

Review

Oxidation of Organic Compounds with Peroxides Catalyzed by Polynuclear Metal Compounds

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Abstract: The review describes articles that provide data on the synthesis and study of the properties of catalysts for the oxidation of alkanes, olefins, and alcohols. These catalysts are polynuclear complexes of iron, copper, osmium, nickel, manganese, cobalt, vanadium. Such complexes for example are: $[\text{Fe}_2(\text{HPTB})(\text{m-OH})(\text{NO}_3)_2](\text{NO}_3)_2 \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$, where HPTB- $\frac{1}{4}\text{N}_4\text{N}_0\text{N}_0\text{N}_0$ -tetrakis(2-benzimidazolylmethyl)-2-hydroxo-1,3-diaminopropane; complex $[(\text{PhSiO}_{1.5})_6]_2[\text{CuO}]_4[\text{NaO}_{0.5}]_4[\text{dppmO}_2]_2$, where dppm-1,1-bis(diphenylphosphino)methane; (2,3- η -1,4- diphenylbut-2-en-1,4-dione)undecacarbonyl triangulotriosmium; phenylsilsesquioxane $[(\text{PhSiO}_{1.5})_{10}(\text{CoO})_5(\text{NaOH})]$; bi- and tri-nuclear oxidovanadium(V) complexes $[\{\text{VO}(\text{OEt})(\text{EtOH})\}_2(\text{L}^2)]$ and $[\{\text{VO}(\text{OMe})(\text{H}_2\text{O})\}_3(\text{L}^3)] \cdot 2\text{H}_2\text{O}$ (L^2 = bis(2-hydroxybenzylidene)terephthalohydrazide and L^3 = tris(2-hydroxybenzylidene)benzene-1,3,5-tricarbohydrazide); $[\text{Mn}_2\text{L}_2\text{O}_3][\text{PF}_6]_2$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane). For comparison, articles are introduced describing catalysts for the oxidation of alkanes and alcohols with peroxides, which are simple metal salts or mononuclear metal complexes. In many cases, polynuclear complexes exhibit higher activity compared to mononuclear complexes and exhibit increased regioselectivity, for example, in the oxidation of linear alkanes. The review contains a description of some of the mechanisms of catalytic reactions. Additionally presented are articles comparing the rates of oxidation of solvents and substrates under oxidizing conditions for various catalyst structures, which allows researchers to conclude about the nature of the oxidizing species. This review is focused on recent works, as well as review articles and own original studies of the authors.

Keywords: hydrogen peroxide; alkanes; alcohols; alkyl hydroperoxides; mechanisms of oxidation



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1. Introduction

Hydrocarbons, in particular, saturated hydrocarbons (alkanes) are the main constituents of petroleum and natural gas. These compounds are raw materials for the chemical industry in production of polymers, pharmaceuticals, fragrances, fuels, etc. One of the ways of converting hydrocarbons is catalytic oxygenation with formation of alcohols, ketones, aldehydes, carboxylic acids, and alkyl peroxides. Usually these processes are carried out under severe conditions (high temperature and pressure using heterogeneous catalysts). New catalytic systems for the oxidation of organic compounds with peroxides were described in recent decades (see reviews) [1–13]. Hydrogen peroxide, alkyl peroxides, peroxy acids, Oxone, as well as molecular oxygen were used in these reactions as oxidants. Derivatives of transition metals are widely employed in such reactions. These reactions are carried out under mild conditions (at low temperatures, even at room temperature; atmospheric pressure and often using environmentally friendly solvents such as water and alcohols). Polynuclear complexes are especially interesting catalysts [14,15]. Indeed, these compounds can in many cases exhibit higher catalytic activity in comparison with simple mononuclear complexes and they oxygenate long and branched alkanes with enhanced selectivity [16,17]. Most frequently such reactions proceed with the formation of radical

intermediate species such as hydroxyl radicals [1,2]. A comparison of such catalytic systems for the oxidation of hydrocarbons with simple catalysts—mononuclear complexes or metal salts, is interesting, because the comparison can shed light on the features of oxidation mechanisms.

2. Oxidations Catalyzed by Soluble Polynuclear Compounds

This Chapter describes oxidation of organic compounds with peroxides catalyzed by di- and polynuclear metal complexes and (as comparison) by some mononuclear complexes of transition metals. Polynuclear complexes are of particular interest both from a practical and an academic point of view, since such compounds can have increased catalytic activity and exhibit unique selectivity in the oxidation of organic compounds, in particular, alkanes.

2.1. Oxidation Catalyzed by Iron Complexes

Iron ions have been known for a long time as initiators and catalysts for the decomposition of hydrogen peroxide [1,18]. Thus, the reaction of H_2O_2 with Fe^{+2} gives hydroxyl radicals and Fe^{+3} (stoichiometric Fenton reaction). The interaction of Fe^{+3} with H_2O_2 causes formation of hydroxyl radicals and Fe^{+2} . The resulting Fe^{+2} ion is further involved into a catalytic cycle of generating hydroxyl radicals with an intermediate participation of the Fenton reaction. Hydroxyl radicals attack organic compounds, for example, with the abstraction of a hydrogen atom. The abstraction of a hydrogen atom from a saturated hydrocarbon (RH) gives rise to an unstable alkyl radical ($\text{R}\bullet$). The latter attaches an O_2 molecule from atmosphere, ultimately forming a relatively stable alkyl hydroperoxide (ROOH) [1].

The formation of alkyl hydroperoxide in the reaction of the binuclear complex **1** $[\text{Fe}_2(\text{HPTB})(\mu\text{-OH})(\text{NO}_3)_2](\text{NO}_3)_2 \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ [HPTB = *N,N,N',N'*-tetrakis(2-benzimidazolylmethyl)-2-hydroxo-1,3-diaminopropane] [19] containing the 1,4,7-triazacyclononane ligand turned out to be almost inactive as a catalyst in the cyclohexane oxidation with H_2O_2 at room temperature. However, the addition of a comparatively small amount of 2-pyrazinecarboxylic acid (PCA), to the reaction solution causes intense alkane oxidation (Figure 1) to form cyclohexyl hydroperoxide which decomposes during the reaction to produce the corresponding cyclohexanone and cyclohexanol. Total turnover number (TON) attained was 240 after 24 h. In kinetic measurements the authors determined only the concentrations of the ketone and the alcohol after the reduction with triphenylphosphine. The iron (III) complex **1** was used as catalyst.

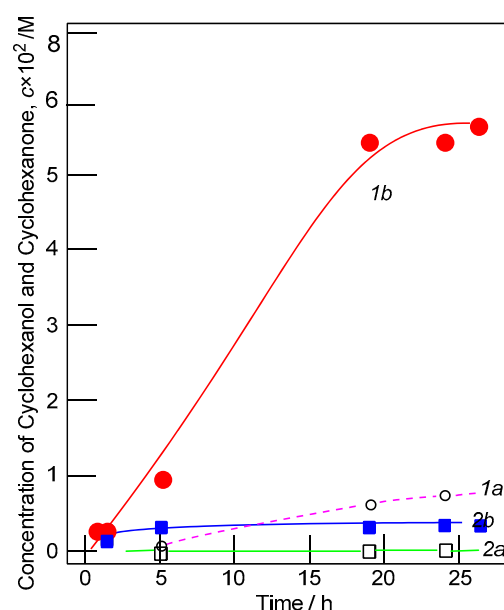


Figure 1. Compound **1** in the absence (curves a) and in the presence of PCA; (curves b) in MeCN at 25 °C. catalyzed the oxidation of cyclohexane by H_2O_2 (0.59 M). Accumulation of cyclohexanol (curves 1b) and cyclohexanone (curves 2b) (concentrations were measured after the reduction with PPh_3 , used method by Shul'pin, which is in comparison with the concentrations of alcohol and ketone in solution samples before and after adding PPh_3) are shown. The data are adapted from [19], Copyright (2004) with permission of Wiley.

Another binuclear iron complex **2** [20] also requires the presence of 2-pyrazinecarboxylic acid (PCA) for the oxidation of alkanes. The accumulation of products during oxidation with hydrogen peroxide catalyzed by complex **2** is shown in Figure 2. As you can see, 2-pyrazinic acid has a dramatic effect on the reaction rate and product yield. As can be seen in the Figure 2, other acids are much less effective in accelerating the reaction compared to 2-pyrazinecarboxylic acid.

In works [21–36] other polynuclear iron complexes have been described. The oxidation of cyclohexane by H_2O_2 and *tert*-butyl hydroperoxide under catalysis by binuclear iron complexes $[(\text{SO}_4)(\text{L})\text{Fe}(\mu\text{-O})\text{Fe}(\text{L})(\text{SO}_4)] \cdot 6\text{H}_2\text{O}$, **3**, and $[\text{Cl}(\text{L})\text{Fe}(\mu\text{-O})\text{Fe}(\text{L})\text{Cl}]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, **4**; 1-(bis-pyridin-2-ylmethylamino)-3-chloropropan-2-ol (L) have been described [21]. The electrochemical analysis showed that the dinuclear species is more stable under reduction in compound **3** than in compound **4**. It was found that compound **4** is more active than compound **3** in oxidation cyclohexane with hydrogen peroxide in acetonitrile at 50 degrees.

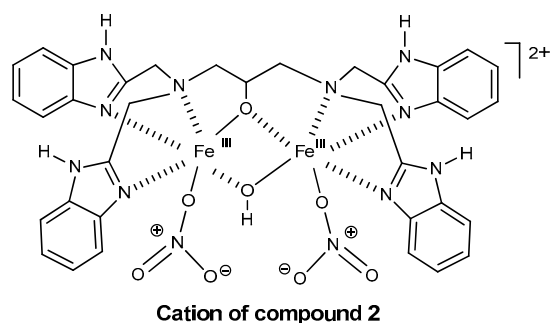


Figure 2. Cont.

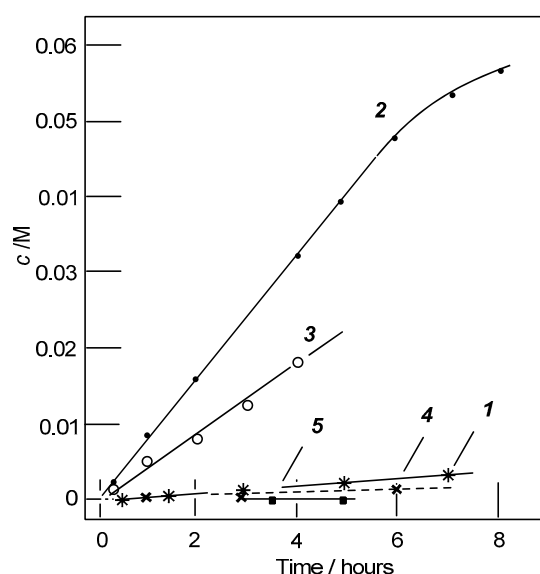


Figure 2. Accumulation of sum of oxygenates (predominantly cyclohexyl hydroperoxide) in the reaction of cyclohexane with hydrogen peroxide (in acetonitrile at 25 °C catalysed by complex 2 in the absence of additives (curve 1) and in the presence of aminoacids: PCA (2), pyrazine-2,3-dicarboxylic acid (3), picolinic acid (4), and pyridine-2,6-dicarboxylic acid (5). Adapted from [20] Copyright (2002), with permission of Elsevier.

Oxidation of alkanes with *m*-chloroperoxybenzoic acid catalyzed by binuclear iron complexes non-heme μ -oxo-bridged diiron(III) complexes $[\text{Fe}_2(\mu\text{-O})(\text{L}_1)_2]$, where $\text{H}_2(\text{L}_1)$ is *N,N'*-*o*-phenylenebis(salicylideneimine), $[\text{Fe}_2(\mu\text{-O})(\text{L}_2)_2] \cdot 2\text{H}_2\text{O}$, where $\text{H}_2(\text{L}_2)$ is *N,N'*-*o*-phenylenebis(3,5-di-*tert*-butylsalicylideneimine), and $[\text{Fe}_2(\mu\text{-O})(\text{L}_3)_2]$, where $\text{H}_2(\text{L}_3) = 1,4\text{-bis}(2\text{-hydroxybenzyl})\text{-}1,4\text{-diazepane}$, occurs with the intermediate formation of the complex $[\text{Fe}_2(\text{O})(\text{L}_2)_2(\text{OOR})]$ and leads mainly to the formation of alcohols and a small amount of ketones [22].

Remarkable results were obtained in the oxidations of alkanes by hydrogen peroxide catalyzed by N-bridged diiron phthalocyanine complex $((\text{FePc tBu}_4)_2\text{N})$ [23], especially very inert methane and ethane. Reactions were performed in MeCN. Formic acid was the main product of the oxidation of methane. Kinetic analysis showed that the ratio of the rates of oxidation of acetonitrile and methane is incompatible with the concept of the participation of the hydroxyl radical in this process. Water was also investigated in this reaction as a solvent. *m*-nitrido complex was supported onto silica. Heterogeneous oxidations of CH_4 were performed in pure H_2O . In this case, the following mechanism was tentatively proposed. In the first stage, $(\text{FePcBu}_4)_2\text{N}$ coordinates H_2O_2 to form hydroperoxo complex $\text{Fe}^{\text{IV}}\text{NFe}^{\text{III}}\text{OOH}$ which is probably in equilibrium with the deprotonated form $\text{Fe}^{\text{IV}}\text{NFe}^{\text{III}}\text{OO}^-$. The heterolytic cleavage of the O–O bond in $\text{Fe}^{\text{IV}}\text{NFe}^{\text{III}}\text{OOH}$ complex and the formation of very strong oxidizing $\text{Fe}^{\text{IV}}\text{NFe}^{\text{V}}=\text{O}$ species was favored in the presence of acid by the protonation of peroxide oxygen.

μ -nitrido diiron phthalocyanine activates H_2O_2 to oxidize CH_4 in water at 25–60 °C to methanol, formaldehyde and formic acid as evidenced. The similar binuclear porphyrin iron complex was also used in the oxidation of methane with *m*-chloroperoxybenzoic acid [24]. It is assumed that oxidation with binuclear complex proceeds with the intermediate formation N-bridged high-valent diiron–oxo species.

