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Homogeneous catalysis in the oxidative functionalization of alkanes in protic media †

E G Chepaikin

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Abstract. Examples of the activation of saturated hydrocarbons and dioxygen as well as oxidative functionalization of saturated hydrocarbons involving the C – H and C – C bonds in the presence of metal complexes in protic media are considered. The mechanisms of processes are analyzed. Attention is focused on the transformations of methane and C_2 – C_4 hydrocarbons as the natural and associated gas components. The bibliography includes 249 references.

I. Introduction

The rational use of natural and associated gases containing saturated $C_1 - C_4$ hydrocarbons is one of the challenges of petrochemistry. At present, these valuable natural resources are mainly used as fuel. The chemical conversion of inert saturated hydrocarbons, the natural gas constituents, to the primary products of petrochemical synthesis requires that the C – H bonds be preliminarily activated.[1]

It was J Halpern, an outstanding catalytic scientist, who drew attention of chemists to the problem of the C – H bond activation in alkanes. He considered this as the most important and difficult task and, at the same time, as the most challenging problem of homogeneous catalysis.[2] The research in this field was preceded by a study by the famous catalytic chemist J Chatt on the intramolecular activation of the C – H bond in a methyl group of the phosphine ligand of the ruthenium complex with 1,2-bis(dimethylphosphino)ethane and on the oxidative addition of naphthalene to this complex.[3]

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Since that time, four decades have elapsed. Over this period, numerous metal complexes capable of activating the C – H bonds in alkanes have been discovered. The activation turned out to be not so problematic, much more difficult is to involve the C – H bond in functionalization, *i.e.*, to substitute a functional group X (X = OH, COOH, Hal, OSO_3H, SO_3H, *etc.*) for the hydrogen atom.

The simplest way of hydrocarbon functionalization is its oxidation with oxygen or hydrogen peroxide and its derivatives. To date, several industrial processes of oxidative functionalization of saturated hydrocarbons exist, for example, ethane or butane oxidation to acetic acid, cyclohexane oxidation to cyclohexanol or cyclohexanone and further to adipic acid, *etc*. Prominent contribution to the progress in studies on hydrocarbon oxidation was made by N M Emanuel and his colleagues and followers.[4]

From studies in the field of biochemistry, it is known that in nature methane and other hydrocarbons are oxidized under very mild conditions under the action of metalloenzymes oxygenases.[5] Numerous metal complex catalysts have been studied for the oxidative functionalization of alkanes at low temperatures under laboratory conditions. Unfortunately, there are no examples of the commercial functionalization of any alkane under conditions of homogeneous catalysis. Moreover, no information is available on a catalyst that could be considered as a real candidate for practical application. However, taking into account the relatively low temperatures of operation of homogeneous metal complexes, the quest for suitable catalysts for some commercial processes of alkane functionalization is still topical. One can also reckon on the development of heterogeneous catalysts as the components of liquid-phase catalytic systems, even if they are heavily deactivated by various

† Dedicated to Academicians I I Moiseev and A E Shilov, who made a great contribution to the development of metal complex catalysts and in connection with their 80th anniversaries.

poisons, for example, sulfur- and arsenic-containing compounds. (Due to the deep oxidation of hydrocarbons, the conventional heterogeneous gas-phase catalysis can hardly provide the required selectivity with the acceptable degree of conversion.)

Special attention was paid to functionalization of methane as the main component of natural gas and the least reactive saturated hydrocarbon. Chemical-processing natural gas is mainly used in the synthesis gas production.

$$CH_4 + H_2O \longrightarrow CO + 3H_2.$$

The CO to H_2 ratio can be varied depending on the conversion conditions. The content of hydrogen in the synthesis gas can be increased by the water gas shift reaction.

$$CO + H_2O \longrightarrow CO_2 + H_2.$$

Synthesis gas is used in the manufacture of ammonia (following conditioning and cleaning), methanol and the hydrocarbons C_nH_{2n+2} ($n \geqslant 2$) by the Fischer–Tropsch process as well as in the hydroformylation and carbonylation reactions.

Higher reactivity of reaction products as compared with that of the starting compounds is one of problems in the oxidative functionalization of alkanes, *e.g.*, their oxidation to alcohols. This necessitates protection of the products from subsequent conversion, for example, transforming alcohols to esters. Esterification requires the presence of an acid in the reaction medium.

$$CH_4 + RCO_2H + \frac{1}{2}O_2 \longrightarrow RCO_2Me + H_2O.$$

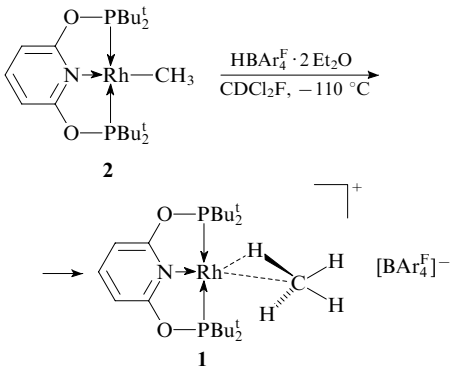
Acidic protic media are most promising for oxidative functionalization of alkanes; in this case, the catalytic systems should be resistant to the action of acids as well as water formed upon esterification.

The activation and functionalization of alkanes has been the subject of numerous publications including monographs (*e.g.*, see Refs 6–14) and reviews (see Refs 15–42). However, the latest monograph [14] published in 2000 covered the material that appeared before 1999, while a considerable part of recent reviews on the oxidative functionalization of alkanes dealt with catalysts based on particular single metals (Pt,[33] Rh,[34] Cu, Ag,[37] Fe (Refs 26, 35, 39), the oxidation of particular compounds (alkylarenes [41]) or considered only part of the problem in question. The present review provides an analysis of publications on the oxidative functionalization of alkanes in protic media in the presence of metal complexes. For the large part, it considers the publications of 1994–2009 and several papers of 2010. The earlier sources are cited only when modern data are discussed or when some classical publications and monographs must be referred to.

II. C–H Bond activation in alkanes

The C–H bond activation in alkanes by metal complexes includes at least the following two stages: alkane coordination (preactivation) and its conversion with the C–H bond cleavage to form alkyl-type or other intermediates.[42,43] Studies on identification of coordinated alkanes, *i.e.*, their molecular complexes, the so-called σ-complexes, are relatively scarce, because it is rather difficult to observe the formation of weak complexes, especially against a large excess of the substrate. The methods that allow *in situ* monitoring, *e.g.*, IR spectroscopy and NMR spectroscopy, are suitable to this end.

The first metal σ-complexes with alkanes were observed in the photochemical generation of coordinatively unsaturated metal pentacarbonyls in a hydrocarbon medium.[44,45] A short-lived methane σ-complex was detected in the methane matrix at 10 K.[45] The data on IR spectral studies of σ-complexes was analyzed in a review.[46] The NMR spectra of the complexes $CpRe(CO)_2(AlkH)$ ($Cp = \eta\text{-}C_5H_5$) were described.[47,48] In the end of 2009, the synthesis of a rather stable methane σ-complex **1** by protonation of rhodium(I) pincer complex **2** at −110 °C was reported.[49] The existence of complex **1** was proved by the data from NMR spectroscopy of this and isotopically modified ($Rh-{}^{13}CH_3$ and $Rh-CD_3$) analogues.



Ar^F is fluorine-containing aryl substituent.

A plethora of theoretical studies were devoted to the alkane C–H bond activation and functionalization. Thus a comparative analysis of two platinum catalysts, *viz.*, the so-called 'cisplatin' ($[Pt(NH_3)_2Cl_2]$) and 'Catalytica' {$[Pt(Bpym)Cl_2]$ (Bpym is 2,2′-bipyrimidine)}, in the methane activation and oxidation was carried out.[50] So far, no alkane complexes with the oxygen atom of the oxo group of metals were detected experimentally; thus, the C–H bond activation by oxo and peroxo complexes was considered only theoretically, *e.g.,* the methyl group transfer from CH_3ReO_3 to OsO_4.[51]

The C–H bond cleavage in alkanes can occur as a result of electrophilic substitution, oxidative addition, metathesis, addition reactions to a multiple bond M=Y (M is a metal), *etc.*

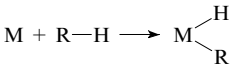
1. Electrophilic substitution.

$$M^{n+}-X + R-H \longrightarrow M^{n+}-R + HX$$

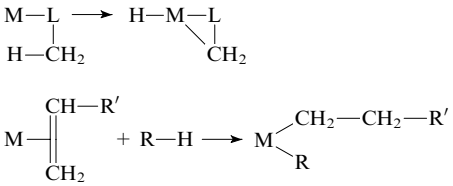
According to A E Shilov,[9] it is more correct to call this mechanism dissociative, bearing in mind that alkanes exhibit virtually no nucleophilic properties. For this reaction to proceed, the remaining group must be as highly nucleophilic as possible and the leaving group must possess only weak complex-forming properties. The driving force of this process could be the presence of an oxidant (Ox), provided the original metal was in a low oxidation state.

$$M^{n+}-X + R-H + Ox \longrightarrow M^{(n+2)+}-R + Ox^{\bullet}H^- + X^-.$$

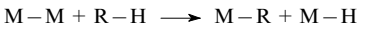
2. Oxidative addition.



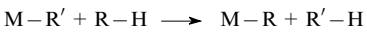
For this process to occur, the metal should exist in a low oxidation state. In its pure form, this reaction is thermodynamically unfavourable. This thermodynamic limitation can be overcome in several ways. The reaction may be promoted by the formation of a coordinatively unsaturated metal complex upon photochemical or thermal impact; by the formation of complexes (metallacycles) with the agostic hydrogen atom formed as a result the C–H bond cleavage in the terminal alkyl substituent in ligand (L) and the proton transfer to the metal atom; by the hydrogen atom transfer from the alkane to a coordinated alkene.



The homolytic cleavage of the metal–metal bond is a special case of oxidative addition.

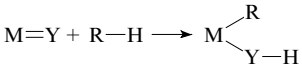


3. Metathesis reaction.

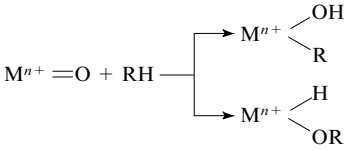


(This thermodynamically neutral reaction can hardly be used in alkane functionalization.)

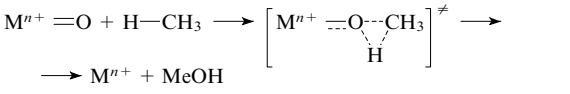
4. Alkane addition to a multiple bond M=Y.



Of no less importance are the naturally occurring mechanisms of the C–H bond cleavage in alkanes involving oxo, peroxo and hydroperoxo complexes.

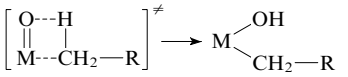


This process can start from the formation of an activated complex with the pentacoordinated carbon atom (insertion of the oxo-oxygen into the C–H bond).

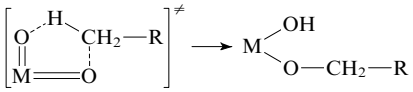


This does not involve the formation of any M–C bonds. The reaction of alkanes with peroxo and hydroperoxo complexes follows the same mechanism.

Let us consider the following two mechanisms of the oxo-group oxygen insertion into the C–H bond: the Baeyer–Villiger mechanism [reaction (1)] and the [3+2] addition (provided several oxo groups are present in the metal complex) [reaction (2)].

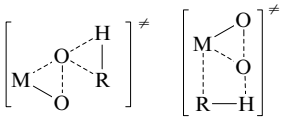


(1)



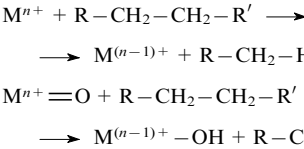
(2)

In the alkane activation with peroxo complexes, the following intermediate states are formed:



Similar structures can be suggested for hydroperoxo complexes.

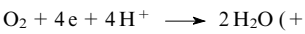
The C–H bond cleavage in alkanes can also occur by the radical route as a result of an electron or a hydrogen atom abstraction from the hydrocarbon (one-electron processes):



Processes accompanied by the formation of radical cations can occur by the non-chain one-electron mechanism. At the same time, the processes with the formation of free radicals follow as a rule the chain mechanism. Such processes, albeit not always selective, are very efficient and widely used in industry, for example, for the oxidation of cyclohexane to cyclohexanol and cyclohexanone in the caprolactam manufacture.

III. Dioxygen activation

Naturally occurring oxygen is fairly inert. Its four-electron reduction to water is a very rare process implemented, for instance, in enzymatic reactions



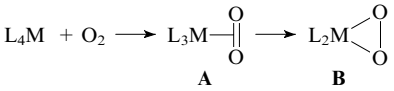
One-electron reactions of oxygen reduction have a negative potential (−0.32 V), which is the reason for the kinetic inertness of dioxygen. Moreover, dioxygen in its ground state is a triplet molecule, whereas the overwhelming majority of substrates (in our case, alkanes) are singlets. According to the spin conservation rule, the reactions of triplet molecules with singlet species are characterized by the high activation energies.

In light of the direct oxidation of hydrocarbons, the mechanisms of dioxygen activation have to be considered. In biological systems, metalloenzymes, oxidases and oxygenases, take part in the dioxygen activation. Most often, the metal involved is the Fe^{3+} ion and more rarely the Cu^{2+} ion. Among the iron-containing oxygenases, cytochrome P450 (a mononuclear complex) and methane monooxygenase (a binuclear complex) are best known. Methane

monooxygenase catalyzes the oxygenation of the simplest and least reactive hydrocarbon, *i.e.*, methane, under mild conditions. The dioxygen activation involves the low-valence Fe^{2+} ion generated under the action of a reducing agent, a reductase, always present in biological systems. In copper-containing oxygenases, the active site contains two or three $Cu^{I(II)}$ ions. The principles of enzyme operation underlie the design of biomimetic systems as highly efficient and selective chemical catalysts. In biomimetic catalytic systems, the role of reducers is played by hydrides, amalgams, dihydropyridines, ascorbic acid, *etc*. Hydrogen and carbon monoxide are also convenient reducing agents; however, they require the addition of extra catalysts to the catalytic system.

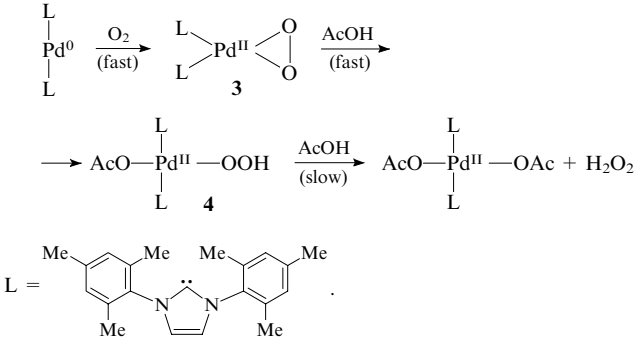
1. Peroxo complexes

Oxygen interacts with low-valence metal complexes to afford π-complexes with oxygen (**A**) and peroxo complexes (**B**).



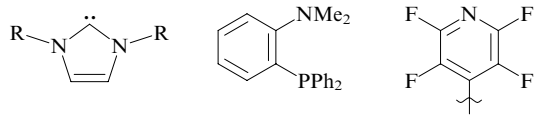
The dioxygen compounds with zero-valent nickel, palladium and platinum triphenylphosphine compounds and their role in the catalytic oxidation of phosphines have been known for a long time.[52] Peroxo complexes of other metals have been documented, for example, $IrCl(CO)(O_2)(PPh_3)_2$ (Ref. 53) and $Ru(O_2)(NCS)$. $.(NO)(PPh_3)_2$ (Ref. 54) and a binuclear rhodium complex with bridging dioxygen $[Cl(Py)_4Rh-O-O-Rh(Py)_4Cl]^{2+}$ (Py is pyridine).[55] The properties of cobalt salen complexes with the reversibly coordinated oxygen molecule that could be used as synthetic oxygen carriers were described in detail.[56] Complexes of platinum metals with oxygen catalyzed the oxidation of not only phosphines but also carbon monoxide (at 100 °C).[57] These complexes were also used in the oxidation of SO_2 , NO, N_2O_4 , CO to the corresponding anions.[56] The structure of complexes of platinum metals with dioxygen was studied by NMR and IR spectroscopy, mass spectrometry and X-ray diffraction analysis.

The reaction of oxygen with a palladium(0) complex containing heterocyclic carbene ligands affords peroxo complex **3**, which, under the action of acetic acid, is transformed to hydroperoxo complex **4** and further to palladium diacetate. The latter process is accompanied by hydrogen peroxide evolution.[58]



Peroxo (**3**) and hydroperoxo complexes (**4**) were characterized by IR, Raman and NMR spectra and electrospray ionization mass spectrometry (ESI-MS). An absorption band at 868 cm^{-1} was observed in peroxo complexes, which shifted to 821 cm^{-1} upon replacement of $^{16}O_2$ by $^{18}O_2$. In hydroperoxides, the absorption bands at 3492 ($Pd-^{18}O-^{18}O-H$) and 2591 cm^{-1} ($Pd-^{16}O-^{16}O-D$) were observed. In the ^1H NMR spectrum, a signal at δ 6.13 corresponds to the hydroperoxide proton in complex **4**. According to the data from X-ray diffraction analysis, the length of the O–O bond was 1.443 Å, which is much longer than that in the oxygen molecule. Complexes of this type catalyzed the aerobic oxidation of alcohols.[59]

In addition to the rhodium binuclear complex with a bridging oxygen molecule, several rhodium peroxo complexes, namely, $RhCl(O_2)(HCCL)(P-N)$ (**5**), $RhCl(O_2)(HCCL)(PPh_3)_2$ (**6**), $RhCl(O_2)(P-N)(PPh_3)_2$ (**7**) and $Rh(O_2)(CNBu^t)(PEt_3)_2(Py^F)$ (**8**), which contain a substituted heterocyclic carbene ligand (HCCL),[60] a P–N-chelating ligand (P–N)[60] and a fluoropyridine substituent (Py^F), were synthesized.



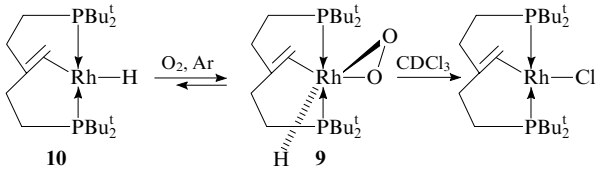
HCCL P–N Ligand Py^F

R = 2,6-$Pr^i_2C_6H_3$, 2,4,6-$Me_3C_6H_2$ (Mes).

These complexes were studied in detail by the methods of ESI-MS, NMR spectroscopy and X-ray diffraction analysis. The O–O distances were 1.450 Å in complexes **5** and **6**, 1.445 Å in complex **7** and 1.452 Å in complex **8**.

The transformation of rhodium peroxide complex **8** to the hydroperoxide, methylperoxide and trimethylsilylperoxide complexes was described (see below).[61]

A unique stable peroxo-alkene-hydride complex $RhH(O_2)\{CH_2{=}C(CH_2CH_2PBu^t_2)_2\}$ (**9**) with the rhodium ion coordination sphere containing two P atoms, a π-bound ethene fragment of the diphosphine ligand, a hydride ion and an oxygen molecule was synthesized.[62] It was synthesized by passing flow of argon containing 2 ppm of oxygen through a benzene solution of air-unstable rhodium alkene-hydride complex **10**.



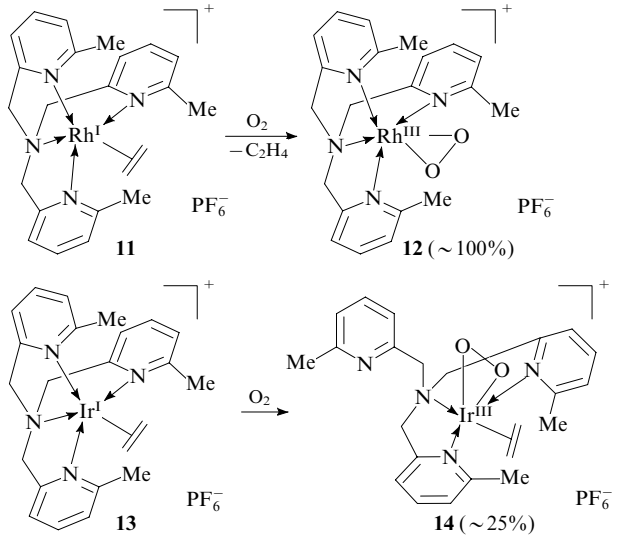
10 **9**

Transition metal complexes containing simultaneously a π-bound alkene and an oxygen molecule in the coordination spheres are the key intermediates in the catalytic oxidation of alkenes. The unique feature of complex **9** is the retention of the hydride ligand. Complex **9** was studied by IR and NMR spectroscopy. According to the data from X-ray diffraction analysis, the O–O bond length in this complex was 1.434 Å. The hydride ion was shown to occupy the *cis*-position with respect to dioxygen and the alkene.

It is interesting that in spite of their *cis*-positions, the hydride ion migrated to neither the dioxygen ligand nor the alkene even when the complex was heated to 60 °C. On

further heating, complex **9** transformed to original complex **10**, which suggests the reversible binding of dioxygen.

The reactions of rhodium(I) and iridium(I) ethene π-complexes $[(C_2H_4)M^IL]^+$ (L is an N-containing ligand) with dioxygen were studied in detail.[63] The reaction of rhodium complex **11** with dioxygen afforded peroxo complex **12** with concomitant loss of one ethene fragment; in the reaction of iridium complex **13** with dioxygen, the coordinated ethylene molecule was retained. In the latter case, the reaction produced alkene-peroxo complex **14**.



The different behaviour of complexes **11** and **13** in the reaction with oxygen was explained by the stronger bond between ethylene and iridium as compared with rhodium. Solid rhodium(I) and iridium(I) ethylene complexes with less bulky N-ligands with no methyl substituents in the pyridine fragments reacted with dioxygen to produce 3-metalla-1,2-dioxolanes as a result of insertion of dioxygen in the metal–alkene bond.

According to crystallographic data, the O–O bond length in iridium complex **14** was 1.430 Å.

Peroxo complexes of metals formed under the action of not only oxygen but also hydrogen peroxide on transition metal complexes.[7] For example,

$$L_nM{=}O + H_2O_2 \longrightarrow L_nM\begin{matrix}OH\\OOH\end{matrix} \longrightarrow L_nM\begin{matrix}O\\O\end{matrix} + H_2O.$$

2. Hydroperoxo complexes

In acidic media, peroxo complexes transform into hydroperoxo complexes. Particularly, the protonation of peroxo complexes $(Ph_3P)_2Pd(O_2)$ and $(Ph_3P)_2Pt(O_2)$ was observed.[64] Pd, Pt and Cu hydroperoxo complexes formed under the action of hydrogen peroxide on the acetate and trifluoroacetate complexes of these metals

$$LL'_nMX + H_2O_2 \longrightarrow LL'_nMOOH + HX.$$

Particularly, the hydroperoxo complexes $(RCO_2)Pd.(OOH)_2$ (R = Me, CF_3),[65] (P–P)Pt(O_2CCF_3)(OOH) (P–P is a diphosphine)[66] and $(AcO)Cu_2(OH)_2(OOH)$[67] were synthesized by the above method.

