et al. [33] discovered that complexes of Ir(III) are homogeneous catalysts with respect to an H—D exchange of alkyl benzenes both into the benzene ring and the side chain at 130°C. The next year, Garnett et al. reported on the activation of alkanes, catalyzed by Na_3IrCl_6 in $CH_3COOD—D_2O$. This catalyst was less active than K_2PtCl_4: for optimum reaction a higher temperature but a lower (25%) concentration of CH_3COOD. was required. At 150 to 170°C, an extensive H—D exchange (up to 70%) of $C_1—C_7$ normal alkanes, cyclopentane and cyclohexane was observed. The exchange, as in the case of Pt(II), is multiple, i.e. several hydrogen atoms are exchanged while an alkane molecule enters the coordination sphere of the metal complex. The initial distribution of isotopes is indicative of the predominant attack of primary C—H bonds [34].

Recently, it has been found [35], that $RhCl_3$ in $CH_3COOD—D_2O$ can also catalyze a homogeneous H—D exchange of cyclohexane (96 h, 130°C). The investigators [35] compared the role of Pt(II), Rh(III) and Ir(III) in the activation of alkanes and arrived at the following conclusions.

(1) $RhCl_3$ is thermally more stable than $PtCl_4^{2-}$. $IrCl_6^{3-}$ is even more stable. Therefore higher temperatures may be used for $RhCl_3$ and $IrCl_6^{3-}$ in reaction of H—D exchange than for $PtCl_4^{2-}$.

(2) In the presence of Rh(III), an H—D exchange is slower than with Pt(II)

or Ir(III), has a higher multiple exchange factor ($M = 3.7$ for benzene), and leads to pronounced deuteration of both the aromatic ring and the side chain in alkyl benzenes.

(3) The orientation of isotopes in the side chain of alkyl benzenes in the case of an exchange with Rh(III) is similar to that in the case of Pt(II) and Ir(III).

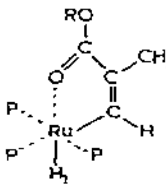
(4) Similarly to Pt(II) and Ir(III) an ortho-steric effect is observed in the presence of Rh(III) for substituted benzenes.

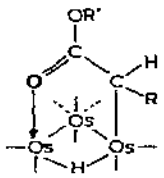
(5) No excessive amount of a mineral acid is required to stabilize the catalytic solution as opposed to a $PtCl_4^{2-}$-system, since excess acid slows down exchange on the rhodium catalyst.

(6) In a system with Rh(III), the deuteration of cyclohexane is much slower than that of benzene. The introduction of polycyclic aromatic compounds such as pyrene intensifies the exchange of cyclohexane in both Rh(III) and Pt(II) systems.

Although in these studies Rh(III) and Ir(III) complexes were used, it may be assumed that compounds of Rh(I) and Ir(I) with a d^8 configuration are responsible for the activation of RH. These, as well as the isoelectronic compounds of Pt(II), are capable of entering into oxidative addition reactions. It is also reported [17] that a Ru(II) complex, namely $RuHCl(PPh_3)_3$, catalyzes an H—D exchange of the alkyl side-chain of phosphine, $(C_6H_5)_2P(CH_2)_n\,CH_3$, with D_2.

Oxidative addition of a vinyl C—H bond in alkyl methacrylate is observed as it interacts with $H_2Ru(PPh_3)_4$ to yield a vinyl-hydride complex of Ru(II), which structure has been confirmed by X-ray study [48]. $H_2Os_3(CO)_{10}$ reacts with two equivalents of ethylene, yielding ethane and vinyl-hydride cluster $HOs_3(CO)_{10}(CH{=}CH_2)$ [49]. Relatively stable "alkyl" hydride triosmium clusters have been isolated. The elimination of "alkane" * from these compounds results in an unsaturated cluster responsible for activation of H_2 and vinyl C—H bonds. Their structure has been defined as a result of NMR studies [50].





Examples were described recently of fast cleavage of a number of C—H bonds (activated sp^3, aromatic sp^2 and sp) under mild conditions by bis(dimethylphosphino)ethane complexes of Fe(0), Ru(0) and Os(0) with formation of stable products characterized as a mixture of *cis*- and *trans*-"alkyl" (aryl) hydrides [124].

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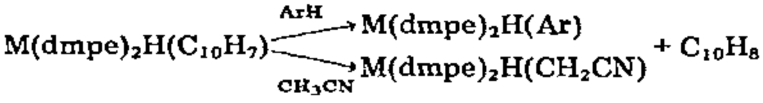
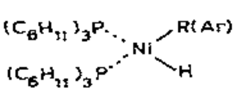
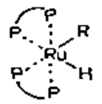
* "Alkanes" and "alkyls" here and elsewhere signify functionally substituted alkanes and alkyls.

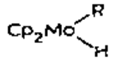


$$M(dmpe)_2H(C_{10}H_7) \begin{cases} \xrightarrow{ArH} M(dmpe)_2H(Ar) \\ \xrightarrow[CH_3CN]{} M(dmpe)_2H(CH_2CN) \end{cases} + C_{10}H_8$$

Alkanes are known to form only unstable complexes even with strong electron acceptors, and charge transfer can hardly be responsible for the activation of C—H bonds by Pt(II) complexes. On the other hand, there are examples of stable alkyl and aryl hydrides such as *trans*-PtH([CH$_2$]$_n$CN) (PPh$_3$)$_2$ where n = 1—3, or o-CH$_2$C$_6$H$_4$ [125], bis-(tricyclohexylphosphine) nickelalkyl (aryl) hydrides [36], bis-diphosphinealkyl hydrides of ruthenium and osmium [37],

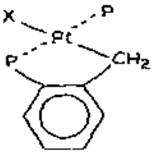


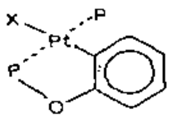


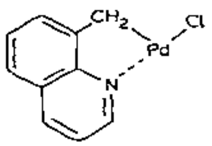


numerous alkyl hydrides of cobalt, alkyl hydrides of iron [38] and molybdenum [39], and an alkyl hydride of tungsten [40].

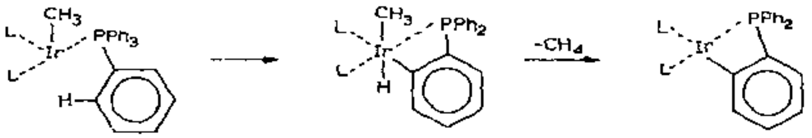
There are known cases of intramolecular insertion of metal complexes into aromatic and aliphatic C—H bonds. These reactions proceed, as a rule, with the formation of a five-membered ring, e.g. in the case of Pt(II) and Pd(II) complexes with triaryl phosphines, triaryl phosphites or 8-methylquinoline [41] and yield chelate alkyl(aryl) hydrides or alkyls (aryls) of metals with



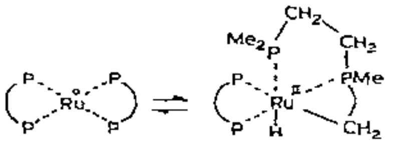


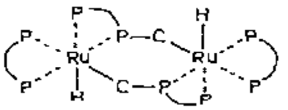


the hydride being split off, in the latter case, normally in the form of HHal or RH.

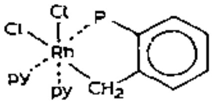


The first published example of reversible insertion of the metal atom into the aliphatic C—H bond of the ligand is the reaction of complex Ru[(CH$_3$)$_2$PCH$_2$CH$_2$P(CH$_3$)$_2$]$_2$, reported by Chatt and Davidson [45].



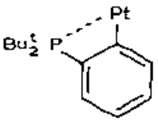


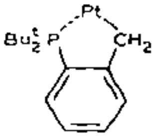
In the crystalline state, the equilibrium is shifted towards the alkylhydride complex of Ru(II),and, according to X-ray diffraction analysis [46], this complex exists in the form of a dimer. The structure of a Rh complex including a five-membered ring [47] was also proved.

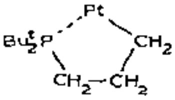


The rate of insertion into a C—H bond is higher in the case of platinum complexes than in the case of palladium complexes and is also dependent on the nature of halogen X, diminishing in order X = Cl > Br ≫ I [41]. In the case of iridium complexes the rate increases with a change in the substituent in the para position of the phenyl ring in the order F < H < OCH_3 < CH_3 [42]. On the basis of a relatively low kinetic isotopic effect, a three-center transition state is assumed for the insertion of reaction into the C—H bond [42]. Intramolecular activation of aromatic C—H bonds has been used for catalytic *ortho*-chlorination of azobenzene [43] and *ortho*-deuteration of triphenyl phosphine [44].

The formation of intramolecular Pt—C bonds is believed to be promoted by steric effects as, for example, in case of phosphines with very bulky substituents [126].





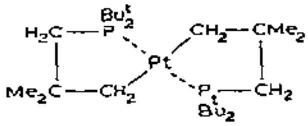


The insertion occurs not only in the primary but also in the secondary and tertiary C—H bond [127].

The products containing five-membered rings are usually more stable than those with four-membered and six-membered rings [127,128].

The reasons why the bulky substituents on phosphorus promote the inner metallation are not yet completely clear [129]. It may be due to the proximity and orientation effects which lead to the decrease of activation enthalpy and to smaller entropy losses in the reaction transition state.

The steric effects on the rate of C—H bond activation is so great that even the neopentyl C—H bond, usually unreactive in intermolecular reactions, was shown to react intramolecularly in phosphine complex of platinum [130]. At



the same time an analogous propyl derivative does not form. The main reason for differences in metallation rates is apparently the degree of approaching the metal, due to the steric overstraining by tertiary phosphine as well as a favourable conformation and an entropy factor created by *gem*-t-butyl and *gem*-dimethyl groups [131].

It is clear that the intramolecular activation of C—H bonds proceeds readily as a result of the chelate effect, while as the mechanism is concerned it is similar to intermolecular activation. Therefore, the results obtained with intramolecular CH activation may be useful in a search for new reactions of alkanes of activation.

Rate differences in intermolecular and intramolecular C—H insertion are explained first of all, by the differences between the bimolecular and monomolecular characters of these reactions. Assuming that E_a for intermolecular and intramolecular reactions for one metal complex with similar ligands is equal, and knowing the values of preexponential factors ($A_{\text{inter}} = 2.5 \cdot 10^8$ l mole^{-1} sec^{-1} [64] and $A_{\text{intra}} = 6 \cdot 10^{11}$ sec^{-1} [27] in agreement with the usual values for bi- and monomolecular reactions), it may be estimated that

$$\frac{W_{\text{intra}}}{W_{\text{inter}}} = \frac{A_{\text{intra}}}{A_{\text{inter}}[\text{RH}]} = 10^5\text{—}10^6 \,,$$

for [RH] = 0.1—0.01 mole l^{-1}. The difference by 5—6 orders of magnitude explains why with the numerous examples of intramolecular reactions of C—H bond available there are only a few cases of direct interaction of alkanes with metal complexes. Taking an experimental $E_a \approx 20$ kcal mole^{-1} for alkane interaction with complexes Pt(II), one may conclude that to overcome the rate differences by 5—6 orders of magnitude, and to observe the direct interaction of alkanes with metal complexes, it is necessary to carry out these reactions at temperatures 100—200° higher than the corresponding intramolecular reactions of C—H bond.

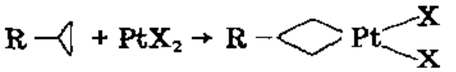
(ii) Activation of C—C bonds

Intermolecular or intramolecular insertion of M in various complexes normally takes place only into C—H but not into C—C bonds. This is probably due to the steric hindrance for C—C bond insertion by a large attacking reagent. At the same time the following order of reactivity of sp^3 bonds is observed during protolysis of alkanes in superacids,

tert C—H > C—C > sec C—H > prim C—H ,

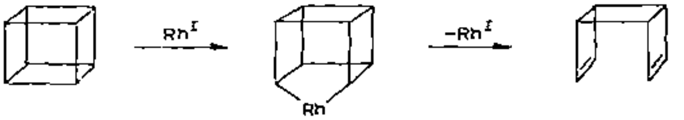
i.e. a C—C bond is easily opened by the relatively small proton. The attack on C—C bond by M becomes possible however, when it is weakened e.g. in strained cyclic compounds. The examples are stereoselective insertions of Pt(II) and Pd(II) complexes into the C—C bond of substituted cyclopropanes [51].

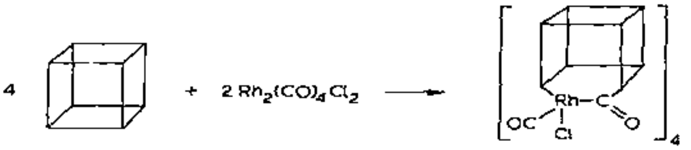
The effect of substituents indicates the importance of donor properties of C—C containing compounds in reaction



where R = alkyl > aryl ≫ CO_2Me, COMe or CN, i.e. the platinum complex plays the role of an acceptor [51]. The products of insertion are characterized by NMR spectre.

The abnormally high multiple exchange factor (see Section C (iii)) during catalysis by Pt(II) of the H—D exchange of cyclobutane is attributed to the cleavage of the C—C bond of cyclobutane by Pt(II) with the formation of a stable five-membered metallocycle [20]. Tetraphenyl cyclobutane is opened by Pt(II) yielding *trans*-stilbene [52]. Other examples of insertion into a C—C bond are known [53—55]. In recent years, many papers have appeared describing catalysis of rearrangements of carbocyclic compounds by transition metal complexes. Studies into the kinetics and products of valence isomerization of cubane into tricyclooctadiene, catalyzed by Rh(I) complexes, have shown that the rate controlling step could be the cleavage of the C—C bond by oxidative addition [56]. Further evidence of this mechanism is the formation of a stable acyl rhodium adduct as a result of interaction of cubane with $Rh_2(CO)_4Cl_2$.





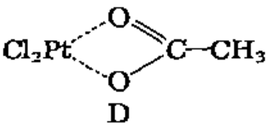
Evidence for intermediate organometal compounds in these ractions has also been obtained by NMR studies. A similarity has been found between the reactions of insertion into a C—C bond and the reactions of respective metal complexes with hydrogen [56].

C. INTERACTION OF ALKANES WITH Pt(II)

(i) Studies into the kinetics and mechanism of H—D exchange of alkanes with solvent protons in the presence of Pt(II) compounds

These have been conducted using water exchange with ethane [57], pentane [58] and other alkanes [59], halogenoalkanes [24] and functional substituted methane and ethane [23] with the aim of elucidating the mechanism of the reactions.

The reaction of hydrogen—deuterium exchange proceeds with a noticeable rate in water and becomes 30 times as fast in 50% acetic acid. This is indicative of a specific solvation of the active particle with the molecules of acetic acid, probably with formation of a weak chelate complex with $PtCl_2$.