The diiron–oxo complex demonstrated significantly stronger oxidizing properties than similar mononuclear complex $[(\text{TMP}^+\text{p})\text{Fe}(\text{IV})(\text{O})]\text{p}$ (TMP 1/4tetramesitylporphyrin) [25].

It is not uninteresting to note that iron mononuclear complex $[\text{FeII}(\text{Me}_3\text{NTB})(\text{CH}_3\text{CN})](\text{CF}_3\text{SO}_3)_2$, ($\text{Me}_3\text{NTB} = \text{tris}(\text{N-methylbenzimidazol-2-ylmethyl})\text{amine}$), exhibits a rather high activity in the oxidation of cyclohexane [26]. It cannot be ruled out that the mononuclear complex in solution forms polynuclear particles that are involved in the oxidation of

alkane. Other compounds appearing on the oxidation of organic compounds with peroxides catalyzed by polynuclear iron derivatives have been also published in works [27–36].

In recent years, polynuclear silsesquioxane complexes of iron have been synthesized and their catalytic activity in the oxidation of alkanes and alcohols with peroxides and oxygen has been investigated [37–40]. Such complexes are usually highly active and contribute to the formation of oxidation products in high yields at low temperatures and atmospheric pressure. Examples of structures of such complexes are presented in Figure 3.

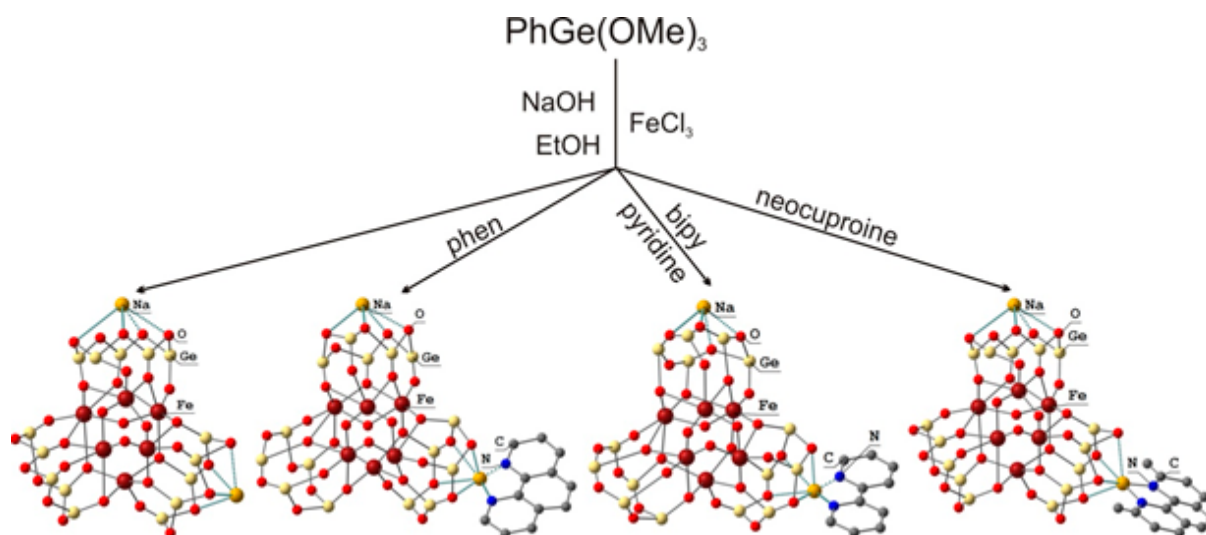


Figure 3. All structures adapted from Ref. [40], Copyright (2016) with permissions of Wiley.

As mentioned above, mononuclear iron derivatives are often less active in alkane oxidation reactions, which proceed according to Fenton-like mechanism involving hydroxyl radicals [41–59].

2.2. Oxidation Catalyzed by Copper Complexes

The large number of works are devoted to catalysts containing copper. Usually these complexes contain N-ligands [60–88]. Formulae and structures of some of the catalysts used in the reactions are shown in Figures 4–9.

Complex 5 (Figure 4) [63] efficiently catalyzes the oxygenation of alkanes with *tert*-butyl hydroperoxide (TBHP) in acetonitrile solution under relatively mild conditions (temperature 50–70 °C, under normal pressure of air). Concentrations of the final products (alcohols and ketones) in the oxidation of cyclohexane gives after 8.5 h cyclohexanol and cyclohexanone in 17% yield (after addition of PPh_3), and the turnover number (TON) attains 800. Complex 6 does not exhibit catalytic activity in the oxidation of alkanes with TBHP, which can be associated with its relatively rapid decomposition or transformation into a catalytically inactive species under the reaction conditions. It should be noted that the oxidation of alcohols with TBHP is effectively catalyzed by both complexes 5 and 6. In the case of the cyclohexanol oxidation the maximum values of TON and yield of cyclohexanone attained 820 and 78%, respectively. However, in oxidation of alcohol the activity of compound 6 is a bit less than activity of compound 5. Both compounds 5 and 6 catalyze the hydrocarboxylation of cycloalkanes to the corresponding cycloalkanecarboxylic acids. In all cases, catalyst 6 shows a slightly higher activity over the dicopper (II) complex 6.

Dinuclear $[\text{Cu}_2(1\kappa\text{NO}^2:2\kappa\text{N}'\text{O}'^2\text{-H}_2\text{L})(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ (7) (Figure 5) and the tetranuclear $[\text{Cu}_4(\mu\text{-}1\kappa\text{NO}^2:2\kappa\text{N}'\text{O}'^2\text{-H}_2\text{L})_2(\mu\text{-NO}_3)_2(\text{H}_2\text{O})_4]\cdot 2\text{C}_2\text{H}_5\text{OH}$ (8) (Figure 6) complexes were used as catalysts for oxidation of alcohols and alkanes [66]. The catalytic activity of both 7 and 8 has been screened toward the solvent-free microwave-assisted oxidation of alcohols and the peroxidative oxidation of alkanes under mild conditions. Complex 7 (Figure 5) exhibits the highest activity for both oxidation reactions, leading selectively to a maximum

product yield of 99% (for the 1-phenylethanol oxidation after 1 h without any additive) and 13% (for the cyclohexane oxidation to cyclohexyl hydroperoxide, cyclohexanol, and cyclohexanone after 3 h).

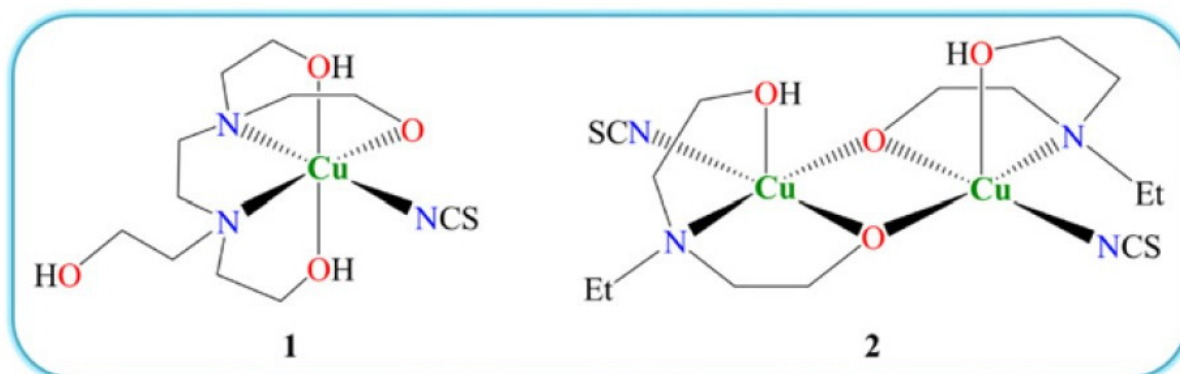


Figure 4. Formulae Complex 5 (left) and 6 (right), which have been used in oxidations with peroxides adapted from Ref. [64], Copyright (2011) with permission of Elsevier.

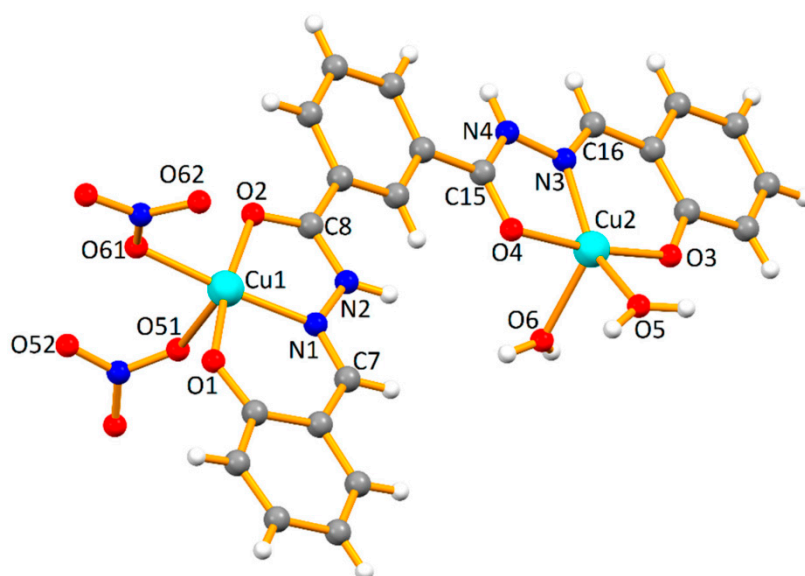


Figure 5. Complex 7 Adapted from Ref. [67], Copyright (2018), Molecules (MDPI), Open Access.

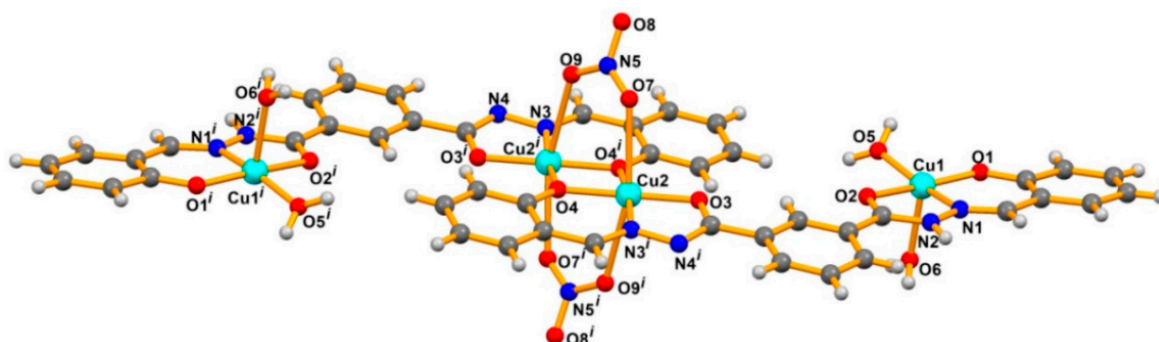


Figure 6. Complex 8 Adapted from Ref. [67], Copyright (2018), Molecules (MDPI).

The catalytic activity of a hexanuclear Cu(II) complex $[\text{Cu}_3(\mu_2\text{-}1\text{kNO}^2, 2\text{kNO}^2\text{-L})(\mu\text{-Cl})_2(\text{Cl})(\text{MeOH})(\text{DMF})_2]_2$ (Figure 7) for the microwave-assisted neat oxidation of alcohols was explored. This Cu (II) complex was found to exhibit high activity under milder

reaction conditions of oxidation of 1-Phenylethanol by *tert*-butyl hydroperoxide. Yield 95% of acetophenone in the presence of catalyst was found [70].

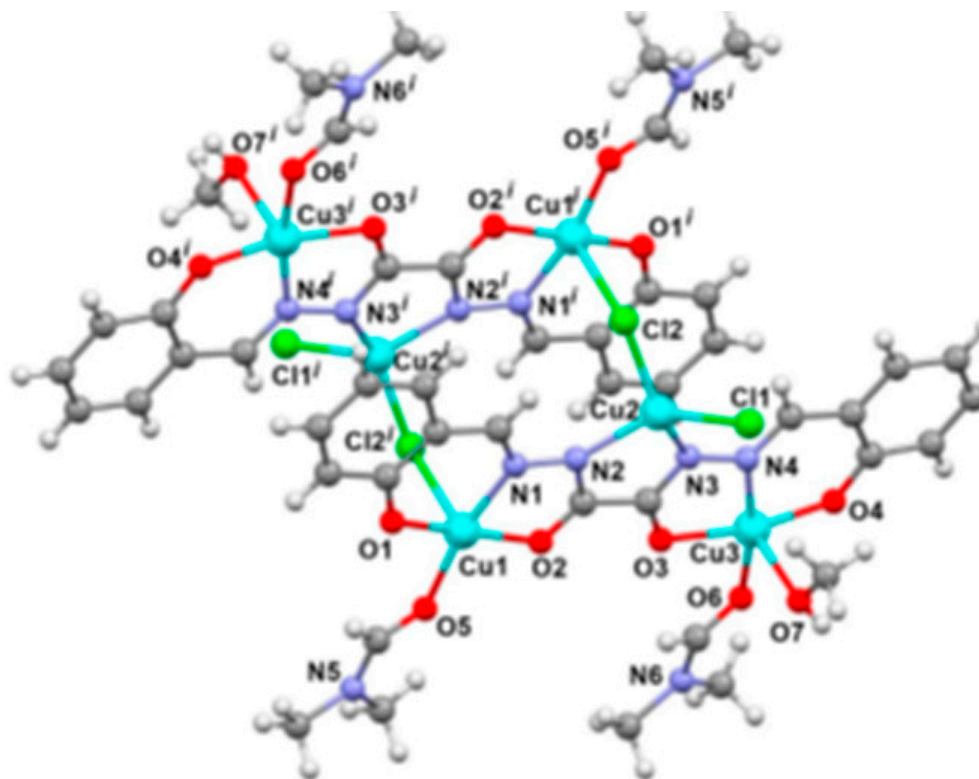


Figure 7. Complex tested in oxidations with peroxides adapted from Ref. [70], Copyright (2020), *Int. J. Mol. Sci.* (MDPI), Open Access.

