

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.

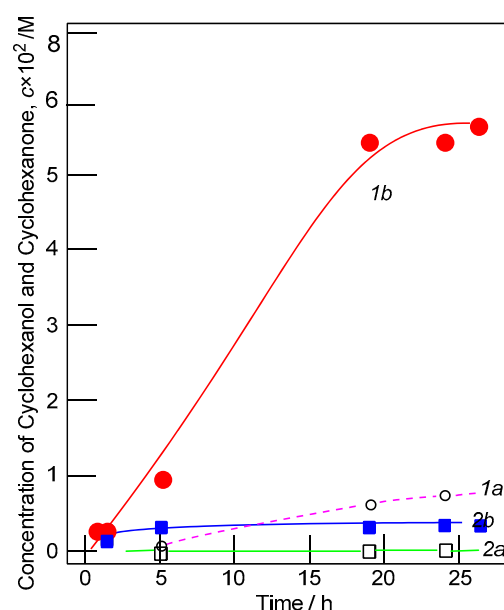


Figure 1. Compound **1** in the absence (curves a) and in the presence of PCA; (curves b) in MeCN at 25 °C. catalyzed the oxidation of cyclohexane by H_2O_2 (0.59 M). Accumulation of cyclohexanol (curves 1b) and cyclohexanone (curves 2b) (concentrations were measured after the reduction with PPh_3 , 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.

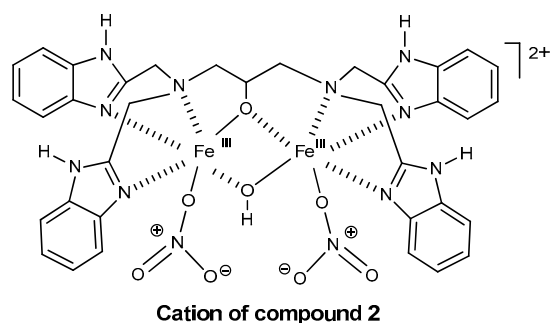


Figure 2. Cont.

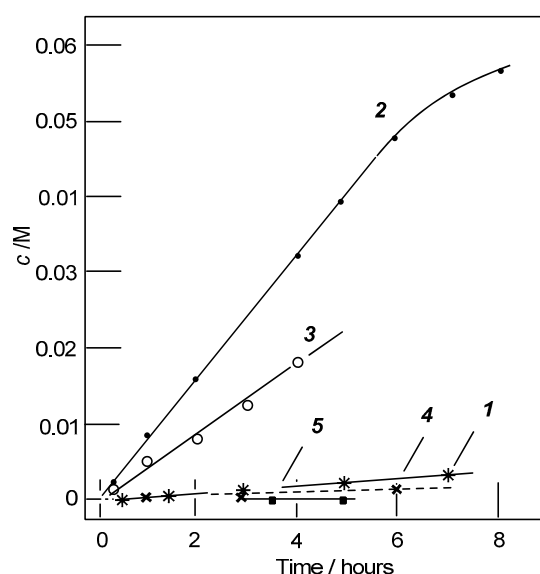


Figure 2. Accumulation of sum of oxygenates (predominantly cyclohexyl hydroperoxide) in the reaction of cyclohexane with hydrogen peroxide (in acetonitrile at 25 °C catalysed by complex 2 in the absence of additives (curve 1) and in the presence of aminoacids: PCA (2), pyrazine-2,3-dicarboxylic acid (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 $[(\text{TMP}^{\text{tp}})\text{Fe}(\text{IV})(\text{O})]\text{p}$ (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.

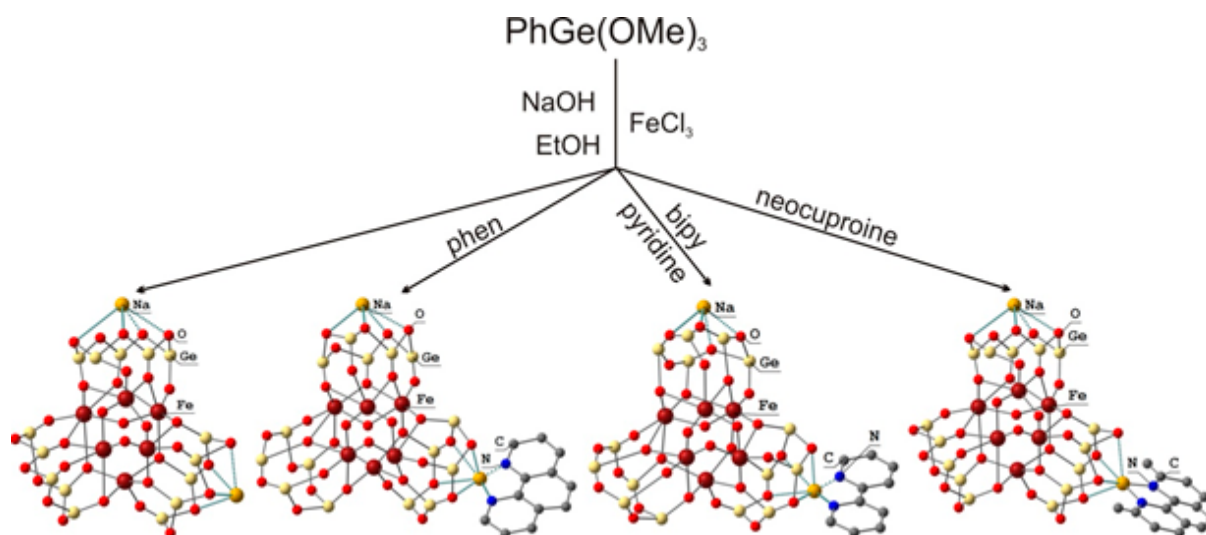


Figure 3. All structures adapted from Ref. [40], Copyright (2016) with permissions of Wiley.

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).

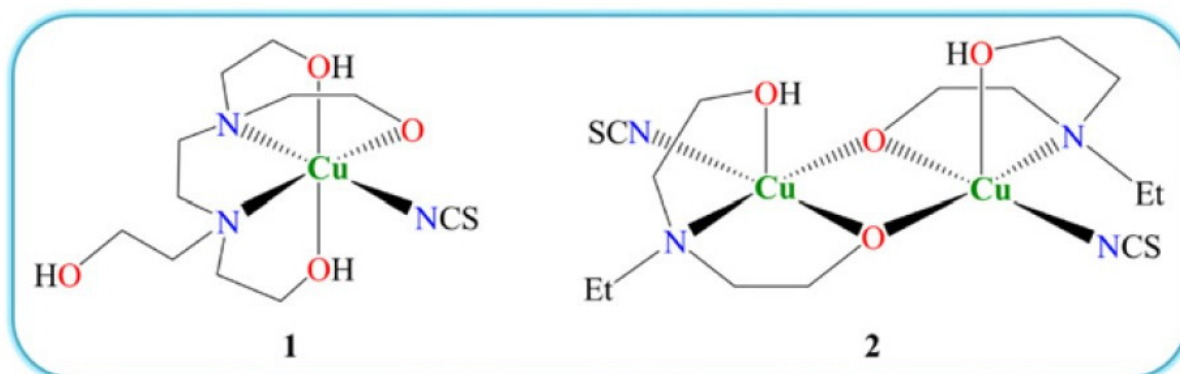
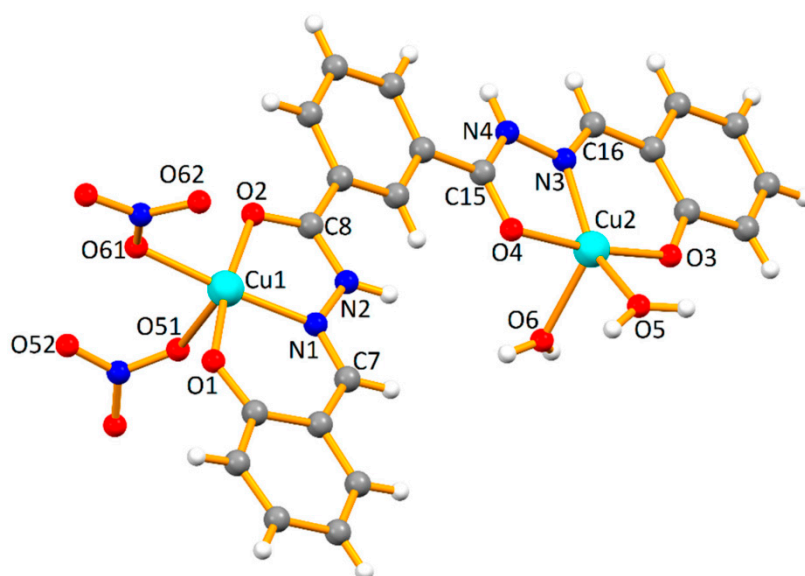


Figure 4. Formulae Complex 5 (left) and 6 (right), which have been used in oxidations with peroxides adapted from Ref. [64], Copyright (2011) with permission of Elsevier.



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

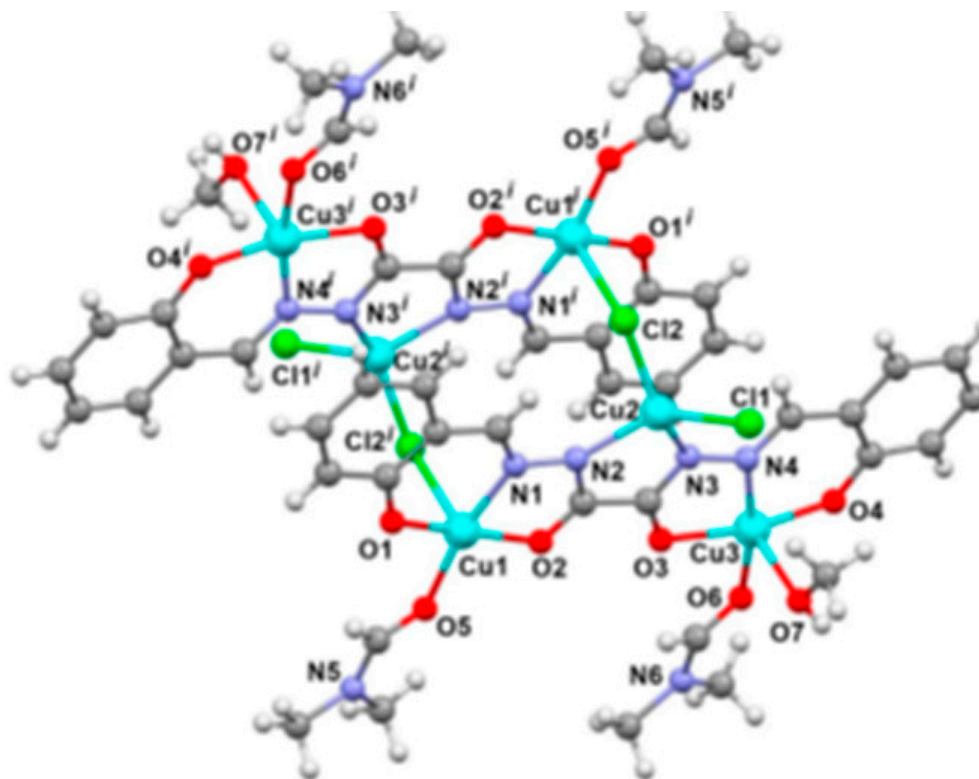


Figure 7. Complex tested in oxidations with peroxides adapted from Ref. [70], Copyright (2020), *Int. J. Mol. Sci.* (MDPI), Open Access.