In a more weakly solvating trifluoroacetic acid, the rate of exchange is lower. The ability of an acetate ion to function as a bidentate ligand has been demonstrated for example in a study of the molecular structure of the complex $RuH(CH_3COO)(PPh_3)_3$ [60]. The H—D exchange is inhibited by chloride ions and is first order with respect to hydrocarbon and fractional order (<1) with respect to K_2PtCl_4. The order of the reaction with respect to chloride changes from 0 to —1 as the concentration of Cl^- increases (Fig. 5). The rate of deuterium exchange is virtually independent of the ionic strength and acidity in the range of 0.2 to 1.0 M. At $HClO_4$ concentrations below 0.2 M the rate of the reaction drops somewhat [57]. The activation energy from 80 to 100° was found to be 18.6 kcal mol^{-1}.

In experiments with CD_4—H_2O and CH_4—D_2O, a noticeable isotopic effect was observed: $k_{CH_4}/k_{CD_4} = 3.0 \pm 0.5$ (100°C) [57]. In the case of cyclohexane, $k_H/k_D = 1.7 \pm 0.1$ (100°C) [58].

Platinum (IV) compounds, such as Na_2PtCl_6 and H_2PtCl_6, also catalyze exchange. However, in this case, accumulation of deuterium in ethane follows an autocatalytic law, with an induction period being observed. Spectrophotometric measurements indicate that during the induction period Pt(IV) complexes are reduced in the solution to Pt(II) complexes which catalyze deuterium exchange. The rate of deuterium exchange, being equal to that of Pt(IV) –Pt(II) transformation, suggests that a Pt(IV) complex, as such, does not catalyze the reaction.

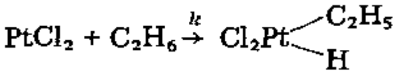
Platinum(II) compounds seem to act as electron acceptors in reaction with alkanes. With this in view, it becomes clear why both Pt(IV) and Pt(0) complexes fail to activate alkanes the former because of the coordinative saturation, and the latter because of weak acceptor properties.

For Pt(II) chloride complexes, which are in equilibrium in a K_2PtCl_4 solution, the acceptor properties have to follow the order: $PtCl_2 > PtCl_3^- > PtCl_4^{2-}$ In fact, analysis of the kinetic results shows that the most active species with respect to hydrocarbons are platinum dichloride molecules, $PtCl_2$ or $PtCl_2S_2$, where S is the solvent [58,64].

The following mechanism for deuterium exchange of alkanes with water, catalyzed by Pt(II), has been proposed [57].

$$PtCl_4^{2-} \overset{K_1}{\rightleftharpoons} PtCl_3^- + Cl^- \tag{1}$$

$$PtCl_3^- \overset{K_2}{\rightleftharpoons} PtCl_2 + Cl^- \tag{2}$$

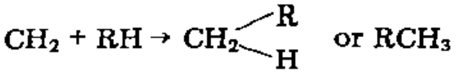


$$PtCl_2 + C_2H_6 \xrightarrow{k} Cl_2Pt\begin{smallmatrix} C_2H_5 \\ H \end{smallmatrix} \tag{3}$$

$$Cl_2Pt\begin{smallmatrix} C_2H_5 \\ H \end{smallmatrix} \rightarrow ClPtC_2H_5 + H^+ + Cl^- \tag{4}$$

$$ClPtC_2H_5 + D^+ + Cl^- \rightarrow PtCl_2 + C_2H_5D \tag{5}$$

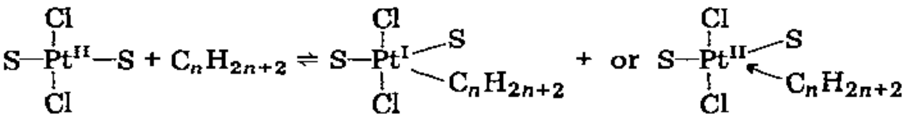
Independence of the rate on the ionic strength, and the isotope effect, indicate that step (3) is limiting. The relatively low value of the isotope effect is in agreement with a suggestion that reaction (3) is an insertion in a C—H bond via the three-membered transition state; this reaction is similar to the intramolecular insertions mentioned above and also to the reaction of insertion of a carbene, such as methylene, into a C—H bond.



$$CH_2 + RH \rightarrow CH_2{<}^{R}_{H} \quad \text{or } RCH_3$$

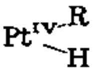
The dependence on Pt(II) and Cl$^-$ concentrations indicates that equilibrium (1) is shifted to the right. From NMR studies on alkanes after the exchange, it follows [58] that the reactivity of different alkane positions with respect to a Pt(II) attack diminishes in the order prim ⩾ sec > tert; that is, opposite to a decrease of the C—H bond strength or to an increase of electrophilic reactivity of these bonds. The methyl or methylene groups adjacent to the quaternary carbon atom exhibit a very low reactivity. Bearing in mind that the rate of H—D exchange sharply decreases with a higher degree of branching in alkanes, the most probable explanation of all these results seems to be steric factors. The decrease in the rate of attack on going from prim C—H to tert C—H is accounted for by a marked increase in steric hindrance in attacking the voluminous Pt(II) complex. Primary metal alkyls are known to be more stable than secondary, and particularly tertiary ones [61,62].

The importance of the electron donor properties of hydrocarbons for interaction with Pt(II) has been demonstrated by finding the correlation between the logarithms of H—D exchange rate constants and the ionization potentials of respective hydrocarbons [58]. It is interesting to note that the points corresponding to n-alkanes and aromatic hydrocarbons lie on the same straight line (Fig. 2). Hodges et al. [58] believe that the initial interaction of an alkane with a catalyst involves transfer of an electron from the delocalized molecular orbital of the alkane to the platinum atom in the complex.



$$S-\overset{Cl}{\underset{Cl}{Pt^{II}}}-S + C_nH_{2n+2} \rightleftharpoons S-\overset{Cl}{\underset{Cl}{Pt^{I}}}{<}^{S}_{C_nH_{2n+2}}\ {}^{+} \quad \text{or} \quad S-\overset{Cl}{\underset{Cl}{Pt^{II}}}{\leftarrow}^{S}_{C_nH_{2n+2}}$$

Such a complex is, in general, similar to CH$_5^+$ and involves coordination of the σ-electron pair of the C—H bond to Pt(II) with the formation of a five-coordinated carbon atom. However, in contrast to H$^+$ which is a hard acid, the platinum atom in Pt(II) complexes is a soft acid and capable of double bonding, and the authors of this review believe that, as a result, the process continues until the insertion product



$$Pt^{IV}{<}^{R}_{H}$$

is formed.

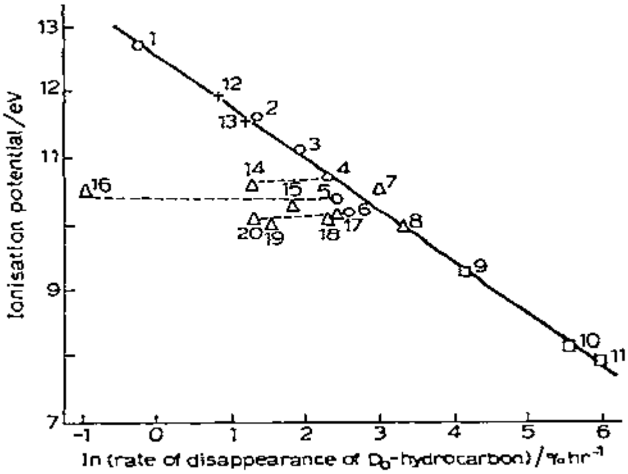


Fig. 2. Rate of H—D exchange versus ionization potential of alkanes and aromatic compounds (1 = methane, 2 = ethane, 3 = propane, 4 = n-butane, 5 = n-pentane, 6 = n-hexane, 7 = cyclopentane, 8 = cyclohexane, 9 = benzene, 10 = naphthalene, 11 = phenanthrene, 12 = 2,2-dimethylbutane, 13 = 1,1-dimethylpropylbenzene, 14 = 2-methylpropane, 15 = 2-methylbutane, 16 = 2,2-dimethylpropane, 17 = 2-methylpentane, 18 = 3-methylpentane, 19 = 2,3-dimethylbutane, 20 = 2,2-dimethylbutane).

Studies of the H—D exchange of substituted alkanes [23,24] are indicative of the inadequacy of this correlation. It is insufficient to take into account the influence of only the induction effects on the reaction center.

Generally speaking, since there is a correlation between the ionization potentials and polar Taft constants, there must be a correlation between the logarithms of H—D exchange rate constants and σ *.

In fact, such a correlation has been found for the series of functional substituted methane and ethane (Fig. 3) [23]. It turned out that the logarithms of the rate constants correlate well through the two-parameter equation

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

i.e. in addition to the polar parameter σ^*, the reaction rate depends on the resonance term $n\psi$. Parameter ψ characterizes the conjugation of the α-substituent with the radical reaction center or a π-system, while n is equal to the number of substituents capable of such a conjugation [63]. The ρ^* value, which was found to be —1.4, suggests that in this reaction Pt(II) manifests moderate electron acceptor properties, while the hydrocarbon is a donor. The presence of the resonance term indicates that the cleavage of the C—H bond in the elementary act of Pt(II) insertion into this bond takes place homolytically, with an unpaired electron forming at the carbon atom under attack. This is in line with the assumption that the single-electron transfer in

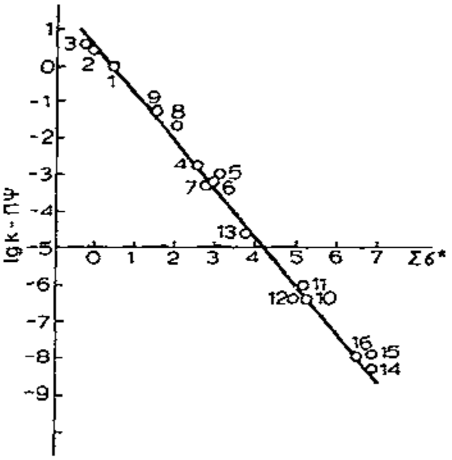


Fig. 3. Rate of H—D exchange (% h^{-1}) vs. Taft polar constants of $H—CXY_2$; X = H, CH_3, C_2H_5, CF_3, OH, COOH, Y; Y = H, F, Cl, Br. (*n* = *0* : 1 = methane, 2 = ethane, 3 = propane, 4 = 1,1,1-trifluoroethane; *n* = 1 : 5 = fluoromethane, 6 = chloromethane, 7 = bromomethane, 8 = acetic acid, 9 = methanol; *n* = 2 : 10 = difluoromethane, 11 = dichloromethane, 12 = fluorochloromethane, 13 = 1,1-difluoroethane; *n* = 3 : 14 = trifluoromethane, 15 = trichloromethane, 16 = tribromomethane).

the sphere of Pt(II) takes place in reaction with alkane [58]. It should be noted that the insertion of CH_2 into the C—H bond is homolytic and probably involves formation of a radical pair [79].

To elucidate further the nature of alkane activation on Pt(II), more studies

TABLE 3

Deuterium exchange of cyclohexane in the presence of Pt^{II} complexes
$[Pt^{II}]$ = 0.0043 M(1,2), 0.02 M(3—12), $[HClO_4]$ = 0.1 M, $[C_6H_{12}]$ = 0.15 M, 100°C

No.	Complex	Time (h)	$\sum_i d_i$	$k \cdot 10^3$ ($l\ mol^{-1}\ sec^{-1}$)	$M = \frac{\Sigma i \cdot d_i}{\Sigma d_i}$
1	$PtCl_2S_2$	2	0.230	7.42	1.93
2	$KPtCl_3S$	2	0.154	4.97	1.74
3	K_2PtCl_4	1.66	0.333	2.78	1.75
4	$K_2Pt(NO_2)Cl_3$	7	0.185	0.366	1.52
5	$KPt(NH_3)Cl_3$	2.5	0.140	0.777	1.65
6	$KPt(py)Cl_3$	12	0.0268	0.025	1.46
7	$KPt(DMSO)Cl_3$	12.5	0.0549	0.056	1.60
8	$Pt(DMSO)Cl(NO_3)$	4	0.0242	0.083	1.62
9	$K_2Pt(NO_2)_2Cl_2$	7	0.0584	0.115	1.41
10	$Pt(PPh_3)_2Cl_2$	16.5	0.0078	0.007	1.34
11	$Pt(acac)_2$	7.5	0.0511	0.094	1.57
12 [a]	$Pt(CF_3COO)_2$	0.3	0.0158	0.732	1.34

[a] Experiment in CF_3COOH at 91°C.

TABLE 4

Effect of anions on the deuterium exchange of cyclohexane in the presence of $PtCl_2S_2$ $[Pt^{II}] = 0.0043$ M, $[X^-] = 0.0086$ M, $[HClO_4] = 0.1$ M, [pyrene] = 0.013 M, $[C_6H_{12}] =$ 0.15 M

X^-	None	CF_3COO^-	F^-	$\frac{1}{2}SO_4^{2-}$	Cl^-	Br^-	I^-	NO_2^-
$k \cdot 10^3$ l mol^{-1} sec^{-1}	6.30	6.28	6.26	6.06	4.10	2.47	0.394	0.115
σ_x	13.05		12.18		9.92	9.22	8.31	5.87
M	2.02	1.94	1.92	1.98	1.77	1.48	1.52	1.41

were required into the effect of ligands on the catalytic properties of Pt(II) complexes [64]. In particular, a study has been made into the deuterium exchange of cyclohexane, catalyzed by $PtLCl_3^-$ ($L = H_2O, Cl^-, NO_2^-$, DMSO, NH_3, py), $PtCl_2L_2$ ($L = H_2O, Cl^-, Br^-, I^-, NO_2^-, CN^-, PPh_3$) and other complexes.

As can be seen from Table 3, the exchange rate constant depending on ligands changes by three orders of magnitude, decreasing towards more basic as well as softer more polarizable ligands, with a growing tendency for double bonding. In Table 4 are the rate constants in the case of catalysis by complexes formed in the system $PtCl_2S_2 + 2X^- \rightleftarrows PtCl_2X_2^{2-} + 2S$.

The decrease in the rate of deuterium exchange of cyclohexane in the series $X = F > Cl > Br > I > NO_2 > CN$ correlates with $pK_{PtX_4^{2-}}$ (Fig. 4), as well as with the overlap integral of the $6p_\sigma$ orbital of platinum and p_σ orbitals of ligands [65] and the softness and hardness parameters (σ_x) of ligands [66]. Evidently, a ligand may affect both the degree of complexation of PtX_2 in

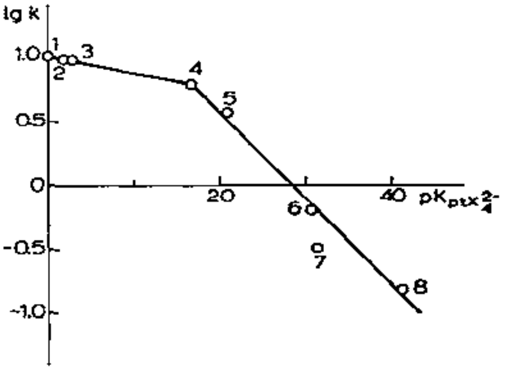


Fig. 4. Rate of cyclohexane H—D exchange (l mol^{-1} sec^{-1}, in systems $PtCl_2 + 2X^-$) vs. stability constants of PtX_4^{2-}; $X = H_2O(1)$, F(2), $\frac{1}{2}SO_4(3)$, Cl(4), Br(5), I(6), $NO_2(7)$, CN (8).