The copper complexes shown in Figure 8 [72] were tested in catalytic oxidation. It should be noted that in the case of binuclear complex **15** (Figure 10), the initial rate of accumulation of oxidation products is higher than for complex **9** (Figure 9), however, the maximum product yield is somewhat lower than in catalysis with mononuclear complex **9**. The authors proposed the following explanation for this fact. This phenomenon is probably due to a higher rate of interaction of **15** with the resulting hydroperoxide in comparison with the situation found for the complex **9** or the dimeric complex **15** effectively decomposes hydrogen peroxide via a catalase pathway that is not associated with the generation of intermediate species of an oxidizing nature, and therefore the yield of oxidizing species decreases. The lowest activity was found for compound **17** (see Figure 11), in which the copper ion is strongly screened by methyl groups in the ligand.

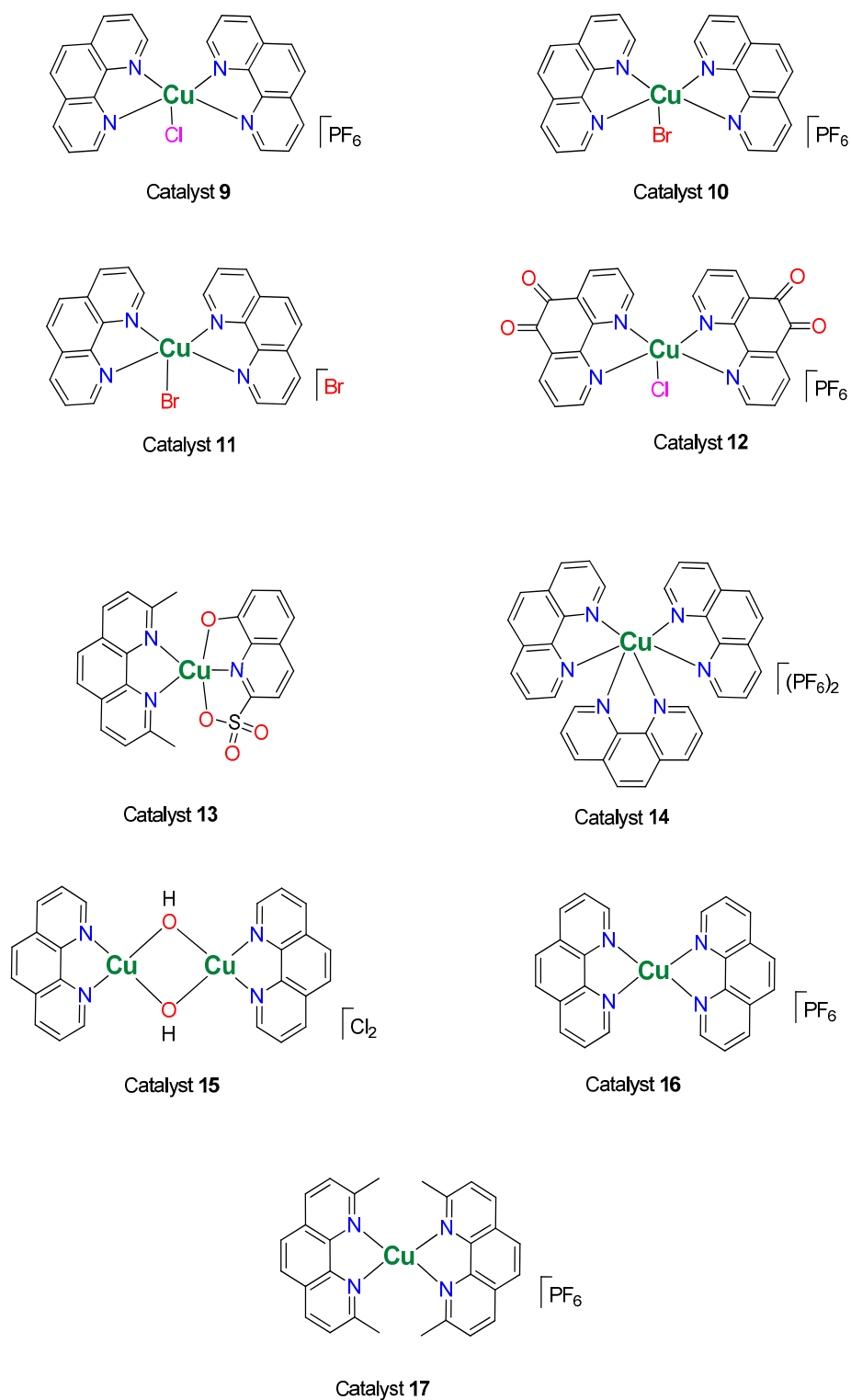


Figure 8. Complexes studied as catalysts, adapted from Ref. [72], Copyright (2020) with permission of Elsevier.

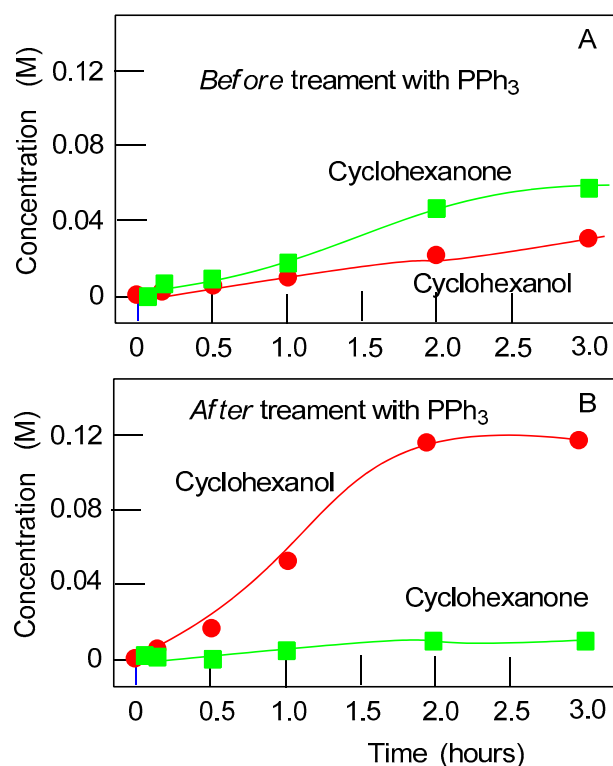


Figure 9. Oxidation of cyclohexane with hydrogen peroxide (50% aqueous) catalyzed by compound **9** in MeCN at 50 °C (Graphs (A,B)); total volume of the reaction solution was 5 mL. Concentrations of cyclohexanone and cyclohexanol were determined before (Graph A) and after (Graphs B) reduction of the aliquots with solid PPh₃. Total yield of products 27% after 2 h, TON = 250 at 50 °C and 30% after 1 h, TON = 280 at 60 °C. adapted from [72], Copyright (2020) with permission of Elsevier.

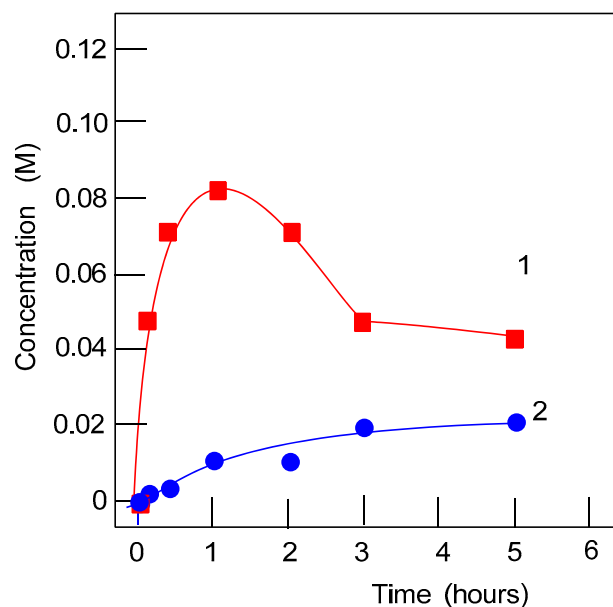


Figure 10. Oxidation of cyclohexane with hydrogen peroxide (50% aqueous;) catalyzed by compound **15** in MeCN at 60 °C. Concentrations of cyclohexanone and cyclohexanol were after reduction of the aliquots with solid PPh₃. Points for cyclohexanol (red) and cyclohexanone (blue) are marked by numbers 1 and 2, respectively. Total yield of products 20% after 1 h, TON = 180. Adapted from [72], Copyright (2020) with permission of Elsevier.

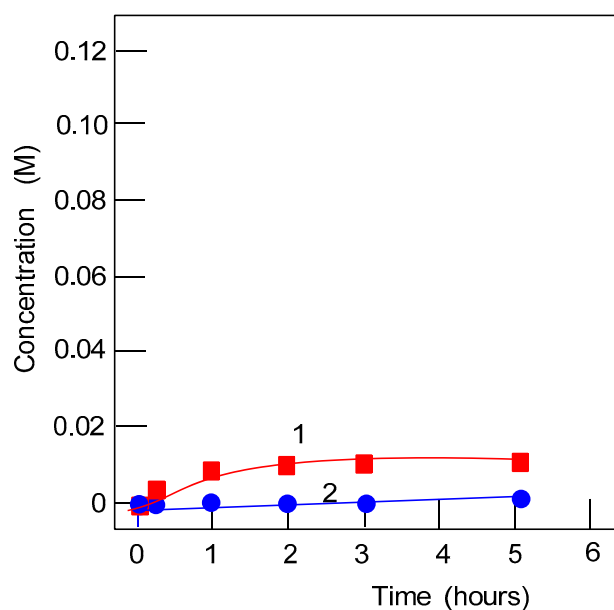
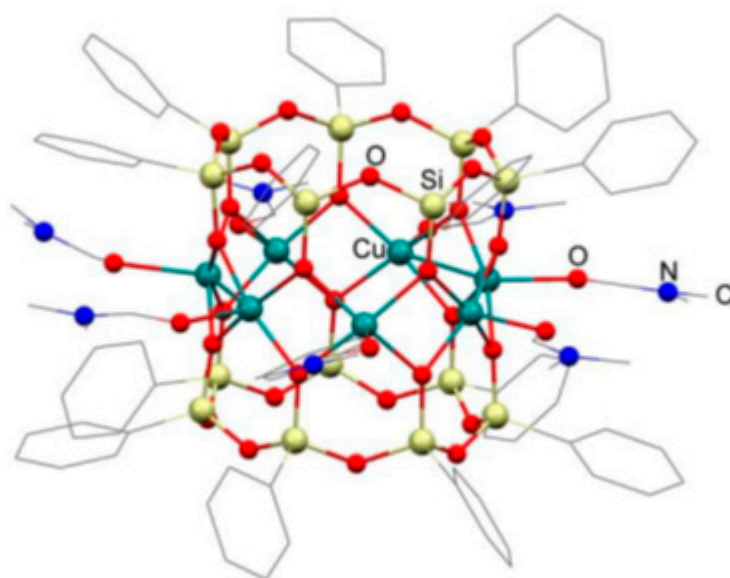


Figure 11. Oxidation of cyclohexane with hydrogen peroxide (50% aqueous) catalyzed by compound **17** in MeCN at 60 °C; Concentrations of cyclohexanone and cyclohexanol were after reduction of the aliquots with solid PPh_3 . Points for cyclohexanol (red) and cyclohexanone (blue) are marked by numbers 1 and 2, respectively. Total yield of products 2.5% after 2 h, TON = 22. Adapted from Ref. [72], Copyright (2020) with permission of Elsevier.

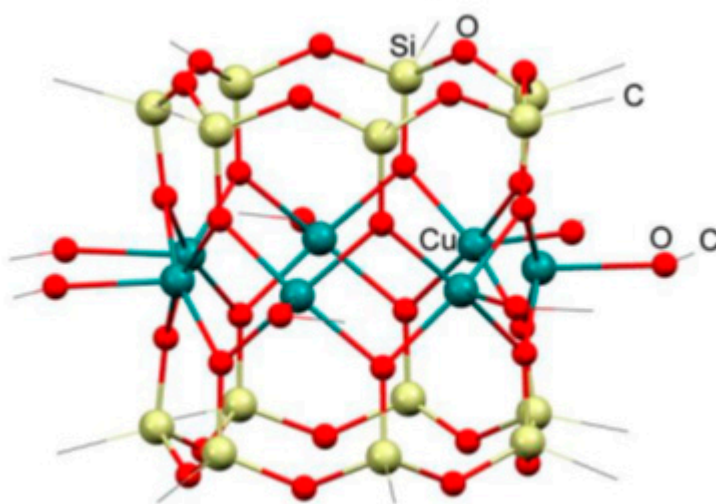
As in the case of iron ions, a large number of works have been devoted to silsesquioxane complexes with copper and their use in catalytic oxidation [73–88]. A few structures of the catalysts used in the most recent years are shown in Figures 12–15.

First examples of heptanuclear cage silsesquioxanes, $(\text{PhSiO}_{1.5})_{14}(\text{CuO})_7$ **18** and $(\text{MeSiO}_{1.5})_{14}(\text{CuO})_7$ **19**, were obtained [81]. It should be noted that in Ref. [81] (Figure 12), the complexes **18** and **19** used in the catalysis of alkane oxidation exhibited somewhat different activity. Compound **18** gave a higher yield of oxidation products. Product accumulation curves are shown in Figure 13. The maximum observed in the Figure 13B and the decrease in the alcohol yield can be explained by the over-oxidation of alcohol with the formation of unidentifiable oxidation products. It is important that the oxidation requires the presence of nitric acid. Under conditions of the experiment shown in Figure 13 the yield of oxygenates was 39%. This is a high value taking into account the pronounced inertness of alkanes. The oxidation of n-heptane allowed to measure the regioselectivity parameters for positions 1, 2, 3 and 4: C (1): C (2): C (3): C (4) = 1.0: 6.0: 6.0: 5.5. This data also indicates that the reaction proceeds with the participation of free hydroxyl radicals generated from hydrogen peroxide. However, these parameters are higher than those usually observed in oxidation with hydroxyl radicals (1: 2: 2: 2). Such an increase in regioselectivity can be explained by the fact that oxidation in the case of complex **18** occurs in the cavities formed by bulky ligands surrounding the reaction centers of the catalyst molecule.

