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Activation and Catalytic Reactions of Alkanes in Solutions of Metal Complexes

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The reactions of saturated hydrocarbons and compounds modelling them with metal complexes, leading to the cleavage of the C-H and C-C bonds, are examined. In particular, processes which result in the formation of organometallic derivatives are described and the mechanism of the oxidation of alkanes by enzymes and their chemical models is discussed. The bibliography includes 355 references.

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I. INTRODUCTION

The relatively low reactivity of saturated hydrocarbons is due to the absence of π and n electrons from their molecules and the low polarity of the C–H and C–C σ-bonds. At the same time, since paraffinic hydrocarbons (the store of which, especially methane, in nature is still large) are one of the types of chemical organic raw materials, the problem of their conversion into functional derivatives (alcohols, ketones, and acids) and also of the synthesis of olefins and aromatic hydrocarbons from alkanes is currently of very great importance. The hydrocracking and isomerisation reactions of paraffins, which make it possible to obtain valuable forms of motor fuel, are also of considerable practical importance. The main industrial processes in which alkanes are used as raw materials occur at high temperatures (above 150–200 °C), frequently in the presence of heterogeneous catalysts (for example, dehydrogenation, aromatisation, the reaction of methane with water which affords the CO + H_2 mixture, the cracking of methane to acetylene and hydrogen, nitration, fluorination by CoF_3, etc.). The radical-chain processes (photochemical chlorination by Cl_2, oxidation by molecular oxygen initiated by light or radicals, sulphochlorination, etc.), which are carried out at low temperatures, constitute a special field. However, the selectivity of these reactions is low and complex mixtures of products are usually formed. Finally, the ability of certain micro-organisms and higher animal cells to oxidise alkanes by oxygen at the usual temperature has long been known. Biological oxidation is usually selective. For example, certain micro-organisms oxidise only the terminal methyl group of hydrocarbons, converting it initially into an alcohol (ω-hydroxylation).

New homogeneous reactions of alkanes, occurring in solution or in the gas phase, have been discovered recently.[1] Thus the reactions of saturated hydrocarbons with electrophiles in solutions of strong acids or superacids have been discovered.[1,2] The proton, the attack of which on the alkane gives the alkonium ion $C_nH_{2n+3}^+$, which subsequently decomposes with cleavage of the C–H and C–C bonds, functions as the electrophilic species in solutions of the acids FSO_3H–SbF_5 or HF–SbF_5. The electrophilic substitution of hydrogen in alkanes by the nitro-group takes place under the influence of $NO_2^+PF_6^-$ in dichloromethane at room temperature, while the reaction of an alkane with Cl_2 in SbF_2–SO_2ClF takes place even at −78 °C. Solutions of fluoranil in HF–HF–SbF_5 oxidise methane, propane, and n-pentane.[3] The dissolution of H_2O_2 or O_3 in FSO_3H–SbF_5–SO_2ClF generates respectively the $H_3O_2^+$ and HO_3^+ species, which attack alkane molecules electrophilically resulting in the formation of various oxygen-containing derivatives. Like ozone, iodoxybenzene $PhIO_2$ oxidises aromatic alkyl-substituted hydrocarbons.[4] In reactions with electrophiles, the reactivity of the bonds in branched alkanes usually diminishes in the sequence 3° > C–C > 2° > 1° (where 1°, 2°, and 3° denote respectively the primary, secondary, and tertiary C–H bonds). In the reaction with $H_3O_2^+$, the reactivity varies in the sequence[2] 3° > 2° > 1° > C–C. An analogous behaviour has been observed also in the interaction of branched alkanes with radical and carbene species.[1] Thus hydroxylation of alkanes by peracids (for example, trifluoroperacetic)[1,5] also proceeds with the "normal" selectivity 3° > 2° > 1°, while the reaction with *cis*- or *trans*-1,2-dimethylcyclohexane proceeds with complete retention of the configuration. The reaction takes place via the "oxenoid" mechanism—with insertion of the oxygen atom in the C–H bond without the formation of intermediate free-radical or ionic species. Thus in all the reactions enumerated the reactants interacting with alkanes are to some extent electrophilic. The reaction of an alkane (methane, ethane, propane) with the phenylium ion $C_6H_5^+$ in the gas phase has been described recently.[6] The product of the insertion of the phenylium cation in the R–H bond of the alkane, resembling the familiar Wheland complex, which is converted into C_6H_5R after transferring H^+ to a base, is formed as an intermediate. The interaction of 1,10-B_{10}.$H_8(N_2)$ with a mixture of CO and CH_4 leads to the formation of $MeB_{10}H_7(CO)_2$ and $Me_2B_{10}H_6(CO)_2$, but the reaction mechanism has not been established.[7]

The first reaction of an alkane with a metal complex in which an organometallic compound, i.e. a derivative containing a metal–carbon bond,[9] is formed as an intermediate was discovered[8] in 1969. This reaction is responsible for the H–D exchange in methane, ethane, and higher alkanes in the C_nH_{2n+2}–D_2O–$PtCl_4^{2-}$ system. The ability of alkanes to be oxidised in the C_nH_{2n+2}–H_2O–$PtCl_4^{2-}$–$PtCl_6^{2-}$ system, also with the intermediate formation of organometallic σ-complex of platinum, was discovered somewhat later.[10] The characteristic features and mechanisms of these reactions have been studied in detail. Section II of the present review review is devoted to such reactions. New reactions in which the alkane molecule is activated in solution with a transition metal complex were discovered subsequently. The number of such reactions continues to increase and an increasing

number of laboratories in various countries are becoming involved in the study of this rapidly developing field. Section III presents a survey of studies on this field carried out during the last decade. Major advances have been achieved recently in the understanding of the mechanism of the bioiogical oxidation of alkanes. The studies on the chemical models of enzymes catalysing the oxidation of alkanes are developing vigorously. It is becoming clear that the active centres interacting with the C–H bond in the alkane include high-valence derivatives of a metal (usually iron), Reactions involving the direct oxidation of alkanes by high-valence metal compounds have been known for many years.[11,12] Section IV deals with the enzymic oxidation of alkanes and the oxidation of the latter by high-valence metal complexes, associated with the enzymic process. The review covers studies published mainly in the 1980's; earlier investigations were described in detail in other reviews.[13–18]

II. REACTIONS OF ALKANES WITH PLATINUM(II) AND PLATINUM(IV) COMPLEXES

The closest analogue of the activation of alkanes involving the dissociation of weakly polar strong C–H or C–C bonds is the activation of the H_2 molecule. Indeed the H_2 and CH_4 molecules exhibit a definite similarity, because they contain only σ-bonds (H–H or C–H), which have virtually identical homolytic dissociation energies D(R–H) = 103–104 kcal mol^{-1} and are characterised by a high ionisation potential and a low electron affinity. At the end of the 1960's considerable advances were made in the solution of the problem of the activation of H_2 by metal complexes (see, for example, James[19]). The key stage of such activation is the oxidative addition of hydrogen in accordance with the scheme

$$M^n + H_2 \rightarrow H—M^{n+2}—H$$

On the basis of the similarity of the properties of H_2 and alkanes, it might have been supposed that the latter are also capable of being activated by metal complexes undergoing the oxidative addition reaction with the latter. As already mentioned, the first such system is represented by the platinum(II) chloride complex.[8] It was subsequently found that the platinum(IV) complex is capable of oxidising alkanes. Analogous reactions are known also for aromatic compounds.

1. Characteristic Features and Kinetics of the Reactions

(a) Deuterium Exchange in the Presence of Platinum(II) Complexes

When methane or another alkane is heated to ~100 °C in a sealed tube containing a solution of $PtCl_4^{2-}$ in the D_2O–CD_3.COOD mixture, the hydrogen atoms in the alkane are replaced by deuterium.[1,8,13–17] The process also occurs in water but in the presence of acetic acid the rate of reaction increases by a factor of 30 (when account is taken of the solubility of alkanes in CH_3COOH). The reaction is of first order with respect to the hydrocarbon. The rate constant k for the deuterium exchange involving cyclohexane in the presence of various platinum(II) complexes decreases in the following sequence for $[C_6H_{12}]$ = 0.15 M, $[HClO_4]$ = 0.1 M, [Pt(II)] = 0.02 M, and 100 °C: K_2PtCl_4 (2.78), $K_2Pt(NO_2)Cl_3$ (0.366), $KPt(NH_3)Cl_3$ (0.777), $KPt(DMSO)Cl_3$ (0.056), KPt.(py)Cl_3 (0.025). The values of 10^3k (litre mol^{-1} s^{-1}) are given in brackets. When the anions X^- are added to the system, new complexes catalysing the H–D exchange in cyclohexane are formed via the reaction

$$S_2PtCl_2 + 2X^- \rightleftarrows X_2PtCl_2^{2-} + 2S\,.$$

The following rate constants for this reaction have been obtained (10^3k, litre mol^{-1} s^{-1}):[13] 6.30 (in the absence of X^-); 6.28 (in the presence of CF_3COO^-); 6.26 (F^-); 6.06 (SO_4^{2-}); 4.10 (Cl^-); 2.47 (Br^-); 0.394 (I^-); 0.115 (NO_2^-); 0.106 (CN^-). Ultimately this led to the establishment of the sequence based on the influence of the ligands in the platinum(II) complex on the rate of H–D exchange:[13]

$$PPh_3 \simeq py < DMSO < CN^- < NO_2^- < NH_3 < I^- < Br^- < Cl^- < F^- \simeq H_2O, \quad (1)$$

This sequence is the opposite to that based on the *trans*-effect of the corresponding ligands. The rate constants for the H–D exchange reaction catalysed by platinum(II) are described satisfactorily by the two-parameter equation

$$\lg(k/k_0) = \rho^*\sigma^* + n\psi\,, \quad (2)$$

where σ* is the Taft constant taking into account the polar influence, ψ the parameter characterising the conjugation of the substituent in the α-position relative to the H atom with the radical reaction centre, and n the number of substituents. The value $\rho^* = -1.4$ indicates weak electron-accepting properties of the platinum(II) complex, while the presence of the resonance term may indicate that the C–H bond is dissociated homolytically. A linear correlation has also been observed between the logarithm of the rate of H–D exchange in hydrocarbons and their ionisation potentials.[13]

Unbranched alkanes are the most reactive in the H–D exchange reaction. On the other hand, in the exchange of branched hydrocarbons the "reverse" reactivity sequence is observed, i.e. 1° > 2° > 3°. Evidently this is associated with the strong influence of steric factors. The low rate of exchange in the methyl and methylene groups adjoining the t-butyl group in 2,2-dimethylpropane and 2,2-dimethylbutane can be explained in the same way. A characteristic feature of the reaction is multiple exchange—the alkane molecule can exchange several H atoms for D without leaving the coordination sphere of the metal complex. The multiple exchange parameter M for different alkanes varies in the range 1.4–1.7 and increases only slightly with decrease of the reaction temperature.

(b) Oxidation by Platinum(IV) Complexes

When a solution of H_2PtCl_6 and Na_2PtCl_4 in H_2O (or in aqueous CF_3COOH) is heated in the presence of alkanes (100–120 °C, 0.25–5 h), a mixture of isomeric alkyl chlorides, alcohols, trifluoroacetates, and ketones is formed, while platinum(IV) is reduced to platinum(II).[1,10,13–17] The kinetics of the reaction with participation of methane have been described in detail.[20] When cyclic alkanes (cyclohexane and decalin) are oxidised, aromatic hydrocarbons (benzene, naphthalene) are obtained. The π-complex of hex-1-ene with platinum(II) has been isolated[21] in 1% yield from the mixture of products formed in the reaction of H_2PtCl_6 with hexane in the CF_3COOH–H_2O mixture. Acetic acid is oxidised by a mixture of Pt(IV) + Pt(II) chloride complexes to chloroacetic acid. The reaction of $PtCl_6^{2-}$ with saturated hydrocarbons is catalysed by added $PtCl_4^{2-}$. In the absence of such additives, an induction period is observed, its duration decreasing with increase of the amount of added $PtCl_4^{2-}$. In the presence of heteropoly-acids, the platinum(II) formed in the reaction can be reoxidised by air and the oxidation of CH_4 to CH_3Cl (CH_3OH is then also oxidised) becomes catalytic.[22] Another catalytic system for the chlorination of alkanes contains K_2PtCl_4, H_2PtCl_6, and $HgSO_4$ immobilised on silica gel.[23]

As in deuterium exchange, the dependence of the rate of oxidation of alkanes (with a constant k_n) in the $PtCl_6^{2-}$ + $[PtCl_{4-n}(H_2O)_n]^{n-2}$ system passes through a maximum with increase of n (at $n = 2$), but in the case of isobutane k_2 = 3.8 litre mol^{-1} s^{-1} differs insignificantly from k_3 and espepecially from k_1 (1.9 and 3.7 litre mol^{-1} s^{-1} respectively). The complexes with $n = 0$ and 4 are almost inactive in the reaction.[1] When the H–D exchange and oxidation reactions of cyclohexane in CF_3COOH catalysed by Pt(II) + Pt(IV) were compared, the following features were discovered:[24] the sum of the rates of the oxidation and H–D exchange reactions is independent of the concentrations of CF_3COOH and Pt(IV), but with increase of [Pt(IV)] keeping [CF_3COOH] = const., the rate of oxidation rises, while with increase of [CF_3COOH] for [Pt(IV)] = const. the rate of H–D exchange increases. These data show that the two processes have a common initial stage.

The oxidation reaction of alkanes containing between 1 and 4 carbon atoms in an aqueous medium is of first order with respect to the hydrocarbon and has a fractional order (0.77) with respect to platinum(II).[14] The activation energy (~20 kcal mol^{-1}) for the oxidation reactions of ethane, propane, or butane is approximately equal to the activation energy for the H–D exchange involving ethane (18.6 kcal mol^{-1}). The chlorination of acetic acid proved to be most convenient for kinetic study. The order of this reaction is unity with respect to platinum(II) and CH_3COOH. At low concentrations of the added Cl^- ions the rate of reaction is proportional to $[Cl^-]^{-1}_{add}$ while at high concentrations it is proportional to $[Cl^-]^{2}_{add}$. The order of the reaction with respect to platinum(IV) varies from 0 to 1. The role of steric factors is strongly manifested in the reaction involving the oxidation of alkanes by the $PtCl_6^{2-}$ + $PtCl_4^{2-}$ system.[1,25] As for the system with [H_2PtCl_6] = 0.02 and [K_2PtCl_4] = 0.05 M in water at 98 °C the oxidation rate constants diminish on passing from normal to branched hydrocarbons; for n-butane and 2-methylpropane, they are respectively 11.5 and 8.2 s^{-1}, for n-pentane, 2-methylbutane, and 2,2-dimethylpropane they are 15.3, 11.2, and 1.0 s^{-1}, and for n-octane and 2,2,4-trimethylpentane the corresponding values are 15.4 and 3.6 s^{-1}. In the series of normal alkanes, the oxidation rate constant increases with increase of the number of carbon atoms atoms: methane (1.6) < ethane (6.6) < propane (9.9). For C_5–C_8 n-hydrocarbons, k is approximately the same (~16 s^{-1}). The latter factor can be accounted for if it is assumed that the chlorine atom substitutes mainly the hydrogen atoms in the 1- and 2-positions in the chain on oxidation by the Pt(IV) + Pt(II) system. In general the number of active (capable of substituting their hydrogen atoms by Cl) carbon atoms n_a in the alkane C_nH_{2n+2} is defined by the formula[25] $n_a = n - n_{tert} - 5n_{quat}$, where n_{tert} and n_{quat} are the numbers of ternary and quaternary carbon atoms in the molecule respectively.

