catalysts

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Review

New Trends in Oxidative Functionalization of Carbon–Hydrogen Bonds: A Review

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Abstract: This review describes new reactions catalyzed by recently discovered types of metal complexes and catalytic systems (catalyst + co-catalyst). Works of recent years (mainly 2010–2016) devoted to the oxygenations of saturated, aromatic hydrocarbons and other carbon–hydrogen compounds are surveyed. Both soluble metal complexes and solid metal compounds catalyze such transformations. Molecular oxygen, hydrogen peroxide, alkyl peroxides, and peroxy acids were used in these reactions as oxidants.

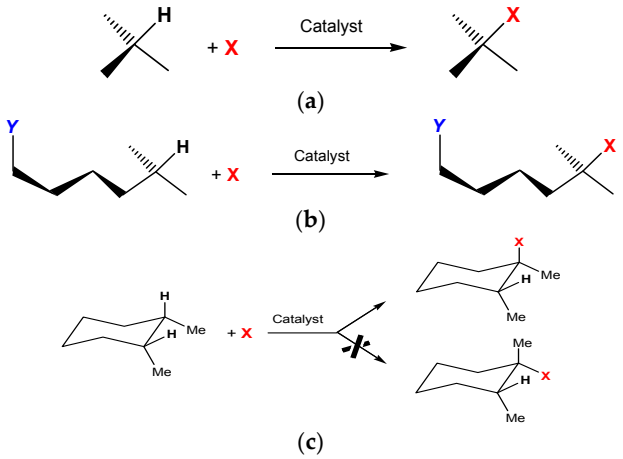
Keywords: alkanes; alcohols; alkyl hydroperoxides; aromatics; hydrogen peroxide; mechanisms of oxidation; metal-complex catalysis; oxygen; oxygenation; peroxyacids

1. Introduction

This review is devoted to functionalization of carbon–hydrogen bonds [1–13] in various organic compounds, which is a very important process both from academic and practical point of view. Replacing hydrogen atoms in carbon–hydrogen compounds by functional groups X leads to valuable functionalized C–X compounds (Scheme 1a).

Remote functionalization of carbon–hydrogen compounds bearing functional groups *Y* under the action of metal complex catalysts can give valuable difunctionalized alkanes (Scheme 1b).

Some catalytic systems are capable of functionalizing carbon–hydrogen bonds stereospecifically (Scheme 1c).



Scheme 1. Functionalization of various C–H bonds.

Functionalization of the carbon–hydrogen bond primarily proceeds via its activation when the reactivity of this σ-bond increases toward a reagent. As a result, the bond is capable of splitting, and in many cases this rupture of a saturated carbon–hydrogen bond is implied in the literature when the term "activation" is used. However, it is necessary to emphasize that splitting the bond is actually *a consequence* of its activation [1]. Alternative definitions have been proposed by Periana and colleagues who

> "*define CH activation as a facile CH cleavage reaction with an 'MX' species that proceeds by coordination of an alkane to the inner-sphere of 'M' (either via an intermediate 'alkane complex' or a transition state) leading to a M–C intermediate*" ([14])

and wrote about

> "*the CH activation reaction as a coordination reaction with a reactive species 'M', that proceeds without the involvement of free radicals, carbocations, or carbanions to generate discrete M–R intermediates*" ([14–17]).

Labinger and Bercaw gave the definition of

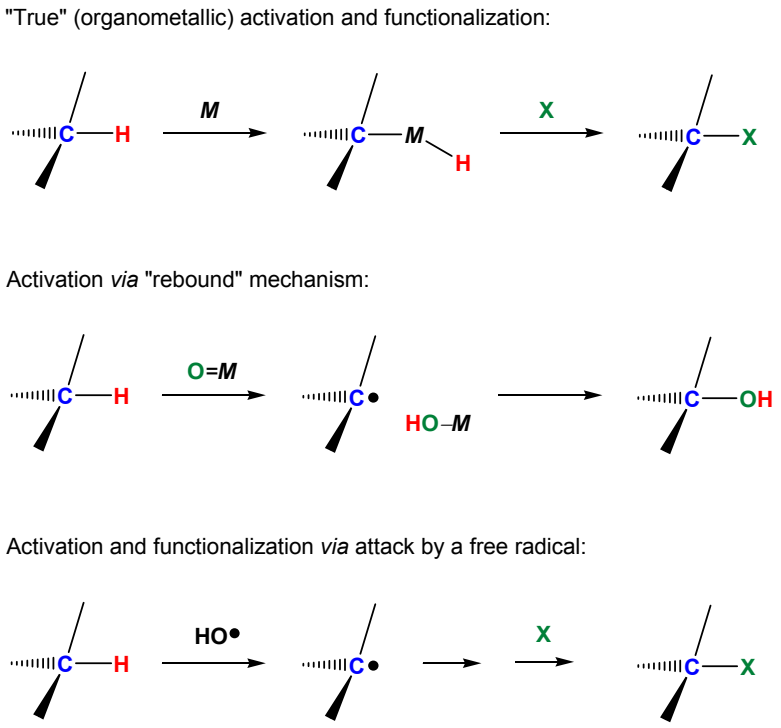
> "*reactions that have clearly been shown to involve bond formation between a metal and an alkane carbon*" ([18])

and Crabtree wrote:

> "*Activation is considered to be the binding of a substrate to a metal center. This can be followed by a functionalization step in which the substrate is transformed...The term 'CH activation' emphasizes the distinct reactivity pattern of low valent metal complexes from that of classical organic reagents which break CH bonds by electrophilic or radical routes. In a classical route, radicals such as* $^{\bullet}OH$ *readily abstract an* $H^{\bullet}$ *atom from alkanes, RH, to give the alkyl radical* $R^{\bullet}$*. Included in this group are some metal catalyzed oxidations, such as the Gif reaction and Fenton chemistry*" ([2]).

Finally, the term "C−H activation" refers to a metal-mediated pathway involving the formation of metal-carbon bonds [19].

In recent years and decades, many reactions of inert saturated hydrocarbons with various metal compounds under mild conditions have been described [1]. Such processes with the participation of metal complexes occur at relatively low temperatures and can be selective. The oxidations of hydrocarbons with molecular oxygen and donors of an oxygen atom (hydrogen peroxide, alkyl hydroperoxides, and peroxy acids) constitute an important field of contemporary catalytic chemistry. We divide all carbon–hydrogen functionalization processes into three types taking into account the mechanistic point of view [1]. The first group includes reactions involving "true" or "organometallic" functionalization of the carbon–hydrogen bond. In these reactions compounds containing metal-carbon σ-bonds (organometallic derivatives) are formed as intermediates or as final products. We include in the second group reactions in which the contact between the complex and the carbon–hydrogen bond is only via a ligand of the complex during the whole process of the carbon–hydrogen bond cleavage. The σ-C–M bond is not generated directly at any stage. In these reactions the function of the metal complex usually consists in abstracting an electron or a hydrogen atom from the carbon–hydrogen compound. In the processes that belong to the third type, a complex activates initially not the hydrocarbon but it reacts with another reactant (for example, with hydrogen peroxide or molecular oxygen). The formed reactive species (for example, hydroxyl radical) then attacks the hydrocarbon molecule without any participation in the latter process of the metal complex. The "direct activation" in this case does not involve the participation of the metal catalyst [1]. The three categories of metal-mediated C–H functionalization processes are shown below Scheme 2.



Scheme 2. Three types of metal-mediated C–H functionalization.

In living organisms under the action of certain metal-containing enzymes, the carbon–hydrogen oxidations proceed as reactions of the second or third type [1]. Although these oxidations occur via the formation of reactive radicals, they are rather selective and produce what is necessary for microorganisms compounds and energy. Biodegradation of hydrocarbons requires also metal-containing enzymes.

The Shilov reaction [1] was the first example of the organometallic (first type) activation which allows us to oxidize alkanes in aqueous solutions under catalysis by platinum(II) complexes. Curiously, the mechanism of this first reaction is very complex and is not completely clear. It will be discussed in more detail later. Numerous publications have appeared since Shilov's discovery which described unambiguous formation of σ-alkyl derivatives in alkane activation by metal complexes. In this review, however, we will discuss mainly the processes of oxygenation of carbon–hydrogen bonds to afford compounds with C-O bonds. All hydrocarbon oxidations occurring in living organisms [1,20–29] from the mechanistic point of view are also of the second or third types. Some non-organometallic complexes, for example, metal derivatives of porphyrins can play the role of models of certain metal-containing enzyme centers. In this review, we will consider recent publications devoted to metal-catalyzed liquid-phase reactions of carbon–hydrogen compounds. Many reviews on some aspects of carbon–hydrogen functionalization have been published in recent years [30–52].

2. Main Characteristics of Catalysts and Catalyzed Reactions

2.1. Definitions

A reaction can be characterized [53] by the yield (%) (Equation (1)):

$$(\text{amount of a product}/\text{amount of either starting substrate or reagent}) \times 100 \quad (1)$$

Important parameters [54,55] characterizing the catalyst are turnover number (TON) (Equation (2))

$$\text{TON} = \text{moles of product}/\text{moles of catalyst} \quad (2)$$

and turnover frequency (TOF) (Equation (3))

$$\text{TOF} = \text{TON}/\text{time}. \quad (3)$$

In functionalization of inert hydrocarbons, these substrate compete with a solvent. In these cases, usually acetic and trifluoroacetic acid [56], acetonitrile [57], and water [58,59] are employed. Alcohols are more easily oxidizable compounds in comparison with alkanes. It is noteworthy, however, that, in the aerobic oxidation of alkanes catalyzed by $FeCl_3$ under visible light irradiation, alcohols can be used as solvents [60]. In the initial stage, photohomolysis of the Fe^{III}–Cl bonds leads to the generation of reactive $Cl^{\bullet}$ radicals [61] which attack both the alkane and the alcohols used as a solvent with comparable rates. This leads to the formation of oxygenation products from the alkanes in quite high yield.

> "*To strengthen the relationship between catalysis and green chemistry, methods making use of neoteric solvents or alternative media rather than hazardous solvents, are more and more considered and represent unique challenges and opportunities for the future of catalysis*" ([62]).

Ionic liquids can be presented as examples [63–66].

In recent decades, traditional methods of stimulating catalyzed reactions (heating) new methods were added: photochemical initiation [67–72], microwave heating [73], electrocatalytic [74], and sonochemical [75] transformations.

2.2. Selectivity

Typically alkanes are transformed into derivatives which are more reactive in comparison with parent hydrocarbons, and this makes the selectivity one of the most important problems in functionalizations of saturated hydrocarbons as well as aromatic and other carbon–hydrogen compounds.

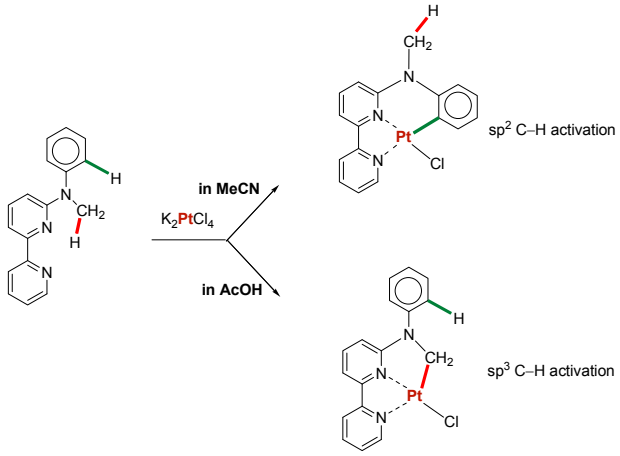
We will begin our discussion here from the term "*substrate selectivity*." It is especially important to discuss the substrate selectivity in the oxidations in living systems because the cell contains myriad of various compounds that might be potential substrates.