The equilibrium formation of a ruthenium hydroperoxo complex was reported.[68]

$$[(Edta)Ru^{III}(H_2O)]^- + H_2O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(Edta)Ru^{III}(OOH)]^{2-} + H_3O^+,$$

H_4Edta is ethylenediaminetetraacetic acid.

The rate constants for the forward (k_1) and reverse (k_{-1}) reactions at 4.5 °C were 17.7 ± 0.5 litre mol^{-1} s^{-1} and 0.08 ± 0.01 s^{-1}, respectively. The reaction kinetics was studied by the stopped flow method at $\lambda = 271$ nm. At 25 °C in acidic media, the hydroperoxo complex was transformed by the heterolytic route to an Ru^V oxo complex and by the homolytic route, to an Ru^{IV} hydroxo complex.

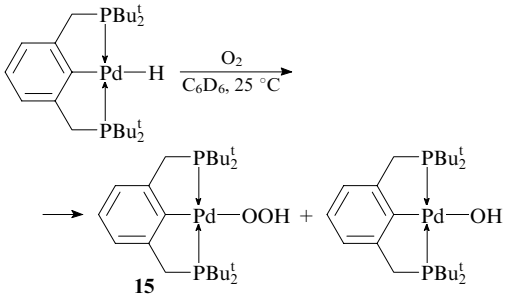
$$[(Edta)Ru^{III}(OOH)]^{2-} \xrightarrow{H^+} \begin{matrix}\xrightarrow{k_2} [(Edta)Ru^V(=O)]^- + H_2O\\ \xrightarrow{k_3} [(Edta)Ru^{IV}(OH)]^- + HO^{\bullet}\end{matrix}$$

The dioxygen insertion reaction in the metal–hydrogen bond to form hydroperoxide complexes is of interest.[7]

$$L_nM-H + O_2 \longrightarrow L_nM-OOH,$$

M = Co, Rh, Pd, Ir, Pt.

The first direct observation of the dioxygen insertion in the Pd–H bond to form palladium hydroperoxo complex **15** was reported.[69]



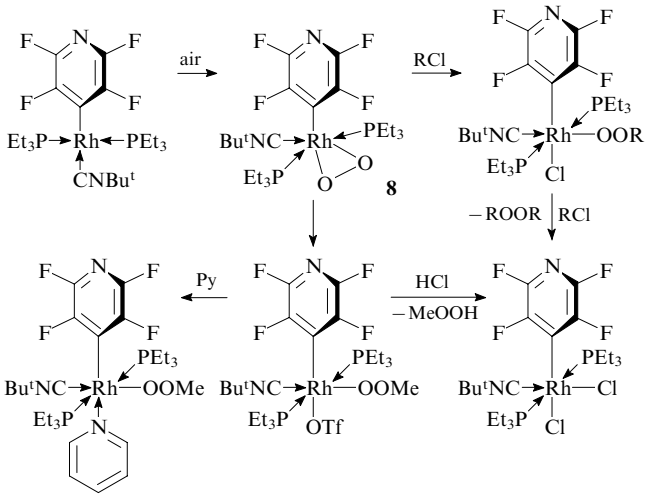
The kinetic isotope effect of this reaction (k_H/k_D) was found to be 5.2. The reaction proceeds by the molecular rather than radical mechanism. The molecular structure of complex **15** was determined. According to X-ray diffraction data, the O–O distance in complex **15** was 1.47 Å, *i.e.*, the O–O bond was substantially longer in hydroperoxo complexes than in peroxo complexes.

The transformations of rhodium peroxo complex **8** to hydroperoxo, methylperoxo and trimethylsilylperoxo derivatives were described (Scheme 1).[61]

According to the acquired structural data, on going from peroxo complex **8** to the corresponding hydroperoxo complex, the O–O distance increased from 1.452 to 1.488 Å. A recent ESI-MS study[70] considered the mechanism of dioxygen activation by cationic complexes of transition metal hydrides, namely, $[M(H)]^+$, $[M(H)(H_2O)]^+$ and $[M(H)(OH)]^+$ (M = Fe, CO, Ni). It was shown for $[M(H)(OH)]^+$ complexes that the reactions proceeded as the insertion of an O_2 molecule into the M–H bond to form hydroperoxo complexes. Certain examples of oxidation of organic substrates by palladium(II) hydroperoxo complexes were discussed.[71]

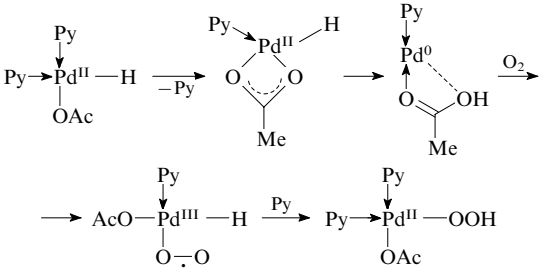
Currently, the mechanism of reactions of palladium hydride complexes with dioxygen is being actively discussed. In a theoretical study[72] of the $(Py)_2Pd(H)OAc$ complex, the following four possible routes were consi-

Scheme 1



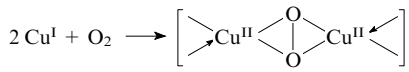
R = H, SiH_3; Tf is trifluoromethylsulfonate.

dered: 1) a homolytic mechanism involving the hydrogen atom abstraction; 2) reductive elimination of AcOH to form a Pd^0 complex and its subsequent reaction with oxygen; 3) insertion of an O_2 molecule into the Pd—H bond; 4) oxidative addition of an O_2 molecule to Pd^{II} to afford Pd^{IV} η^2-peroxo complex. Preference was given to the second mechanism. At the same time, the quantum chemical calculations by Goddard *et al.*[73] for a complex [(sparteine)Pd^{II}(Cl)(H)] and a model compound [(2,2′-bipy)Pd^{II}(Cl)(H)] (bipy is bipyridine) have shown that preference should be given to the homolytic mechanism. Furthermore, the authors of the latter study[73] disclosed an unprecedented kinetically favourable mechanism that involved the formation of a complex with the superoxide ligand in place of the peroxo complex.

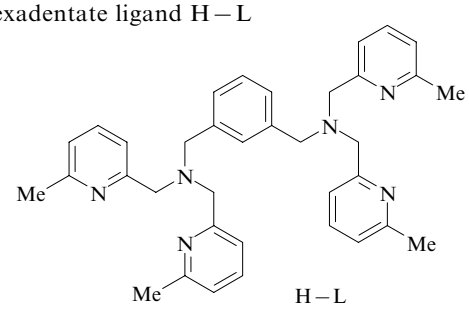


3. Complexes with the bridging peroxo group

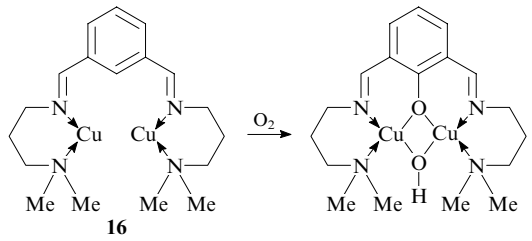
These complexes attract attention because the active site of a copper-containing oxygenase involves two and even three copper ions, which interact with oxygen to form bridging structures.[74,75] For example, a simplified oxidation mechanism of phenols to *o*-quinones by tyrosinase was presented.[75] This process included the interaction of two copper(I) ions with an oxygen molecule to form a complex in which both oxygen atoms are bound to both copper ions. As a result, a (μ-η^2 : η^2-peroxo)dicopper(II) species becomes a component of this biocatalyst.



It was shown that the $[Cu_2(H-L)O_2]^{2+}$ complex with a hexadentate ligand H—L



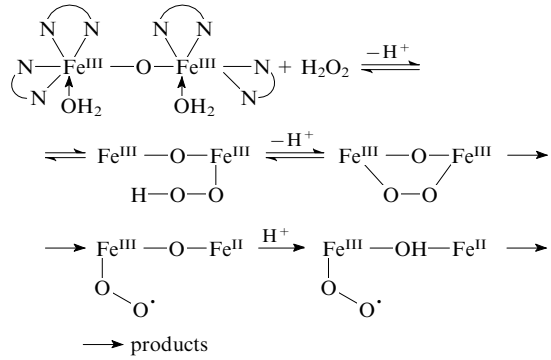
containing the active (μ-η^2 : η^2-peroxo)dicopper(II) species was capable of activating and oxidizing the C—H bonds in different substrates.[76] A comparison of the $[Cu_2(H-L)O_2]^{2+}$ complex and the cumylperoxo radical has shown that they exhibited the same activity, *i.e.*, the $[Cu_2(H-L)O_2]^{2+}$ catalyst could initiate a wide spectrum of oxidation reactions including the C—H bond oxidation in alkanes. Recently, the hydroxylation of the benzene ring in the 1,3-bis[(3-(*N*,*N*-dimethylamino)propyl)iminomethyl]-benzene ligand (DAPA) of the $[Cu_2(DAPA)]^{2+}$ complex (**16**) was carried out.[77]



16

It was assumed that in this case the oxygen activation also proceeded *via* the transition complex Cu_2^{II}(μ-η^2 : η^2-O_2) and that this process simulated the effect of tyrosinase. The formation of a similar intermediate was also assumed in the reaction of dioxygen with a hexaazamacrocyclic dicopper(I) complex.[78]

The reaction of hydrogen peroxide with the diiron complex $[Fe_2^{III}(\mu\text{-}O)(phen)_4(H_2O)_2]^{4+}$ (phen is phenanthroline) was also accompanied by the formation of a peroxo-bridged adduct.[79]



is a phenanthroline ligand, which is omitted for sake of simplicity.

The reaction of the complex $K[Ru^{III}(HEdta)Cl]$ with hydrogen peroxide afforded a peroxo complex containing the $Ru^{IV}-O-O-Ru^{IV}$ moiety with $\lambda_{max} = 390$ nm.[80] The absorption band at 870 cm^{-1} in the IR spectrum was ascribed to the $-O-O-$ group in this moiety.

4. Oxo complexes

Metal oxo complexes also take part in redox reactions. It is generally agreed that Fe^{IV} oxo complexes are involved in the biological oxidation of substrates. The first X-ray diffraction study of a non-heme Fe^{IV} oxo complex **17** synthesized by the reaction

$$LFe^{II}(OTf)_2 + PhIO \xrightarrow[-48\ ^\circ C]{MeCN} \left[\begin{matrix} O \\ \| \\ LFe^{IV}(MeCN) \end{matrix}\right](OTf)_2,$$

17

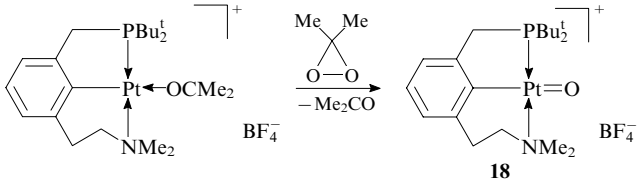
L is 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane.

was reported.[81]

The Fe=O bond length was found to be 1.646 Å. Complex **17** was characterized by several spectral techniques. Its UV-Vis and IR spectra demonstrated absorption bands at 820 nm and 834 cm^{-1}, respectively. This oxo complex oxidized Ph_3P to $Ph_3P=O$.

Currently, it was shown by several examples that the oxygen atom bound to a high-valence transition metal atom can insert into the C–H bond of alkanes to afford a transition state with pentacoordinated carbon (such reactions were surveyed in a monograph [11]). It was also assumed that on the surface of heterogeneous oxidation catalysts, the M=O species were present. Particularly, it was shown that in the interaction of methyl radicals with the oxygen-pretreated surface of monolythic rhodium, the methoxy groups were present in addition to methyl groups. Simultaneously, formaldehyde was observed in the gas phase.[82]

As we travel in the Periodic System from left to right, the trend of metals for the formation of oxo complexes decreases.[83] Until recently, nothing was known on palladium, platinum and gold oxo complexes, although ruthenium and osmium oxo complexes have been synthesized long ago. This is explained by the strong π-donor properties of the oxo group; this is why the stabilization of oxo complexes of metals with more than five valence d-electrons requires the introduction of strong π-acceptors. For example, in the $[Mes_3Ir=O]$ complex, the d-electron interaction with an oxo group was found to be minimum due to the tetrahedral configuration of iridium and the acceptor properties of the aromatic ligands.[84] The stability of $Na[Re^{I}(O)(Ph-C\equiv C-Ph)_2]$ was associated with the acceptor properties of the tolane ligands.[85] The first publications on the synthesis and structural studies of oxo complexes appeared only in 2004–2007 for platinum(IV),[86] palladium(IV) (Ref. 87) and gold(III).[88] The synthesized complexes were stabilized by polytungstate ligands, which are strong π-acceptors. The Pt^{IV} pincer oxo complex **18** was synthesized; its structure was optimized by the density functional theory method.[89]



18

In contrast to compounds considered above, complex **18** contains no strong π-acceptor ligands. So far, this compound could not be prepared as single crystals suitable for X-ray diffraction analysis; however, it was characterized by quite a number of other physicochemical methods. In the IR spectrum, the absorption band at 783 cm^{-1} was attributed to the Pt=O bond vibrations. Oxo complex **18** exposed at room temperature for 7–10 h underwent an intramolecular transformation with the transfer of an oxygen atom to the phosphorus atom in the phosphine fragment, in stochiometric reactions it oxidized KH, H_2, CO, PPh_3 and reacted with water to afford the corresponding dihydroxo compound. No information on its reactions with alkanes is available. Compound **18** and other analogous complexes were discussed in more detail elsewhere.[90]

5. Hydrogen peroxide generation from dioxygen

One of the methods for industrial production of hydrogen peroxide includes catalytic hydrogenation of 2-ethylanthraquinone followed by the reaction of 2-ethylanthrahydroquinone with oxygen.[7] The direct reaction of hydrogen with oxygen in the presence of heterogeneous palladium catalysts in liquid media is also studied.[91–93] Likholobov and coworkers.[94] showed that the reaction of oxygen with carbon monoxide in the presence of $(Ph_3P)_2Pd(OAc)_2$ in a biphasic system dichloridomethane–water produced hydrogen peroxide under very mild conditions

$$(Ph_3P)_2Pd(OAc)_2 + CO + H_2O \longrightarrow (Ph_3P)_2Pd + 2\,AcOH + CO_2,$$

$$(Ph_3P)_2Pd + O_2 \longrightarrow (Ph_3P)_2Pd\begin{matrix} O \\ | \\ O \end{matrix},$$

$$(Ph_3P)_2Pd\begin{matrix} O \\ | \\ O \end{matrix} + 2\,AcOH \longrightarrow (Ph_3P)_2Pd(OAc)_2 + H_2O_2.$$

The overall reaction was as follows:

$$CO + H_2O + O_2 \longrightarrow CO_2 + H_2O_2. \qquad (3)$$

The aqueous phase represented a 3% $Ti(SO_4)_2$ solution which served as the trap for H_2O_2

$$Ti(SO_4)_2 + H_2O_2 \longrightarrow H_2[TiO_2(SO_4)_2].$$

The overall equation (3) is confirmed by the fact that CO_2 and H_2O_2 formed in the equimolar ratio.

In a patent filed in 1997 and subsequent publications, Italian authors presented the results of their studies on reaction (3) in biphasic systems in the presence of palladium phosphine and arsine complexes[95] and palladium complexes with 2,2′-bipyridine and different substituted phenanthrolines.[96] The phosphine and arsine complexes proved to be inactive due to the ligand oxidation by oxygen. Among the nitrogen-containing ligands, the best results were obtained with 2,9-dimethyl-4,7-diphenylphenanthroline.[96]

The transient formation of H_2O_2 or other peroxide species was postulated in the reaction of the Cu^{I} (Refs 97, 98) and Fe^{II} (Ref. 99) ions with oxygen. In the oxidation of copper(I), the accumulation of considerable amounts of hydrogen peroxide was observed.[100]

Summarizing the presented material, it should be noted that there is a considerable body of information for design-

ing catalytic systems capable of stereoselective oxidation of alkanes. However, in the majority of cases this could not be attained due to impossibility to find conditions for integrating the stages of alkane and dioxygen activation and for conducting mild oxidation.

IV. Principles of designing catalytic systems for the oxidative functionalization of alkanes

A catalyst or a component of a catalytic system must activate the alkane C–H bond and the oxygen molecule, provided O_2 is used as the oxidant. Two-electron oxidants in which oxygen is already in the active form are often used. These oxidants include hydrogen peroxide, alkali metal persulfates and hypochlorites, iodosylbenzene, SO_3, NO_2, *etc*. In catalyzed radical processes, hydrogen peroxide or persulfates generate strong oxidants, *viz*., the $HO^{\bullet}$ radicals and $SO_4^{-\bullet}$ radical anions capable of abstracting a hydrogen atom from the alkane. In this case, there is no need in activation of the C–H bond.[12] Alkyl radicals initiate the chain oxidation reaction, which is non-selective. However, with the appropriate choice of catalysts and conditions, it is possible to direct this processes along a route with the oxygen atom transfer, *i.e*., by the molecular mechanism, and carry out the stereoselective oxidation of alkanes with retention of their configuration.

Let us consider two approaches to the design of a catalytic systems for oxidative functionalization of alkanes. One of them consists of the formation of the $R-M^{n+}X$ bond by one of the mechanisms considered in Section II. Upon the introduction of an oxidant to the system, the active site transforms to the complex $RM^{(n+2)+}X_3$ with the metal in the high-valence state from which the reductive elimination of the reaction product is possible

$$RM^{(n+2)+}X_3 \longrightarrow M^{n+}X_2 + RX,$$

$X = OH^-, RCOO^-, Cl^-$.

If SO_3 or NO_2 are used as the oxidants (Red-O), the reduced form (Red) is converted to the oxidized form by a reaction with oxygen.

$$M^{n+}X_2 + RH \longrightarrow RM^{n+}X + HX,$$

$$RM^{n+}X + \text{Red-O} + 2HX \longrightarrow RM^{(n+2)+}X_3 + \text{Red} + H_2O,$$

$$RM^{(n+2)+}X_3 \longrightarrow M^{n+}X_2 + RX,$$

$$RX + H_2O \longrightarrow ROH + HX,$$

$$\text{Red} + \frac{1}{2}O_2 \longrightarrow \text{Red-O}.$$

The overall equation is as follows:

$$RH + \frac{1}{2}O_2 \longrightarrow ROH. \quad (4)$$

According to this scheme, the catalytic systems of Periana (SO_3) and Bao (NO_2) were designed. The Shilov catalytic system[6] employed Pt^{IV} as the oxidant, but Pt^{II} was not transformed to Pt^{IV} under the action of oxygen.

The second approach consists of designing catalytic systems in which one component (catalyst A) is responsible for the alkane activation and the second (co-catalyst B) is responsible for the oxygen activation. For example, in reactions of copper(I) and iron(II) complexes (as co-catalysts) with oxygen, the transient formation of hydroperoxides of these metals, *i.e*., two-electron oxidants, was observed. In this case, in order to transform the oxidized metal to its low-valence state thus closing the catalytic cycle, a certain reducing agent should be added to the system. Then, the following reaction sequence can be proposed:

$$A^{n+}X_2 + RH \rightleftharpoons RA^{n+}X + HX,$$

$$2B^{m+}X + O_2 + HX \rightleftharpoons B^{(m+1)+}(OOH)X + B^{(m+1)+}X_2,$$

$$RA^{n+}X + B^{(m+1)+}(OOH)X + 2HX \longrightarrow RA^{(n+2)+}X_3 + B^{(m+1)+}(OH)X + H_2O,$$

$$B^{(m+1)+}(OH)X + HX \longrightarrow B^{(m+1)+}X_2 + H_2O,$$

$$RA^{(n+2)+}X_3 \longrightarrow A^{n+}X_2 + RX,$$

$$RX + H_2O \longrightarrow ROH + HX,$$

$$B^{(m+1)+}X_2 + H_2 \longrightarrow 2B^{m+}X + 2HX.$$

The overall reaction is

$$RH + H_2 + O_2 \longrightarrow ROH + H_2O. \quad (5)$$

The liberated water dilutes the catalytic system. If carbon monoxide is used in place of H_2, the overall reaction is as follows:

$$RH + CO + O_2 \longrightarrow ROH + CO_2. \quad (6)$$

This approach employs an element of biomimetics, namely, a reducing agent is added to activate oxygen. It is according to this scheme that the systems proposed by Sen,[16] the author of the present review (see Ref. 29) and (partly) Neumann[36] operated.

An alcohol is oxidized faster than an alkane; hence, the former should be protected, *e.g*., by esterification. For this purpose, the alkane oxidation is carried out in solutions of acids (H_2SO_4, CF_3CO_2H). It should be borne in mind that in actual practice, the catalytic systems designed according to the above approaches could operate by different, often more complex mechanisms.

V. Stoichiometric reactions of the oxidative functionalization of alkanes involving the C–H bonds

Let us consider several examples of stoichiometric oxidation of methane by metal salts and oxides.‡

The oxidation of methane by palladium acetate in trifluoroacetic acid was reported[101] to give trifluoromethyl acetate as the reaction product (yield >60%). However, these results could not be reproduced by two research groups.[102–104] This is probably associated with the fact that the palladium acetate trimer contained traces of the coordinated nitrite anion,[105] which oxidized the acetate ion to MeOH.[104, 105] Table 1 shows the results of oxidation of methane with metal trifluoroacetates and oxides. (It is assumed that the oxides transformed into trifluoroacetates upon dissolution in CF_3CO_2H.) The discrepancies between

‡ Oxidation of alkanes by high-valence manganese and chromium compounds is beyond the scope of this review being discussed in detail in a monograph.[12]

Table 1. Methane oxidation with metal compounds in CF_3CO_2H.

