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Activation of the C–H bond by metal complexes

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ABSTRACT. Reactions involving the cleavage of C–H bonds by metal complexes in saturated and aromatic hydrocarbons and also in other compounds are examined. Some of these processes occur with formation of a carbon–metal bond, whilst in others the interaction of the complexes with the hydrocarbon takes place without direct contact between the metal atom and the C–H bonds. Metal compounds are widely used as initiators of the liquid-phase oxidation of hydrocarbons at relatively low temperatures. There is a prospect of creating new technologies for the chemical processing of petroleum and gas hydrocarbons, whereby they can be converted into valuable products, for example, into alcohols, ketones, and carboxylic acids, on the basis of processes involving metal complexes. The study of the metal complex activation of the C–H bond also makes it possible to understand and model the metalloenzyme-catalysed hydrocarbon oxidation reactions in the living cell.

The bibliography includes 340 references.

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I. Introduction

The catalytic reactions occuring with cleavage of the C–H bond in hydrocarbons and other compounds on treatment with metal complexes[1] constitute an extensive and important field of metal complex catalysis.[2] The problem of the activation of the C–H bond in fully saturated hydrocarbons (alkanes) which contain no π- or *n*-electrons and are therefore inert to many reagents which are usual in organic chemistry, is of special interest. Many fundamentally new stoichiometric reactions of alkanes (and arenes) with metal complexes (usually in a low oxidation state) were discovered in recent years, but to this day there is an acute need to seek procedures for the metal-complex catalysed introduction of functional groups into these hydrocarbons, i.e. for replacing hydrogen atoms by hydroxy-, carbonyl-, amino-, and other groups and also for obtaining alkenes and halogeno-derivatives from alkanes.

Bearing in mind the process mechanism, all the C–H bond activation reactions can be subdivided into three groups. Processes where organometallic derivatives, i. e. compounds containing an M–C σ-bond (M = transition metal), are formed as an intermediate or as the final product can be conveniently assigned to the *first group*.[3] The σ-ligand in the resulting compound is an organyl group (alkyl, aryl, vinyl, ethynyl, acyl, etc.). Subsequently the M–C σ-bond may be ruptured; naturally, in catalytic processes the dissociation of this bond is obligatory. The cleavage of the C–H bond with direct participation of a transition metal ion proceeds via the oxidative addition (OA) mechanism:

$$RH + M \rightarrow R—M—H$$

or an electrophilic substitution:

$$RH + M^{(n+)} \rightarrow R—M^{(n+)} + H^+.$$

In the case of electrophilic metallation of the aromatic nucleus, the reaction proceeds in two stages, the electrophilic species adding to the arene in the first stage with formation of a Wheland intermediate. The intermediate formed in the interaction of a saturated hydrocarbon with an electrophile is much less stable. It is therefore not surprising that the reactivities of alkanes and arenes in electrophilic substitution reactions are not the same (the reactivity of the latter is much higher). At the same time, the mechanism of the interaction of both saturated and aromatic hydrocarbons with complexes of metals in a low oxidation state is in principle the same (oxidative addition). The reactivities of arenes and alkanes in oxidative addition reactions with respect to metal complexes therefore usually differ insignificantly. Furthermore, the C–H bond in alkenes is cleaved via the same mechanism. Thus the first group includes reactions involving "true" metal complex activation of the C–H bond if such activation is understood as a process as a result or in the course of which the activated molecule is cleaved at the C–H bond and enters in the form of an organyl σ-ligand into the coordination sphere of the metal complex. The formation of weak inner- or outer-sphere adducts of alkanes with metal complexes or of π-complexes of aromatic and other unsaturated molecules with metal-containing fragments need not by any means necessarily lead to the subsequent cleavage of the C–H bond; such coordination may be referred to as preactivation of the C–H bond of the compound.

In the *second group*, it is useful to include reactions in which the C–H bond is cleaved on treatment with a metal complex but the C–M σ-bond is not generated directly at any stage. The function of the metal complex usually consists under these conditions in abstracting an electron or an H atom from the RH molecule. The radical-ions RH^+ or radicals $R^\cdot$ formed then interact with other

species present in solution, for example, with molecular oxygen. One of the ligands of the metal complex can also serve as a species of this kind. An example is provided by the hydroxylation of an alkane by an oxo-complex of a high-valence metal:

$$RH + O{=}M^{(n+)} \rightarrow R^{\cdot} + HO{-}M^{((n-1)+)} \rightarrow ROH + M^{((n-2)+)}.$$

Here the oxo-complex is an oxidant of the type CrO_4^{2-} or MNO_4^- and also, for example, one of the states of the cytochrome P-450 enzyme (an oxoferryl species containing the $P^+.Fe^V = O$ species). It is noteworthy that the reaction with the intermediate participation of radicals can result in the formation of alkyl σ-complexes {for example, via the mechanism $RH + M^{(n+)} \rightarrow R^{\cdot} + M^{((n-1)+)} + H^+ \rightarrow R{-}M^{(n+)} + H^+$} and the reaction should then be assigned to the first group. Since the alkyl σ-derivative is frequently unstable, it is occasionally difficult to demonstrate its intermediate formation. The mediated (i.e. without contact with the metal ion) activation of RH by a complex can apparently be effected also via a molecular mechanism where RH is in direct contact only with a ligand of the complex. Finally the metal complex is capable of activating not only a hydrocarbon but also other reactants. Thus the active centre of cytochrome P-450 initially causes the transition of the oxygen molecule to a reactive state (one of the two atoms of dioxygen is coordinated to the iron ion, forming an oxo-ligand), after which it activates the hydrocarbon molecule.

Whereas the reactions included in the second group require direct contact between a molecule of the C–H compound and the metal complex (albeit via the ligand), in the processes belonging to the *third group* the complex activates initially not the hydrocarbon but the other reactant, for example, O_2 and H_2O_2, and the reactive species formed (a radical or carbene) rarely attacks the hydrocarbon molecule. In the H_2O_2–Fe(II) system, such a species is $HO^{\cdot}$. Sometimes the reaction initiated via this mechanism can lead to the formation of an organyl σ-derivative of the metal and the entire process then belongs to the first group. For example, the photochemical metallation of a C–H compound by a metal chloride can proceed in accordance with this scheme:

$$RH + [M{-}Cl]^* \rightarrow R^{\cdot} + M + H^+ + Cl^- \rightarrow \sigma\text{-}R{-}M + H^+ + Cl^-.$$

Evidently the unambiguous assignment of a process to a particular group requires a detailed knowledge of the reaction mechanism. However, at the present time the mechanisms of many processes have not been elucidated even in broad outline. We may note that the mechanisms of reactions included in the last two groups are in general not the same for paraffins, on the one hand, and aromatic hydrocarbons, on the other, although the products of these reactions can be frequently of the same type (for example, alcohols and phenols). Hence follows the possibility that arenes and alkanes may exhibit different reactivities in each specific reaction.