The term "*product selectivity*" is a concept more important for the reactions made *in vitro*. Indeed, the same interaction of a few reactants can lead depending on conditions to different distribution of products. By optimizing the conditions, a chemist can obtain predominantly one desirable product (isomer).

Usually, reactions give rise to the formation of a few possible positional isomers, such as monosubstituted benzenes. Electrophilic substitution in monosubstituted benzenes C_6H_5X gives comparable amounts of the three isomers. The distribution of isomers is *ortho* ≈ *para* > *meta* if X is an electron-releasing group and *meta* > *ortho* ≈ *para* if X is an electron-withdrawing group. In reactions of homolytic arylation, both withdrawing and releasing groups X direct the substituent mainly into *ortho*- and *para*-positions. Normal alkanes contain carbon–hydrogen bonds of two types: primary carbon–hydrogen bonds of two terminal methyl groups and secondary carbon–hydrogen bonds of internal methylene groups. Reactivities of methylene carbon–hydrogen bonds relative reactivity of the methyl group often depend on the nature of an oxidizing species and thus can give valuable information on the mechanism of the oxidation. Parameter C(1):C(2):C(3):C(4) is relative normalized (calculated taking into account the number of hydrogen atoms at each carbon) reactivities of hydrogen atoms at carbons 1, 2, 3, and 4 of the chain of normal alkane. This parameter is often discussed in mechanistic studies. Substitution of hydrogen atoms in normal alkanes with the participation of very reactive radicals like $Cl^{\bullet}$ or $HO^{\bullet}$ proceeds non-selectively, which is reflected by low selectivity parameter: C(1):C(2):C(3):C(4) ≈ 1:5:5:5. The stochiometric uncatalyzed oxygenations of normal alkanes with peracids occur without the participation of free radicals and exhibit high selectivity; more inert methyl groups are not oxidized at all. Some catalytic systems direct the substituent predominantly to only one position (region). We say that such reactions are "*regioselective*" or

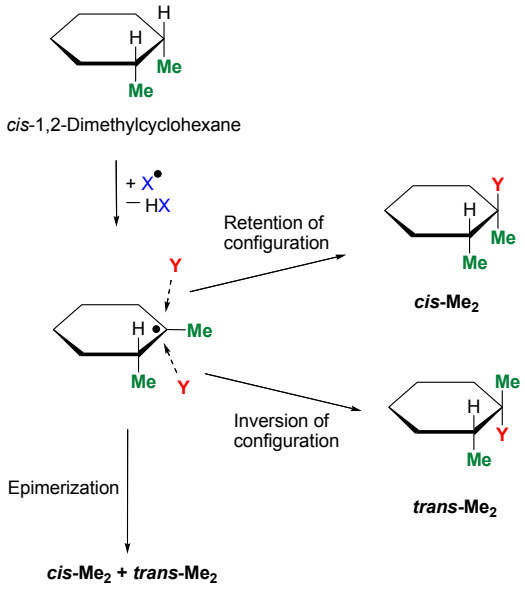
regiospecific. Regioselectivity is the preferential formation of one constitutional isomer over another (constitutional isomers of the same molecular formula differ in how their atoms are connected).

In reactions of branched alkanes, the bond selectivity parameter 1°:2°:3° is widely used. This value is relative normalized reactivities of hydrogen atoms at primary, secondary, and tertiary carbons of a branched alkane. Reactions that involve free radicals are usually less selective compared to reactions that proceed via concerted non-radical mechanism. In some reactions, the nature of a solvent can influence dramatically changing preferable carbon–hydrogen bonds in the same molecule [76] Scheme 3:



Scheme 3. Activation of aryl or methyl C–H groups by the Pt(II) complex.

An investigation of "*stereoselectivity*" helps to understand the mechanism of the interaction between the active species and carbon–hydrogen bonds. The transformation of a test compound *cis*-1,2-dimethylcyclohexane with or without retention of configuration is shown in Scheme 4.



Scheme 4. Activation of *cis*-1,2-dimethylcyclohexane.

If two methyl groups in the product (in the case Y = OH) are in *cis*-orientation, we say that the reaction proceeds with retention of configuration. In the second case, if methyls are in mutual *trans*-orientation, we say about inversion of configuration. Usually, both reactions proceed

with comparable rates and give ***cis*-Me$_2$** and ***trans*-Me$_2$** isomers in approximately equal amounts (epimerization). If the reaction proceeds without the participation of reactive radicals but via a concerted mechanism (as in the cases of peracids), the products are generated with partial or complete retention of configuration.

2.3. Effect of Additives: Pyrazine-2-Carboxylic Acid (PCA)

It is known that the addition of some compounds can dramatically change the reaction rate (increasing or decreasing it) and also affect the selectivity of the reaction. Thus, pyridine present in the solution of Gif systems induces the transformation of initially formed alkyl hydroperoxide into the corresponding ketone ("ketonization" of the alkane occurs). Light irradiation of the emulsion of cyclohexane with an aqueous solution of $Fe(ClO_4)_3$ in air exclusively gives cyclohexanone [77]. One can propose that water, like pyridine, dehydrates the cyclohexyl hydroperoxide. This is supported by finding that irradiation of the solution of cyclohexyl hydroperoxide and $Fe(ClO_4)_3$ in water selectively gave cyclohexanone.

Some time ago, we found [78–80] that pyrazine-2-carboxylic acid (PCA) and analogous compounds (2,3-pyrazinedicarboxylic, picolinic, and dipicolinic acids) can be used as highly active co-catalysts in the vanadate-catalyzed oxidations of alkanes, arenes, alcohols, and other substrates, under mild conditions by peroxides in air. The $[VO_3]^-$/PCA/H_2O_2 system has been studied in detail [81–92]. We then continued studies of alkane oxidations in the presence of PCA under catalysis by complexes of some other metals: iron [93–96], manganese [97,98], and rhenium [99].

The complex $(OC)_3Fe(\mu\text{-}PhS)_2Fe(CO)_3$ (compound **1**; see Figure 1) catalyzes the oxygenation of alkanes and benzene with hydrogen peroxide in air in an acetonitrile solution [100]. Alkyl hydroperoxides are formed as the main reaction products in the alkane oxidation (turnover numbers of 2300 were attained); benzene is transformed into phenol. The addition of PCA improves the oxidation. The duration of the lag period in the oxygenate accumulation can be substantially reduced if pyridine is added. Some dependencies are shown in Figure 1. Interestingly, the addition of picolinic acid (PIC) instead of PCA leads to the complete oxidation inhibition (Figure 1A).

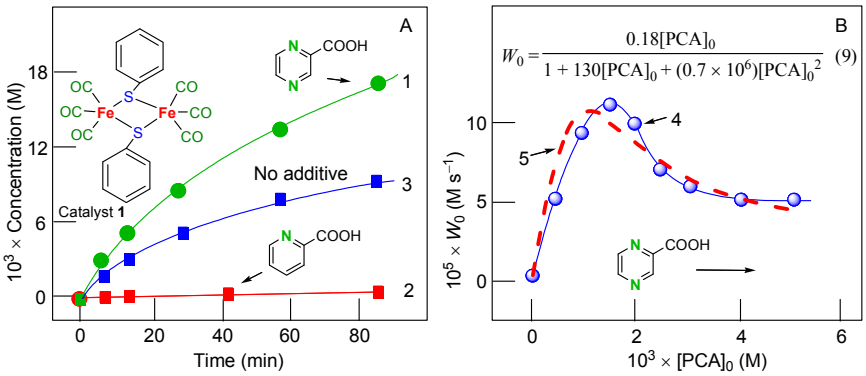


Figure 1. Graph (**A**). Accumulation of oxygenates (cyclohexyl hydroperoxide + cyclohexanol + cyclohexanone) with time in the cyclohexane oxidation with H_2O_2 catalyzed by compound **1** in acetonitrile in the presence of two different co-catalysts: PCA (3.0×10^{-3} M; curve 1) and PIC (3.0×10^{-3} M; curve 2) or in the absence of additives (curve 3). Conditions: $[\mathbf{1}]_0 = 2.0 \times 10^{-4}$ M, $[pyridine]_0 = 0.2$ M, $[H_2O_2]_0 = 0.64$ M, $[cyclohexane]_0 = 0.37$ M, 50 °C. Graph (**B**). Curve 4: dependence of the initial rate W_0 of oxygenate accumulation in the cyclohexane oxidation with H_2O_2 catalyzed by **1** in acetonitrile on the initial concentrations of PCA. Curve 5: simulated dependence of the initial rate W_0 on $[PCA]_0$ corresponding to Equation (6). Conditions: $[\mathbf{1}]_0 = 2.0 \times 10^{-4}$ M, $[pyridine]_0 = 0.1$ M, $[H_2O_2]_0 = 0.64$ M, $[cyclohexane]_0 = 0.37$ M, $[H_2O]_{total} = 1.21$ M, 50 °C. Adapted from Ref. [100].

The dependence of the initial oxidation rate W_0 on the initial concentration of added co-catalyst PCA in the presence of pyridine is presented by curve 1 in Figure 1B. For the kinetic Equations (4)–(7).

$$1 + n\,\mathrm{py} \rightleftharpoons 1 \cdot (\mathrm{py})_n \tag{4}$$

$$\mathbf{1} \cdot (\mathrm{py})_n + \mathrm{PCA} \overset{K_1}{\rightleftharpoons} \mathbf{1} \cdot (\mathrm{py})_{n-1} \cdot \mathrm{PCA} + \mathrm{py} \tag{5}$$

$$\mathbf{1} \cdot (\mathrm{py})_{n-1} \cdot \mathrm{PCA} + \mathrm{PCA} \overset{K_2}{\rightleftharpoons} \mathbf{1} \cdot (\mathrm{py})_{n-2} \cdot (\mathrm{PCA})_2 + \mathrm{py} \tag{6}$$

$$\mathbf{1} \cdot (\mathrm{py})_{n-1} \cdot \mathrm{PCA} + \mathrm{H_2O_2} \overset{k}{\rightarrow} \mathrm{X} \tag{7}$$

where X is a species active in the cyclohexane oxidation, we have Equation (8)

$$W_{\mathrm{X}} = \frac{kK_1[1 \cdot (\mathrm{py})_n]_0[\mathrm{PCA}]_0[\mathrm{H_2O_2}]_0}{1 + K_1[\mathrm{PCA}]_0 + K_1K_2[\mathrm{PCA}]_0{}^2} \tag{8}$$

$$W_0 = \frac{0.18[\mathrm{PCA}]_0}{1 + 130[\mathrm{PCA}]_0 + (0.7 \times 10^6)[\mathrm{PCA}]_0{}^2} \tag{9}$$

It is easy to obtain Equation (9) shown in Figure 1B for conditions of the discussed experiments.

More recently, further research of other chemists has resulted in new interesting catalytic systems based on the combination of PCA. For example, Pombeiro and colleagues described catalytic oxidations with complexes of iron, copper, vanadium as well as gold nanoparticles [101–104] (see also reviews [105,106]).

3. New Catalysts and Ligands

New types of catalysts for efficient oxidation of carbon–hydrogen compounds have been reported in recent years: heteropolycompounds [107–110], supported complex catalysts [111,112], and porous materials [113–122].

3.1. Metal Ions Most Active in Oxidation Catalysis

In the early stages of development of homogeneous carbon–hydrogen oxidations only a few transition metals were more or less carefully studied as catalysts [1]. These ions were iron, copper, manganese, *etc.* During the past several decades, many metals have been studied in catalytic activation and functionalization of carbon–hydrogen bonds. The reader is directed to selected recent examples with gold [123], cobalt [124–126] chromium [127], copper [128–131] iron [132–135], iridium [136], manganese [137–139], molybdenum [140], nickel [141], osmium [142–148], palladium [149–151], rhenium [152], rhodium [153,154], ruthenium [155,156], and vanadium [157,158].