It has been found recently that, when a solution of H_2PtCl_6 and n-hexane in CH_3COOH is irradiated by light ($\lambda > 300$ nm) or γ-quanta, a π-complex of hex-1-ene with platinum(II), isolated in the form of the pyridine adduct [$CH_3(CH_2)_3$. .$CH{=}CH_2$]$PtCl_2$py, is formed.[26–29] The yield of the π-complex in the γ-induced reaction reaches 17%. The photochemical reaction is of first order with respect to hexane.

2. Intermediate Organometallic Compounds

In earlier studies[1,13–17] it was postulated on the basis of the investigation of the kinetics of the reactions of alkanes with platinum complexes, and certain indirect evidence, that the interaction of alkanes with both platinum(II) and platinum(IV) leads to the intermediate formation of alkyl π-complexes of platinum. In recent years new indirect and direct evidence has been obtained for the involvement of these complexes in the process.

(a) The Stages in the H–D Exchange and Oxidation Reactions

The H–D exchange and oxidation reactions apparently begin with the attack by the reactive form of the platinum(II) complex on RH, which results in the formation of an alkylplatinum(II) σ-complex:

$$PtCl_4^{2-} \rightleftarrows PtCl_3^- + Cl^- , \quad (3)$$

$$PtCl_3^- \rightleftarrows PtCl_2 + Cl^- , \quad (4)$$

$$PtCl_2 + RH \rightleftarrows RPtCl + H^+ + Cl^- . \quad (5)$$

In the absence of platinum(IV), the alkyl σ-derivative undergoes electrophilic attack by the D^+ ion (for the cleavage of the M–C bond by electrophiles—see, for example, Kochi[30]):

$$RPtCl + D^+ + Cl^- \rightarrow RD + PtCl_2 . \quad (6)$$

On the other hand, if a platinum(IV) derivative is present in the system, it interacts with the platinum(II) σ-complex and converts it into an alkylplatinum(IV) σ-complex. The latter reacts with the nucleophile X (H_2O or Cl^-) and affords ROH or RCl:

$$RPt(II) + Pt(IV) \rightarrow RPt(IV) + Pt(II) , \quad (7)$$

$$RPt(IV) + X^- \rightarrow RX + Pt(II) . \quad (8)$$

At a temperature above 100 °C and a low platinum(IV) concentration the rate of reaction depends on [Pt(IV)] and on the acidity of the medium and stage (7) is apparently rate-limiting. The activation energy for this stage is low (~9 kcal mol^{-1}). At a temperature below 100 °C and for a low platinum(IV) concentration, the rate of the entire reaction is determined by the rate of stage (5). The activation energy for the reaction under the given conditions (~20 kcal mol^{-1} for C_2–C_4 alkanes) is naturally close to that for H–D exchange (18.6 kcal mol^{-1} for ethane).[14] Since the platinum(II) complex, used for the initial activation of RH, returns to the system in stage (7), the alkane oxidation reaction is catalytic with respect to platinum(II) and the platinum(IV) acts as an oxidant.

Evidence for the formation of intermediates or organometallic compounds in this process is presented below.

(b) Isolation of Aryl σ-Complexes and Their Properties

It is well known that transition metal complexes, in particular platinum complexes, are capable of cleaving the C–H bond intramolecularly with formation of cyclometallated compounds.[31,32] Compounds containing both sp^2-hybridised carbon atoms (aromatic rings) and groups with sp^3-hybridised carbon atoms (CH_2 and CH_3) are capable of entering into the cyclometallation reaction.[33–37] Calculation has shown[14] that the intramolecular metallation of the C–H bond should be 10^3–10^6 times faster than the intermolecular reaction.

In order to confirm the possibility of the formation of complexes with a C–Pt(IV) σ-bond in intermolecular reactions with $PtCl_6^{2-}$, use was made of aromatic compounds, since it was known that the reaction with benzene and other arenes gives rise to oxidation products (especially chlorobenzene) analogous to the alkane oxidation products and that aryl σ-complexes should be much more stable than the alkyl σ-complexes. It was found that heating of a solution of H_2PtCl_6 and an aromatic compound ArH in the CF_3COOH–H_2O mixture or in CH_3COOH leads to the formation of fairly stable

aryl σ-complexes of platinum(IV) in yields up to 95%, which can be isolated in the form of anionic adducts with ammonia after chromatography on silica gel containing NH_3:[38-42]

$$ArH + PtCl_6^{2-} \xrightarrow[2)\ SiO_2,\ NH_3]{1)\ CF_3COOH-H_2O} [\sigma\text{-}ArPtCl_4NH_3]NH_4 \quad . \qquad (9)$$

Complexes of naphthalene and *o*-nitrotoluene have been characterised by X-ray diffraction[38,43] and ^{195}Pt NMR spectra have been obtained for a number of complexes.[44] The kinetics of the accumulation of the complexes and of their decomposition, leading to the formation of ArAr, ArCl, and platinum(II), have been investigated.[42,45-48] The accumulation of the aryl σ-complex is accompanied by its *para–meta* isomerisation: if in the initial instant the substitution takes place mainly (to the extent of ~90%) in the *para*-position in toluene, then the statistical distribution $m:p = 2:1$ is gradually attained. The substituent does not enter the *ortho*-position for steric reasons. It has been established by the method of competing reactions[42,49] that the relative rates of reactions with participation of C_6H_5X decrease in the following sequence of X: OH (16), OCH_3 (8.5), CH_3 (3), C_2H_5 (2.7), OC_6H_5 (2.0), $CH(CH_3)_2$ (1.9), H (1.0), C_6H_5 (0.9), F (0.3), $COCH_3$ (0.1), COOH (0.09), Cl (0.08), NO_2 (0.04). The logarithms of these quantities are correlated with the Hammett constant σ and the Brown constant σ^+ (with the parameters $\rho = -3.0$ and $\rho^+ = -1.5$). On the basis of the data obtained, a mechanism has been proposed[42] for the reaction—electrophilic substitution in the aromatic ring.[48] In terms of its behaviour in the arene metallation reaction and also as regards the behaviour of the aryl σ-complexes formed in relation to nucleophiles (arenes, olefins),[50-53] platinum(IV) resembles palladium(II).[54] The gold(III) chloride complex apparently metallates arenes also via the electrophilic substitution mechanism.[55] Arenes interact with Na_2PtCl_4 on heating with a solution in $CF_3COOH-H_2O$ or CH_3COOH.[56] This apparently entails the formation of aryl σ-complexes of platinum(II) which are comparatively unstable but can be converted by treatment with H_2PtCl_6 into aryl σ-complexes of platinum(IV). Thus the platinum(II) chloride complex apparently behaves as an electrophile in the reaction with arenes. On the other hand, the reaction of arylplatinum(II) σ-complexes with $PtCl_6^{2-}$ can be regarded as a model of stage (7) in the oxidation of alkanes.

Reaction (9) can be induced not only by heating but also by light[26,28,48,57] or γ-irradiation.[27] The arenes C_6H_5X form the following series in terms of substituents X based on the variation of the relative rate of the photochemical reaction with $PtCl_6^{2-}$:[26] OH (8), OC_2H_5 (4.1), OCH_3 (4.0), OC_6H_5 (1.9), CH_3 (1.0). The logarithms of these quantities are correlated with the constants σ_n^+ ($\rho^+ = -1.5$). It has been suggested[48] that the radiation-induced reactions begin with electron transfer from the arene to platinum(IV) and then the Wheland complex is formed, as in the case of a thermal reaction.

All the reactions of arenes considered here apparently proceed by the electrophilic substitution mechanism postulating the delocalisation of the positive charge of the arene ring in the Wheland complex formed as an intermediate. Since such delocalisation is impossible for fully saturated hydrocarbons, the reaction with arene must be regarded merely as confirmation of the possibility of the formation of compounds with an M–C bond when alkanes are activated; on the other hand, the mechanisms of the interaction of the metal complexes with a C–H bond in alkanes and arenes should differ.

(c) Alkane σ-Complexes

The reactions involving the oxidative addition of alkyl halides to transition metal complexes containing phosphine or amine ligands, resulting in the formation of a compound with M–C bonds, are well known.[9,58] However, it has been found only recently[59] that the chloride complex $PtCl_4^{2-}$, not containing "stabilising" ligands, combines with CH_3I at room temperature in aqueous solution to form a methyl σ-complex of platinum(IV). An interesting feature of the reaction is that the sixth coordination site in the octahedral molecule of the product is occupied by water, while the I^- ion is bound to another molecule of the platinum(II) complex (PtI_2 is formed and precipitates). The reaction with C_2H_5I [60,61] and CH_3COCH_2I [62] proceeds analogously:

$$RI + PtCl_4^{2-} \xrightarrow{H_2O} RPtCl_4(H_2O)^- + I^- \quad . \qquad (10)$$

In the presence of an excess of I^- ions at 80 °C, RI is converted rapidly and quantitatively into the alkane, the platinum(II) complex functioning as the catalyst:[63]

$$RI + I^- + H^+ \xrightarrow{Pt^{II}} RH + I_2 \quad . \qquad (11)$$

The methyl σ-complex formed in reaction (10) ($R = CH_3$) eliminates CH_3Cl with formation of a platinum(II) complex:

$$CH_3PtCl_5^{2-} \rightarrow CH_3Cl + PtCl_4^{2-} \ ; \qquad (12)$$

$$CH_3PtCl_4(H_2O)^- + Cl^- \rightarrow CH_3Cl + PtCl_4^{2-} + H_2O \quad . \qquad (13)$$

It has been concluded[64] on the basis of the kinetic parameters of the decomposition of the methylplatinum(IV) σ-complex that the steady-state concentration of this complex, formed in the reaction of CH_4 with the Pt(II) + Pt(IV) system at a methane pressure of 1.01×10^7 Pa, [Pt(II)] = 0.1 M, and 120 °C, should not exceed 10^{-6} M in aqueous solution. However, owing to the increase of the concentration of CH_4 and the higher rate of its reaction with platinum(II) in the $CF_3COOH-H_2O$ solution, this value may be higher by 1–2 orders of magnitude.

Similar alkyl σ-complexes of platinum(IV) can be obtained in the reaction of $PtCl_6^{2-}$ with certain alkyl derivatives of non-transition metals. Thus $PtCl_6^{2-}$ reacts slowly[65] with $(CH_3)_4Sn$ in CD_3COOD at room temperature with formation of $CH_3PtCl_5^{2-}$. The reaction is accelerated by the addition of $PtCl_4^{2-}$ and is of first order with respect to platinum(II):

$$(CH_3)_4Sn + PtCl_6^{2-} \xrightarrow{PtCl_4^{2-}} CH_3PtCl_5^{2-} + (CH_3)_3SnCl \quad . \qquad (14)$$

In the absence of $PtCl_6^{2-}$, tetramethyltin reacts with Na_2PtCl_4 in aqueous acetone, also forming a methylplatinum(IV) σ-complex. The precipitation of metallic platinum is then observed. The reaction partly proceeds as oxidative addition of the components involved in the Me_3Sn-Me bond to platinum(II). As in the case of RI [reaction (10)], one component adds to the platinum(II) atom, while the other is bound by another platinum(II) species (reducing the latter):

$$(CH_3)_4Sn + 2PtCl_4^{2-} + H_2O \rightarrow CH_3PtCl_4(H_2O)^- + Pt + (CH_3)_3SnCl + 3Cl^- . \qquad (15)$$

The reaction involving the transfer of the methyl group from methylcobalamine to platinum(IV) is likewise catalysed by a platinum(II) complex.[66] It is noteworthy that reaction (14) to a certain extent models the interaction of the Pt(IV) + Pt(II) system with saturated hydrocarbons. Reaction (15) probably also has features in common with the reaction of alkanes with the platinum(II) complex. The cleavage of the $Sn-CH_3$ bond by the $PtCl_6^{2-}$ complex is accelerated by light.[65] The formation of the complex $C_2H_5PtCl_5^{2-}$ (in addition to CH_3.$PtCl_5^{2-}$) has been observed by ^1H NMR in the photochemical reaction of $PtCl_6^{2-}$ with $(CH_3)_2Sn(C_2H_5)_2$ in CD_3COOD. Light apparently accelerates the conversion of the ethyl σ-complex into the ethylenic π-complex.

Thus the reactions in which there is a possibility of the formation of platinum(IV) derivatives and alkyl fragments containing a hydrogen atom in the β-position, mainly the photoinduced reactions of the ethyl derivatives of tin and germanium with $PtCl_6^{2-}$, oxidative addition of ethyl iodide or n-hexyl iodide to $PtCl_4^{2-}$, and thermal or photochemical reactions of hexane with $PtCl_6^{2-}$, lead to olefinic π-complexes of platinum(II). The most probable mechanism of the conversion of alkyl σ-complexes into olefinic π-complexes involves the β-elimination of hydrogen with reduction of platinum(IV) to platinum(II):

$$RCH_2CH_2PtCl_5^{2-} \xrightarrow{-Cl^-} (RCH{=}CH_2)\underset{\displaystyle H}{\underset{|}{}}PtCl_4^{2-} \xrightarrow{-H^+,\,-Cl^-} (RCH{=}CH_2)PtCl_3^- \quad (16)$$

The formation of the methyl σ-complex of platinum(IV) in the reaction of CH_4 with the Pt(II) + Pt(IV) system in H_2O has been demonstrated directly.[20] It was found that treatment of the reaction mixture, after the removal of methane from the latter, with sodium tetrahydroborate leads to the evolution of CH_4, formed on reduction of the complex $CH_3 \cdot PtCl_5^{2-}$. The kinetic curve corresponding to the concentration of the methyl σ-complex determined in this way has a maximum corresponding to the same reaction time as the points of inflection on the kinetic curves for the consumption of $PtCl_6^{2-}$ or the accumulation of the final products (CH_3OH and CH_3Cl). The activation energy for the decomposition of the methyl σ-complex is 26 ± 2 kcal mol^{-1}, the decomposition rate constant at 120 °C is 0.14 s^{-1}, and the maximum concentration of the complex is 7.7×10^{-5} M. Hence it is possible to calculate the rate of decomposition of the complex at its maximum concentration (1.1×10^{-5} mol $litre^{-1}$ s^{-1}), which is close to the maximum rate of consumption of platinum(IV) or accumulation of the product (1.0×10^{-5} mol $litre^{-1}$ s^{-1}). Finally the σ-complex formed in the reaction with methane was characterised by the ^1H NMR spectrum, which proved to be identical with the spectrum of the complex obtained in reaction (10).