Run	Compound	P_{CH_4}/MPa	T/°C	Reaction time/h	Yield of CF_3CO_2Me (%)	Ref.
1	$Pd(O_2CCF_3)_2$	3.0	180	3	$\leqslant 0.1$	103
2	$Pd(O_2CCF_3)_2$	4.1	180	3	7.8	106
3	$Mn(O_2CCF_3)_3$	3.0	180	3	30 ± 5	103
4	Mn_3O_4	4.1	180	3	100	106
5	$Co(O_2CCF_3)_2$	3.0	180	3	90 ± 10	103
6	Co_3O_4	4.1	180	3	17.1	106
7	$Cu(O_2CCF_3)_2$	3.0	180	3	0.1	103
8	$Cu(O_2CCF_3)_2$	4.1	180	3	0.0	106
9	$Fe(O_2CCF_3)_3$	3.0	180	3	0.0	103
10	$Pb(O_2CCF_3)_4$	3.0	180	3	10 ± 3	103
11	PbO_2	4.1	180	3	38.3	106
12	$Ce(SO_4)_2$	4.1	180	3	8.7	106
13	AgO_2CCF_3	4.1	180	3	18.0	106
14	$(Bipym)PtCl_2-Cu(O_2CCF_3)_2$	4.1	180	3	14.8	106
15	$Pt_2(O_2CCF_3)_6$, $Pt(O_2CCF_3)_4$, $Pt(O_2CCF_3)_2$, $Rh(O_2CCF_3)_3$	5–20	70–150	see [a]	0.5–5	104

[a] The reaction time was several hours.

the numerical data obtained by different authors are observed. For instance, the contradicting results for the oxidation by cobalt and manganese compounds [103, 106] (compare Entries 3 and 4, 5 and 6) are probably associated with the fact that manganese and cobalt oxides used in one study [103] produced water upon dissolution in trifluoroacetic acid.

All studies were carried out in solutions of the mentioned compounds in trifluoroacetic acid, because the latter is a strong acid (pK_a 0.3) with a low dielectric permittivity and poor ability to solvate ions, which favours the increase in the electrophilic properties of the metal compounds.[15] It is also known that the peroxide oxidation in such solvents proceeds much more efficiently than in acetic acid.[107] In the alkane oxidation to alcohols, the formation of trifluroacetates, on the one hand, prevents the further oxidation; on the other hand, such esters are easily hydrolyzed to afford target products. In addition to data shown in Table 1, mention should be made of the use of mercury and gold. Thus, methane was oxidized in virtually quantitative yields in the presence of $Hg(OTf)_2$ in TfOH at a pressure of 3.45 MPa and 180 °C (Ref. 108) and by gold(III) hydrogensulfate according to the following reaction:[109]

$$3\,CH_4 + 2\,Au(HSO_4)_3 \xrightarrow[180\ ^\circ C,\ 2\ h]{P_{CH_4} = 2.7\ MPa} 3\,CH_3-O-SO_3H + 2\,Au + 3\,H_2SO_4.$$
$$(\sim 90\%)$$

VI. Catalytic oxidative functionalization of alkanes involving the C—H bonds

In 1967, Garnet and Hodges [110] discovered that the platinum(II) salts catalyzed the deuterium–hydrogen exchange of aromatic compounds with the medium ($AcOD-D_2O$). Somewhat later, Shilov and co-workers [111] showed for the first time that in this system, the methane activation and its catalytic deuterium–hydrogen exchange were possible. Later, it was found that in the $Pt(II)-Pt(IV)-H_2O-AcOH$ system, alkanes were catalytically transformed to alkyl chlorides [112] and acetic acid was converted to chloroacetic acid.[113]

After the first publications by Shilov and co-workers, the platinum system was studied by several research groups.[6, 9–12, 14, 24, 33] The putative mechanisms of the action of this platinum system, which are referred to as the 'Shilov-type Chemistry', were considered in detail.[24, 33] In the $Pt^{II}-Pt^{IV}$ system, the Pt^{II} complex served as the catalyst of methane activation and functionalization, while Pt^{IV} was the oxidant. It was proved that in the primary methyl complex, Pt^{II} was oxidized to Pt^{IV} due to the electron transfer along the chloride bridges. In the reductive elimination, MeCl was obtained from the Pt^{IV} methyl complex, whereas methanol was produced under the action of water.[10, 14]

$$MePt^{II}Cl + [Pt^{IV}Cl_6]^{2-} \longrightarrow [MePt^{IV}Cl_5]^{2-} + Pt^{II}Cl_2$$

$$[MePt^{IV}Cl_5]^{2-} \longrightarrow MeCl + Pt^{II}Cl_2$$
$$[MePt^{IV}Cl_5]^{2-} \xrightarrow{H_2O} MeOH + [Pt^{II}Cl_4]^{2-} + HCl$$

The $MePt^{IV}$ fragment was detected by ^1H NMR spectroscopy (a signal at $\delta = 3.04$) after the reaction of methane ($P \approx 10$ MPa) with the $[PtCl_6]^{2-}-[PtCl_4]^{2-}$ system for 30 min followed by fast cooling.[114] (However, no $MePt^{IV}$ signal was detected by the *in situ* NMR studies of the methane chlorination in a sapphire ampoule at high pressure.[115])

So far, there is no agreement concerning the step of C—H bond activation. It was assumed that an alkane forms an associate (σ-complex) with a coordinatively unsaturated Pt^{II} compound. In this associate, a carbon atom is located closer to the platinum ions than the hydrogen atoms. The associated methane is deprotonated by water to form $MePt^{II}$ (Ref. 116). According to the discoverers of this system,[6] the methane activation process could start as the oxidative addition of CH_4 to Pt^{II} and finish with synchronous processes of the formation of the $Me-Pt^{II}$ fragment

and the liberation of a proton and a chloride ion. The purely oxidative addition of methane is thermodynamically unfavourable, and the mechanism of electrophilic substitution contradicts the kinetics of this process.[114]

1. Catalytic reactions involving active oxidants

a. Oxidation with sulfuric acid

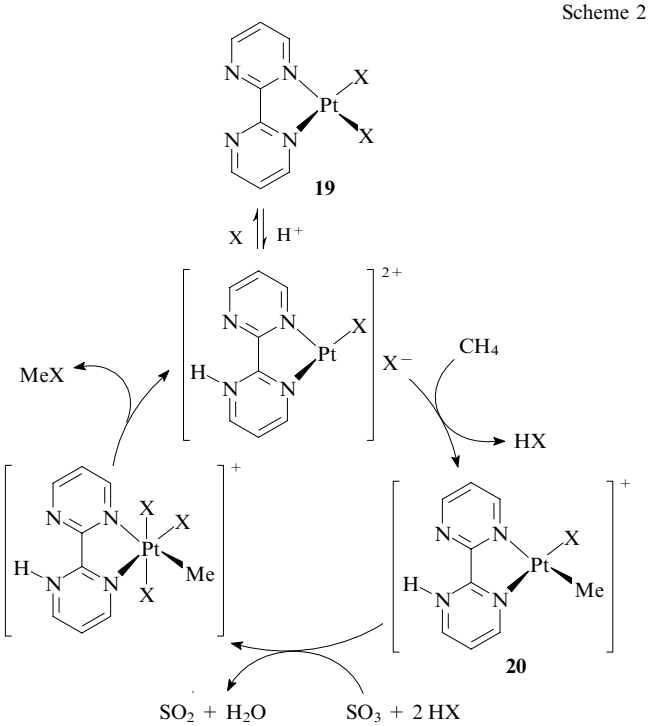
In 1950, a patent was granted[117] for the oxidation of methane in fuming sulfuric acid in the presence of mercury(II) sulfate. At 263 °C, this reaction produced methyl hydrogensulfate and methanesulfonic acid with the total yield of 44% (see Section VII).

Rudakov[12,116] made a noticeable contribution to studies of the kinetics and mechanism of alkane activation. Particularly, he has shown that the alkane oxidation in sulfuric acid was catalyzed by mercury(II) salts with the transient formation of alkylmercury hydrogensulfate $RHgOSO_3H$. Later, Periana *et al.*[108] studied the oxidation of methane in this system at 180–210 °C and 3.4 MPa. Presumably, in the first step, methane formed a complex with the coordinatively unsaturated $[Hg(OSO_3H)]^+$ cation and the electrophilic substitution in this complex produced methylmercury hydrogensulfate. The latter could also be obtained at room temperature but it transformed to methyl hydrogensulfate at 180 °C. Thus, the overall process can be written as follows:

$$CH_4 + 2\,H_2SO_4 \xrightarrow{Hg^{II}} MeOSO_3H + 2\,H_2O + SO_2.$$

The most efficient catalyst of this process was a Pt^{II} complex with 2,2′-bipyrimidine **19**[118] stable in sulfuric acid. At the 90% conversion of methane at 220 °C, the yield of methyl hydrogensulfate was 73%. The main side product was CO_2. The specific activity of the catalyst was low, ~3.6–8.4 mol mol^{-1} Pt h^{-1}. The putative mechanism is shown in Scheme 2.

Scheme 2



X = Cl, HSO_4.

The key intermediate was Pt^{II} methyl complex **20** identified by ^{1}H NMR spectroscopy. In contrast to the methylmercury derivative, which was stable in H_2SO_4 for several days, complex **20** was observed to evolve methane gradually at room temperature and instantaneously under the conditions of the catalytic reaction (180–220 °C). The multiple (repeated) deuterium–hydrogen exchange of methane was observed in a solution of complex **20** in D_2SO_4 at 75 °C. The exchange rate was found to depend linearly on the solvent acidity.[119]

It was assumed that one of uncoordinated nitrogen atoms in complex **19** quaternized under the action of an acid.[119,120] To check this assumption, its analogue containing a methyl group at one of nitrogen atoms was synthesized and its catalytic activity in the isotope exchange of methane with D_2SO_4 was studied.[121] It was shown that methylation had no effect on the activity of this complex and that methyl hydrogensulfate probably formed from the methyl group under the action of H_2SO_4. It also deserves mention that the stability of the catalyst was due to the high affinity of the bipyrimidine ligand to platinum. Under the conditions of catalysis in the presence of the Bpym group, even metallic platinum dissolved

$$Pt^0 + Bpym + 3\,H_2SO_4 \longrightarrow (Bpym)Pt(HSO_4)_2 + SO_2 + 2\,H_2O.$$

So far, the methane activation step has not been elucidated. It could be either the oxidative addition followed by fast deprotonation or the electrophilic substitution.

Both theoretical and purely applied aspects of the action of the $(Bpym)PtCl_2$ catalyst (**19**) were discussed.[119,120] A possible flow chart of the process that included the SO_2 oxidation step to SO_3 by atmospheric oxygen was proposed. The requirements to the catalyst recommended for commercialization were also formulated (see Conclusion). The kinetics of oxidation of methane in sulfuric acid in the presence of platinum compounds was studied in detail.[122]

Deactivation of the $(Bpym)PtCl_2$ catalyst (**19**) resulting from accumulation of water is an obstacle to its use. To surmount this difficulty, it was proposed to carry out the reaction in ionic liquids.[123] The most efficient catalytic system included H_2PtCl_6 (0.05 mmol) and 1-methylimidazolium chloride (0.3 mmol) in 1 ml of sulfuric acid. For P_{CH_4} = 3.4 MPa and 200–220 °C, the system retained its activity even in 96% H_2SO_4 where the $(Bpym)PtCl_2$ catalyst was inactive. Nonetheless, in oleum, complex **19** was nearly twice as efficient.

Another route of modifying the $(Bpym)PtCl_2$ catalyst (**19**) consisted of using cross-linked polymers containing triazine fragments as the macroligands.[124] The complexation of this polymer with K_2PtCl_4 afforded a heterogenous catalyst, which operated in oleum and could be used repeatedly.

A cationic gold catalyst prepared from Au_2O_3 or metallic gold effected methane oxidation[109] (P_{CH_4} = 3.4 MPa) in 96% sulfuric acid in the presence of selenic acid (3 mol litre^{-1}).

$$CH_4 + H_2SeO_4 \xrightarrow[180\ ^\circ C,\ 10\ h]{96\%\ H_2SO_4,\ Au^{III}} \underset{(0.35\ mol\ litre^{-1})}{CH_3{-}OX} + H_2SeO_3 + CO_2 \qquad (3\%)$$

X = HSO_3, $HSeO_3$.

Apparently, the role of H_2SeO_4 was to reoxidize Au^0 or Au^I to Au^{III}. In the ^{13}C NMR spectrum of the crude product, the signal for the protons of the methyl groups in CH_3-O-SO_3H and $CH_3-O-SeO_3H$ were detected in a $\sim 20:1$ ratio. (It should be noted that a solution of selenic acid in sulfuric acid oxidized methane even in the absence of catalysts.[109])

The Hg-, Pt- and Au-containing catalysts discussed above were compared with one another.[125] Presumably, these catalysts operated by similar mechanisms, but the activity of the Pt systems was *ca.* three times higher. The C–H bond activation by these catalysts (solutions in sulfuric acid) proceeded by the electrophilic mechanism and SO_3 served as the oxidant.[125]

In sulfuric acid, $PtCl_2$ catalyzed the oxidative carbonylation of methane.[126]

$$CH_4 + CO + H_2SO_4 \xrightarrow[180\,^\circ C]{PtCl_2} AcOH + H_2SO_3.$$

The catalytic activity of platinum increased with the introduction of $CuCl_2$ and O_2 into the system. Probably, methyl hydrogensulfate transiently formed in this reaction. It was found[127] that the use of palladium in place of platinum resulted in a one-step synthesis of acetic acid by the oxidative condensation of methane:

$$2\,CH_4 + 4\,H_2SO_4 \xrightarrow{PdCl_2} AcOH + 4\,H_2SO_3 + 2\,H_2O.$$

Later, these results were confirmed in another publication.[128] It was shown that upon the addition of oxygen, almost all palladium solubilized thus increasing its catalytic activity. Experiments with labelled $^{13}CH_4$ showed that both carbon atoms of acetic acid originated from methane. At the same time, condensation of $^{13}CH_4$ with $^{12}CH_3OH$ affords $^{13}CH_3-{}^{12}COOH$. Hence, the methyl group of acetic acid originated from methane, whereas the carbon atom of the carbonyl group most probably came from methyl hydrogensulfate. The mechanism of this process can be represented by the following reaction sequence:

$$Pd^{II}(OSO_3H)_2 + CH_4 \longrightarrow [MePd^{II}OSO_3H] + H_2SO_4,$$

$$[MePd^{II}OSO_3H] \longrightarrow Pd^0 + MeOSO_3H,$$

$$Pd^{II}(OSO_3H)_2 + MeOSO_3H + H_2SO_4 \longrightarrow$$

$$\longrightarrow Pd^{II}(CO)(OSO_3H)_2 + 2\,H_2SO_3 + H_2O,$$

$$Pd^{II}(CO)(OSO_3H)_2 + H_2O \longrightarrow Pd^0 + CO_2 + H_2SO_4,$$

$$Pd^{II}(CO)(OSO_3H)_2 \rightleftharpoons Pd^{II}(OSO_3H)_2 + CO,$$

$$[MePd^{II}OSO_3H] + CO \longrightarrow [MeC(O)Pd^{II}OSO_3H] \longrightarrow$$

$$\longrightarrow Pd^0 + AcOSO_3H,$$

$$AcOSO_3H \xrightarrow[-H_2SO_4]{H_2O} AcOH,$$

$$Pd^0 + 3\,H_2SO_4 \longrightarrow Pd^{II}(OSO_3H)_2 + H_2SO_3 + H_2O.$$

It was assumed that the low stability of this system was caused by the slow reoxidation of Pd^0 to Pd^{II}. From our point of view, the decomposition of formic acid derived from methanol present in the reaction mixture in equilibrium with methyl hydrogensulfate could result in the formation of CO.

$$MeOH \xrightarrow{[O]} HCO_2H + H_2O,$$

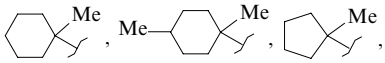
$$HCO_2H \longrightarrow CO + H_2O.$$

Quantum chemical calculations[129] of Pd^{II}-catalyzed oxidation of methane to acetic acid in sulfuric acid have shown that methane activation was the slow step and that the redox transformations $Pd^{IV} \rightleftarrows Pd^{II}$ were more probable than $Pd^{II} \rightleftarrows Pd^0$.

Carbonylation of alkanes in the presence of copper and silver carbonyls and of Pd, Pt, Os and Hg cationic carbonyl complexes in sulfuric acid, superacids and a BF_3-H_2O mixture was performed.[130] The reactions proceeded at room or slightly elevated temperature and atmospheric pressure but required the presence of alcohols or alkenes as the source of carbocations. The resulting carbocation accepts a hydride ion from the alkane, the new carbocation is carbonylated and its subsequent reaction with water affords a carboxylic acid.

$$(R^1)^+ + R^2H \longrightarrow R^1H + (R^2)^+,$$

$$(R^2)^+ + CO \xrightarrow{Cu(CO)_3^+} R^2CO^+ \xrightarrow{H_2O} R^2CO_2H,$$

R^1 = Alk; R^2 = 

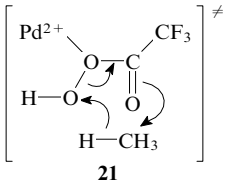
tert-C_5H_{11}, tert-C_6H_{13}.

The yield of oxygenates (oxidation products) reached 40%–95% based on the original alkane.

b. Oxidation by hydrogen peroxide

Hydrogen peroxide acts at moderate temperatures and is a convenient oxidant. However, due to the metal ion-catalyzed decomposition of H_2O_2, the yield of oxidation products rarely exceeds 25%.[7]

The oxidation of methane in a mixture of trifluoroacetic anhydride and H_2O_2 in the presence of palladium(II) compounds was described[101,131] Presumably, peroxytrifluoroacetic acid formed was the oxidant. This reaction was assumed to proceed by the molecular mechanism including the electrophilic substitution of a hydrogen atom in methane. Methane did not interact with Pd, but rather formed outer-sphere transition state **21**.



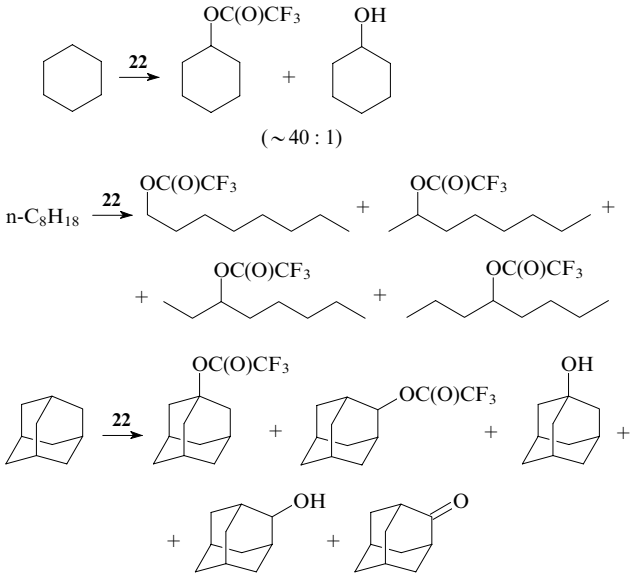
21

The role of palladium consisted of polarization of the O–O bond in the peroxy acid. The electrophilic molecular mechanism was confirmed by the fact that the aromatic ring of *p*-xylene was oxidized 100 times faster than the rather weak benzyl C–H bond. Moreover, the oxidation of *cis*- and *trans*-1,2-dimethylcyclohexanes with peroxytrifluoroacetic acid proceeded with complete retention of their configuration.[132]

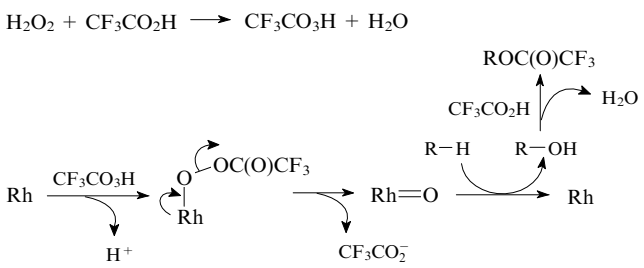
The complexes $Pd(hfacac)_2$ and $Cu(hfacac)_2(H_2O)_2$ (hfacac is hexafluoropentane-2,4-dionate) were studied as the catalysts under the same conditions.[133] The palladium

complex turned out to be more active than the copper complex. Ethane and propane were oxidized to the corresponding trifluoroacetates much more easily as compared with methane. It is noteworthy that the ratio of isopropyl and propyl esters was ~6.7 for Pd, and ~40 for Cu. No data on the formation of acetone and propionic acid and on the bond cleavage in ethane and propane are available. It was assumed that the reaction proceeds *via* an outer-sphere transition state with the structure analogous to **21**. The coordination of peroxytrifluoroacetic acid to palladium enhanced its electrophilic properties.

Cyclohexane, octane and adamantane were oxidized in an $H_2O_2-CF_3CO_2H$ system.[134] Different Rh, Pd, Ru, Pt and Fe compounds were studied as the catalysts. The $[Rh_3O(OAc)_6(H_2O)_3]OAc$ complex (**22**) exhibited the highest activity. Cyclohexanol and cyclohexyl trifluorophosphate in the ratio ~1 : 40 were obtained from cyclohexane, whereas all three isomeric secondary trifluoroacetates in the approximately equal ratio and a small amount of primary trifluoroacetate were obtained from octane. The oxidation of adamantane produced a ketone in addition to alcohols and esters.

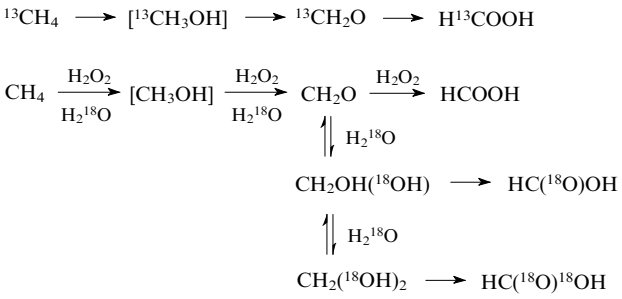


A mechanism involving the alkane activation on a rhodium oxo complex was put forward.



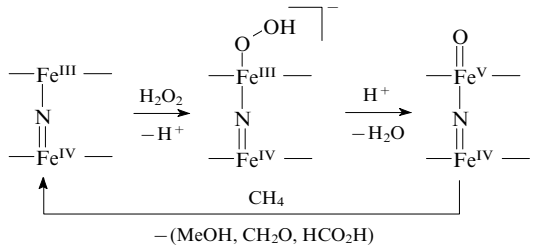
The synthesis of binuclear iron phthalocyanine complexes with a nitride bridge was reported.[135] Tetrabutylphthalocyanine complexes were soluble in acetonitrile and catalyzed the oxidation of methane by hydrogen peroxide to methanol, formaldehyde and formic acid. Unfortunately, acetonitrile was also oxidized. The silica gel-supported μ-nitridobis(iron phthalocyanine) was shown to catalyze the oxidation of methane (P = 3.2 MPa) by hydrogen peroxide in water. In 0.1 M H_2SO_4, the rate of this reaction increased five- to sixfold, because methanol was quickly oxidized to formaldehyde and formic acid and could not be detected in aqueous catalyzates.