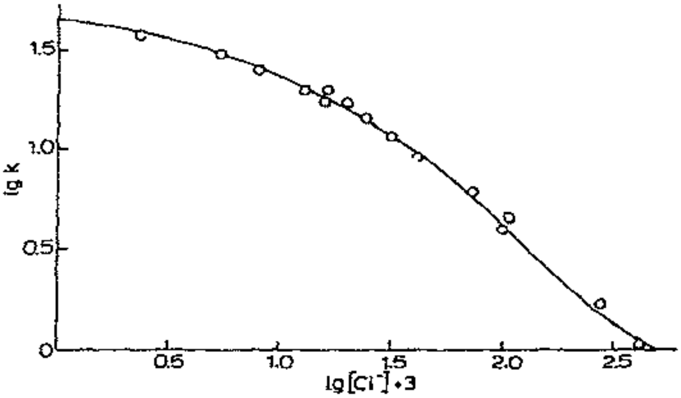


Fig. 5. Rate of cyclohexane H—D exchange (l mol^{-1} sec^{-1}) versus chloride ion concentration (mol l^{-1}) (points = experimental values, solid line = calculated at $k_1 : k_2 : k_3 = 100:14:0.6$, $K_1 = 3 \cdot 10^{-2}$, $K_2 = 5 \cdot 10^{-2}$ mol l^{-1}).

solution and the electronic properties of the complex as a whole. The profound effect of a ligand on the electronic properties of a catalytically active particle is shown particularly when comparison is made of complexes of the $[PtCl_3L]^-$ type, where L = Cl^-, H_2O, NH_3, DMSO. The stability constants of aquo-complexes of platinum and platinum complexes with DMSO are close, i.e. the concentrations of active $PtCl_2(DMSO)S$ and $PtCl_2(H_2O)S$ complexes in the solution are approximately the same, while the cyclohexane deuterium exchange rate constants, in the case of catalysis by these complexes, differ more than ten times. Dimethylsulfoxide, being a strong π-acceptor, is expected to create a higher positive charge of the central ion, which, in accordance with the donor nature of the hydrocarbon, should lead to a higher rate of deuterium exchange (as in the $H_2O > NH_3$ series). The slower rate of deuterium exchange, which is actually observed, is presumably due to the greater softness (higher double bonding capacity) of the ligands containing sulfur instead of oxygen. It is well known that soft ligands stabilize Pt(II) complexes with respect to the transition to Pt(IV). All the ligands tested can be arranged, as to their effect on the rate of deuterium exchange of cyclohexane, in the following order: $PPh_3 \approx Py < DMSO < CN^- < NO_2^- < NH_3 < I^- < Br^- < Cl^- < F^- \approx H_2O$. This order is opposite to that of the *trans*-effect of ligands in substitution reactions of square Pt(II) complexes. Thus, this result is not consistent with the alternative mechanism of direct substitution of a hydrocarbon for the ligand in Pt(II), $RH + Pt^{II} - Cl \rightarrow [H^{\delta+} \cdots R \cdots Pt \cdots Cl^{\delta-}]^{\ddagger} \rightarrow H^+ + RPt + Cl^-$ which is similar to the mechanism of substitution in square complexes of platinum and, hence, should correspond to the normal *trans*-effect series. The order of ligands effect is, in our opinion, in agreement with the homolytic cleavage of RH by the Pt(II) complex with Pt—H and Pt—R bonds being formed.

The logarithm of the rate constant for homolytic H-atom or R-group abstraction by an active particle is linearly dependent on the bond strength of the resulting bond of this particle with H or R [63]: $\log k = a + b\mathrm{D}(\mathrm{Pt{-}H}$ or $\mathrm{Pt{-}R})$. As can be inferred from ref. 68, the vibration frequency of the Pt—C bond and, hence, probably the strength of this bond, in *trans*-$\mathrm{Pt(CH_3)X(PEt_3)_2}$ decreases in the order $\mathrm{X = NO_3^-, NCS^- >> Cl^- > Br^- > NO_2^- > I^- > CN^-}$, which is again the reversed *trans*-effect order. The vibration frequency of the Pt—H bond in $\mathrm{PtA_2LH}$ and the strength of this bond diminishes with the nature of L in a similar order $\mathrm{L = NO_3^- > Cl^- > Br^- > I^- > NO_2^- > SCN^- > CN^-}$ [69].

Thus, the exchange rate constant k must, in general, depend on the degree of complexing of $\mathrm{PtX_2}$ *, determining the concentration of free $\mathrm{PtX_2}$ in solution, as well as on the nature of ligands X in $\mathrm{PtX_2}$. Bearing in mind that in the series $\mathrm{PtX_2}$, $\mathrm{PtX_3^-}$, and $\mathrm{PtX_4^{2-}}$ the $\mathrm{PtX_2}$ complex is the most active, to a first approximation $k = k_1[\mathrm{PtX_2}]_0/\phi$, where ϕ is the function of the degree of complexing of $\mathrm{PtX_2}$ by a ligand in a solution. For chloride complexes of platinum

$$k = \frac{(k_1 + k_2K_2[\mathrm{Cl^-}] + k_3K_{12}[\mathrm{Cl^-}]^2)[\mathrm{PtCl_2}]_0}{1 + K_2[\mathrm{Cl^-}] + K_{12}[\mathrm{Cl^-}]^2}$$

and, from the dependence of k on $[\mathrm{Cl^-}]$ (Fig. 5), one can evaluate constants k_1, k_2 and k_3 for complexes $\mathrm{PtCl_2S_2}$, $\mathrm{PtCl_3S^-}$ and $\mathrm{PtCl_4^{2-}}$ which are in the state of equilibrium in the solution, K_1 and $K_{12} = K_1 \cdot K_2$ being the constants for these equilibria. We have found that $k_1 : k_2 : k_3 = 100 : 14 : 0.6$ at 100°C. For an exchange involving $\mathrm{PtCl_2S_2}$ the temperature dependence of the exchange rate constant was measured in the range of 81 to 112°C: $k_1 = 2.5 \cdot 10^8 \exp(-18\,200/RT)$ 1 $\mathrm{mol^{-1}\ sec^{-1}}$.

The activation parameters $\Delta H^\ddagger = 17.5$ kcal $\mathrm{mol^{-1}}$, $\Delta S^\ddagger = -22.6$ cal $\mathrm{deg^{-1}\ mol^{-1}}$ can be compared with respective parameters for bonding of $\mathrm{H_2}$ with $\mathrm{IrCl(CO)(PPh_3)_2}$ [71]: $\Delta H^\ddagger = 10 - 13$ kcal $\mathrm{mol^{-1}}$, $\Delta S^\ddagger = -14 - -24$ cal $\mathrm{deg^{-1}\ mol^{-1}}$. The similar values of $\Delta S^\ddagger$ for processes $\mathrm{Ir^I + H_2 \rightarrow Ir^{III}}\!<^{\mathrm{H}}_{\mathrm{H}}$ and $\mathrm{Pt^{II} + RH \rightarrow Pt^{IV}}\!<^{\mathrm{R}}_{\mathrm{H}}$ are consistent with similar mechanisms.

(ii) Demonstration of alkyl platinum formation in homogeneous activation of saturated hydrocarbons

Studies into the kinetics and mechanism of H—D exchange of saturated hydrocarbons in the presence of Pt(II) complexes suggest that the activation of alkanes proceeds by way of their oxidative addition to Pt(II) with formation of unstable alkyl derivatives of Pt(II). Evidence for intermediate formation of alkyl compounds of Pt(II) would be provided by direct observation of these compounds in a solution using different physical methods, or, which would be even more desirable, by isolating them from the solution. This

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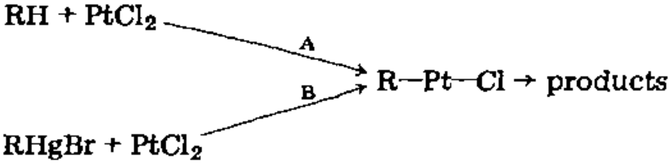
* Further solvolysis of $\mathrm{PtX_2}$, according to ref. 70, in the case of not very low [Pt], does not make a significant contribution to the equilibria of Pt complexes in solution.

seems to be difficult because of the thermal instability of these compounds and their high reactivity. However, in the case of transformation of these intermediate Pt(II) alkyls to more stable and less reactive compounds of Pt(IV), they become detectable. As will be shown later, the oxidation of alkanes and benzene with compounds of Pt(IV), catalyzed by Pt(II), are also consistent with intermediate formation of PtRCl and $PtRCl_3$. Some non-stoichiometric relationships at the initial stage of the reaction were accounted for [72,73] by the intermediate formation of relatively stable alkyl compounds $RPtCl \xrightarrow{Pt(IV)} RPtCl_3 \rightarrow RCl + PtCl_2$, slowly decomposing to yield the end products. Circumstantial evidence for the presence of $ArPtCl_3$ in the solution is provided by the occurrence of benzene under the effect of a reducing agent [72]: $ArPtCl_3 \xrightarrow{2H_2} ArH + Pt + 3HCl$.

An attempt has been made also to synthesise platinum alkyls in a solution using conventional methods [75].



In this case, the formation of platinum alkyls in homogeneous activation of alkanes is corroborated by the identity of the products yielded in reactions A (direct activation) and B (alkylation of $PtCl_2$), provided these reactions are conducted under similar conditions.

In the case of interaction of K_2PtCl_4 with organomercuric compounds of the RHgBr ($R = CH_3, C_2H_5, C_3H_7, C_4H_9$) type in $CH_3COOD—D_2O$ (1:1) at 100°C, deuterohydrocarbons and alkylhalides are formed, the latter containing practically no deuterium in the akyl group, i.e. the same products which are obtained in a direct reaction involving alkanes.

Table 5 shows the distributions of deuteromethanes in a reaction of CH_3HgBr with K_2PtCl_4 and direct H—D exchange of CH_4 catalyzed by K_2PtCl_4 under identical conditions ($Pt^{II} : Hg^{II} : DCl = 1 : 1 : 3$). Close agree-

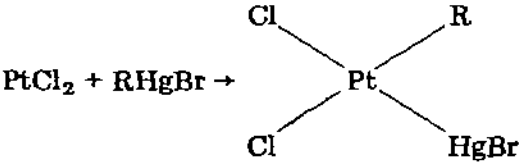
TABLE 5

Distributions of d-methanes in methylation Pt(II) and direct H—D exchange

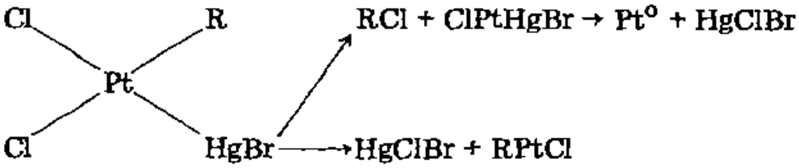
Direction	Conditions	$\alpha_i = d_i/\Sigma d_i$				D (%)	*M*
		α_1	α_2	α_3	α_4		
A	$K_2PtCl_4 : HgCl_2 : DCl = 1 : 1 : 3$; $P_{CH_4} = 760$ torr 100°C; 9 h	0.650	0.251	0.0735	0.0296	0.915	1.49
B	$K_2PtCl_4 : CH_3HgBr : DCl = 1 : 1 : 3$; 100°C; 0.3 h	0.630	0.268	0.0815	0.0212	35.0	1.49

ment between the distribution of d-methanes in methylation of Pt(II) and direct H—D exchange is convincing evidence for the formation of platinum alkyls in homogeneous activation of saturated hydrocarbons.

The interaction of organomercuric compounds with K_2PtCl_4 seems to follow the mechanism of oxidative addition

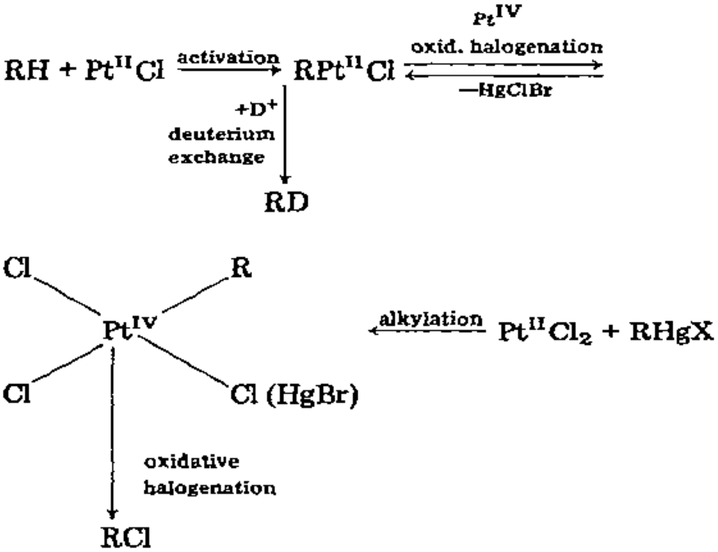


The Pt(IV) complex may then decompose by way of reductive elimination of RCl or HgClBr.



The first reaction is similar to one of the stages of halogenation of alkanes in platinum salt solutions. The second reaction yields the same alkyl compound of Pt(II) which is obtained in homogeneous activation of alkanes.

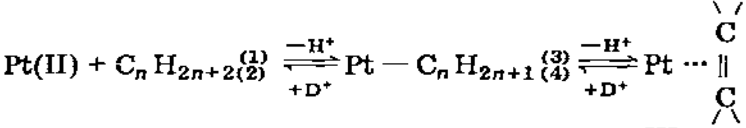
The relationship between the activation of saturated hydrocarbons with formation of alkyl platinum, reactions of deuterium exchange and oxidative halogenation of alkanes in platinum salt solutions and alkylation of Pt(II) with organomercuric compounds is illustrated by the following schematic representation



The alkyl derivative of Pt(IV) is the key compound for halogenation, while the Pt(II) alkyl is the key compound for simple and multiple deuterium exchange. The identical distribution of deuteromethanes in the reactions of methane and CH_3HgBr can be explained by the fact that both reactions have common intermediate compounds for deuterium exchange.

(iii) Mechanism of multiple exchange in the presence of Pt(II). Pt(II) carbenes as intermediates

As mentioned above, the deuterium exchange of alkanes with solvents, catalyzed by Pt(II) compounds, is multiple, i.e. each hydrocarbon molecule entering into the reaction may exchange several hydrogen atoms at a time without leaving the complex [57,58]. In heterogeneous catalysis, the multiple exchange of alkanes is usually explained by the intermediate formation of surface π-complexes. A similar mechanism was suggested by analogy for the homogeneous exchange in the case of ethane and higher hydrocarbons [57, 76].