III. REACTIONS WITH COMPOUNDS OF OTHER METALS

As early as 1969, it was reported that the complex $H_3Co \cdot (PPh_3)_3$ catalyses the H–D exchange between methane and D_2 in benzene solution.[8] Other hydride or low-valence metal complexes, inducing the H–D exchange in aromatic and aliphatic hydrocarbons, have been discovered in recent years. For example, processes of this kind have been described for the naphthalene–C_6D_6–$ReH_5(PMe_2Ph)_2$ [67] and H_2–C_6D_6–$ReH_7[P(C_6H_{11})_3]_2$ systems.[68] In solution in C_6D_6 the isopropyl or cyclohexyl groups R in the complexes $RuH_4 \cdot (PR_3)_3$ are involved in the H–D exchange.[69] The photolysis of a solution of toluene or ethylbenzene in C_6D_6 in the presence of $CpMoH_3(Me_2PCH_2CH_2PMe_2)$ (Cp = cyclopentadienyl) leads to the substitution of H by D both in the aromatic ring and in the alkyl chain.[70] Under the influence of light, H–D exchange has been observed between $IrH_3(CO)(Ph_2PCH_2 \cdot CH_2PPh_2)$ and C_6D_6.[71] The exchange between alkanes and D_2 is catalysed by the allyl hydride complex of rhodium immobilised on silica gel.[72,73] All the reactions enumerated apparently include the stage involving oxidative addition to the metal complex and in certain cases can begin with the elimination of H_2 from the hydride derivative.

In the presence of $TiCl_4$, Cp_2TiCl_2, or VCl_4, dimethylaluminium chloride exchanges the hydrogen atoms of the methyl group for deuterium atoms from CD_4.[74,75] CH_2D_2 is formed preferentially, CH_3D and CD_3H being produced in addition. The proposed reaction mechanism includes the reversible disproportionation of the methyl groups linked to the transition metal atom M, which leads to the formation of a carbenium complex, the latter combining in its turn with deuteriomethane. The electronic structures of the complexes H_nMCH_3 and H_mMCH_2 (M = Ti, V, or Cr) have been calculated by the LCAO-MO SCF method.[76] It was found that the capacity of these compounds for the formation of the carbenium complex ($MCH_3 \rightarrow MCH_2 + H_2$) varies in the sequence Ti < V < Cr.

Under the influence of Cp_2V, methane exchanges the hydrogen atoms for deuterium atoms from D_2 (the overall yield of CH_3D, CH_2D_2, CHD_3, and CD_4 is 2–6% after 24 h in the presence of 35% of methane and at a pressure of 250 mmHg; the product ratios are 1.0 : 0.2 : 0.3 : 0.12).[74,77,78] Benzene used as the solvent also enters into the H–D exchange reaction. The process mechanism includes the following stages:

$$\begin{gathered} M + CH_4 \rightleftarrows H{-}M{-}CH_3, \\ H{-}M{-}CH_3 + D_2 \rightleftarrows D{-}M{-}CH_3 \rightleftarrows H{-}M{-}CH_2D, \\ H{-}M{-}CH_3 + D_2 \rightleftarrows H{-}M{-}D + CH_3D, \\ M + D_2 \rightleftarrows D{-}M{-}D, \\ D{-}M{-}D + CH_4 \rightleftarrows D{-}M{-}H + CH_3D. \end{gathered} \quad (17)$$

It is of interest that the H–D exchange between CD_4 and C_6H_6 under the influence of Cp_2V is strongly accelerated in the presence of ethylene, which may be associated with the fact that the addition of methane to the ethylene complex via the mechanism

$$M(\pi\text{-}CH_2{=}CH_2) + CD_4 \rightleftarrows CD_3{-}M{-}CH_2CH_2D \quad (18)$$

is dynamically more favourable than the addition involving the formation of an alkyl hydride complex. In the CD_4–C_2H_4–C_6H_6 system the ethylene molecule plays the role of agent transferring deuterium from methane to benzene.

Iridium(III) and rhodium(III) chlorides catalyse the H–D exchange with the solvent (CH_3COOD–D_2O) in arenes and alkanes.[1,13–15,79] As for the platinum(II) complexes, multiple exchange is observed, arenes react faster than alkanes, and the exchange does not occur in the *ortho*-position in substituted arenes. Finally we may note that the interaction of alkanes with metal atoms or ions M (see, for example, Refs. 80–87) leads to the cleavage of the C–H and C–C bonds and the formation of M–H and M–C bonds.

(a) Isolation of Alkyl Hydride Complexes

In certain cases the alkyl hydride complexes formed on oxidative addition (accompanied by the dissociation of a C–H bond) of arenes, alkyl groups linked to aromatic rings, and even alkanes are fairly stable and can be isolated. For example, on heating or photolysis, the complexes Cp_2WH_2, Cp_2WCO, and Cp_2WHCH_3 give rise to a coordination-unsaturated tungstocene species Cp_2W, which readily combines with aromatic or aromatic alkyl-substituted hydrocarbons.[88] For example, in the reaction with toluene the products are $Cp_2 \cdot W(H)C_6H_4CH_3$ and $Cp_2W(CH_2Ph)C_6H_4CH_3$, i.e. tungsten is inserted both in a C–H bond in the aromatic ring and in a bond involving an sp^3-hybridised carbon atom. The thermal reaction of Cp_2W with mesitylene affords $Cp_2W(H)CH_2C_6H_3 \cdot (CH_3)_2$. However, cyclohexane and neopentane do not give rise to insertion products in this instance. The oxidative addition of alkanes with formation of alkyl hydride complexes was first demonstrated directly in studies using iridium complexes. Thus the iridium dihydride derivative $Cp'Ir(H)_2 \cdot PMe_3$ (Cp′ = pentamethylcyclopentadienyl) produces, after irradiation in solution in cyclohexane or neopentane, the complexes $Cp'(PMe_3)Ir(H)(C_6H_{11})$ and $Cp'(PMe_3)Ir(H) \cdot CH_2C(CH_3)_3$ in a satisfactory yield.[89–91] Other saturated hydrocarbons and benzene also readily add to an iridium complex. The alkyl hydride complexes obtained have been characterised by ^1H and ^{13}C NMR and infrared spectra. By

treatment with $CHBr_3$ at −60 °C, these complexes were converted into the more stable derivatives $Cp'(PMe_3)Ir(Br)R$. Irradiation of $Cp'Ir(H)_2PMe_3$ in the $C(CH_3)_4 + C_6D_{12}$ mixture led to the formation of $Cp'(PMe_3)Ir(H)CH_2C(CH_3)_3$ and $Cp'.(PMe_3)Ir(D)C_6D_{11}$ with very small admixtures of cross-addition products. Thus both components involved in the R–H bond add to the same metal atom. The reaction of alkanes with the complex $Cp'Rh(H)_2PMe_3$ takes place analogously under irradiation conditions at a temperature below −30 °C.[89,92,93] It is of interest that the cyclopropyl hydride complex rearranges to the rhodacyclobutane derivative.[94] The relative rates of the reactions with various hydrocarbons have been determined by the method of competing reactions[89,92] (Table 1). The selectivity (both substrate and positional selectivity) proved to be much higher for the rhodium complex than in the case where an iridium complex was used. When the cyclohexyliridium hydride complex (I) or the n-pentyliridium hydride derivative (II) was heated for 50 h at 140 °C in a mixture of 91.5% of cyclohexane and 8.5% of n-pentane, the following equilibrium was established:

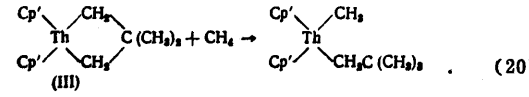
$$\underset{\text{(I)}}{Cp'(PMe_3)Ir(H)C_6H_{11}} + CH_3(CH_2)_3CH_3 \overset{K}{\rightleftarrows} \underset{\text{(II)}}{Cp'(PMe_3)Ir(H)(CH_2)_4CH_3} + C_6H_{12} \quad (19)$$

and the ratio (II) : (I) was 1.0 ± 0.1. Hence the constant $K = [(II)][C_6H_{12}]/[(I)][n\text{-}C_5H_{12}] = 10.6$, which corresponds to $\Delta G^\circ = -2.0$ kcal mol^{-1}. It has been suggested that the entropy changes in the reaction are small and, assuming that the CH_2 and CH_3 bond energies in cyclohexane and n-pentane are 94.5 and 98 kcal mol^{-1} respectively, we find that the energy of the M–C bond in the complex (II) is higher by 5.5 kcal mol^{-1} than in the complex (I).[95] It follows from the estimates that the methyliridium hydride complex $Cp'.(PMe_3)Ir(H)CH_3$ should also be thermodynamically very stable. It was obtained in 58% yield on heating (at 140 to 150 °C) a solution of the complex (I) in cyclo-octane in the presence of methane (20 atm).[89,95]

Table 1. The relative rates of reaction of the complex $Cp'M(H)_2PMe_3$ with hydrocarbons via a C–H bond (irradiation at −60 °C).[89,92]

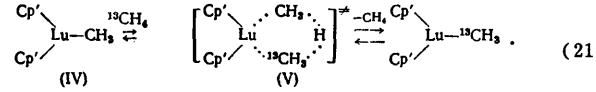
Hydrocarbon	Relative rate		Hydrocarbon	Relative rate	
	M=Rh	M=Ir		M=Rh	M=Ir
Benzene	19.5	3.9	Ethane	2.0	—
Cyclopropane	10.4	2.1	Cyclopentane	1.8	1.1
Hexane (1°)	5.9	2.7	Neopentane	—	1.14
Hexane (2°)	0.1	0.2	Cyclohexane	1.0	1.0
2-Methylpropane	3.6	—	Cyclodecane	—	0.23
Propane (1°)	2.6	1.5	Cycloheptane	0.14	—
Propane (2°)	0.1	0.3	Cyclo-octane	0.06	0.09
Ethylene	2.4	—			

Irradiation of the solution of the carbonyl complex $Cp'Ir(CO)_2$ in perfluorohexane at room temperature in a CH_4 atmosphere (10 atm) led to the formation of $Cp'Ir(CO)(H)CH_3$ in 20% yield.[96] The study of the kinetics of the reaction of the complex $Cp'Rh(H)_2PMe_3$ with arenes and alkanes led to the conclusion that in the case of arenes the oxidative addition is preceded by the coordination of the aromatic hydrocarbons via one of the double bonds and that the Rh–C_6H_5 bond is more stable by approximately 13 kcal mol^{-1} than the Rh–CH_3 bond.[97] In reaction (20) of the cyclic derivative of thorium(III) with methane (60 °C, in cyclohexane) the methyl group is bound to the metal and hydrogen adds to the ligand carbon atom:[98]



(20)

This is confirmed by the fact that the reaction with CD_4 (which is 6 times slower than that with CH_4) leads to the formation of a deuteriated complex, evolving neopentane-d_1 after hydrolysis. The exchange reaction (21) of methane with a lutetium complex[99,100] apparently proceeds via a similar mechanism. It has been suggested that reaction (21) takes place via the transition state (V):

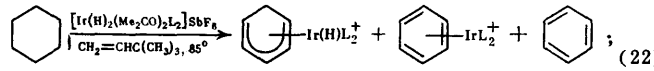


(21)

Since lutetium in the complex (IV) is in the +3 oxidation state, it is unlikely that the exchange with $^{13}CH_4$ takes place via the usual oxidative addition, since the latter should result in the formation of the alkyl-lutetium hydride complex (V). In the mechanism involving the transition state (V), the metal atom has electrophilic properties. The rhodium complex immobilised on silica gel, which reacts with methane, is also an electrophile.[101] The reaction proceeds via two pathways, one of which leads to a methylrhodium(III) hydride derivative. When the methylrhodium hydride complex is treated with chlorine, CH_3Cl is formed.