Labelling studies have shown that the process proceeds by the following scheme:



Based on the data from electron spectroscopy, EPR spectroscopy and ESI MS, a mechanism that involved the methane activation and oxidation by a high-valence oxo complex was proposed (Scheme 3).[135] μ-Nitrido iron phthalocyanine was the axial ligand with respect to the oxo iron phthalocyanine moiety. The role of nitride consisted of stabilization of the high-valence iron states.

Scheme 3



—Fe— is iron phthalocyanine.

Thus, the catalyst under consideration is efficient in water and can be regarded as a proper model of cytochrome P450.

The formation of a nitride bridge was postulated for the catalysis by the $[Cl_4(O)Os^{VIII}{\equiv}N{\rightarrow}M^{III}]$ complex, where M^{III} is a Lewis acid [$FeCl_3$ or $Sc(OTf)_3$].[136] This catalytic system was active in the oxidation of alkanes and cycloalkanes by hydrogen peroxide and alkyl hydroperoxides in CH_2Cl_2-AcOH or CH_2Cl_2-MeCN mixtures. These reactions afforded alcohols and ketones in good yields under very mild conditions (~23 °C). The following data corroborate the molecular mechanism:

— the yield of products and their ratio was virtually independent of the presence of oxygen;

— the addition of $BrCCl_3$ to the system had no effect on the yield of products;

— hydroxylation of *cis*- and *trans*-1,2-dimethylcyclohexanes proceeded with complete retention of their configuration.

As opposed to the models of cytochrome P450, which are sufficiently well developed (*e.g.*, see Ref. 13), the modelling of non-heme oxygenases dramatically lags behind. This is associated with the more complex structure of active sites in such enzymes and the kinetic instability of simple complexes with mono- and bidentate ligands. Among the studies on this subject, mention should be made of investigations by Shteinman *et al.*[26, 39, 137–143] in which different

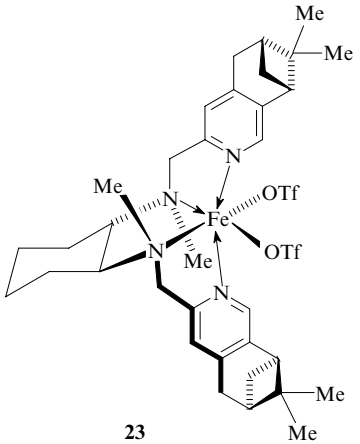
N,O-polydentate ligands were used in building models of methane monooxygenase (MMO). Particularly, tetranuclear iron complexes with the octadentate ligand 2,6-bis{3-[*N*,*N*-bis(2-pyridylmethyl)amino]propoxy}benzoic acid (L—H) containing two Fe—O—Fe binuclear cores have recently been synthesized and studied.[142] The distance between the cores was about 10 Å, and the Fe—O distances were approximately 3.1 Å. Such complexes catalyzed the oxidation of *cis*-1,2-dimethylcyclohexane by peroxide proceeding with retention of configuration, which pointed to the molecular reaction mechanism. The aqua complex $[Fe_2(m\text{-}O)_2L(H_2O)_2]_2(ClO_4)_6$ exhibited the highest activity, the TON was 6.5 at 20 °C.

The larger TON (43 in 28 h) in this reaction was demonstrated by the $[Fe_2(\mu\text{-}O)L_2(H_2O)_2](ClO_4)_2$ complex, where L—H is *N*,*N*-bis(2-pyridylmethyl)pyridine-2-carboxamide.[141]

In the cyclohexane oxidation, the ratio of products cyclohexanol : cyclohexanone was 7 : 1, whereas for the adamantane oxidation, the ratio 3-isomer : 2-isomer was 6 : 1. These results together with the 97% retention of the configuration in the oxidation of *cis*-1,2-dimethylcyclohexane confirmed the molecular mechanism of this reaction.

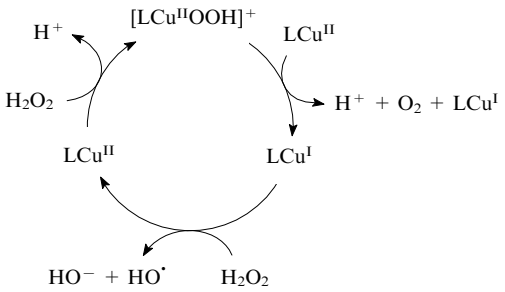
The effect of several iron complexes with polydentate ligands in the peroxide oxidation of cycloalkanes was compared for low and high H_2O_2 concentrations.[143] It was found that for high H_2O_2 concentrations, two types of active intermediates operated. Thus, a complex containing an $Fe^V(O)(OH)$ fragment was responsible for the alcohol formation and a complex containing an $Fe^V(O)(OOH)$ group was involved in the formation of both an alcohol and a ketone.

Iron complex **23** containing a sterically constrained bis(pyridylmethylamino) ligand proved to be fair MMO model.[144] Under the action of H_2O_2, this complex catalyzed the hydroxylation of *cis*-1,2-dimethylcyclohexane and menthyl acetate in 50% aqueous acetic acid, with the yields of about 60% and high degree of stereoselectivity.



23

The design of models of copper-containing MMO that operated extremely efficiently under mild conditions in acetonitrile with hydrogen peroxide as the oxidant was reported.[145–149] A simple and convenient synthesis of copper(II) bi-, tri- and tetranuclear complexes containing triethanolamine as the bridging ligand was carried out.[145] These complexes catalyzed oxidation of cyclohexane to cyclohexanol and cyclohexanone. The tetranuclear complex $[(O)Cu_4(tea)_4(BOH)_4](BF_4)_2$ (LCu^{II}, H_3tea is triethanolamine) exhibited the highest activity, more precisely, one order of magnitude higher than the activity of $Cu(NO_3)_2$. Later, the kinetics of this process was studied and a mechanism in which the alkane was attacked by a hydroxyl radical formed in the reaction between Cu^I and H_2O_2 was proposed.[146]



The promoting role of acid and water was noted. Apparently, they were involved in the generation of active Cu^I species. Mono- and binuclear and polymeric copper complexes based on *N*-butyldiethanolamine[147] as well as the coordination polymer $Cu_2(H_3tea)(\mu_4\text{-}pma)]_n$ (H_4pma is pyromellitic acid) were synthesized as the MMO models.[148] They proved to be fairly efficacious and apparently operated according to a mechanism analogous to those of catalysts described above.[145, 146]

Yet another MMO model has recently been synthesized, *viz*., the heterotrimetallic complex $[FeCuCoL_3(NCS)_2.(MeOH)_2]_2 \cdot 3.2\,H_2O$ (H_2L is diethanolamine), which contained two Cu—Co—Fe cores.[149] This complex catalyzed the oxidation of cyclohexane and cyclopentane by hydrogen peroxide in acetonitrile to afford cyclic alcohols as the main products and cycloalkanones in lower amounts. The catalytic activity and selectivity of this complex in this reaction was substantially higher as compared with those comprising individual metals, which can be explained by synergism.

Thus, the considered catalysts (except for Cu-containing ones) operate by a molecular mechanism, which involves the metal oxo complexes formed from hydrogen peroxide. The high degree of stereoselectivity of these transformations was mentioned. For copper-containing catalysts, hydrogen peroxide produces the $HO^\bullet$ radicals that attack the alkanes.

c. Oxidation by potassium persulfate

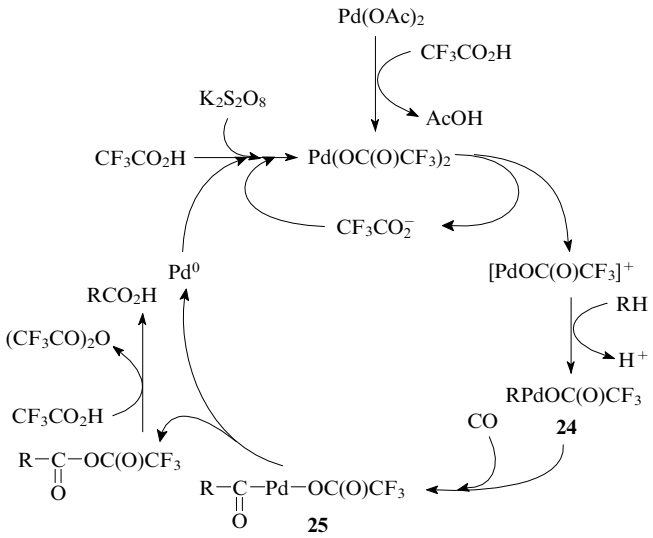
Fujuwara *et al.*[25, 150–152] studied alkane carbonylation in solutions of palladium and/or copper complexes with potassium persulfate as the oxidant. It was found that cyclohexane underwent carbonylation in the $Pd(OAc)_2$–$Cu(OAc)_2$ system at 80 °C and a CO pressure of 2.0 MPa to yield cyclohexanecarboxylic acid (4.3% relative to the substrate). The TON was ~20 in 20 h. Other co-catalysts, namely, metallic iron, $FeCl_2$, $FeCl_3$, $Co(OAc)_2$, $Ni(OAc)_2$, $Zn(OAc)_2$ proved inefficient. The activity of $Pd(OAc)_2$ itself was ~2.6 cycles over the same time and the activity of $Cu(OAc)_2$ was 1.5 cycles. Under the same conditions, ethane and propane afforded propionic (TON = 76) and butyric acids (TON = 71), the ratio of isobutyric and butyric acids being ~3.4.

It should be noted that methane carbonylation to acetic acid proceeded ~3 times more efficiently in the $Cu(OAc)_2$–$K_2S_2O_8$ system as compared with $Pd(OAc)_2$–$Cu(OAc)_2$–$K_2S_2O_8$. In the former case, the TON of the catalyst reached ~40 in 25 h. Such a noticeable difference

was explained by the different mechanisms operating in the $Pd(OAc)_2-Cu(OAc)_2$ system and $Cu(OAc)_2$ alone. Copper acetate acted by the one-electron mechanism to be discussed below in Section VIII. To elucidate the role of copper in the $Pd(OAc)_2-Cu(OAc)_2$ system, spectral studies were carried out.[151] It was found that $Pd(OAc)_2$ and $Cu(OAc)_2$ form a catalytically active heteronuclear complex with the 1 : 1 composition The data from XPS and ^{19}F NMR spectroscopy suggest partial electron density transfer from the Pd atom to the Cu atom, which enhanced the electrophilicity of palladium. XRD analysis of the 1 : 1 $Pd(OAc)_2-Cu(OAc)_2$ complex demonstrated new signals, while those corresponding to the constituents were not observed.

Presumably, in the Pd and Pd–Cu systems under consideration the mechanism of electrophilic substitution of alkanes was realized (Scheme 4).[25]

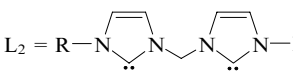
Scheme 4



The kinetic isotope effect for the carbonylation of C_6H_{12} and C_6D_{12} ($k_H/k_D \sim 3$) suggests that the attack of a strong electrophilic species $Pd(O_2CCF_3)^+$ on the alkane C–H bond to form intermediate **24** is the limiting step (see Scheme 4). This is followed by the CO coordination and insertion into the $Pd-C_{Alk}$ bond to form acyl complex **25**. The reductive elimination affords a mixed anhydride, which gives the reaction product, *i.e.*, a carboxylic acid, under the action of an excess of CF_3CO_2H.

Methane is selectively oxidized by persulfate in the absence of CO. For instance, in trifluoroacetic acid with addition of TFA, palladium biscarbene complex **26** manifested fairly high activity.[153]

$$CH_4 + CF_3CO_2H + K_2S_2O_8 \xrightarrow{L_2PdBr_2\,(\mathbf{26})} CF_3CO_2Me + 2\,KHSO_4,$$

L_2 =  (R = Me, Bu^t).

The reaction at 80 °C and $P_{CH_4} = 3$ MPa yielded 30 mol of methyl trifluoroacetate in 14 h. Under these conditions, the (Bpym)$PtCl_2$ catalyst and the Pd phenanthroline complex were totally inactive, while $Pd(OAc)_2$ proved to be 2.5-times less efficient.

Other examples of using $K_2S_2O_8$ as the oxidant pertain to radical processes and are considered in Section VIII.

2. Catalytic reactions involving dioxygen

Dioxygen is the most environmentally friendly oxidant. The essence of operation of iron-containing biocatalysts is that under the action of reducing agents, dioxygen is converted into the following species acceptable for the oxidation of alkanes:[11]

$$Fe-O{=}O + e + H^+ \longrightarrow Fe-O-O-H,$$
$$Fe-O-O-H + H^+ \longrightarrow Fe^+{=}O + H_2O.$$

In model systems, hydrogen, sodium borohydride, zinc, ascorbic acid, carbon monoxide, *etc.* were used as the reducing agents.[10, 11, 14] We believe that CO is one of the most convenient reducing agents because its oxidation affords CO_2, which can easily be removed from the reaction zone.

a. Alkane oxidation reactions in the absence of reducing agents

The examples of the oxidation of alkanes where the oxygen activation did not require the presence of a reducing agent are documented. Moiseev and co-workers [102, 103] found that cobalt(III) trifluoroacetate performs stoichiometric oxidation of methane in CF_3CO_2H solutions at 30 atm and 180 °C to afford methyl trifluoroacetate:

$$CH_4 + 2\,Co(O_2CCF_3)_3 \longrightarrow$$
$$\longrightarrow CF_3CO_2Me + 2\,Co(O_2CCF_3)_2 + CF_3CO_2H.$$

Cobalt(II) trifluoroacetate could be reoxidized by dioxygen to produce the cobalt(III) salt:

$$2\,Co(O_2CCF_3)_2 + \frac{1}{2}\,O_2 + 2\,CF_3CO_2H \longrightarrow 2\,Co(O_2CCF_3)_3 + H_2O.$$

Evidently, these two reactions represent overall the catalytic oxidation of methane by dioxygen:

$$CH_4 + \frac{1}{2}\,O_2 + CF_3CO_2H \longrightarrow CF_3CO_2Me + H_2O.$$

The low yield of methyl trifluoroacetate (4 mol per oxidation equivalent of Co) was associated with the formation of insoluble cobalt fluorides. In the gas phase, CO_2 was detected in a yield independent of the methane pressure. Apparently, CO_2 resulted from decarboxylation of trifluoroacetic acid or its anion.

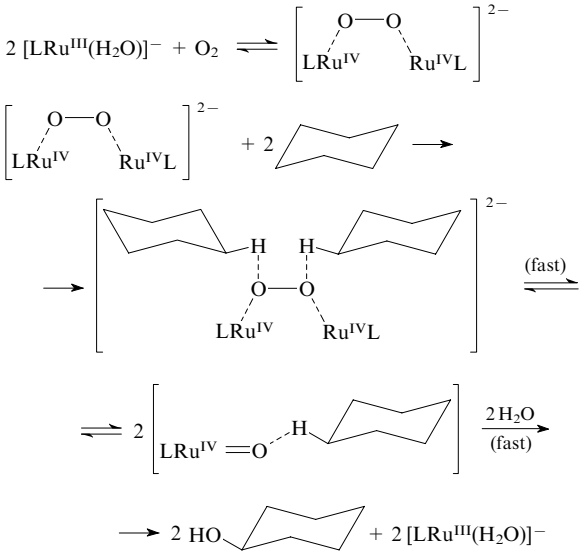
In a recent publication,[106] UOP LLC, a Honeywell Company, presented data on oxidation of methane by dioxygen in the presence of $Mn(O_2CCF_3)_3$ prepared *in situ* from Mn_2O_3 (of 99.999% purity) in CF_3CO_2H at 180 °C. About 30 min after the beginning of the process, the catalyst activity sharply decreased. With the introduction of SiO_2, the catalyst service life increased to 100 min. In the steady-state region, the reaction afforded 0.24 mmol of CF_3CO_2Me in 1 min. The process rate can be calculated as $\sim$0.1 mol litre^{-1} h^{-1} ; the specific catalytic activity and the TON per Mn oxidation equivalent were 14.4 h^{-1} and 24, respectively.

Presumably, the catalyst deactivation was associated with the formation of inactive MnF_2.

The formation of inactive fluoride (CoF_2), which has also been observed earlier,[103] is associated with the instability of CF_3CO_2H at high temperatures in the presence of oxygen. Apparently, silica gel sorbed the fluorine compounds thus preventing the formation of MnF_2. This was

the reason for the decrease in the catalyst life time. The aforementioned data [106] are of certain interest; however, due to quick deactivation, the catalysts can hardly be employed.

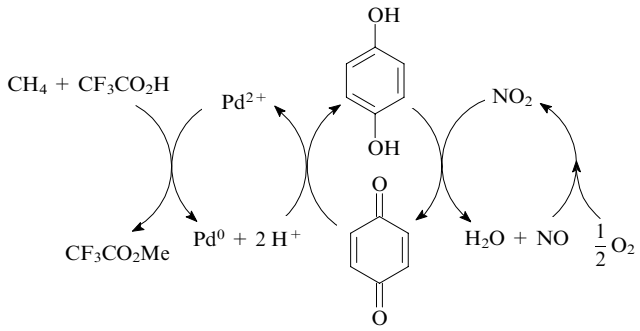
The K[Ru(HEdta)Cl] complex can be mentioned as a single-component catalyst that operates in the absence of specially added re-oxidant. This complex catalyzed oxidation of cyclohexane to cyclohexanol and cyclohexanone under mild conditions in water–dioxane mixtures.[154] The catalyst activity increased ~40-fold upon the addition of cetyltrimethylammonium chloride. This quaternary salt not only was the phase-transfer catalyst but also could increase the solubility of cyclohexane in water at the interface. The kinetics of this process was studied in detail and an interesting mechanism involving the formation of μ-peroxodiruthenium unit was put forward.



L = $Edta^{4-}$.

A catalytic system including re-oxidants was described by Chinese scientists.[155] Methane reacted with oxygen in the presence of the $Pd(OAc)_2$–benzoquinone–$NaNO_2$ system. Presumably, oxidation of methane by palladium trifluoroacetate underlies this process (Scheme 5).

Scheme 5



Sodium nitrite rapidly decomposed in CF_3CO_2H to NO; the latter was easily oxidized to NO_2:

$$NaNO_2 + CF_3CO_2H \longrightarrow HNO_2 + CF_3CO_2Na,$$

$$2\,HNO_2 \longrightarrow NO + NO_2 + H_2O,$$

$$NO + \frac{1}{2}O_2 \longrightarrow NO_2.$$

However, Scheme 5 seems doubtful. As has already been noted, methane could not be oxidized under the action of $Pd(O_2CCF_3)_2$.[102–105] It is a Pd nitrite complex that could serve as the oxidant. Its action may be described in a simplified form by the following equation:

$$2\,Pd^{II}(O_2CCF_3)(NO_2) + CH_4 + 3\,CF_3CO_2H \longrightarrow$$
$$\longrightarrow 2\,Pd^{II}(O_2CCF_3)_2 + CF_3CO_2Me + 2\,NO + 2\,H_2O.$$

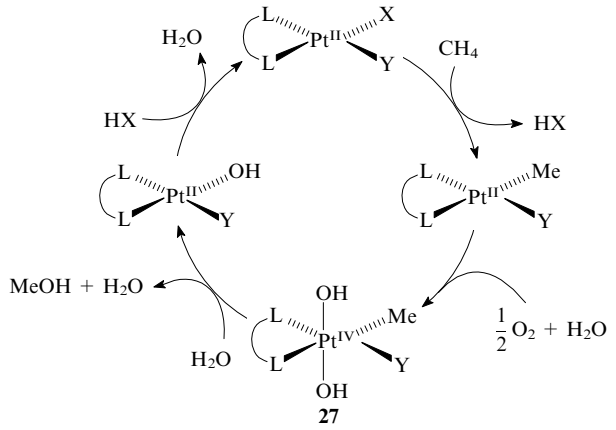
The regeneration of the nitrite complex proceeded by the reaction

$$2\,Pd^{II}(O_2CCF_3)_2 + NO + NO_2 + H_2O \longrightarrow$$
$$\longrightarrow 2\,Pd(O_2CCF_3)(NO_2) + 2\,CF_3CO_2H.$$

The role of quinone is not fully clear, because NO_2 itself can act as the re-oxidant. Probably, quinone stabilizes palladium in the low-valence state.

The complex $(Bpym)PtCl_2$ and heteropolyacids were used in the development of a catalyst for mild oxidation of metane.[156] Methylation of the bipyrimidine ligand afforded a cationic complex which served as the counter-ion for the $[PV_2Mo_{10}O_{40}]^{2-}$ anion by the ion-exchange procedure. The thus formed heteropolyacid was wet impregnated onto silica gel and used in the oxidation of methane in aqueous media. The reaction products contained methanol, formaldehyde and acetaldehyde. Several routes of acetaldehyde formation were considered. It was shown using labelling experiments ($H_2{}^{18}O$ and $^{18}O_2$) and oxidation of $^{13}CH_3OH$ that the most likely route was the oxidation of methane to formaldehyde *via* methanol, followed by its coupling with methane. A catalytic cycle that included intermediate **27** containing a methyldihydroxyplatinum(IV) fragment was proposed earlier [28] (Scheme 6). Presumably, the presence of the heteropolyacid favoured the aerobic oxidation of Pt^{II} to Pt^{IV}.

Scheme 6



Y is solvent, X is anion, L⌒L is bidentate *N*,*N*-heteroaromatic ligand.

An example of using the catalytic 'Shilov chemistry' was described.[157] It was found that the Pt^{II}–Pt^{IV}–Cl^- system can be replaced by Pt^{II}–Cu^{II}–Cl^-. At 150 °C and the oxygen pressure of 8.26 MPa, in an aqueous solution acidified with H_2SO_4, the following substrates were oxidized: methane-, ethane- and propanesulfonic acids, propionic acid and ethylphosphonic acids. As the result, the corresponding hydroxy compounds were obtained. The low reactivity of methanesulfonic acid was explained by the strong electron-withdrawing effect of the sulfonate group.

It is the methyl groups of ethane- and propanesulfonic acids that is preferably oxidized. Presumably, this serves as evidence for the electrophilic two-electron mechanism rather than the radical mechanism. Moreover, in the competitive oxidation of ethane and ethanesulfonic acid, the ratio of reaction products remained virtually unchanged on moving from the $Pt^{II}-Pt^{IV}-Cl^-$ system to the $Pt^{II}-Cu^{II}-Cl^-$ system. This also corroborates the two-electron mechanism. Note that the deuterium – hydrogen isotope exchange in non-consumed substrates with the medium proceeded both in the presence and in the absence of oxygen. In the presence of oxygen, the degree of exchange was higher, which was explained by the permanent generation of catalytically active species. This also involved the sufficiently active exchange in the methylene groups, for example, in position 3 of n-butanesulfonic acid. In the absence of oxygen, the degree of isotope exchange in CH_3 and 3-CH_2 groups increased. Probably, an alternative reaction route was realized to a small extent.