A new method of synthesis of heterometallic coordination compounds by spontaneous self-assembly (SSA) [159] led recently to complexes which turned out to be very efficient catalysts in oxidations with peroxides. For example, Nesterov *et al.* prepared the heterobimetallic complex with a Schiff-base ligand $[Co_4Fe_2OSae_8]$ (compound **2**; where Sae = L^4 and H_2Sae is salicylidene-2-ethanolamine (Figure 2)) [160]. In oxidation of cyclohexane into cyclohexyl hydroperoxide under the action of H_2O_2, this compounds exhibits a very high TON of 3570, which is the highest value ever observed for an iron-containing catalyst. It has been indicated [160] via mass spectral and comprehensive kinetic studies that hexanuclear **2** dissociates when dissolved in CH_3CN to form a trinuclear particle $[Co_2Fe(L^4)_4]^+$. This particle, observed in concentrated (1×10^{-4} M) solutions of **2**, is the catalytically active species responsible for the fast reaction rates greater than 3×10^4 M·s^{-1} (maximum turnover frequency TOF = 11,200 h^{-1} = 3.1 s^{-1}). The catalytic system is believed to proceed by free-radical pathways with the hydroxyl radical as the main attacking species.

A few years ago, we discovered that the salt of non-transition metal aluminum catalyzes the alkane hydroperoxidation with hydrogen peroxide [161]. It has been proposed that interacting with an

aluminum derivative hydrogen peroxide is decomposed to afford hydroxyl radicals that attack the alkane molecule. This reaction is by no means a Fenton-like process because, in a Fenton reaction with Fe(II) or a Fenton-like reaction (for example with Fe^{III}), a transition metal can change its oxidation state ($Fe^{II} \rightleftharpoons Fe^{III}$) in the course of the hydrogen peroxide decomposition. Aluminum cation is unable to change its valency. To explain the catalytic action of aluminum cation, our co-authors Kozlov and Kuznetsov [162] assumed that, in the case of Al^{III}, not one but simultaneously *two* H_2O_2 molecules interact (entering into cation's coordination sphere). The first H_2O_2 molecule—as a model of the electron-rich Fe^{II} ion—delivers one electron (like in the Fenton mechanism) to the system, and this leads to the splitting the O–O bond in the second H_2O_2 molecule. Figure 3 presents a catalytic cycle generating two free radicals, $HO^{\bullet}$ and $HOO^{\bullet}$. According to DFT calculations, H_2O_2 molecule in complex **4** is highly activated toward the homolysis in the free hydrogen peroxide (6.1 *vs.* 39.4 kcal/mol). This approach has been used for some other non-transition metals [163–167]. The overall activation barriers (kcal/mol) of the generation of hydroxyl radicals were calculated: Ga (19.5) < Sc (22.2) < In (23.5) ≈ Y (23.7) < La (25.2) ≈ Al (25.6).

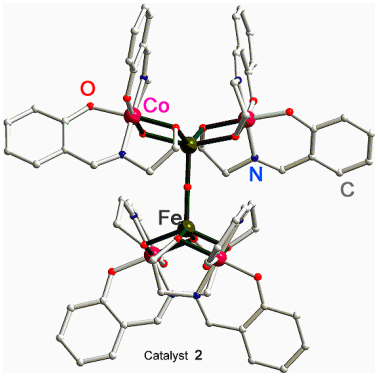


Figure 2. Molecular structure of $[Co^{III}_4Fe^{III}_2O(L^4)_8]\cdot 4DMF\cdot H_2O$ (complex **2**). Solvated DMF and water molecules have been omitted for clarity. Adapted from Ref. [160].

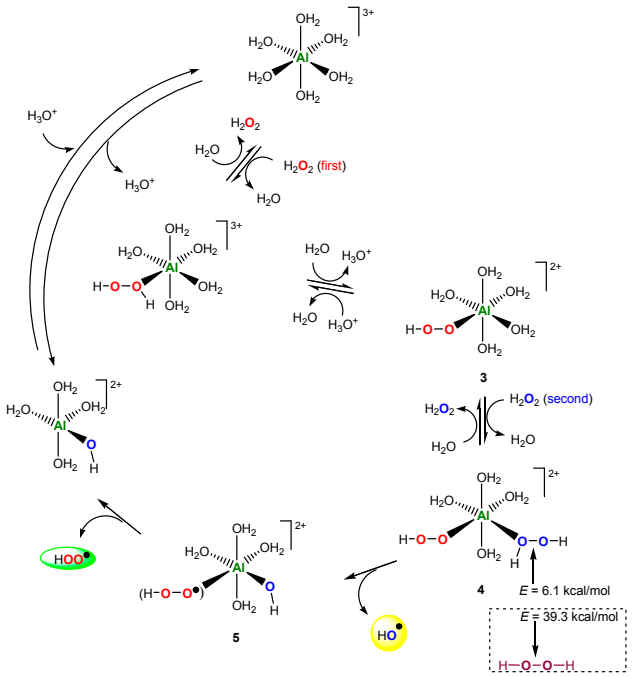


Figure 3. The Al-catalyzed decomposition of hydrogen peroxide. Adapted from Ref. [162].

Very recently, Meyerstein and colleagues used our approach involving two H_2O_2 molecules in DFT calculations of Fenton-like reactions with the participation of transition metals [168]. It was also shown that the Fenton-like reaction of $Co(H_2O)_6^{2+}$ proceeds via the binding of three H_2O_2 molecules to the cobalt(II) ion forming the transient $(H_2O)_3Co^{II}(OOH)_2(H_2O_2)$ [169]. Harvey studied the mechanism of the Fenton reaction via computational methods [170].

3.2. New Types of Ligands and Catalysts

In this section, we will briefly consider work that has been published in recent years describing new types of ligands and catalysts. Some examples have been discussed in previous sections (for example, see Figure 3).

Heme and nonheme oxidation catalysts have been intensively used in oxidations of alkanes aromatics, as well as in epoxidations [171–174]. Metalloporphyrins [175–178] play a very important role in such studies; they are models of enzyme reaction centers.

Sorokin and colleagues used phthalocyanines as catalysts in oxidations with peroxides [179,180]. Thus, mild oxidation of ethane to acetic acid by H_2O_2 was catalyzed by supported mu-nitrido diiron phthalocyanes [181], methane was oxidized to methanol, formaldehyde, and formic acid [182]. Maksimov, Karakhanov, and colleagues used analogous catalysts containing ions of iron and copper [183].

Talsi, Bryliakov, and colleagues published a series of papers on the C–H oxidations with H_2O_2 in the presence of aminopyridine complexes of manganese(II) of the types **6**–**10**. It was shown that complexes **6**–**8** efficiently (with TON up to 970) induce the oxidation of substrates containing aliphatic carbon–hydrogen groups, such as cyclohexane, adamantane, and (-)-acetoxy-*p*-menthane (Figure 4), with high regioselectivity (preferential oxidation of tertiary C–H bonds) [184]. Along with a few more catalysts, Mn-aminopyridines have been regarded as demonstrating good promise for practical use [185]. The introduction of electron-donating groups (complexes **9** and **10**) improved the oxidation selectivity; furthermore, catalysts **9** and **10** surprisingly demonstrated a much better efficiency in the benzylic oxidation of cumenes and ethylbenzene compared to the parent catalyst **6** [186]. All Mn-aminopyridine catalysts were active in acetonitrile solutions with the addition of co-catalytic additive (acetic acid), and typically required only 0.1 mol. % catalyst loadings and 1.3 equiv. of H_2O_2 (*vs*. substrate). Some examples of preparative oxidations on catalysts of this type are presented in Figure 4.

The mechanism of carbon–hydrogen bond oxidation in the presence of Mn-aminopyridine complexes was considered. The authors confirmed the electrophilic nature of the active oxidizing species. The latter demonstrated high $3^\circ/2^\circ$ ratios (40–49), alcohol/ketone ratios > 5, and high stereospecificity in the oxidation of *cis*-1,2-dimethylcyclohexane [187]; kinetic studies revealed a sizable kinetic isotopic effect (k_H/k_D 4.5–4.7), indicating that that the H atom lies on the reaction coordinate and participates in the C–H bond breaking step. Altogether, the experimental data provided indirect evidence in favor of the participation of a high-valent (presumably oxometal(V) [188]) species, ruling out the contribution of a free-radical-driven oxidation pathway. The key findings pointing to the oxomanganese(V) active species were (i) the incorporation of ^{18}O from added $H_2{}^{18}O$ into the oxidizing product, corroborating the "water-assisted" mechanism and (ii) partial inversion of *cis* configuration during the oxidation of *cis*-1,2-dimethylcyclohexane, apparently proceeding via formation of relatively short-lived carbon-centered tertiary radicals typical of the classic "rebound mechanism," postulated for the oxoferryl-driven cytochrome P450 reaction cycle. So far, no direct spectroscopic evidence for the oxomanganese(V) reactive species in Mn-aminopyridine-based systems has been reported. However, in catalyst systems relying on isostructural Fe catalysts, such evidence was gained by EPR spectroscopy taking advantage of the low-spin ($S = {}^1/_2$) structure of known oxoiron(V) intermediates [189].

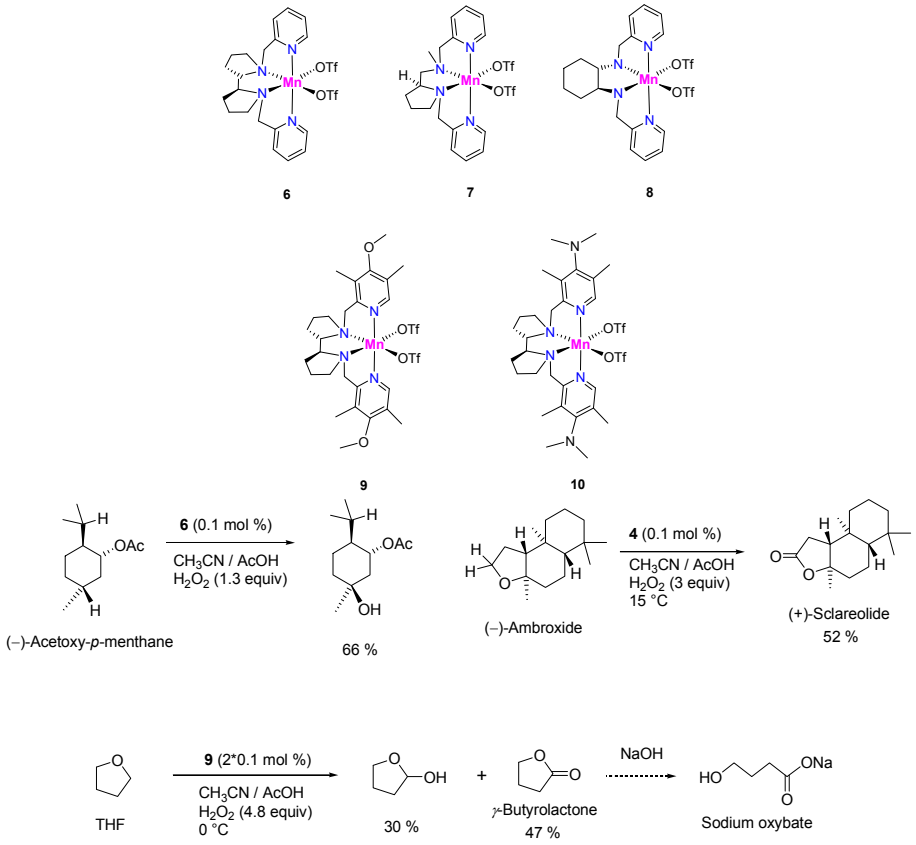


Figure 4. Examples of preparative-scale selective C–H oxidations catalyzed by Mn-aminopyridine complexes.