(b) Dehydrogenation of Alkanes

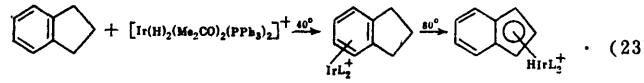
As already mentioned, platinum chloride complexes dehydrogenate alkanes. The complexes of certain metals in a low oxidation state can also abstract hydrogen from aliphatic substituents in phosphine ligands or alkanes. For example, the reaction of $[(\text{cyclo-octene})_2MCl]_2$ (M = Rh or Ir) with tricyclohexylphosphine in boiling toluene leads to the formation of the derivative $[P(C_6H_{11})_3]M[P(C_6H_9)(C_6H_{11})_2]Cl$, in which the M atom is π-coordinated to the double bond in the cyclohexene group C_6H_9.[102] The cycloalkanes are dehydrogenated in the presence of 3,3-dimethylbutene by the cationic iridium complexes $[Ir(H)_2(Me_2CH)_2L_2]SbF_6$, where L = PPh_3 or $(p\text{-}FC_6H_4)_3P$.[103,104] The complex $[CpIr(H)L_2]SbF_6$ is formed from cyclopentane in 82% yield. Cyclohexane affords the mixture of the products (VI) and (VII) as well as benzene in yields of 5, 45, and 32% respectively:



(22)

L = $(p\text{-}FC_6H_4)_3P$. (VI) (VII)

The reaction with cyclo-octane leads to the formation of $[Ir(COD)L_2]SbF_5$, where COD = 1,5-cyclo-octadiene and L = $(p\text{-}FC_6H_4)_3P$, in 75% yield. However, in the presence of 1,8-di(dimethylamino)naphthalene as the base, the process becomes catalytic (8 cycles) and its product is cyclo-octene. Iridium compounds with arenes ArH give rise to complexes which dehydrogenate cyclopentane with formation of a Cp derivative of iridium and the liberation of the free arene.[105] The indan dehydrogenation process is accompanied by an intramolecular rearrangement:[105]

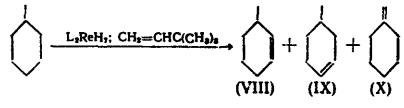


(23)

All the reactions with cationic iridium complexes take place under homogeneous conditions. To demonstrate this, a special test was developed using dibenzo[*a*, *e*]cyclo-octatetrane, which makes it possible to detect the formation of a

heterogeneous catalyst from the soluble complex.[106] It has been suggested that the dehydrogenation by the cationic complex includes the oxidative addition to the alkane via a C–H bond to the iridium atom with subsequent dehydrogenation.[103]

The dehydrogenation of alkanes has been studied in detail in relation to reactions with rhenium polyhydride complexes. Thus heating of a solution of L_2ReH_7 (L = PAr_3, where Ar = p-FC_6H_4, C_6H_5, or p-$CH_3C_6H_4$) in cycloalkane in the presence of 3,3-dimethylbutene leads to the formation of the complex $CpRe(H)_2L_2$ in the case of cyclopentane[107] or of cycloalkenes in the case of cyclohexane, cycloheptane, and cyclo-octane.[108] When low concentrations of the heptahydride and 3,3-dimethylbutene are used, the dehydrogenation reaction of the alkanes C_nH_{2n} (n = 6, 7, 8) becomes catalytic in relation to rhenium hydride (up to 9 cycles).[109] Under these conditions, methylcyclohexane produces a mixture of three olefins (no other products, for example benzene, have been detected):



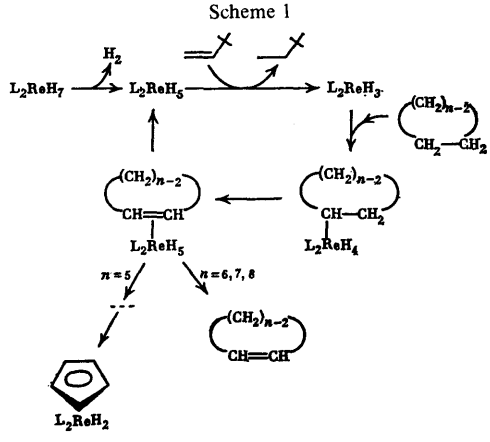
(24)

The ratio of the isomers (VIII), (IX), and (X) depends on the nature of the ligand L (Table 2).[109] The selectivity series CH_3 > CH_2 > CH has been observed in the reaction, but for steric reasons the reagent does not attack the most shielded hydrogen atom (in CH_3 and 2- and 6-CH_2). In the case of the less bulky ligand Et_3P, the content of compound (X) increases at the expense of compound (IX). The proposed process mechanism (Scheme 1) includes the first stage involving the elimination of H_2 followed by the oxidative addition of RH to L_2ReH_3 and the β-elimination of the hydrogen atom with formation of an olefinic π-complex:

Table 2. The ratio of the isomers (in %) formed in reaction (24) as a function of the nature of the ligand L.[109]

L	(VIII)	(IX)	(X)
$(p$-$FC_6H_4)_3P$	29	65	6
Ph_3P	28	63	9
Et_3P	27	45	28

Scheme 1

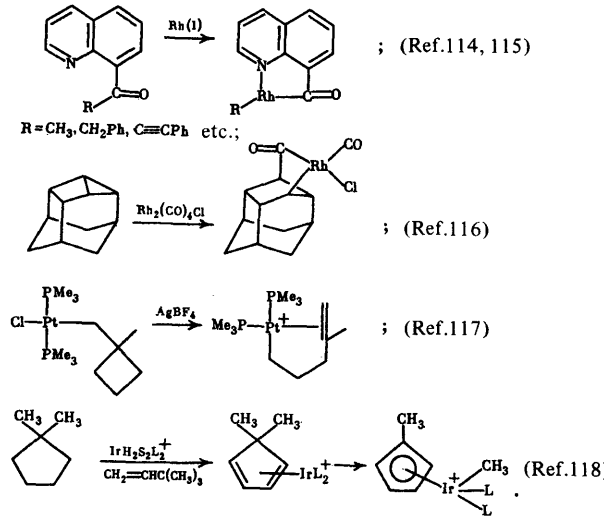


The reaction of $(PPh_3)_3ReH_7$ with n-alkanes leads to the formation of the diene complexes $(RCH{=}CH{-}CH{=}CH_2)Re.(PPh_3)H_3$, which, on treatment with $(MeO)_3P$, give rise to alk-1-enes in yields of more than 95% and a selectivity in excess of 98%.[110] The polyhydrides of other metals, in particular, $(iso\text{-}Pr_3P)_2IrH_5$, $[(p\text{-}FC_6H_4)_3P]_2IrH_5$, and $[(p\text{-}FC_6H_4)_3P]_3RuH_4$ dehydrogenate catalytically (45 to 70 cycles) cyclo-octane to cyclo-octene in the presence of 3,3-dimethylbutene at 150 °C.[111] The dehydrogenation reaction can occur also under the influence of metal atoms. For example, the condensation of tungsten with cyclopentane and PMe_3 gives a 10% yield of $CpW(PMe_3)H_5$,[112] while the interaction of tungsten atoms with cyclohexane and PMe_3 affords the complex $C_6H_6W(H)_2(PMe_3)_2$.[113]

(c) The Cleavage of the C–C Bond

Compared with the C–H bond, the bond between carbon atoms in saturated fragments of alkane molecules is much more resistant to the action of metal complexes. Only reactions involving the opening of the cyclopropane ring and the insertion of Rh in the C–CO bond or bonds in saturated but strained cyclic hydrocarbons are known.[9] Certain examples of such reactions are presented in Scheme 2.

Scheme 2



; (Ref.114, 115)

; (Ref.116)

; (Ref.117)

(Ref.118)

An instance of the cleavage of a C–C bond in an alkane by metal complexes is known: when octane was heated at 180 °C for 15 h in an atmosphere of H_2 (50 atm) in the presence of $Re_2(CO)_{10}$ + $Al(C_2H_5)_3$, the hydrocarbon was hydrogenolysed with 48% conversion.[119] There are data showing that, in the presence of $Co_2(CO)_8$, the fragmentation of alkanes by γ-radiation is retarded and at the same time the complexes $Co_3(CO)_9CR$, where R = CH_3, C_2H_5, or $CH(CH_3)_2$, are formed.[120]

(d) The Hydroalkylation of Multiple Bonds by Alkanes

Like hydrogen (hydrogenolysis), methane can rupture a metal–alkyl bond (alkanolysis):

$$M{-}R + CH_4 \rightarrow M{-}CH_3 + RH \quad (25)$$

The first examples of such reactions were the formation of ethane in the interaction of methane with organoaluminium compounds in the presence of $TiCl_4$, Cp_2TiCl_2, VCl_4, and other complexes.[74,75,121]

As already stated, the possibility of such processes was then demonstrated in the reaction of methane with lutetium and thorium complexes [reactions (20) and (21)]. Taking into account the occurrence of reaction (25), on the one hand, and knowing the mechanism of the multiple bond hydrogenation reaction, on the other, it is reasonable to postulate[74,121,122] the possibility of the addition of R–H to the multiple bond (hydroalkylation):

$$\begin{gathered} M + R{-}H \rightleftarrows H{-}M{-}R\,, \\ H{-}M{-}R + CH_2{=}CH_2 \rightleftarrows CH_3CH_2{-}M{-}R \rightarrow M + CH_3CH_2R\,, \\ CH_3CH_2{-}M{-}R + RH \rightarrow M{-}R + CH_3CH_2R\,. \end{gathered} \qquad (26)$$

Indeed, in the reaction of methane with ethylene ($CH_4/C_2H_4 > 10$, 20 °C, 10 h), propane is formed under the influence of the catalyst $Ti(OC_4H_9)_4 + Al(C_2H_5)_3$ in benzene in a yield of about 20% relative to ethylene.[122] Methane adds to acetylene with formation of propene when acted upon by $Al(C_2H_5)_3$ and and $Fe(acac)_3$ [74,121] or nickel stearate, naphthenate, and naphthenehydroxamate deposited on the surface of nickel hydroxide.[123]

IV. CHEMICAL MODELS OF THE BIOLOGICAL OXIDATION OF ALKANES

1. Enzymic Oxidation

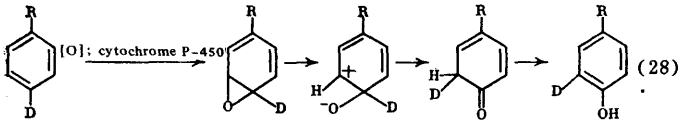
It is well known that various organic compounds, including alkanes, can be oxidised by oxygen in the cells of bacteria, insects, fish, warm-blooded animals, and man as well as higher plants. The group of enzymes catalysing the hydroxylation of CH-containing compounds by oxygen, namely oxygenases, can induce the insertion of only one oxygen atom from O_2 in the C–H bond, while the second oxygen atom is reduced with formation of water:

$$C{-}H + O_2 + AH_2 \rightarrow C{-}OH + H_2O + A\,. \qquad (27)$$

In this case the enzymes are referred to as monoxygenases.[124–129] The hydrogen donors AH_2 are NADH, NADPH, the ascorbate anion, and other biological reductants. Certain monooxygenases contain cytochrome P-450—a protein which contains haem as the prosthetic group.[124–134]

(a) Oxidation with Participation of Cytochrome P-450

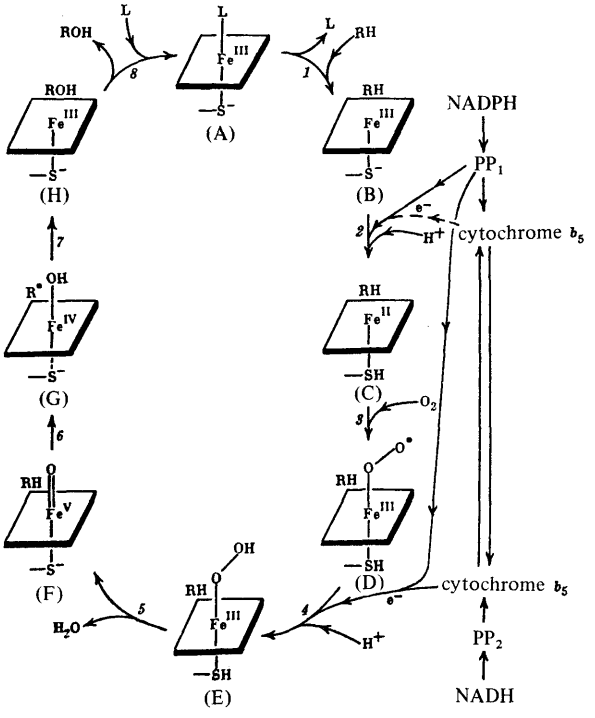
The oxidation of organic substrates by oxygen has been investigated in greatest detail in the liver cell microsomes of warm-blooded animals and also by bacterial monoxygenases containing cytochrome P-450. For example, the monoxygenases of the bacterium *Pseudomonas putida* hydroxylate camphor, while the monoxygenases from the mitochrondria and microsomes in the adrenal cortex cause the side chain of cholesterol to be split off with subsequent hydroxylation of the saturated C–H bonds. It is important that, in the presence of liver microsomes, alkanes and aliphatic acids are hydroxylated predominantly at the terminal (ω) carbon atom. The C–H bonds at the neighbouring (ω − 1) carbon atom of the aliphatic chain are much less reactive. Thus the oxidation of decanoic acid results in the formation of 92% of 10-hydroxydecanoic and 8% of 9-hydroxydecanoic acid. Since the oxidation in the ω- and (ω − 1)-positions is inhibited by carbon monoxide to different extents, presumably the C–H bond activation processes in these positions are catalysed by different monoxygenases. The isotope effect discovered in the hydroxylation of [11-D_2]lauric acid amounts to 3.6. On the other hand, monoxygenases are known (for example those isolated from rat liver microsomes) which hydroxylate alkanes with the "usual" selectivity (thus 1°: 2°: 3° = 1: 15.4: 113 for isopentane). A characteristic feature of the oxidation in the presence of monoxygenases is the retention of the configuration of the substrate. The hydroxylation of aromatic compounds proceeds as electrophilic substitution (the ratio $o:m:p$ = 59: 13: 28 for toluene) and is accompanied by the so called NIH shift. This phenomenon, consisting in the transfer of a hydrogen (deuterium) atom to a neighbouring position relative to that at which hydroxylation takes place, may be accounted for by the following scheme:



(28)

The oxidation of organic compounds RH by oxygen in the presence of cytochrome P-450 includes at least 8 stages (Scheme 3).[124] The following notation has been adopted in the scheme: PP_1 = NADPH-cytochrome P-450 reductase, PP_2 = NADH-cytochrome b_5 reductase, and S = cysteine residue.

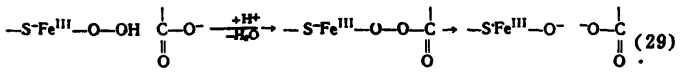
Scheme 3



The formation of the complex (B) in the first stage converts cytochrome P-450 from the low-spin form into the high-spin form. Reduction takes place in the second stage of the process, after which an O_2 molecule is coordinated to the Fe(II) atom. X-Ray diffraction analysis of the complex of myoglobin with O_2 showed that oxygen is coordinated in such a way that the molecular axis of O_2 forms an angle of 120° with the plane of the porphyrin ring [Pauling's structure (D)]. The fourth and fifth stages terminate with the reduction of the complex and the elimination of a water molecule. This results in the formation of the oxenoid (F), whose structure can be represented by several formulae:

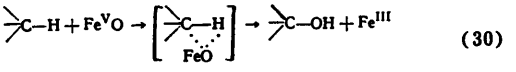
$$-S^-Fe^{V}O^{2-} \leftrightarrow -S^-Fe^{IV}O^- \leftrightarrow -S^-Fe^{III}O \leftrightarrow -S^+Fe^{III}O^-\,.$$

The thiol ligand S^- behaves in this instance as an electron donor. The carboxy-group of one of the aminoacids of cytochrome P-450 and the intermediate acyl peroxide participate in the cleavage of the O–O bond:[124]



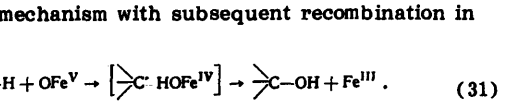
(29)

The sixth stage consists in the rupture of a C–H bond in the substrate molecule. Two alternative mechanisms have been proposed[124,125,134]—the oxenoid mechanism:



(30)

and the radical mechanism with subsequent recombination in the cage:

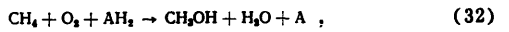


(31)

It may be that the real mechanism of the elementary process includes two stages, the first of which is close to the H atom abstraction mechanism but proceeds without the formation of radicals and the reaction terminates with formation of an alcohol.