Although the H_2O_2–Fe(II) system, capable of hydroxylating aromatic compounds, was discovered as early as the past century,[4] the 1930s should apparently be regarded as the start of investigations into the activation of C–H compounds with participation of transition metal complexes. During this period, the reaction involving the electrophilic auration of arenes was discovered,[5] the radical chain autoxidation of hydrocarbons initiated by metal derivatives was developed,[6,7] and a method was proposed for the oxidation of alkenes and arenes by hydrogen peroxide in the presence of oxo-complexes.[8] The second spurt in the pioneering research into this field occurred in the 1960s. Reactions involving the cyclometallation (i.e. the cleavage of the C–H bond in a ligand linked to the metal via an atom of nitrogen, phosphorus, or another element) of the aromatic nucleus[9] and of an sp^3-hybridised carbon atom[10] were discovered. It was found that palladium(II) derivatives induce the oxidative coupling of arenes[11] and the arylation of alkenes,[12] while platinum(II) salts catalyse the H–D exchange with D_2O in benzene[13] and also in methane and other alkanes (a cobalt complex can also catalyse such processes).[14] It has now become evident that organometallic derivatives are formed as intermediates in all these instances. It was shown in the 1970s that alkanes are oxidised by platinum(IV),[15] palladium(II),[16] and ruthenium(IV)[17] compounds, that iridium(III)[18] and titanium(II)[19] complexes catalyse the H–D exchange, that Ziegler–Natta catalysts induce the hydrometallation of ethylene by methane with formation of propane,[20] and that the $PtCl_6^{2-}$ ion effects the electrophilic metallation of arenes.[21] The next decade was marked by a vigorous development of studies on the activation of alkanes (and arenes) by low-valence metal complexes via the oxidative addition mechanism with formation of alkyl σ-derivatives or alkenes.[22–27]

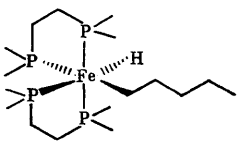
The number of known examples of the activation of the C–H bond by complexes of metals in a high oxidation state with formation of organometallic compounds is so far very small. Thus $PtCl_6^{2-}$ photochemically dehydrogenates alkanes and platinates arenes,[28] while the methyllutetium σ-complex enters into an exchange reaction with $^{13}CH_4$.[29] At the end of the 1980s, the intensity of investigations of the activation of the C–H bond by low-valence metal complexes began to diminish somewhat and interest gradually shifted to the field involving the oxidation of hydrocarbons by high-valence metal oxo-compounds and oxygen. Attention is being especially concentrated nowadays on biological oxidation and its chemical models. Studies on the modelling of cytochrome P-450 were stimulated by the use of iodosobenzene as the donor of an oxygen atom in catalytic oxidation reactions and of metalloporphyrin as a model of the active centre of the enzyme.[30] The Gif system, used for the selective oxidation of alkanes and consisting of O_2, an iron complex, a reductant, a carboxylic acid, and pyridine,[31] is of interest.

Studies on the activation of the C–H bond published up to 1987 were described in our previous review.[32] Therefore mainly publications during 1987–1990 will be discussed here. During this period, several books and reviews, wholly or partly devoted to the metal complex activation of C–H compounds, appeared.[2,33–51] We may also note that abstracts of the reports of the IInd All-Union Symposium on Homogeneous Catalysis "New Pathways in the Reactions of Saturated Hydrocarbons" have been published (Donetsk, 1988). All the papers in the special edition of the journal *Nouv. J. Chim.*, 1989, **13**, Nos. 10–11, are concerned with the activation of alkanes. The biological oxidation of hydrocarbons and the oxidation of hydrocarbons modelling the biological process (biomimetic oxidation) as well as the activation of oxygen have been described in abstracts published in a special issue of the journal *J. Inorg. Biochem.*, 1989, **36**, Nos. 3 and 4.

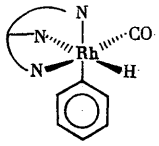
II. Activation of hydrocarbons via the oxidative addition mechanism

1. The formation of organyl σ-derivatives of metals

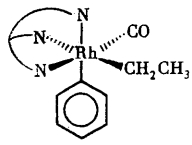
Numerous reactions involving the oxidative addition of the components of the C–H bond to metal complexes, in accordance with the scheme RH + $ML_n \rightarrow R-ML_n-H$ were discovered and investigated in detail in recent years. Alkanes, arenes, alkenes, and monosubstituted acetylenes enter into such reactions. The reaction frequently occurs in solution at room temperature, but sometimes heating is required. Certain reactions are stimulated by irradiation. An increased temperature or light are essential for the abstraction of several ligands from the initial complex and the formation of a coordinatively unsaturated species capable of effecting the oxidative addition of the C–H compound to itself. Thus irradiation at −90 °C of the phosphine complex $(PP)_2Fe(H)_2$, where PP = 1,2-bis-(dimethylphosphino)ethane, leads to the abstraction of a hydrogen molecule and the formation of the $Fe(PP)_2$ species. n-Pentane undergoes oxidative addition to this species with formation of the alkyl metal hydride complex (I).[52]



(I)

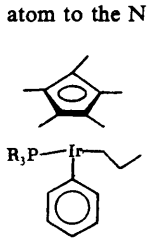


(II)

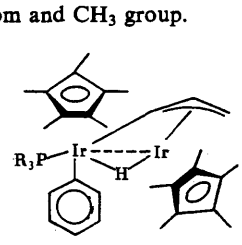


(III)

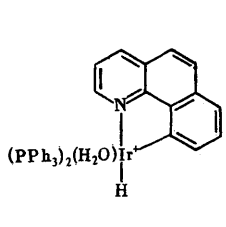
Sometimes thermal and photochemical activation can result in the formation of different products. For example, whereas heating of the solution of the ethylenerhodium carbonyl complex $[RhHBPz^*_3(CO)(C_2H_4)]$, where Pz* = 3,5-dimethylpyrazole, in benzene entails the elimination of the ethylene π-ligand and the formation of phenylrhodium hydride (II),[53] on irradiation of this solution, the hydride ligand adds not to the metal atom but to the ethylene molecule, which results in the appearance of an ethyl σ-group in the complex (III).[54] The hydrogen atom can add also to the allyl π-ligand: thermolysis of the complex $Cp^*Ir(H)(\eta^3\text{-}C_3H_5)$, where Cp* = pentamethylcyclopentadienyl, in benzene in the presence of phosphine leads to the formation of the propyl σ-derivative (IV).[55] It was of interest that at high concentrations of the initial complex the dimer (V) is obtained. It follows from the examples quoted that alkanes and arenes interact with metal complexes via the oxidative addition mechanism in a similar manner. However, differences are also sometimes observed. For example, the cyclometallation of 7,8-benzoquinoline by the complex $[LIr(PPh_3)_2]SbF_6$, where L = cycloocta-1,5-diene, in moist CH_2Cl_2 affords compound (VI),[56] whereas the analogous reaction with 8-methylquinoline does not entail the cleavage of the C–H bond in the methyl group and leads merely to the coordination of the Ir atom to the N atom and CH_3 group.



(IV)

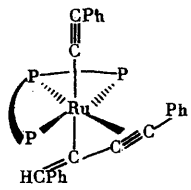


(V)

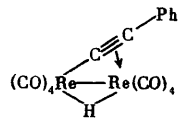


(VI)

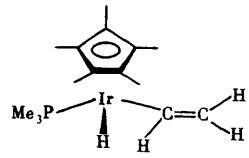
Complexes readily cleave the C–H bond in acetylenes and acetylene molecules frequently also enter into other reactions. Thus the interaction of $RuH_4(Cyttp)$, where Cyttyp = $PhP[(CH_2)_3P(C_6H_{11})_2]_2$, with an excess of phenylacetylene gives rise to compound (VII).[57] Irradiation of a solution of phenylacetylene and $Re_2(CO)_{10}$ in ether leads to the dinuclear rhenium hydride derivative (VIII).[58]



(VII)



(VIII)



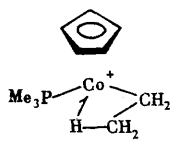
(IX)

Relatively few examples of the oxidative addition of ethylenes to the C–H bond are known. The thermolysis of the cyclohexyliridium hydride complex $Cp^*Ir(PMe_3)(H)(C_6H_{11})$ in solution in cyclohexane in the presence of ethylene results in the formation of the products of insertion in the C–H bond (IX) and of the ethylene π-complex $Cp^*Ir(PMe_3)(C_2H_4)$.[59] Finally, the components of the C–H bond in the allyl position are also capable of the oxidative addition to metal complexes: irradiation of a solution of the propene π-derivative $Cp^*Re(CO)(CH_2CHCH_3)$ affords the η^3-allylrhenium hydride complex $Cp^*Re(CO)(H).(\eta^3\text{-}CH_2CHCH_2)$.[60]