Costas in recent years has carried out many valuable works on functionalization of carbon–hydrogen bond catalyzed by nonheme complexes with polyamino ligands [190–193]. Additionally, very important works on complexes with polydentate ligands as catalysts have been reported by Nam and colleagues [194].

Complexes with ligands of new types have been recently synthesized, and in some cases these complexes turned out to be efficient catalysts for C–H functionalization. We have to mention here $Tp^{X}M$ complexes which were used by Pérez and other authors for alkane functionalization by carbene insertion [195–200].

The nature of ligand and ligand robustness play a very important role in metal-complex catalysis [201]. New types of ligands have been proposed in recent decades which form efficient catalysts with transition metal ions. These ligands are: N-heterocyclic carbene (NHC) [202,203], pincer-like [204–208], redox-active ligands [209–212], and scorpionates [213–218].

3.3. Polynuclear Metal Complexes As Catalysts

Multi-metallic metal complexes often have higher catalytic activity in comparison with mononuclear compounds [219,220].

Recently, Bilyachenko *et al.* have proposed a new convenient route to metallasilsesquioxanes and synthesized a series of complexes containing various transition metal ions. The most simple compound is the binuclear cage-like copper silsesquioxane $[(PhSiO_{1.5})_{10}(CuO)_2(NaO_{0.5})_2\ 4EtOH]$ (complex **11**) with a "Cooling Tower" structure (Figure 5) [221]. In addition, isomers containing four [222] and six [223] copper ions have been isolated. Their structures are presented in Figures 6 and 7 respectively. Al these compounds exhibited high catalytic activity in oxidation of benzene, alkanes, and alcohols with peroxides [224].

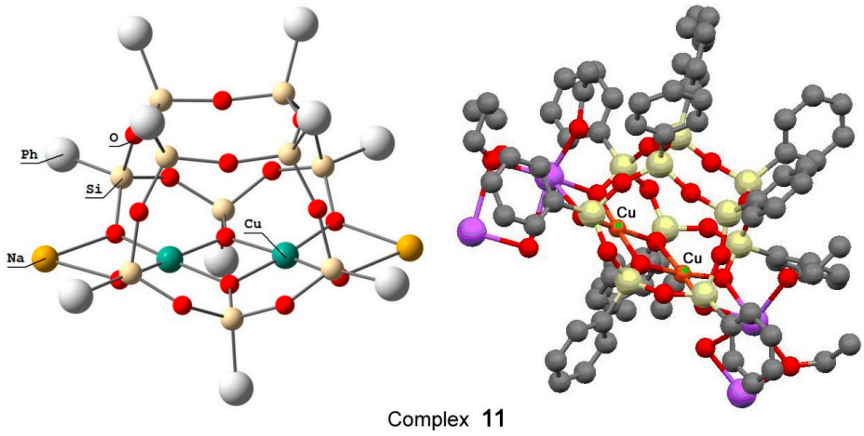


Figure 5. The structure of compound $[(PhSiO_{1.5})_{10}(CuO)_2(NaO_{0.5})_2$ 4EtOH] (**11**) (left) and a fragment of polymeric structure (right). Adapted from Ref. [221].

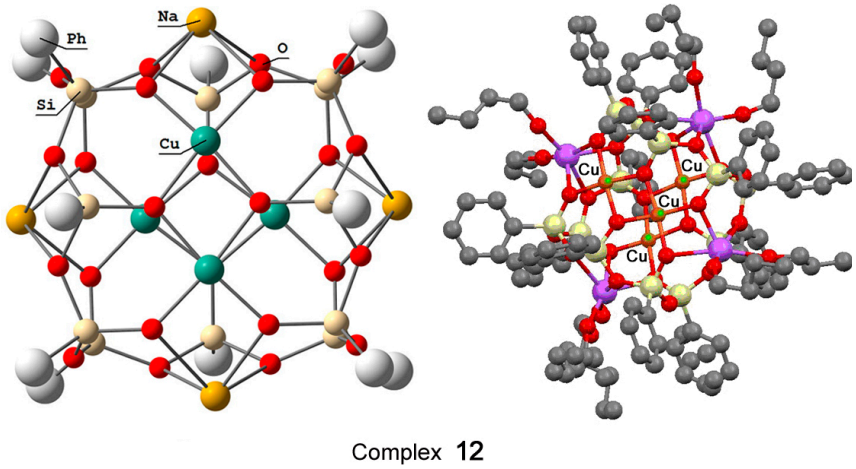


Figure 6. The structure of "Globule"-like compound $[(PhSiO_{1.5})_{12}(CuO)_4(NaO_{0.5})_4]$ (**12**). Adapted from Ref. [222].

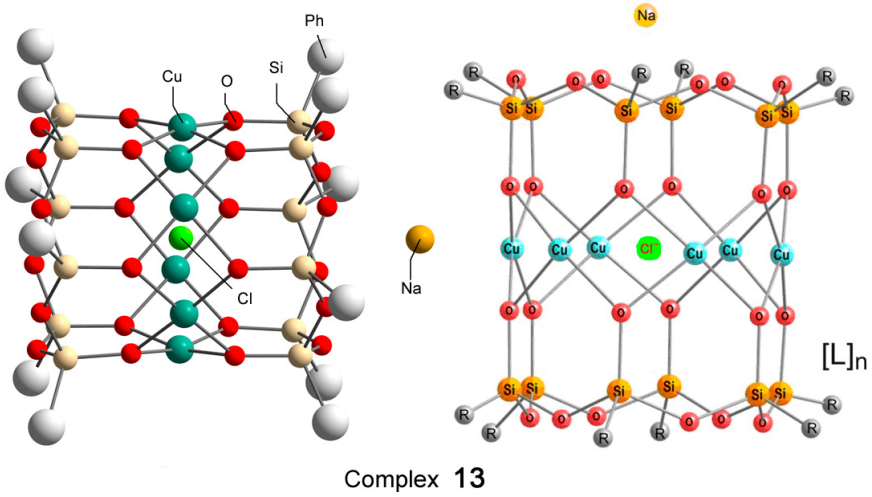


Figure 7. The structure of hexanuclear cylinder-like copper silsesquioxane $[(PhSiO_{1.5})_{12}(CuO)_6$ $(NaCl)(C_4H_8O_2)_{12}(H_2O)_2]$ (**13**), L = 1,4-dioxane/H_2O. Adapted from Ref. [223].

The hexanuclear oxo cluster $[(PhSiO_{1.5})_{20}(FeO_{1.5})_6(NaO_{0.5})_8(C_7H_8)(C_4H_9OH)_9]$ **14** (for the strucure, see Figure 8) containing iron and sodium cations efficiently catalyzed oxidation of cyclohexane and benzene in acetonitrile solution to the corresponding alkyl hydroperoxides and phenol, respectively, by hydrogen peroxide in air in the presence of nitric acid [225]. Another hexairon complex **15** [226] (for the structure, see Figure 9) catalyzed the oxidation of cyclohexane affording the products in 46% yield (Figure 10), which is very high for oxidation of alkanes.

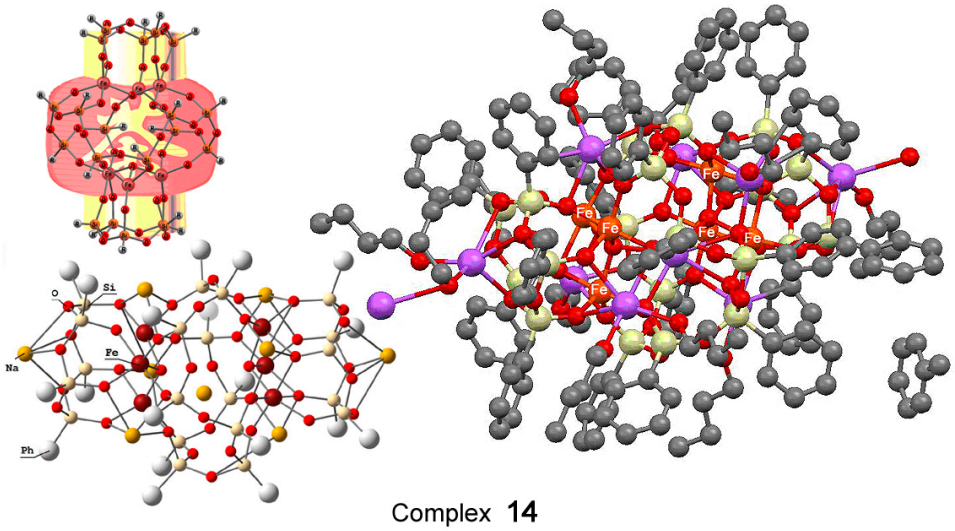


Figure 8. The structure of heteronuclear Na_8Fe_6-oxo cluster bearing silsesquioxane ligands $[(PhSiO_{1.5})_{20}(FeO_{1.5})_6(NaO_{0.5})_8(C_7H_8)(C_4H_9OH)_9]$ (**14**). Adapted from Ref. [225].

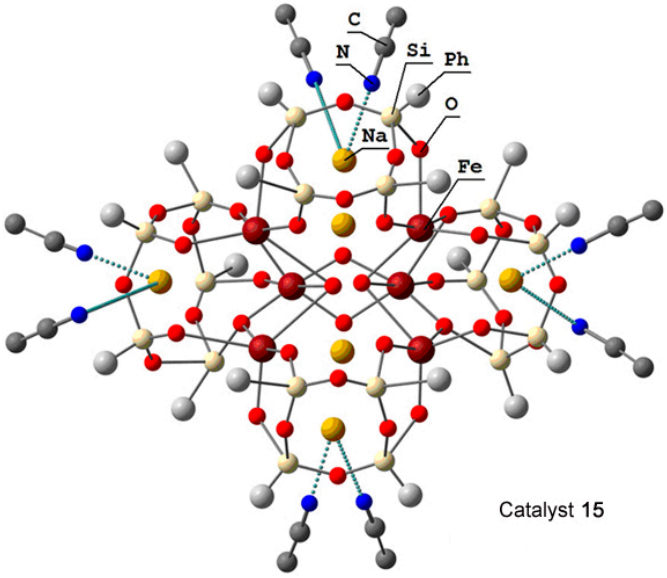


Figure 9. Molecular structure of hexairon compound **15**. Adapted from Ref. [226].