Complex **20** [82] (see Figure 14) was found to be a good catalyst in oxidations of alcohols and alkanes with TBHP and H_2O_2 , respectively. 1-Phenylethanol and heptanol-2 could be converted into corresponding ketones in yields up to 94% and 50%, respectively. Hydroperoxidation of alkanes by H_2O_2 was found when complex **20** is used as a catalyst. Cyclohexane has been converted into cyclohexyl hydroperoxide which was gradually transformed in a mixture of cyclohexanol and cyclohexanone over the course of the oxidation.



Complex 18



Complex 19

Figure 12. Molecular structures of **18** and **19**. Color code: Si—yellow, O—red, Cu—green, N—blue, adapted from [81] Copyright (2018) with permission from Wiley.

Not only silsesquioxane complexes, but germesquioxanes, which are precatalysts in the oxidation of organic compounds, were obtained and described [86–88]. An example of structure of such catalysts is given in Figure 15. Germanium-based sesquioxane copper complex exhibits an extremely high nuclearity ($\text{Cu}_{42}\text{Ge}_{24}\text{Na}_4$) and unusual encapsulation features. This compound is a very active catalyst in the oxidation of alkanes and alcohols [87].

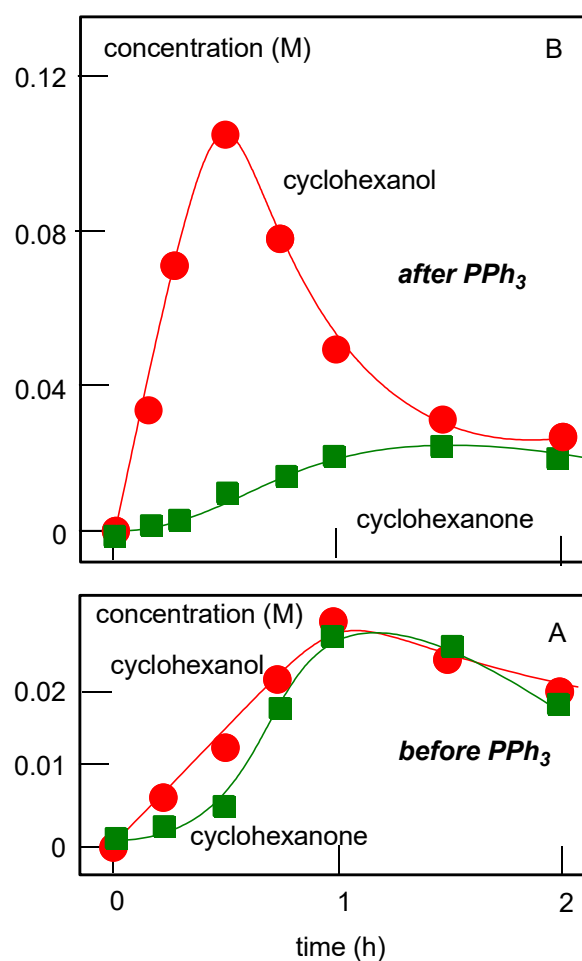


Figure 13. Oxidation of cyclohexane with H₂O₂ (50%) catalyzed by complex 18 at 60 °C. Concentrations of cyclohexanol and cyclohexanone were measured both before (A) and after reduction (B) with PPh₃ (used method of Shul'pin). Adapted from [81], Copyright (2018) with permission of Wiley.

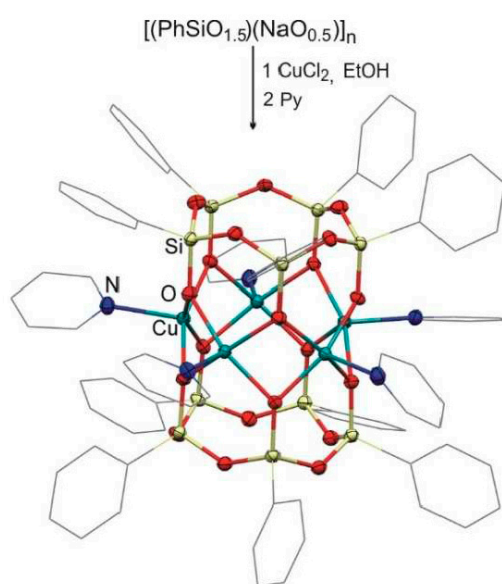


Figure 14. Scheme synthesis Complex 20 used in oxidation alkanes with peroxides is presented on this figure, adapted from Ref. [82], Copyright (2018) with permission of Elsevier.

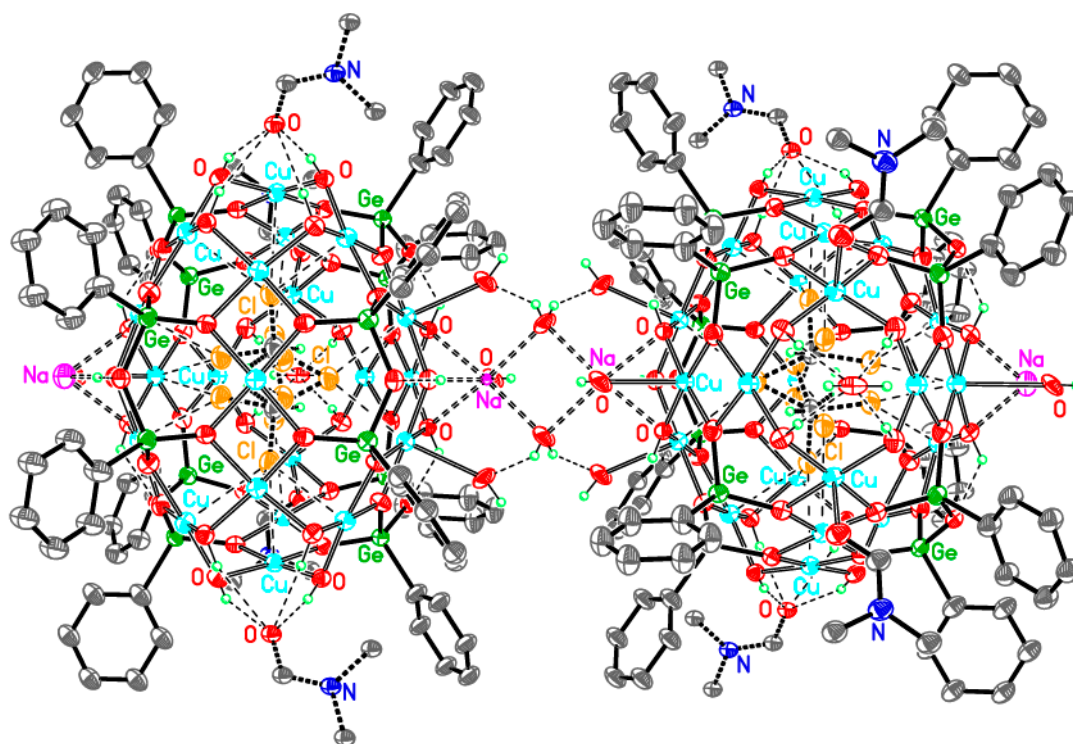


Figure 15. The copper complex with germesquioxane surroundings. Adapted from Ref. [87], Copyright (2018), Catalysts, MDPI.

A recent publication [89] described the synthesis and catalytic properties of complex **21** (see Figure 16). The kinetic study allowed authors to propose the mechanism of the oxidation reaction of alkanes and alcohols with hydrogen peroxide and *tert*-butyl hydroperoxide. Complex **21** exhibited high catalytic activity in the oxidation of cyclohexane and other alkanes with H_2O_2 in acetonitrile in the presence of nitric acid. The following selectivity parameters were obtained for the oxidation of *n*-heptane: $\text{C}(1):\text{C}(2):\text{C}(3):\text{C}(4) = 1.0:5.6:5.6:5.0$. These data as well as the character of dependence of the initial cyclohexane oxidation rate on the initial hydrocarbon concentration (approaching a plateau at $[\text{cyclohexane}]_0 > 0.3 \text{ M}$) (see Figure 17) indicate that the reaction occurs with the participation of hydroxyl radicals and alkyl hydroperoxides are formed as the main primary products. However, the regioselectivity in the oxidation of *n*-heptane (see above) is noticeably higher than the regioselectivity usually observed for oxidation with hydroxyl radicals (1: 2: 2: 2). The increased regioselectivity in the case of catalysis by complex **21** can be explained by the fact that steric hindrances arise in the molecule of this complex around the copper-containing reaction center. Previously, for most of the catalytic systems studied, based on the data on the selectivity of alkane oxidation, it was concluded that the oxidizing species is a hydroxyl radical. This conclusion has received kinetic confirmation see Ref. [20]. On the one hand, the calculated ratio of the constants of the rates of reactions of the interaction of an oxidizing species with acetonitrile and cyclohexane k_2/k_3 is much higher than for the reactions ratio characterized the reactions involving hydroxyl radicals [20,86]. The obtained value ($k_2/k_3 = 0.033$) is very different from the 0.006–0.01.

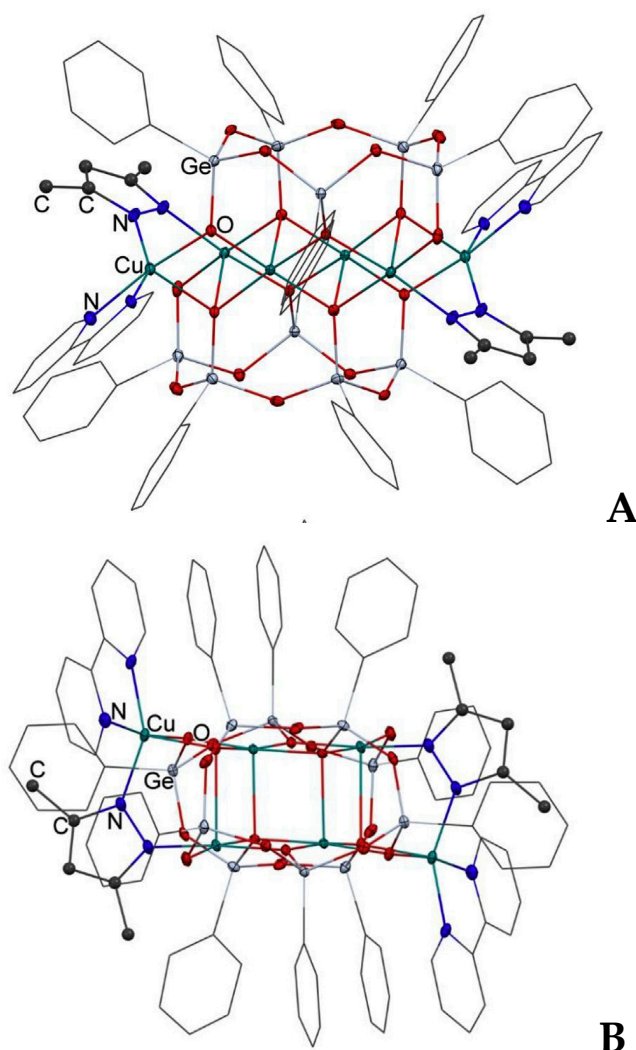


Figure 16. Molecular structure of complex **21**. (A): side view. (B): top. View. Color code: Ge: grey, O: red, Cu: green, N: blue. Adapted from [89], Copyright (2019) with permission of Elsevier.

On the other hand, the low selectivity of the effect of oxidizing species ($Z = \text{HO}\bullet$) is close to the selectivity found for reactions involving hydroxyl radicals, indicates that hydroxyl radicals are generated in the catalytic system studied in the work [89]. Similar results (a decrease in the relative reactivity of the oxidizing species for cyclohexane in comparison with acetonitrile) were obtained earlier [86]. Thus, based on the kinetic data and selectivity parameters in alkane oxidation, authors came to different conclusions about the nature of the oxidizing species in the **21**/ H_2O_2 catalytic system. This contradiction can be resolved if it is assumed that the concentrations of acetonitrile and cyclohexane near the reaction center (that is, at the place where the oxidizing species originated) differ from their concentrations in the volume. In this model, the results obtained indicate that the ratio of acetonitrile and cyclohexane concentrations inside the cluster of the catalytic species (near the reaction center) exceeds their ratio in volume. Such a difference may occur due to a higher concentration of acetonitrile and hydrogen peroxide inside a cavity in the catalyst cage.

As can be seen from the above, polynuclear copper complexes have great potential as catalysts in the oxidation of alkanes and alcohols. For comparison, we present several references to articles devoted to mononuclear copper complexes in oxidative catalysis [90–96]. These works investigated mononuclear complexes that exhibit significant activity.