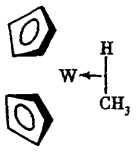
2. The reaction mechanism

The cleavage of the C–H bond can be preceded by the coordination of the saturated compound or fragment to the metal complex. Numerous complexes with hydrogen molecules have become known in recent years[61–64] and intramolecular coordination of the hydrogen atom of the C–H bond to the metal atom of the complex has been observed (the agostic C–H→M bond).[61,65] Such a bond occurs, for example, in complex (X).[66] The study of the kinetics of the reductive elimination of the CH_4 molecule from the complexes $Cp^*_2W(CH_3)H$ [67] or $Cp_2W(CH_3)H$ [68] led to the discovery of the intermediate formation of the methane "σ-complex" (XI). The existence of an analogous intermediate has been postulated in the reaction involving the elimination of CH_4 from the methylrhenium hydride derivative.[69] Presumably the alkane σ-complexes arise in the oxidative addition reaction, which leads to the formation of alkylmetal hydrides. In the photochemical reaction involving the cleavage of the Si–H bond by the $CpMn(CO)_3$ complex, which models such a process, the first stage may be the displacement of one of the CO ligands by the R_3Si-H ligand with formation of the structure (XII).[70] The adducts of alkanes with metal complexes formed at a low temperature can be detected by IR spectroscopy.[71] It has been established[72] that methane inhibits the reaction of butyllithium with butyl iodide. It has been suggested that this effect is due to the coordination of methane to the lithium alkyl in the reaction or prereaction complex. The interaction of the C–H bond with the metal complex can occur with mediation by the ligand. Thus the C–H...O=Re interaction in the oxorhenium complex has been demonstrated by X-ray diffraction.[73] The

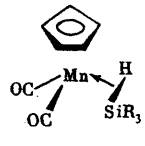
application of the NMR method led to the detection of the short-lived adducts of bis[hydrotris(pyrazolyl)borato]cobalt with alkanes in solution.[74] Outer-sphere interaction between the components takes place in this case.



(X)



(XI)



(XII)

The previous section presented examples of reactions which undoubtedly occur via the oxidative addition mechanism and in which the metal complex functions as a nucleophile. The kinetics and thermodynamics of such processes have now been investigated in fair detail[32,39,40,75,76] and quantum-chemical calculations have been carried out.[77,78] At the same time several reactions are known where attempts to describe their mechanisms as oxidative addition have encountered certain contradictions. In the first place, this applies to the activation, known for a long time, of alkanes by platinum(II) salts, which exhibit both nucleophilic and electrophilic properties. The activation of an alkane by a platinum(II) complex apparently begins as the oxidative addition of the C–H bond but the H atom acquires acid properties and is abstracted by a base (for example, the water forming part of the composition of the complex[79]):

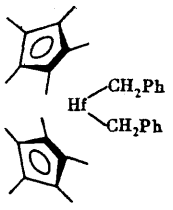
$$L_4Pt + RH \rightleftarrows [L_4Pt(H)R] \rightleftarrows L_3PtR + H^+ + L^-.$$

The rotation of the alkyl group R in the coordination sphere entails an appreciable intensification of the nucleophilic properties of the carbon atom, which should facilitate the electrophilic attack on the latter by the deuterium cation D^+:

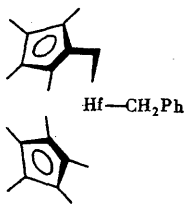
$$L_3PtCH_2R + D^+ \rightleftarrows L_3PtCHDR + H^+.$$

The alkyl group rotates synchronously with the approach of D^+ and the C–H→Pt agostic bond is formed. Since it is evident that several H atoms can be substituted by D in the alkyl group R before it is split off from Pt, the proposed mechanism explains satisfactorily the multiplicity of different types of H–D exchange in the presence of platinum(II) complexes.[79] It is believed[79] that such "alkyl" mechanisms agree better with certain features of the exchange reaction than the carbene and alkane–alkyl mechanisms proposed previously.[1,32,80]

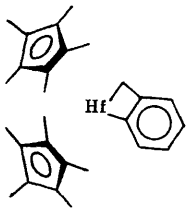
The intermolecular activation of the C–D bond in benzene-d_6 by the complex $(PMe_3)_2Pt(CH_2CMe_3)(SO_3CF_3)$ apparently begins with the formation of the coordinatively unsaturated species $[(PMe_3)_2Pt(CH_2CMe_3)]^+$, which gives rise to an arylplatinum hydride complex with C_6D_6 as a result of oxidative addition.[81] The product $(PMe_3)_2Pt(C_6D_5)(SO_3CF_3)$ is formed after the elimination of CH_2DCMe_3. However, Brainard et al.[81] do not rule out the possibility that the positively charged species carries out an electrophilic attack on the benzene ring. Thermolysis of complex (XIII) in benzene-d_6 leads to the appearance of the intramolecular metallation product (XV).[82] The reaction takes place in several stages and the intermediate complex (XIV) has been isolated. The introduction of several substituents into the benzene ring has virtually no effect on the rate of metallation, which enabled the authors[82] to regard the transformation (XIV)→(XV) not as typical electrophilic metallation by the Hf(IV) ion but as a process which proceeds via a four-membered transition state.



(XIII)



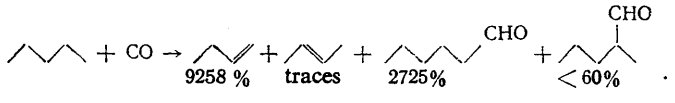
(XIV)



(XV)

3. Catalytic Processes

Metal complexes induce a whole series of reactions involving the substitution of hydrogen atoms in hydrocarbons by the atoms of other elements—processes involving the introduction of a functional group into the C–H bond. The complex very often catalyses such reactions. A considerable proportion of the processes proceed via the oxidative addition mechanism. Thus the complex $Li_2Pd_2Cl_6$ catalyses the H–D exchange in the allylic position in alkenes with CD_3COOD.[83] It has been suggested that the exchange proceeds with the reversible intermediate formation of an alkene π-complex of palladium(II) and its conversion into allylpalladium(IV) hydride π-derivative. The H–D exchange involving alkylsilanes catalysed by an osmium complex has been described.[84] Metal complexes dehydrogenate alkanes to alkenes. In a dark reaction, cyclohexene is formed from cyclohexane in the presence of $[PtCl_2(SnCl_3)_2]^{2-}$,[85] the complexes $[Ir(H)_2(\eta^2\text{-}O_2CCF_3)(PR_3)_2]$ dehydrogenate alkanes in the presence of 3,3-dimethylbutene, both on heating and on irradiation.[86] $RhCl(CO)(PMe_3)_2$ proved to be an effective photocatalyst of the dehydrogenation of alkanes.[87] Under the same conditions, arenes enter into an oxidative coupling reaction with alkenes, which results in the formation of substituted styrenes.[88] Finally, the above catalyst has been used for the photochemical introduction of functional groups into alkanes and arenes. Thus a complex mixture of products has been obtained from pentane and CO (the yields of the product relative to the catalyst are given below):[89]



It is of interest that the composition of the products depends on the wavelength. On irradiation of decane with light at a wavelength in the range $420 > \lambda > 295$ nm, the principal products are non-1-ene and undecanal. At $\lambda > 325$ nm, mainly isomeric C_{11} aldehydes are formed, while non-1-ene is not detected at all.[90] Irradiation with light of a solution of $RhCl(CO)(PBu_3)_2$ in pentane in the presence of cyclohexyl isocyanide leads to the formation of imines in low yields.[91] Finally, under the same conditions it is possible to silylate arenes with triethylsilane or hexamethyldisilane.[92] It is noteworthy that, on photosensitisation with mercury, dicyclohexane, cyclohexylmethanol, and ethylene glycol are formed from cyclohexane and methanol.[93]