Thus, in the study under discussion, the principle of designing palladium–re-oxidant catalytic systems developed for the alkene oxidation[22] was realized for the oxidative functionalization of alkanes.

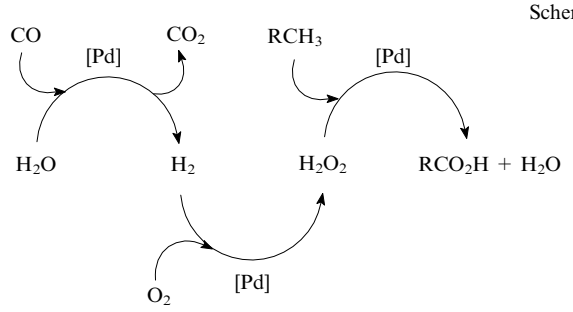
b. Alkane oxidation reactions involving reducing agents

Sen and co-workers[16,158–160] studied the oxidation, in the presence of Pd/C and Pd/C(or K_2PdCl_4)–$CuCl_2$ catalytic systems, of methane, ethane and butane and of several saturated organic compounds containing functional groups. Carbon monoxide was used as the reducing agent. The use of hydrogen proved to be less efficient, because hydrogen peroxide formed rapidly decomposed to H_2O and O_2, which decreased the hydrogen pressure.

It was shown that in D_2O acidified with DCl, in the presence of Pd/C, the efficient ethane oxidation to ethanol, acetic and formic acids occurred.[158] Presumably, transient formation of ethanol took place only at 70 °C. As the temperature increased, the yield of formic acid passed through a maximum, which was most probably associated with its decomposition to CO and H_2O. In the absence of CO or DCl, no reaction occurred. Labelling experiments with ^{13}CO showed that all CO_2 was formed from CO. Running the reaction in the absence of a substrate resulted in formation of 0.002 mol litre^{-1} of hydrogen peroxide. The Pt/C catalyst proved to be less effective than Pd/C due to the greater tendency of platinum to decompose hydrogen peroxide. The transient formation of H_2O_2 was also proved by independent experiments. For example, when hydrogen peroxide was added as the oxidant at 30 °C, ethane was oxidized slowly to ethanol, acetic and formic acids. Because the use of ^{13}CO failed to afford $CH_3{}^{13}CO_2H$, it is evident that the $^{\bullet}CH_3$ radical was not the intermediate (*vide infra*). Hence, the two-electron mechanism was realized (Scheme 7).[16]

However, it seems improbable that H_2O_2 was formed from H_2 generated in the water gas conversion. Even if this reaction did proceed, the H_2 activation was hardly probable under the conditions of the high CO content in the original gas. At least, an induction period associated with the transformation of a considerable part of CO by the reaction of water gas conversion should be observed. At the same time, as was mentioned above, information on the direct reaction of CO with oxygen and water to afford H_2O_2 is available.[94–96]

Scheme 7



R = H, Me, Pr^n.

Methane was oxidized much less efficiently as compared with ethane[158] and produced formic acid as the main product. The substitution of CF_3CO_2H for water did not increase the Pd/C efficacy but the simultaneous introduction of $CuCl_2$ led to the formation of an active catalytic system for methane selective oxidation to methyl trifluoroacetate.[159] A similar effect was achieved when $Cu(O_2CCF_3)_2$ and 2 equiv. of NaCl were added as the co-catalysts. The substitution of K_2PdCl_4 for Pd/C resulted in sharp acceleration of the reaction. Ethane and butane exhibited the higher reactivity as compared with methane. Moreover, for ethane and butane, the C–C bond activation and cleavage were observed.

We believe that the extremely high activity of the $K_2PdCl_4-CuCl_2$ system is associated with the effect of colloidal palladium. Most probably, the colloidal palladium particles enlarge as the reaction proceeds and the activity of the system decreases. When a Pd complex was used, the carbonylation reactions could occur because such complexes are known to be the most active catalysts of alkene carbonylation.[161] Insofar as no acetic acid was detected that could be formed in the oxidation of methane in the presence of CO by the radical mechanism, it was assumed that the mentioned catalytic systems operated by the two-electron mechanism.[159] Carbon monoxide is known to be an efficient trap of methyl radicals; the rate constant for this reaction in water was found to be 2×10^6 litre mol^{-1} s^{-1} (Ref. 162).

The Pd/C–$CuCl_2$ catalytic system in the presence of an O_2 + CO mixture in aqueous CF_3CO_2H also turned out to be efficient in the oxidation of 'remote' C–H bonds and the cleavage of C–C bonds in functionalized derivatives of hydrocarbons, namely, propionic and butyric acids, ethane- and propanesulfonic acids, ethylphosphonic acid, 1-chloropropane, cumene and 4-isopropylbenzoic acid.[160] Thus, propionic acid transformed to 3-hydroxypropionic, acetic and formic acids. The addition of mercury inhibited the oxidation process, which substantiated the effect of heterogeneous palladium. The following arguments were advanced for the two-electron mechanism: first, sufficiently high selectivity of the attack on the stronger primary C–H bond was observed; second, the chlorination of 1-chloropropane (a radical reaction) proceeded exclusively at position 2, whereas its oxidation occurred at the methyl group; third, in the competitive oxidation of ethane and cumene (or 4-isopropylbenzoic acid), ethanol was the main product despite the much lower concentration of ethane.

It deserves mention that gradual introduction of hydrogen peroxide into the reaction mixture using a syringe pump brought about hydroxylation of n-propanol to 1,3- and 1,2-propanediol in the presence of $CuCl_2$; this did not occur on Pd/C.[160] At the same time, Pd/C, like $CuCl_2$, catalyzed the

oxidative cleavage of the C–C bonds, *i.e.*, the reaction produced acetic and formic acids. It was thus concluded that the functions of catalytic system components were clearly differentiated. The role of Pd/C consisted of the converting the $CO + O_2$ mixture to hydrogen peroxide under the action of water, whereas $CuCl_2$ in the presence of H_2O_2 catalyzed the hydroxylation of alkanes. Taking into account that the activity of the $Pd/C - CuCl_2$ system passes through a maximum depending on the $CuCl_2$ concentration, the following assumption can be made. The palladium surface atoms are blocked by $CuCl_2$ species that are in equilibrium with the former, which affects the catalytic activity of the system. An alternative and presumably a more probable pathway of hydrogen peroxide formation includes the following reaction sequence:

$$2\,CuCl^+ + CO + H_2O \xrightarrow{[Pd]} 2\,CuCl + CO_2 + 2\,H^+,$$

$$2\,CuCl + O_2 + 2\,H^+ \longrightarrow 2\,CuCl^+ + H_2O_2.$$

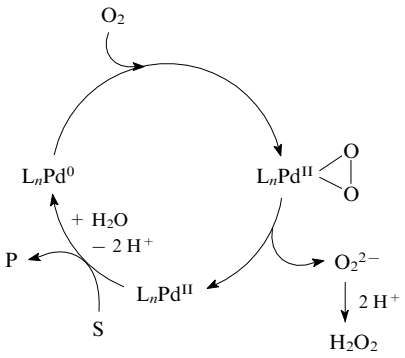
As was discussed above, in several cases the oxidation of copper(I) and iron(II) with dioxygen in protic media involved the formation of not only water but also hydrogen peroxide.[97–100] The regeneration of Cu^I occurred by the palladium-catalyzed reduction of Cu^{II} with carbon monoxide.

The difference in the oxidation products of n-propanol with hydrogen peroxide in the presence of Cu^{II} and Pd/C makes it possible to assume that the mechanisms of C–H and C–C bond activation substantially differ, *i.e.*, on Cu^{II} species, the methyl group is hydroxylated, while on Pd/C particles, the cleavage of C(1)–C(2) and C(2)–C(3) bonds occurs.

The catalytic systems of alkane oxidation usually involve copper, iron and vanadium compounds as the co-catalysts. As has recently been reported,[163] tetrachlorobenzoquinone (TQ) was used in combination with Pd/C for the oxidation of methane in aqueous trifluoroacetic acid. The reaction proceeded at 140 °C and for CH_4, CO and O_2 pressures equal to 2.5, 1.0 and 0.5 MPa, respectively, to afford CF_3CO_2Me and HCO_2H. In the absence of TQ, formic acid was the main product. The addition of TQ decreased the yield of HCO_2H and sharply increased the yield of methyl trifluoroacetate. In the reaction mixture, the formation of hydrogen peroxide was also observed and its content depended linearly on the TQ concentration.

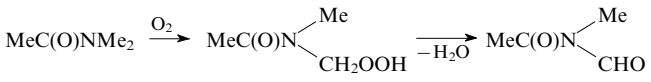
Let us consider the reactions of alkane oxidation that make use of hydrogen as the reducing agent. Thus in the presence of Pd/Al_2O_3 and co-catalysts, *i.e.*, iron and vanadium compounds, cyclohexane was oxidized to a mixture of cyclohexanol and cyclohexanone in a ~3 : 1 ratio.[164] The reaction was carried out in a solution of propionic acid at 36 °C for the H_2 and O_2 pressures of 64 MPa and the N_2 pressure of 6.4 MPa. (Nitrogen was added to avoid explosion.) The role of the palladium catalyst lies in the generation of hydrogen peroxide according to Scheme 8, while iron- or vanadium-containing compounds catalyzed the cyclohexane oxidation by hydrogen peroxide; the latter mechanism was not shown. Under the above-mentioned conditions, the specific activity of the catalyst per equivalent amount of Fe or V was 25–38 cycles per h. From Scheme 8, it follows that alkenes and alcohols can be used as the reducing agents along with H_2 and CO.

Scheme 8

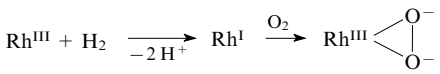


S is substrate, P is product; S = RCH=CH_2, P = RC(O)Me; S = RCH_2OH, P = RCHO; S = H_2, P = H_2O; S = CO, P = CO_2.

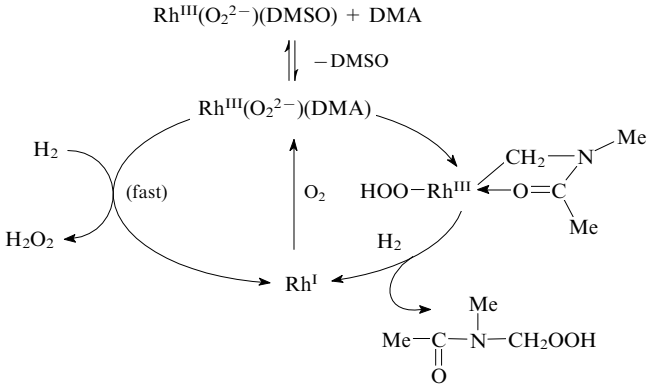
An interesting example of the oxidation of the =N–Me group in *N*,*N*-dimethylacetamide catalyzed by the $RhCl_3(DMSO)_3$ complex was reported.[165] The reaction proceeded in the substrate solution at 50 °C with the partial O_2 and H_2 pressures of 34.7 and 66.7 kPa, respectively, to furnish hydrogen peroxide and *N*-hydroperoxymethyl-*N*-methylacetamide. The latter was dehydrated to *N*-methyl-*N*-formylacetamide either during the experiment or in the course of its analysis by gas chromatography



Dioxygen was assumed to be activated through the oxidative addition to rhodium(I)



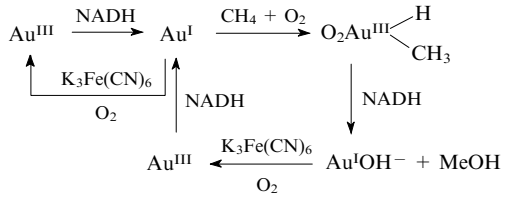
In the absence of H_2, no oxidation was observed. If an aerobic solution was treated with hydrogen for a certain time, the absorption of H_2 and O_2 resumed. The introduction of H_2O_2 or Bu^tO_2H in place of the H_2 and O_2 mixture resulted in a decrease in the reaction rate by a factor of 5–8. The role of hydrogen is believed to consist of the primary reduction of rhodium(III) to rhodium(I) and the prevention of the formation of inactive polynuclear complexes. The kinetic data corroborated the mechanism depicted below.[165]



Other catalytic systems for the oxidation of alkanes with dioxygen in the presence of hydrogen will be considered in Section VIII devoted to one-electron reactions.

Gold-containing catalysts were studied by Shilov and co-workers.[166–168] First, it was found that the Au-protein from the aurophilic bacteria *Micrococcus luteus* utilized gold in the methane activation and its oxidation to methanol in aqueous media. Gold ions were bound by hydroxyl groups of rutin as a co-factor. A functional model of the active site of the Au-protein that involves $HAuCl_4$, rutin and $K_3Fe(CN)_6$ was suggested. This system oxidized methane with dioxygen in the presence of the reduced form of nicotinamide adenine dinucleotide (NADH).[167] At a concentration of $HAuCl_4$ of 0.33 μmol litre^{-1}, production of methanol at room temperature reached 33 μmol litre^{-1} in 90 h.§ To provide the solubility of the Au–rutin complex, 33% of ethanol was added to the reaction mixture. It is of note that methane increased the NADH-oxygenase activity of both the protein and the model system. However, the choice of $K_3Fe(CN)_6$ as the system component and its functions have not been rationalized. According to the proposed mechanism (Scheme 9),[167] it can be concluded that $K_3Fe(CN)_6$ favours the activation of dioxygen and the oxidation of Au^{I} to Au^{III}. $K_3Fe(CN)_6$ could effect the electron transport from NADH to dioxygen to form an unidentified two-electron oxidant.

Scheme 9



A quantum chemical study of the methane activation with different gold(III) aqua chloride complexes has shown that the reaction of $[Au(H_2O)_2Cl_2]^+$ with methane is characterized by a rather low energy barrier.[169]

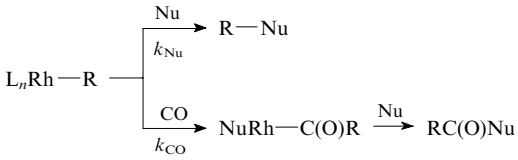
c. Oxidation and oxidative carbonylation of alkanes in the presence of catalytic systems based on rhodium complexes and co-catalysts

In 1994, Lin and Sen[170] described a promising catalytic system for the catalytic functionalization of methane, which contained $RhCl_3$, KI and NaCl (or DCl) in D_2O. At 95 °C and partial pressures of CH_4, CO and O_2 of 6.8, 1.36 and 0.68 MPa, respectively, the major reaction product was acetic acid (27.6 mol per mol of Rh in 420 h). Methanol and formic acid formed in insignificant amounts. Analysis of these data allowed us to assume that the rate of this process can be increased on moving from water to a water-organic medium, particularly, to water–carboxylic acid mixtures. Examples of this kind of effects are known for reactions of alkene carbonylation in the presence of metal complexes.[171,172] Indeed, it was shown that the efficiency of the rhodium–iodide–chloride system considerably increased in aqueous heptafluorobutyric,[173] acetic[174,175] or trifluoroacetic[176,177] acids.

§ Later, different flavones were studied in this reaction but only quercetin proved to be an efficient ligand for the complex with gold so that the yield of methanol in the presence of 0.2 μmol litre^{-1} of this catalyst was 12 μmol litre^{-1} in 48 h (Ref. 168).

The oxidation and the oxidative carbonylation of methane and other alkanes in an aqueous solution of heptafluorobutyric acid ($C_3F_7CO_2H : D_2O = 6:1$) were studied.[173] Alkanes C_2–C_4 were more reactive; not only their C—H bonds were involved but the C—C bonds were also cleaved. Using labelling (^{13}C) experiments, it was proved that the carbonyl group of acetic acid originated from CO. The main amount of CO_2 formed from CO rather than from CH_4. In competitive reactions ($^{13}CH_4 + {}^{12}CH_3OH$) it was shown that methane is more reactive than methanol; moreover, acetic acid formed exclusively from methane. Thus, the mechanism of this process differs substantially from that of carbonylation of methanol in the Monsanto process, which includes the formation of MeI and the oxidative addition to Rh^{I} (Refs 178, 179). The methane activation step was not considered in the analysis of the mechanism[173] and the ratio of the reaction products was interpreted to be a consequence of the ratio of the constants k_{Nu} and k_{CO} dependent on the properties of the medium (Scheme 10).

Scheme 10



Nu = HO^-, $C_3F_7CO_2^-$.

The role of the iodide co-catalyst was not rationalized and an active oxygen species ('O') was assumed to form by the reaction

$$H_2 + O_2 \longrightarrow H_2O + \text{'O'},$$

while hydrogen formed upon water gas conversion. Above, the low probability of such a process for palladium was noted. As a rule, rhodium compounds catalyzed the conversion of carbon monoxide with water in basic media.[180] In the Monsanto process, this reaction proceeded but at very high HI concentrations.[171,178,179] Moreover, we have experimentally shown that at 95 °C, the CO pressure of 0.64–1.84 MPa and the mole fraction of water in CF_3CO_2H of 0.64–0.91, the rhodium–iodide–chloride system of methane oxidation did not catalyze the water gas conversion reaction.[176,177]

By invoking different published data and analyzing their own data, Sen and co-workers[173] were inclined to believe that the two-electron mechanism is more probable in comparison with the radical mechanism. In particular, methane proved to be 5 times more reactive than methanol, despite the lower energy of the C—H bond homolytic cleavage in the latter. The investigations of the simultaneous functionalization of C_2H_6 and C_2D_6 revealed the primary isotope effect $k_H/k_D = 2.65$ for the formation of ethyl heptafluorobutyrate. This result is inconsistent with the one-electron transfer mechanism according to which only a modest secondary isotope effect would be observed. Presumably, in the presence of an excess of I^- in the reaction medium, one cannot expect the appearance of a radical more reactive than $I^{\bullet}$ or an oxidant stronger than I_2. None of these reagents react with methane. Activation of the alkane C—H bond apparently occurred within the coordination sphere of the rhodium complex. However, the presence of oxygen was ignored as well as the possibility

of formation of some active oxygen-containing species that can be involved in the process.

Several studies aimed at increasing the efficiency of the rhodium–iodine-containing catalytic system and elucidating certain aspects of its operation were performed at the Institute of Structural Macrokinetics and Materials Science of the Russian Academy of Sciences.[174–177, 181–183] Soon after the appearance of the cited paper,[173] we reported on the possibility of methane oxidation and oxidative carbonylation in the presence of the rhodium–iodide–chloride catalytic system in the $CD_3CO_2D-D_2O-DCl$ mixture.[174, 175] As in water, acetic acid was the main reaction product. In addition, the reaction mixture contained methanol, methyl trifluoroacetate and formic acid. The total efficiency of the catalyst under comparable conditions turned out to be 5–6 times higher than in water. Probably, deuterated hypoiodic acid generated in the reaction between DI and O_2 is an intermediate oxidant. The formation of acetic acid involving IO^- is thermodynamically favourable ($\Delta G = -21$ kJ mol^{-1}).

$$CH_4 + CO + IO^- \longrightarrow AcOH + I^-.$$

It was also shown that methanol and methyl iodide could not be carbonylated under the conditions of methane conversion. Methanol transformed into methyl acetate, while methyl iodide was converted to methyl chloride. Thus, as in the above publication,[173] the mechanism of the process differed from that stated for the Monsanto process. It also deserves mention that carrying out the latter involved the use of very high HI concentrations.[178, 179]

The analysis of the data on both the stoichiometric and catalytic alkane oxidation and the preparative synthesis of oxygen-containing compounds[107] made it possible to conclude that trifluoroacetic acid is one of the best solvents. This increased the efficiency of the rhodium–iodide–chloride system as compared with methane oxidation and oxidative carbonylation in heptafluorobutyric and acetic acids.[176, 177]

It turned out that in the presence of the system under study (with DCl in place of NaCl) in aqueous trifluoroacetic acid, the yields of the reaction products (CH_3OD, $CF_3CO_2CH_3$, HCO_2D, CH_3CO_2D) passed through maxima depending on concentrations of water and the iodide ions and CO pressure. As the NaCl concentration increased to 0.2 mol litre^{-1}, the yield of CH_3CO_2D also increased, whereas the yields of the other products somewhat decreased. Further increase in the NaCl concentration inhibited the formation of all products.[176, 177]

The solvent-induced kinetic isotope effects were found to be $k_H/k_D \approx 2.0$ for methanol, methyl trifluoroacetate, acetic acid and carbon dioxide and $k_H/k_D \approx 1.7$ for formic acid.

Special experiments have shown that under the conditions of methane oxidation and oxidative carbonylation, metallic titanium was also oxidized.[184] The intensity of titanium oxidation passed through a maximum at the same water concentration as the yield of organic products from methane. Apparently, both methane and titanium were oxidized with the same oxidant formed from dioxygen, the reducing agent and the medium components. Hydrogen peroxide or its analogues could serve as the oxidant (*vide infra*). It is known that titanium is oxidized due to the destruction of its protective oxide film by the following reaction:

$$TiO_2 + H_2O_2 \longrightarrow H_2TiO_4.$$

Bearing in mind the volatility of iodine, the high corrosivity of hydroiodic acid and the possibility of precipitation of RhI_3 at low CO pressures in the rhodium–iodide–chloride system, it seems promising to develop an iodine-free system. Being a true oxidant, hydrogen peroxide can be generated under specific conditions upon oxidation of copper(I) to copper(II) or iron(II) to iron(III).[97–100] Indeed, it was shown that the $RhCl_3-Cu_2O(CuO)-NaCl$ and $RhCl_3-FeO(Fe_2O_3)-NaCl$ systems in aqueous trifluoroacetic acid efficiently catalyzed the oxidation and oxidative carbonylation of methane.[181–183]

The introduction of copper or iron oxides as the primary co-catalysts facilitates experimental procedures and allows studying this process at low chloride ion concentrations. Under these conditions, copper oxides quickly transformed to trifluoroacetates and, probably, partly to chlorides. On the whole, the effects of rhodium–copper–chloride and rhodium–iodide–chloride systems were similar, namely, the same products were obtained and similar dependences of the yield of products on the chloride ion concentration and the CO pressure were observed. Neither system catalyzed the isotope exchange of methane with the medium (similar values of the kinetic isotope effect were obtained, *vide infra*) but both oxidized metallic titanium. However, differences between the systems were observed. The former was approximately 1.5 times more active in the methane conversion as compared with the latter, less sensitive to the water content and less corrosive with respect to titanium. Moreover, the solvent-induced kinetic isotope effects of products were also different.