(b) Methane Monoxygenases

The enzymes isolated from methane oxidising bacteria are known under the general name of methane monoxygenases.[1,135–137] The oxidation takes place in accordance with the scheme



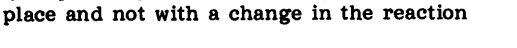
(32)

where AH_2 = NADH or NADPH. The methane monoxygenases isolated from *Methylococcus capsulatus* and *Methylosinus trichosporium* contains proteins incorporating non-haem iron and possibly copper.[1] The enzymes also include cytochrome *c*, but its presence does not influence the activity of methane monoxygenases. The enzyme from *M. capsulatus* oxidises alkanes ranging from methane to butane and, as the chain length increases, the rate of oxidation falls. Pentane, cyclohexane, and aromatic hydrocarbons are not oxidised.[137] We may note that the activity maximum for cytochrome P-450 corresponds to alkanes containing 8 and 12 carbon atoms. The difference in the activity is apparently associated with the size of the hydrophobic pocket in the enzyme where oxidation takes place and not with a change in the reaction mechanism.

2. Chemical Models

(a) "Direct" Oxidation by High-Valence Metal Compounds

Aromatic, aromatic alkyl-substituted, and saturated hydrocarbons are oxidised by cobalt(III) compounds.[1,11,14,15,138,139] For example, cobalt(III) trifluoroacetate oxidises cyclohexane in solution in CF_3COOH at 30 °C in the course of 23 h to cyclohexyl trifluoroacetate in 35% yield. The proposed mechanism includes the formation of the R· radical from the hydrocarbon RH under the conditions of the elimination of a proton synchronous with the reduction of cobalt(III):



(33)

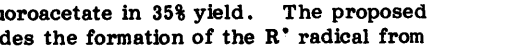
or in the decomposition of the alkyl σ-complex of cobalt(III):



(34)

The radicals enter into further reactions leading to the formation of the final products. Numerous studies of the direct oxidation of alkanes and aromatic alkyl-substituted hydrocarbons by compounds of other high-valence metals are known. Thus, on interaction with manganese(III) or lead(IV) acetates in CF_3COOH, adamantane produces 1-adamantyl trifluoroacetate.[140] Lead(IV) acetate oxidises n-heptane and other alkanes at room temperature[12,141] and copper(III) complexes convert cyclohexane into cyclohexanol, cyclohexanone, and benzene in aqueous solution at room temperature.[142]

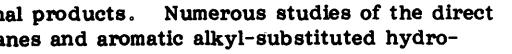
In highly acid media, in particular in concentrated H_2SO_4, certain complexes, for example those of palladium(II), platinum(III), and mercury(II), oxidise alkanes with formation of olefins, aromatic compounds, and carbonium ions.[143,144] The reactions with all oxidants in acid media apparently have a similar mechanism in the rate-limiting stage—homolytic cleavage of the C–H bond with participation of the ligand L:[143]



(35)

(b) Oxidation by the Oxo-Compounds of High-Valence Metals

There is some similarity between the oxidation of alkanes and other compounds by monoxygenases, on the one hand, and the oxygen derivatives of high-valence metals, on the other. For example, the migration of the substituent, analogous to the NIH shift,[124] has been observed in the hydroxylation of arenes by the chromium(VI) derivatives $CrO_2(OAc)_2$.[124] The reactions of alkanes with chromium(VI) oxo-compounds apparently take place with the intermediate formation of radicals:



(36)

However, not all the radicals formed are liberated in the solution, since the oxidation of (+)-3-methylheptane by chromic acid involves the formation of (+)-3-methyl-3-heptanol with retention of configuration to the extent of 70–85%. The normal selectivity has been observed in the hydroxylation of branched alkanes. The addition of ruthenium(IV) or iridium(IV) chloride complexes increases the rate of the reaction leading to the formation of the chloroalkanes.[145–147] The selectivity of the oxidation in the presence of ruthenium(IV) ($1°:2°:3° = 1:100:1000$) is different from that in the oxidation catalysed by iridium(IV) (1:30:250); in the latter case, the primary C–H bond is relatively more reactive. One of the possible causes of the greater oxidising capacity of chromium(VI) compounds is the formation of the mixed complex $[Cl_4RuOCrO_3]^{3-}$.[147] Strong acids accelerate the reaction similarly (the rate of oxidation is proportional to the acidity of the medium), giving rise to protonated species, for example $O=Cr(OH)_3^+$ and $HCrO_3^+$. In solution in CF_3.COOH, permanganate oxidises alkanes at room temperature.[148] The cation MnO_3^+ is apparently the active species. The selectivity of the reaction corresponds to $1°:2°:3° = 1:60:2100$. Finally, we may note that the ruthenium(IV) complex $[Ru(terpyridyl)(bipyridyl)(O)]^{2+}$ catalyses the electrochemical oxidation of aromatic alkyl-substituted hydrocarbons to alcohols, ketones, and acids.[149]

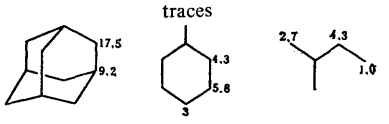
(c) Oxidation of Alkanes Coupled with the Oxidation of Metal Compounds

A whole series of systems hydroxylating organic substrates in a process coupled with the oxidation of a low-valence metal derivative by oxygen are regarded as chemical models of monoxygenases. Copper(I), titanium(III), molybdenum(O), molybdenum(III), iron(II), etc. compounds have been used for this purpose.[1] The hydroxylation of alkanes by oxygen in the presence of $SnCl_2$ in acetonitrile at room temperature has been studied in greatest detail.[1,150] The reaction selectivity corresponds to $1°:2°:3° = 1:5.1:12.5$. It has been established that the interaction of O_2 with $SnCl_2$ involves a

branched chain mechanism with formation of hydroxy-radicals, which react with alkanes.

(d) The GiF System

Molecular oxygen effectively oxidises alkanes in the presence of powdered iron, a carboxylic acid, pyridine, and water (the so called GiF system).[151] It was noted in the first studies that traces of H_2S initiate the reaction.[152,153] Soluble iron complexes are active in the system and zinc dust can be used as the source of electrons.[151,154] Oxidation in the course of 15–20 h at 30 °C leads to the formation of ketones and aldehydes (or an alcohol in the case of a tertiary C–H bond) with the following yields expressed as percentages (indicated by numbers opposite the corresponding positions within the molecule):



It has been suggested that the unusual selectivity of the oxidation reaction (the low reactivity of a weak tertiary bond compared with the primary and secondary bonds) is associated with the involvement in the process of a carbene complex of iron as an intermediate, but it has been shown[155,156] that the selectivity is independent of the nature of the metal. When copper, tin, and cobalt were used instead of iron, (and in general in the absence of a metal in the initiation of the oxidation) similar results were achieved. The unusual selectivity is apparently determined by the formation of the radicals $HO_2^{\bullet}$ or $RO_2^{\bullet}$ in the presence of pyridine and acid (part of the pyridine should be protonated). It has been suggested[155,156] that the "solvated oxygen cation" pyO^+ (or $pyO^{\ddagger}$), formed from $HO_2^{\bullet}$ or $RO_2^{\bullet}$ in the presence of protonated pyridine, is active in the oxidation of alkanes:

$$HO_2^{\bullet} + pyH^+ \rightleftarrows H_2O + pyO^+ . \qquad (37)$$

The pyO^+ species can react with the hydrocarbons as a three-electron oxidant with the elimination of H^+ from the carbon atom undergoing hydroxylation:

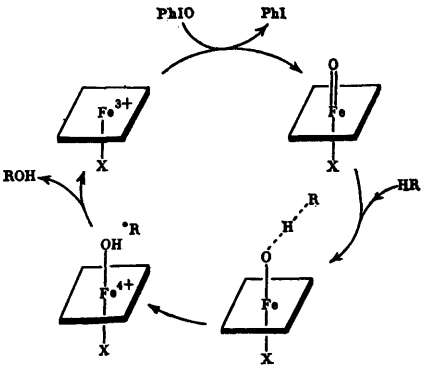
$$-\overset{|}{\underset{|}{C}}-H + pyO^+ \rightarrow -\overset{|}{\underset{|}{C}}^{\bullet} + H^+ + py \quad (H,\ OH) . \qquad (38)$$

The radical formed is converted into a ketone or an aldehyde on further oxidation or into an alcohol on reduction. Naturally, this mechanism does not operate in the case of a tertiary C–H bond, which may account for the unusual selectivity of the oxidation process.

(e) Oxidation by Metalloporphyrin Complexes of Oxygen

The closest models of the hydroxylating system based on cytochrome P-450 are oxygen derivatives of metalloporphyrins. Mainly oxidation with participation of iron and manganese complexes, using O_2, iodosobenzene PhIO, and KO_2 as sources of atomic oxygen, has been investigated.[157–170] The mechanism of the oxidation of alkanes catalysed by iron-porphyrins involves the initial oxidation of iron(III) with the simultaneous transfer of an oxygen atom to iron and the formation of the oxoferryl complex $[P-Fe^{IV}=O]^+$ (P = porphyrin), which affords an alcohol on reaction with RH (Scheme 4).

Scheme 4



The oxidation of cyclohexane by the PhIO + TPPFeCl system (TPP = tetraphenylporphyrin) leads to the formation of a mixture of cyclohexanol and cyclohexanone in proportions of 15:1 in 8% yield. The ratio 3°:2° = 25–48:1. The oxoferryl complex can also be obtained by the interaction of the oxygen complex of iron(III) with the acylating agent AcX (X = OAc, Cl, or OH):[161,165]

$$[P-Fe^{III}O_2]^- + AcX \xrightarrow[-X^-]{} P-Fe^{III}-O-O-Ac \xrightarrow[-OAc^-]{} [P-Fe^{IV}=O]^{\ddagger} . \qquad (39)$$

It is of interest that the use of the tetramesitylporphyrin (TMP) complex, in which approach to the iron atom is sterically hindered, makes it possible to alter the selectivity.[165] Thus, whereas 1°:2°:3° = 1:12:40 for the hydroxylation of isopentane in the presence of the TPP-complex while C(1):C(2):C(3) = 1:10:10 for hexane, the corresponding ratios obtained in the presence of the TMP-complex were respectively 1:6:16 and 1:7:3. By increasing the steric shielding of the active centre, it is possible to achieve an even greater change in the selectivity. Particles of the tetrakis(p-hexadecyloxyphenyl)-porphyriniron chloride–PhIO–cyclodextrin system, dispersed in aqueous solution, were used as a model of the active centre of cytochrome P-450. Iron-porphyrin is incorporated in the liposomes formed by dimyristoylphosphatidylcholine. In the hydroxylation of hexane, we have the ratios C(3):C(2):C(1) = 1:1.8:0.59 when β-cyclodextrin is used and 1:2.1:0.77 for permethylated β-cyclodextrin.[166] These results confirm the hypothesis concerning the cause of the unusual selectivity observed in many instances of the biological oxidation of alkanes, according to which the high reactivity of the ω- and (ω − 1)–C–H bond is due to the steric hindrance generated around the active centre of cytochrome P-450.

The system based on the nickel(II) complex with a macrocyclic nitrogen-containing ligand, which hydroxylates arenes, is close to the metalloporphyrin models.[171] The complex forms an adduct with O_2 in aqueous solution, which then oxidises benzene.

V. THE MECHANISMS OF THE CLEAVAGE OF THE C–H BOND

1. Saturated Hydrocarbons and Their Fragments as Ligands in Complexes

From the standpoint of the usual ideas, the formation of any complexes by saturated hydrocarbons is impossible owing to the lack of π or n-electrons in their molecules. However,

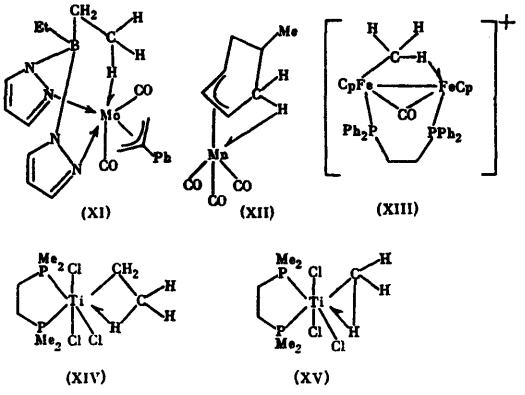
compounds containing hydrogen and other three-centre bonds,[172] for example B...H...B and Al...CH_3...Al, are well known and fairly stable complexes of molecular hydrogen, namely (iso-$Pr_3P)_2(CO)_3W(H_2)$ [173] and $Cr(CO)_5(H_2)$,[174,175] have been characterised recently. If these data are taken into account, one can imagine the possibility of the existence of complexes of alkanes. On the other hand, bearing in mind that saturated hydrocarbons are extremely weak electron donors and poor electron acceptors,[176] one can postulate that alkane complexes should be extremely unstable. Thus, when iodine or oxygen is dissolved in saturated hydrocarbons, contact donor–acceptor complexes are formed,[177] the equilibrium formation constant of which is close to zero. The bond energy in these complexes is very low and both components are oriented with respect to one another in an arbitrary fashion. A quantum-chemical calculation for the $CH_4 + O_2$ system showed that,[178] if the C–H σ-bond is located along the axis of the π orbital of oxygen in such a way that the O...H distance is 2.05 Å, a minimum corresponding to a bond energy between the components of ~0.5 kcal mol^{-1} appears on the potential curve. The paramagnetic shifts of the ^{13}C NMR signals, induced by a nitroxy-radical (the di-t-butylnitroxy-radical) dissolved in the saturated hydrocarbon, indicate the formation of a complex between the radical and the alkane.[178,179] The paramagnetic shift Δδ diminishes on passing from the terminal atom of n-pentane to atoms in the 2- and 3-positions. Thus, at a radical concentration of 1 M, Δδ = 3.8, 2.4, and 2.3 p.p.m. respectively. In the case of 2,2-dimethylbutane, the paramagnetic shifts of the signal due to the CH_3 groups in the t-butyl and ethyl fragments are respectively 3.1 and 3.4 p.p.m., the shift for CH_2 amounts to 2.3 p.p.m., while for a quaternary carbon atom it is only 0.13 p.p.m. All the shifts are directed downfield, which indicates a transfer from the radical to the carbon atoms of alkanes having a positive spin density. The data presented led to the conclusion that an alkane forms a complex by interacting via its hydrogen atoms with the π orbital of the radical occupied by the unpaired electron and distributed approximately equally between the N and O atoms. According to the calculation for the model system CH_3H...ONH_2 by the INDO method,† the stabilisation energy of the complex for a O...H distance of ~2.0 Å does not exceed 1 kcal mol^{-1}.[181]

(a) Diffraction and Spectroscopic Studies

Fairly numerous complexes in which there is an intermolecular bond between the metal atom and one of the CH groups of the ligand according to X-ray diffraction data, confirmed by infrared and NMR spectra, have been discovered in recent years.[182] The bonds formed by saturated hydrocarbon fragments, especially methyl groups, are of special interest. It has been suggested[182] that such a bond be referred to as "agostic" and to designate it by half an arrow: C–H ⇀ M. Thus the term "agostic" bond refers to the case where the hydrogen atom is simultaneously bound covalently by a three-centre two-electron bond to carbon and transition metal atoms. Scheme 5 presents examples of complexes containing the agostic C–H ⇀ M bond. The presence of an agostic bond in the complexes has been demonstrated by X-ray diffraction (XD) and neutral diffraction (ND) methods.