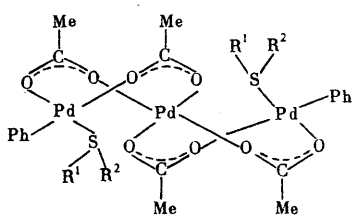
The kinetics of the hydromethylation of acetylene by methane have been investigated in the presence of organonickel catalysts.[94] The use of $^{13}CH_4$ in an analogous system made it possible to show that propene is formed via at least two pathways and that the contribution of the pathway involving methane is only about 20%.[95] At the same time, a detailed study of the hydromethylation of acetylene by methane in the presence of $Pt(bipy)Cl_2$ in dimethylformamide showed that the products of the reaction of a mixture of $^{13}CH_4$ and C_2H_2 do not contain ^{13}C and do not differ as regards composition and quantitative yield from the products of the reaction of pure C_2H_2.[95]

III. Reactions of hydrocarbons with compounds of high valence metals

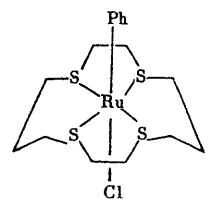
Whereas the interaction of C–H compounds with complexes of metals in a low oxidation state usually proceeds as oxidative addition, the reactions of arenes or alkanes with the derivatives of metals in high oxidation states are usually processes involving direct electrophilic substitution leading to the formation (final or intermediate) of an organometallic compound or are electron transfer or hydrogen atom abstraction processes, which are followed by the reactions of the resulting radical-cation or radical.

1. Direct electrophilic metallation of the C–H bond

In recent years electrophilic substitution by metal complexes of a hydrogen atom in aromatic compounds has been studied in detail in relation to cyclometallation reactions and in particular *ortho*-palladation (see, for example, Refs. 96–101). The reaction involving the intramolecular and intermolecular exchange of a cyclopalladated ligand in complexes has been discovered.[99–101] Previously such transfer of an aryl σ-ligand between complexes of the same metal had been observed for platinum(IV) derivatives[102] and also thallium(III) and mercury(II) derivatives. Palladocyclic compounds can be used to introduce functional groups into arenes.[103] It is well known that arylpalladium(II) σ-complexes, not stabilised by chelating ligands, are unstable and readily decompose with formation of biaryls (see, for example, Ignatenko et al.[104]). However, it has been recently possible to isolate the first phenylpalladium(II) σ-derivative, obtained directly by palladating benzene. When palladium(II) acetate was heated in benzene in the presence of dialkyl sulphides, complexes (XVI) were obtained.[105] A similar reaction has been discovered for ruthenium(II): the chloride complex with a thio-crown-ether in the presence of $Al_2(CH_3)_6$ gives rise to the phenyl derivative (XVII) on heating in benzene.[106]



(XVI)



(XVII)

The complexes formed by metallating arenes with the $PtCl_6^{2-}$ ion are sufficiently stable to be able to isolate them in a crystalline state (they can be stored for several months at room temperature), but prolonged heating of a solution of an arene and $PtCl_6^{2-}$ in $CF_3COOH-H_2O$ or CH_3COOH leads to the formation of biaryls and platinum(II) derivatives.[107] Metallation of arenes by heating with the $PtCl_6^{2-}$ ions can be achieved only in an acid medium. At the same time the rate of the light-induced reaction, occurring in acetic acid in the case of anisole with a quantum yield of 0.08 (λ = 365 nm), is independent of the acidity of the medium; the reaction can be carried out also in CH_2Cl_2.[108] Intermediate platinum(III) complexes apparently arise in the reaction.[109] The unstable arylplatinum(IV) σ-complexes, formed in the thermal reaction of arenes with $PtBr_6^{2-}$ in a $CF_3COOH-H_2O$ mixture, were not isolated, but biaryls were detected in the products.[110]

All the reactions described above, in which the formation of aryl σ-derivatives of metals was demonstrated, proceed as typical electrophilic substitution processes.[111] Nevertheless, their first stage can consist in electron transfer from the arene to the metal and the formation of an arene radical-cation, after which a Wheland intermediate is formed. However, the radical-cation may not recombine with the reduced metal ion, undergoing instead further reactions with participation of other species, for example, nucleophiles.[112–114] In this case, the arene or alkylarene is activated by the metal complex without the intermediate formation of an organometallic compound.

Metal complexes with strong electrophilic properties are capable of reacting with alkanes.[115–117] Thus, on heating a solution of CH_4 and $Pd(OOCMe)_2$ in CF_3COOH, metallic palladium and CH_3OOCCF_3 are formed in a yield greater than 60% relative to palladium(II).[116,117] It has been suggested that the product is formed when a solvent molecule attacks the methylpalladium(II) σ-complex arising as a result of electrophilic substitution. Under these conditions, arenes are activated much more readily: the trifluoroacetate group substitutes a hydrogen atom in the *p*-xylene ring more than 50 times faster than in the methyl group. It has been suggested[118] that the oxidation of alkanes by oxygen in aqueous solutions of mercury(II) salts under UV irradiation involves the intermediate formation [as a result of the electrophilic attack by Hg(II)* on RH] of alkylmercury compounds, but proof of this requires additional studies. The intermediate formation of alkylplatinum(IV) σ-complexes on photochemical dehydrogenation of n-hexane to the hexeneplatinum(II) π-complex has not been demonstrated either.[32] The possibility of the occurrence of such a process, with participation of a stage involving the β-elimination of hydrogen from the alkyl chain, has been confirmed in a study[119] where it was shown that the β-elimination from the ethylplatinum(IV) complex is the principal route to its decomposition.

2. Functionalisation on treatment with oxygen-containing complexes

Oxo-compounds of transition metals (in the first place chromium and manganese) are effective oxidants for C–H compounds.[120] Such derivatives are used in organic synthesis; for example, the $KMnO_4-NEt_3$ system oxidises the benzyl group to the ketone group with a satisfactory yield.[121] There exist also other oxo-complexes capable of oxygenating hydrocarbons: $[Ru^{VI}L_2(O)_2]^{2+}$ (L = 6,6′-dichlorobipyridyl) [122] and $[Os^{VI}(CN)_4(O)_2]^{2-}$.[123] The second complex activates the C–H bond on irradiation.

The oxidation of alkanes and of aromatic alkyl-substituted compounds by oxo-derivatives of chromium(VI) has been investigated on irradiation with light.[124–127] CH_3COOH, CH_3CN, and CH_2Cl_2 have been used as solvents; the products are alcohol

and carbonyl compounds. The reaction apparently begins with the abstraction of a hydrogen atom from the C–H bond of the oxo-complex by an excited species. On irradiation with light, the oxidation of alkanes and arenes by vanadium(5+) oxo-complexes in organic acids is greatly accelerated.

Transition metal,[128] for example palladium[129] and chromium,[130] peroxide compounds are capable of effecting the stoichiometric oxygenation of alkanes. Various chromium,[131–134] ruthenium,[135] and vanadium[136,137] complexes catalyse the oxidation of alkanes by peroxides. In many reactions of this kind, either metal peroxides are formed or the substrate is oxygenated by the oxo-compound, which is regenerated on interaction with ROOH. An alternative mechanism may be the formation of $HO^{\cdot}$ radicals when ROOH is acted upon by the complex. The hydroxylation of benzene by the H_2O_2–Fe(II) system takes place in this way.[138] Cyclohexane has been oxidised to cyclohexanol by molecular oxygen at room temperature in solution in aqueous dioxane.[139] The reaction was catalysed by the ruthenium(III) complex of ethylenediaminetetraacetic acid (EDTA). It has been suggested that a μ-peroxo-complex or an oxo-complex is formed in the first stage and then hydroxylates the alkane:

$$LRu^{III} + O_2 \rightleftarrows LRu^{IV}\,O \ldots O \ldots Ru^{IV}\,L \leftrightarrow 2LRu^{V} = O.$$