The oxidation of metallic titanium can be considered as a test for the presence of H_2O_2 or its equivalents, namely, peroxytrifluoroacetic acid, hypoiodous acid (in the iodide system) and copper(II) hydroperoxide (in the copper-containing system). Hence, it was assumed that hydrogen peroxide was the primary intermediate in the dioxygen interaction with the medium. This oxidized HI to HIO in the rhodium–iodide–chloride system. The narrow range of activity of this system as a function of the water concentration can be associated with the fact that in this interval both the conditions of HIO stability and those required for the methane activation and oxidation are fulfilled. The generation of hypoiodous acid can be considered as the conjugated oxidation of HI and CO by the reactions

$$2HI + O_2 \longrightarrow H_2O_2 + I_2,$$

$$HI + H_2O_2 \longrightarrow HIO + H_2O,$$

$$I_2 + CO + H_2O \xrightarrow{[Rh]} 2HI + CO_2.$$

The overall reaction can be written as follows:

$$HI + O_2 + CO \longrightarrow HIO + CO_2.$$

In both catalytic systems, the solvent-induced kinetic isotope effect in the oxidation reaction of CO to CO_2 was primarily associated with the equilibrium deprotonation of a rhodium(III) aqua carbonyl complex[185] by the reaction

$$[Rh(CO)_2(H_2O)Cl_3] \rightleftharpoons [Rh(CO)_2(OH)Cl_3]^- + H^+.$$

The $[Rh(CO)_2(H_2O)Cl_3]$ complex is a weak acid and the dissociation constants of weak acids in D_2O are 2–3 times smaller than in H_2O.[186] It is generally agreed that if the solvent-induced k_H/k_D ratio is >1, then H(D)–An (An is an anionic species) bond dissociation precedes the first irreversible step or is the first irreversible step itself. Examples of such reactions are known in the homogeneous metal complex catalysis, *e.g.*,

1) the ethylene oxidation to acetaldehyde in the presence of aqueous solutions of palladium chloride, $k_H/k_D \sim 4$;[187]

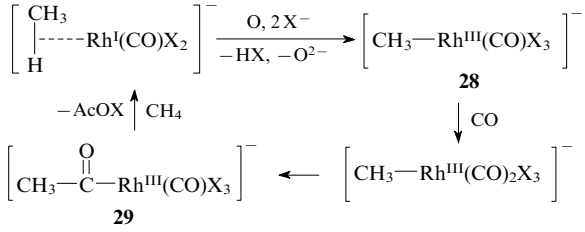
2) the water gas shift reaction in CF_3CO_2H in the presence of palladium phosphine complexes, $k_H/k_D \sim 3$;[188]

3) the oxidative carbonylation of acetylene in ethanolic solutions of palladium complexes, $k_H/k_D \sim 1.7-1.8$.[189]

The oxidation of methane in rhodium–iodide–chloride and rhodium–copper–chloride systems proceeded by a mechanism similar to the molecular mechanism, being independent of the presence of radical traps. Neither system catalyzed the deuterium–hydrogen isotope exchange with the medium.

The kinetic isotope effects of methane were ~ 4.3 for the $Rh^{III}-I^--Cl^-$ system and ~ 3.9 for $Rh-Cu^{I/II}-Cl^-$.[190] These data suggest the molecular mechanism and imply that the C–H bond cleavage is the limiting step in both systems. Then, for the formation of methane-derived products, the solvent-induced kinetic isotope effect should manifest itself in the preceding steps, most likely, in the step of active oxidant formation. In this case, in the $Rh^{III}-I^--Cl^-$ system, the formation of HIO and its reaction with rhodium should be associated with the dissociation of either HI, which can become a weak acid in a $CF_3CO_2H-H_2O$ system, or HIO, which is a very weak acid.

Let us consider two mechanisms of methane activation. The dissociative route resulting in methylrhodium(III) carbonyl complex **28** under the action of an oxidant ('O') is an adequate rationale for the formation of acetic acid.[176, 177]



X = Cl, I.

In the step of CO insertion in the $Rh-CH_3$ bond, the equilibrium constant was 3.2×10^3 at 35 °C.[179] For the Monsanto process, the oxidative addition of methyl iodide to rhodium(I) and insertion steps were reversible and heating of acetyl complex **29** afforded methyl iodide rather than methane.[178, 179] This is a possible reason for the lack of the deuterium exchange of methane with the medium. Of two possible versions of the rhodium oxocomplex formation, preference should be given to the reaction of rhodium with IO^-, because this better explains the solvent-induced kinetic isotope effect.

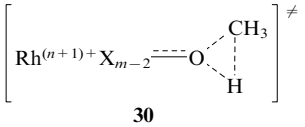
$$Rh^{n+}X_m \underset{X^-}{\overset{OI^-}{\rightleftharpoons}} Rh^{n+}X_{m-1}OI \longrightarrow$$

$$\longrightarrow Rh^{(n+1)+}X_{m-2}{=}O + I^- + X^-.$$

The second version, *i.e.*, the oxygen atom insertion into the Rh–H bond to form a hydroperoxo complex and then an oxo complex, was less probable, because the equilibrium of the reaction

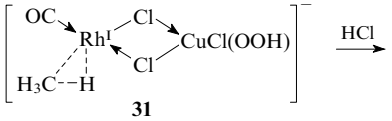
$$[Rh(CO)_2X_2] \underset{-HX}{\overset{HX}{\rightleftharpoons}} [HRh(CO)_2X_3]^-$$

was strongly shifted to the left.[171] The formation of methanol is the result of the oxygen atom insertion into the C–H bond in transition state **30**.



30

In rhodium–copper (iron)–chloride catalytic systems, the formation of a rhodium oxo complex and the oxidation of methane to methanol occurred under the action of any two-electron oxidant that could be generated in these systems (H_2O_2, CF_3CO_3H, MOOH, *etc.*). For acetic acid, the following mechanism involving the formation of a heterobinuclear intermediate was proposed: first, methane formed a weak associate such as σ-complex **31** with the coordinatively unsaturated rhodium(I) complex, which was followed by the transfer of two electrons from the Rh^I atom along a chloride bridge and the copper atom to the hydroperoxide group, which increased the electrophilicity of the rhodium ion and resulted in the formation of the $Rh^{III}-CH_3$ bond. The evolved proton was bound to afford water.



31

$$\longrightarrow [MeRh^{III}(CO)Cl_3]^- + CuCl(OH) + H_2O.$$

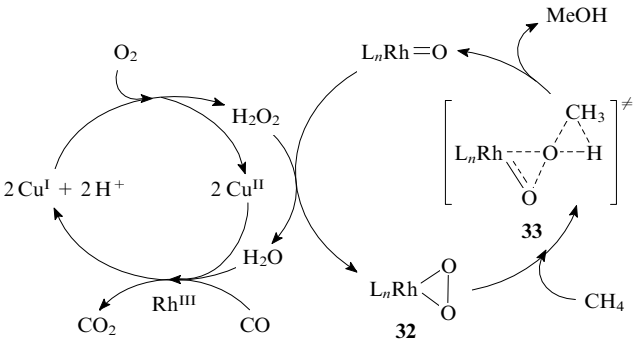
Later, in a joint study carried out by scientists from two research teams,[190] methane was oxidized in the presence of a rhodium–copper–chloride catalytic system under the action of the isotope $^{18}O_2$ in a 'light' liquid phase and conversely, under the action of $^{16}O_2$ in an $H_2{}^{18}O-CF_3C(O){}^{18}OH$ mixture.

The obtained data suggest that the oxygen atom was incorporated into the oxidation products from dioxygen, because the composition of oxygenates was similar to the gas phase composition. The transient formation of rhodium peroxo or hydroperoxo compounds, rather than an oxocomplex, agreed better with the experimental data. In the latter case, the isotope composition of products should correspond to the liquid phase composition due to the isotope exchange of the oxygen atom from the oxo group.

$$M{=}{}^{18}O + H_2{}^{16}O \rightleftharpoons M{=}{}^{16}O + H_2{}^{18}O.$$

The analysis of products has also shown that the primary oxidation product of methane was methanol, which later underwent esterification to CF_3CO_2Me.

Scheme 11



L = H_2O, Cl^-.

A mechanism of this process was proposed (Scheme 11), which involved the formation of rhodium peroxo compound **32**. Hydrogen peroxide or its analogues were generated in a cycle that was catalyzed by copper and involved rhodium (see Scheme 11, left cycle). The methane activation occurred under the action of one of oxygen atoms of the peroxo group to afford transition state **33**.[190]

According to Scheme 11, the formation of an active oxidant did not require the dissociation of any weak acid, which agreed with the observed solvent-induced kinetic isotope effect equal to ~1. Later, it was found that no oxidation of methane was virtually observed where carbon monoxide was totally replaced by hydrogen. This fact required explanation, because these compounds are similar as regards their reducing activity.

When considering peroxo compounds, we learnt that both rhodium and copper compounds could form complexes with the bridging peroxo group.[55,76,77] To explain the role of CO in the oxidation of methane with the mixture of CO and O_2, a mechanism involving a rhodium(IV)–copper(II)-containing heteronuclear complex with the bridging carbonyl and peroxo groups can be proposed (Scheme 12). The existence of complexes analogous to Rh^{IV} complexes has been reported earlier.[191]

According to Scheme 12, the catalytically active intermediate represents heteronuclear μ-carbonyl-μ-peroxo complex **34**. This intermediate proved to be capable of oxidizing both CH_4 and CO; moreover, the larger part of the latter was converted by the conventional route.[185] Scheme 12 explains all experimental facts obtained by kinetic and isotope methods.[181,182,190] This scheme explains the inability of hydrogen to be an active component of the gas phase At the same time, in the rhodium–iodide–chloride system, hydrogen operated as a reducing agent, being less efficient than carbon monoxide.

As was mentioned above, the equilibrium constant for the reaction of rhodium hydride formation in acidic media is very small.[162] Furthermore, the hydride bridges are weak and exist only in the presence of another stronger bridge. It is also important that coordinated CO is the stabilizing ligand.[56] The formation of palladium–cobalt, palladium–nickel and palladium–copper heteronuclear complexes bound by acetate bridges was reported.[192] Later, the structure of the $PdCo(OAc)_4$ complex was established by X-ray diffraction analysis,[193] which served as evidence for the existence of heteronuclear complexes.

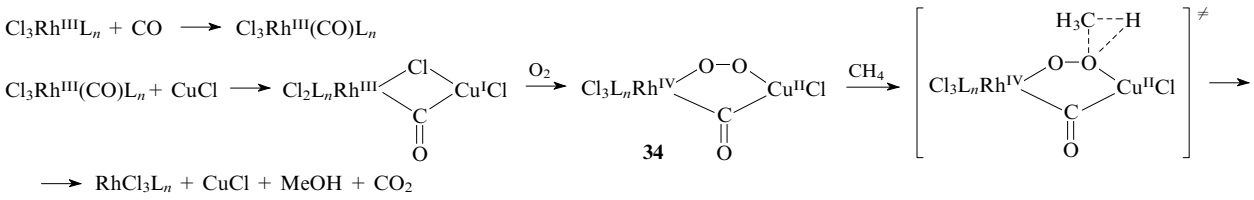
For the cyclohexane oxidation under the action of the $H_2 + O_2$ mixture in propionic acid in the presence of the $Pd/Al_2O_3 - V^{V}$(or Fe^{III}) system, palladium was assumed to play the role of the catalyst of the H_2O_2 synthesis. The hydrocarbon was oxidized on V^{V} (or Fe^{III}) with H_2O_2 that evolved, which has been confirmed by independent experiments.[164] As an alternative to the above mechanism, an analogous mechanism can be considered for the operation of the rhodium–copper–chloride catalytic system in the methane oxidation. The latter mechanism probably includes two conjugated catalytic cycles. In the first cycle, the rhodium-catalyzed CO oxidation occurs and Cu^{I} is constantly generated. In the second cycle, Cu^{I} reacts with oxygen to form $Cu^{II}-OOH^-$ or $\mu\text{-}CO-\mu\text{-}O_2-Cu^{II}_2$ and the latter oxidizes methane. Thus, CO not only serves as the reducing agent but can also assist in the formation of Cu^{II} dimers that activate dioxygen. Copper(I) carbonyls are well known (*e.g.*, see Ref. 185) and the oxidation of C–H bonds with copper(II) hydroperoxo complex was reported.[194]

In connection with the process of methane oxidative carbonylation to acetic acid discussed above, mention should be made of the heterogeneous version of this reaction that proceeds in the presence of a carbon-supported $Rh_4Se_{18}Cl_{10}$ catalyst at 400–450 °C and atmospheric pressure.[195,196]

VII. Alkane reactions involving the C–C bonds

There are two reasons that were thought[197,198] to be responsible for the more difficult activation and cleavage of the C–C bond in alkanes as compared with the C–H bond. One of them is the stereochemical hindrance due to the ligand environment of the metal. The second factor is that an MHR species arises upon cleavage of the C–H bond, while the break of the C–C bond affords the MR_2 species. Insofar as the M–H bond is stronger than the M–R bond, the cleavage of the C–H bond is energetically more favourable than that of the C–C bond. The cleavage

Scheme 12



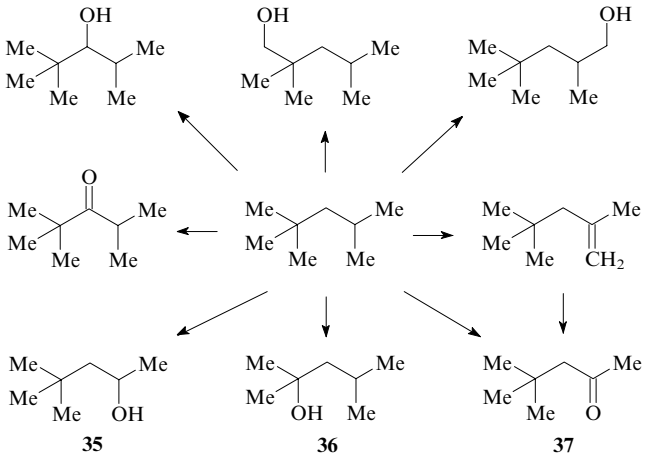
L = H_2O.

of the C–C bond was observed in the reactions of alkanes with a 'naked' metal cation in the absence of stereochemical hindrance.[199, 200]

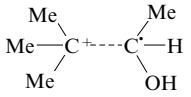
In contrast to the large number of examples of the C–H bond activation and oxidation in alkanes, only few studies were devoted to reactions with the C–C bond cleavage. It was shown by Moiseev and co-workers[201] that ethane and propane can be oxidized in CF_3CO_2H by either cobalt(III) trifluoroacetate or a $Co^{II}-O_2$ system to afford ethyl and isopropyl trifluoroacetates, respectively, as the main products. The reactions were carried out at 130–200 °C under the alkane pressure of 0.5–4.0 MPa and the oxygen pressure of 0–1 MPa. Isopropyl trifluoroacetate results from isomerization of initially formed propyl trifluoroacetate, as confirmed by special experiments. Small amounts of $(CF_3CO_2CH_2)_2$, AcOH and CF_3CO_2Me in the ratio 5 : 3 : 2 also formed from ethane, while CF_3CO_2Me, CF_3CO_2Et, AcOH, $Me_2C(O)$ and $CF_3CO_2CH(Me)CH_2O_2CCF_3$ formed from propane upon further oxidation of ethyl and isopropyl trifluoroacetates. It was assumed that these processes proceeded by the one-electron mechanism according to Scheme 13 proposed for the ethane oxidation.[201]

The process begins with the formation of $C_2H_6^{+\bullet}$, which later undergoes transformations by two pathways. In the first pathway, the C–C bond is cleaved. The resulting CH_3^+ species is transformed to methyl trifluoroacetate, while $CH_3^\bullet$ in the presence of O_2 affords CO_2. The second pathway consists of the C–H bond cleavage in $C_2H_6^{+\bullet}$ to form a proton and the ethyl radical. The latter reacts with O_2 to afford $C_2H_5O_2^\bullet$ and further AcOH or forms first $C_2H_5^+$ and then ethyl trifluoroacetate. Ethyl trifluroacetate is oxidized by cobalt(III) to a radical cation. The latter transforms to the corresponding ethylene glycol diester or acetic acid due to the cleavage of an extra C–H bond. Apparently, neither the C–C bond cleavage in an alkane, nor the formation of glycols from the latter were observed earlier.

Studying of the peroxide oxidation of isoalkanes in the presence of V^V in acetic acid has shown that their oxidation could involve the C–C bond cleavage.[202] For instance, the oxidation of isooctane results in a mixture of products of which compounds **35**–**37** had smaller number of carbon atoms.



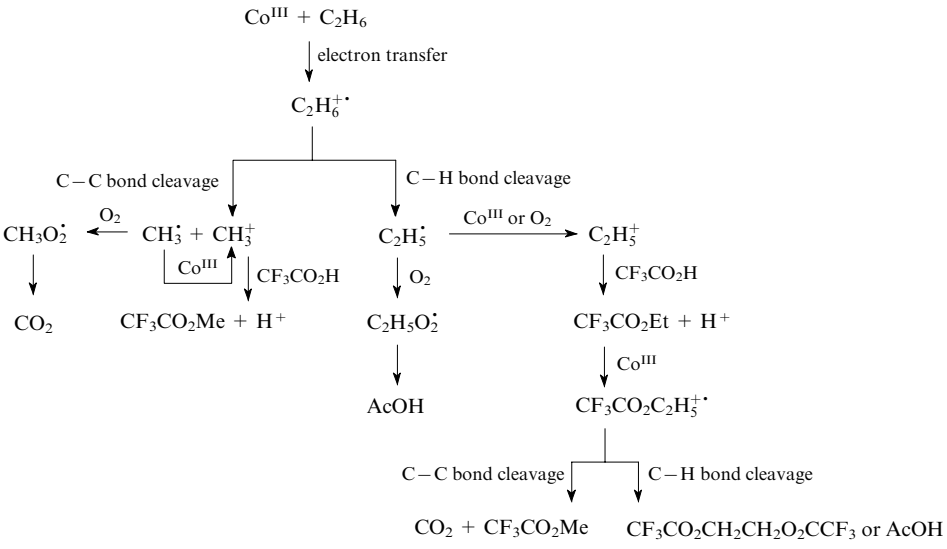
It was assumed that the formation of the following radical-ion pair occurs simultaneously with the C–H bond oxidation in the active site:



The reaction of this radical-ion pair with oxygen brings about the R–CH_3 bond cleavage.

The C–C bond oxidative functionalization was carried out in the presence of a rhodium–iodide–chloride system in a heptafluorobutyric acid–water mixture.[173] Methanol, ethanol and their esters as well as acetic acid formed as the functionalization products of ethane. Propionic acid was detected only in trace amounts, which was explained by considerably stronger susceptibility of the rhodium ethyl complex to the nucleophilic attack as compared with its methyl analogue and also by the absence of a carbonylation step. With the use of ^{13}CO, it was shown that 80% of acetic acid formed from ethane and 20% formed due to the ethane C–C bond cleavage followed by the generation of a CH_3-Rh species, which was followed by carbonylation of the latter. The use of labelled ethane, $^{13}C_2H_6$, exclusively

Scheme 13



produced labelled methanol and methyl heptafluorobutyrate. The same result was obtained when $^{13}C_2H_6$ and $^{12}C_2H_5OH$ were simultaneously introduced to the reaction, *i.e.*, methanol did not originate from ethanol. The reaction of propane furnished mainly isopropyl and n-propyl heptafluoroacetates in the 5 : 1 ratio and acetone as well as considerable amounts of methanol, ethanol and acetic acid.

The use of butane was the most spectacular example of the C—C bond functionalization.[173] Virtually all the products resulted from the C—C bond cleavage. Several putative mechanisms were considered. It was assumed that the transient formation of radical cations upon alkane ionization and the C—C bond homolysis were highly improbable, whereas the C—C bond activation and cleavage occurred in the coordination sphere of rhodium. As the result of substitution of $K_2S_2O_8$ for the $O_2 + CO$ mixture and the catalyst, ethylene glycol and its esters formed in the ethane reaction. No such products were observed in the catalytic reaction. Apparently, the process occurred by the following scheme:

$$S_2O_8^{2-} \longrightarrow SO_4^{-\bullet},$$

$$C_2H_6 \xrightarrow{SO_4^{-\bullet}} C_2H_5^{\bullet} \xrightarrow{SO_4^{-\bullet}} C_2H_5^{+} \underset{}{\overset{-H^+}{\rightleftharpoons}} C_2H_4 \xrightarrow{CF_3CO_2H} \longrightarrow ROCH_2CH_2OR,$$

R = H, $CF_3C(O)$.

This agrees with the other data [201] on the involvement of the radical cations in the oxidation of ethane and propane by the $Co^{II} + O_2$ mixture or under the action of $Co(O_2CCF_3)_3$.

In the presence of the rhodium–copper–chloride catalytic system in aqueous CF_3CO_2H, under the action of the $O_2 + CO$ mixture, the transformations of C_2–C_4 alkanes with the C—C bond cleavage were also observed.[203, 204] Moreover, the composition of products differed from that reported in other publications,[173, 201] particularly, no formation of glycols and their esters was observed. According to the ^1H NMR spectroscopic, GC and GC–MS studies,[203, 204] primary and secondary alcohols and their esters (as a result of the C—H bond cleavage by metal complexes) as well as ketones and acids formed from saturated hydrocarbons (Table 2). Aldehydes were detected in trace amounts probably due to their fast oxidation. The process was accompanied largely by the C—C bond cleavage. Thus from all alkanes studied, CF_3CO_2Me and HCO_2H formed. Additionally, AcOH and CF_3CO_2Et were detected in the oxidation of propane and butane, while acetone and $CF_3CO_2Pr^i$ were observed in the oxidation of isobutane. Note that methyl trifluoroacetate and isopropyl trifluoroacetate formed in approximately equal amounts and the respective kinetic curves run in parallel.

A considerable number of oxidation products from C_2–C_4 hydrocarbons suggests the low selectivity of the process. As applied to processing of the natural and associated gas, it is desirable to obtain the minimum set of compounds from all C_2–C_4 hydrocarbons, for instance, lower alcohols and acetic acid. It should be noted that 'heavy' products (butyl esters and propionic acid) form in small amounts, while the main fraction consist of relatively 'light' C_1–C_3 oxygenates (see Table 2) in which a considerable fraction belongs to formic acid. It can be assumed that in the presence of the rhodium–copper–chloride catalyst, the activation of the C—C bond occurs through abstraction of an electron by the electrophilic fragment of the catalytically active intermediate to produce a reactive radical cation pair.[201, 202] This follows from the approximately equal yields of CF_3CO_2Me and CF_3CO_2Et from propane (and of CF_3CO_2Me and $CF_3CO_2Pr^i$ from isobutene). Data in favour of the stepwise conversion of, *e.g.*, propane to alcohols, acetone and propionic acid are abundant (Scheme 14).