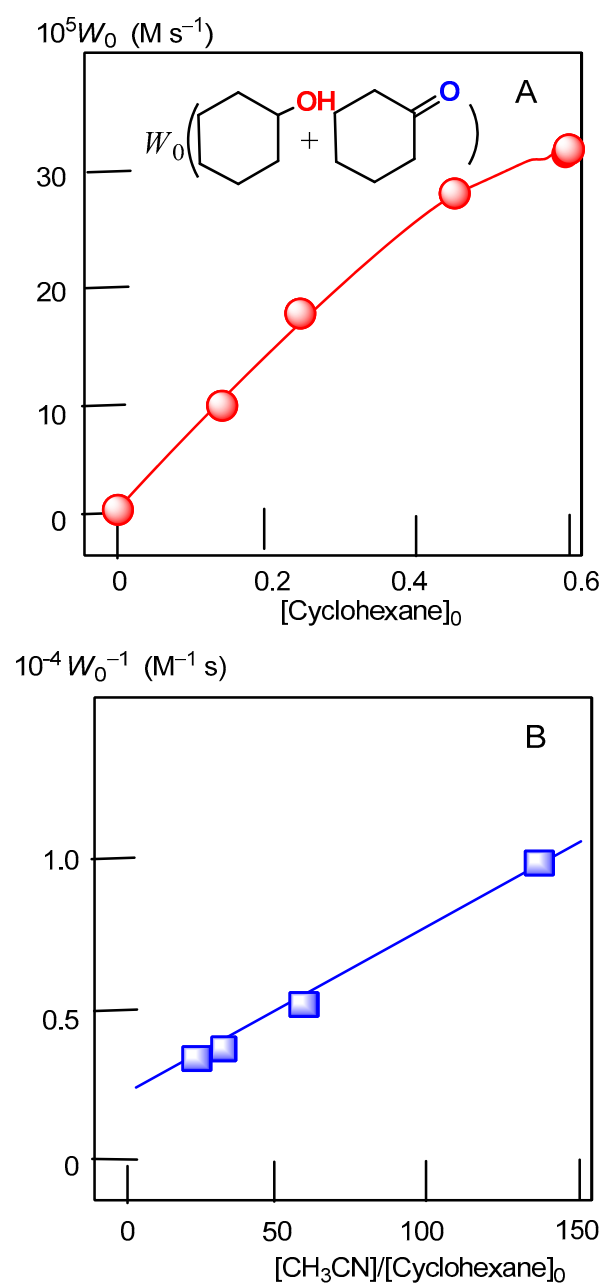


Figure 17. Cont.

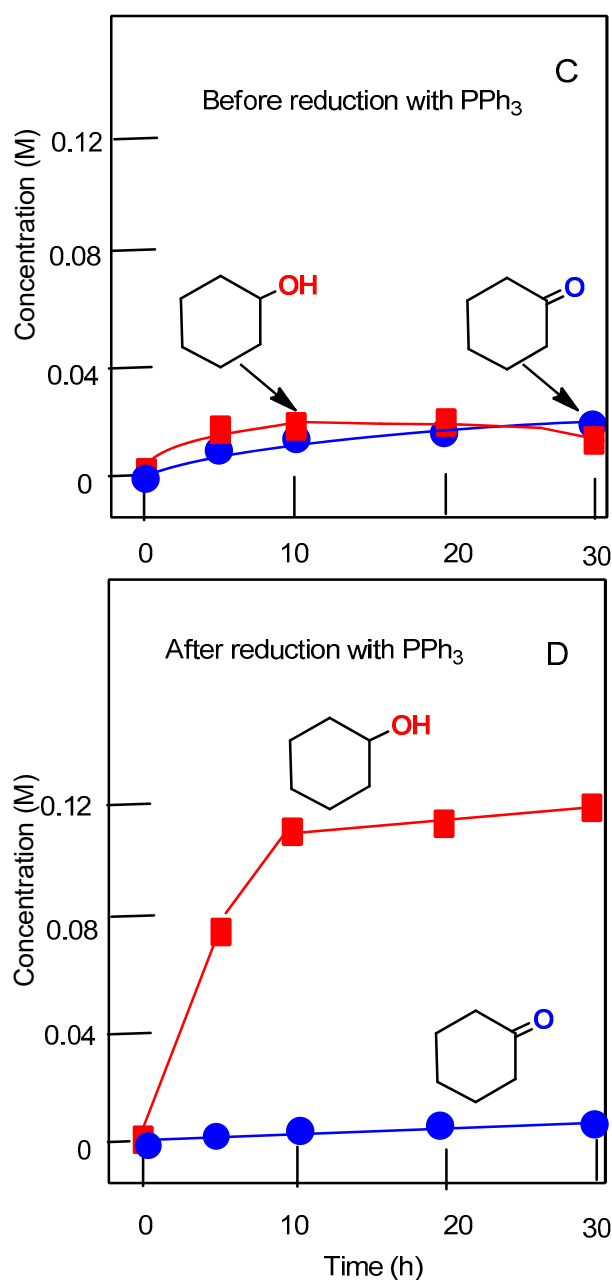
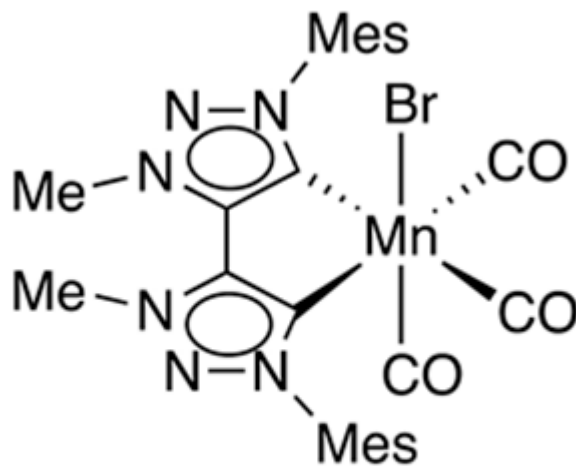


Figure 17. Accumulation of cyclohexanol and cyclohexanone in oxidation of cyclohexane with hydrogen peroxide catalyzed by compound **21** in MeCN at 50 °C. Dependence of the initial rate of oxygenate formation W_0 on initial concentration of cyclohexane is shown in graph (A). Linearization of curve from graph (A) in coordinates $W_0^{-1} - [\text{CH}_3\text{CN}]/[\text{C}_6\text{H}_{12}]$ is presented in graph (B). Concentrations of cyclohexanone and cyclohexanol were determined after reduction of the aliquots with solid PPh₃. Accumulation of cyclohexanol and cyclohexanone (under conditions given above) is shown when their concentrations were measured before (graph (C)) and after treating the reaction sample with PPh₃ (graph (D)). Adapted from [89], Copyright (2019) with permission of Elsevier.

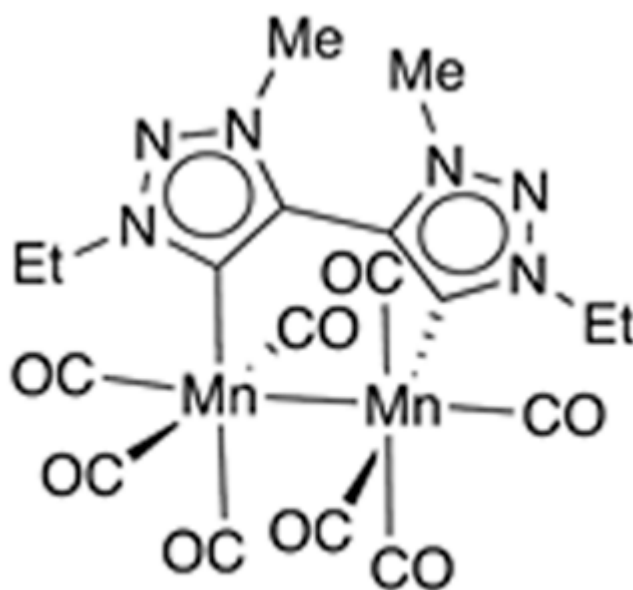
2.3. Polymanganese Complexes in Oxidations with H₂O₂

Manganese complexes are active in the oxidation of hydrocarbons and alcohols [97–120]. Carbonyl manganese complexes with chelating or bridging mesoionic di(1,2,3-triazolyldiene) ligands were synthesized and characterized of a bimetallic manganese(0) complex **23** [99]. (Figure 18). This complex exhibited high activity (yields up to 99%) and selectivity in the catalytic oxidation of secondary alcohols and benzyl alcohol with *tert*-butyl hydroperoxide). Comparison of the mono- and bimanganese complexes

22 and **23** showed that the binuclear complex is more active in the oxidation of spites by *tert*-butyl hydroperoxide. The yield of acetophenone in the reaction with complex **23** attained 99% at 40 °C after 2 h. A similar yield was obtained by carrying out the reaction without solvent.



Complex 22



Complex 23

Figure 18. Carbonyl manganese compounds as a catalysts in oxidation with peroxides, Adapted from Ref. [99] Copyright (2019) with permission from Royal Society of Chemistry.

In 1998, the effective catalytic action of the binuclear manganese (IV) complex **24** (Figure 19) was described in the oxidation of organic compounds with hydrogen peroxide in acetonitrile at low temperatures [100,101]. This system works efficiently only in the presence of an added organic acid. This acid was acetic acid, and later it was found that oxalic acid is even more effective [112–117]. Thus, for example, the system complex **24**/oxalic acid/H₂O₂/O₂ gives products in oxidation cyclohexane with yield up to 50% (TON = 2700) [115]. Other organic acids also accelerate the oxidation reaction [102–120].

The work [109] on the oxidation of organic compounds in water is of particular interest. In oxidation of *n*-heptane TON was attained 160 at 50 °C after 3 h. That study revealed a remarkable regio-selectivity in the oxidation of higher *n*-alkanes.

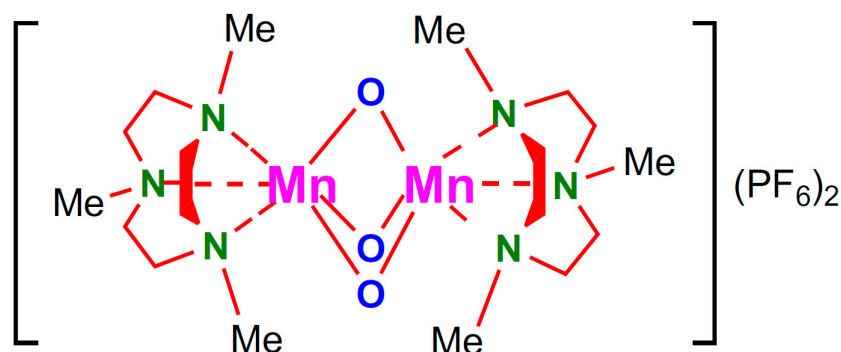
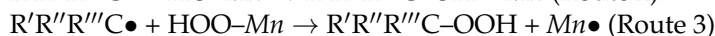
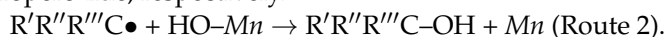


Figure 19. Binuclear manganese complex **24** which catalyzes a very efficient oxidation with peroxides, Adapted from [120], Copyright (2017) with permission of Elsevier.

Further, this system was investigated in more detail [119,120]. The kinetic study led to the conclusion about the oxidation mechanism proposed in [120], which includes the formation of intermediate complexes. A catalytic cycle shown in Figure 20 (see below). Many catalytic reactions of alkane oxidation into alkyl hydroperoxides contain as a crucial step the abstraction of a hydrogen atom from the alkane with subsequent fast interaction of the formed alkyl radical with atmospheric dioxygen (Route 1 in Figure 20). The data obtained in the present study show that, on the one hand, the transformation of the alkane $R'R''R'''C-H$ into the corresponding alkyl hydroperoxide $R'R''R'''C-OOH$ proceeds with the formation of alkyl radical $R'R''R'''C\bullet$ which rapidly reacts with atmospheric molecular oxygen. On the other hand, alkyl radicals can be generated via hydrogen abstraction from the alkane not by hydroxyl radicals but most likely by manganyl $Mn=O$ fragments. A catalytic cycle shown in Figure 20 is in good agreement with all experimental data and allowed authors to explain all features of the reaction. In the first step of the process carboxylic acid protonates one of the oxygen bridges between two manganese (IV) centers, resulting in the formation of a vacant site at one Mn (IV). The generated complex $[Mn^{IV}(\mu-O)_2Mn^{IV}(OH)]^{3+}$ then adds one hydrogen peroxide molecule and the formed hydroperoxo derivative $[(HOO)Mn^{IV}(\mu-O)_2Mn^{IV}(OH)]^{2+}$ eliminates hydroperoxyl radical to afford the catalytically active Mn(III)Mn(IV) species $[Mn^{III}(\mu-O)_2Mn^{IV}(OH)]^{2+}$ shown in Figure 20. The interaction with a second H_2O_2 molecule leads to the formation of the dihydroperoxo complex of Mn(III)Mn(IV). The protonation of the $MnOOH$ ligand and subsequent evolution of the water molecule gives the high-valent oxomanganese species which abstracts a hydrogen atom from the alkane $R'R''R'''C-H$ to produce an alkyl radical. The recombination in the solvent cage of this radical and either $HO-$ or $HOO-$ ligand (oxygen rebound or hydroperoxyl rebound) produces either alkanol or alkyl hydroperoxide, respectively.



where Mn is a fragment of the binuclear intermediate species. Reactions of the manganyl fragment formation and hydrogen atom abstraction are rate-limiting stages. Thus, this mechanism is a crypto-radical one but not a radical-chain process.