†For the description of different quantum-chemical methods for calculations on molecules, the molecular structure of coordination compounds, the symmetry-based classification of orbitals, etc., see, for example, Minkin et al.[180]

Scheme 5



Certain distances in the crystal, determined by these methods, are presented in Table 3. When the agostic bond is formed, the C–H bond usually lengthens by 5–10%, but in the case where it is formed by the C(sp^3)–H fragment virtually no increase in length is observed. The M–H bond is also somewhat longer (by 15–20%) than in the usual hydride. The M–C bond length is always appreciably smaller than the sum of the van der Waals radii of M and C. The appearance of the agostic bond is reflected in the NMR spectra (upfield shift of the ^1H and ^{13}C signals) and IR spectra (decrease of the stretching vibration frequency of the C–H bond to 2700–2350 cm^{-1}). Thus a system with a C–H ⇀ M agostic bond is, as it were, on the reaction pathway between the C–H + M system and the alkyl hydride derivative C–M–H.

Table 3. Certain interatomic distances in complexes containing the agostic C–H ⇀ M bond.[182,183]

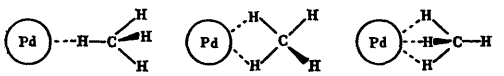
Complex	Method	Distance, Å		
		C–H	M–H	M–C
(XI)	XD	0.97(8)	2.27(8)	3.06
(XII)	ND	1.19(1)	1.84(1)	2.34(1)
(XIII)	XD	1.06(4)	1.64(4)	2.101(3)
(XIV)	XD	1.02	2.29	2.516(10)
(XV)	XD	1.00(2)	2.03(4)	2.149(5)
(XV)	ND		2.45	

Dissolution of chromium trisacetylacetonate in 1-chlorobutane entails a paramagnetic shift of the ^{13}C signals of the solvent in the NMR spectra.[184] It is of interest that the shift Δδ along the chain initially diminishes and then again increases for the terminal CH_3 group; the ratios of the Δδ are C(1):C(2):C(3):C(4) = 1.00:0.30:0.14:0.62. These results indicate the transfer of electron spin density from the complex to the methyl group of the chlorobutane coordinated to it and, since the complex is coordination-saturated, the interaction apparently takes place via the acetylacetonate ligand of the complex (outer-sphere coordination). The formation of adducts of cyclohexane with the paramagnetic bis-[hydrotris(1-pyrazolyl)borato]cobalt(II) complex has been observed[185] by ^1H NMR.

Finally the formation of methane, hexane, and methylcyclohexane complexes with the $Cr(CO)_5$ species in a matrix has been detected.[186–188]

(b) Quantum-Chemical Calculations for Complex Formation

The problem of the coordination of saturated hydrocarbons or molecular fragments to metal complexes has recently attracted the attention of theoretical chemists. It has been suggested that the interaction of saturated C–H bonds with transition metals is due to the overlap of the diffuse outer orbitals of the transition metal with the localised orbitals of the saturated bond.[189,190] The simplest system modelling the interaction of the C–H bond with an unoccupied diffuse orbital of the metal is a CH_4 molecule coordinated to a palladium atom. A calculation has been carried out for this system by the non-empirical SCF MO method.[191] Three possible symmetrical structures, differing in the number of hydrogen atoms coordinated directly to the Pd atom, were examined: two structures with the C_{3v} symmetry [(XVI) and (XVIII)] and one with the C_{2v} symmetry [structure (XVII)]:



(XVI) (XVII) (XVIII)

The calculated CH_4...Pd bond energies decrease in the sequence (XVI) > (XVII) > (XVIII), although they are similar for all three structures [8.4 and 7.3 kcal mol^{-1} for (XVI) and (XVIII) respectively]. Coordination leads to a slight transfer of electron density from methane (mainly from H atoms) to the 5*s* and 5*p* orbitals of palladium via a donor–acceptor mechanism; this entails some redistribution of electron density in the individual AO of both components. Thus the electron density in the $4d_{z^2}$ AO of the palladium atom decreases in all three structures. There is a simultaneous increase of electron density in the 5*s*, $5p_\pi$, and $5p_\sigma$ AO but the overall negative effective charge on palladium increases. The changes in the populations of the AO of methane (much smaller) show that the electron density is to some extent transferred also via a dative mechanism. Since a carbon and not a hydrogen atom plays the main role in structure (XVIII), where the methane molecule is oriented towards the palladium atom via three hydrogen atoms [the equilibrium Pd...H distance in (XVIII) is 2.2 Å against 1.7 Å in (XVI)], the dative transfer of electron density from palladium mainly to a carbon atom is most clearly expressed precisely in this structure.

It is of interest that the bond energy in the Pd...H_2 system, calculated by the same method, is almost twice as high as the bond energy in the methane complex. The donor–acceptor transfer in the alkane complex is much smaller than in the complex with H_2. On the other hand, in general, since the HOMO energy in CH_4 is higher than in H_2 (the ionisation potentials are 12.7 and 15.4 eV respectively), methane should be a better electron donor. However, according to the calculation, the opposite behaviour obtains. One can therefore conclude that the interaction is in this instance determined by the overlap of the corresponding orbitals and not by the difference between the energy levels.[189,191]

The electronic structure of complexes activating alkanes—square planar and pseudo-square chloride and aquochloride derivatives of platinum(II), as well as the interaction of these complexes with CH_4 have been investigated by the semiempirical MO-LCAO SCF method in the CNDO approximation.[192] Calculation for the complexes $[PtCl_{4-n}(H_2O)_n]^{n-2}$ with n = 0, 1, 2, 3, 4 and *trans*-$[PtCl_2(H_2O)(OH)]^-$ showed that the changes in their quantum-chemical characteristics are monotonic and are independent of the symmetry (thus the positive charge on platinum increases monotonically with the increase of n). It was concluded that, when the interaction of such complexes with an axial ligand is controlled by the LUMO, then this is an interaction with an *s* AO and to a lesser extent a d_{z^2} AO of platinum. The methane molecule was considered as the ligand and the calculation was performed for the CH_4...$PtCl_4^{2-}$, CH_4...*trans*-$PtCl_2(H_2O)(OH^-)$, CH_4...*trans*-$PtCl_2(H_2O)_2$, and CH_4...$Pt(H_2O)_4^{2+}$ systems. It was found that coordination involves a redistribution of electron density in CH_4, as a result of which the polarity of the CH bonds increases and the bonds (particularly those coordinated to Pt or an equatorial *acido*-ligand) are weakened. Furthermore, an increase in the free valence of the carbon atom of methane was noted. This actually results in the activation of the CH_4 molecule, facilitating the attack on the latter by polar species. Analysis of the distribution of electron density in methane complexes showed that the alkane is bound as a result of the interaction of the 1*s* AO of the hydrogen atoms and the 2*s* and $2p_z$ AO of the carbon atom with the 6*s* and $6p_z$ AO of platinum. Thus the involvement of the *d* AO of the metal in such complex formation is smaller than the involvement of the outer *s* and *p* AO. For virtually any mode of coordination of CH_4 to the platinum(II) complex (coordination via the vertex, edge, and face of the methane tetrahedron to platinum and also simultaneously to platinum and the acido-ligand was considered), the resulting transfer of electron density from methane entails its decrease at the H atoms. However, owing to the contribution by the dative interaction, the electron density on the carbon atom increases. It is essential to note that the acceleration of the H–D exchange reaction, observed experimentally after the replacement of the $PtCl_4^{2-}$ or $Pt(H_2O)_4^{2+}$ catalysts by $PtCl_2(H_2O)_2$, could not be related to any calculated quantum-chemical parameters. It was therefore postulated[192] that an optimum combination of the donor–acceptor and dative mechanisms of the transfer of electron density is essential for the effective alkane–platinum(II) complex interaction. Since the contribution of the former increases and that of the latter diminishes with increase of the positive charge on the complex, the optimum combination can be achieved for the complex with zero charge. Somewhat earlier the presence of a catalytic activity maximum for the complex $PtCl_2(H_2O)_2$ was attributed to the influence of the symmetry of the ligand environment.[193] On the basis of the hypothesis that the formation of a bond with the activated alkane takes place mainly on interaction with the d_{z^2} AO of the complex, the rates of reaction were correlated with the contribution by this orbital to the LUMO of the platinum(II) complex. Symmetry considerations led to the conclusion that, for n = 0 and n = 4, the LUMO of the complex is formed solely by the $d_{x^2-y^2}$ AO and cannot contain an admixture of the d_{z^2} state. As a consequence of the decrease of symmetry for n = 1, 2, 3, such admixture exists but the n = 2 complex occupies a special place (thus the contribution of the d_{z^2} AO orbital for the *trans*-isomer with n = 2 should be greatest). It is believed[192] that this approach, based on the crystal field theory, is insufficiently complete, since, according to the MO theory, the d_{z^2} AO of platinum participates in the binding of equatorial ligands even in highly symmetrical complexes, i.e. in these complexes too this orbital, being partly unoccupied, can be involved in the donor–acceptor interaction with the alkane.

The total energies have been calculated by the extended Hückel method[194] for alkanes coordinated to the $PtCl_3(H_2O)^-$ species and it has been shown that the coordination of the terminal atom, for example, in pentane, is most preferred. The MO analysis of the agostic interaction in the methyl complexes of metals has been carried out.[195]

2. Types of Reactions

(a) Electrophilic Substitution

Reactions involving the electrophilic substitution of hydrogen in arenes by metal complexes are known for transition metal complexes: Pd(II),[54] Au,[55,195–197] Pt(II),[56] Pt(IV),[38–49] and Rh(III).[198] This series can be extended if account is taken of the cyclometallation reactions.[31,32,199] Arenes are also readily metallated by compounds of the non-transition elements Hg(II), Tl(III), and Pb(IV). All these reactions apparently proceed with the intermediate formation of Wheland complexes. Less information is available about the electrophilic substitution of hydrogen involved in the formation of the $C(sp^3)$–H bond. For example, reaction (21) between methane and a lutetium(III) complex proceeds in this way. The oxidation of alkanes by palladium(II) complexes in acid media can proceed via the cyclic transition state in which palladium(II) behaves as the electrophile.[200,201] The saturated H_2 molecule can also be split by a transition metal ion via an electrophilic mechanism:[202]

$$H_2 + Cu^{2+} \rightarrow CuH^+ + H^+ . \qquad (39a)$$

Analysis of the thermodynamics of electrophilic substitution reactions

$$L_nM + RH \rightarrow L + L_{n-1}M^--R + H^+ \qquad (40)$$

yielded[176] the expression

$$\Delta E = E_{M-L} - Q^c_L - Q^c_{L_{n-1}M} + Q^c_{L_nM} \qquad (41)$$

(where ΔE is the energy expenditure on the formation of the coordination vacancy and Q^c are the heats of solvation), from which it follows that substitution is favoured by a low bond energy E_{M-L} and a high heat of solvation Q^c_L.

(b) Oxidative Addition

The interaction of arenes with low-valence transition metal complexes, leading to the formation of aryl σ-complexes, is a reaction involving the oxidative addition of the components involved in the Ar–H bond to the metal. The cleavage of the Ar–H bond is usually preceded by the formation of a coordination-unsaturated species via the elimination of hydride, alkyl, and halide ligands. An example of such a process is the insertion of Cp_2W in an aromatic C–H bond[88] (see Section III). The metal complex, to which arenes add via an oxidative mechanism, functions as a nucleophilic species. Thus in the reaction of the complex $HMNp(Me_2.PCH_2CH_2PMe_2)_2$ (Np = 2-naphthyl, M = Fe or Ru) with various arenes, the retarding effect of electron-donating substituents and the accelerating effect of electron-accepting substituents in the aromatic ring was noted. For example, the hydrogen atom in the *para*-position in toluene is 2.5 times more reactive than the D atom in C_6D_6 (where M = Fe).[203] Reactions involving the substitution of hydrogen in aromatic compounds by rhodium(I), iridium(I),[204] manganese(I),[205] rhodium(III), and iridium(III) [206] complexes, which exhibit nucleophilic properties, are known. Examples of the reactions of alkanes, which undoubtedly proceed as oxidative addition, were presented in Section III. The complexes inserted into the aromatic C–H bond are frequently capable of activating also the saturated hydrocarbons or the corresponding fragments via the same mechanism. For example, $HMN_p(Me_2PCH_2CH_2PMe_2)_2$ (M = Fe, Ru, or Os) is inserted oxidatively in the C–H bond of the methyl group of acetonitrile.[207] Estimation of the heat of oxidative addition via the mechanism[202]

$$L_nM + RH \rightarrow R{-}L_nM{-}H$$

demonstrated that this reaction is usually endothermic with $\Delta H \cong +10$ kcal mol^{-1} (the following typical dissociation energies were used for the calculation: $D_{M-H} = 60$, $D_{M-R} = 30$, and $D_{R-H} = 100$ kcal mol^{-1} [208]). Oxidative addition with cleavage of the C–C bond via the mechanism

$$L_nM + R{-}R \rightarrow R{-}L_nM{-}R$$

should be thermodynamically even less favourable. This does not apply to the cleavage of C–C bonds in strained hydrocarbons, for example, in the reaction[202]

$$L_nPt(II) + \Delta \rightarrow L_nPt(IV)\langle\rangle . \qquad (42)$$

It is noteworthy that the above considerations refer to complexes of the first transition series of metals, because there are no data on the bond energies in the complexes of heavier metals. The alkyl–metal bonds can be stronger in the case of heavy metals, although, for example, the D_{M-CH_3} for the M^+–CH_3 ions in the gas phase indicate the absence of a distinct tendency towards an increase of this parameter on passing from light to heavy metals within a given Group.[209] The calculated[210] $\bar{D}_{Pt-C} = 36$ kcal mol^{-1} [for *cis*-$Me_2Pt(PH_3)_2$] and $\bar{D}_{Pt-H} = 60$ kcal mol^{-1} [for *cis*-$(H)_2Pt(PH_3)_2$] made it possible to estimate the enthalpies of the oxidative addition to $Pt(PH_3)_2$ of hydrogen (−16 kcal mol^{-1}, exothermic reaction), methane via the CH_3–H bond (+9 kcal mol^{-1}, which agrees with Halpern's estimate[202]), and ethane via the CH_3–CH_3 bond (+19 kcal mol^{-1}, highly endothermic reaction). On the other hand, the complex *cis*-$OsHMe(CO)_4$ is apparently thermodynamically stable and does not exhibit a tendency towards intermolecular reductive elimination of CH_4 (see below). It has been suggested[202] that the $Os(CO)_4$ species, generated photochemically, is capable of combining oxidatively with the alkanes, this addition process being thermodynamically favourable. Thus the kinetic barrier to the oxidative addition of RH to low-valence metal complexes is fairly low and the inability of many 16-electron complexes to activate alkanes can be associated with the thermodynamic causes.[202] Indeed, the rate of addition of CH_4 to Cp'IrCO depends only very slightly on temperature.[211] The nature of L (CO + PMe_3) has little influence on the reactivity of the complexes Cp'IrL in relation to alkanes, which can also indicate that the activation barrier is low.[202] The energy of the oxidative addition of RH to L_nM is determined by the equation[176]

$$E_{M-R} + E_{M-H} - E_{R-H} \simeq E_{M-M} \qquad (43)$$

and hence can be estimated from E_{M-M}. The highest value of E_{M-M} has been obtained for platinum and in addition it has been shown that the reaction involving Group VIII and I transition metals is energetically favourable.