Further oxidation of acetone according to the Baeyer–Villiger mechanism and the transformation of propionic acid within the rhodium inner coordination sphere afford shorter-chain products. It was experimentally demonstrated that isopropyl alcohol is oxidized to acetone, acetone is oxidized to methyl trifluoroacetate and acetic acid and the latter is oxidized to methyl trifluoroacetate (see Scheme 14, pathway *a*). Propanol is oxidized to propionic acid, which is oxidized to acetic acid *via* transient 3-hydroxypropionic and malonic acids (see Scheme 14, pathway *b*). This was confirmed by the formation of CH_2DCO_2D in the oxidation of $EtCO_2H$ in a deuterated medium, because deuterium could be incorporated into the acetic acid methyl group only through the decarboxylation of $DO_2CCH_2CO_2D$. The second pathway of propionic acid oxidation represents a sequence of reactions in which CO is inserted in the Rh—propionate bond and the further decarboxylation affords a rhodium propionyl complex. The latter produces ethanol (ethyl trifluroacetate) by decarbonylation and hydrolysis (acidolysis) (see Scheme 14, pathway *c*) as confirmed by the formation of CF_3CO_2Et upon oxidation in a deuterated medium. The transformation of acetic acid to CF_3CO_2Me is much similar.

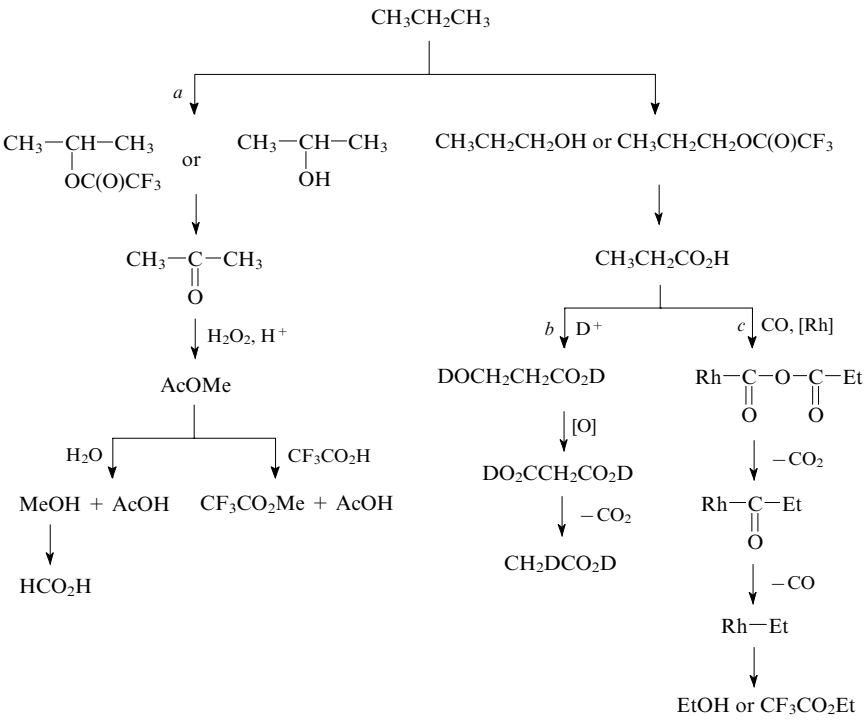
The C(1)—C(2) bond oxidative cleavage in primary alcohols and vicinal diols was described [205] for their stoichiometric reaction with polyoxometallate $H_5[PMo_{10}V_2O_{40}]$

Table 2. Conversion of C_1–C_4 alkanes in a CF_3CO_2H–H_2O mixture in the presence of the $RhCl_3$–$Cu(O_2CCF_3)_2$–NaCl catalytic system.

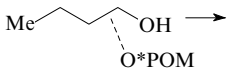
Products	Alkanes [a]				
	CH_4	C_2H_6	C_3H_8	n-C_4H_{10}	iso-C_4H_{10}
HCO_2H	0.10	0.20	0.30	0.16	0.21
CF_3CO_2Me	0.15	0.23	0.07	0.32	0.24
AcOH	0.05 [b]	0.02	0.03	0.19	—
CF_3CO_2Et		0.84	0.09	0.18	—
$CF_3CO_2Pr^i$			0.24	—	0.27
$CF_3CO_2Pr^n$			0.16	0.01	—
$EtCO_2H$			0.01	traces	—
Me_2CO			0.15	—	0.39
$CF_3CO_2Bu^i$				—	0.02
$CF_3CO_2Bu^s$				0.03	—
$CF_3CO_2Bu^n$				0.04	—
AcOEt				0.02	—

Note. $[RhCl_3] = 2.5 \times 10^{-3}$ mol litre^{-1}, $[Cu(O_2CCF_3)_2] = 5 \times 10^{-2}$ mol litre^{-1}, $[NaCl] = 7.5 \times 10^{-3}$ mol litre^{-1}. The volume of the reaction mixture was 2.5 ml with 0.5 mole fraction of water. [a] The amount of product is in mol litre^{-1}; for reactions involving methane, $T = 95$ °C, time 2 h, pressure, MPa: 6.0 (CH_4), 0.56 (O_2), 1.8 (CO); in the other cases, ~12 mmol of alkane were condensed, $T = 80$ °C, pressure, MPa: 3.6 (He), 0.8 (O_2), 1.6 (CO). [b] Acetic acid was formed by oxidative carbonylation of methane.

Scheme 14



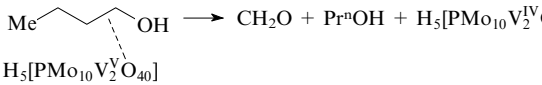
(POM). The ^{13}C NMR spectrum of a mixture of butanol with POM demonstrated the appearance of signals at δ 30.3 and 65.8, which were attributed to the POM-bound C(1) and C(2) atoms of the alcohol. For n-butanol, the reaction products were butyl formate and butyl propionate. However, it was assumed that aldehydes, namely, formaldehyde and propionic aldehyde, were the primary products. Aldehydes were quickly oxidized to acids and the latter were converted to the identifiable esters. The reaction was first order with respect to POM and the deuterium–hydrogen kinetic effects were $\sim$1. The oxygen atom in products originated from POM, as confirmed by labelling experiments with ^{18}O-polyoxometallate. A mechanism including the transfer of electrons and an oxygen atom (the ET–OT mechanism) was proposed. The rate determining step can be represented as reaction (7).



$$\longrightarrow CH_2O^* + EtCHO^* + H_5[PMo_{10}V_2^{IV}O_{39}] + 2H^+. \quad (7)$$

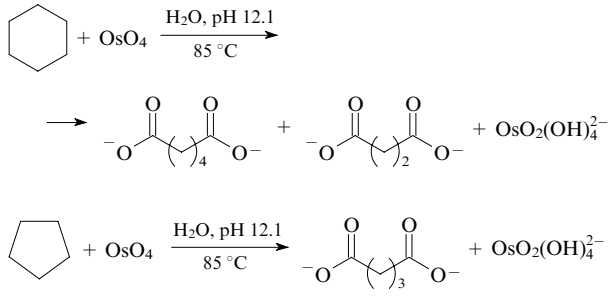
(The designation O*POM stands for the ^{18}O atom incorporated in polyoxometallate.)

In our opinion, Eqn (7) is not completely correct from the viewpoint of stoichiometry. The formation of aldehydes should be expected when two POM molecules react with an alcohol molecule, whereas for their equimolar ratio, the reaction should afford an aldehyde and an alcohol, for example, CH_2O and Pr^nOH.



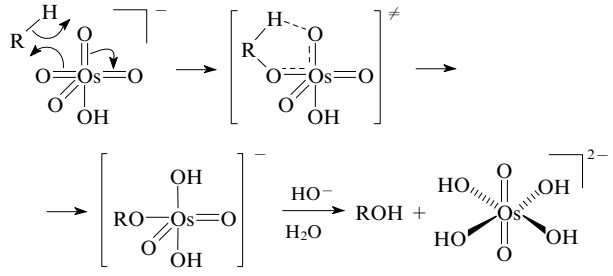
Hence, it can be assumed that in the slow step, propanol remains bound to POM to be later quickly oxidized by the second $H_5[PMo_{10}V_2O_{40}]$ molecule to afford the aldehyde.

The stoichiometric oxidation of cyclohexane and cyclopentane under the action of OsO_4 was also described.[206] Cyclohexane was oxidized to adipic and succinic acids, while cyclopentane was oxidized to glutaric acid.



Presumably, the process occurred *via* cyclohexanol. Thus *cis*-decalin oxidation to *cis*-decalin-9-ol proceeded with retention of configuration by the concerted molecular [3 + 2] mechanism (Scheme 15). The mechanism according to which two vicinal carbon atoms of cyclohexane or cyclopentane interact with two vicinal oxygen atoms in OsO_4 has not been discussed.[206]

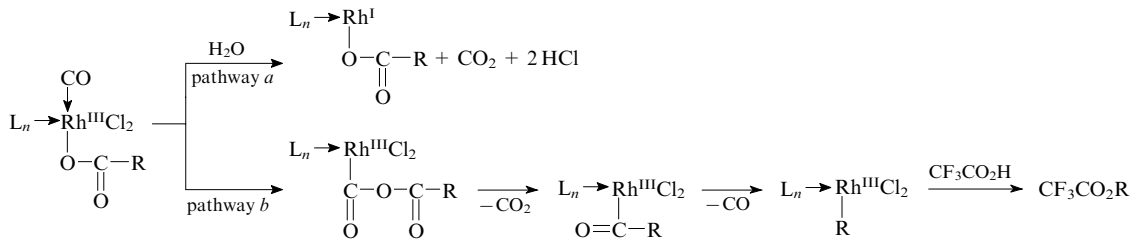
Scheme 15



R–H is *cis*-decalin.

The C–C bond cleavage can be exemplified by the formation of acetic acid upon oxidation of 2-cyanoethanol

Scheme 16



R = Me, Et; L = H_2O, AcOH, $EtCO_2H$.

38

with hydrogen peroxide in the presence of $OsCl_3$ and oxidation of isopropyl alcohol in the presence of $FeCl_3$.[207]

The destruction of acetic and propionic acids occurred under the action of an $O_2 + CO$ mixture in the presence of the rhodium–copper–chloride catalytic system in aqueous solutions of the corresponding acids.[208, 209]

$$2\,RCO_2H + CO + O_2 \longrightarrow RCO_2R + 2\,CO_2 + H_2O,$$

R = Me, Et.

The conversion of propionic acid should be supplemented by the following reactions:

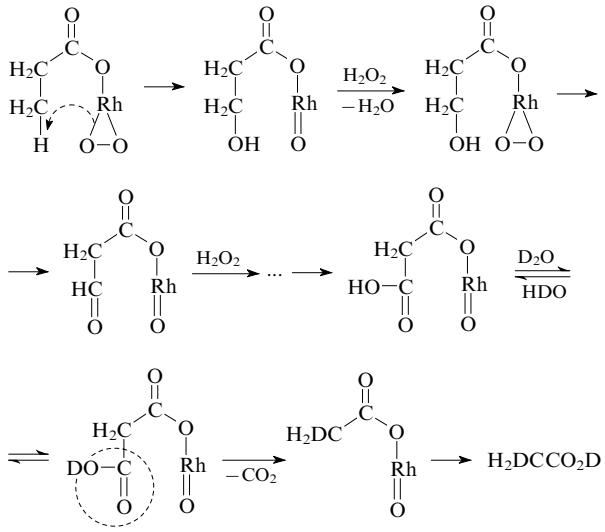
$$EtCO_2H + \frac{1}{2}O_2 \longrightarrow AcOH + CO_2 + H_2O,$$

$$2\,EtCO_2H + 2\,O_2 \longrightarrow EtCO_2Me + 2\,CO_2 + 2\,H_2O.$$

The formation of methyl acetate from acetic acid and of ethyl propionate from propionic acid was explained by the CO insertion into the metal–carboxylate bond, *i.e.*, a reaction well known in coordination chemistry,[210] which was followed by the decarboxylation to afford an acyl derivative (Scheme 16). The nucleophilic attack of water on the carbon atom within the coordinated carbonyl group leads to the formation of CO_2 (pathway *a*). This step is involved in the catalytic cycle of CO oxidation. Acyl complex **38** formed upon decarboxylation is subjected to decarbonylation to afford an ethyl derivative and the latter reacts with the acid to produce the ester.

The dependence of the yield of ethyl propionate on the concentrations of H_2O and H_2SO_4 differed from the corresponding dependences for acetic acid and methyl propionate. Moreover, under the reaction conditions, C_2D_5OD was not oxidized to acetic acid but underwent esterification. This showed that acetic acid and methyl propionate were synthesized by a mechanism different from that involved in formation of ethyl propionate.

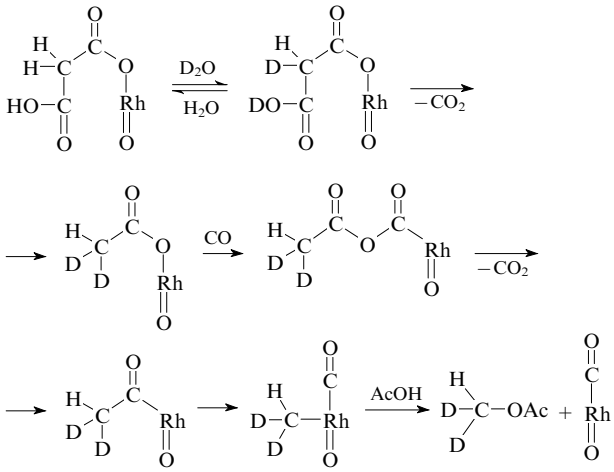
Scheme 17



A mechanism of formation of acetic acid with the transient formation of malonic acid was suggested.[208, 209] This was confirmed by the incorporation of a deuterium atom from the medium to the methyl group of acetic acid (Scheme 17).

The esters $EtCO_2CH_nD_{3-n}$ ($n = 0-3$) were detected as the products, which suggested that the acetic acid oxidation could proceed according to Scheme 18.

Scheme 18

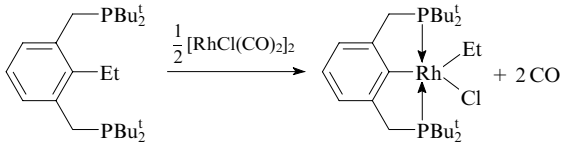


The transient formation of malonic acid was confirmed [160] by the fact that the carbon atom of the methylene group of propionic acid could become the primary atom in the formed acetic acid as a result of oxidation,

$$CH_3{}^{13}CH_2CO_2H \xrightarrow{\text{`O'}} {}^{13}CH_3CO_2H + CO_2 + H_2O.$$

This reaction could occur only according to the reaction sequence considered above (Schemes 17, 18).

The ability of metal compounds to activate the C–C bond was reliably confirmed for the reaction of pincer complexes with arylalkanes. Thus the oxidative addition of a rhodium complex to substituted ethylbenzene afforded compound **39**.[211]



39

VIII. One-electron processes

The oxidation reactions of ethane and propane in the presence of cobalt compounds[201] and of higher alkanes in the presence of vanadium compounds,[202] which were considered in Section VII, proceed by the one-electron non-chain route.

Likholobov and co-workers[212–215] used the H_2+O_2 mixture as the cyclohexane oxidant. Such a choice is rationalized on the basis of the fact that oxidation with hydrogen peroxide was often characterized by low selectivity. These studies differed from those described, *e.g.*, in Ref. 164 in the fact that it is a platinum-coordinated hydroxyl radical rather than hydrogen peroxide that is formed as the oxidant from the H_2+O_2 mixture. Two types of a catalyst were studied. The first represented a Pd(or Pt)/SiO_2–heteropolyacid catalytic system. The catalyst activity increased in the following series of heteropolyacids: $H_6[P_2Mo_{18}O_{62}] < H_4[PMo_{11}VO_{40}] < H_4[PMo_{10}V_2O_{40}]$. The catalytically active species formed upon the adsorption of heteropolyacids from solution on the Pd(or Pt)/SiO_2 catalyst. The second type was a two-component catalyst prepared from the $[Pt(NH_3)_4]\cdot[H_2PMo_{12}O_{40}]_2\cdot 7H_2O$ complex salt by calcination followed by reduction.

Cyclohexane oxidation was assumed to occur by a non-chain radical mechanism (Scheme 19).[215]

Scheme 19

$$Pt^0 + O_2 \rightleftharpoons Pt^0(O_2)\,(ads),$$

$$Pt^0(O_2)\,(ads) + H^+ \longrightarrow (Pt-OOH)^+,$$

$$2\,(Pt-OOH)^+ + Pt^0 + 4H^+ \longrightarrow$$

$$\longrightarrow 2\,(Pt-O^{\bullet}H)^{2+} + Pt^{2+} + 2H_2O,$$

$$(Pt-OOH)^+ + Mo^{5+} + 2H^+ \longrightarrow$$

$$\longrightarrow (Pt-O^{\bullet}H)^{2+} + Mo^{6+} + H_2O,$$

$$(Pt-O^{\bullet}H)^{2+} + C_6H_{12} \longrightarrow Pt^{2+} + {}^{\bullet}C_6H_{11} + H_2O,$$

$$(Pt-O^{\bullet}H)^{2+} + {}^{\bullet}C_6H_{11} \longrightarrow Pt^{2+} + C_6H_{11}OH,$$

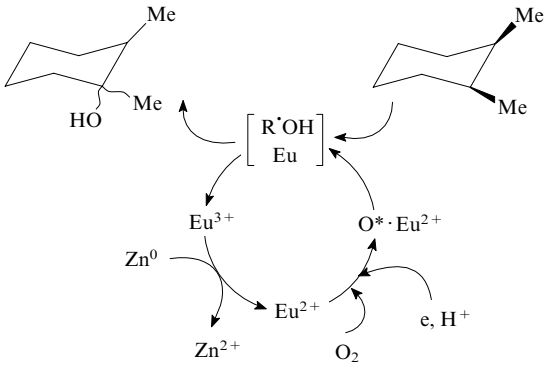
$$Pt^{2+} + H_2 \longrightarrow Pt^0 + 2H^+,$$

$$2Mo^{6+} + H_2 \xrightarrow{[Pt]} 2Mo^{5+} + 2H^+.$$

Methane was selectively oxidized with dioxygen to methanol (or methyl trifluoroacetate) in CF_3CO_2H in the presence of $EuCl_3$ at room temperature and atmospheric pressure with zinc powder used as the reducing agent.[216,217] Under similar conditions, ethane was oxidized mainly to ethyl trifluoroacetate and acetaldehyde, while propane oxidation afforded isopropyl trifluoroacetate, acetone and propionic aldehyde. In the process, a large amount of CO_2 was obtained; moreover, as the alkane pressure increased the CO_2 formation rate decreased. According to the obtained results, the only route of CO_2 formation could be the decarboxylation of CF_3CO_2H. Ethane and propane were also oxidized in acetic acid but with the lower efficiency.

The oxidation of a series of hydrocarbons in the presence of the $Eu^{III}-O_2-Zn$ system was described.[217] Scheme 20 shows the mechanism proposed for *cis*-1,2-dimethylcyclohexane. According to UV-spectroscopic data, certain difference was observed in the absorption of initial Eu^{3+}, the zinc-reduced species, presumably, Eu^{2+} and oxygen-treated Eu^{2+}.

Scheme 20

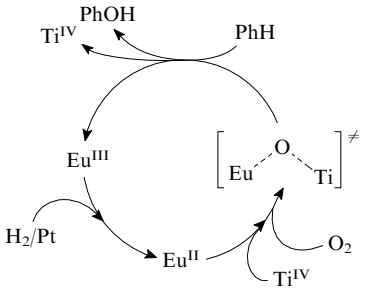


R is 1,2-dimethylcyclohexyl.

Europium(III) was reduced with zinc to europium(II) and the latter activated dioxygen by transferring it into an 'electrophilic' form of some unknown structure (designated as $O^*\cdot Eu^{2+}$ in Scheme 20). The $1^0:2^0:3^0$ parameter, *i.e.*, the total amount of products oxygenated at the primary, secondary and tertiary C–H bonds (mol) per number of the respective bonds (the position selectivity) in the $EuCl_3$ system was estimated as 1:6:19 from the results of the oxidation of hexane and adamantane, which pointed to the low electrophilicity of the active oxygen-containing species. For the co-oxidation of cyclopentane and cyclohexane, the parameter $C_5:C_6 = 0.66$ was determined, which implies that the H atom is preferentially abstracted from cyclohexane. The oxidation of *cis*- and *trans*-1,2-dimethylcyclohexanes proceeded without retention of their configuration and pointed to the radical mechanism of this process. The kinetic isotope effect equal to 2.6 for hexane means that the limiting step was the H atom abstraction from the alkane.

The further elaboration of Eu-containing systems has shown that zinc can be replaced by hydrogen activated on Pt/SiO_2.[217] The system $Eu-Pt/SiO_2-O_2-H_2$ was studied for the oxidation of benzene. The reaction was largely promoted by $TiO(acac)_2$ (acac is acetylacetonate). The highest yield of phenol is attained if the mole fraction of the additive is *ca.* 1/6 of the amount of Eu. The catalytic system $Eu(OTf)_3-TiO(acac)_2-Pt_xO_y/SiO_2$ operating in acetic acid at atmospheric pressure and 40 °C demonstrated the highest activity. In toluene, it was the benzene ring that was oxidized preferentially. The active intermediate was assumed to contain the atoms of Eu, Ti and electrophilic oxygen (Scheme 21).

Scheme 21



It was shown[218] that methane ($P = 4-7.5$ MPa) was oxidized with air ($P = 1$ MPa) at 23–75 °C in acetonitrile in the presence of $Bu^n_4NVO_3$ together with pyrazine-2-carboxylic acid (PCA) taken as the catalyst to afford methyl hydroperoxide, formaldehyde and formic acid. Hydrogen peroxide, which in this case acted as the promoter, had also to be added to the reaction mixture. Prior to analysis, methyl hydroperoxide was reduced with triphenylphosphine:

$$MeOOH + PPh_3 \longrightarrow MeOH + O{=}PPh_3.$$

Oxidation of cyclohexane with labelled dioxygen, $^{18}O_2$, has shown that 75% of cyclohexanol (following reduction with triphenylphosphine) contained ^{18}O. In triphenylphosphine oxide, ^{18}O atoms were also found. This served as evidence for the alkane oxidation with dioxygen.