On irradiation under anaerobic conditions, alkanes dissolved in CH_3CN are converted by treatment with heteropolyacids into alkenes, dimers, *N*-alkylacetamides, alkylmethyl ketones, and also H_2.[140,141] The reaction begins with electron or H atom transfer from RH to a photoexcited polyoxometallate species. The resulting $R^{\cdot}$ radical is converted into an alkene or interacts with a solvent molecule. The reduced species derived from the oxo-compound is reoxidised by Pt(O), evolving H_2. The use of the ROOH–CCl_4 (or CBr_4) system in dark reactions catalysed by heteropolyacids induces the halogenation of the alkane, while in the interaction of alkanes with the ROOH–$C(NO_2)_4$ system nitroalkanes are formed.[142]

IV. Oxidation of saturated and aromatic alkyl-substituted hydrocarbons by oxygen

1. Initiation of the oxygenation process by metal complexes

It is well known that variable-valence metal compounds are capable of initiating in solution radical chain hydrocarbon oxidation processes.[1] Chain initiation occurs, for example in accordance with the scheme $M^{3+} + RH \rightarrow M^{2+} + R^{\cdot} + H^{+}$, after which $R^{\cdot}$ interacts rapidly with oxygen: $R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$. Chain propagation takes place via the reaction $ROO^{\cdot} + RH \rightarrow ROOH + R^{\cdot}$. Complexes are usually active in the decomposition of the hydroperoxides formed (see, for example, Lauterbach et al.[143]). The participation of a metal ion in a low oxidation state in the reaction leads to chain branching. Thus, in the cobalt bromide catalysis of the oxidation of hydrocarbons,[144,145] which is of practical importance, the interaction of one $ROO^{\cdot}$ radical with Co(II) leads to the formation of three new radicals (Scheme 1):

Scheme 1

$$ROO^{\cdot} + Co\,(II) + H^{+} \rightarrow ROOH + Co\,(III)$$
$$\downarrow Co(II) \qquad Br^{-}\downarrow RH$$
$$RO^{\cdot} + Co\,(III) \qquad R^{\cdot}$$
$$Br^{-}\downarrow RH \qquad \downarrow O_2$$
$$2ROO^{\cdot} \xleftarrow{O_2} 2R^{\cdot} \qquad ROO^{\cdot}$$

In this process, bromide ions catalyse the oxidation of RH by a cobalt(III) derivative via the reaction

$$Co\,(III) + Br^{-} \rightarrow Co\,(II) + Br^{\cdot};\quad Br^{\cdot} + RH \rightarrow Br^{-} + H^{+} + R^{\cdot}.$$

The oxidation process may not have a chain mechanism in relation to the $ROO^{\cdot}$ radicals, as shown for the oxidation of *p*-ethylnitrobenzene at 140 °C in the presence of $Mn(OOCCH_3)_2$.[146]

In the reactions mentioned above, the role of the metal complex (and also the role of the ligand, as in cobalt bromide catalysis) consists in chain initiation and propagation. However, the complex can only generate reactive species which subsequently enter into a non-chain process, which proceeds with dissociation of C–H bonds. Thus, on interaction with copper(I) and H^{+} ions, molecular oxygen gives rise to the $HO^{\cdot}$ radicals ($2Cu^{+} + O_2 + 2H^{+} \rightarrow 2Cu^{2+} + H_2O_2$; $Cu^{+} + H_2O_2 + H^{+} \rightarrow Cu^{2+} + HO^{\cdot} + H_2O$), which then hydroxylate benzene to hydroquinone. The resulting copper(II) may be reduced electrochemically.[147] The interaction of O_2 with the copper(I) complex $Py_4Cu_4Cl_4$ leads to the formation of the copper(II) oxo-complex $Py_3Cu_4Cl_4O_4$, which is capable of catalysing the oxidative coupling of 2,6-dimethylphenol.[148]

2. Photocatalytic liquid-phase oxygenation

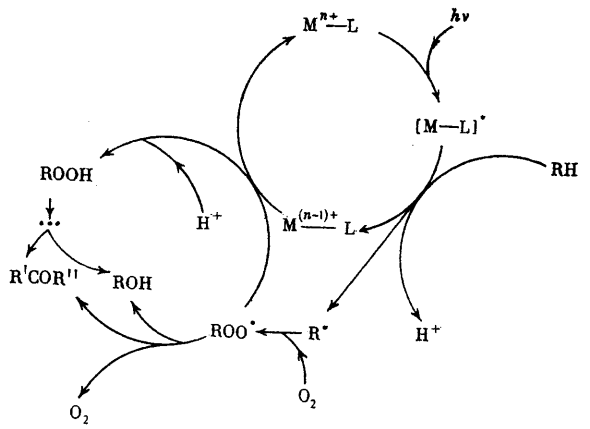
The metal complex-catalysed photochemical oxidation of hydrocarbons by air in solutions at room temperature is of great practical interest because it can serve as a basis for new processes for the conversion of hydrocarbon raw material using sunlight as the source of energy. We shall differentiate two principal groups of metal compounds capable of effectively catalysing the photooxygenation of alkanes: the halide complexes (usually chlorometallates) and the oxo-complexes (usually polyoxometallates).

The following systems for the photochemical oxidation of hydrocarbons have been discovered and(or) studied in detail in recent years: $FeCl_3$ in CH_3COOH [149,150] and in CH_3CN;[151,152] $CuCl_2$ in CH_3CN;[151,153] $AuCl_4^{-}$ in CH_3CN [154] and CH_3COOH;[155] $Cr_2O_7^{2-}$ and $Cr_4O_{13}^{2-}$ in CH_2Cl_2;[156,157] iso- and hetero-polyacids in H_2O,[158,159] CH_3CN,[160] CH_3COOH or CH_3OH,[161] and CH_2Cl_2;[162] vanadates in CH_2Cl_2;[162] UO_2^{2+} in CH_3COOH or CH_3CN.[163] The complexes $PtCl_6^{2-}$, $PtCl_4^{2-}$, $RuCl_3$, $RhCl_3$, $IrCl_6^{2-}$, and $OsCl_6^{2-}$ can also serve as photooxygenation catalysts in acetonitrile. Cyclohexane, isobutane, toluene, ethylbenzene, and other hydrocarbons are used as substrates. The methane oxidation reactions in the presence of polyoxotungstate in H_2O [158,189] or of $HAuCl_4^{-}$ [154] and UO_2Cl_2 [163] in CH_3CN afford formaldehyde (as well as methanol and formic acid). Irradiation of a solution of an alkane (adamantane, cyclohexane) in CH_3CN in the presence of cerium ammonium nitrate gives rise to alcohols and ketones.[164]

The proposed mechanism of the photochemical oxidation processes described, including the formation on treatment with the photoexcited metal complex species of the $R^{\cdot}$ radical (in the case of

oxo-complexes, an H atom from RH apparently adds to the oxygen ligand), is presented in Scheme 2.

Scheme 2



However, in fact the mechanism is apparently more complex, at least when halides are used. Thus the photooxygenation of alkanes catalysed by the complex $AuCl_4^-$ takes place with an induction period (which proved to be particularly long in the case of the bromides $CuBr_2$, $FeBr_3$, and $PtBr_6^{2-}$). The induction period becomes shorter after the introduction of an inductant into the solution. Presumably, the oxidation proceeds also via a second pathway in which the catalyst is a low-valence metal complex obtained from the initial complex during the initial period of the reaction. Thus the complex combines with an oxygen molecule and the metal peroxide derivative formed subsequently oxidises the hydrocarbon (one cannot rule out the possibility that this process takes place under the influence of light). Furthermore, the peroxide derivative can be converted into an oxo-complex of the metal in a higher oxidation state, which subsequently reacts with the alkane.