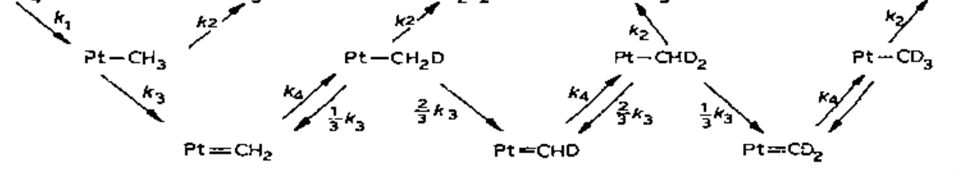
$$\mathrm{Pt(II)} + C_nH_{2n+2} \underset{+D^+}{\overset{-H^+}{\underset{(2)}{\overset{(1)}{\rightleftharpoons}}}} \mathrm{Pt}-C_nH_{2n+1} \underset{+D^+}{\overset{-H^+}{\underset{(4)}{\overset{(3)}{\rightleftharpoons}}}} \mathrm{Pt}\cdots \begin{smallmatrix}\diagdown\ \diagup\\ C\\ \|\\ C\\ \diagup\ \diagdown\end{smallmatrix}$$

I II III

Each I—II—I or II—III—II cycle results in a single deuterium atom being introduced into the alkane molecule since $D^+ \gg H^+$. If the rates of decomposition in directions (3) and (2) are comparable, one I—II—I cycle may include several II—III—II cycles, which will result in a number of deuterium atoms being introduced into the alkane molecule within a single act of coordination of alkane with platinum. In the case of ethane, the average number of deuterium atoms $M = \Sigma i d_i/d_i$ is equal to 1.7 in $CH_3COOD:D_2O$ (1:1). For other alkanes, $M = 1.5$ to 2.0 depending on the number of carbon atoms in the alkane, as well as the nature of solvent and temperature.

Multiple exchange in methane may be explained in a similar way assuming intermediate formation of a complex of methylene with platinum: $Pt{=}CH_2$.

The distribution of deuterohydrocarbons, independent of time at initial stages of exchange, can be calculated by the stationary state method, e.g. for methane exchange.



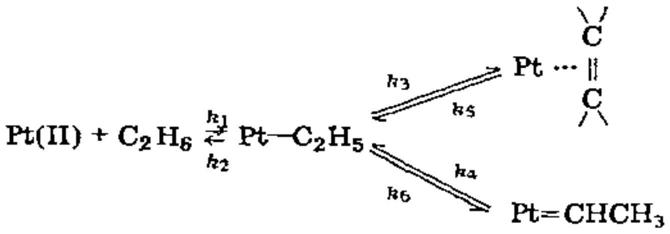
The amount of each deuteromethane present in the mixture $\alpha_i = d_i/\Sigma d_i$ may be expressed in terms of a factor $p = k_3/k_2$ unambiguously.

The calculation of the distribution (i.e. α_i) of deuterohydrocarbons for the exchange of methane and ethane in $CH_3COOD—D_2O$ (1 : 1) indicates that this scheme adequately represents the experimental results. The distribution of deuterohydrocarbons in experiments carried out in $CH_3COOD—D_2O$ (1 : 1) is smoothly descending, i.e. a lower amount of the hydrocarbon is observed (α_i) with an increase in the number (i) of D atoms in it.

Experiments on the deuterium exchange of ethane in pure water [77] have revealed, however, an unusual stepwise distribution including two groups $\alpha_1 - \alpha_3$ and $\alpha_4 - \alpha_6$, the distribution in each of these groups being ascending. It follows from MS for these experiments that in deuteroethanes $d_2 - d_4$ asymmetrical molecules (CHD_2CH_3, CD_3CH_3, CD_3CH_3D) are prevalent.

The pattern of distribution of deuteroethanes for deuterium exchange in water (predominance of $d_1—d_3$ over $d_4—d_6$ and the same ascending pattern in each group) suggests that the exchange takes place, first, in one methyl group of ethane, then, after the molecule turns round, in the other. Obviously, such a distribution is inconsistent with the π-complex mechanism of multiple exchange when both carbons must be equivalent.

There is a logical explanation for the stepped distribution if it is assumed that the multiple exchange in ethane is similar to that in methane, involving intermediate formation of complexes with carbenes. To account for the appearance of deuteroethanes with the number of deuterium atoms exceeding three, it is necessary to introduce an elementary act of molecular rotation, probably via the π-complex.



Calculation of the distribution of deuterohydrocarbons by the method of stationary concentrations in accordance with the above scheme yields results which agree well for experiments in water. It is interesting to note that in experiments with a smoothly descending distribution (i.e. in 50% acetic acid) good agreement is observed in calculations using both the π-complex mechanism and carbene mechanism. However, it is more logical to assume that the carbene intermediate is always present than to infer that it appears spontaneously when conditions change. Therefore carbene mechanism appears to be a general one.

In the case of other alkanes [78], just as in the case of ethane, a stepwise distribution is observed with the group $\alpha_1—\alpha_3$ always standing distinctly apart (Fig. 6). As in the case of ethane, this is indicative of platinum being preferably bonded with one (terminal) carbon of alkane, i.e. 1-(alkyl)- and 1,1-(carbene)-bonded intermediates rather than 1,2(olefin)- bonded fragments. Platinum shifts take place via 1,2-bonded fragments (or π-complexes) from

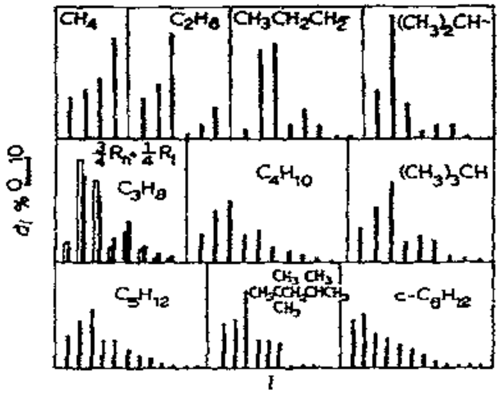
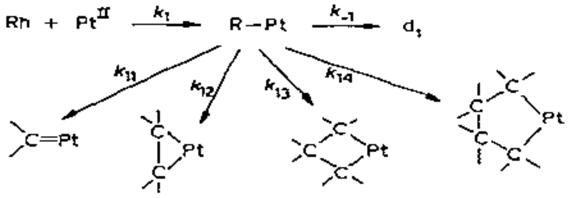


Fig. 6. Distributions of deuteroalkanes.

1- to 2-(etc) carbons of alkane (1,1 → 1,2 → 2,2 or 1,1 → 1 → 1,2 → 2 → 2,2).

In the case of propane, one should take into consideration the possibility of platinum attacking the primary or secondary carbon atoms, and the distribution of deuteropropanes during exchange must be a superposition of these partial distributions. To corroborate this, platinum was alkylated with n-propyl and isopropyl bromides of mercury (RHgBr) [78] in a deuterium exchange reaction. As can be seen from Fig. 6, the distribution in the case of H—D exchange of propane agrees well with that obtained as a sum of the partial distributions with respective coefficients $R = 0.75\ R_H + 0.25\ R_{iso}$, which are proportional to the constants of the rates at which platinum attacks the primary and secondary carbons. Bearing in mind that in propane there are 6 primary and 2 secondary C—H bonds, the selectivity of the attack on a C—H bond can be expressed through the following relationship: prim : sec ≈ 1 : 1.

The presence of the second step α_4—α_5 in the distribution of deuteropropanes in alkylation with the n-propyl of mercury is consistent with the 1,2-shift of platinum along the carbon chain; however, the markedly higher value of α_6 is indicative of a possibility and higher probability of a 1,3-shift of platinum. Such a shift is assumed [132] to involve an intermediate particle, which may be regarded as a complex of platinum with cyclopropane. As is known, when hydrocarbons of the cyclopropane series interact with K_2PtCl_4 in a solution, they readily yield compounds of such a structure [51]. The role of 1,3-intermediates in multiple exchange becomes prevalent in the case of such hydrocarbons as isobutane and isooctane in which the formation of 1,2-intermediates is difficult because of spatial factors. The triplets of groupings in the case of these hydrocarbons (see Fig. 6) is indicative of a 1;3-shift, while the appreciable contribution to the distribution of the α_4—α_6 group suggests that it proceeds easily enough. The distinct group α_7—α_9 for isobutane and the conspicuous absence of α_{10} (in contrast to butane) indicate that the hydrogen atom attached to a tertiary carbon does not participate in the exchange either by way of primary attack or by way of a 1,2-shift. Since the rate at which platinum attacks the CH_3 and CH_2 groups associated with the quaternary atom of carbon is extremely low [19], the presence of groups α_7—α_9 in the exchange of isooctane is suggestive of a 1,4-shift. The possibility of formation of 1,4-(cyclobutane) intermediate complexes is corroborated by the study of the H—D exchange of cyclobutane in K_2PtCl_4 solutions [20]. More remote migrations of platinum are possible as well



The absence of exchange of the tenth hydrogen atom in isobutane is explained by a substantial increase in steric hindrance in transition to the tertiary C—H bond. Thus, the selectivity of the attack of platinum on a C—H bond of an alkane is prim : sec : tert ≈ 1 : 1 : 0. This selectivity, derived in studying the distribution of deuteroproducts, agrees well with the constants of the rates of interaction between alkanes and platinum.

Accurate calculation of multiple exchange patterns for hydrocarbons higher than ethane is a difficult task; however, analysis of distribution in the absence of steric hindrances shows that the rate constants seem to decrease in the series $k_{11} \gg k_{12} > k_{13} > k_{14}$. Analysis of the ascending distribution in the case of methane exchange in water, in which it was compared with calculations using different patterns, shows that dehydrogenation is confined to methylene complexes with no methine complexes (Pt≡CH) being formed. The dependence of M on the experimental conditions (temperature, dielectric constant of the medium, ionic strength, acidity and concentration of Cl^-) is consistent with the following mechanism of multiple exchange.

$$\mathrm{RPtCl} \overset{K}{\rightleftharpoons} \mathrm{RPt^+} + \mathrm{Cl^-}$$

$$\mathrm{RPtCl} + \mathrm{D^+} \xrightarrow{k'_{-1}} \mathrm{RD} + \mathrm{PtCl^+}$$

$$\mathrm{RPt^+} + \mathrm{D^+} \xrightarrow{k''_{-1}} \mathrm{RD} + \mathrm{Pt^{2+}}$$

$$\mathrm{RPt^+} \xrightarrow{k''_2} \text{double bonded platinum complexes} + \mathrm{H^+}$$

$$k''_2 = k_{11} + k_{12} + k_{13} + k_{14}$$

In accordance with this mechanism, the dependence of k''_2/k_{-1} (= p) on $[H]^+$ and $[Cl^-]$ can be expressed as ($k'_{-1} \gg k''_{-1}$)

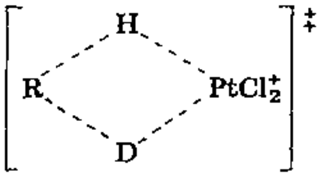
$$p = \frac{k_2''K}{k_{-1}'[\mathrm{D}^+][\mathrm{Cl}^-]}$$

i.e. as the acidity and $[\mathrm{Cl}^-]$ increase, the degree of dehydrogenation and multiple exchange factor M decrease.

The increase in M observed when changing over from an aqueous—acetic acid medium to water is associated with an increase in the acidic dissociation of the alkyl complex of Pt(II) as a result of a higher dielectric constant of the medium.

(iv) Nature of transition state

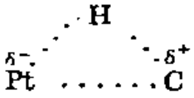
Different mechanisms have been discussed in the literature to explain deuterium exchange of alkanes, catalyzed by Pt(II). The mechanism proposed by Littlecott and McQuillin [21], involving a simultaneous process of addition of D^+ and splitting off of H^+ with the participation of $\mathrm{DPtCl_2^+}$ through a 4-center transition state,



can be ruled out, since the intermediate formation of platinum alkyls seems beyond doubt. Any mechanism of alkane activation with Pt(II) complexes must be considered with this fact in view.

The following alternatives can be proposed for the transition state of a reaction yielding Pt—R.

A



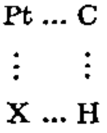
Insertion, oxidative addition

B

$\mathrm{Pt^I \ldots CH_4^+}$

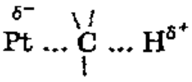
Electron transfer with formation of a complex with a cation radical

C



Four-membered transition state

D



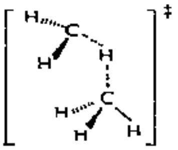
$\mathrm{S_E2}$

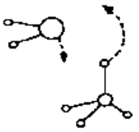
As can be inferred from the available data, in our opinion, transition state A is the most probable. This transition state is mostly associated with reactions involving Pt(II) having electron configuration d^8 and tending, therefore, to oxidative addition reactions to give the stable d^6 configuration of Pt(IV). Transition state B with complete electron transfer from the alkane to platinum seems to be unlikely because of very high ionization potentials of methane and its homologs, although the correlation between the rate constants and ionization potential is indicative of the partial electron transfer in the transition state as well as of the donor—acceptor nature of the interaction.

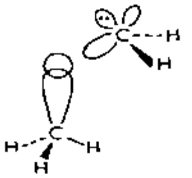
In the case of the four-membered transition state C, one would expect a correlation with the basicity of ligand X (heterolytic mechanism) or with the strength of its bond with H and Pt (homolytic mechanism), which is not found. Transition state D, as already mentioned, is difficult to correlate with the effect of the substitutent in the hydrocarbon (the presence of a non-polar conjugation) or a change of the Pt(II) ligand (reverse *trans*-effect series).

It should be noted here that the regularities observed in the case of intramolecular cleavage of the C—H bond in the ligand, where the mechanism of oxidative addition via transition state A is quite certain (formation of an alkyl hydride), are similar to those established for the reaction of free alkanes with Pt(II). This is other evidence for the mechanism involving transition state A.

The transition state of the Pt(II) + RH reaction seems to be similar to that of the insertion reaction of a singlet carbene into a C—H bond, for example, $CH_2 + CH_4$. For the latter reaction, a calculation has been made of the potential energy surface by Hoffman and co-workers [79] by means of extended Hückel method, and by Dewar and co-workers [80] by means of the MINDO/2 method, both arriving at the conclusion that insertion is a concerted reaction with CH_2 being attacked almost along the C—H axis, similar to reactions of H-abstraction by radicals. The transfer of hydrogen from methane to carbene takes place only when the carbon atoms are spaced 2 Å apart, the remaining stage of the reaction being similar to the recombination of a pair of methyl radicals. This radical-type transition state was assumed earlier by Benson [144] for the carbene insertion reaction.

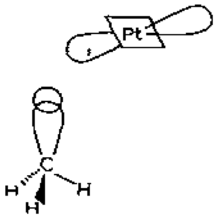


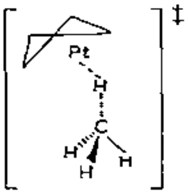


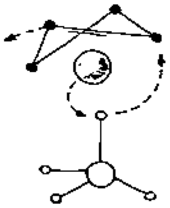


Calculations show that in such a transition state, a negative charge is localized on the methylene carbon, while on the methane carbon a positive charge occurs. The appearance of electron density on methylene is consistent with an attack on methane inolving a vacant orbital. The interaction of this vacant orbital results in electron density loss in the case of an alkane carbon and in its transfer to carbene carbon.

Square Pt(II) complexes have a vacant p_z-orbital with a relatively low energy. This orbital can play an important role in the initiation of the transition state in a reaction involving hydrocarbons as well as in substitution reactions proceeding in accordance with an associative mechanism [81].