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.

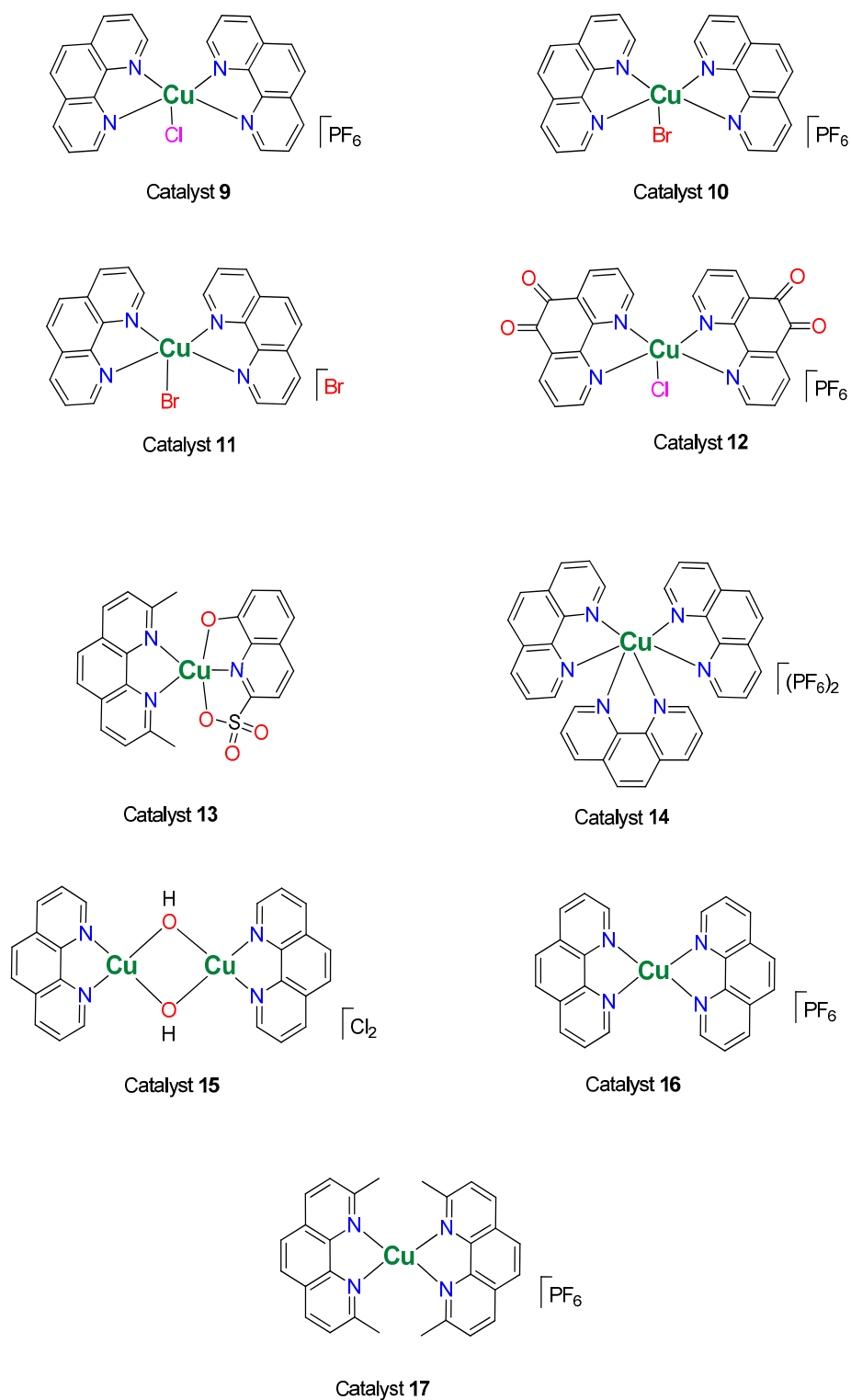


Figure 8. Complexes studied as catalysts, adapted from Ref. [72], Copyright (2020) with permission of Elsevier.

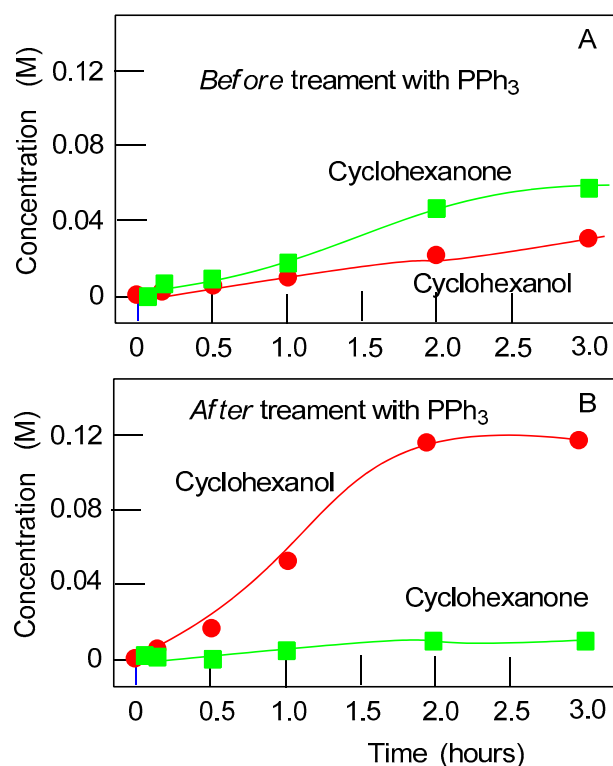


Figure 9. Oxidation of cyclohexane with hydrogen peroxide (50% aqueous) catalyzed by compound **9** in MeCN at 50 °C (Graphs (A,B)); total volume of the reaction solution was 5 mL. Concentrations of cyclohexanone and cyclohexanol were determined before (Graph A) and after (Graphs B) reduction of the 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.

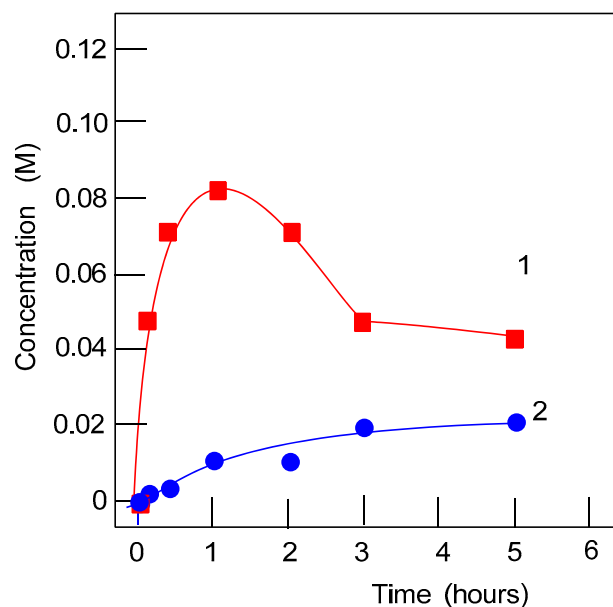


Figure 10. Oxidation of cyclohexane with hydrogen peroxide (50% aqueous;) catalyzed by compound **15** in MeCN at 60 °C. Concentrations of cyclohexanone and cyclohexanol were after reduction of the aliquots with solid PPh₃. Points for cyclohexanol (red) and cyclohexanone (blue) are marked by numbers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

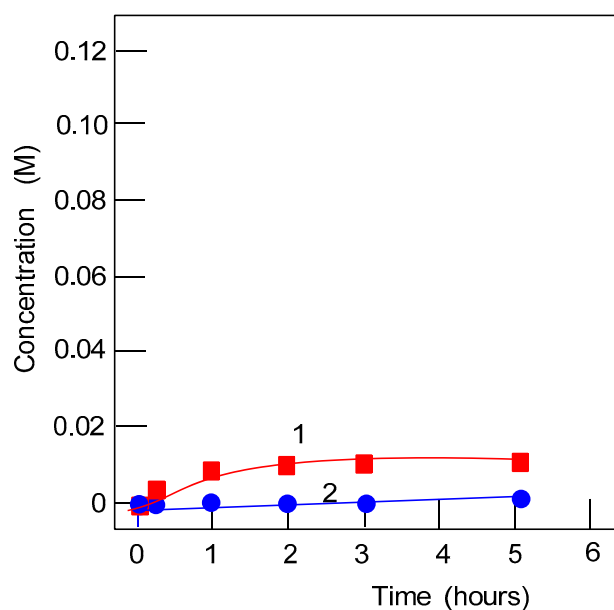
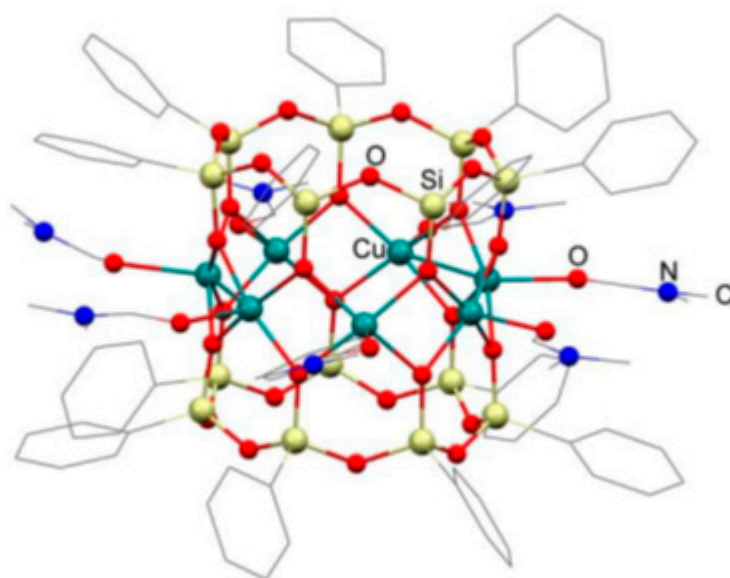


Figure 11. Oxidation of cyclohexane with hydrogen peroxide (50% aqueous) catalyzed by compound **17** in MeCN at 60 °C; Concentrations of cyclohexanone and cyclohexanol were after reduction of the aliquots with solid PPh₃. Points for cyclohexanol (red) and cyclohexanone (blue) are marked by numbers 1 and 2, respectively. Total yield of products 2.5% after 2 h, TON = 22. Adapted from Ref. [72], Copyright (2020) with permission of Elsevier.