The components involved in saturated bonds can add oxidatively simultaneously to two metal complex molecules:

$$M + R{-}R + M \rightarrow 2M{-}R .$$

It may be that reaction (15) proceeds as two-centre oxidative addition of the components of the $(CH_3)_4Sn$ molecule, namely CH_3 and $Sn(CH_3)_3$, to two platinum(II) species. Finally, one cannot rule out the possibility that, in the interaction of the Pt(II) + Pt(IV) system with methane, the methyl group adds oxidatively to the platinum(II) in the molecule, forming $CH_3Pt(IV)$, while the second component, the hydride, reduces platinum(IV) to platinum(II). Information about the oxidative addition mechanism can be obtained from the study of the reverse process—reductive elimination.[212,213] For example, since the interaction of $OsH(CD_3)(CO)_4$ and $OsD.(CH_3)(CO)_4$ results in the formation of a mixture of CH_4, CH_3D, CD_3H, and CD_4, one may conclude that the reductive elimination proceeds as a bimolecular process:

$$2OsH(CH_3)(CO)_4 \rightarrow CH_4 + (OC)_4HOsOs(CH_3)(CO)_4 . \qquad (44)$$

However, the reaction is kinetically of first order, i.e. its rate-determining stage is unimolecular. In the presence of amines or phosphines (L = py, PPh_3, or PEt_3) a first order is also observed but the reaction proceeds as intramolecular elimination.[214] At the rate-determining stage, an intramolecular rearrangement takes place with insertion of CO in the $Os-CH_3$ bond. The acyl complex formed reacts in a rapid stage with a second molecule of the initial compound.

Processes involving the oxidative addition of the components involved in the saturated H–H or R–H bonds to metal complexes or metal atoms as well as the reductive elimination of RH have been investigated by quantum-chemical methods.[215–223] We shall consider the general case of the interaction of a metal complex with the simplest saturated molecule, namely H_2.[218] In the interaction of the bonding σ orbital of hydrogen with the unoccupied acceptor orbital of the complex and of the antibonding σ^* orbital with the occupied donor orbital, four orbitals of a new hydride derivative are generated. The two low-lying orbitals are filled with electrons, one being symmetrical and the other antisymmetrical relative to the twofold axis or the mirror symmetry plane. A symmetrical combination is formed, for the MH bond generated, from the occupied orbital of the hydrogen molecule and such electron transfer from $\sigma_g(H_2)$ to ML_n weakens the H–H bond and strengthens the M–H bond. The electron transfer in the opposite direction, namely donor orbital → σ_u^*, also weakens H–H and strengthens M–H. One can assume that the occupied a_1 orbitals and the three degenerate t_2 orbitals in CH_4 correspond to the σ_g orbital of the hydrogen molecule. Since the energy of the t_2 orbital is greater by 2 eV than the energy of the $\sigma_g(H_2)$ orbitals, the CH_4 molecule is a somewhat stronger donor.

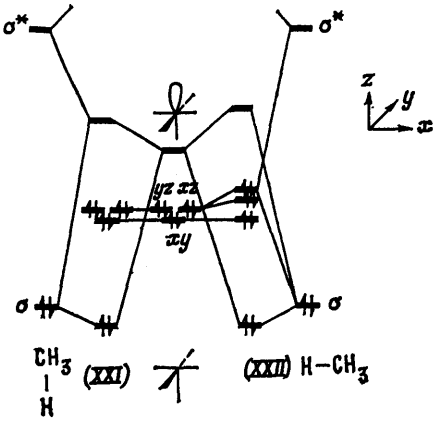
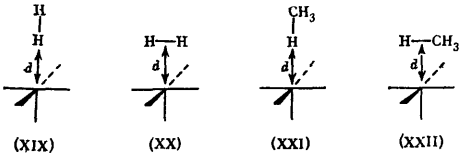


Figure 1. The interaction of orbitals in the formation of the structures (XXI) and (XXII).[218]

The total energy of the $H_2...Cr(CO)_5$ system has been calculated by the extended Hückel method.[218] The interaction energy is negative for both the perpendicular orientation (XIX) and the parallel orientation (XX) of the H_2 molecule approaching the $Cr(CO)_5$ fragment, which has the C_{4v} symmetry. However, in the case of the parallel approach of H_2 the energy of the system has a much more distinct minimum. When H_2 is replaced by CH_4, the curve for the perpendicular approach has approximately the same form but the parallel approach becomes extremely unfavourable.

Whereas the d_{xz} orbital (which functions as the donor orbital in the complex) is lowered for (XX), in the case of CH_4 [structure (XXII)] the energies of both d_{xz} and d_{yz} orbitals increase (Fig. 1).



(XIX) (XX) (XXI) (XXII)

If the CH_4 approaches $Cr(CO)_5$ in such a way that the $H-CH_3$ axis forms an angle θ with the height of the pyramid, the structure is stable for $d(M-H) = 2.0$ Å and $\theta \leq 130°$. However, the perpendicular orientation ($\theta = 180°$) remains the most favourable. The reactions involving the oxidative addition of H_2 and CH_4 to $Rh(CO)_4^+$ and the corresponding isolobal complex CpRh(CO) and to the metallic surfaces of nickel and titanium have also been analysed.[218]

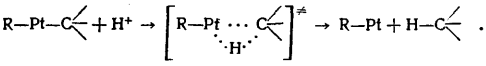
(c) The Mechanism with a Three-Centre Transition State

The first stage in the reaction of alkanes with the platinum(II) complex proceeds via a mechanism which cannot apparently be identified with either typical oxidative addition or the usual electrophilic substitution. Indeed the correlation (2) yields $\rho^* = -1.4$, indicating weak electrophilic properties of the metal complex. On the other hand, the series characterising the influence of ligands on the rate of the H–D exchange [reaction (1)] is the opposite to the *trans*-effect ligand series for the substitution reaction, which takes place with square platinum(II) complexes, but this does not agree with the mechanism involving the direct substitution of the ligand at platinum(II) by the alkane:

$$RH + Pt(II)-Cl \rightarrow [H \cdots R \cdots Pt \cdots Cl]^{\neq} \rightarrow H^+ + RPt + Cl^- .$$

We may note that, in the cyclometallation of arenes, the rhodium(I) and iridium(I) complexes behave as nucleophiles, the palladium(II) complex exhibits electrophilic properties, and the platinum(II) complex occupies an intermediate position.[204]

Presumably the reaction of the chloroaquoplatinum(II) complex with alkanes begins as oxidative addition, proceeds through a three-centre transition state, and terminates by the synchronous formation of a Pt–C bond with elimination of H^+ (which can be transferred to a H_2O molecule).[18,176,223] A similar mechanism has been proposed for the cyclometallation of 8-alkylquinolines by palladium(II).[224] It has also been suggested that the reverse process—the protolysis of the Pt(II)–C bond in alkyl and aryl complexes—involves a three-centre transition state:[225–227]

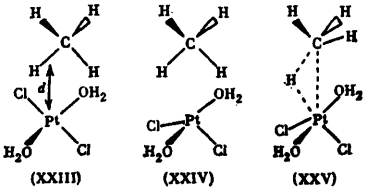


(45)

At the same time the photolysis of the Pt–C bond in *trans*-$[PtH(CH_2CN)(PPh_3)_2]$ takes place in two stages: the oxidative addition of H^+ to the metal and the subsequent elimination of CH_3CN with formation of *trans*-$[PtHCl(PPh_3)_2]$.[228]

The cleavage of the C–H bond in methane by the *trans*-$PtCl_2(H_2O)_2$ complex has been subjected to quantum-chemical analysis by the extended Hückel method,[176,223] It was shown that the approach of CH_4 to the square planar platinum(II) complex [structure (XXIII)] leads to strong four-electron repulsion, the main cause of which is the interaction between the t_2 orbitals of methane and the occupied orbitals of the metal complex localised in the region of the free coordination site (HOMO consisting mainly of the d_{z^2} orbital and also the low-lying d_{yz} orbital). When the distance between the Pt

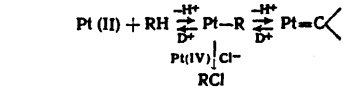
atom and the centre of the C–H bond reaches d = 2.8 Å, the distortion of the metal complex [structure (XXIV)] lowers the repulsion energy. The composition of the HOMO then changes, namely the contribution of the d_{z^2} orbital diminishes and that of the $d_{x^2-y^2}$ orbital increases, which entails a decrease of the electron density in the region of the free coordination site. The $d_{x^2-y^2}$ orbital is hybridised with the s, p_z, and d_{z^2} orbitals of the metal, as a result of which the low acceptor MO of the complex becomes extended in the axial direction.



(XXIII) (XXIV) (XXV)

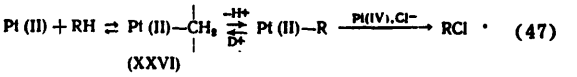
The overlap of the acceptor orbital with the σ orbital of the C–H bond increases and hence the contribution of the transfer of electron density via the donor–acceptor mechanism also increases. This is accompanied by the simultaneous increase of the dative interaction, the main contribution to which is made by the charge transfer from the d_{z^2} and d_{yz} orbitals to the σ* orbitals of methane. In the second stage, the deformation distortion of the methane molecule occurs starting with d = 2.4 Å and the repulsion energy diminishes still further. At the same time the angle of the displacement of the ligands from the plane of the complex increases from 10° to 36°. The populations of the Pt–C and Pt–H bonds reach 30–40% and the C–H bond is loosened to the extent of 20–30%. Under these conditions, the overlap of the d_{yz} and t_2 orbitals diminishes. Since an analogue of an unshared pair oriented towards the complex appears at the carbon atom, namely the 3a′ component at the t_2 level (Fig. 2), the donor–acceptor interaction is enhanced. The transition state (XXV) arises for d = 1.8 Å, whereupon the Pt–C and Pt–H bond lengths reach the usual values and the angle of deviation of the ligand in the complex is 36°. When the C–H bond is extended by 0.28 Å, a maximum appears on the curve describing the energy of the system and the C–H, Pt–C, and Pt–H bonds become approximately equivalent. The extension of the C–H bond enhances both the donor–acceptor and dative interactions; the main contribution to the latter comes in this case from the transfer of electron density to the 3a$_1$ component of the t_2^* level. This transfer plays a decisive role in the rupture of the C–H bond. It is noteworthy that, when the C–H bond is extended, the four-electron repulsion increases faster than the interactions of both types and only when CH_4 and the complex are close together do the repulsion and dative interaction energies become equalised. Calculation[223] has shown that, on passing from *trans*-$PtCl_2(H_2O)_2$ to $PtCl_4^{2-}$, the activation energy for the reaction with the alkane should increase by 0.24 eV, which agrees with the experimental data (these yield a difference ⩾0.17 eV). In the first stages of the process, up to the appearance of the transition state, the C–H bond is polarised, which increases the acidity of the hydrogen atom. This is apparently why in the presence of bases stronger than the platinum(II) complex, it is easier for the system to transfer hydrogen in the form of H^+ to the molecule of the base, which may be H_2O. Thus the reaction may be completed by the synchronous formation of the Pt–C bond and the elimination of H^+, i.e. can proceed as "soft" electrophilic substitution.

The study of the kinetics of the H–D exchange and of the oxidation of alkanes as well as the analysis of the multiple exchange parameter led to the hypothesis[229] that the reaction does not proceed via the alkyl–carbene mechanism



(46)

but via the alkane–alkyl mechanism



(47)

(XXVI)

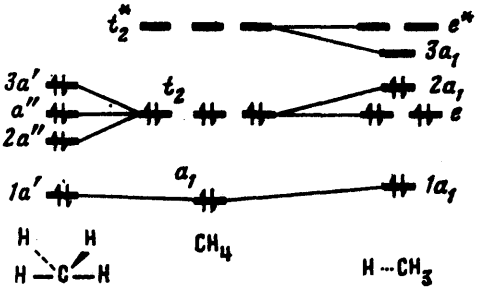
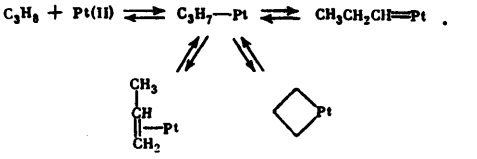


Figure 2. The change in the orbitals of the methane molecule on deformation of the angles and following an increase in the C–H bond length.[223]

It has been suggested that the first kinetically significant intermediate in this reaction is the Pt(II)–alkane complex (XXVI), which is an analogue of alkonium ions of the type CH_5^+, whose formation is associated with the deformation of both the planar complex and of the tetrahedral hydrocarbon molecule. The multiple H–D exchange in alkanes under the influence of platinum(II) can also be due to the formation of olefinic π-complexes and metallocycles[1] (Scheme 6).