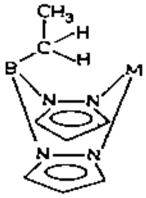


The transition state of the Pt(II) + RH reaction is attained, in all probability, by the alkane carbon closely approaching Pt(II) without any substantial stretching of the C—H bond. As soon as this approach takes place, the hydrogen atom is transferred to Pt(II) with simultaneous distortion of the square Pt(II) to form, at a certain stage, a trigonal bipyramid of Pt(III) in pair with the $R^{\cdot}$ radical. The process terminates in a recombination of $R^{\cdot}$ and Pt(III) to form an octahedral alkyl hydride of Pt(IV).

Studies into multiple exchange of alkanes reveal a tendency of Pt(II) to covalent double bonding which is another indication of its carbenoid properties. As mentioned above, the relatively small isotopic effect and the value of activation entropy agree well with transition state A. Such a transition state, requiring close approach of the reagents to one another, accounts for the serious steric hindrances in the Pt(II) + RH reaction. And, finally, transition state A agrees well with the effect of the substituents in hydrocarbons, and changes of ligands in Pt(II).

Some data obtained for the other metals are in good agreement with the above interpretation of C—H bond interaction with a metal atom in the complex.

The interaction of hydrogen from a C—H bond with a metal atom in a complex is known from X-ray work. For example, the interaction of vinyl hydrogen with Pd in complex $PdBr—(PPh_3)_2(CCO_2Me)_4H$ leads to a Pd ··· H distance of 2.3 Å which is considerably less than the van der Waals radii sum (3.1 Å) [133]. In the alkylpyrazolylborate complexes of Ni and Mo, where an ethyl group is on the B atom, the methylene C—H bond approaches a metal atom due to the favourable molecule conformation [134].



The NMR spectra of these complexes display a considerable signal shift of protons close to metal. The shift may be both to high and low fields depending on the electronic properties of metal and C—H bond orientation. In such complexes the M ··· H distance is close to 1.9—2.1 Å, and the interaction may be viewed as a three-centre two-electron bond including C, H and Mo or Ni [135]. The interaction of aliphatic C—H bonds with a metal atom may successfully compete with the metal—olefin interaction [136]. Essential for all these complexes is the availability of an empty low-lying orbital at the metal. A trend to reach a filled electron shell is, by all evidence, the driving force of the M ··· H interaction.

D. REACTIONS OF OXIDATION OF ALKANES IN SOLUTIONS OF METAL COMPLEXES

The problem of oxidation of hydrocarbons remains of importance from the standpoint of both basic and applied science. The use of metal complexes opens up new possibilities in this respect [82,83].

The observation that Pt(IV) is reduced to Pt(II) in acetic acid solutions led to a discovery of the reaction of alkane oxidation in solutions of platinum chlorides [84,85]. Acetic acid, cyclohexane and other hydrocarbons, including such inert ones as methane and ethane, are capable of reducing Pt(IV) in an aqueous solution at 100—120° C, to Pt(II), the latter catalyzing this reaction (Table 6).

A similar result was obtained for cyclohexane [86]. Earlier, the reaction of chorination and oxidative coupling of benzene was discovered [87]. When this reaction is conducted in D_2O—CH_3COOD, the products of benzene oxidation, namely chlorobenzene and diphenyl, contain deuterium in an amount exceeding that of the unreacted benzene. The distribution of deuterium in chlorobenzene is consistent with the mechanism of chlorination via intermediate formation of Pt—C_6H_5.

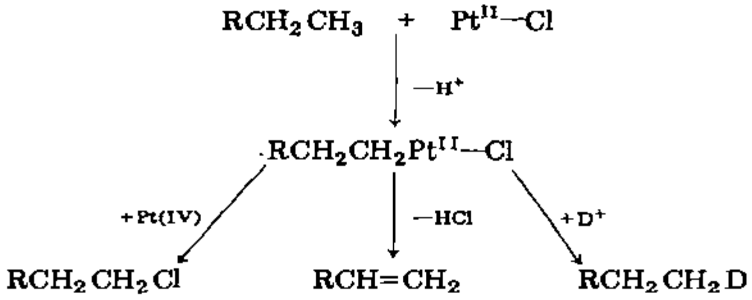
It can be assumed that the reactions of chlorination and dehydrogenation of alkanes involve their interaction with Pt(II), just as in the case of deuterium exchange. Thus, all of these reactions can be summarized as follows.

TABLE 6

Products of oxidation of hydrocarbons in aqueous solutions of H_2PtCl_6—Na_2PtCl_4

No.	Alkane	t°C/time (h)	Products (relative yield, %)
1	Methane, 50 atm	120/4	Methyl chloride
2	Ethane, 20 atm	120/4	Ethyl chloride
3	Propane, 6 atm	120/4	n-C_3H_7Cl(75), iso-C_3H_7Cl(25)
4	Pentane	120/0.25	n-$C_5H_{11}Cl$(56), sec-$C_5H_{11}Cl$(44)
5	Isopentane	120/0.25	prim-$C_5H_{11}Cl$(78), sec-$C_5H_{11}Cl$(22)
6	Hexane	110/5	n-$C_6H_{13}Cl$(40), n-$C_6H_{13}OCOCF_3$(30,5), $C_4H_9COCH_3$(23,9), sec-$C_6H_{13}OCOCF_3$, sec-$C_6H_{13}Cl$(1,4)
7	Cyclohexane	110/5	C_6H_6(77.6), C_6H_5Cl(11), $C_6H_{11}Cl$(5,4), $C_6H_{11}OCOCF_3$(5), cyclohexanone, traces of alcohol and dichloride
8	Methyl cyclohexane	110/5	Toluene (61,6), n-chlorotoluene (11,2), $CH_3C_6H_{10}Cl$(9,1), $CH_3C_6H_{10}OCOCF_3$(8,2), $C_6H_{11}CH_2Cl$(4,1), ketone (4,1)
9	Decalin	110/5	Naphthalene

Experiments 1—5 in H_2O, 0.5 M Pt(IV), 0.05 M Pt(II); 6—9 in 8.7 M CF_3COOH, 0.18 M Pt(IV), 0.02 M Pt(II).



In the chlorination reaction, Pt(II) acts as a catalyst, while Pt(IV) performs the function of the oxidant. Oxidation of hydrocarbons yields, in addition to chloroderivatives, alcohols, esters, ketones, aromatic compounds, as well as olefinic and aryl platinum complexes, organic acids and products of oxidative coupling of hydrocarbons [72,73]. Chloroalkanes are the primary products. Dehydrogenation of cyclic hydrocarbons also seems to proceed by initially yielding chloroalkanes. In the course of the reaction, the concentration of cyclohexyl chloride passes through a maximum; a similar picture is observed in other cases.

Olefins (e.g. cyclohexene) have not been found among the reaction products, probably because they are rapidly oxidized further or form stable complexes with Pt(II). Evidence for the latter, formed as a result of oxidation of hexane, is given in ref. 72. In the presence of platinum salts, both cyclohexene and cyclohexyl chloride yield benzene, probably through successive stages of chlorination and dehydrochlorination. The rates of reduction of Pt(IV) by cyclohexene and cyclohexyl chloride are close to each other and exceed the rate of reduction of Pt(IV) by cyclohexane and benzene.

The following facts support primary formation of chloroderivatives.

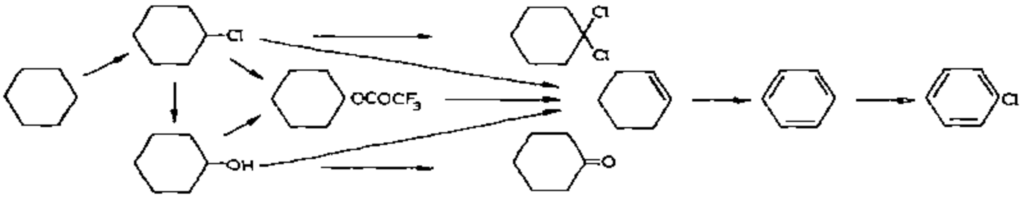
(1) At the initial stage of the reaction of Pt(IV) reduction with cyclohexyl chloride, only benzene is yielded, while there is no trace of chlorobenzene which is a product of dehydrogenation, i.e. no direct dehydrogenation takes place.

(2) Halogen derivatives are the only products of the reaction in cases where they are stable enough, for example, in the case of acetic acid or benzene. In a non-aqeous medium (sulfolane), the only product of cyclohexane oxidation was cyclohexyl chloride.

(3) The selectivity in isomeric products, measured at low conversion, approaches that of the primary attack of Pt(II) on a C—H bond in deuterium exchange reactions.

(4) In the case of oxidation of a mixture of 1- and 2-chlorohexanes, only the former remains in the products, while 1-hexene does not yield 1-chlorohexane under the reaction conditions.

The sequence in which products are yielded, e.g. in oxidation of cyclohexane, can be represented as follows.



The rate of further transformations of chlorides is higher than the rate of their formation [88]. As a result, the yield of primary products per Pt in the case of n-alkanes is often below 5%. The quantitative yield of chloroacetic acid is determined by both its greater stability with respect to solvolysis and high excess of acetic acid in the reaction solution. The total yield of the main products of cyclohexane oxidation is about 40%, while that of products of benzene oxidation is as high as 80%. The selectivity to terminal oxidation of alkanes does not reflect merely the ratio of rate constants of primary reaction; it is the result of faster further transformations of secondary and tertiary chlorides [72].

The kinetics of interaction of alkanes with platinum chloride complexes was studied by a number of investigators [85,88–91]. For C_1—C_4 alkanes in water, the reaction is first order with respect to hydrocarbon, and fractional (0.77) with respect to Pt(II). The relative rates of Pt(IV) reduction with ethane, propane, butane and isobutane, agree well with the data on deuterium exchange of these hydrocarbons. The activation energies of about 20 kcal mol^{-1} for halogenation of C_2—C_4 alkanes are also consistent with E_a for exchange of ethane (18.6 kcal mol^{-1}). The kinetics of catalytic oxidative halogenation of a C—H bond in the presence of Pt(II) has been studied in detail for acetic acid transformation to monochloroacetic acid [85,89].

$$PtCl_6^{2-} + CH_3COOH \rightarrow PtCl_4^{2-} + ClCH_2COOH + HCl$$

The concentration of Pt(IV) decreases in accordance with the autocatalytic rate law. The observed induction period is eliminated by adding small amounts of bivalent platinum. The kinetic curves for acetic acid are similar to those for hydrocarbons (cyclohexane, hexane, pentane, isopentane), which is consistent with a similar mechanism of activation of C—H bonds. The order of the reaction with respect to both Pt(II) and acetic acid is 1. A slower reaction rate is observed on addition of acid and Cl^-, and at a higher concentration of Cl^- the reaction rate is proportional to $[Cl^-]^{-2}$. The order of the reaction with respect to Pt(IV) changes from 0 to 1. A mechanism has been proposed on the basis of kinetic studies, which seems to be common for compounds containing sp^3 hybridized C—H bonds, including saturated hydrocarbons.

$$PtCl_4^{2-} \rightarrow PtCl_3^- + Cl^- \tag{6}$$

$$PtCl_3^- \overset{K}{\rightleftarrows} PtCl_2 + Cl^- \tag{7}$$

$$PtCl_2 + RH \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} RPtCl + H^+ + Cl^- \quad (8)$$

$$RPtCl + PtCl_6 \xrightarrow{k_2} RCl + 2PtCl_3^- \quad (9)$$

Stages (8) and (9) may be composite, for example:

$$PtCl_2 + RH \xrightarrow{k_1} RPtHCl_2 \quad (10)$$

$$RPtHCl_2 \xrightarrow{fast} RPtCl + H^- + Cl^- \quad (11)$$

$$RPtCl + PtCl_6^{2-} \xrightarrow{k_2} RPtCl_3 + PtCl_4^{2-} \quad (12)$$

$$RPtCl_3 \xrightarrow{fast} RCl + PtCl_2 \quad (13)$$

Under these conditions, stage (8) or (9) may be limiting since stages (6) and (7) proceed rapidly and reversibly.

At temperatures above 100° C and low concentrations of Pt(IV), when the reaction rate depends on Pt(IV) and H^+, stage (9) seems to be limiting. As the temperature decreases and the concentration of Pt(IV) increases, the dependence on acidity and Pt(IV) disappears, i.e. under these conditions the reaction of Pt(II) along the C—H bond becomes limiting.

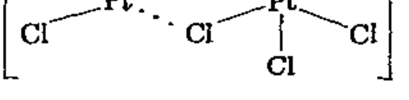
The following kinetic equation can be obtained on the basis of a stationary state method for the above scheme.

$$W = \frac{k_1 k_2 K[RH][Pt^{II}][Pt^{IV}]}{([Cl^-] + K)(k_{-1}[H^+][Cl^-] + k_2[Pt^{IV}])}$$

The equation accounts for the experimental results.

The temperature dependence of the reaction rate corresponds to two activation energies 80—100° $E_{eff} = 22.5$ kcal mol^{-1} and 100—130° $E_{eff} = 8.6$ kcal mol^{-1}. At temperatures below 100° C and low concentrations of chloride when the reaction rate is practically independent of $[Cl^-]$, equilibrium (8) seems to be completely shifted to the right, and one can neglect Cl^- as compared to K, and $k_{-1}[H^+][Pt^{II}]$ as compared to $k_2[Pt^{IV}]$. Therefore we come to $W = k_1[RH][Pt^{II}]$. Accordingly the activation energy in this region is close to that in exchange reactions.

At temperatures above 100° C, the limiting stage is that of interaction of an alkyl derivative of Pt(II) with Pt(IV). The low activation energy corresponds to the nature of elementary process (9), which is an exchange reaction in a binuclear activated (or intermediate) complex, probably formed by bridges.



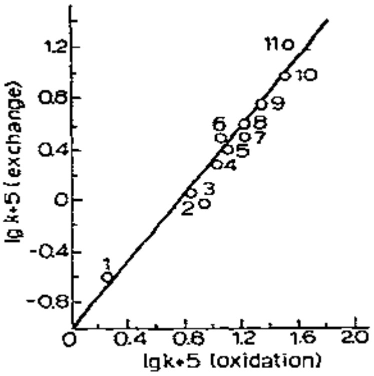


Fig. 7. Correlation between rates (sec^{-1}) of H—D exchange and oxidation (1 = methane, 2 = ethane, 3 = iso-butane, 4 = propane, 5 = 3-methylpentane, 6 = n-butane, 7 = n-pentane, 8 = n-hexane, 9 = cyclopentane, 10 = cyclohexane, 11 = benzene).

This mechanism is in agreement with the higher rate of oxidation of benzene [86] and alkanes [92] in systems with a bromide ion which is a better bridge than Cl^-, as well as with the lower rate of oxidation in a system in which the ratio between halogenide-ligands and Pt is less than 2.5—3 [92]. The rate constants for oxidation of a number of alkanes range from 2 to $8 \cdot 10^{-3}$ l mol^{-1} sec^{-1} at 98° C in an aqueous solution of chlorides of Pt(II)—Pt(IV) [90].

According to ref. 90, there is a distinct correlation between the rates of oxidation and H—D exchange (Fig. 7). The oxidation rate constants turned out to be proportional to the number of carbon atoms available to attack in the hydrocarbon: $k = k_0 n_0$ where $k_0 = (0.4\text{—}1.2) \cdot 10^{-3}$ l mol^{-1} sec^{-1} and $n_0 = n - n_{tert} - 5n_{quatern}$.