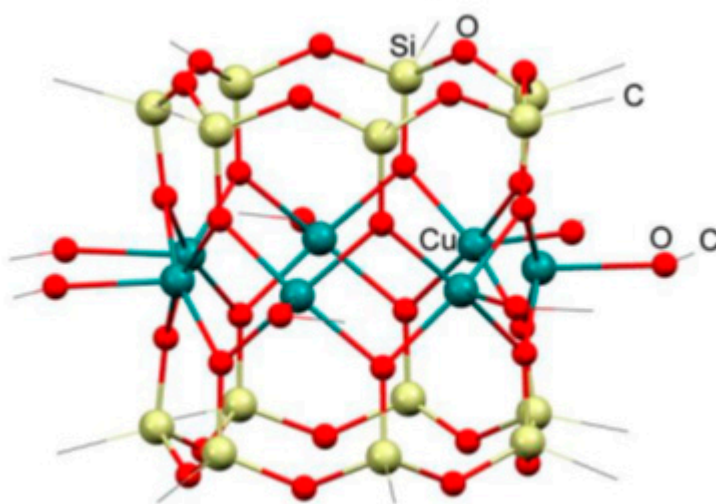
As in the case of iron ions, a large number of works have been devoted to silsesquioxane complexes with copper and their use in catalytic oxidation [73–88]. A few structures of the catalysts used in the most recent years are shown in Figures 12–15.

First examples of heptanuclear cage silsesquioxanes, (PhSiO_{1.5})₁₄(CuO)₇ **18** and (MeSiO_{1.5})₁₄(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 H₂O₂, respectively. 1-Phenylethanol and heptanol-2 could be converted into corresponding ketones in yields up to 94% and 50%, respectively. Hydroperoxidation of alkanes by H₂O₂ 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].

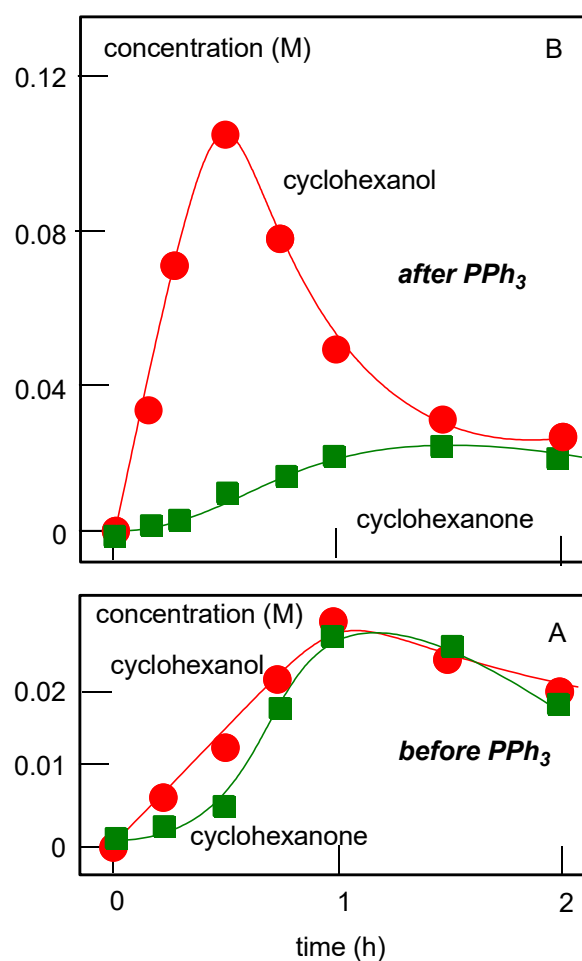


Figure 13. Oxidation of cyclohexane with H₂O₂ (50%) catalyzed by complex 18 at 60 °C. Concentrations of cyclohexanol and cyclohexanone were measured both before (A) and after reduction (B) with PPh₃ (used method of Shul'pin). Adapted from [81], Copyright (2018) with permission of Wiley.

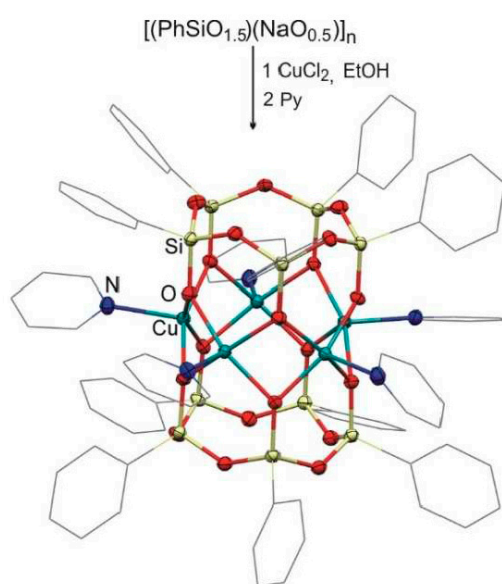


Figure 14. Scheme synthesis Complex 20 used in oxidation alkanes with peroxides is presented on this figure, adapted from Ref. [82], Copyright (2018) with permission of Elsevier.

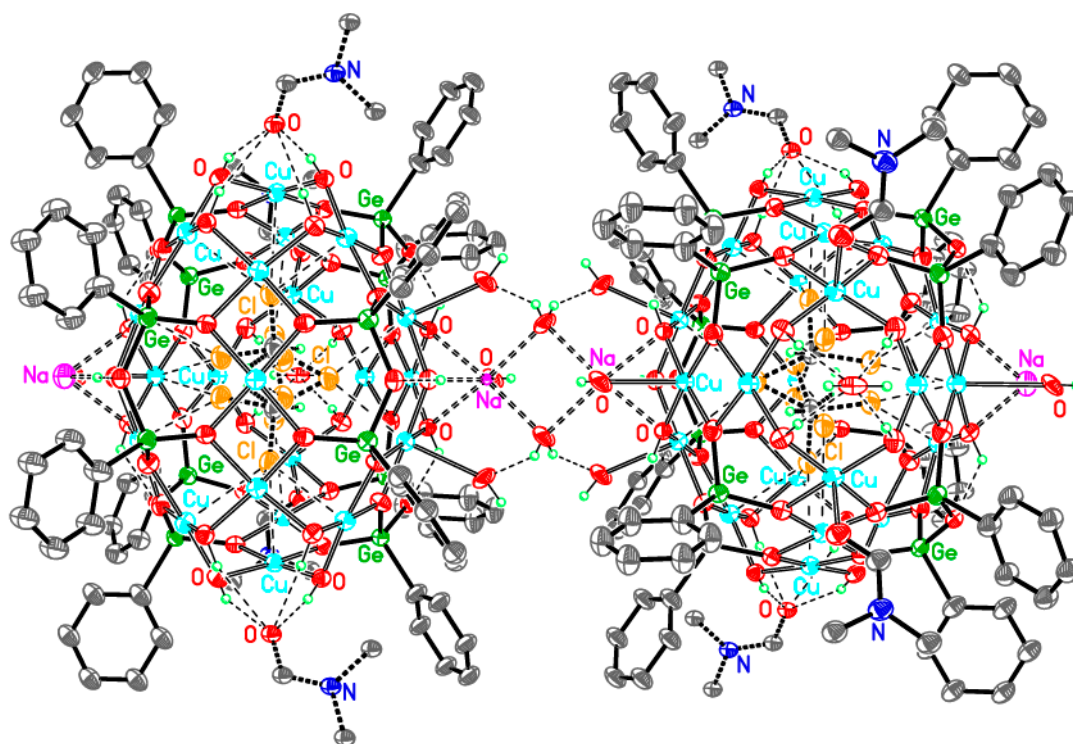


Figure 15. The copper complex with germesquioxane surroundings. Adapted from Ref. [87], Copyright (2018), Catalysts, MDPI.

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.

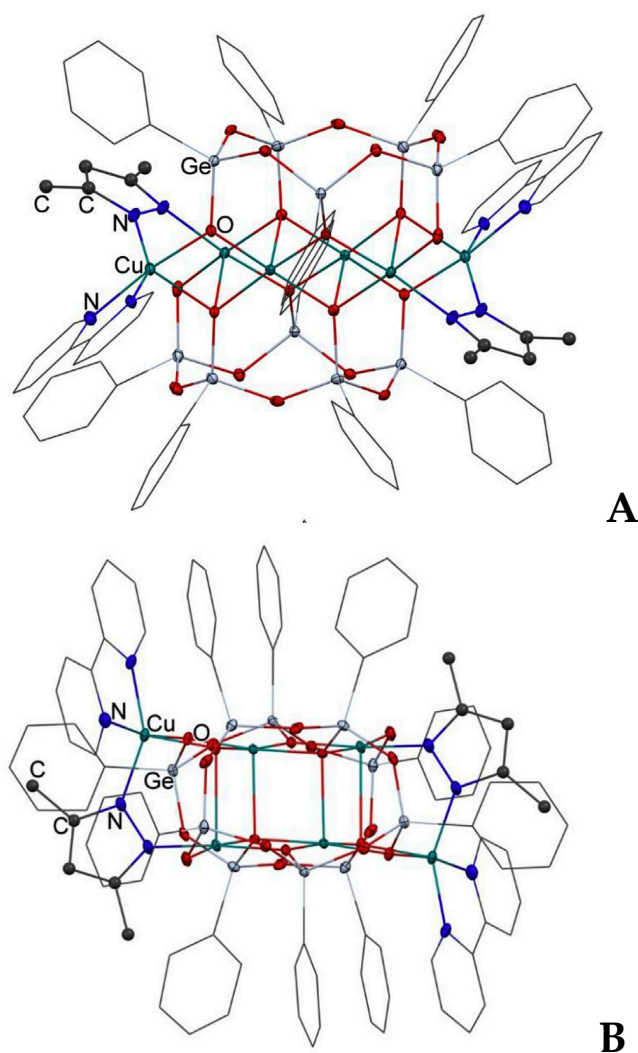


Figure 16. Molecular structure of complex **21**. (A): side view. (B): top. View. Color code: Ge: grey, O: red, Cu: green, N: blue. Adapted from [89], Copyright (2019) with permission of Elsevier.