3. Coupled oxidation

A whole series of systems containing complexes are capable of effecting the oxidation of alkanes and arenes by oxygen only in the presence of a reductant. In this case, coupled oxidation takes place.[165] Detailed study of the oxidation of cyclohexane by atmospheric oxygen in the presence of hydrazobenzene (a reductant), benzoic acid, and the complex Py_4FeCl_2 (catalyst) in acetone led to the hypothesis that the reaction proceeds with the intermediate formation of an iron hydroperoxide derivative, which hydroxylates alkanes.[165] Hence it was concluded that, despite the participation of the iron complex, molecular oxygen, and the reductant in the process, the system cannot be regarded as a model of cytochrome P-450. At the same time the oxenoid species $Fe^V = O$, which is inserted in a C—H bond (X = OH, $OCOCH_3$), plays an active role in the oxidation of alkanes by the Gif system:

$$X_2Fe^{II} + {}^{\cdot}O_2H \rightarrow X_2Fe^{III}—O—O—H \xrightarrow{H^+,\ X^-} X_3Fe^V{=}O + H_2O.$$

Thus the authors of the study[167] in which evidence for the formation of such a species was secured believed that the Gif system can be regarded as a model of cytochrome P-450. However, there exists also an alternative idea about the nature of the Gif system,[168,169] according to which the active centre is a solvated oxygen cation PyO^+ formed via the reaction $HO_2^{\cdot} + PyH^+ \rightleftarrows PyO^+ + H_2O$. This radical-cation, capable of oxidising hydrocarbons, was generated electrochemically[168] and by the photochemical oxidation of pyridine *N*-oxide.[169]

V. Biological oxidation and its chemical models

Alkanes or arenes are surprisingly easily oxidised by atmospheric oxygen in cells of organisms at room temperature and the usual pressure. For example, various fungi hydroxylate camphor derivatives,[170] testosterone and other steroids,[171] and the side chain in alkylbenzenes.[172] Under the influence of the *Pseudomonas putida* bacteria, benzene has been converted into *cis*-1,2-dihydroxycyclohexa-3,5-diene.[173] The cells of higher animals and man are also capable of oxidising compounds containing C—H bonds, hydroxylation occurring with the invariable participation of a reductant, whereupon one of the two atoms in the O_2 molecule is inserted into the C—H bond, while the other is reduced to H_2O. This is referred to as the monoxygenase mechanism (the catalysis is effected by monoxygenase enzymes). In all the biological oxidation reactions, hydroxylation is preceded by the activation of oxygen by the metalloenzyme.[174] The creation of chemical models of the enzymic oxidation of alkanes and arenes makes it possible not only to understand better its mechanism but also to develop what are likely to be fundamentally new processes for the conversion of the hydrocarbon raw material.[175]

1. Cytochrome P-450

Cytochrome P-450 is a widely distributed enzyme in living nature; it belongs to the group of monoxygenases and is capable, in particular, of oxidising alkanes, arenes, and their derivatives (for example, prostaglandins and aliphatic acids).[176—178] The active centre of the enzyme incorporates haem iron (whose ion forms a complex with the porphyrin). On treatment with O_2 and a reductant, the $Fe^V = O$ fragment arises in the active centre and oxidises the alkane in accordance with the scheme

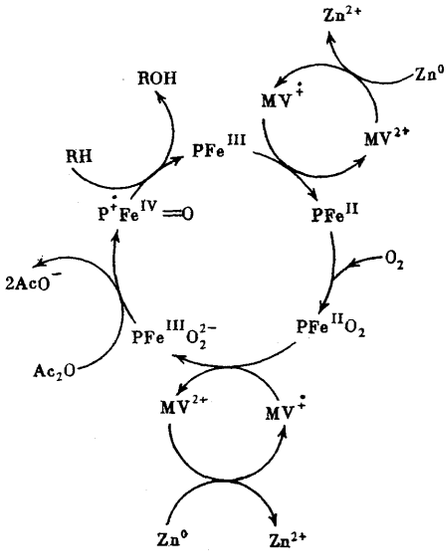
$$Fe^V = O + RH \rightarrow Fe^{IV}—OH + R^{\cdot} \rightarrow Fe^{III} + ROH.$$

The mechanism of the action of cytochrome P-450 has been described in detail in reviews[32,179] and other publications.[180,181]

In modelling cytochrome P-450 (see the reviews[32,175,179,182—184]), porphyrin complexes of iron(III) as well as manganese(III), chromium(III), and ruthenium(III) are usually employed as catalysts. If molecular oxygen is the oxidant, a reductant is required whose role may be assumed by an electric current.[185,186] Metallic zinc can also serve as the reductant.[187—189] The catalytic cycle involving the last system, which includes, apart from the porphyrin complex

PFe^{III}, an electron transferring agent (methylviologen MV^{2+}) and acetic anhydride, is illustrated in Scheme 3.[189]

Scheme 3

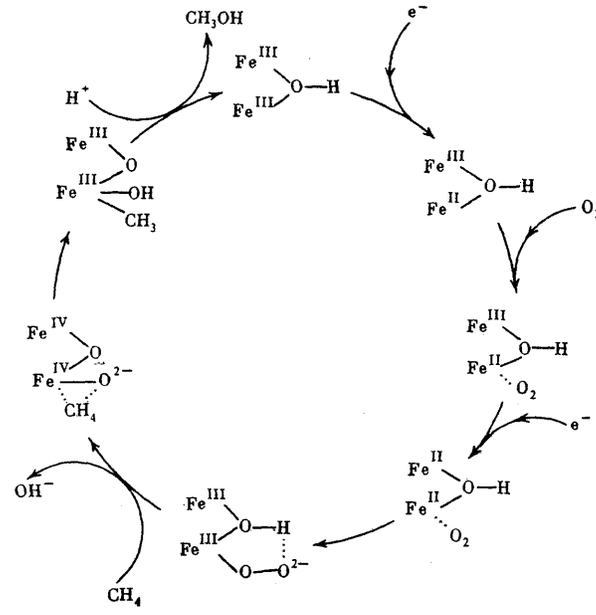


Instead of the O_2—reductant pair, one can employ oxo-compounds containing an oxygen atom which is already partly reduced: PhIO,[190] H_2O_2,[191–193] NaOCl,[194,195] $KHSO_5$,[196] and XeO_3.[197] We may note that, in the oxidation of alkanes in the presence of cytochrome P-450 or its models, the kinetic isotope effect reaches high values—up to 21.9 for the oxidation of cyclohexane by the tetramesitylporphyriniron chloride—NaOCl system.[198] For the oxygenation of hydrocarbons by various oxygen atom donors, fairly simple complexes were used as catalysts in certain studies: CrO_3 or $VOCl_2$ in the presence of α-picolinic acid (oxidation by PhIO),[199,200] $Fe(ClO_4)_2$ (oxidation by peroxybenzoates),[201] $[Fe(MeCN)_4](ClO_4)_2$ (oxidation by H_2O_2),[202] and $RuCl_2L_2$ (oxidation by LiOCl).[203]

2. Methane monoxygenase

Among the monoxygenases containing non-haem iron (the ligands are apparently aminoacid residues), methane monoxygenase (MMO) is of special interest. It catalyses the oxidation of alkanes, methane showing the highest activity among them in this reaction.[1,32] Ethane is also readily oxygenated by this enzyme.[204] It has been shown that MMO from *Methylococcus capsulatus* contains 4 atoms of non-haem iron and 1 atom of Cu per molecule with a molecular weight of 240 000.[205] The active centre of MMO apparently contains a dinuclear iron complex.[206] The proposed mechanism of the oxygenation of methane at this dinuclear centre is illustrated in Scheme 4.[207]

Scheme 4



Several systems which can serve as models of MMO in the oxidation of alkanes according to the authors have been described: the system incorporating a dinuclear μ-oxo-complex of iron, O_2, CH_3COOH, and Zn;[208] the cluster $Mn_{3-4}O_{1-2}Py_xRCOO_y^-$ combined with $(CH_3)_3COH$;[209] the complex $Fe_2O(OOCCH_3)_2Cl_2$. .$(bipy)_2$ together with $(CH_3)_3COOH$;[210] the complex $Fe_2O(bipy)_4Cl_4$ combined with H_2O_2.[211]