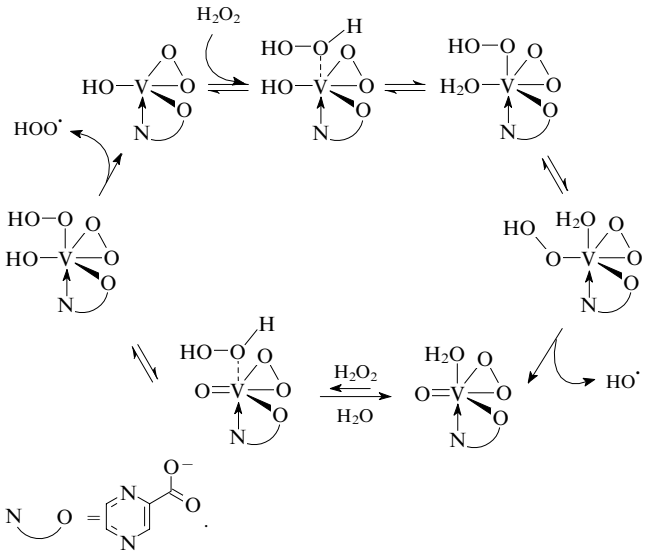
The oxidation of methane ($P = 7.0$ MPa) also occurred in aqueous solution in the presence of KVO_3 and PCA at 20–90 °C under the action of air ($P = 1.0$ MPa) and H_2O_2.[219] Formic acid was the main reaction product and its yield considerably increased upon introduction of strong acids. The oxidation of methane in the presence of the V^v–PCA system proceeded by the radical chain mechanism. The formed $HO^{\bullet}$ radical abstracted a hydrogen atom from the alkane. The alkyl radical quickly reacted with dioxygen to produce the hydroperoxyl radical. The latter produced alkyl hydroperoxide under the reaction conditions.

Formic acid was the main oxidation product of methane ($P = 3.0$ MPa) with H_2O_2 as the oxidant in the presence of $VOSO_4$ in acetonitrile.[220] The reaction probably proceeded by a mechanism involving V^V species. For the oxidation of C_1-C_4 alkanes, heptane and cyclohexane and of *cis*- and *trans*-1,2-dimethylcyclohexanes, a catalytic system $H_2O_2-NaVO_3-H_2SO_4$ was proposed, which was active in acetonitrile and less efficient in water.[221] Alkyl hydroperoxides were the main reaction products. Dimethylcyclohexanes were oxidized to the corresponding alcohols without retention of configuration. The products could be detected following reduction of alkyl hydroperoxides with triphenylphosphine. The oxidation was initiated by the hydroxyl radical.

Tetra-n-butylammonium salts with the heteropolyacid anions (phosphomolybdovanadates $[PMo_{11}VO_{40}]^{4-}$ and $[PMo_6V_5O_{39}]^{12-}$) were reported[222] to efficiently catalyze the oxidation of ethane, octane, cyclooctane, adamantane and decalin with hydrogen peroxide in acetonitrile. The main products, *i.e.*, the corresponding alkyl hydroperoxides, were gradually transformed to aldehydes and ketones. For example, cyclooctane was oxidized in 9 h at 60 °C to produce oxygenates in the yield of 30% with the TON of ~1000. One H_2O_2 molecule was assumed to reduce V^V to V^{IV} and the other one reacted with V^{IV} to produce a hydroxyl radical. The hydroxyl radical abstracted a hydrogen atom from the alkane. The resulting alkyl radical was transformed to hydroperoxide.

The catalytic system vanadate anion–PCA–H_2O_2 was studied by kinetic, spectroscopic and theoretical methods.[223] The mechanism of action of this system was elucidated to be well consistent with all previously obtained experimental data (Scheme 22). This mechanism involved the generation of $HO^{\bullet}$ and $HOO^{\bullet}$ radicals in the catalytic cycle by vanadium complexes containing one peroxo group.

Scheme 22



Methane carboxylation was accomplished under the action of carbon monoxide and carbon dioxide in the presence of vanadium complexes.[224] In the presence of sodium vanadate in an aqueous solution (pH 7.3), formic acid, methanol and formaldehyde were produced from methane. Air served as the oxidant. Acetic acid and methyl hydroperoxide were the reaction products in the catalytic system sodium vanadate–PCA in the presence of hydrogen peroxide. Both reactions proceeded by the one-electron mechanism.

Presumably, the use of carbon dioxide as the carboxylating agent implies its initial reduction by alkyl and/or hydroxyl radicals to carbon monoxide. Then the process proceeds with abstraction of a hydrogen atom from methane and the reaction of the methyl radical with CO to form the acetyl radical. The latter reacts with dioxygen and produces ultimately peracetic acid.

Alkane oxidation with hydroperoxides catalyzed by osmium compounds was described.[225] A carbonylosmium complex, $Os_3(CO)_{11}(\pi\text{-alkene})$, efficiently catalyzed the oxidation of alkanes and cycloalkanes in acetonitrile solutions. The original Os^0 was oxidized and generation of radicals occurred:

$$Os^{II} + H_2O_2 \longrightarrow Os^{III} + HO^{\bullet} + HO^-,$$

$$Os^{III} + H_2O_2 \longrightarrow Os^{II} + HOO^{\bullet} + H^+.$$

In the reaction of alkane oxidation with hydroperoxides, different transition metal chlorides were studied of which $OsCl_3$ proved to be most active.[226] In contrast to the earlier study,[225] it was assumed[226] that the active species were those containing Os^{III} and Os^{IV}, which reacted with H_2O_2 to generate the $HO^{\bullet}$ and $HOO^{\bullet}$ radicals.

Organic hydroperoxides were also efficient in the alkane oxidation reactions. The latter could be catalyzed by, *e.g.*, osmium(II, III) compounds,[225] cobalt azaporphins,[227] soluble and immobilized manganese(III) complexes with substituted salicylaldoximes.[228]

Unusual results were obtained[229] in studies of the oxidation of methane, ethane and propane with hydrogen peroxide in perfluorocarboxylic acids in the absence of metal complexes. The reaction was initiated by ethylene or propylene at their content of 1600 ppm. Under these con-

ditions, methane did not react, propane was oxidized to isopropyl alcohol and acetone, while ethane underwent a chain radical reaction involving trifluoroacetic anhydride to form propionic acid and ethyl trifluoromethyl ketone. Hence, the COOH group of propionic acid and the CF_3 group of the ketone formed from trifluoroacetic acid. The reason for such unique behaviour of ethane as compared with propane remains obscure. No alkene was required when *m*-chloroperoxybenzoic acid, azo-2,2-bis(isobutyronitrile) or tetraethyllead served as the initiators. The reaction initiated by $PbEt_4$ was especially efficient producing up to 500 equiv. of products per equiv. of $PbEt_4$. The yields of products were studied as a function of concentrations of trifluoroacetic anhydride, propylene and hydrogen peroxide. The addition of $Pd(O_2CCF_3)_2$ and H_2O_2 shifted this reaction to its usual two-electron route with the electrophilic mechanism. In this case, methane was also oxidized. The radical-chain process was assumed to follow Scheme 23.

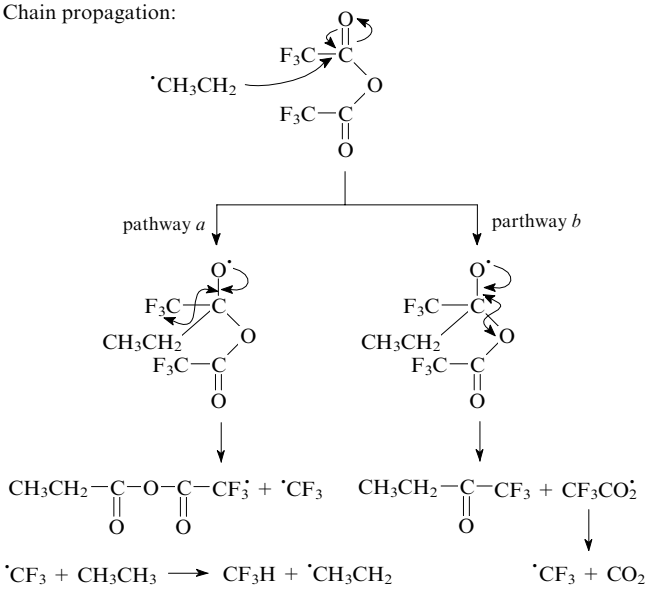
Scheme 23

Chain initiation:

$$R^{\bullet} + CH_3CH_3 \longrightarrow RH + {}^{\bullet}CH_3CH_2$$

$R^{\bullet}$ is the radical formed at the initiator decomposition.

Chain propagation:



$${}^{\bullet}CF_3 + CH_3CH_3 \longrightarrow CF_3H + {}^{\bullet}CH_3CH_2 \qquad {}^{\bullet}CF_3 + CO_2$$

The possibility of methane sulfonation in sulfuric acid has been mentioned.[117] Later, this process was studied in more detail.[230–233]

$$CH_4 \xrightarrow{H_2SO_4,\ SO_3} MeSO_3H.$$

It was shown that the reaction follows the radical-chain mechanism being initiated by potassium persulfate, mercury sulfate and hydrogen peroxide[230,231] and metal peroxides.[232,233] CaO_2 served as the best radical initiator that operated at a sufficiently low temperature (65 °C).[233] In CF_3CO_2H and CF_3SO_2OH, the reaction proceeded much more slowly than in sulfuric acid. Note that $PdSO_4$ and $PdCl_2$ proved to be inefficient initiators.

Several studies were devoted to the oxidative functionalization of alkanes with potassium persulfate. An unusual aminomethylation reaction of alkanes with trimethylamine *N*-oxide in trifluoroacetic acid in the presence of copper acetate as the catalyst and potassium persulfate as the co-oxidant was described.[234]

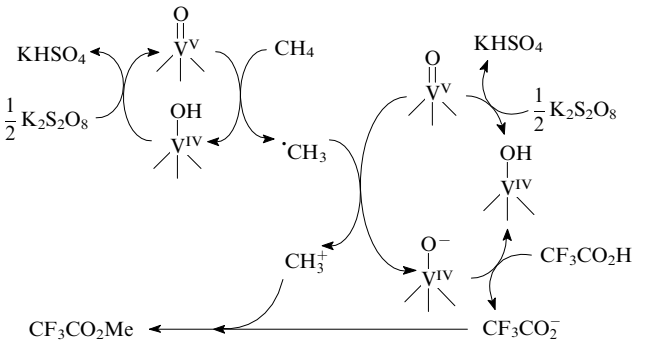
Ethane and propane afforded dimethylpropylamine and isobutyldimethylamine, respectively. Propane gave also isopropyl trifluoroacetate and a small amount of dimethylamine.

$$C_3H_8 + Me_3N{\rightarrow}O + CF_3CO_2H \longrightarrow$$
$$\longrightarrow Bu^iNMe_2 + CF_3CO_2Pr^i + Me_2NH + H_2O.$$

Methyl trifluoroacetate was found as the reaction product of methane. *N*-Methylpiperidine, pyrrolidine and *N*-methylmorpholine *N*-oxides also reacted with propane. The details of this mechanism are unclear but, since the reaction was inhibited with free radical traps, it was assumed to follow the one-electron mechanism. *N*-Oxides and CF_3CO_2H were assumed to form alkylcopper and the Mannich bases as the intermediate species.

Methane oxidation with a catalytic system comprising the Keggin heteropolyacids and $K_2S_2O_8$ as the oxidant in trifluoroacetic anhydride–trifluoroacetic acid efficiently affords methyl trifluoroacetate and trace amounts of methyl acetate.[235] The highest activity was manifested by $H_5[PV_2Mo_{10}O_{40}]$, $H_5[SiVW_{11}O_{40}]$ and $H_5[PV_2W_{10}O_{40}]$. The yields of the reaction products reached 95% (based on methane) at 80 °C and the CH_4 pressure of 0.5 MPa in an autoclave of small volume (25 cm^3). Depending on the amount of added trifluoroacetic anhydride, the yield of products passed through a maximum, which corresponded to TON of 490 in 20 h. Scheme 24 illustrates the proposed reaction mechanism.

Scheme 24



The methyl radical was generated in the reaction of the $V^V{=}O$ fragment obtained in the oxidation of V^{IV} with potassium persulfate. Next, $V^V{=}O$ abstracted an electron from the methyl radical and the resulting CH_3^+ cation reacted with the CF_3COO^- anion to afford methyl trifluoroacetate. The origin of methyl acetate was not explained.[235]

The fact of carbonylation of methane to acetic acid in the presence of $CaCl_2$ and $K_2S_2O_8$ as the oxidant in trifuoroacetic acid seems surprising.[236] Labelling experiments with $^{13}CH_4$ and ^{13}CO confirmed that it is by the methane carbonylation route that acetic acid formed. According to IR spectra, $CaCl_2$ was first transformed to $Ca(O_2CCF_3)_2$. The active species that abstracted the hydrogen atom from methane was assumed to be $CaO^{\bullet}$ generated from $Ca(O_2CCF_3)_2$ under the action of $K_2S_2O_8$ and CO. The one-electron mechanism of this process was confirmed by its inhibition by free-radical traps such as 2,4,6-tri-*tert*-butylphenol, tetrachloro-*p*-benzoquinone and 2,2,6,6-tetramethylpiperidine. Other alkanes including ethane reacted in

the analogous way.[237] For ethane, the total yield of acids was 88% of which 22% accounted for acetic acid formed in the ethane oxidation.

The oxidative carbonylation of ethane in CF_3CO_2H with potassium persulfate as the oxidant and rhenium complexes was studied.[238] Upon the substitution of $CaCl_2$ for rhenium complexes, only traces of propionic acid could be detected, which cast doubt on the reproducibility of quantitative results[237] obtained in the catalysis on $CaCl_2$.

In trifluoroacetic acid, Co compounds, especially cobalt acetate, effected oxidative carbonylation of alkanes except for methane and ethane.[239] The reaction was carried out under rather mild conditions (CF_3CO_2H, 60–80 °C, P_{CO} = 2.0–3.0 MPa) in the presence of persulfate as the oxidant. Butyric and isobutyric acids and isopropyl trifluoroacetate were obtained from propane, the TON was 9.1 in 15 h. Cyclohexane converted the most easily of cylic hydrocarbons. Presumably, the active species, *i.e.*, the $Co^{III}-O^{\bullet}$ radical, acted as the initiator abstracting a hydrogen atom from the alkane. The methyl radical accepted CO, while the acyl radical transformed into a cation and the latter formed a mixed anhydride in the reaction with the solvent.

$$Co^{III}-O^{\bullet} + RH \longrightarrow Co^{III}OH + R^{\bullet},$$

$$R^{\bullet} + CO \longrightarrow R-CO^{\bullet},$$

$$R-CO^{\bullet} + Co^{III} \longrightarrow R-CO^{+} + Co^{II},$$

$$R-CO^{+} + CF_3CO_2H \longrightarrow RC(O)OC(O)CF_3.$$

Under analogous conditions (CF_3CO_2H, $K_2S_2O_8$), heteropolyacids $H_4[PMo_{11}VO_{40}]$, $H_5[PMo_{10}V_2O_{40}]$ and $H_6[PMo_9V_3O_{40}]$ proved to be efficient catalysts,[240] manifesting TON of 3000 in the carboxylation of methane to acetic acid (yield 20%) and ~12 000 in the carboxylation of ethane to propionic acid (yield 70%) and of propane to butyric and isobutyric acids (the overall yield 65%).

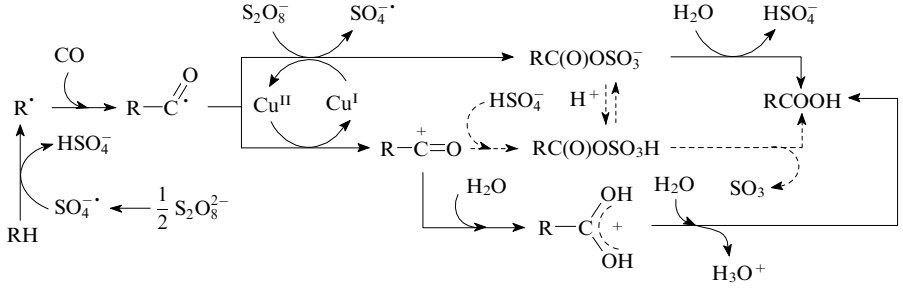
A comparative study of oxides of the Group 5–7 metals in the oxidative carbonylation reaction of alkanes under the action of $K_2S_2O_8$ in trifluoroacetic acid was carried out.[241] A trend of the oxide activity to vary along the diagonal of the Periodic Table was revealed, *i.e.*, V > Re > Mo. Moreover, for the case of methane, only V and Re oxides proved to be active. The process followed the free radical mechanism with the transient formation of alkyl, alkoxyl and alkylperoxyl radicals.

Vanadium complexes play a significant role in the oxidative functionalization of alkanes by the one-electron mechanism. The results of synthetic, catalytic and theoretical studies of the mechanism of action of $Ca[V(HIDPA)]_2$, $Ca[V(HIDA)]_2$ (synthetic amavadine), where HIDPA and HIDA are the basic forms of 2,2′-(hydroxyimino)dipropionic or -diacetic acid, respectively, and of related compounds are available.[242–244] It was found that the conversion of methane under the action of $K_2S_2O_8$ in trifluoroacetic acid could also occur in the absence of CO; moreover, it was initially assumed that it is from methane rather than from CF_3CO_2H that the carbon atom of the carboxyl group originated.[242] Later, it was found that the carboxyl group could also originate from CF_3CO_2H.[243] Different dependences of the yield of acetic acid on the CO pressure were observed for different vanadium compounds; apparently, the same factor determined the contributions of CO and CF_3CO_2H to the acetic acid formed. In the functionalization of ethane under the analogous conditions, acetic acid was formed both in the ethane oxidation (preservation of the C–C bond) and in the reaction of the ethyl radical with CO or CF_3CO_2H (cleavage of the C–C bond).[244]

Recently, the results of studies have been published on the carboxylation of alkanes in the presence of $K_2S_2O_8$ in aqueous acetonitrile where the use of CF_3CO_2H could be avoided.[245,246] The reactions were carried out typically at 60 °C and P_{CO} = 2.0 MPa in both the presence and the absence of a metal catalyst. The highest efficiency was exhibited by the tetranuclear complex $[(O)Cu_4\{N(CH_2.CH_2O)_3\}_4(BOH)_4](BF_4)_2$. The yields of acids calculated based on the initial alkane were as follows (%): 72 for cyclohexane, 45 for hexane, 38 for propane, 30 for butane, 23 for pentane, 22 for cyclopentane and 9 for ethane (methane did not react under these conditions). In the absence of metal, the conversion of ethane and pentane afforded the same product yields, while other alkanes reacted much less efficiently, for instance, the yield of cyclohexanecarboxylic acid was only 12.3%.

A mechanism was proposed (Scheme 25) according to which the alkyl and acyl radicals and the acyl cation were the key intermediates. The $SO_4^{-\bullet}$ radical anion formed upon thermolysis of persulfate abstracts a hydrogen atom from the alkane. The alkyl radical and CO furnish the acyl radical and transformation of the latter could follow the two pathways. According to the first pathway, the oxidation of the acyl radical with persulfate leads to acyl sulfate which is hydrolyzed to a carboxylic acid. The second pathway involves a metal compound, *i.e.*, the metal in the reduced form abstracts an electron to afford the acyl cation, which reacts with water to form the protonated form of the carboxylic acid. When $H_2{}^{18}O$ was used, the main product was $RCO^{18}OH$, which pointed to the role of water as the hydroxylating agent. Hydrogen peroxide and *tert*-butyl hydroperoxide were inefficient in this process. The dashed arrows in Scheme 25 indicate insignificant steps.[245]

This reaction was studied in detail by the example of carboxylation of C_5–C_8 cycloalkanes and adamantane.[246] It was shown that *cis*- and *trans*-1,2-dimethylcyclohexanes



Scheme 25

RH = C_2H_6, C_3H_8, n-C_4H_{10}, n-C_5H_{12}, cyclo-C_5H_{10}, cyclo-C_6H_{12}.

reacted without retention of their configuration, which suggested the radical mechanism.

IX. Conclusion

In closing this review, we consider how can the results of studies on the oxidative functionalization of alkanes carried out so far be implemented in practice. According to Periana,[120] the specific activity (a) of a catalyst should be equal to 1 s^{-1}. However, this requirement seems to be overestimated. In a real catalytic system of the Monsanto process (synthesis of acetic acid by methanol carbonylation), the reaction rate was ~ 6 mol litre^{-1} h^{-1} for $[Rh] = 3 \times 10^{-3}$ mol litre^{-1}, $P_{CO} = 3.0$ MPa and 170 °C. It can easily be calculated that in this case $\alpha = 0.28$ s^{-1}. Taking into account the difference in reactivities of methane and methanol, let us assess the acceptable activity level as *ca.* 0.1 s^{-1}. The activity of the (Bpym)$PtCl_2$ catalyst was 10^{-3} s^{-1}; however, it was characterized by the high degree of methane conversion and the absence of external reducing agents. Its serious drawback was the use of sulfuric acid as the solvent and the oxidant. The isolation of methanol from methyl hydrogensulfate formed requires hydrolysis and hence is associated with the formation of large volumes of highly diluted sulfuric acid. Thus, the profitability of the Catalytica process seems doubtful.

The use of potassium persulfate as the oxidant is hardly profitable as well because it involves the formation of large amounts of sulfate. The processes utilizing hydrogen peroxide or dioxygen appear to be more promising. The efforts of several research groups, mainly the Shul'pin and Pombeiro teams, provided considerable breakthrough in the peroxide oxidation of alkanes. The efficient catalytic systems for direct oxidation of alkanes require an external reducing agent for activating dioxygen. Unfortunately, in contrast to biological systems, the efficiency of a reducing agent in chemical systems is 5%–10%. The $RhCl_3$–$Cu^{I/II}$–Cl^- catalytic system has an index $\alpha \approx 0.09$ s^{-1} at 95 °C and, apparently, approaches the practically important systems as regards this parameter. However, this system operates in trifluoroacetic acid, which is toxic. Furthermore, 9–10 moles of carbon monoxide is consumed per mole of converted methane. The drawbacks also include the very high corrosion activity (dissolution of metallic titanium) and the corresponding requirements to the reactor material. Thus, in their traditional form, the so far known homogeneous catalysts for direct oxidation of alkanes and their oxidative carbonylation can hardly found any practical application.

A possibility of the practical use of achievements in homogeneous catalysis is carrying out processes in the film mode on the surface of a support. For instance, acetoxylation of ethylene was carried out in an acetic acid liquid layer on the Pd/SiO_2 surface.[22] One can also apply solutions of metal complexes in high-boiling solvents onto solid porous supports in the same fashion as in gas chromatography. The development of such hybrid catalysts would allow the advantages of homogeneous and heterogeneous catalyses to be combined. At relatively low temperatures (100–200 °C) that provide the high selectivity of the process, there is no need in solvents and the distillation stage to separate the solvent from the catalyst.

The inevitable difficulties associated with the quest for an oxidation–resistant stationary liquid phase and with heat transfer appear to be surmountable. At least, it is known that the metal complex solutions in ionic liquids that were either applied on the surface of support materials [247] or incorporated into their pores,[248] were actively studied recently in the reactions of quasi-gas-phase hydroformylation of alkenes. Silica gel was preferred as the support. The prospects of using such catalysts in catalytic processes were discussed.[249]

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