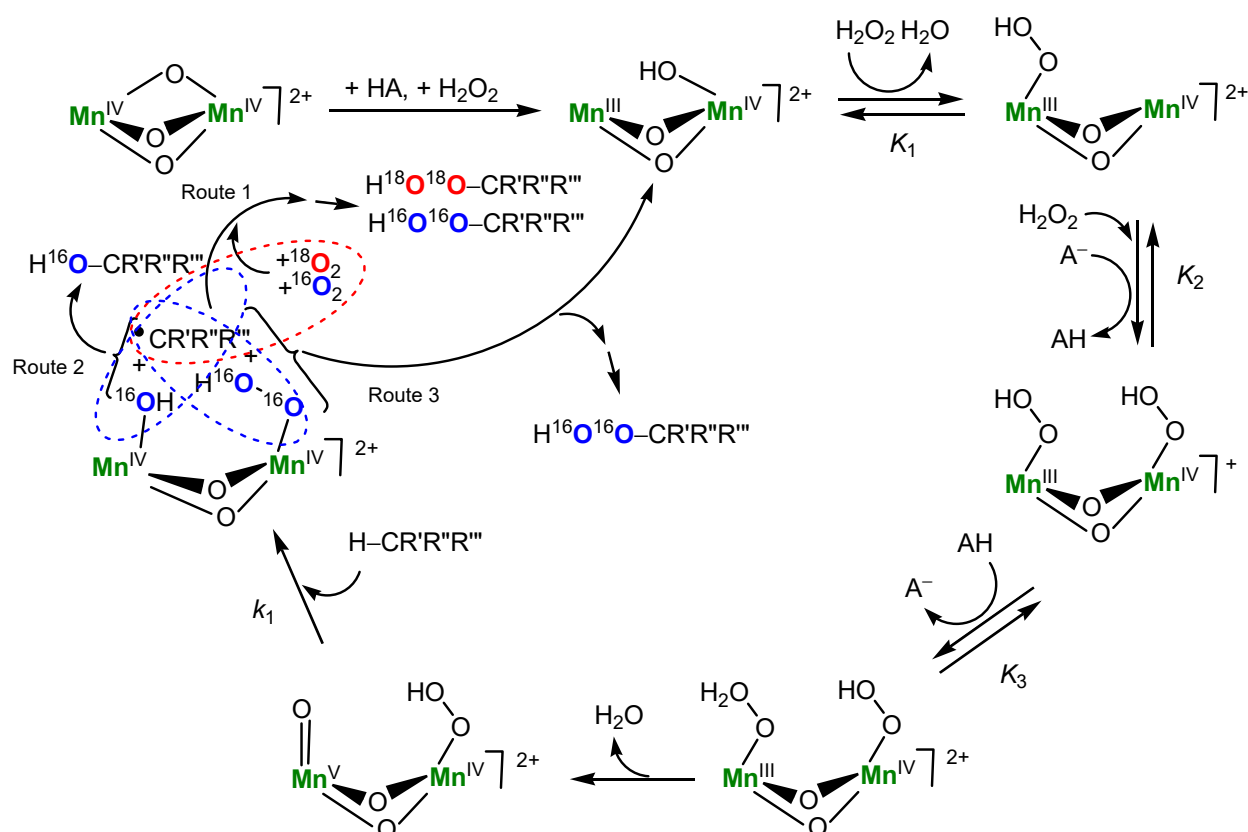


Figure 20. A catalytic cycle proposed for the alkane hydroperoxidation in the presence of $^{18}\text{O}_2$ (in an atmosphere $^{16}\text{O}_2 + ^{18}\text{O}_2$). AH is a carboxylic acid where A is its anion. Adapted from [120], Copyright (2017) with permission of Elsevier.

2.4. Oxidation Catalyzed by Polyvanadate Ions

Vanadium ions play an important role in biological systems and are effective catalysts for the oxidation of organic compounds with peroxides (See recent papers and reviews Refs. [5,121–155]). Monovanadate anion forms polyvanadate ions under the action of strong proton acids. Such polyvanadates are capable of catalyzing the oxidation of organic compounds with peroxides [121–157]. Examples of such compounds the di- and tetra-nuclear complexes of vanadium are described in paper Ref. [156]. The catalytic properties of mono-(25), di-(26) and tetranucleovanadium (27) complexes Figure 21 have been studied [156]. Interestingly, the three complexes exhibit catalytic activity only in the presence of pyrazine-2-carboxylic acid (PCA). The vanadium complexes differ significantly in their catalytic behavior, the most efficient catalyst being complex 25. This compound catalyzes oxidation of cyclohexane with high initial rate and high TON after 24 h (TON = 1400). The binuclear complex 26 catalyzes the reaction with approximately the same activity, but the behavior of complex 27 containing strongly complexing chelating and voluminous ligands is remarkable because it gives rise to the formation of almost pure cyclohexyl hydroperoxide.

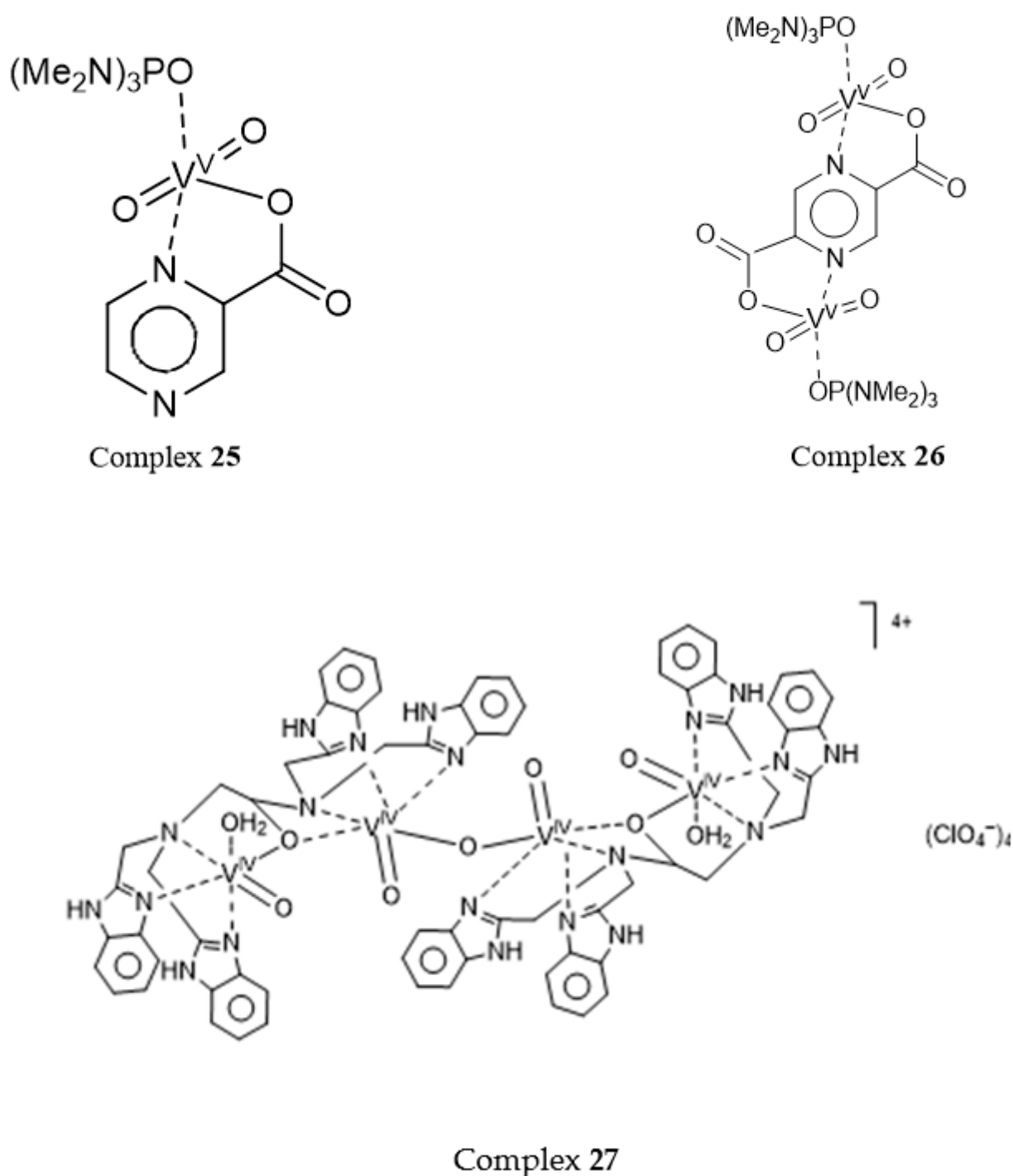


Figure 21. Structures of vanadium complexes 25–27, Adapted from [156], Copyright (2009) with permission of Elsevier.

The formation of oligovanadates in the presence of protons from strong acids was described in Ref. [158]. In reactions with hydrogen peroxide catalyzed by oligovanadate, the adjacent vanadate fragment is the carrier of H^+ to the vanadate ion. Similarly to how PCA works in reactions catalyzed by monovanadates, the scheme for generating catalytically active species is shown below. The possible catalytic cycles for generating radicals $\text{HOO}\bullet$ and $\text{HO}\bullet$ with the participation of model divanadate (Figure 22A) and monovanadate (Figure 22B) have been analyzed. The activity of the polyvanadate ion, in contrast to monovanadate, can be explained by the fact that, in the presence of an adjacent $\text{V}=\text{O}$ fragment in polyvanadate, the formation of a hydroperoxyl complex form a complex

with coordinated H_2O_2 molecule with the participation of a six-membered transition state is facilitated (Figure 23) [158].

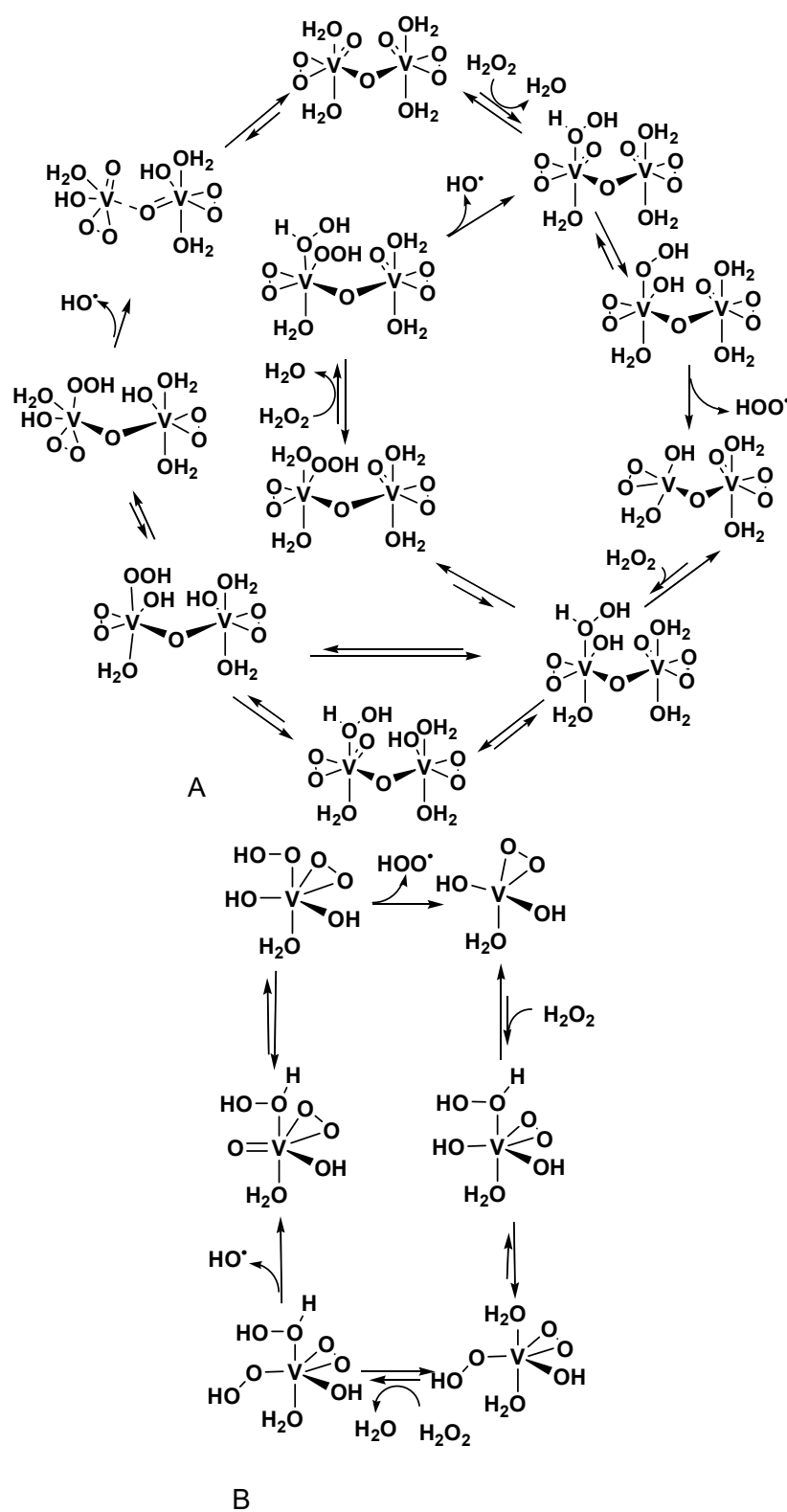


Figure 22. Catalytic cycles of radical generation involving divanadate (A) and monovanadate (B). Adapted from [158], Copyright (2011) with permission of American Chemical Society.

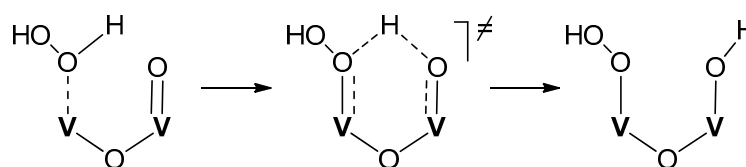
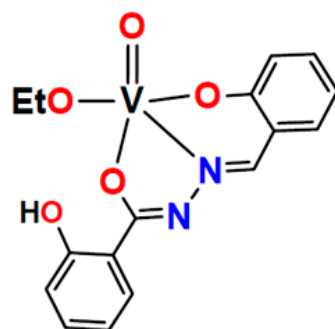


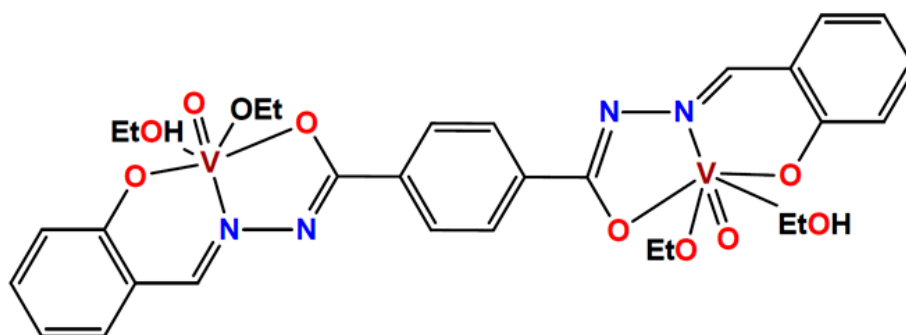
Figure 23. Proton transfer between two vanadium-containing fragments. Adapted from Ref. [158], Copyright (2011) with permission of American Chemical Society.