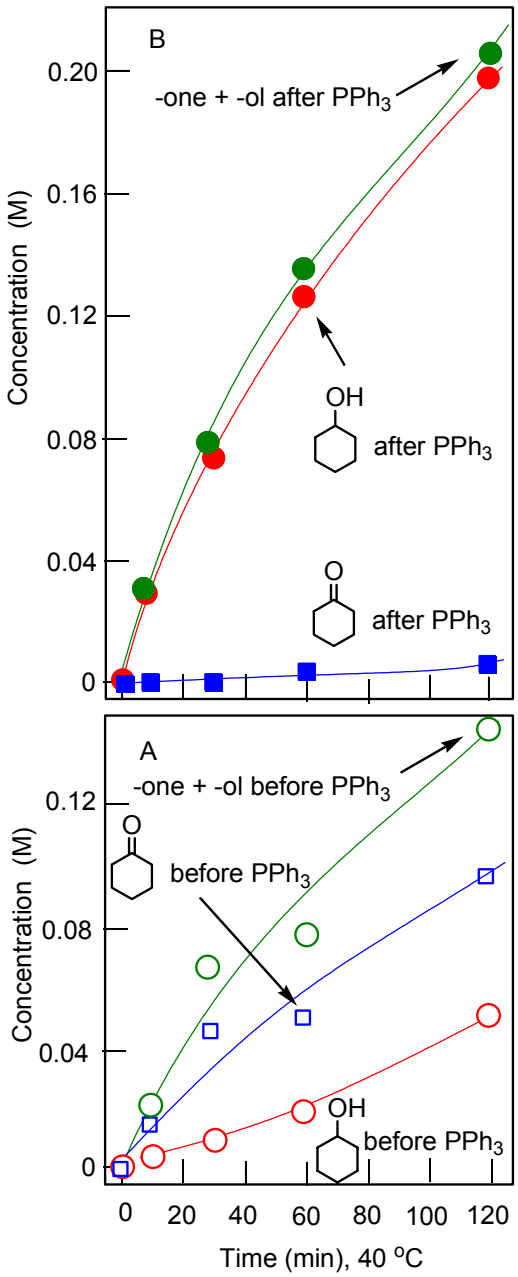


Figure 10. Accumulation of cyclohexanol and cyclohexanone with time in the cyclohexane (0.45 M) oxidation with H_2O_2 (50%, aqueous, 1.5 M) catalyzed by compound **15** (5×10^{-4} M) in the presence of CF_3COOH (0.05 M). Solvent was acetonitrile (total volume of the reaction solution was 5 mL); temperature was 40 °C. Concentrations measured before (Graph **A**) and after (Graph **B**) reduction of the samples with PPh_3 are shown.

Cations of cobalt and nickel gave cylinder-type complexes phenylsilsesquioxane $[(PhSiO_{1,5})_{10}(CoO)_5(NaOH)]$ (compound **16**) [227] and $(PhSiO_{1.5})_{12}(NiO)_6(NaCl)$ (compound **17**) [228]. Their "drum-like" structures are presented in Figures 11 and 12 respectively. Compound **16** exhibited activity in catalytic highly stereoselective oxidation of 1,2-cyclohexane with *m*-CPBA (Table 1).

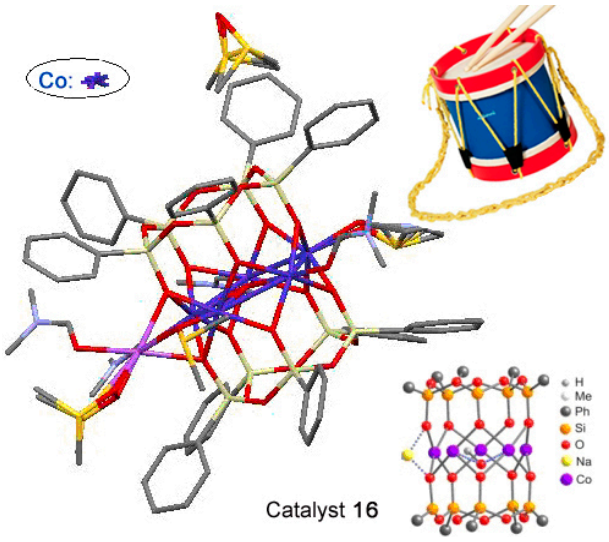


Figure 11. Molecular structure of compound $[(PhSiO_{1,5})_{10}(CoO)_5(NaOH)]$, **16**. Adapted from Ref. [227].

Table 1. Oxygenation of isomeric dimethylcyclohexanes with *meta*-chloroperoxybenzoic acid (*m*-CPBA) catalyzed by hexanuclear cobalt complex **16** [227] [a].

Entry	Substrate	T (°C)	$[HNO_3]$ (M)	Time (min)	Reduction with PPh_3	*t*-Dimethyl-Alcohol (mM)	c-Dimethyl-Alcohol (mM)	Yield (%)	Ratio t/c
1 [b]	*cis*-1,2-DMCH	40	0	120	yes	4	5.7	7	0.70
2 [b]	*cis*-1,2-DMCH	50	0	30	yes	4	5	6	0.77
3 [b]	*cis*-1,2-DMCH	50	0.05	30	yes	3	21	17	0.13
4 [b]	*cis*-1,2-DMCH	40	0.05	300	yes	3	15	13	0.20
5	*cis*-1,2-DMCH	40	0.05	30	yes	4	83	62	0.05
6	*cis*-1,2-DMCH	40	0.05	15	no	3	55	41	0.05
7	*cis*-1,2-DMCH	40	0.05	15	yes	3	55	41	0.05
8	*trans*-1,2-DMCH	40	0.05	15	yes	33	2	25	16
9	*cis*-1,4-DMCH	40	0.05	15	yes	19	59	56	0.32
10	*trans*-1,4-DMCH	40	0.05	15	yes	33	2	25	16

Notes: [a] Reactions were performed in MeCN. Concentrations: $[Substrate]_0 = 0.14$ M, $[m\text{-CPBA}]_0 = 0.26$ M, $[catalyst\ \mathbf{16}]_0 = 5 \times 10^{-4}$ M. [b] In the absence of catalyst **16**.

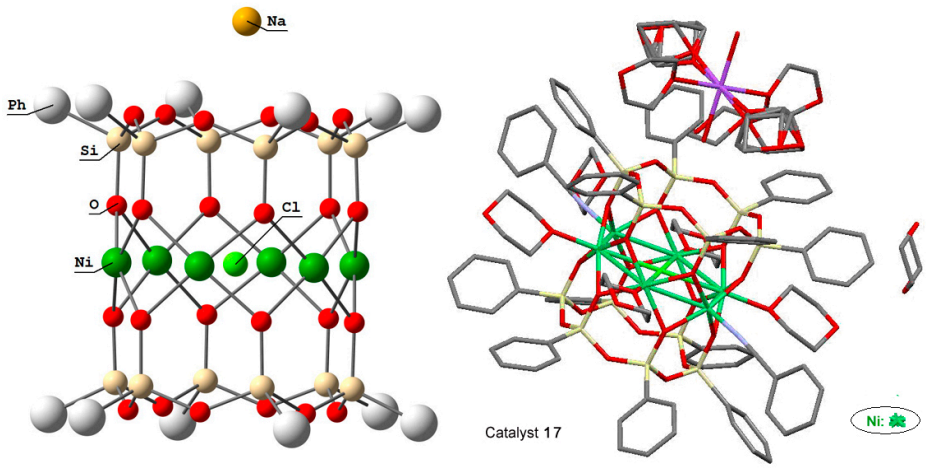


Figure 12. Molecular structure of compound $(PhSiO_{1.5})_{12}(NiO)_6(NaCl)$, **17**. Adapted from Ref. [228].

Metal-organic frameworks (MOFs), or porous coordination polymers, have attracted the attention of chemists [229–233]. Pombeiro, Martins, Guedes da Silva [234–238], Kirillov [234,235,239–241], and other scientists [242] synthesized various polynuclear complexes, coordination polymers, and derived

metal integrated mesoporous matrices and demonstrated high catalytic activity of these materials in oxidations with peroxides. Figures 13–15 show the examples of such catalysts.

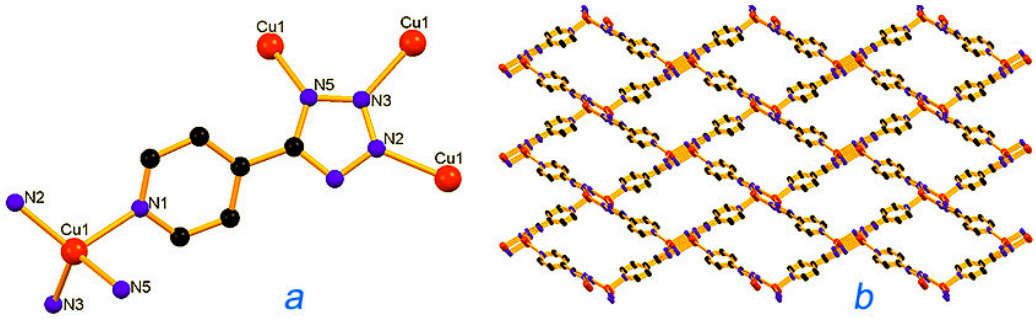


Figure 13. Structural fragments of the Cu(I) catalyst $[Cu(mu_4\text{-}4\text{-}ptz)]_n$ [4-ptz = 5-(4-pyridyl)tetrazolate], **18**, representing (**a**) the basic unit; (**b**) a view of rhomboid voids along the *a*-axis. Adapted from Ref. [238].

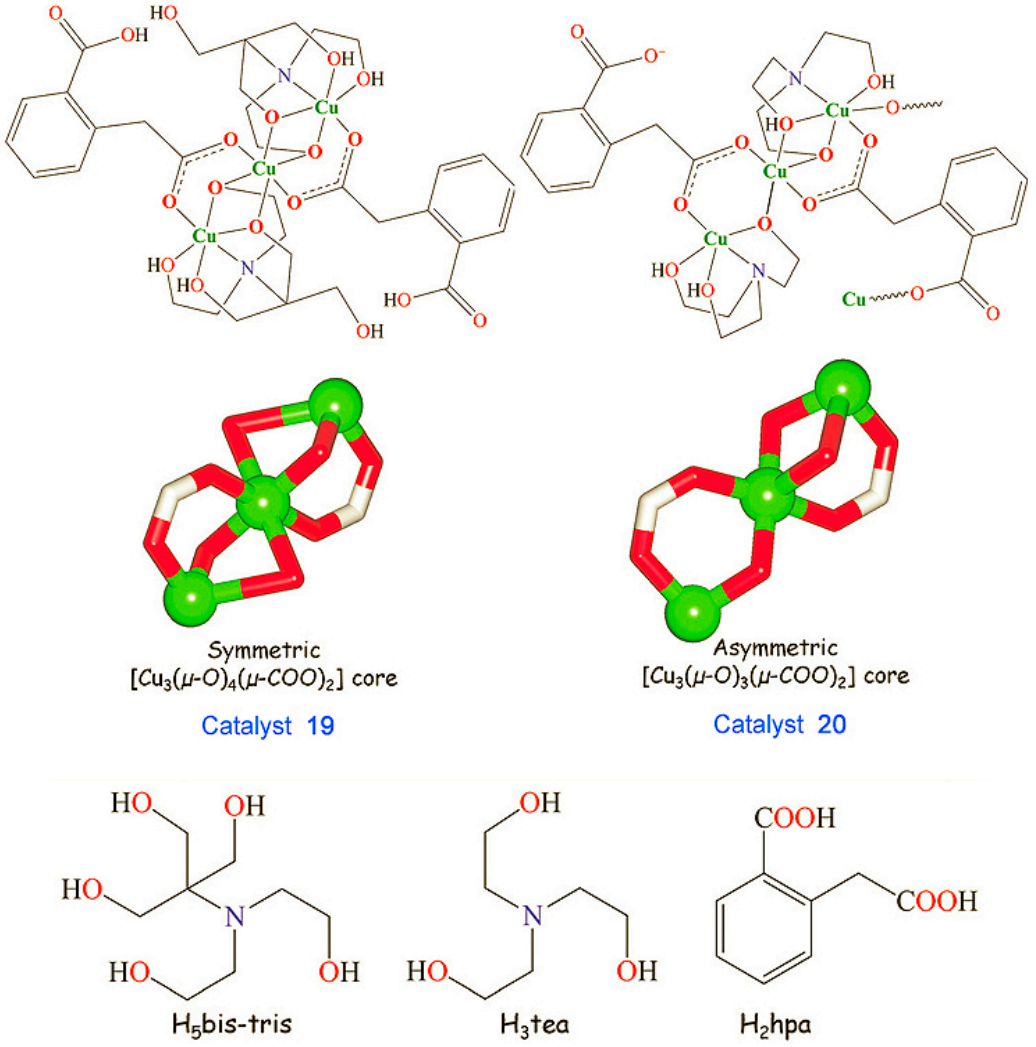


Figure 14. Catalysts $[Cu_3(\mu_2\text{-}H_3bis\text{-}tris)_2(\mu_2\text{-}Hhpa)_2]\cdot H_2O$ (**19**) and $[Cu_3(\mu_2\text{-}H_2tea)_2(\mu_2\text{-}hpa)(\mu_3\text{-}hpa)]_n$ (**20**) bearing distinct tricopper(II) cores where H_3tea is triethanolamine, H_2hpa is homophthalic acid, H_5bistris is bis(2-hydroxyethyl)amino-tris(hydroxymethyl)methane. Adapted from Ref. [241].