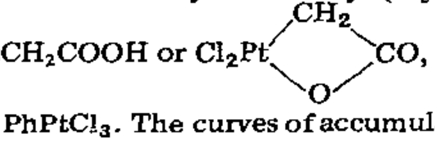
The data published in several papers [24,72,73,87,89,137] indicate that the values of rate constants and activation energies for oxidation often coincide with those for H—D exchange when both reactions proceed under similar conditions (see Table 7).

TABLE 7

Comparison of k and E_a for exchange and oxidation in CH_3COOD—D_2O at 100°C

Hydrocarbon	k, (l mol^{-1} sec^{-1})		E_a, (kcal mol^{-1})	
	exchange	oxidation	exchange	oxidation
Benzene	$6 \cdot 10^{-3}$	$\geq 5.5 \cdot 10^{-3}$	25.7	25
Acetic acid	$0.9 \cdot 10^{-4}$	$1.25 \cdot 10^{-4}$	23.7	22.5
Hexane	$1.8 \cdot 10^{-3}$	$1.6 \cdot 10^{-3}$	18.6 (C_2H_6) 18.4 (C_6H_{12})	

Evidently these results show that the rate determining step of both reactions is the same. Thus, the data suggest that halogenation of alkanes, as well as H—D exchange, involve intermediate formation of platinum alkyls. In studying the kinetics of oxidation of benzene [86], cyclohexane and other cycloalkanes [73], as well as acetic acid [73], it was revealed that at the initial stage of the reaction a drastic change in the stoichiometry takes place. For acetic acid, e.g. the decrease in the amount of Pt(IV) is several times greater than the amount of the chloroacetic acid formed. This effect is apparently due to the formation of relatively stable alkyl (aryl) compounds of Pt(IV) [72,73], such as Cl_3PtCH_2COOH or



$RPtCl_3$, $PhPtCl_3$. The curves of accumulation of these intermediate compounds, calculated from the difference between the change in $[Pt^{IV}]$ and the total concentration of the products, correspond to a lower stability of $AlkPtCl_3$ as compared to $ArPtCl_3$. A relatively high concentration of $PhPtCl_3$ comparable with that of H_2PtCl_6 is also responsible for the formation of an appreciable amount of diphenyl in the case of oxidation of benzene, which seems to proceed as follows

$$PhPtCl_3 + PhPtCl \rightarrow Ph_2PtCl_2 \rightarrow Ph{-}Ph + PtCl_2$$

In the presence of an external oxidant, the process may become catalytic with respect to platinum. The oxidants for Pt(II) were dioxygen (air), cupric chloride (systems $H_2PtCl_6{-}CuCl{-}O_2$ or $Na_2PtCl_4{-}CuCl_2{-}O_2$) and quinones. When controlled amounts of HCl were introduced in the course of the process, the yield of the product was found to correspond to 5 cycles per Pt, i.e. a catalytic process was achieved, consuming CH_3COOH, HCl and O_2. When more than 0.2 M of $ClCH_2COOH$ are accumulated in the solution, further chlorination becomes noticeable.

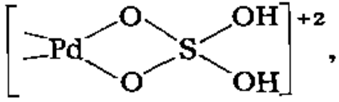
A catalytic process involving Pt(IV) at 100°C is limited by the rate of oxidation of Pt(II) by an external oxidant. However, the rate of accumulation of chloroacetic acid in the catalytic system is several times higher than that of oxidation of Pt(II) under these conditions. This is probably indicative of direct oxidation of the intermediate complexes of RPt(II) by an external oxidant in the absence of H_2PtCl_6.

$$RPtCl + O_2 \xrightarrow{2HCl} RPtCl_3 + H_2O_2$$

It was also found [94] that alkanes (n-hexane and cyclohexane) reduce Pd(II) trifluoroacetate at 92° C in trifluoroacetic acid to Pd(0). $Pd(OCOOCF_3)_2$ itself is quite stable when heated in CF_3COOH even in the presence of palladium black, but cyclohexane is dehydrogenated by homogeneous solutions of palladium trifluoroacetate in accordance with the stoichiometric equation

$$3Pd(CF_3COO)_2 + C_6H_{12} \rightarrow 3Pd(0) + C_6H_6 + 6CF_3COOH$$

The reaction rate does not depend on the acidity of the medium. One can assume that the interaction of hydrocarbons with Pd(II) is similar to activation at Pt(II), although no deuterium exchange of alkane catalyzed by $Pd(OCOCF_3)_2$ is observed. In fact, alkylation of $Pd(OCOCF_3)_2$ with organomercuric compounds RHgBr ($R = CH_3, C_2H_5$) under conditions of deuterium exchange results in yielding ethane, in the first case, and ethylene, in the second case, neither containing deuterium.

Solutions of $PdSO_4$ in sulfuric acid were shown recently [93] to absorb alkanes at 90° C. The reaction is first order with respect to both hydrogen and palladium sulfate, $-d[RH]/dt = k[RH][Pd^{II}]$, and is accompanied by formation of SO_2 and metallic palladium. Presumably, an olefin is formed first, which is then subject to fast reactions of sulfonation, oxidation and dehydrogenation. In the case of cyclohexane, benzene and benzene sulfonic acids are formed. The strong dependence of the rate constant of this reaction on acidity was explained by the presence in the reaction of the doubly protonated complex , with a high oxidation potential. Later work [144] showed that a Pt(II, IV) sulfate, probably of the composition $H_{2n}[Pt_2(SO_4)_2(OH)_4]_n$, in 80—100% H_2SO_4 rapidly oxidizes hydrocarbons, and the kinetic characteristics of this process are similar to those established for Pd(II): first order with respect to RH and Pt, the same kinetic isotopic effect $k_{C_6H_{12}}/k_{C_6D_{12}} = 1.9$—$2.0$ (90° C) a "normal" order of selectivity of attacking C—H bonds (tert > sec > prim), and an exponential growth of k with increasing acidity of the medium. The mechanism of alkane oxidation in sulfuric acid seems to be different from that of oxidation in H_2O, CH_3COOH or CF_3COOH.

Various oxidants can participate in alkane oxidation in sulphuric acid besides Pt(II) and Pd(II). They are: Hg(II), Cr(VI), Mn(III), Mn(III)—Ru(III—IV), NO_2^+, $H_2S_2O_8$, carbocations and H_2SO_4 itself [138]. Under the same conditions, weaker oxidants such as Ag(I) and Fe(III) are inactive. Apparently, the rates of these reactions correlate with redox potentials of metal ions. The similarity of the reactions suggests a common mechanism which is still to be determined. A strong dependence of the reaction rates on acidity may be explained by coupling acid—base and redox processes.

In our opinion, the rate determining step of the reaction might be a synchronous transfer of two hydrogen atoms from a protonated carbon of solvated alkane [139] to an oxidant molecule, similarly to the mechanism of alkane dehydrogenation by the benzyl cation in acid media [139].

Chloride complexes of Ru(IV) substantially accelerate the oxidation of alkanes in aqueous solutions of chromic acid (see table 8) [95,96].

Alkyl chlorides are the primary products of transformation of alkanes. The dependence of the oxidation rate constant of propane and n-butane on $[Cl^-]$ passes through a maximum at a concentration of about 0.5 M. The selectivity of attacking a C—H bond, prim : sec : tert = $1 : 10^2 : 10^4$, is close

TABLE 8

Constants of alkane oxidation rates in system Ru(IV)—Cr(VI) at 88°C

Alkane	Ethane	Propane	n-butane	Isobutane
$k \cdot 10^5 (\text{sec}^{-1})$	0.5	60	200	1,500 (18)[a]

$[K_2Ru(OH)Cl_5] = 5 \cdot 10^{-2}$ M, $[K_2Cr_2O_7] = 8.3 \cdot 10^{-3}$ M, $[LiCl] = 3.0$ M.

[a] The value of k in the absence of Ru(IV).

to that for acid-catalyzed oxidation of saturated hydrocarbons with chromic acid in acetic acid [97]. At $[Cl^-] > 0.5$ M, the reaction rate was little dependent on the acidity and ionic strength, while in the case of $[Cl^-] < 0.5$ M, higher acidity results in a considerably higher rate. The following mechanism is assumed [96] from the kinetic data

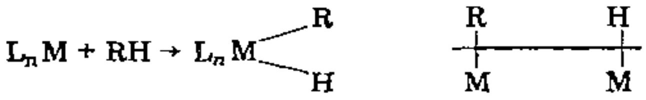
$$\mathrm{RH + Ru(IV)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{Ru(IV) \cdot RH}$$

$$\mathrm{Ru(IV) \cdot RH + Cr(IV)} \xrightarrow{k_2} \text{reaction products}$$

The nature of the Ru(IV) · RH complex is not specified.

E. COMPARISON OF HOMOGENEOUS AND HETEROGENEOUS ACTIVATION OF ALKANES IN THE PRESENCE OF PLATINUM GROUP METALS AND THEIR COMPLEXES

There is a growing belief that there is a strong similarity between heterogeneous and homogeneous catalysis, both being regarded as coordination catalysis. Surface complexes in heterogeneous catalysis have much in common with complexes in solution. It is therefore interesting to compare the results obtained in recent years on homogeneous exchange with those accumulated over many years on heterogeneous H—D exchange of alkanes [98,99]. Table 9 gives certain characteristics for such a comparison. The common factor for exchange in a solution and on the surface of a metal is the dissociative mechanism, determined by the energetics of splitting C—H and forming M—C bonds



$$L_nM + RH \rightarrow L_nM\begin{matrix} R \\ H \end{matrix} \qquad \begin{matrix} R & & H \\ | & & | \\ M & & M \end{matrix}$$

Platinum seems to be most active both in homogeneous and heterogeneous exchange [102] since it forms the strongest M—C bonds. The relative reactivity of different hydrocarbons varies with their ionization potentials, the catalyst being an electron acceptor and the hydrocarbon, an electron donor. The exchange of hydrocarbons with deuterium or D_2O takes place more

TABLE 9

Comparison of homogeneous deuterium exchange of alkanes with heterogeneous exchange on metals

Parameters	Homogeneous		Heterogeneous	
Mechanism and first relatively stable intermediate	Dissociative, M—R, D(Pt—R) > D(Pd—R)			
Relative reactivity	$CH_4 < (CH_3)_4C < C_2H_6 < C_3H_8 \cdots < c\text{-}C_6H_{12}$ Correlation with I.P. for n-alkanes $c\text{-}C_5H_{10} < c\text{-}C_6H_{12}$		$c\text{-}C_5H_{10} > c\text{-}C_6H_{12}$	
Selectivity	prim ⩾ sec > tert		prim < sec < tert	
Order of metal activity	Pt > Ir > Rh > Pd, Ru		Pt > Rh > Pd > Ru [100]	
Activation energy for C_2H_6	18.6 (Pt(II))		12.5 (Pt) 18.2 (Pd)	
Isotopic effect	3.0 ± 0.5 (CH_4, 100°C) 1.7 ± 0.1 (C_6H_{12}, 100°C)		3(C_6H_{14}, Pd) [101]	
Multiple exchange intermediates	1,1-(carbenic), 1,2-(olefinic), 1,3-(cyclopropanoic), 1,4-(cyclobutanoic), double bonded complexes			
Predominant intermediate for C_2H_6	1,1		1,2	
$E_{11}-E_{-1}$	<0		>0	
Distribution	CH_3COOD continuously descending	D_2O ascending stepwise	U-shaped or continuously descending	
M (for C_2H_6)	1.7 (Pt)	3.2 (Pt)	4.8 (Pd)	3.5 (Pt)

readily than C—C bond splitting, despite the fact that C—H bonds are much stronger than C—C ones.

A marked difference is observed in the selectivity of attacking primary, secondary and tertiary C—H bonds. While in heterogeneous exchange the selectivity is consistent with the relative strength of these bonds, in homogeneous exchange it is inversely related to bond strength. This is due to the prevalence of steric factors over electronic ones in homogeneous reactions. At the same time, the lower reactivity of C—H bonds adjacent to the quaternary carbon atom is indicative of the greater role of the hyperconjugative component in the cleavage of a C—H bond. For example, the selectivity on Ni is prim : sec : tert = 1 : 30 : 90, while in the case of Pd, Rh, Ir and Pt the difference between primary and secondary atoms is small. However, in all cases, tertiary atoms exchange faster than primary and secondary ones. For example, multiple exchange of isobutane on Rh yields a great amount of d_{10} at the initial stage, in sharp contrast with the absence of d_{10} in homogeneous deuterium exchange of isobutane on Pt(II). The continuous distribution of deuteromethanes in homogeneous exchange contrasts with the stepped distribution in heterogeneous exchange; analysis of the distributions is indicative of the absence or an insignificant role of triple-bonded intermediates of the Pt≡CH type, as distinct from heterogeneous exchange. As a rule, in heterogeneous exchange, no effect of temperature on distribution is observed, or the degree of multiple exchange increases with temperature.

1 : 1-Bonded intermediates are predominant in homogeneous exchange, the probability of their formation being almost the same for methane and ethane: $k_{11}/k_{-1} = 4.9$ (CH_4), 4.8 (C_2H_6).

In heterogeneous exchange, the mechanism with intermediate formation of 1 : 1-bonded complexes is realized only in exceptional cases when there is no possibility for 1 : 2-bonding, i.e. only in the case of methane, neopentane and other similar molecules. In the case of ethane, 1 : 1-bonded complexes are not observed for any metal or under any conditions. In the case of heterogeneous exchange, $E_{11} \gg E_{-1}$, i.e. the contribution of the carbenic mechanism to the exchange increases with temperature, while in homogeneous exchange on Pt(II) the role of carbenic complexes for saturated hydrocarbons increases as the temperature drops, $E_{11} - E_{-1}$ (kcal) being equal to -5 (CH_4), -14 (C_2H_6) and -3 (C_6H_{12}). The constants for the rate of formation of 1 : 2-bonded complexes of platinum in homogeneous exchange are lower than k_{11}, e.g. in an aqueous medium for ethane, $k_{11}/k_{-1} = 4.8$ and $k_{12}/k_{-1} = 0.2$. The pattern of distribution of deuteroethanes in multiple exchange also differs greatly. Normally, more noticeable multiple exchange is observed on the surface of metals than in solution. Marked changes in heterogeneous multiple exchange are observed already in the condensed phase as compared with the gaseous one [103]. The distribution becomes descending, and multiple exchange becomes less profound (M becomes lower). In the case of Pt/C, NMR analysis reveals only a slight predominance of exchange in the secondary C—H bond as compared to the primary one (1.26 : 1).

Stepwise distribution was never observed in heterogeneous exchange of C_2H_5 with D_2 on the surface of metals, and the distribution of deuterohydrocarbons in heterogeneous exchange is explained well by the formation of surface π-complexes or 1 : 2-bonded hydrocarbon fragments. At the same time, heterogeneous multiple exchange in methane and neopentane $C(CH_3)_4$ (almost exclusively in a single methyl group) seems to involve metal—carbenic intermediates. Thus, the carbenic mechanism may take place on the surface of metals, although the π-complex mechanism is preferable, while in solution preference is given to the carbenic mechanism.