3. Certain other enzymes

A whole series of other enzymes containing metals capable of oxidising C—H compounds are known. They are less important than cytochrome P-450 and have been less thoroughly investigated. We shall list some of the enzymes and their models which oxidise hydrocarbons. Pteridine-dependent monoxygenases, which hydroxylate phenylalanine to tyrosine, containing non-haem iron, while the hydroxylase isolated from *Chromobacterium violaceum* incorporates copper.[212] Systems which have been known for a long time, such as Fenton's reagent, which includes iron(II), H_2O_2, and EDTA, Udenfrend's system containing iron(II), O_2, ascorbate, and EDTA, and Hamilton's system whose composition includes iron(III), O_2, and catechol, can serve as models of hydroxylases (with certain stipulations).[212] Ruthenium analogues of these systems have been proposed recently: ruthenium(III) together with H_2O_2, ascorbate, and EDTA [213] and ruthenium(III) with O_2, ascorbate, and EDTA.[214] Copper(I) complexes with chelating ligands are capable of hydroxylating the benzene ring of the ligand on treatment with O_2,[215,216] while on treatment with PhIO they promote the introduction of an OH group into the α-position in pyridine.[217]

Ketoglutarate-dependent dioxygenases oxidise C—H compounds in the presence of ketoglutaric acid which decomposes into succinic acid and CO_2 in a reaction coupled with the hydroxylation of the substrate.[1] A chemical model of such an enzyme, including an iron

compound and pyruvic acid, has been proposed.[218] In particular, catechol 1,2-oxygenase isolated from *Alcaligenes paradoxus* contains non-haem iron and catalyses the cleavage of the catechol ring.[219] A system consisting of a copper complex and an amine, which is capable of catalysing the oxidation of cyclohexanone, initially to α-hydroperoxycyclohexanone, is a model of pyrocatechase, a copper-containing dioxygenase.[220]

VI. Conclusion

The field of chemical science devoted to the activation of the C–H bond continues to develop vigorously. During the preparation of the manuscript for the press, several tens of articles describing a wide variety of processes occurring with the cleavage of the C–H bond and requiring the participation of metal complexes were published. Some of them are listed below.

Some of the communications describe the reactions of alkanes and arenes with complexes of metals in a low oxidation state, which proceed via the oxidative addition mechanism. Biscyclopentadienyltitanium(III) hydride complexes stimulate the deuterium–hydrogen exchange between methane and dihydrogen under mild conditions in solution in cyclohexane. Multiple exchange takes place in methane, while cyclohexane does not enter into the reaction.[221] The iridium-containing centre of the complex $[(PPh_3)_2IrH_2]_3PW_{12}O_{40}$ activates the C–H bond in arenes, alkanes, and allyl groups.[222] The methyl group of the substituent in a ruthenium-containing cluster undergoes oxidative addition to the ruthenium centre.[223] Oxidative addition of methane has been observed in the photolysis of the complex $CpIr(CO)H_2$ in a methane matrix at 12 K.[224] In the presence of silane, the complex $Cp_2Ta(CH_3)(PMe_3)$ reacts with benzene on photolysis (at 350 nm) or on heating (at 100 °C) with formation of methane and the compound $Cp_2Ta(C_6H_5)(PMe_3)$.[225] The silanes R_3SiH react with the hydride $ReH_7(PPh_3)_2$, which results in the cleavage of the Si–H bond and the formation of the derivative $ReH_6(SiR_3)(PPh_3)_2$ and H_2.[226] The formation of a η^2-arene complex with the $Cp^*Rh(PMe_3)$ species, which can be converted into the arylrhodium hydride $Cp^*Rh(PMe_3)(H)Ar$, has been observed.[227] The functionalisation of compounds containing C–H bonds by the insertion of the isonitrile group has been described. The complexes Cp^*ML_2 [228] or $RhCl(PR_3)_2(CNR')$ participate in this reaction.[229] The interaction of aromatic and aliphatic C–H bonds with terminal alkynes on photocatalysis by the complex $RhCl(CO)(PMe_3)_2$ results in the formation of 1,1-disubstituted ethylenes. Thus the reaction of n-hexane with phenylacetylene affords the product of the addition of hexane exclusively to the methyl group: 2-phenyloct-1-ene.[230] The intramolecular hydrogen transfer from the alkyl substituent of the phosphine ligand to the metal atom on UV irradiation of the $WH_4(PRPh_2)_4$ complexes was demonstrated even earlier and the possibility, in principle, of the photochemical activation of the methane bonds by the phosphinemolybdenum hydride complexes $MoH_4(PMePh_2)_4$ was demonstrated.[231] Cycloalkanes can be dehydrogenated under mild conditions in the presence of Group VIII metal complexes and active spongy uranium U*.[232] The interaction of the complexes $(PMe_3)_3RhMe$ with benzene or toluene at 70 °C results in the formation of the derivatives $(PMe_3)_3RhAr$.[233] The reactions of the radical species derived from the tetramesitylene-porphyrinatorhodium complex TMPRh* with methane in solution in benzene afford the complexes TMPRhMe and TMPRhH.[234] The organomagnesium compounds $C_6H_5Mg_nX$ (n = 2–4, X = halogen), formed on cocondensation of aryl halides and magnesium in the gas phase, react with alkanes even at room temperature. The degree of conversion of n-hexane per mole of the organomagnesium compound reaches 640. The composition of the products depends on the degree of reaction. A mixture of saturated C_4–C_8 hydrocarbons, mainly with a branched structure, is formed from n-hexane. With increase in the reaction time, the fraction of the C_4–C_8 products falls, but the yield of hydrocarbons containing eight and more carbon atoms increases.[235]

The mechanism of the reactions of low-valence metal complexes with alkanes and arenes has been investigated (see Ryabov's review[236]). Non-empirical calculations of the structure and relative energy characteristics of the ion-molecule complexes $Cu^+.CH_4$ and $Cu^+.C_2H_6$ have been performed. Tridentate coordination of the methane molecule is most favourable for the $Cu^+.CH_4$ ion. At moderately high temperatures, the Cu^+ cation is capable of quasi-free migration around the methane molecule.[237] Complexes of alkanes with the $W(CO)_5$ species in the gas phase[238] and the mechanism of the substitution of n-heptane by hex-1-ene in the photochemically generated species $[(n\text{-heptane})Cr(CO)_5]$ [239] have been investigated. The mechanisms of the cleavage of the Si–H bond by metal complexes has been discussed.[240,241] A detailed study has been devoted to the mechanism of the activation of C–H bonds in tetramethylsilane and mesitylene by tetrakis(triphenylphosphine)-hydridoneopentylosmium(II).[242] Finally, it has been shown that the reaction involving the photochemical dehydrogenation of alkanes in the presence of catalytic amounts of the complex $Rh(PMe_3)_2(CO)Cl$ begins with the abstraction of the CO ligand.[243]

Communications describing the oxidation of alkanes and arenes directly by high-valence metal complexes and also reactions occurring in the presence of such complexes have been published. The study[116,117] of the oxidative functionalisation of alkanes and arenes by palladium(II) acetate in trifluoroacetic acid has been continued.[244] It is essential to note that Stolyarov et al.[245] were unable to observe the oxidation of methane by a palladium(II) compound under the conditions described previously.[116,117,244] At the same time, methane is selectively oxidised by cobalt(III) trifluoroacetate with a 90 ± 10% yield of methyl trifluoroacetate relative to cobalt(III).[245] In the presence of palladium(II) acetate, cyclohexane and other alkanes are carboxylated with the aid of CO in CF_3COOH to cyclohexanecarboxylic and benzoic acids.[246,247] Irradiation of a solution of adamantane in acetonitrile with UV light under an oxygen atmosphere in the presence of palladium(II) or copper(II) trifluoroacetate leads to the formation of products resulting from the oxidation of mainly the third carbon atom.[248]