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.

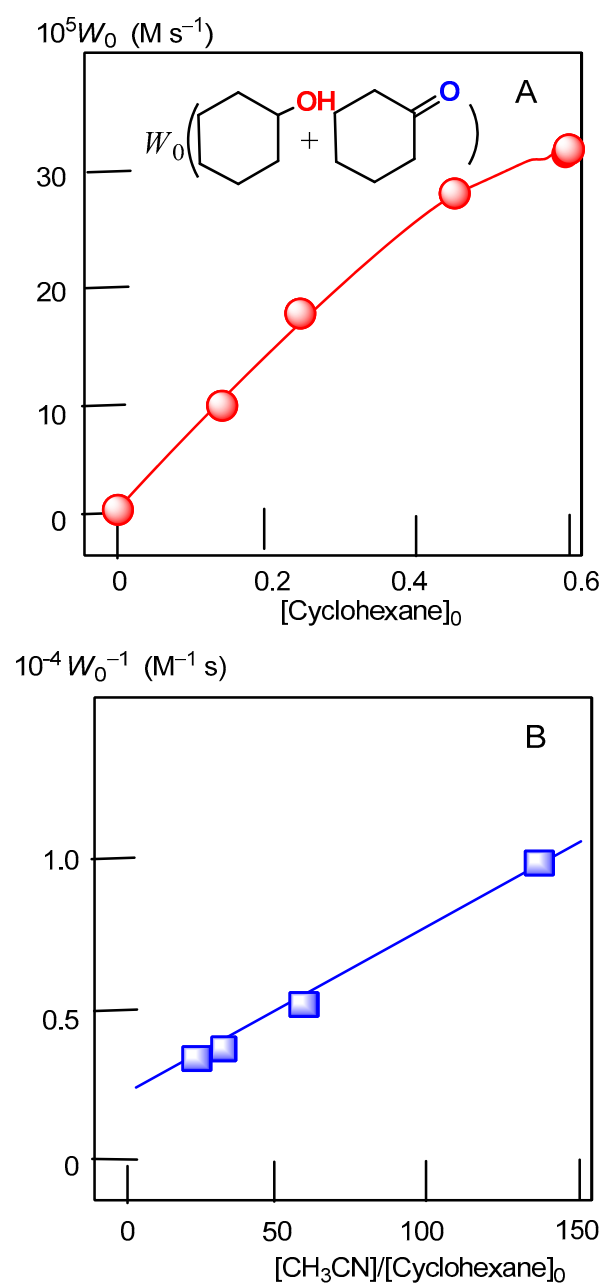


Figure 17. Cont.

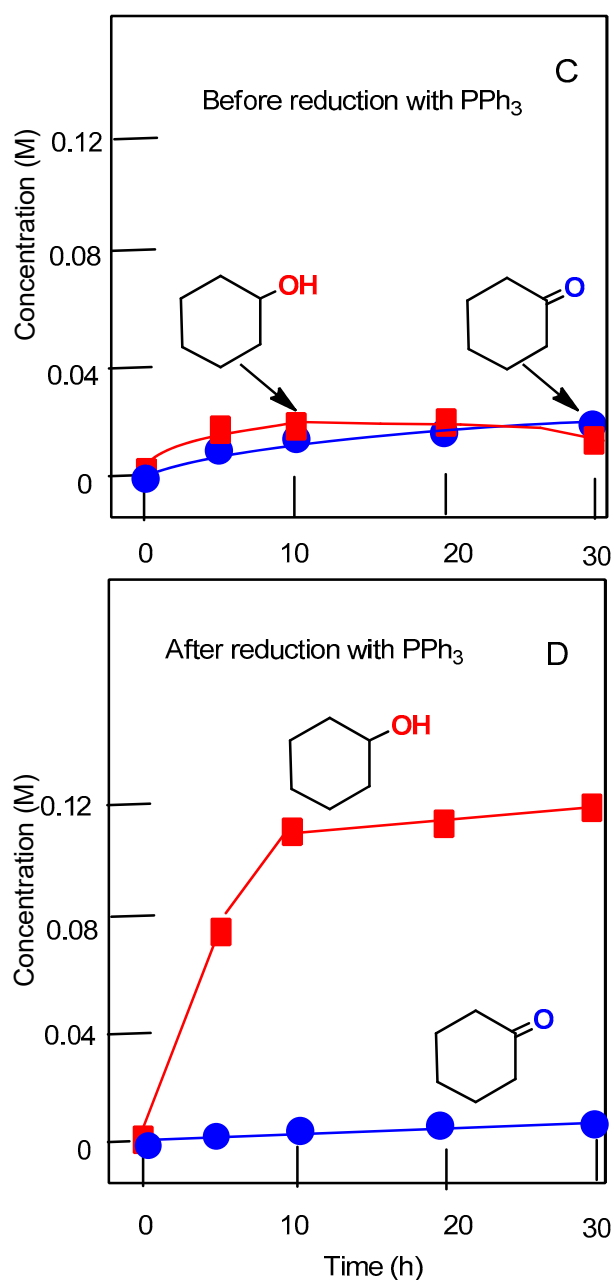
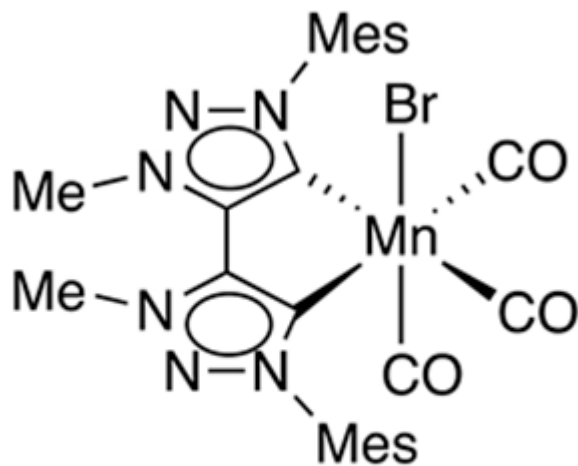


Figure 17. Accumulation of cyclohexanol and cyclohexanone in oxidation of cyclohexane with hydrogen peroxide catalyzed by compound **21** in MeCN at 50 °C. Dependence of the initial rate of oxygenate formation W_0 on initial concentration of cyclohexane is shown in graph (A). Linearization of curve from 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.

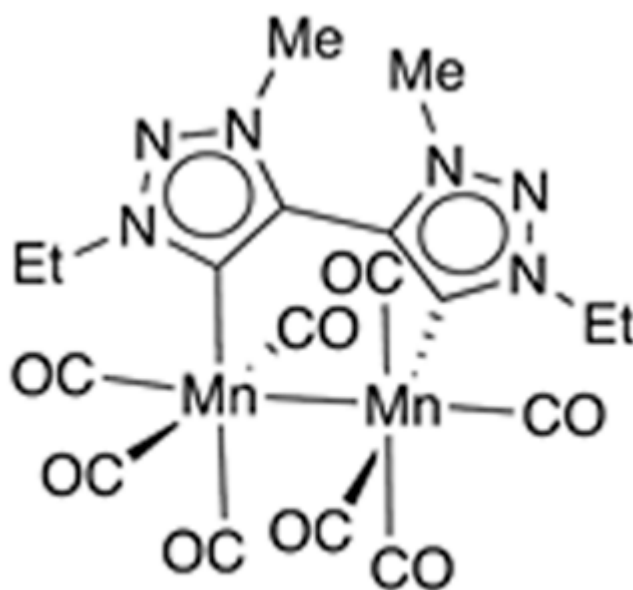
2.3. Polymanganese Complexes in Oxidations with H₂O₂

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.

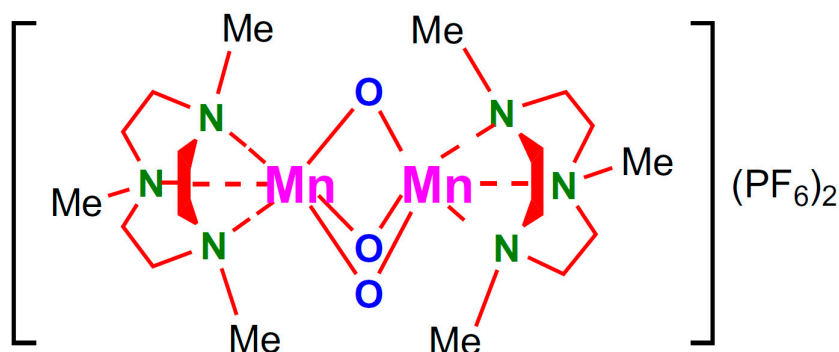
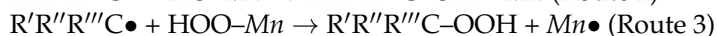
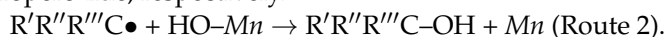


Figure 19. Binuclear manganese complex **24** which catalyzes a very efficient oxidation with peroxides, Adapted from [120], Copyright (2017) with permission of Elsevier.

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.