Scheme 6



(d) Cleavage with Formation of Radicals

In contrast to the activation of an alkane by a platinum(II) complex, the reaction of RH with Pd^{2+} may begin as electron transfer.[230] The hydroxylation of alkanes by oxygen complexes also proceeds with formation of radicals (see Section IV). In the latter case the interaction of the metal with the C–H bond takes place via a bridging ligand.[143,144,231,232] The formation of a benzylrhodium(III) σ-complex on interaction of the porphyrinrhodium dimer with toluene apparently begins with attack by the P–Rh(II)• radical species on the C–H bond.[233] The reaction of $PtCl_6^{2-}$ with hexane induced by light or γ-radiation[26–29] begins with the homolysis of the Pt–Cl bond in the excited species $[PtCl_6^{2-}]^*$,[234–236] which

results in the formation of a platinum(III) complex and the $Cl^{\bullet}$ radical species. The latter can apparently attack the hexane molecule in the solvent (CH_3COOH) cage. The hexyl radical formed recombines with $Pt^{III}Cl_5^{2-}$ to produce a hexylplatinum(IV) σ-complex, which eliminates HCl reductively and is converted into the hexeneplatinum(II) π-complex. The hexyl radical can also be oxidised or can disproportionate with formation of hexene. The olefin readily reacts with[237] the platinum(II) or platinum(IV) chloride complex, affording the hexene π-derivative.

3. Polar, Orbital, and Steric Control

The reactions of metal complexes and other reagents with saturated compounds containing a C–H bond can be subdivided into three types depending on the factors which have a decisive effect on the course of the process. According to perturbation theory,[238] the total energy change ΔE on partial formation of a bond between the atom s of an electron-donating molecule S and the atom t of an electron-accepting molecule T in a solvent with an effective dielectric constant ε is expressed by an equation incorporating the electrostatic and covalent terms:

$$\Delta E = -\frac{q_s q_t}{R_{st}\varepsilon} + \frac{2\,(c_s^m c_t^n \Delta\beta_{st})^2}{E_m^* - E_n^*} \quad , \qquad (48)$$

where q_s and q_t are the total charges on the atoms s and t in the isolated molecules, R_{st} is the distance between the atoms s and t, c_s^m and c_t^n are the coefficients of the corresponding AO, $\Delta\beta_{st}$ is the change in the resonance integral on interaction of the orbitals of the atoms s and t, and E^* are quantities characterising the energies of different MO in the isolated molecules.

When atoms carrying large opposite charges interact, an increase in the contribution of the first, electrostatic term in Eqn.(48) favours the reaction. If the difference between the energy levels of the occupied MO of the donor and the unoccupied MO of the acceptor is large, the contribution of the covalent term is insignificant. Interactions of this type refer to reactions controlled by the charge (polar control).[238] In order that alkanes, which are weak donors, should enter into reactions of this type, very strong acceptors are required. Here one can apparently include the reactions of alkanes with complexes of metals in a high oxidation state. The variation of the selectivity in the sequence $3° \gg 2° \gg 1°$ is characteristic of such processes involving alkanes. In this case the role of the medium (especially the acidity) is large. The C–H bond in arenes is cleaved much more readily than in alkanes. Clearly this class includes typical electrophilic substitution reactions. On the other hand, if the HOMO of the donor and the LUMO of the acceptor have very similar energies, the denominator $E_m^* - E_n^*$ becomes extremely small and the second term in Eqn.(48) is very large. Such processes are classified as orbital-controlled. The reactions of alkanes with complexes of metals in low and moderate oxidation states [for example platinum(II), iridium(I), and rhodium(I)] are close to this type. The energy of the metal–carbon bond formed and of the C–H bond ruptured should be particularly important in this connection. Polar factors are not then significant and the influence of the medium is usually small. Bearing in mind that the changes in the M–C and C–H bonds cancel out, the selectivity as regards the point of attack on the molecule is low and different molecules with the C–H bond have similar reactivities. Finally, steric factors can play a decisive role in the process. In this case the selectivity series are of the type $1° > 2° \gg 3°$ and $\omega > (\omega - 1) \gg (\omega - 2)$; methane may prove to be the most reactive molecule. Biological oxidation is apparently closest to processes of this type, although steric factors are also clearly important in reactions involving metal complexes.

In the real processes involving alkanes account must be taken of all three factors. Their quantitative assessment for different reactions still needs to be carried out.

VI. CONCLUSION

During the 18 years which have elapsed since the discovery of the first reactions of alkanes in solutions of metal complexes, this field of chemistry has developed vigorously, particularly in recent times. There is no doubt that one may expect the discovery of new, especially catalytic, processes with participation of methane and its homologues, which will find practical applications. In its turn, this will intensify the interest in alkanes from the standpoint of their involvement in selective chemical processes and the new chemistry of alkanes thus established will be in line with the ever more urgent need for economy in the consumption of the existing resources of this chemical raw material on our planet, which have accumulated during the billions of years of its existence.

The rapid development of this field of chemistry is also reflected in the fact that, during the period required to prepare the manuscript of this review for the press, several tens of articles solely or partly devoted to the activation of the C–H bond in hydrocarbons and dealing with related problems have appeared in the literature. Reviews have been published on individual problems of the activation of alkanes by metal complexes.[239–244]

The reactions of the hydride, cyclopentadienyl, and other complexes of transition metals in a low oxidation state with alkanes,[245–252] olefins,[253–256] and arenes,[257–260] which proceed as a rule via the oxidative addition mechanism, have been investigated vigorously. The complexes catalyse the H–D exchange in methane[245,246] and benzene.[246,257] Organyl σ-derivatives can be isolated in the case of rhenium,[247,251] thorium,[248] iridium,[249,254–256,258] rhodium,[250] platinum,[252] iron,[253] and osmium[260] complexes. Evidence has been obtained that the addition of an alkane to the $C_5Me_5RhPMe_3$ species takes place with the intermediate formation of an alkane η^2-complex (with an agostic bond).[250] Factors promoting the initial activation of the C–H bond have been discussed.[261] The iridium hydride complex catalyses the thermal and photochemical alkane dehydrogenation reaction.[262] The possibility of hydromethylating carbon monoxide (with formation of acetaldehyde from CH_4 and CO or ethyl methyl ketone from CH_4, CO, and C_2H_4) in the presence of the Cp_2TiCl_2–$(CH_3)_2AlCl$ system has been demonstrated.[263] The reaction involving the "metathesis" of the σ-bonds between the pentamethylcyclopentadienylscandium complex Cp_2^*ScR and the hydrocarbons R'H ($^{13}CH_4$, arenes, and styrenes) via the mechanism $Cp_2^*ScR + R'H \rightleftharpoons Cp_2^*ScR' + RH$ has been described.[264] The bipyridyl complexes of platinum(II) catalyse the addition of methane to acetylene with formation of propene.[265] A number of studies[269–276] have been devoted to cyclomethylation (see the relevant reviews[266]) with cleavage of saturated and aromatic C–H bonds. The thermodynamic and kinetic parameters of the reversible cyclomethylation of the C–H alkyl bonds have been determined[273,274] and the intermolecular cleavage of such bonds in a chelate cobalt complex has been described.[275] The dimers of octaethylporphyrin complexes of rhodium[277] or iridium[278] react with aromatic alkyl-substituted compounds via an aliphatic C–H bond with the simultaneous formation of alkyl σ-derivatives and hydride derivatives (see also Wayland and Del Rossi[233]). The activation of

H–H and C–H bonds by ML_n species with the d^0 configuration, for example, Cp_2LuR, has been analysed by the extended Hückel method.[279] The interaction of the d^6 ML_5 fragments with H_2 involving the η^2-H_2 type of coordination of hydrogen to the metal and the formation of the dihydride derivative, has been investigated by the same method.[280] The dihydrogen complexes $M(CO)_3(PR_3)_2(\eta^2\text{-}H_2)$, where M = Mo or W, have been isolated and characterised.[281] The adducts of saturated hydrocarbons with the paramagnetic complexes $Cr(acac)_3$ and $Fe(acac)_3$ have been detected by ^{13}C NMR in solutions in $CHCl_3$ and CCl_4.[282]

Examples of the cleavage of C–C bonds by metal complexes have been described in a number of studies.[283–286] The reaction of pentamethylcyclopentadiene with $Mn_2(CO)_{10}$ proceeds, in particular, with the cleavage of a C–C bond, which results in the formation of tetramethylcyclopentadienyltricarbonylmanganese.[284] A compound containing a π-bond between iridium and monomethylcyclopentadiene is formed from 1,1-dimethylcyclopentane and the complex $[Ir.(H)_2(Me_2CO)_2L_2]^+$, where L = $(p\text{-}FC_6H_4)_3P$.[285] Cycloalkylrhodium hydride complexes rearrange to rhodacycloalkanes.[286] The reactions of alkanes with transition metal atoms, ions, and complexes in the gas phase and in the matrix at low temperature, which proceed with the cleavage of C–H and C–C bonds, have been described.[287–296]

The interaction of aromatic, alkyl-substituted aromatic, and saturated hydrocarbons with compounds of metals in a high oxidation state usually takes place as electrophilic substitution or involves the formation of radicals. Thus, detailed study of the reactions of arenes with the octaethylporphyrin complex of rhodium(III) in the presence of Ag^+ (this ion eliminates chlorine from the metal complex) has shown[297] that the aryl σ-derivative is formed on electrophilic substitution. The logarithms of the relative rates of methylation of substituted benzenes are correlated with the σ parameters ($\rho = -5.43$). It is of interest that photolysis of solutions of aryl σ-complexes in benzene leads to the homolytic cleavage of the Rh–C bond, which results in the formation of 4-substituted biphenyls.[297] A study has been devoted[298] to the mechanism of the methylation of arenes by mercury(II) and thallium(III) compounds. In a study of the products of the decomposition of the *meta*- and *para*-isomers of the tolylplatinum(IV) σ-complex, formed in the reaction between H_2PtCl_6 and toluene in aqueous CF_3COOH, it was observed that, together with the "expected" 3,3′-, 4,4′-, and 3,4′-bitolyl isomers, a large amount of the 2,3′- and 2,4′-bitolyls is formed after a long induction period.[299] Such products of *ortho*-substitution relative to the methyl group are apparently formed on interaction of *meta*- and *para*-platinised toluenes with free toluene present in solution. It has been shown[300,301] that the oxidation of methylbenzenes by palladium(II) complexes in an acid medium can occur via two pathways: electrophilic substitution in the arene ring with formation of an organometallic intermediate and one-electron transfer from the arene to the palladium atom with participation of the arene radical-cation as an intermediate. The oxidation of mesitylene by the $PtCl_6^{2-}$ ion, which leads to the formation of diarylmethane, apparently takes place with electron transfer.[302] Irradiation by light of a solution of anisole and the $OsCl_6^{2-}$, $IrCl_6^{2-}$, or $RhCl_3$ complex in acetic acid affords a mixture of bianisyl isomers.[303] It has been suggested that in the first stage of the reaction an electron is transferred from the arene to the excited metal complex species and the resulting radical-cation attacks a free anisole molecule.[303] When solutions of the $AuCl_4^-$ [304] or $PtCl_6^{2-}$ [305] ions are irradiated in the presence of alkanes, excited metal complex species are generated,[306] after which the Au–Cl or Pt–Cl bonds undergo homolysis with formation of Cl radical species, which chlorinate alkanes. In the case of $PtCl_6^{2-}$, a hexeneplatinum(II) π-complex is formed as a second reaction product[26–29,305] in addition to the chlorohexane isomers.[305] The reactions involving the free-radical halogenation of alkanes by halogeno-derivatives of hydrocarbons (for example, CCl_4) can be initiated by carbonyl complexes such as $Re_2(CO)_{10}$, $Cr(CO)_6$, etc.[307] The homolytic reactions involving the introduction of functional groups into oxygen-containing compounds are initiated by variable-valence metal derivatives.[308] It has been shown that the oxidation of toluene derivatives by oxygen, catalysed by cobalt acetate in the presence of NaBr, takes place in two stages and that in the first rapid stage chain propagation takes place via the reaction between the peroxy-radical and the cobalt bromide complex.[309] It has been suggested that hydrocarbons are oxidised by lead tetraacetate via a free-radical mechanism.[310] On the other hand, the acyloxylation of toluene by oxygen at the methyl group, catalysed by the $Pd(OAc)_2$–$Cu(OAc)_2$ system, is apparently heterolytic.[311] The activation of a C–H bond in allyldialkylruthenium(IV) complexes has been described.[312]

Several studies have been published on the oxygenation of hydrocarbons by oxygen-containing compounds of high-valence metals. Irradiation of polyoxotungstate by light in the presence of zerovalent platinum and an alkane involves the introduction of a functional group into the hydrocarbon.[313] It has been found that irradiation accelerates the oxidation of alkyl-substituted aromatic hydrocarbons, cyclohexane, and adamantane by oxo-complexes of chromium(VI) both in a homogeneous solution in acetic acid and in water in the presence of tetrabutylammonium bromide.[314] Chromyl trifluoroacetate proved to be an exceptionally powerful oxidising agent capable of oxidising alkanes to ketones at room temperature in solution in CCl_4.[315] Anhydrous $FeCl_3$ in dry acetonitrile activates hydrogen peroxide; the reaction of this system with cyclohexane gives rise to cyclohexyl chloride, cyclohexanol, and cyclohexanone.[316] It has been suggested that the process does not proceed via a radical mechanism. The kinetics and selectivity of the oxidation of alkanes to aromatic hydrocarbons by permanganate in aqueous solutions have been described.[317]

A series of further detailed studies of the Gif system have been published recently.[318–325] The system is effective in the oxidation of natural products, for example, steroids;[318,321–323]; the mechanism of the oxidation has been discussed.[320] The metallic zinc in the oxidising system can be replaced by a cathode (the electrochemical version has been called the Gif–Orsay system).[324,325]

Several studies[330–337] have been devoted to cytochrome P-450 and hydrocarbon oxidation reactions with its participation (see the relevant reviews[326–329]). Increasing attention has been paid to hydrocarbon oxidation reactions catalysed by metalloporphyrins, which model the action of cytochrome P-450 (see the relevant reviews[338–341]). It has been suggested that $KHSO_5$ [342] and NaOCl [343] be used as donors of atomic oxygen in such processes. The stage involving the cleavage of the O–O bond in the porphyrin derivative of iron has been observed;[344] the cleavage of this bond in the analogous manganese(III) complex can take place both heterolytically and homolytically.[345] A change in the selectivity of the oxidation of alkanes with increase of the steric shielding of the active centre of the metalloporphyrin catalyst has been demonstrated in a number of studies.[346–349] Hydrocarbons are oxidised by iodosobenzene in catalysis by phthalocyanine complexes of iron on a zeolite[350] or by oxygen in catalysis by haemin immobilised on the surface of silica.[351]

Finally we may mention several studies on the introduction of functional groups into alkanes without the involvement of metal complexes: photohydroxylation with the aid of H_2O_2,[352] oxidation by peracids[353] and ozone,[354] and the formation of

carboxylic acids from alkanes and CO in the HF–SbF_5 mixture.[355]

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