The paper Ref. [159] (Figure 24) describes in detail the preparation of mono-, di-, tri-nuclear complexes of vanadium (**28–30**) (Figure 25). Compounds **28**, **29**, and **30** were tested as homogeneous catalysts for microwave oxidation of cyclohexane with hydrogen peroxide to produce cyclohexyl hydroperoxide (CyOOH), cyclohexanol, and cyclohexanone (see Figure 25). Advantages of these catalytic systems are mildness and environmental friendliness. The formation of CyOOH was shown by the Shulpin method. GC analysis of the products showed a noticeable increase in the amount of cyclohexanol (after the reduction of CyOOH by PPh_3) and a decrease of cyclohexanone amount in comparison with the nonreduced sample. In the case of the catalysis by complex **30** the maximum yield of all products after the reduction of PPh_3 attained 39% based on initial amount of cyclohexane. In this work, a reaction mechanism was proposed. The authors proposed the mechanism which is a bit different from those usually accepted for the oxidizing systems containing H_2O_2 and an metal ion. The mechanism proposed in Ref. [159] includes at the first step coordination of H_2O_2 to the catalyst molecule, proton transfer from ligated H_2O_2 to the methoxy ligand and elimination of the formed methanol molecule and coordination of the second H_2O_2 molecule followed by HO–OH bond cleavage to give $\text{HO}\bullet$. The activation of the H_2O_2 towards this cleavage is associated with the redox active nature of the ligand in the catalyst molecule, which acts (instead of the metal) as the reducing agent of the H_2O_2 ligand. Generated hydroxyl radicals attack the substrate molecules.

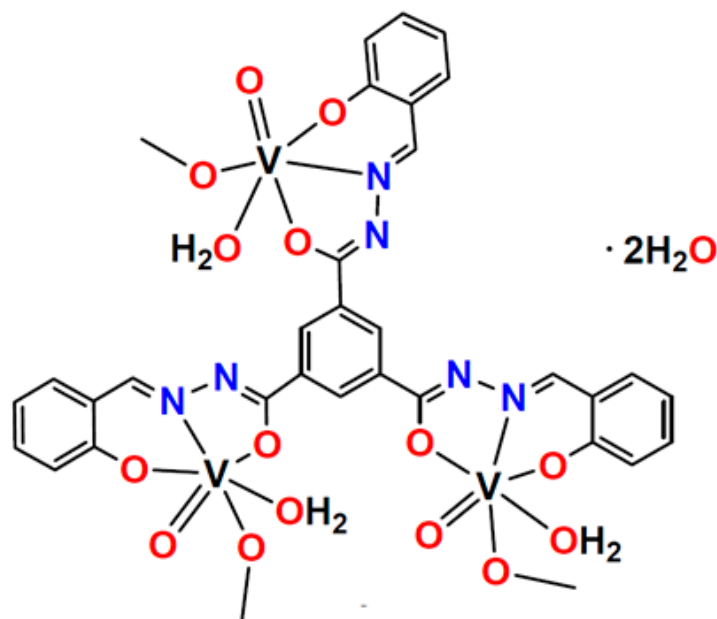
Theoretical DFT calculations were in agreement with previous works on oxidation involving vanadium complexes (Ref. [145]), and led to the conclusion that the global radical type mechanism involves the formation of $\text{RO}\bullet$ radicals (or $\text{HO}\bullet$ if H_2O_2 is used as an oxidizing agent). Then this radical oxidizes the alkane, a hydrogen atom is removed from the R–H molecule to form the corresponding alkyl radical $\text{R}\bullet$. The latter species react with molecular oxygen from the atmosphere, ultimately forming the alkyl hydroperoxide ROOH . The trinuclear vanadium complexes shown in Figure 26 were investigated as catalysts for the oxidation of dopamine by hydrogen peroxide [160]. Kinetic studies showed that the reaction follows a Michaelis-Menten like kinetics. The conversion of dopamine to aminochrome with different catalysts showing high activity under mild conditions with good conversions (Figure 27).



Compound 28



Compound 29



Compound 30

Figure 24. Vanadium Compounds tested as catalysts in oxidation with peroxides. Adapted from [159], Copyright (2019) with permission of Royal Society of Chemistry.

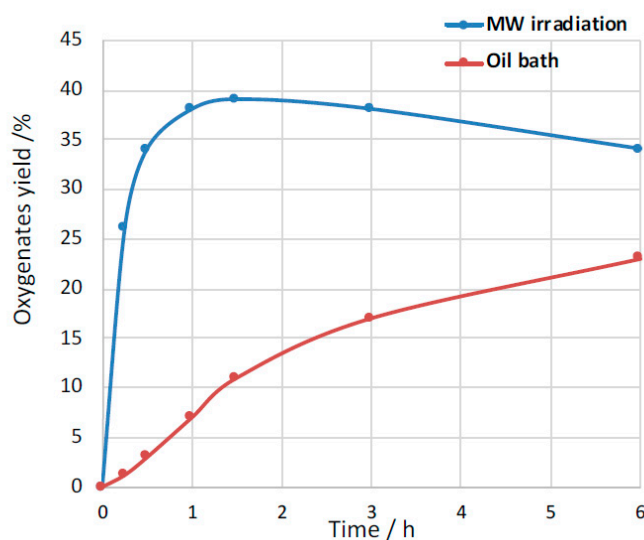
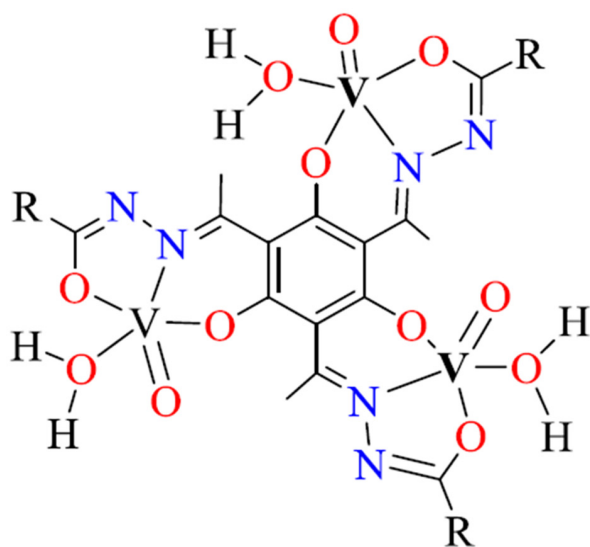


Figure 25. Effect of the heating mode (MW irradiation or oil bath) on the total yield of cyclohexanol and cyclohexanone obtained by neat oxidation of cyclohexane with aq. H_2O_2 catalyzed by complex **30**, adapted from Ref. [159], Copyright (2019) with permission of Royal Society of Chemistry.



R	Complexes
	$[\{\text{V}^{\text{IV}}\text{O}(\text{H}_2\text{O})\}_3(\text{ptk}(\text{bhz})_3)]$
	$[\{\text{V}^{\text{IV}}\text{O}(\text{H}_2\text{O})\}_3(\text{ptk}(\text{fah})_3)]$
	$[\{\text{V}^{\text{IV}}\text{O}(\text{H}_2\text{O})\}_3(\text{ptk}(\text{inh})_3)]$
	$[\{\text{V}^{\text{IV}}\text{O}(\text{H}_2\text{O})\}_3(\text{ptk}(\text{nah})_3)]$

Figure 26. Structural formulae of the $\text{V}^{\text{IV}}\text{O}$ -complexes prepared in this work. Adapted from Ref. [160], Copyright (2020) with permission of Royal Society of Chemistry.

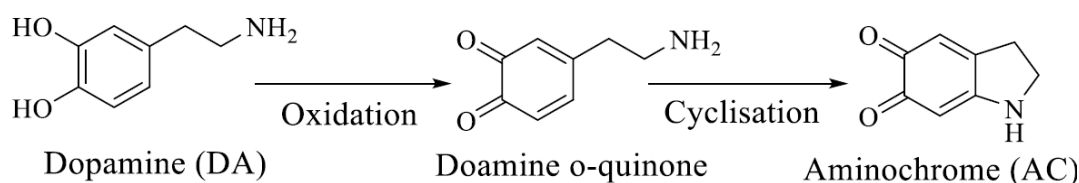


Figure 27. Scheme of oxidation of dopamine.

Figure 28 shows the structure of binuclear vanadium complex **31**. Although the molecule of the complex-**31** contains two fragments inclusive vanadium, these fragments are separated by a large bridge and are located at a long distance from each other. Therefore, it is more reasonable to attribute compound **31** to mononuclear complexes. In the work Ref. [150] was studied in details the oxidation of cyclic, linear and branched alkanes

with the **31**/PCA/H₂O₂ system in acetonitrile solution (typical temperature of 50 °C). Oxidation of cyclohexane is shown in Figure 29. The accumulation of oxygenates at different concentrations of complex **31** is shown in the presence of and in the absence of PCA.

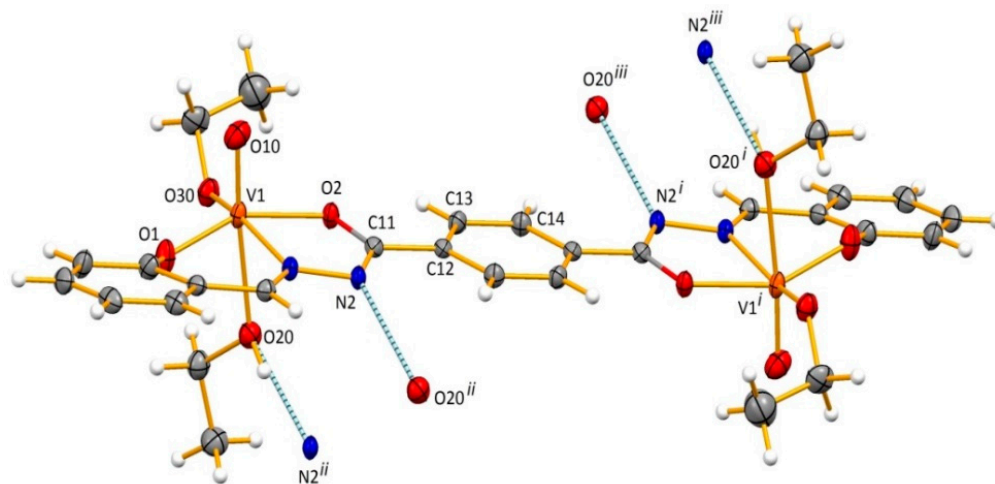


Figure 28. Structure of complex **31** (C₃₀H₃₆N₄O₁₀V₂) Adapted from Ref. [150], Copyright (2013) with permission of Royal Society of Chemistry.

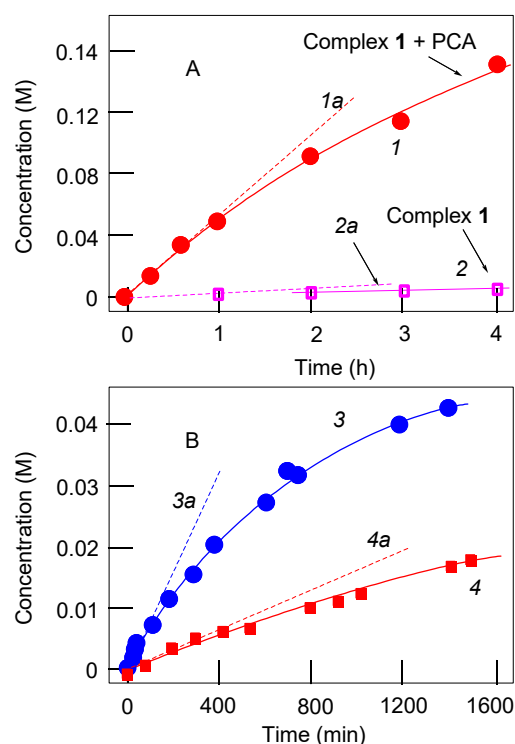
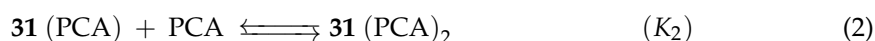


Figure 29. Oxidation of cyclohexane with the H₂O₂/**31**/PCA/CH₃CN–H₂O (curve 1). Curve of accumulation of oxygenates (predominantly cyclohexyl hydroperoxide) in the absence of PCA (curve 2) are shown. For Graph (A): [catalyst **31**]₀ = 2.0 × 10^{−5} M; [PCA]₀ = 0.005 M; [H₂O₂]₀ = 2.2 M (50% aqueous), [H₂O]_{total} = 4.2 M; [cyclohexane]₀ = 0.46 M; MeCN; 50 °C. For Graph (B): [catalyst **31**]₀ = 1.0 × 10^{−6} M (curve 3) or 5.0 × 10^{−7} M (curve 4); [PCA]₀ = 6 × 10^{−4} M; [H₂O₂]₀ = 0.4 M (50% aqueous), [cyclohexane]₀ = 0.4 M; MeCN; 50 °C. Maximum initial rates *W*₀ were determined from the slopes of tangents (two examples are depicted with straight dotted lines 1a, 2a, 3a and 4a) to the kinetic curves in the intervals where the rate attains maximum (in these cases in the beginning of the oxidation reaction). Adapted from Ref. [150] Copyright (2013) with permission of Royal Society of Chemistry.

It has been shown earlier [6–11] that a vanadium complex as catalysts and PCA as a cocatalyst is a very efficient catalytic system if H_2O_2 is used as an oxidant. The addition of strong acids to the monovanadate ion solution leads to an increase the catalyst activity. This phenomenon is due to the formation of polyvanadate species. (see Section 2.4). The kinetic study of alkane oxidation by the **31**/PCA/ H_2O_2 CH₃CN–H₂O system the dependences of the initial rate of oxygenate accumulation W_0 . Examples are presented by the dotted straight lines in Figure 29. The follow kinetic scheme was proposed for the oxidation reaction catalyzed by vanadium complexes:



Reactions (1) and (2) are the equilibria stages of adduct formation between compound **31** and one or two PCA molecules, respectively. A rate-limiting stage is reaction (3) in the sequence of transformations which are induced by the interaction of **31**. (PCA) and H_2O_2 . These transformations lead to the generation of species Z (in many cases $\text{Z} = \text{HO}\bullet$) and regeneration of the catalyst active form. The rate W_Z of the Z generation in reaction (3) is equal to

$$W_Z = k_3[\mathbf{31}(\text{PCA})][\text{H}_2\text{O}_2] \quad (4)$$

The data on the kinetics of cyclohexane oxidation and further calculations based on confirmed the assumption about the participation of hydroxyl radicals as key species Z in the oxidation catalyzed by compound **31**.