It is interesting to note that 1 : 1, 1 : 2 and 1 : 3-intermediates are found to be involved in heterogeneous exchange of RH with D_2 on the surface of metals, 1 : 3-intermediates being more stable on platinum than on other metals.

Thus, a close similarity is observed for intermediate fragments in homogeneous and heterogeneous alkane exchange. The difference in heterogeneous exchange, residing in $k_{12} > k_{11}$, is easily explained by the fact that two adjacent platinum atoms can be used on the surface to yield 1 : 2-fragments, these fragments being preferable to any 1 : 1-fragments with one or two metal atoms.

The other differences between homogeneous and heterogeneous exchange of alkanes still remain to be explained, although the common features of these two types of coordination activation of saturated hydrocarbons have been firmly established.

F. ACTIVATION OF SATURATED HYDROCARBONS BY COMPLEXES OF NON-PLATINUM METALS

So far, few examples are known of homogeneous activation of saturated hydrocarbons with complexes of non-platinum metals. In heterogeneous catalysis, W, Mo, Ta, Ti and Ni are active for H—D exchange of alkanes, whereas the activity of Co and Fe is low. Since the intramolecular or intermolecular oxidative addition of an aromatic C—H bond is known for practically all transition metals, as can be seen from the case with Pt(II), under certain conditions complexes of these metals may activate an aliphatic C—H bond as well.

In this review, we do not include numerous and well studied cases of catalysis of radical-chain reactions of hydrocarbons by transition metal ions (Mn, Co, Fe and others), which do not react directly with alkanes but participate at elementary stages of the chain oxidation by reacting with other particles (e.g. hydroperoxides at the stage of chain branching).

However, in some cases, the alkane molecule seems to be attacked. We should first of all note the effect of metal complexes acting as strong electron acceptors.

For example, alkanes are known to be activated and oxidized by Co(III) and Mn(III) which are powerful oxidants. Cyclohexane is oxidized by Co(III) perchlorate in $CH_3CN—H_2O$ at 20°C [104] or by Co(III) trifluoracetate [105]; cycloalkanes are oxidized by acetates of Co(III) and Mn(III) in CH_3COOH at 80°C [106]; butane, isobutane and pentane are oxidized by Co(III) acetate at 100—125°C [107], and n-hexane, 2-methylpentane, etc. are oxidized by Co(III) acetate in the presence of catalytic amounts of strong acids at 20°C [108]. These reactions exhibit remarkable features: an unusual selectivity, differing from that for radical attack (tert-CH is less reactive than sec-CH) and indicative of the important role of steric factors; a low isotope effect ($k_H/k_D = 0.86$) [106]; and reactivities of n-alkanes (n-butane > n-pentane > n-undecane) arranged in reverse order relative to the radical one [107]. Additions of Cu(II) acetate which is an effective trap for free radicals do not affect the rate of oxidation [106]. The reaction of oxidation of n-heptane by acetate of Co(III) in the presence of CF_3COOH is first order with respect to hydrocarbon, second order with respect to Co(III) and —1 order with respect to Co(II). The reaction may involve electron transfer, possibly with the participation of Co(IV) formed as a result of disproportionation of two particles of Co(III): $2Co(III) \rightleftarrows Co(IV) + Co(II)$.

In this system alkyl acetates are formed in the absence of oxygen, alcohols and ketones — in the presence of O_2, and alkyl chlorides — in the presence of CCl_3COOH without O_2. In all cases, the methylene group adjacent to the terminal methyl group is preferably attacked, indicative of the importance of the hyperconjugative factor. These results are accounted for [108] by the intermediate formation of radicals $RH + Co(III) \rightarrow R^{\cdot} + Co(II)$.

In ref. 108 it is assumed that the radicals are the result of decomposition of the initially formed alkyl compound of Co(III): RH + Co(III) → RCo(III) → R˙ + Co(II).

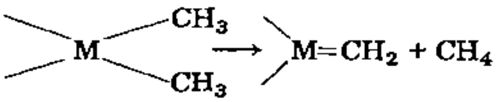
This assumption explains the serious steric hindrances to attacking the C—H bond.

The mechanism of outersphere oxidation with the unstable cation—radical formation [105] which was earlier thought to be analogous to the reaction with aromatic compounds does not take place for alkanes [74]. When oxidizing substituted adamantanes by trifluoroacetates of Pb(IV), Co(III) and Mn(III), the fragmentation products of a possible intermediate cation—radical are absent, unlike in electrochemical oxidations when the radical is always formed. This indicates that with metal compounds the oxidation proceeds by a direct attack on C—H bond.

Only limited information is available so far on the action of low-valency transition metal complexes on alkanes, which is expected to involve oxidative addition. Isotopic exchange of methane with deuterium in the presence of a triphenylphosphine complex of Co(I) [14] has already been mentioned. The mechanism of this reaction is likely to be similar to that of alkane activation by other d^8 metal complexes, though the reaction still requires more detailed study.

Of great interest is the report on activation of methane in the presence of Ziegler's catalysts based on Ti and V: $TiCl_4 + AlMe_2Cl$; $Cp_2TiCl_2 + AlMe_2Cl$, and $VCl_3 + AlMe_2Cl$ [120].

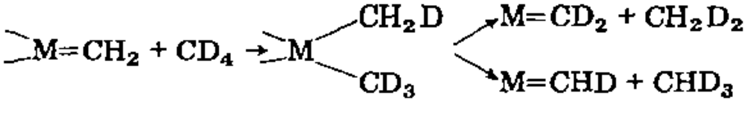
In the presence of these systems, H—D exchange of CD_4 with the methyl groups of the catalytic system is observed in heptane at 20—50° C. Carbene intermediates have been postulated [120]



or

$$2\ {\geq}M{-}CH_3 \rightarrow {\geq}M{-}CH_2{-}M{\leq} + CH_4 \quad [121].$$

The formation of CH_2D_2 and CH_3D is thought to be due to the reaction of these complexes with CD_4, e.g.



In fact, hydrolysis of the catalytic system after the experiment yields a mixture of deuteromethanes in amounts corresponding to the above representation, the balance between the number of H atoms in the reaction products and that of D atoms in the hydrolysis products being observed with sufficient accuracy. It is interesting to note, in connection with this work, that $Cp_2Ti(CH_3)_2$ catalyzes the exchange of benzene with D_2 at 130° C [122].

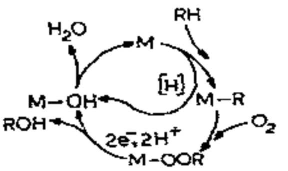
Recently, Grigorian and D'yachkovskii [142] report that $(\pi\text{-}C_5H_5)_2V$ catalyzes isotopic exchange of methane and ethylene, as well as benzene and ethylene, the exchange being multiple. It should be noted that although being a strong electron donor, vanadocene must at the same time exhibit acceptor properties since this molecule includes an empty (a_{1g}) and a partially empty (e_{2g}) anti-bonding orbital [143]. This seems to provide the right conditions for oxidative addition of the alkane molecule.

A study has been made into the photoinduced insertion of Cp_2W into the methyl C—H bond of n-xylene and mesitylene [123].

$$Cp_2WH_2 \xrightarrow[(CH_3)_3C_6H_3]{h\nu} Cp_2W[CH_2(3,5\text{-}Me_2C_6H_3)]_2$$

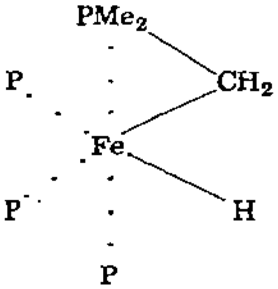
This field seems to be particularly promising in view of the data on biological oxidation of paraffins. As is known, enzymes such as monooxygenase catalyze oxidation of paraffin hydrocarbons, yielding intermediate products such as primary alcohols. In the case of higher hydrocarbons, the important role in this process is played by cytochrome P-450, and the ferric ion of the cytochrome molecule seems to activate O_2 rather than the alkane molecule, while RH enters into a reaction with the metal-activated oxygen molecule (in most cases, so called oxenoid mechanism [110] is assumed).

There are indications, however, that the enzymes catalyzing oxidation of methane and its nearest homologs act by an entirely different mechanism, probably involving alkane activation by a metal ion [109]. For example, the strong isotopic effect in oxidation of methane by bacteria, $k_{CH_4}/k_{CD_4} = 12.5$ (30°C) indicates that at the limiting stage of the reaction the C—H bond is cleaved. The relative reactivity of hydrocarbons is $CH_4 : C_2H_6 : C_3H_8 = 100 : 8 : 1$. In the case of a deficiency in O_2, the methane-bacteria system yields H_2 (D_2 and HD from CD_4) [111], which points directly to activation of the methane molecule. The bacterial methane oxidizing systems are devoid of cytochrome P-450 although, iron, cobalt and copper have been found in the enzyme system. The enzyme activating the methane seems to include one or more of these metals. Considering that cobalt acts effectively on the growth of methane bacteria and is found in the B_{12} coenzyme, one can assume that B_{12} systems participate in the activation of methane. The bacteria enzyme systems oxidize methane in the same way as monooxygenase, and hence, the anticipated oxidation cycle can be represented as follows (M — metal enzyme)



During the cycle, the H atom may be stored in the 5'-deoxyadenosyl group. The insertion of O_2 into a Co—R bond is well known [112]. The activation of methane may, in principle, proceed similarly to enzymatic insertion of coenzyme B_{12} into an inactivated C—H bond, the radical mechanism of this process having been established [113—115] and corroborated by model studies [116,117]. Activation of methane according to this mechanism is consistent with the isotopic effect ($k_H/k_D \approx 13$),i.e. close to that in bacterial oxidation of methane; at the same time, a mechanism, involving oxidation by Co(III) seems unlikely because the latter reaction has a very low isotope effect (see above).

If the active species in reactions catalyzed by coenzyme B_{12} is a derivative of Co(I) [118], then the mechanism of these reactions and activation of methane may be similar to that of alkane activation by other d^8 metal complexes including, as already mentioned, a Co(I) complex. On the other hand, copper and iron may also serve as active centers. Chlorination of methane with a melt of CuCl—$CuCl_2$—KCl at 310—400°C is described in ref. 119. The rate of chlorine formation under these conditions is too low to account for the rate of chlorination of methane, and Kunugi et al. [119] believe that the rate determining stage is direct interaction of methane with cupric chloride. Recently, intramolecular reactions proceeding under rather mild conditions through an aliphatic C—H bond of a ligand linked to Fe(O), with formation of the corresponding "alkyl" hydrides of Fe(II), have become known [124, 140].



More studies are expected shortly in this fascinating field, which will supply more coherent data on the mechanism of biological activation of methane and its homologs and provide effective models for this process, thereby contributing to the low-temperature chemistry of alkanes.

G. CONCLUSION

The results presented in this review show that a new field of homogeneous catalysis came into being in recent years and is rapidly developing — activation and catalytic reactions of saturated hydrocarbons. This field is still at the beginning of its development and if it is compared with activation of molecular hydrogen, its present period is comparable to that from 1930—1960 when relatively simple compounds of transition metals were studied in reactions with dihydrogen. More complex catalysts for activation of H_2 have been developed since.

It is hoped that homogeneous activation of alkanes will follow this trend. One can expect substantial broadening of the range of metals and ligands, as well as an increase in the number of new homogeneous catalytic reactions involving alkanes. Of particular interest is the introduction into these reactions of new complexes of non-platinum metals, especially metals of the 1st and 2nd transition periods. Alkyl derivatives of these metals feature higher reactivity than those of the platinum group. In particular, they are capable of inserting O_2 into an M—R bond. This is essential insofar as activation of alkanes can be used in a number of significant processes.

At the same time, it should be pointed out that homogeneous catalytic reactions of saturated hydrocarbons are determined not only by activation of RH with which this paper is primarily concerned. In some cases, activation of reagents interacting with the hydrocarbons may be sufficient. Such cases include, for example, the well known radical-chain reactions of oxidation of hydrocarbons, as well as biological oxidation of higher alkanes where the reaction is extremely selective and seems to involve no radicals. The development of effective chemical models for enzymic oxidation of this type is another very important problem.

Thus, parallel development of several trends is expected in the future; these should provide radically new alkane processes, some of which will undoubtedly be of practical value.

REFERENCES

1 J. Halpern, Advan. Catal., 9 (1959) 301.
2 J. Smidt, W. Hafner, R. Jira, R. Sieber, J. Sedlmeier and A. Sabel, Angew. Chem. Int. Ed., 1 (1962) 80;
I.I. Moiseev, Kompleksoobrazovanie v katalize (Complexing in Catalysis), Nauka, Moscow, 1968, p. 38.
3 J.L. Garnett, Catal. Rev., 5 (1971) 229.
4 C.W. Bird, Chem. Rev., 62 (1962) 283.
5 G. Henrici-Olive and S. Olive, Angew. Chem., 86 (1974) 1;
A.V. Savitsky and V.I. Nelyubin, Usp. Khim., 44 (1975) 214.
6 A.E. Shilov, Usp. Khim., 43 (1974) 863.
7 J. Halpern, Discuss. Faraday Soc., 46 (1968) 7.
8 P.J. Davidson, M.F. Lappert and R. Pearce, Accounts Chem. Res., 7 (1974) 209.
9 N.M. Emanuel, E.T. Denisov and Z.K. Maizus, Tsepnye reaktsii okisleniya uglevodorodov v zhidkoi phaze (Chain Reactions of Hydrocarbon Oxidation in Liquid Phase), Nauka, Moscow, 1965; R.A. Sheldon and J.K. Kochi, Oxid. Comb. Rev., 5 (1973) 135.
10 A.I. Shatenshtein, Usp. Khim., 24 (1955) 377.
11 G.A. Olah, Angew. Chem. Int. Ed., 12 (1973) 173.
12 F. Asinger, Paraffins, Chemistry and Technology, Pergamon Press, Oxford, 1968.
13 D. Kram, Osnovy khimii karbanionov (Fundamentals of Carbanion Chemistry), Mir, Moscow, 1967.
14 N.F. Goldshleger, M.B. Tyabin, A.E. Shilov and A.A. Shteinman, Zh. Fiz. Khim., 43 (1969) 2174.