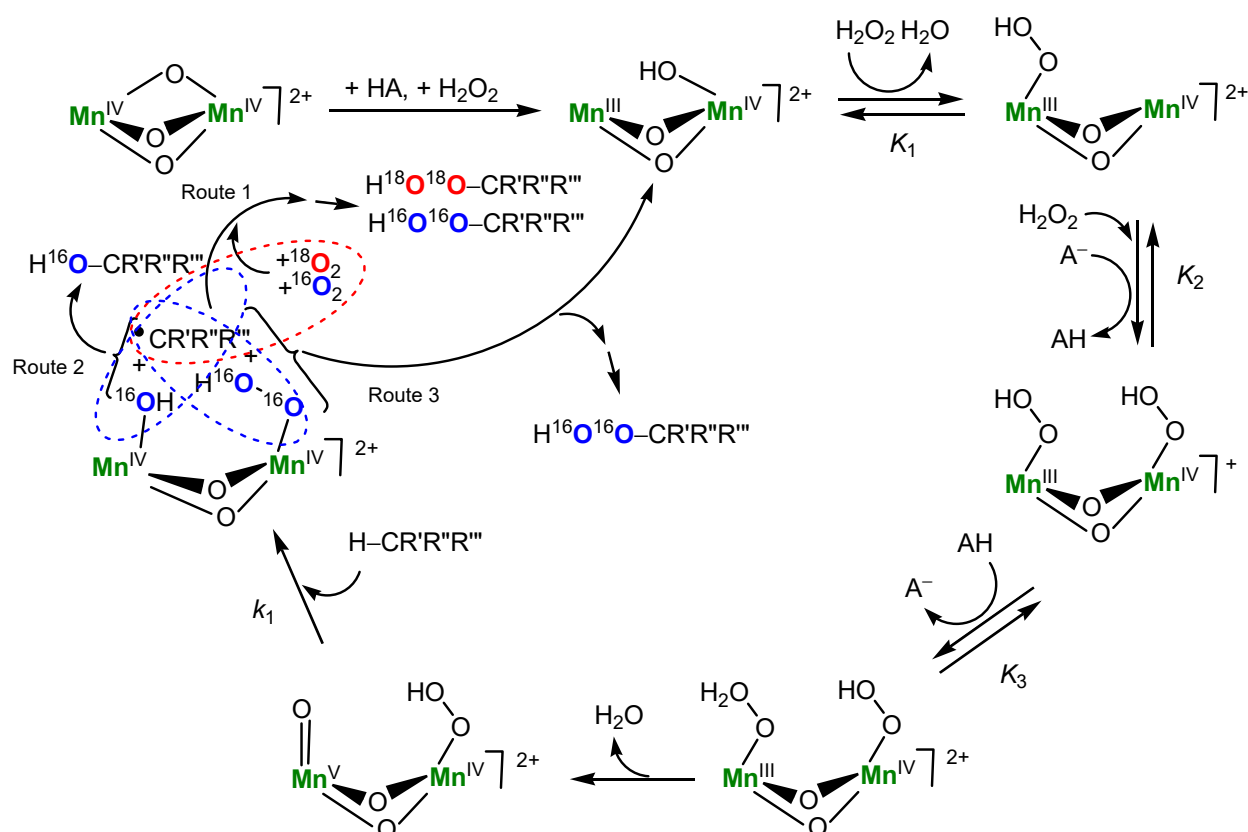


Figure 20. A catalytic cycle proposed for the alkane hydroperoxidation in the presence of $^{18}\text{O}_2$ (in an atmosphere $^{16}\text{O}_2 + ^{18}\text{O}_2$). AH is a carboxylic acid where A is its anion. Adapted from [120], Copyright (2017) with permission of Elsevier.

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.

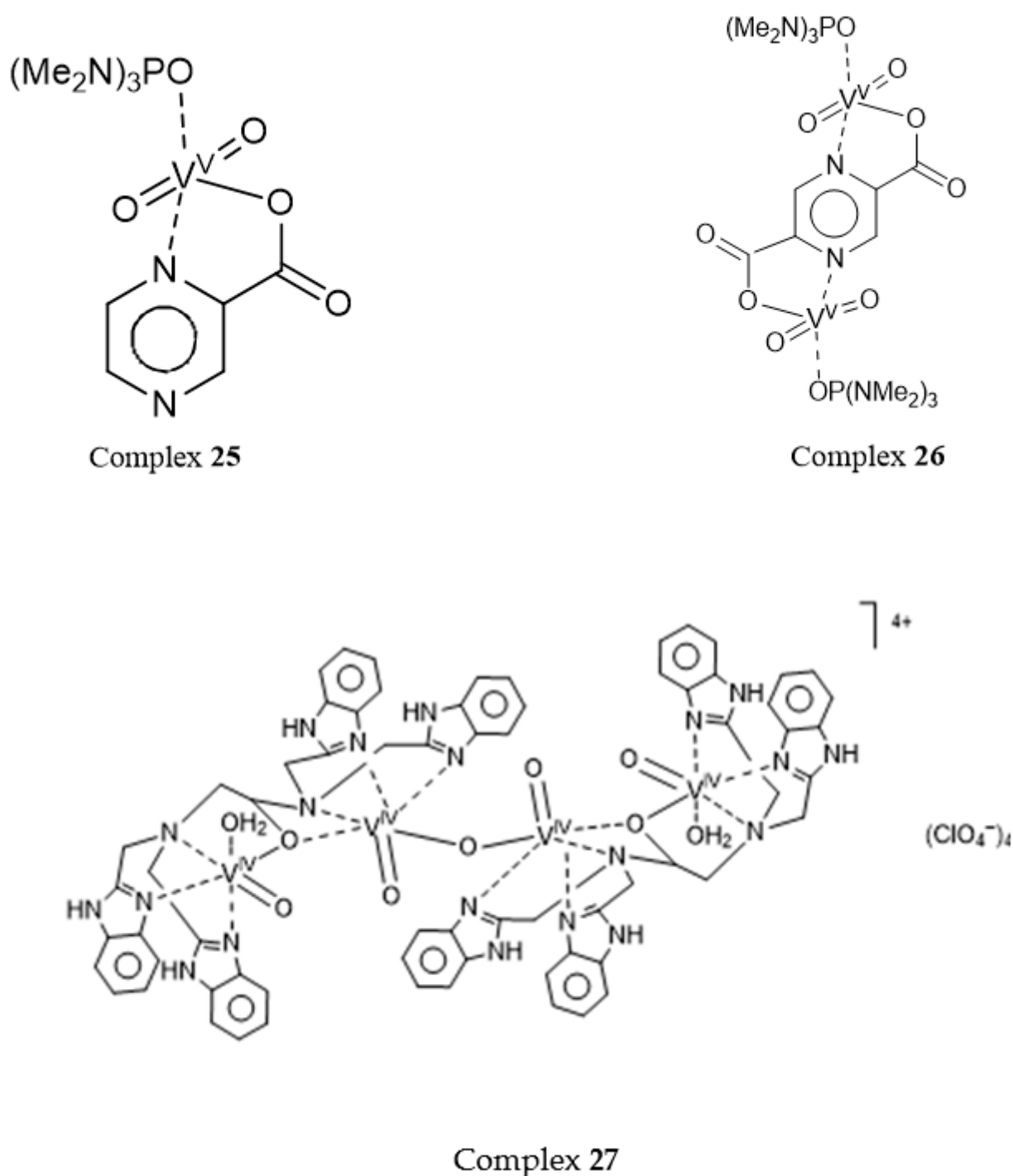


Figure 21. Structures of vanadium complexes 25–27, Adapted from [156], Copyright (2009) with permission of Elsevier.

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].

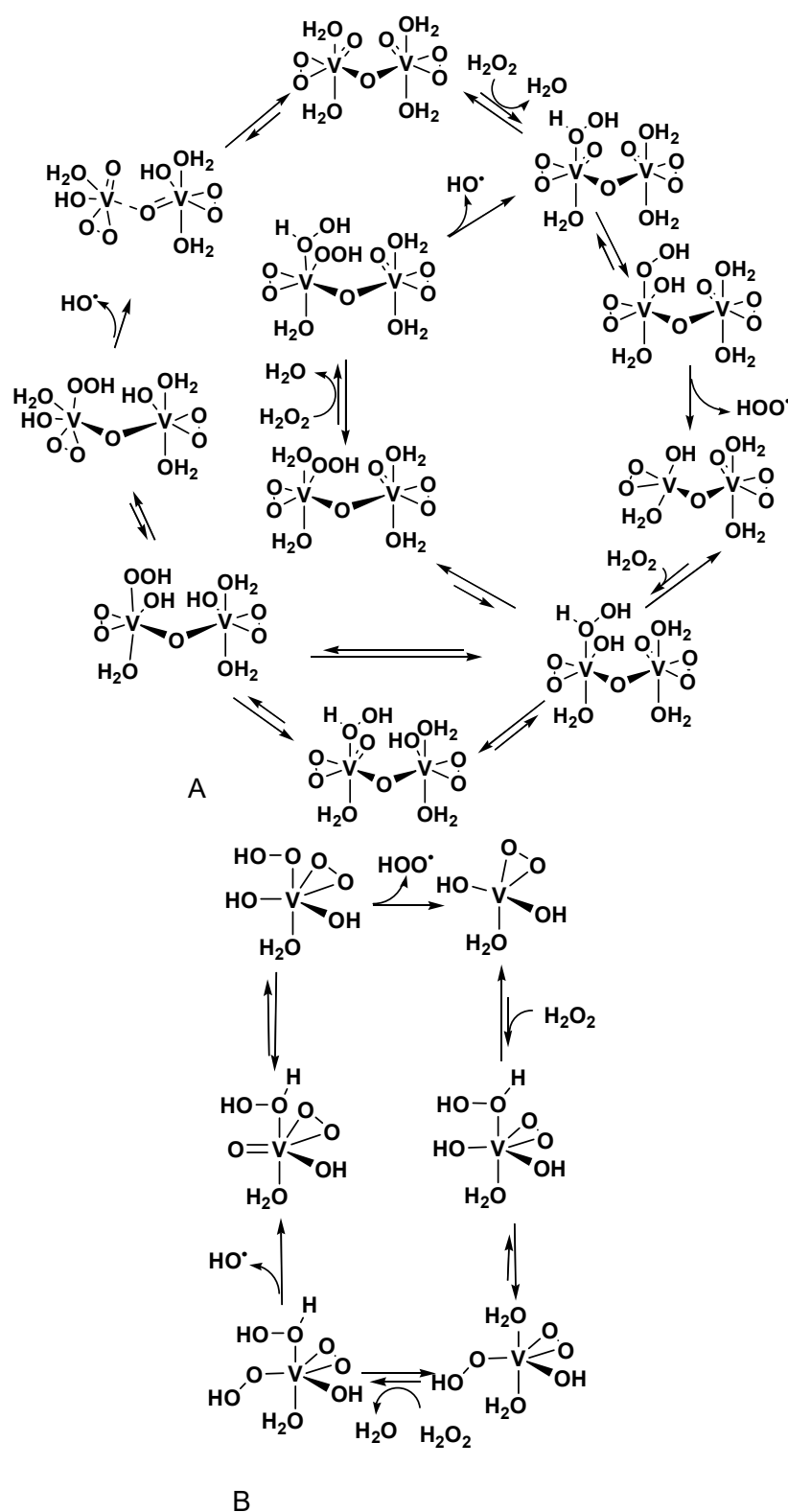


Figure 22. Catalytic cycles of radical generation involving divanadate (A) and monovanadate (B). Adapted from [158], Copyright (2011) with permission of American Chemical Society.