Basing on the results of all studies of vanadium complexes, both mononuclear and polynuclear, we can conclude that they all have approximately the same activity in the oxidation of organic compounds by peroxides. Of particular note is the simplest and cheapest system $\text{VO}_3^-/\text{PCA}/\text{H}_2\text{O}_2$. The system was discovered in 1993. This reaction takes place at low temperatures in a solution of acetonitrile [122–124]. Later, this system was studied in detail. As substrates were used: alkanes, olefins, arenes, and alcohols and as oxidants: hydrogen peroxide, tert-butyl hydroperoxide, and other peroxides [125–149].

2.5. Oxidation Catalyzed by Other Metal Complexes

Complexes of other metals have been reported as catalysts in oxidations by peroxides. Some of these catalysts are demonstrated in Figures 30–33. Nickel complexes were used in the oxidation of alkanes most often with the use of *m*-chloroperoxybenzoic acid–(*m*-CPBA) turned out to be a good oxidant [161–166]. An example of oxidation catalyzed by the nickel complex was described in Ref. [161] Complex oxidized cyclohexane with *m*-CPBA at room temperature in a mixture of methylene chloride and acetonitrile. The reaction gave cyclohexanol and cyclohexanone in ratio 8:1 with total TON = 612.

Another example of nickel catalyst is presented by compound **32** (Figure 30, Ref. [164]).

Complex **32** catalyzes the oxidation of cyclohexane *m*-CPBA to afford cyclohexanol and cyclohexanone. The ketone/alcohol ratio is not changed in the chromatograms made before and after reduction of samples with triphenylphosphine. This indicates that cyclohexyl hydroperoxide is not formed in the course of the oxidation. The yield of oxygenates was 24%. The oxidation of *n*-octane (0.12 M) with (0.13 M) *m*-CPBA in the presence of compound **32** (5×10^{-4} M) and co-catalyst HNO_3 (0.05 M) at 60 °C during 3 h gave rise to the formation of a mixture of 2-, 3-, and 4-octanones (0.009, 0.009, and 0.008 M, respectively; yield 22%). The oxidation of methylcyclohexane under similar conditions gave predominantly isomeric ketones and *tert*-alcohol. Alkyl hydroperoxides have not been formed in this reaction.

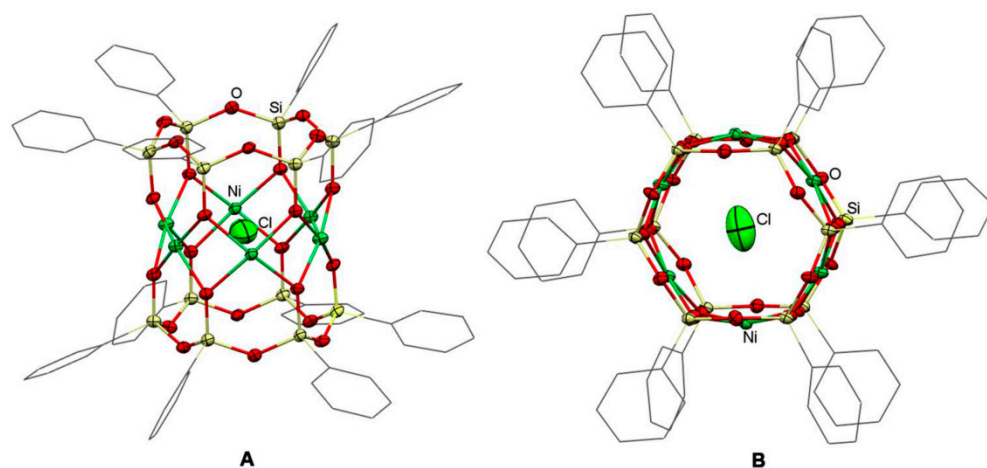


Figure 30. Molecular structure of compound **32** ((A)—side view, (B)—top view). Solvating ligands and counter ion Na^+ are omitted for clarity. Adapted from Ref. [164], Copyright (2016) from Molecules MDPI (Open Access).

Complexes containing cobalt and zinc MOF [166] can also exhibit catalytic activity in the oxidation of alcohols and alkanes. A pentanuclear “cylinder”-like cobalt(II) phenylsilsesquioxane $[(\text{PhSiO}_{1.5})_{10}(\text{CoO})_5(\text{NaOH})]$ [165] (**33**) (see Figure 31) exhibits a high catalytic activity and stereoselectivity in the oxidation of alkanes and alcohols. Complex **33** efficiently (yield 62%) catalyzes stereoselective (trans/cis ratio = 0.04) cis-1,2-dimethylcyclohexane oxidation with *meta*-chloroperoxybenzoic acid (m-CPBA) and 1-phenylethanol’s oxidation (yield 99%) with TBHP.

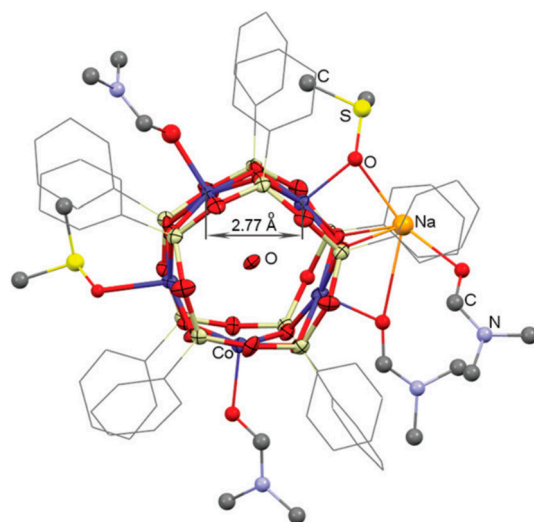
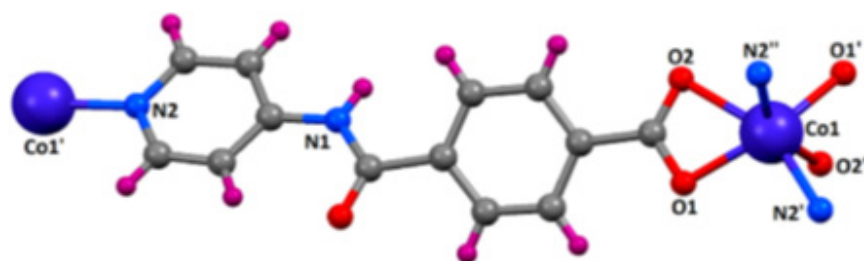
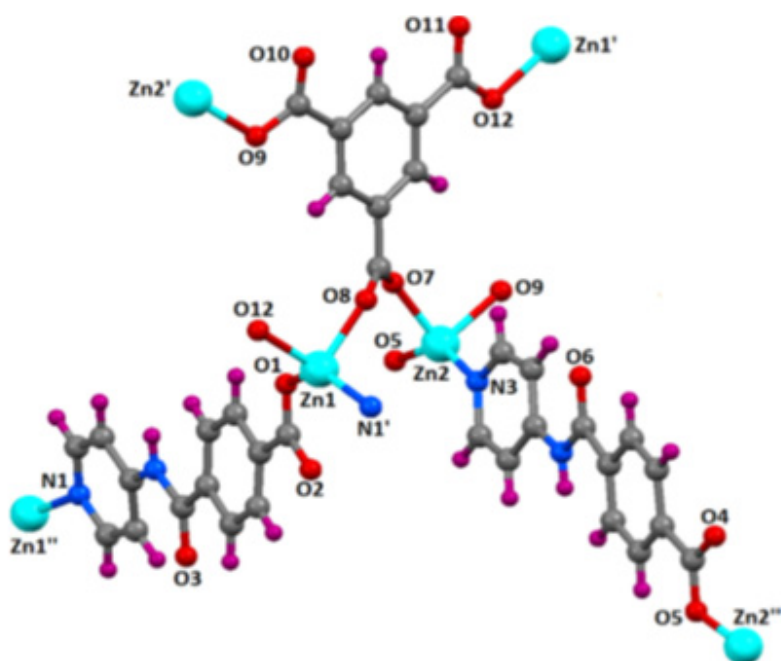


Figure 31. Crystal structure of complex **33**. Color code: Co, blue; Na, orange; Si, light yellow; O, red; C, grey; S, yellow; N, light blue. Adapted from Ref. [165], Copyright (2016) with permission from Royal Society of Chemistry.

The heterogeneous catalytic activity of compounds **34** and **35** (Figure 32), under eco-friendly conditions, was assessed in benzyl alcohol oxidation [166]. Complex **34** has good activity in the solvent-free microwave-assisted oxidation of benzyl alcohol to benzaldehyde using *tert*-butyl hydroperoxide (t-BuOOH, TBHP) as oxidizing agent (yields up to 89%). Although with a lower activity, MOF **35** with a redox inactive Zn(II) site, also catalyzes such alcohol oxidation (yields up to 27%).



Complex 34



Complex 35

Figure 32. Structures complexes cobalt and zinc used as catalyst in oxidation with peroxides, adapted from Ref. [166], Copyright (2020) with permission from Elsevier.

Three Os (0)—carbonyl complexes [167–170] (see Figure 33) are active in the oxidation of alkanes and alcohols by peroxides in acetonitrile. Thus, oxidation, for example, upon catalysis of alkanes by triosmium dodecacarbonyl, $\text{Os}_3(\text{CO})_{12}$ with hydrogen peroxide, gave product yields above 60% and TON above 60,000 [167]. In this review, other complexes of osmium, cobalt, and nickel are not described in detail.

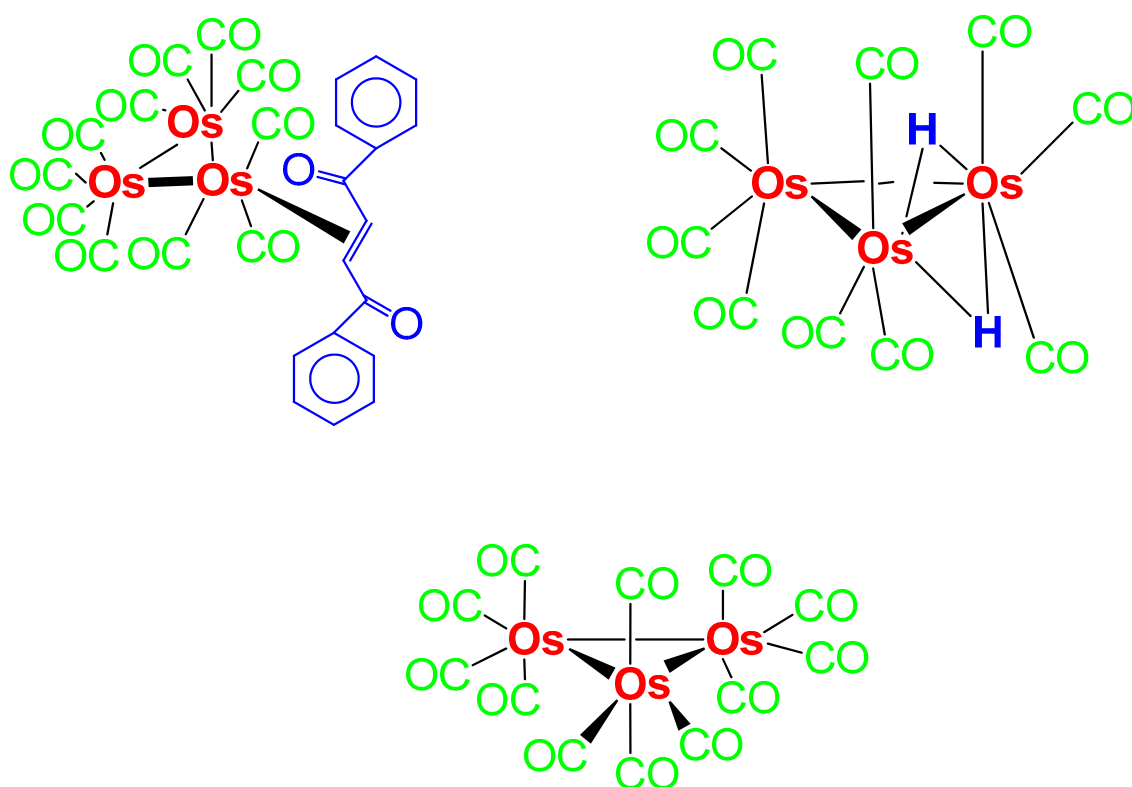


Figure 33. Osmium carbonyls derivatives which extremely efficiently catalyzed the oxidation of alkanes and alcohols with peroxides.

3. Conclusions

In many cases polynuclear complexes of transition metals exhibit higher catalytic activity in oxidations of organic compounds by peroxides in comparison with simple mononuclear derivatives. Moreover, such complexes oxidize long-chain and branched saturated hydrocarbons with non-conventional selectivity. These features can be successfully use in fine chemical technology. Examination of the oxidation reactions with peroxides shows that both mono and polynuclear complexes of transition metals are often active catalysts in these reactions. However, they all require either the presence of a redox-active ligand in the molecule or amine-containing organic compounds added to the solution, which changes the mechanism of the reaction of hydrogen peroxide with a metal (in the absence of such ligands or additives, only the reaction of hydrogen peroxide decomposition with the formation of oxygen and water takes place).

Author Contributions: G.B.S. and L.S.S. wrote the paper. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: All links are given to publications that are in the open press and are easily available.

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0007), as well as by the Initiative Program in the frames of the State Tasks 0082-2014-0004 and 0082-2014-0007 “Fundamental regularities of heterogeneous and homogeneous catalysis”; the Program of Fundamental Research of the Russian Academy of Sciences for 2013–2020 on the re-search issue of IChP RAS No. 47.16. Access to electronic scientific resources was provided by INEOS RAS with the support of Ministry of Science and Higher Education of the Russian Federation.

Conflicts of Interest: The authors declare no conflict of interest.

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