15 A.E. Shilov and A.A. Shteinman in F. Marta and D. Kallo (Eds.), Mechanisms of Hydrocarbon Reactions, A. Symposium, Academiai Kiado, Budapest, 1975, p. 479; Kinet. Katal., 14 (1973) 149; E.S. Rudakov, A.E. Shilov and A.A. Shteinman, Second Soviet—French Catalysis Seminar, Abstracts, Kiev, 1974, p. 141.
16 K. Davis, J.L. Garnett, K. Hoa, P.S. Kenyon and M. Long in J.W. Hightower (ed.), Proc. Vth. Internat. Congress Catalysis, Palm Beach, Florida, North-Holland, Amsterdam, 1973, p. 1973.
17 G.W. Parshall, Accounts Chem. Res., 8 (1975) 113; Specialist Periodical Report on Catalysis, Am. Chem. Soc. (1976).
18 D.E. Webster in Advances in Organometal. Chem., vol. 15, (1977).
19 R.J. Hodges, D.E. Webster and P.B. Wells, Chem. Commun., (1971) 462.
20 I.J. Harvie and F.J. McQuillin, Chem. Commun., (1974) 806.
21 G.W. Littlecott and F.J. McQuillin, Tetrahedron Lett., (1973) 5013.
22 J.L. Garnett and R.S. Kenyon, Aus. J. Chem., 27 (1974) 1023, 1033; Chem. Commun., (1970) 698; (1971) 1227.
23 L.F. Repka and A.A. Shteinman, Kinet. Katal., 15 (1974) 805.
24 R.J. Hodges, D.E. Webster and P.B. Wells, J. Chem. Soc. Dalton, (1972) 2577.
25 A.I. Mustafin and A.A. Shteinman, Kinet. Katal., 16 (1975) 953.
26 C. Masters, Chem. Commun., (1972) 1258; P.A. Kramer and C. Masters, J. Chem. Soc. Dalton, (1975) 849.
27 C. Masters, Chem. Commun., (1973) 191; A.A. Kiffen, C. Masters and L. Raynand, J. Chem. Soc. Dalton (1975) 853.
28 J.L. Garnett and R.J. Hodges, J. Am. Chem. Soc., 89 (1967) 4546.
29 J.L. Garnett in Mechanism and Kinetics of Complex Catalytic Reactions, Nauka, Moscow, 1970.
30 R.J. Hodges and J.L. Garnett, J. Catal., 13 (1969) 83.
31 C. Bond, Chem. Soc. Ann. Rep., 63 (1967) 27.
32 A.S. Berenblyum and I.I. Moiseev, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 474.
33 J.L. Garnett, M.A. Long, A.B. McLaren and K.B. Peterson, Chem. Commun., (1973) 749.
34 J.L. Garnett, M.A. Long and K.B. Peterson, Aust. J. Chem., 27 (1974) 1823.
35 M.R. Blake, J.L. Garnett, I.K. Gregor, W. Hannan, K. Hoa and M.A. Long, Chem. Commun., (1975) 930.
36 K. Jonas and G. Wilke, Angew. Chem. Int. Ed., 8 (1969) 519.
37 J. Chatt and R.G. Hayter, J. Chem. Soc., (1963) 6017.
38 V.D. Bianco, S. Doronzo and M. Aresta, J. Organometal. Chem. 42 (1972) C63.
39 A. Nakamura and S. Otsuka, J. Am. Chem. Soc., 94 (1972) 1886.
40 L.J. Green and P.J. Knowles, J. Chem. Soc. A, (1971) 1508.
41 E.W. Ainscough and S.D. Robinson, Chem. Commun., (1971) 130.
42 M.A. Bennett and D.L. Milner, J. Am. Chem. Soc., 91 (1969) 6983.
43 D.R. Fahey, J. Organometal. Chem., 27 (1971) 283.
44 G.W. Parshall, W.H. Knoth and R.A. Schunn, J. Am. Chem. Soc., 91 (1969) 4990.
45 J. Chatt and J.M. Davidson, J. Chem. Soc., (1965) 843.
46 F.A. Cotton, D.L. Hunter and B.A. Frenz, Inorg. Chim. Acta, 15 (1975) 155.
47 R. Mason and A.D.C. Towl, J. Chem. Soc. (A) (1970) 1601.
48 S. Komiya and A. Yamamoto, Chem. Lett., 475 (1976); S. Komiya, T. Ito, M. Cowie, A. Yamamoto and J.A. Ibers, J. Am. Chem. Soc., 98 (1976) 3874.
49 J.B. Keister and J.R. Shapley, J. Organometal. Chem., 85 (1975) C29.
50 J.B. Keister and J.R. Shapley, J. Am. Chem. Soc., 98 (1976) 1056.
51 K.G. Powell and F.J. McQuillin, Tetrahedron Lett., (1971) 3313.
52 H. Hogeveen and B.J. Nusse, Tetrahedron Lett., (1973) 3667.
53 K.B. Wiberg and K.C. Bishop III, Tetrahedron Lett., (1973) 2727.
54 M. Lavanda, R. Ros, M. Graziani and U. Belluco, J. Organometal. Chem. 65 (1974) 407.

55 P. Chum and J.A. Roth, J. Catal., 39 (1975) 198.
56 J. Halpern, Proc. XIV Intern. Conf. Coord. Chem., Toronto, Canada (1972) p. 698.
57 M.B. Tyabin, A.E. Shilov and A.A. Shteinman, Dokl. Akad. Nauk, SSSR., 198 (1971) 380.
58 R.J. Hodges, D.E. Webster and P.B. Wells, J. Chem. Soc. A, (1971) 3230.
59 R.J. Hodges, D.E. Webster and P.B. Wells, J. Chem. Soc. Dalton, (1972) 2571.
60 A.C. Skapski and F.A. Stephens, Chem. Commun. (1969) 1008.
61 J. Chatt, R.S. Coffey, A. Gough and D.T. Thompson, J. Chem. Soc. A, (1968) 190.
62 M.A. Bennett and R. Charles, J. Am. Chem. Soc., 94 (1972) 666.
63 A.A. Shteinman, Kinet. Katal., 15 (1974) 831.
64 N.F. Goldshleger and A.A. Shteinman, React. Kinet. Catal. Lett., 6 (1977) 43.
65 C. Langford and H.B. Gray, Protsessy zameshcheniya ligandov (Process of Substitution of Ligands), Mir, Moscow, 1969, p. 49.
66 Ya. D. Fridman, Koord. Khim., 1 (1975) 1155.
67 D.R. Armstrong, R. Fortune and P.C. Perkins, Inorg. Chim. Acta, 9 (1974) 9.
68 D.M. Adams, J. Chatt and B.L. Shaw, J. Chem. Soc., (1960) 2047.
69 J. Chatt and B.L. Shaw, J. Chem. Soc., (1962) 5075.
70 L.I. Elding, Acta Chem. Scand., 24 (1960) 1527.
71 P.B. Chock and J. Halpern, J. Am. Chem. Soc., 88 (1966) 3511.
72 J.R. Sanders, D.E. Webster and P.B. Wells, J. Chem. Soc. Dalton, (1975) 1191.
73 N.F. Goldshleger, V.V. Lavrushko, A.P. Khrushch and A.A. Shteinman, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 2174.
74 S.R. Jones and J.M. Mellor, Chem. Commun. (1976) 385.
75 N.F. Goldshleger, I.I. Moiseev, M.L. Khidekel' and A.A. Shteinman, Dokl. Akad. Nauk SSSR, 198 (1971) 380.
76 E.S. Rudakov and A.A. Shteinman, Kinet. Katal. 14 (1973) 1346.
77 A.I. Mustafin, E.S. Rudakov, A.E. Shilov and A.A. Shteinman, Kinet. Katal., 16 (1975) 1173.
78 A.I. Mustafin and A.A. Shteinman, React. Kinet. Catal. Lett., 6 (1977) 153.
79 R.C. Dobson, D.M. Hayes and R. Hoffman, J. Am. Chem. Soc., 93 (1971) 6188.
80 N. Bodor, M.J.S. Dewar and J.S. Wasson, J. Am. Chem. Soc,. 94 (1972) 9095.
81 D.S. Martin, M.A. Tucker and A.J. Kassman, Inorg. Chem., 5 (1966) 1298.
82 A.E. Shilov and A.A. Shteinman, Kinet. Katal., 14 (1973) 149.
83 R.A. Sheldon and J.K. Kochi, Oxidat. Combust. Rev., 5 (1973) 135.
84 N.F. Goldshleger, V.V. Yes'kova, A.E. Shilov and A.A. Shteinman, Fiz. Khim., 46 (1972) 1353.
85 V.V. Yes'kova, A.E. Shilov and A.A. Shteinman, Kinet. Katal. 13 (1972) 534.
86 J.L. Garnett and J.C. West, Syn. Inorg. Metal-Org. Chem., 2 (1972) 25; Aust. J. Chem. 27 (1974) 129.
87 R.J. Hodges and J.L. Garnett, J. Phys. Chem. 72 (1968) 1673.
88 V.P. Tretyakov, V.A. Zhugastarova and R.I. Rudakova, React. Kinet. Catal. Lett., 1 (1974) 203.
89 V.V. Lavrushko, A.E. Shilov and A.A. Shteinman, Kinet. Katal., 16 (1975) 1479.
90 V.P. Tretyakov, E.S. Rudakov, A.A. Galenin and R.I. Rudakova, Dokl. Akad. Nauk SSSR, 125 (1975) 583.
91 V.P. Tretyakov and L.I. Arzamaskova, Kinet. Katal., 17 (1976) 119.
92 V.P. Tretyakov, E.S. Rudakov, R.I. Rudakova, A.A. Galenin and G.P. Zimtseva, Zh. Fiz. Khim., 51 (1977) 1026.
93 E.S. Rudakov, V.V. Zamashchikov, N.P. Belyaeva and R.I. Rudakova, Zh. Fiz. Khim., 47 (1973) 2732.
94 N.F. Goldshleger, M.L. Khidekel', A.E. Shilov and A.A. Shteinman, Kinet. Katal., 15 (1974) 261.

95 V.P. Tretyakov, L.N. Arzamaskova and Yu. I. Yermakov, Kinet. Katal., 15 (1974) 638.
96 L.N. Arzamaskova, Yu.I. Yermakov, V.A. Likholobov and V.P. Tretyakov, React. Kinet. Catal. Lett., 3 (1975) 183.
97 K.B. Wiberg and R. Eizenthal, Tetrahedron, 20 (1964) 1151.
98 C. Kemball, Advan. Catal., 11 (1959) 223.
99 B.A. Kazansky and A.L. Liberman, Neftekhimiya, 12 (1972) 147.
100 R.L. Burwell, Catal. Rev., 7 (1972) 25.
101 N.R. Avery, J. Catal. 24 (1972) 92.
102 D.W. McKee, J. Phys. Chem., 70 (1966) 525.
103 J.G. Atkinson, N.O. Luke and R.S. Stuart, Chem. Commun., (1969) 283.
104 T.A. Cooper and W.A. Waters, J. Chem. Soc. B, (1967) 687.
105 R. Tang and J.K. Kochi, J. Inorg. Chem., 35 (1973) 3845.
106 A. Onopchenko and J.G.D. Schulz, J. Org. Chem., 38 (1973) 3729; 40 (1975) 3338.
107 A. Onopchenko and J.G.D. Schulz, J. Org. Chem., 38 (1973) 909.
108 J. Hanotier, Ph. Camerman, M. Hanotier-Bridoux and P. de Radzitsky, J. Chem. Soc. Perkin II, (1972) 2247.
109 V.S. Belova, R.I. Gvozdev, Yu.R. Malashenko, A.P. Sadkov and V.V. Yuzchenko, Biokhimiya, 41 (1976) 1903.
110 G.A. Hamilton, J. Am. Chem. Soc., 86 (1964) 3391.
111 E. Zajic, Developments in Industrial Microbiology, 6 (1965) 16.
112 F.R. Jensen and R.C. Kiskis, J. Organometal. Chem., 49 (1973) C46.
113 B.M. Babior, Accounts Chem. Res., 8 (1975) 376.
114 D. Dodd and M.D. Johnson, J. Organometal. Chem., 52 (1973)
115 R.G. Eagar, W.W. Bachovchin and J.H. Richards, Biochemistry, 14 (1975) 5523.
116 P. Dowd, M. Shapiro and K. King, J. Am. Chem. Soc., 97 (1975) 4754.
117 R. Breslow and P.L. Khanna, J. Am. Chem. Soc., 98 (1976) 1297.
118 G.N. Schrauzer, R.N. Katz, J.H. Grabe and T.M. Vichrag, Angew. Chem. Int. Ed., 15 (1976) 170.
119 T. Kunugi, H. Tominaga, A. Sawanobosi and M. Nushi, Kogyo Kagaku Zasshi, 72 (1969) 2385.
120 E.A. Grigorian, F.S. D'yachkovsky and I.R. Mullagaliev, Dokl. Akad. Nauk SSSR, 224 (1975) 859.
121 F.S. D'yachkovsky and N.E. Khrushch, Zh. Obshch. Khim., 41 (1971) 1779.
122 V.B. Shur, E.G. Berkovich, E.I. Mysov and M.E. Vol'pin, Izv. Akad. Nauk, Ser. Khim., (1975) 1908.
123 K. Elmitt, M.L.H. Green, R.A. Forder, I. Jefferson and K. Prout, Chem. Commun., (1974) 747.
124 S.D. Ittel, C.A. Tolman, A.D. English and J.P. Jesson, J. Am. Chem. Soc., 98 (1976) 6073.
125 R. Ros, R. Bataillard and R. Roulet, J. Organometal. Chem. 118 (1976) C53.
126 A.J. Chency, B.E. Mann, B.L. Shaw and R.M. Slade, Chem. Commun., (1970) 1176; C. Masters, W.S. McDonald, G. Raper and B.L. Shaw, Chem. Commun., (1971) 210.
127 D.F. Gill and B.L. Shaw, Chem. Commun. (1972) 65.
128 D.F. Gill, B.E. Mann and B.L. Shaw, J. Chem. Soc., Dalton (1973) 270.
129 A.J. Cheney, B.E. Mann, B.L. Shaw and R.M. Slade, J. Chem. Soc. A, (1971) 3833.
130 R. Mason and M. Textor, Chem. Commun., (1976) 292.
131 B.L. Shaw, J. Am. Chem. Soc., 97 (1975) 3856.
132 E.S. Rudakov, Dokl. Akad. Nauk SSSR, 229 (1976) 149.
133 D.M. Roe, P.M. Bailey, K. Moseley and P.M. Maitlis, Chem. Commun., (1972) 1273.
134 S. Trofimenko, J. Am. Chem. Soc., 89 (1967) 6288; 90 (1968) 4754; Inorg. Chem. 9 (1970) 2493.
135 F.A. Cotton, T. LaCour and A.G. Stanislowski, J. Am. Chem. Soc., 96 (1974) 754.
136 F.A. Cotton and V.W. Day, Chem. Commun., (1974) 415.

137 L. Blackett, V. Gold and D.M.E. Reuben, J. Chem. Soc. Perkin II, (1974) 1869.
138 E.S. Rudakov, V.V. Zamashchikov and A.I. Lucik, Teor. Eksp. Khim., 12 (1976) 474.
139 P. van Pelt and H.M. Buck, J. Am. Chem. Soc. 98 (1976) 5864.
140 J.W. Rathke and E.L. Meutterties, J. Am. Chem. Soc., 97 (1975) 3272; H.H. Karsch, H.-F. Klein and H. Schmidbauer, Angew. Chem. Int. Ed., 14 (1975) 637.
141 E.S. Rudakov, V.V. Zamashchikov, A.I. Lucik and G.P. Zimtseva, Zh. Fiz. Khim., 49 (1975) 2729.
142 E.A. Grigorian and F.S. D'yachkovskii, Abstracts Internat. Congr. Coord. Chem., Hamburg (1976).
143 J.W. Lauher and R. Hoffmann, J. Am. Chem. Soc., 98 (1976) 1729.
144 S.W. Benson, Adv. Photochem., 2 (1964) 1.