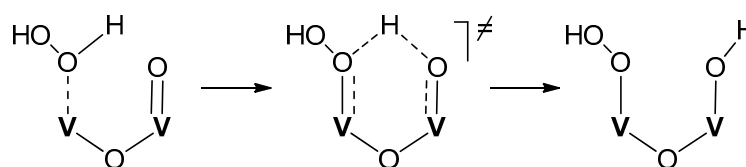
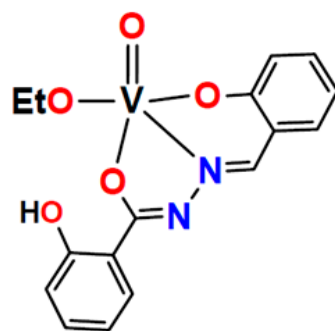


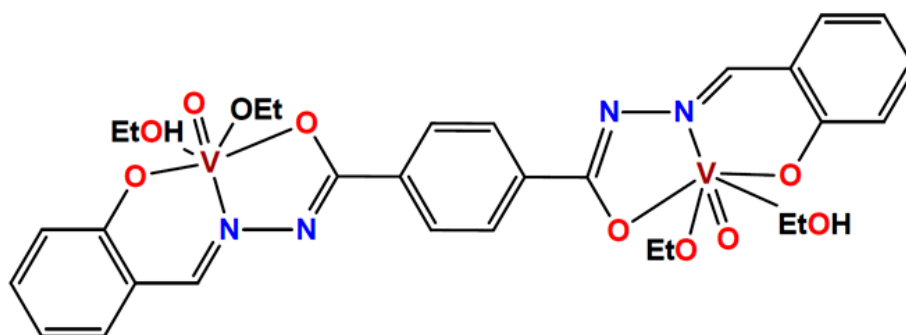
Figure 23. Proton transfer between two vanadium-containing fragments. Adapted from Ref. [158], Copyright (2011) with permission of American Chemical Society.

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 PPh₃) 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 PPh₃ 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 H₂O₂ and an metal ion. The mechanism proposed in Ref. [159] includes at the first step coordination of H₂O₂ to the catalyst molecule, proton transfer from ligated H₂O₂ to the methoxy ligand and elimination of the formed methanol molecule and coordination of the second H₂O₂ molecule followed by HO–OH bond cleavage to give HO•. The activation of the H₂O₂ 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 H₂O₂ ligand. Generated hydroxyl radicals attack the substrate molecules.

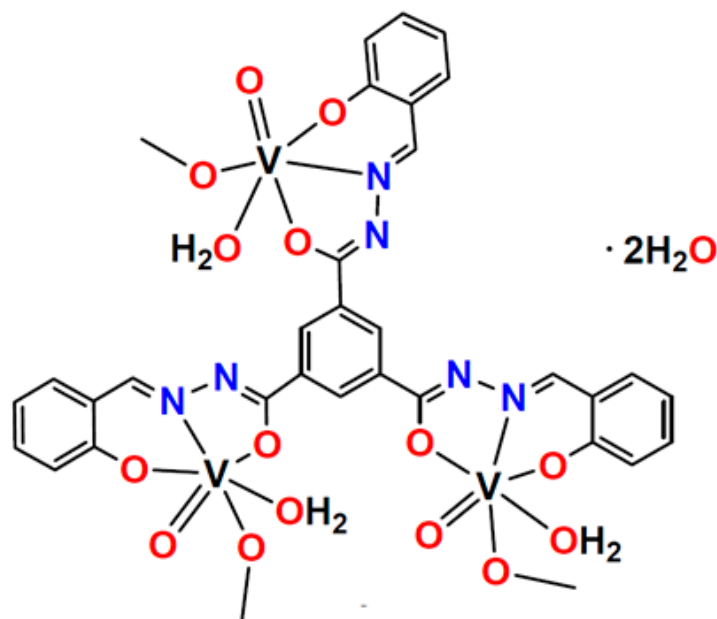
Theoretical DFT calculations were in agreement with previous works on oxidation involving vanadium complexes (Ref. [145]), and led to the conclusion that the global radical type mechanism involves the formation of RO• radicals (or HO• if H₂O₂ is used as an oxidizing agent). Then this radical oxidizes the alkane, a hydrogen atom is removed from the R–H molecule to form the corresponding alkyl radical R•. 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.

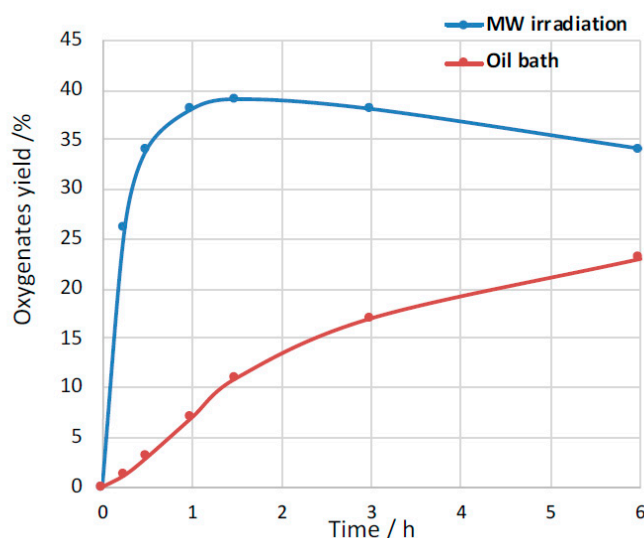
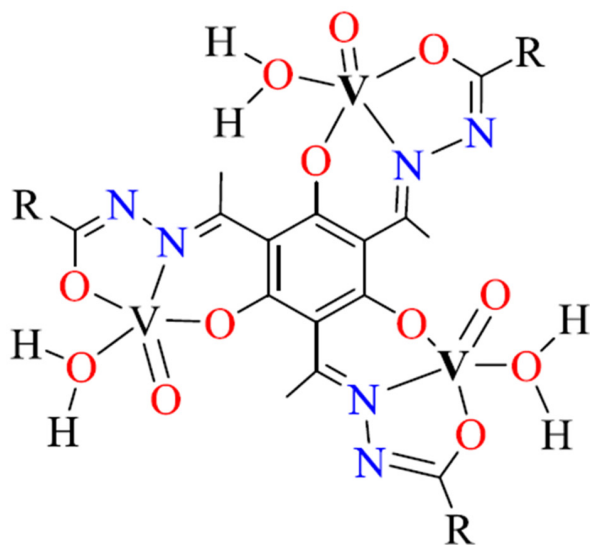


Figure 25. Effect of the heating mode (MW irradiation or oil bath) on the total yield of cyclohexanol and cyclohexanone obtained by neat oxidation of cyclohexane with aq. H_2O_2 catalyzed by complex **30**, adapted from Ref. [159], Copyright (2019) with permission of Royal Society of Chemistry.



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.

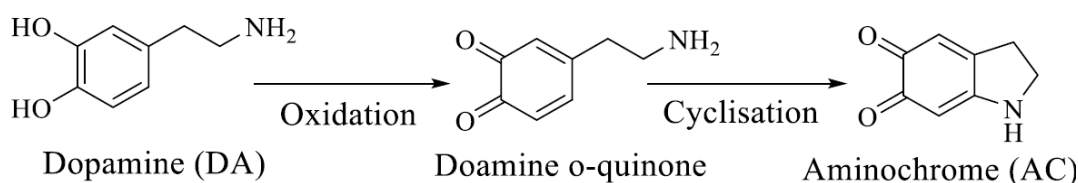


Figure 27. Scheme of oxidation of dopamine.

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.

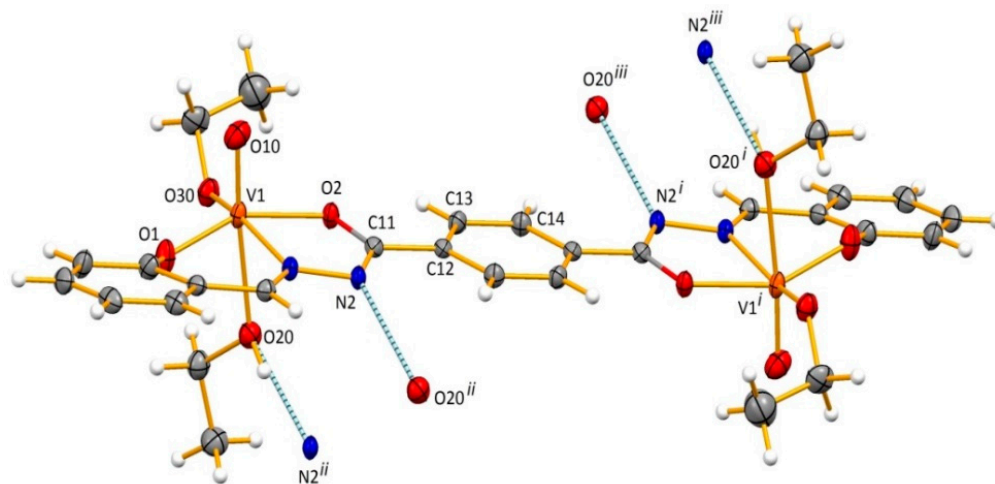


Figure 28. Structure of complex **31** (C₃₀H₃₆N₄O₁₀V₂) Adapted from Ref. [150], Copyright (2013) with permission of Royal Society of Chemistry.

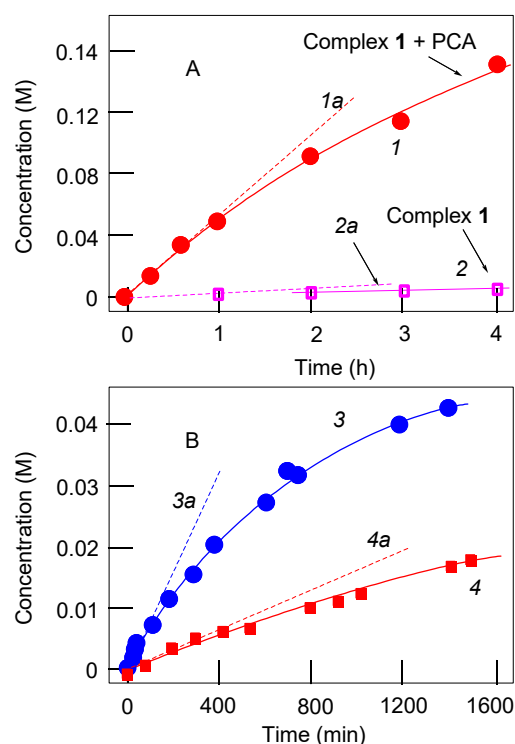
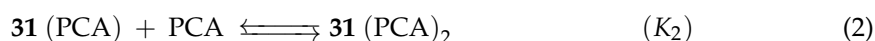


Figure 29. Oxidation of cyclohexane with the H₂O₂/**31**/PCA/CH₃CN–H₂O (curve 1). Curve of accumulation of oxygenates (predominantly cyclohexyl hydroperoxide) in the absence of PCA (curve 2) are shown. For Graph (A): [catalyst **31**]₀ = 2.0 × 10^{−5} M; [PCA]₀ = 0.005 M; [H₂O₂]₀ = 2.2 M (50% aqueous), [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.