Irradiation with light of a solution of an alkane (or benzene) in CF_3COOH in the presence of the polyvanadate ions formed on dissolution of KVO_3 affords an alkyl trifluoroacetate and a ketone (or phenyl trifluoroacetate). When n-hexane is oxidised, the relative reactivities of the hydrogen atoms in the 3-, 2-, and 1-positions in n-hexane are 1.0 : 2.9 : 0.43.[249] Ruthenium(V) oxo-complexes oxidise cyclohexane and adamantane in solution in acetonitrile at 25 °C to cyclohexanone (yield 60% relative to the complex) and 1-adamantanol (40%) respectively.[250] Ruthenium(VI) and osmium(VI) dioxo-complexes oxidise alkanes on irradiation with light.[251] A number of studies have been devoted to the catalytic photochemical functionalisation of alkanes in the presence of polyoxometallates.[252–254] The photodimerisation of cyclohexene and methane on treatment with the $W_{10}O_{32}^{4-}$ ions has been investigated by the molecular orbital method.[255]

The heteropolyanion $SiRu(H_2O)W_{11}O_{39}^{5-}$ catalyses the oxidation of alkanes by persulphate, periodate, alkyl hydroperoxides, and iodosobenzene.[256] Chromium complexes catalyse the oxidation of adamantane by alkyl hydroperoxides.[257] Hydrogen peroxide in CF_3COOH in the presence of vanadium(5+) [136,137] oxidises even methane.[258] Alkanes are hydroxylated by periodate in the presence of $RuCl_3$ with the intermediate formation of RuO_4.[259] The rhodium complex of 1,2-bis(diphenylphosphino)ethane catalyses the oxidation of alkanes by hypochlorite.[260] *N*-Benzoyl-2-methylaniline is *ortho*-hydroxylated by trimethylamine oxide in the presence of a copper(II) salt with the intermediate formation of a copper(III) derivative.[261] The addition of iron(III) salts increases the quantum yields of the products of the photochemical hydroxylation of benzoic acid by hydrogen peroxide,[262] especially in the presence of methylene blue.[263] It has been concluded[264] that the abstraction of a hydride ion is the most likely mechanism of the activation of alkanes by carbonium ions and metal complexes — soft Lewis acids.

Reactions involving the oxidation of alkanes and arenes by molecular oxygen in the presence of metal complexes have been studied vigorously. It has been found that, in the gas-phase oxidation of propane (at 313 °C), the process is inhibited by the polyphthalocyanine complex of copper, whereas similar complexes of iron, cobalt, and manganese, present in small amounts, accelerate the reaction without altering the qualitative composition of the products. Analysis of the catalysts by EPR and IR spectroscopy demonstrated the absence of changes in their structure during the reaction.[265]

A whole series of studies have been devoted to the initiated radical chain oxidation of alkanes in the liquid phase[266–269] and also to cobalt bromide catalysis.[270] A trinuclear ruthenium carboxylate complex proved to be an effective catalyst of the oxidation of alkanes by atmospheric oxygen at 75 °C.[271] It has been concluded[272] that all the reactions of organic substrates with dioxygen are catalysed by metal ions which are bound to be present as impurities.

The photochemical oxygenation of alkanes and aromatic alkyl-substituted compounds by dioxygen catalysed by metal oxo-complexes, described in an earlier study[273] (see also Refs. 156–163), was developed in investigations by other workers.[274] A new system based on palladium acetate and phenanthroline, permitting the hydroxylation of benzene to phenol by molecular oxygen, was discovered.[275] Benzene is hydroxylated by dioxygen in the presence of palladium and copper complexes and molecular hydrogen.[276] The hydroxylation of benzene by dioxygen in the presence of $FeCl_3$, catechol, and pyridine in acetonitrile has also been described.[277] Finally, it has been found that methane is functionalised by cross-dimerisation with methanol in the reaction initiated by atomic oxygen; oxygen atoms are formed in their turn on interaction of photoexcited mercury atoms with N_2O.[278]

Detailed study of the Gif system[279–282] and of its models based not on dioxygen but on peroxides[283,284] and of the mechanism of the functioning of the system[285] has been continued. An analogous system incorporating a complex of iron with picolinic acid and dixoygen[286] or hydrogen peroxide[287] was proposed. Such systems can be regarded as models of oxygenases. The mechanism of the hydroxylation of aromatic compounds by the $Cu^+ - H_2O_2$ system has been discussed.[288]

Most communications have been devoted to the study of the biological and biomimetic oxidation of compounds at C–H bonds and several books have been published on this topic.[289–292] Attention has been concentrated on oxidation with participation of cytochrome P-450 [293–295] and also on the modelling of such processes (see the review of Mansuy et al.[296]), usually using porphyrin complexes of metals as catalysts.[297–306] It has been found that azidoporphyrinato-complexes and other complexes of chromium(III), manganese(III), and iron(III) catalyse the selective hydroxylation of alkanes at low temperatures by molecular oxygen in the absence of a reductant.[307–309] A fully inorganic model of cytochrome P-450 has been proposed in which the catalyst is iron deposited on a zeolite and the oxidation is effected either with H_2O_2 or with the $O_2 - H_2$ couple. In the oxidation of n-octane with participation of H_2O_2 on Fe/ZSM-5, the main product is 1-octanol.[310] The mechanism of the functioning of cytochrome P-450 and of its models has been discussed.[311–314]

The oxidation of 1,1-dimethylcyclopropane[315] and ethane[316] catalysed by MMO has been described. The substrate specificity in the oxidation by the soluble form of the above enzyme isolated from *Methyloccocus capsulatus* has been discussed in detail.[317] It was of interest that the hydroxylation of methane with participation of *Methylosinus trichosporium*, which leads to the formation of methanol, has been observed only when the microorganisms were treated with cyclopropane.[318] A dinuclear iron complex with bridging oxo-ligands can serve as a structural model of MMO.[319]

Photochemical models of the monoxygenase oxidation by dioxygen have been proposed,[320,321] the role of light consisting in exciting a sensitiser capable of generating the reducing component necessary for the reaction. The reactions involving biomimetic oxygenation by a system based on iodosobenzene and metal complexes with bleomycin, modelling cytochrome P-450, have been discussed.[322]

Data have been published on the oxidation of alkanes and arenes by other enzymes — hydroxylases,[323–327] dioxygenases,[328,329] and chloroperoxidase.[330] The reaction of dioxygen with a dinuclear copper(I) complex leads to the hydroxylation of the benzene ring of the ligand and can be regarded as a model of the process catalysed by tyrosinase[331] (see also Kitajima et al.[332]). The models of ligninase, a peroxidase which oxidises lignin (C–C bonds are then cleaved and the benzene rings are hydroxylated), are based on metalloporphyrin complexes and use hydrogen peroxide[333] or persulphate[334] as the oxidant. The model of the vanadium-containing bromoperoxidase includes a vanadyl complex,[335] while the complex $[Mn_4O_2(OCCPh_3)_6(H_2O)_2]$, modelling the oxygen-evolving centre of the photosystem II, catalyses the oxidation of alkanes by alkyl peroxides or iodosobenzene.[336] In the presence of a nitrogen-containing base in iron complexes with bisimidazolyl-methane, the methylene group is oxidised by atmospheric oxygen. Such complexes model the coordination of metal ions in certain metalloproteins, while the oxidation process itself may be similar to oxidation catalysed by lipoxygenases.[337] The complexes $V_2W_4O_{19}^{4-}$, $V_{10}O_{28}^{6-}$, and others catalyse the oxidative cleavage of catechol and model catechol dioxygenase.[338] Iron phenoxide complexes, obtained from Schiff bases, can serve as models of dioxygenases.[339] Finally, we may note that the insertion of oxygen into an aromatic ring, catalysed by complexes which are models of catechol dioxygenases, has been investigated by the extended Hückel method.[340]

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