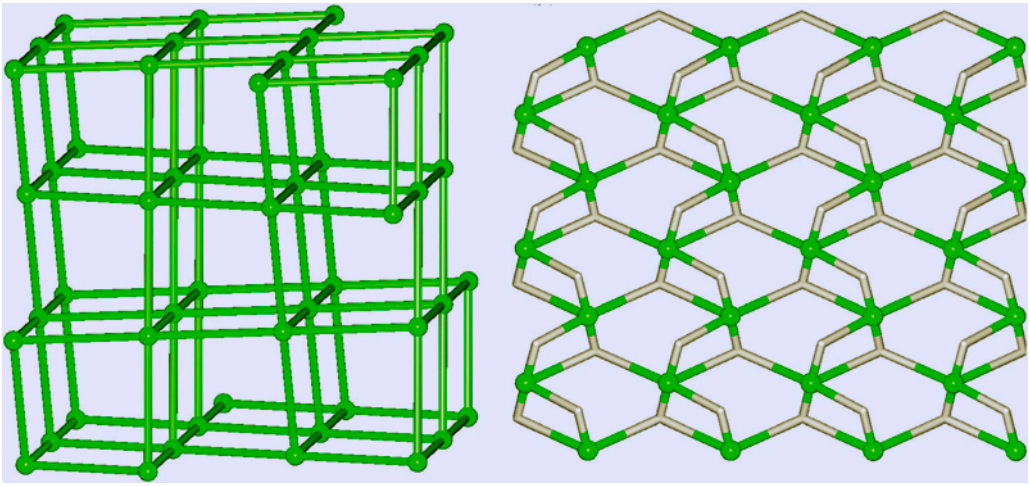


Figure 15. Topological representations of the H-bonded networks in catalysts **19** (left) and **20** (right). Green balls correspond to centroids of 6-connected or 5-connected molecular nodes. Adapted from Ref. [241].

4. Mechanism of Oxidation by Peroxides: Radical, or not Radical, That is the Question

In many cases, organic reactions occur with the formation of free carbon- and oxygen-centered radicals [243–246], and alkyl hydroperoxides are formed. A few tests can be used to detect the formation of ROOH from RH.

4.1. Detection and Determination of Alkyl Hydroperoxides Comparing GC before and after Treating Samples with PPh_3

We proposed and developed a simple method for analysis of alkyl hydroperoxides generated in various alkane oxidations in solutions [11–13,247–252]). A chemist can find that, if the direct injection of a reaction sample into the chromatograph gave comparable amounts of cyclohexanol and cyclohexanone (Figure 16, Figure 17a), the reduction of the sample with PPh_3 prior to GC analysis led to the noticeable predominance of the alcohol (Figure 17b). The comparison of the results obtained before and after the reduction clearly indicates that cyclohexyl hydroperoxide was formed as the main primary product. We can estimate the *real* concentrations of the alkyl hydroperoxide, alcohol, and ketone present in the reaction solution comparing the intensities of peaks attributed to the alcohol and ketone *before* and *after* the reduction. This method gives the very valuable information on the existence or non-existence of alkyl peroxides in the reaction mixture and allows us to estimate concentrations of the three products (ketone, alcohol, and alkyl hydroperoxide) formed in the reaction. In some cases, using non-polar columns and/or very clean detector, we can see in chromatogram a peak of alkyl hydroperoxide (Figure 16, Figure 17a), which disappears under the action of PPh_3 (Figure 17b).

Generally speaking, the [alcohol]/[ketone] ratio (presented in many publication as the A/K ratio) has no meaning and gives valuable information only if [alkyl hydroperoxide] = 0 [253]. Thus, it is more correct to write "the A/K ratio determined after reduction of the sample with PPh_3" [254,255]. Evidently, in this case, [A] = [alcohol] + [alkyl hydroperoxide].

When we have only the chromatogram obtained *after* the addition of PPh_3, we cannot definitively say that ROOH is present in the reaction solution (for example, [256]). In cases when the difference between chromatograms obtained *before* and *after* reduction of samples with PPh_3 indicates the formation of cyclohexyl hydroperoxide (that is when the investigator knows definitely that ROOH is present in the reaction mixture), it is convenient to characterize the reaction by the following ratio: ([alkyl hydroperoxide] + [alcohol])/[ketone]. This ratio is measured by GC for the samples *after* treating with PPh_3, and ([alkyl hydroperoxide] + [alcohol]) = $[alcohol]_{after\ PPh3}$. Although this rough parameter (see, for example, a recent paper by Kühn [257]) does not give the information on the amount of alkyl

hydroperoxide that is present in the reaction mixture, it approximately describes the selectivity relative to the three products (alkyl hydroperoxide, alcohol and ketone).

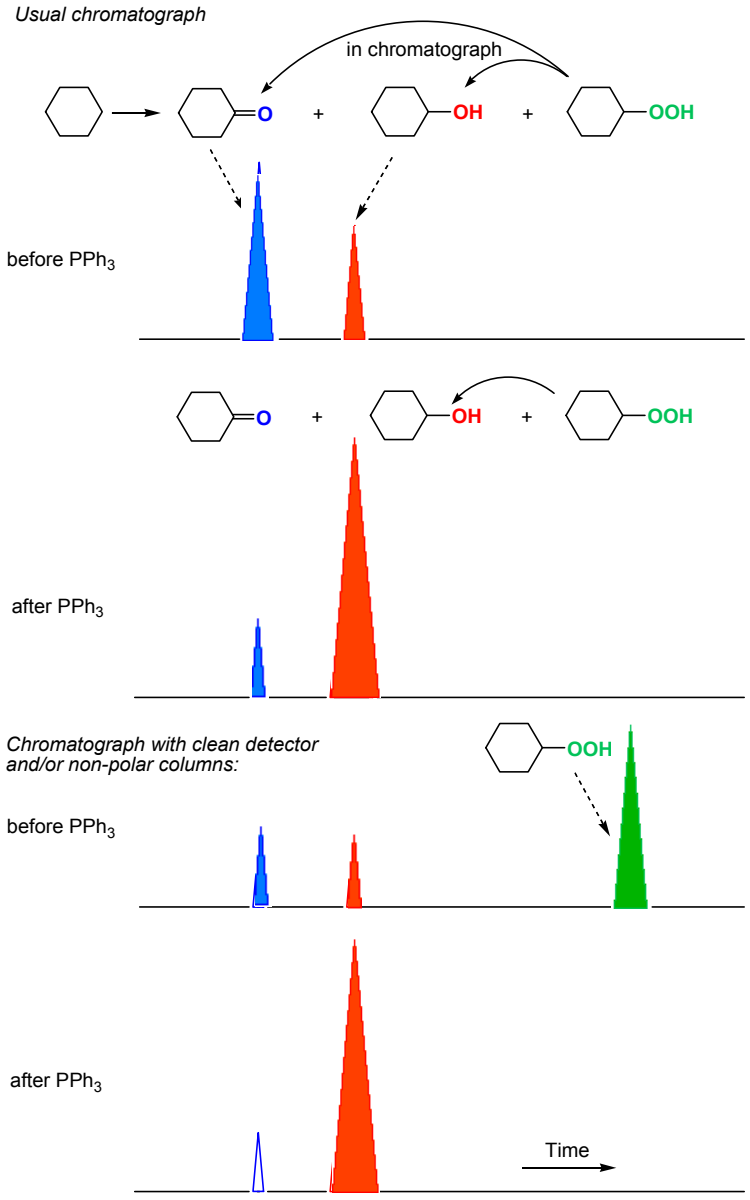


Figure 16. Detection of alkyl hydroperoxide ROOH by GC.

The so-called Shul'pin method [257–259] of analysis of oxygenates discussed above in this section and based on GC and PPh_3 has been used by other authors (selected examples are given in Refs. [260–278]). Finally, if the GC analysis shows that there is no difference between chromatograms obtained before and after reduction with PPh_3, it indicates that the samples do not contain alkyl hydroperoxides. Consequently, the reaction proceeds without the participation of free radicals, unless it was proposed, for example, for an oxidation with hydrogen peroxide via hydroxyl radicals (Fenton-like scheme): $H_2O_2 \rightarrow HO^{\bullet}$; $HO^{\bullet} + RH \rightarrow R^{\bullet}$; $R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$; $ROO^{\bullet} \rightarrow \rightarrow ROOH$. Possibly, we have a concerted mechanism in this case. Examples of such reactions are given below in Table 1 and Figure 17c,d for the catalyzed oxidation of 1,2-dimethylcyclohexane with *m*-CPBA.

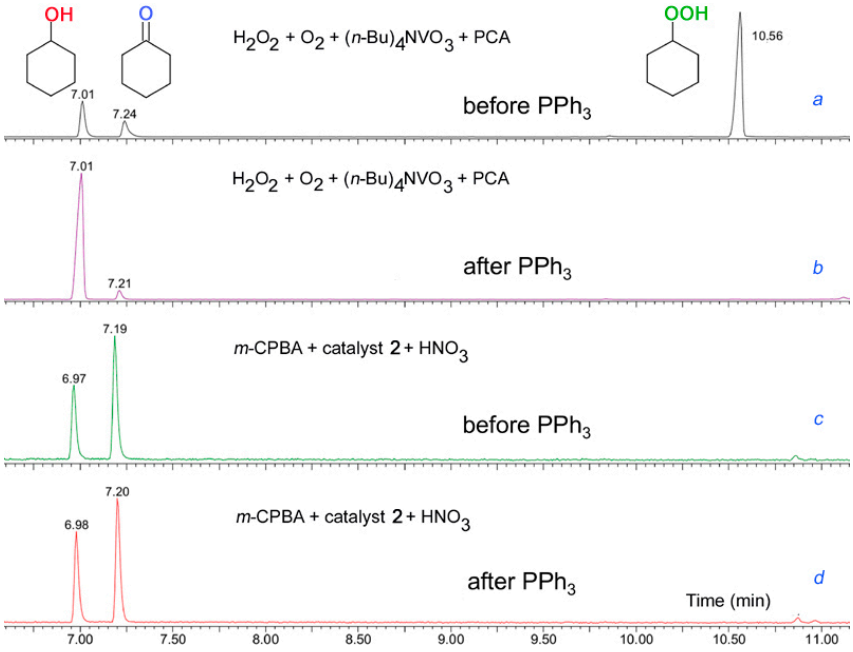


Figure 17. Chromatograms of reaction products obtained in the cyclohexane oxidation in acetonitrile by the H_2O_2/O_2/vanadate anion/PCA reagent [78–92] and the *m*-CPBA/catalyst **2**/HNO_3 system (see below [160]). For both systems the chromatograms were recorded before and after the addition of PPh_3. Conditions: $[cyclohexane]_0$ = 0.46 M; (***a*** and ***b***): $[H_2O_2]_0$ = 0.75 M, $[(n\text{-Bu})_4NVO_3]_0$ = 1×10^{-4} M, $[PCA]_0 = 4 \times 10^{-4}$ M, 40 °C; (***c*** and ***d***): $[m\text{-CPBA}]_0$ = 0.028 M, [complex **2**]$_0$ = 2.7×10^{-6} M, $[HNO_3]_0 = 5.5 \times 10^{-3}$ M, 50 °C. A Perkin-Elmer Clarus 600 gas chromatograph, equipped with non-polar capillary columns (SGE BPX5; 30 m × 0.32 mm × 25 μm) was used for analyses of the reaction mixtures. Adapted from Ref. [160].