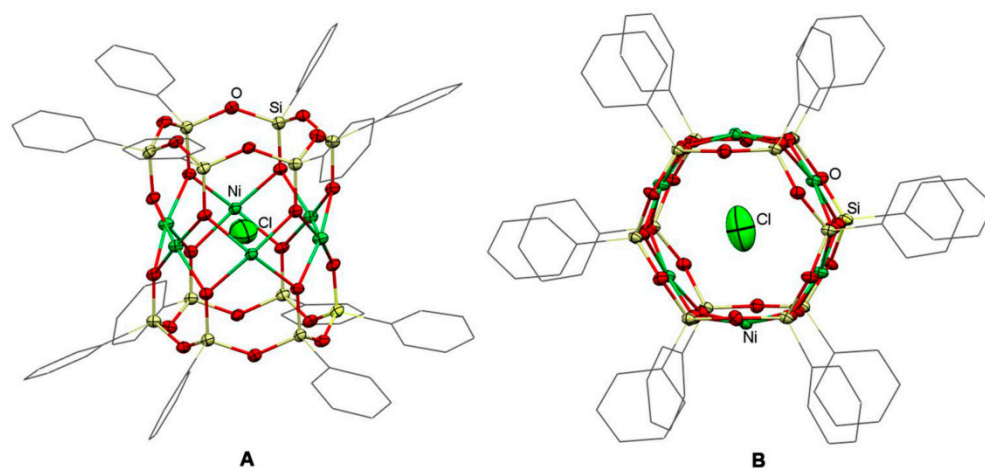


Figure 30. Molecular structure of compound **32** ((A)—side view, (B)—top view). Solvating ligands and counter ion Na^+ are omitted for clarity. Adapted from Ref. [164], Copyright (2016) from Molecules MDPI (Open Access).

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.

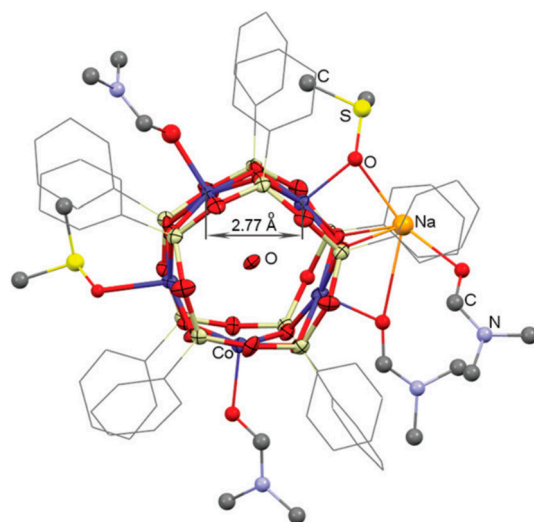
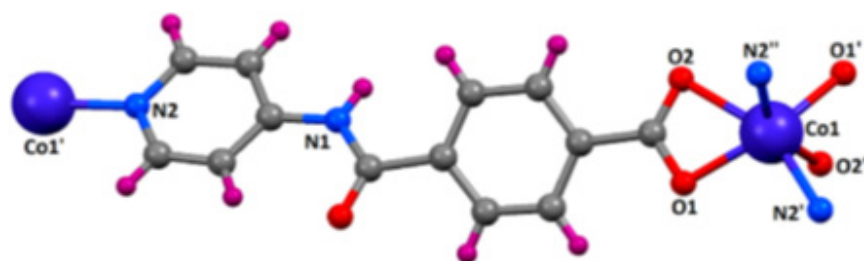
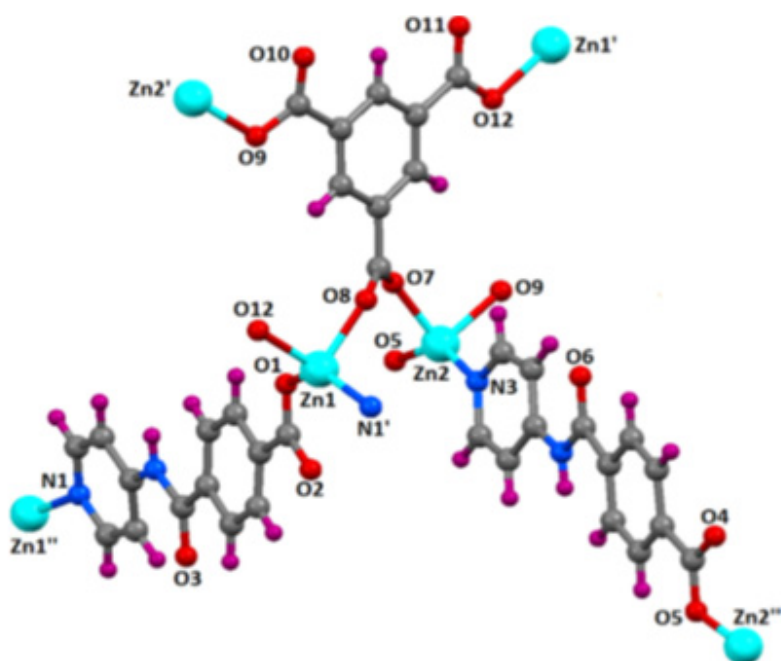


Figure 31. Crystal structure of complex **33**. Color code: Co, blue; Na, orange; Si, light yellow; O, red; C, grey; S, yellow; N, light blue. Adapted from Ref. [165], Copyright (2016) with permission from Royal Society of Chemistry.

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.

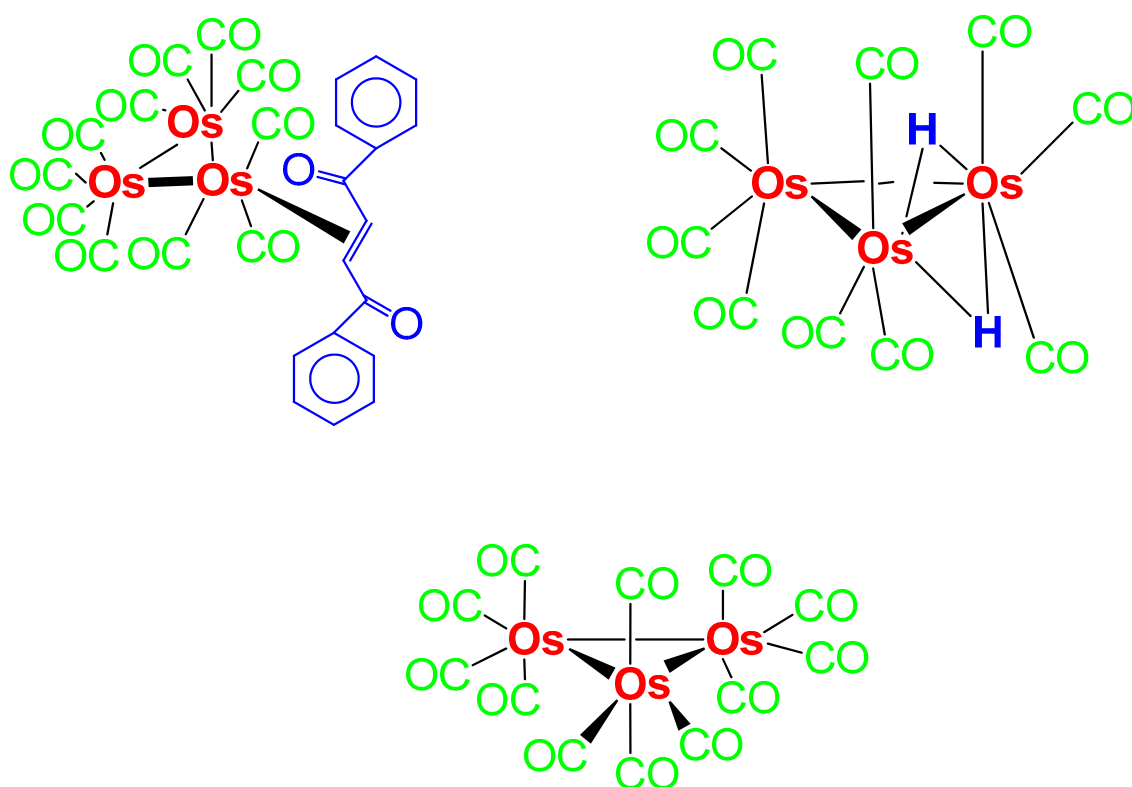


Figure 33. Osmium carbonyls derivatives which extremely efficiently catalyzed the oxidation of alkanes and alcohols with peroxides.