4.2. Competitive Oxidation of Alkane and Solvent

Kozlov demonstrated that the mode of dependence of the initial rate of oxygenate formation W_0 on initial concentration of cyclohexane (W_0 is approaching to a plateau at relatively high concentrations of cyclohexane; an example is shown in Figure 18A) can lead to the conclusion on the participation of hydroxyl radicals in the reaction (see, for, example, Ref. [160]) by the competitive interaction of hydroxyl radicals both with cyclohexane and acetonitrile. The following kinetic scheme describes the dependence of W_0 on $[cyclohexane]_0$ with the plateau:

$$H_2O_2 + \text{catalyst} \rightarrow HO^{\bullet} \quad (\text{rate } W_5) \tag{10}$$

$$HO^{\bullet} + CyH \rightarrow Cy^{\bullet} \rightarrow \rightarrow CyOOH \quad (\text{constant } k_6) \tag{11}$$

$$HO^{\bullet} + CH_3CN \rightarrow \rightarrow \text{products} \ (\text{constant } k_7) \tag{12}$$

Here, the initiation stage (10) corresponds to the catalytic generation of hydroxyl radicals with rate W_5, stage (11) corresponds to the sequence of transformations of CyH into CyOOH (with kinetically rate-limiting interaction between $HO^{\bullet}$ and CyH), and stage (12) is the reaction of $HO^{\bullet}$ with acetonitrile. The analysis of this kinetic scheme in the quasi-stationary approximation relative concentration of hydroxyl radicals leads to the following equation:

$$W_0 = -\frac{d[CyH]}{dt} = \frac{d[CyOOH]}{dt} = \frac{W_i}{1 + \frac{k_7[MeCN]}{k_6[CyH]}} \tag{13}$$

The term

$$\frac{1}{\frac{d[CyOOH]}{dt}} \quad (14)$$

should be a linear function of $1/[CyH]_0$ (see Figure 18B). The following ratio can be obtained:

$$\frac{k_7[MeCN]}{k_6} = 8 \times 10^{-2}\,M \quad (15)$$

If we assume [MeCN] = 18 M in the reaction solution, we obtain $k_7/k_6 = 4.4 \times 10^{-3}$. Values $k_7[MeCN]/k_6$ (0.08 M) and k_7/k_6 (0.0044) are close to the corresponding parameters obtained for oxygenation of cyclohexane in acetonitrile with H_2O_2. The experimental data are in agreement with this dependence, which is shown in Figure 18A.

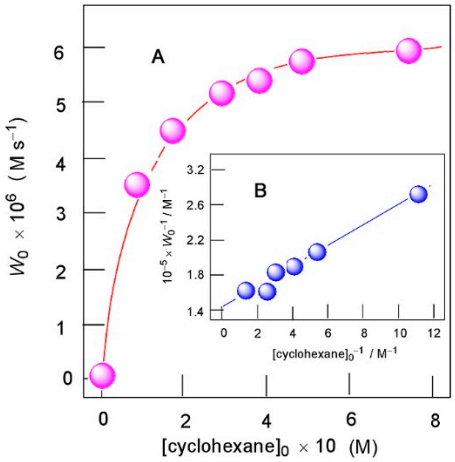


Figure 18. Oxidation of cyclohexane with H_2O_2 (1.0 M) catalyzed by compound **2** (3.2×10^{-5} M) in the presence of HNO_3 (0.04 M) in MeCN at 50 °C. Graph **A**: dependence of the initial rate of oxygenate formation W_0 on initial concentration of cyclohexane. Graph **B**: anamorphosis of curve shown in Graph A in coordinates [cyclohexane]$_0^{-1}$ – W_0^{-1}. Adapted from Ref. [160].

4.3. On the Rebound and Concerted Mechanisms

Radicals can be generated in the solvent cage, as in the so-called "oxygen rebound mechanism" [279–282]: M=O + RH → M–OH + R$^\bullet$ → M + R–OH. The regioselectivity of such reactions is relatively high, e.g., C(1):C(2):C(3):C(4) ≈ 1:40:40:40 (compare with the parameter typical for free-radical oxidation: 1:5:5:5). Reactions of such type are in many cases stereoselective and even stereospecific, *i.e.*, for the oxidation of *cis*-1,2-dimethylcyclohexane parameter trans/cis <<1. However, if radicals R$^\bullet$ partly leave the solvent cage and react with O_2, the formation of ROOH is possible. The $H_2O_2/[Mn_2(TMTACN)_2O_3]^{2+}$ (**21**)/RCOOH system has been assumed to oxidize via a "crypto-radical" ("hydroperoxo-rebound") mechanism (Figure 19) [283].

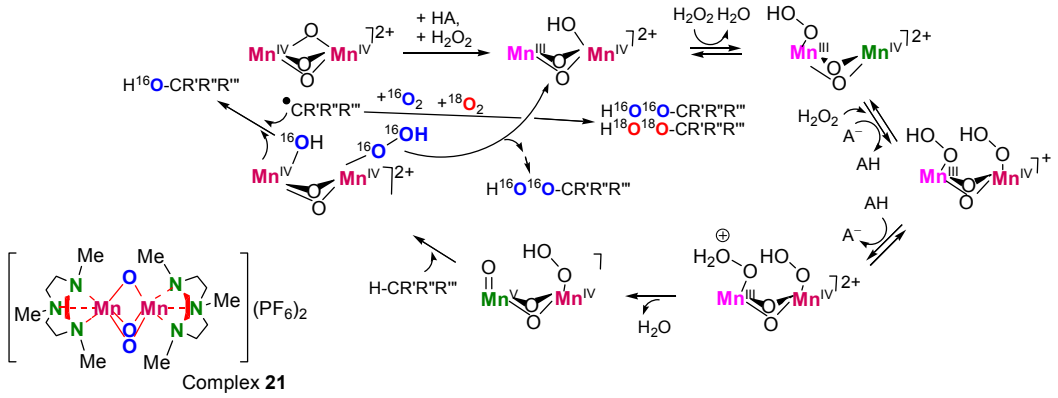


Figure 19. A catalytic cycle proposed for the alkane hydroperoxidation catalyzed by complex **21** in the presence of $^{18}O_2$ (in an atmosphere $^{16}O_2$+$^{18}O_2$). AH is a carboxylic acid where A^- is its anion. Adapted from Ref. [283].

m-Chloroperbenzoic acid in the presence of certain metal compounds efficiently oxidizes alkanes at low temperature with a very high degree of stereoselectivity (*trans*/*cis* << 1) [160,227,284,285]. Apparently, radicals are not produced intermediately in the course of such oxidation, which occurs via a "concerted" mechanism.

5. Some New Reactions

5.1. Shilov Chemistry

So-called Shilov chemistry [1,286–291] includes two reactions (discovered in 1969 and 1972 [1]). It was demonstrated that $Pt^{II}Cl_4^{2-}$ ion catalyzes H/D exchange in methane in a D_2O/CD_3COOD solution and, if $Pt^{IV}Cl_6^{2-}$ is added, the latter oxidizes methane to methanol. The catalytic cycle in which σ-methyl complexes of platinum(II) and platinum(IV) are involved is shown in Figure 20.

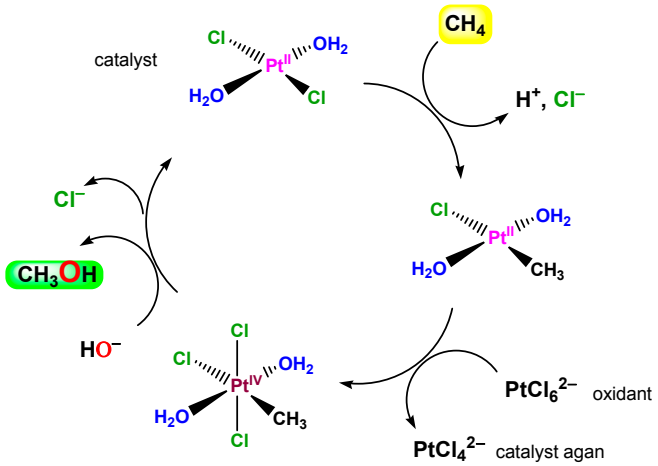


Figure 20. A schematically depicted catalytic cycle proposed for Shilov chemistry (the methane oxidation to methanol by $Pt^{IV}Cl_6^{2-}$ catalyzed by $Pt^{II}Cl_4^{2-}$).

The initial step of the reaction between alkane and ion $Pt^{II}Cl_4^{2-}$ is the formation of a σ-alkyl platinum(II) derivative, which in the second step is oxidized by platinum(IV) present in the solution to give alkanol (and also alkyl chloride):

$$Alk - H + Cl - Pt^{II} - Cl \rightarrow Alk - Pt^{II} - Cl + HCl$$

$$Alk - Pt^{II} - Cl + Pt(IV) + H_2O \rightarrow Alk - OH + Pt^{II} + Pt(II) + HCl$$

Recently, Rudakov [287] proposed an intimate mechanism for the first step of organometallic alkane activation by the Pt^{II} species (Figure 21). An active form of the aquachloride species $Cl_2(H_2O)_2Pt^{II}$ (**A**) is an adduct of the hydride $^{\bullet}Pt^{III}$ derivative with hydroxyl radical in the form of unseparated radical pair $Cl_2(H_2O)H(^{\bullet}Pt^{III})\cdots O^{\bullet}H$ (**B**). This coordinatively unsaturated complex has a vacancy to add an R fragment from the reacting alkane, RH. Indeed, coordinated hydroxyl radical can abstract a hydrogen atom from RH to produce radical $R^{\bullet}$. A collapse of radical pair ($^{\bullet}Pt^{III}$) and $R^{\bullet}$ affords an alkylhydride derivative of platinum(IV) (**C**) postulated for one stage of the catalytic cycle [1,287]. Thus, considering such a hypothesis, we can say that one of the main peculiarities of Shilov chemistry is a crypto-radical character of its intimate mechanism ("rebound mechanism"; see Section 4.3). It is possible to compare the platinum complex $Cl_2Pt^{II}(OH_2)_2$ (**A**) with a wasp, which "pricks" (activates) alkanes using its sting (coordinated hydroxyl radical). It is useful to remember that Bach and Dmitrenko [292] proposed a mechanism of alkane oxidation catalyzed by cytochrome P450. It involves the rearrangement (somersault motion) of the metal hydroperoxide to its inverted isomeric form with a hydroxyl radical that is hydrogen bonded to the metal oxide: MO-OH → M=O ··· HO•. The coordinated hydroxyl radical abstracts a hydrogen atom from the alkane carbon–hydrogen bond. This mechanism has similarities with the hypothetical platinum "wasp's sting mechanism" described in this paragraph (Figure 21).

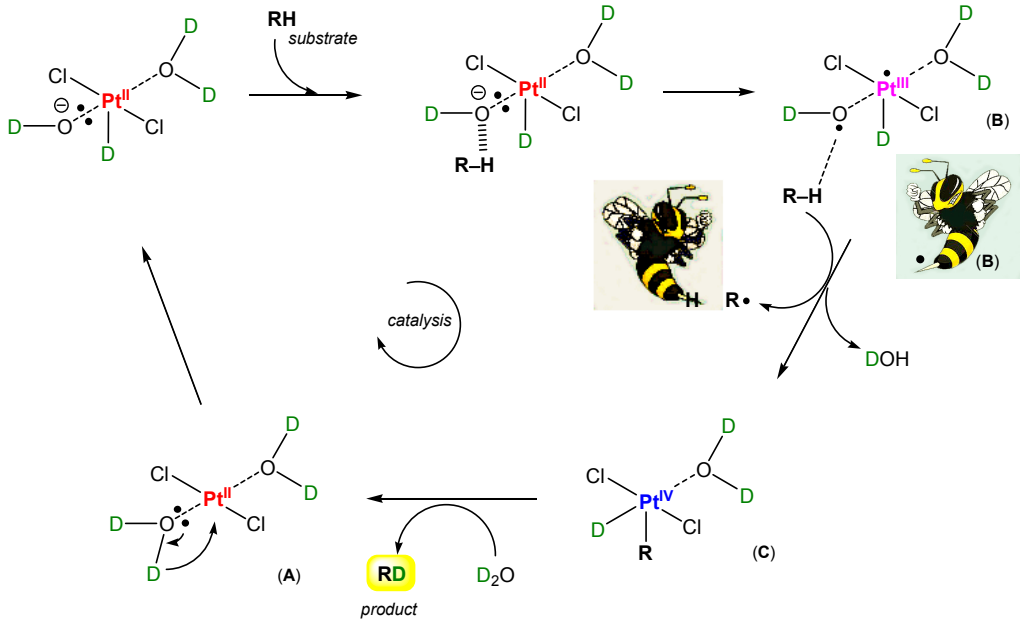
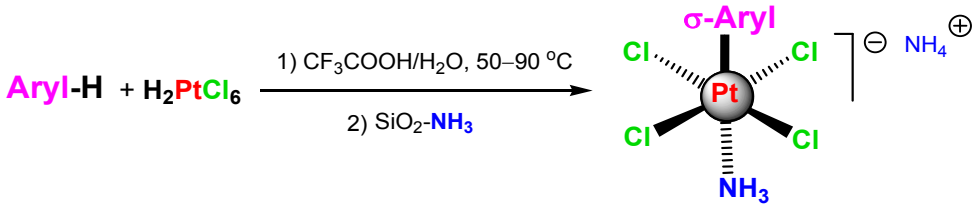


Figure 21. A hypothetical "wasp's sting mechanism" of the first step of Shilov chemistry (interaction between methane and $Pt^{II}Cl_4^{2-}$).

Hexachloroplatinate used originally as the stoichiometric oxidant in alkane reactions is a very expensive reagent and is not convenient to use in the synthesis. The Pt(II)–Pt(IV)–H_2O_2 system used by Thorn and colleagues to hydroxylate *n*-propanol selectively to 1,3-propanediol [293] exhibited very low efficiency: The amount of 1,3-propandiol corresponded to 1.3 turnovers of the entire platinum content (about 0.09 h^{-1}).

Sigma-aryl complexes of platinum(IV) obtained via the electrophilic substitution reaction between H_2PtCl_6 and arenes in CF_3COOH or CH_3COOH (so-called Shul'pin reaction as noted by Matsumoto [294], Sanford [295], and Jones [296]) (Scheme 5) turned out to be more stable than sigma-alkyl complexes and have been isolated in the form stabilized by NH_3 ligands. These complexes were demonstrated to play the role of models of sigma-alkyl platinum complexes generated as

intermediates in the reactions with alkanes [1,287,297–299]. For selected recent original publications on organoplatinum chemistry including carbon–hydrogen bond functionalizations, see [300–304].



Scheme 5. The reaction of H_2PtCl_6 with arenes to afford σ-aryl derivatives of Pt(IV).

5.2. Periana System

Platinum complexes derived from the bidiazine ligand family, discovered by Periana and colleagues [305–307], catalyze oxidation of methane by sulfuric acid to a methanol derivative in >70% one-pass yield based on methane. These complexes are very stable in concentrated sulfuric acid at relatively high temperature and are among the most effective catalysts for methane conversion. A simplified scheme of the catalytic cycle is shown in Figure 22.

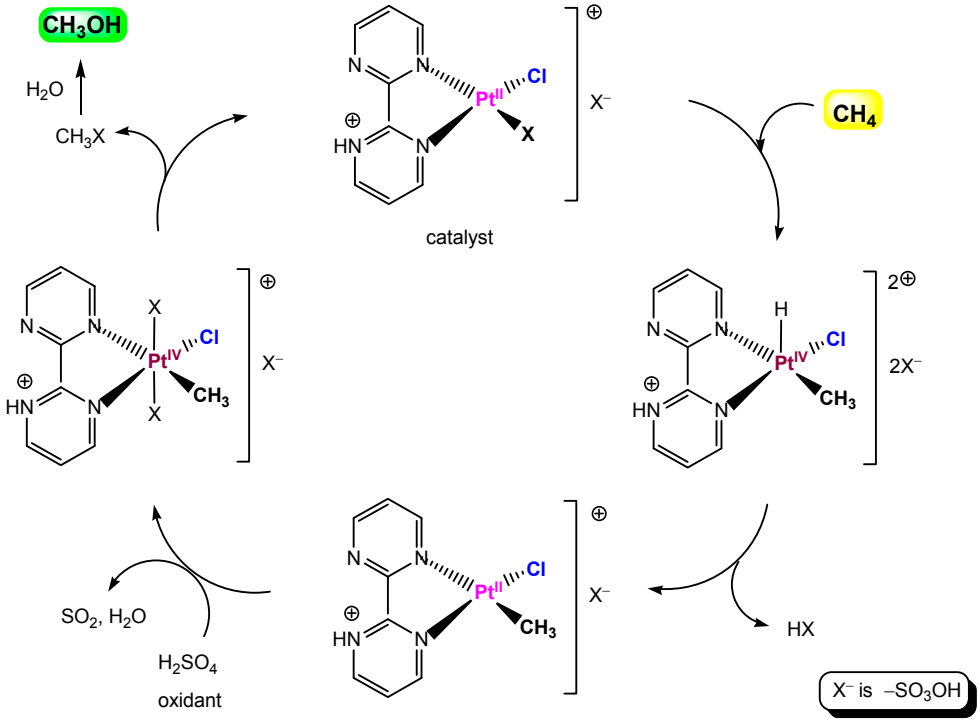


Figure 22. A catalytic cycle for the methane oxidation by Periana system.

5.3. Carboxylation of C–H Compounds (Sen-Fujiwara-Pombeiro Reaction)

In 1992, Sen reported that, in aqueous medium anion-radical $SO_4^{-\bullet}$ (generated from $S_2O_8^{2-}$) abstracts,

> *"a hydrogen atom from methane and ethane to form the corresponding alkyl radicals which could be trapped efficiently by carbon monoxide, the resultant acyl radicals being ultimately converted into the homologous carboxylic acids"* ([308]).

The reaction can be presented by Figure 23.

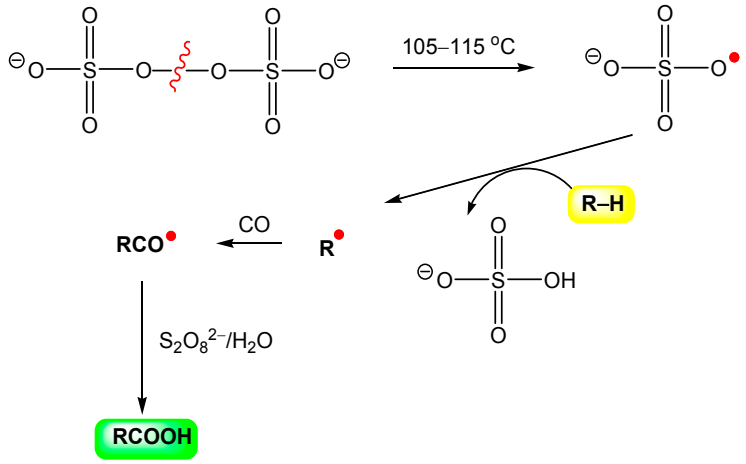


Figure 23. Hydrocarbonylation of alkane, RH, with hexaoxo-μ-peroxodisulfat, $S_2O_8^{2-}$, and CO. Adapted from Ref. [308].

Later, Fujiwara [309–311] and Pombeiro [312–315] demonstrated that this reaction can be sufficiently improved if various catalysts are used. Derivatives of copper, vanadium, and other metals served as catalysts. A simplified scheme of this reaction is shown in Figure 24. A number of works have been published by other authors in recent years [316].

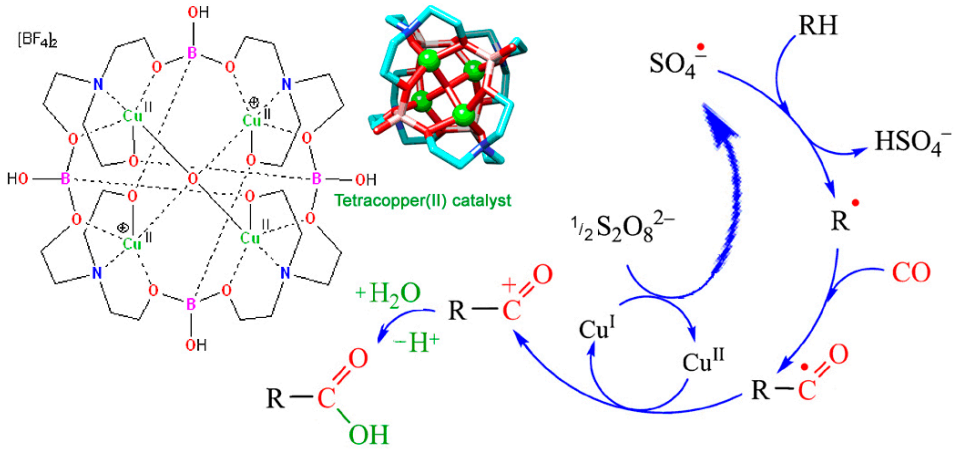


Figure 24. Alkane (RH) carboxylation with $S_2O_8^{2-}$/CO system catalyzed by a copper salt. Adapted from Refer. [313].

6. Outlook

We can see a few routes to further develop the field of metal-catalyzed functionalization of C–H compounds. One of these ways is the search of complexes of as yet unexplored metals. It has been found recently that osmium complexes catalyze the alkane oxidation with huge TONs [144–146,148]. For example, the oxidation of cyclohexane with hydrogen peroxide at 60 °C and low concentration of Os-catalyst (10^{-7} M) gave a turnover number (TON) of 200,000 after 24 h. [146].

Polynuclear metal complexes containing voluminous organic [63,66,118,119,129–131,186,213–218,234–241] or siloxane [221–228] ligands are also very efficient in oxidations of organic compounds including saturated hydrocarbons with peroxides. For example, dinuclear copper complex **11** [221,224] and hexairon complex **15** (for the structure, see Figure 9) affording the products of cyclohexane oxidation in a very high yield of 46% (see Figure 10 [226]) can be considered as "inorganic models of methane monooxygenases." These enzymes contain dinuclear copper [317,318] and iron [319] reaction centers,

respectively. A new method of synthesis of heterometallic coordination compounds by spontaneous self-assembly (SSA) gave complexes which are very efficient catalysts in oxidations with peroxides (turnover frequency TOF was up to 11200 h^{-1} = 3.1 s^{-1}) [160]. This approach modeling natural enzymes can be called biomimetic route. Various polynuclear complexes [320–322] including siloxane derivatives [221–228] containing bulky ligands are especially attractive as catalysts in oxidations with peroxides. Bulky ligands around the reaction centers give rise in these cases to the selectivity enhancement [12,323].

Another route that uses as oxidants dioxygen or even concentrated sulfuric acid [305–308] that require high temperatures seems to be more attractive from the point of view of industrial applications. It is noteworthy that the Periana reaction occurring under severe conditions employs a metal complex catalyst (but not a simple salt). We may hope that new practically useful systems will be discovered in the near future.

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