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

References

1. Denisov, E.T.; Afanas'ev, I.B. *Oxidation and Antioxidants in Organic Chemistry and Biology*; Taylor & Francis Group: Abingdon, UK, 2005; ISBN 0-8247-5356-9.
2. Shilov, A.E.; Shul'pin, G.B. *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*; Kluwer Academic Publishers: New York, NY, USA; Boston, MA, USA; Dordrecht, The Netherlands; London, UK; Moscow, Russia, 2002; p. 548. ISBN 978-0-306-46945-9.
3. Ma, Z.; Mahmudov, K.T.; Aliyeva, V.A.; Gurbanov, A.V.; Pombeiro, A.J.L. TEMPO in metal complex catalysis. *Coord. Chem. Rev.* **2020**, *423*, 213482. [\[CrossRef\]](#)
4. Beller, M.; Bolm, C. (Eds.) *Transition Metals for Organic Synthesis*, 2nd ed.; Wiley-VCH: Weinheim, Germany; New York, NY, USA, 2004; ISBN 3-527-30613-7.
5. Shul'pin, G.B. Selectivity in C–H functionalizations. In *Comprehensive Inorganic Chemistry II*, 2nd ed.; Reedijk, J., Poeppelmeier, K., Casella, L., Eds.; Elsevier: Amsterdam, The Netherlands, 2013; Chapter 6.04; Volume 6, pp. 79–104. [\[CrossRef\]](#)
6. Pombeiro, A.J.L. (Ed.) *Advances in Organometallic Chemistry and Catalysis*; Wiley: Hoboken, NJ, USA, 2014; Chapter 1; pp. 3–14. ISBN 978-1-118-51014-8. [\[CrossRef\]](#)
7. Pombeiro, A.J.L.; Guedes da Silva, F.C. (Eds.) *Alkane Functionalization*; Wiley: Hoboken, NJ, USA, 2018; ISBN 978-1-119-37924-9.
8. Bryliakov, K. (Ed.) *Frontiers of Green Catalytic Selective Oxidations*; Springer-Nature: Berlin/Heidelberg, Germany, 2019. [\[CrossRef\]](#)
9. Shilov, A.E.; Shul'pin, G.B. Activation of C–H Bonds by Metal Complexes. *Chem. Rev.* **1997**, *97*, 2879–2932. [\[CrossRef\]](#) [\[PubMed\]](#)
10. Shul'pin, G.B. Metal-catalysed hydrocarbon oxygenations in solutions: The dramatic role of additives: A review. *J. Mol. Catal. A Chem.* **2002**, *189*, 39–66. [\[CrossRef\]](#)
11. Shul'pin, G.B. Metal-catalysed hydrocarbon oxidations. *Comptes Rendus Chim.* **2003**, *6*, 163–178. [\[CrossRef\]](#)
12. Shul'pin, G.B. Hydrocarbon Oxygenations with Peroxides Catalyzed by Metal Compounds. *Mini-Rev. Org. Chem.* **2009**, *6*, 95–104. [\[CrossRef\]](#)
13. Shul'pin, G.B. New Trends in Oxidative Functionalization of Carbon–Hydrogen Bonds: A Review. *Catalysts* **2016**, *6*, 50. [\[CrossRef\]](#)
14. Shul'pin, G.B.; Kozlov, Y.N.; Shul'pina, L.S. Metal Complexes Containing Redox-active Ligands in Oxidation of Hydrocarbons and Alcohols: A Review. *Catalysts* **2019**, *9*, 1046. [\[CrossRef\]](#)
15. Levitsky, M.M.; Bilyachenko, A.N.; Shul'pin, G.B. Oxidation of C–H compounds with peroxides catalyzed by polynuclear transition metal complexes in Si- or Ge-sesquioxane frameworks: A review. *J. Organomet. Chem.* **2017**, *849–850*, 201–218. [\[CrossRef\]](#)
16. Shul'pin, G.B. Selectivity enhancement in functionalization of C–H bonds: A review. *Org. Biomol. Chem.* **2010**, *8*, 4217–4228. [\[CrossRef\]](#)
17. Shul'pin, G.B. C–H functionalization: Thoroughly tuning ligands at a metal ion, a chemist can greatly enhance catalyst's activity and selectivity, Perspective. *Dalton Trans.* **2013**, *42*, 12794–12818. [\[CrossRef\]](#)
18. Kozlov, Y.N.; Nadezhdin, A.D.; Purmal, A.P. Mechanism of initiation in the Fe(3+) + H₂O₂ system. *Kinet. Catal.* **1973**, *14*, 141–148.
19. Shul'pin, G.B.; Nizova, G.V.; Kozlov, Y.N.; Gonzalez Cuervo, L.; Süß-Fink, G. Hydrogen peroxide oxygenation of alkanes including methane and ethane catalyzed by iron complexes in acetonitrile. *Adv. Synth. Catal.* **2004**, *346*, 317–332. [\[CrossRef\]](#)
20. Nizova, G.V.; Krebs, B.; Süß-Fink, G.; Schindler, S.; Westerheide, L.; Gonzalez Cuervo, L.; Shul'pin, G.B. Hydroperoxidation of methane and other alkanes with H₂O₂ catalysed by a dinuclear iron complex and an amino acid. *Tetrahedron* **2002**, *58*, 9231–9237. [\[CrossRef\]](#)
21. Parrilha, G.L.; Ferreira, S.S.; Fernandes, C.; Silva, G.C.; Carvalho, N.M.F.; Antunes, O.A.C.; Drago, V.; Bortoluzzid, A.J.; Horn, A., Jr. Properties of (m-Oxo)di-iron Complexes and Catalytic Activity Toward Cyclohexane Oxidation. *J. Braz. Chem. Soc.* **2010**, *21*, 603–613. [\[CrossRef\]](#)
22. Mayilmurugan, R.; Stoekli-Evans, H.; Suresh, E.; Palaniandavar, M. Chemoselective and biomimetic hydroxylation of hydrocarbons by non-heme l-oxo-bridged diiron(III) catalysts using *m*-CPBA as oxidant. *Dalton Trans.* **2009**, 5101–5114. [\[CrossRef\]](#)
23. Sorokin, A.B.; Kudrik, E.V.; Bouchub, D. Bio-inspired oxidation of methane in water catalyzed by N-bridged diiron phthalocyanine complex. *Chem. Commun.* **2008**, 2562–2564. [\[CrossRef\]](#)
24. Kudrik, E.V.; Afanasiev, P.; Alvarez, L.X.; Dubourdeaux, P.; Cle'mancey, M.; Latour, J.-M.; Blondin, G.; Bouchu, D.; Albrieux, F.; Nefedov, S.E.; et al. An N-bridged high-valent diiron-oxo species on a porphyrin platform that can oxidize methane. *Nat. Chem.* **2012**, *4*, 1024–1029. [\[CrossRef\]](#)
25. Groves, J.T.; Haushalter, R.C.; Nakamura, M.; Nemo, T.E.; Evans, B.J. High-valent iron-porphyrin complexes related to peroxidase and cytochrome P-450. *J. Am. Chem. Soc.* **1981**, *103*, 2884–2886. [\[CrossRef\]](#)

26. Seo, M.S.; Kim, N.H.; Cho, K.-B.; So, J.E.; Park, S.K.; Clémancey, M.; Garcia-Serres, R.; Latour, J.-M.; Shaik, S.; Nam, W. A mononuclear non-heme iron(IV)-oxo complex which is more reactive than cytochrome P450 model compound I. *Chem. Sci.* **2011**, *2*, 1039–1045. [\[CrossRef\]](#)
27. Karslyan, E.E.; Shul'pina, L.S.; Kozlov, Y.N.; Pombeiro, A.J.L.; Shul'pin, G.B. Oxygenation of saturated and aromatic hydrocarbons with H₂O₂ catalyzed by the carbonyl thiophenolate iron complex (OC)₃Fe(PhS)₂Fe(CO)₃. *Catal. Today* **2013**, *218–219*, 93–98. [\[CrossRef\]](#)
28. Rabe, V.; Frey, W.; Baro, A.; Laschat, S.; Bauer, M.; Bertagnolli, H.; Rajagopalan, S.; Asthalter, T.; Roduner, E.; Dilger, H.; et al. Syntheses, Crystal Structures, Spectroscopic Properties, and Catalytic Aerobic Oxidations of Novel Trinuclear Non-Heme Iron Complexes. *Eur. J. Inorg. Chem.* **2009**, 4660–4674. [\[CrossRef\]](#)
29. Romakh, V.B.; Therrien, B.; Süß-Fink, G.; Shul'pin, G.B. Synthesis, molecular structure and catalytic potential of the tetrairon complex [Fe₄(N₃O₂-L)₄(μ-O)₂]⁴⁺ (L = 1-carboxymethyl-4,7-dimethyl-1,4,7-triazacyclononane). *Inorg. Chem.* **2007**, *46*, 3166–3175. [\[CrossRef\]](#) [\[PubMed\]](#)
30. Jarenmark, M.; Turitsyna, E.A.; Haukka, M.; Shteinman, A.A.; Nordlander, E. A monocarboxylate-bridged diiron(III) I-oxido complex that catalyzes alkane oxidation by hydrogen peroxide. *New J. Chem.* **2010**, *34*, 2118–2121. [\[CrossRef\]](#)
31. Nesterov, D.S.; Chygorin, E.N.; Kokozay, V.N.; Bon, V.V.; Bocča, R.; Kozlov, Y.N.; Shul'pina, L.S.; Jezierska, J.; Ozarowski, A.; Pombeiro, A.J.L.; et al. Heterometallic Co^{III}₄Fe^{III}₂ Schiff Base Complex: Structure, Electron Paramagnetic Resonance, and Alkane Oxidation Catalytic Activity. *Inorg. Chem.* **2012**, *51*, 9110–9122. [\[CrossRef\]](#)
32. Quesne, M.G.; Senthilnathan, D.; Singh, D.; Kumar, D.; Maldivi, P.; Sorokin, A.B.; de Visser, S.P. Origin of the enhanced reactivity of μ-nitrido-bridged diiron(IV)-oxo porphyrinoid complexes over cytochrome P450 Compound I. *ACS Catal.* **2016**, *6*, 2230–2243. [\[CrossRef\]](#)
33. Gomez, L.; Canta, M.; Font, D.; Prat, I.; Ribas, X.; Costas, M. Regioselective Oxidation of Nonactivated Alkyl C–H Groups Using Highly Structured Non-Heme Iron Catalysts. *J. Org. Chem.* **2013**, *78*, 1421–1433. [\[CrossRef\]](#)
34. Olivo, G.; Cussy, O.; Borrell, M.; Costas, M. Oxidation of alkane and alkene moieties with biologically inspired nonheme iron catalysts and hydrogen peroxide: From free radicals to stereoselective transformations. *J. Biol. Inorg. Chem.* **2017**, *22*, 425–452. [\[CrossRef\]](#)
35. Karmakar, A.; Martins, L.M.; Yahorava, Y.; Guedes da Silva, F.; Pombeiro, A.J.L. Synthesis, Structures, Electrochemistry, and Catalytic Activity towards Cyclohexanol Oxidation of Mono-, Di-, and Polynuclear Iron(III) Complexes with 3-Amino-2-Pyrazinecarboxylate. *Appl. Sci.* **2020**, *10*, 2692. [\[CrossRef\]](#)
36. Lyakin, K.P.; Talsi, E.P. Non-heme oxoiron(V) intermediates in chemo-, regio- and stereoselective oxidation of organic substrates. *Coord. Chem. Rev.* **2019**, *384*, 126–139. [\[CrossRef\]](#)
37. Ouyang, J.; Haotian, S.; Liang, Y.; Commisso, A.; Li, D.; Xu, R.; Yu, D. Recent Progress in Metal-containing Silsesquioxanes: Preparation and Application. *Curr. Org. Chem.* **2017**, *21*, 2829–2848. [\[CrossRef\]](#)
38. Levitsky, M.M.; Bilyachenko, A.N.; Shubina, E.S. Cagelike metallagermanates and metallagermoxanes: Synthesis, structures and functional properties. A review. *Coord. Chem. Rev.* **2019**, *386*, 209–239. [\[CrossRef\]](#)
39. Bilyachenko, A.N.; Levitsky, M.M.; Yalymov, A.I.; Korlyukov, A.A.; Vologzhanina, A.V.; Kozlov, Y.N.; Shul'pina, L.S.; Nesterov, D.S.; Pombeiro, A.J.L.; Lamaty, F.; et al. A heterometallic (Fe₆Na₈) cage-like silsesquioxane: Synthesis, structure, spin glass behavior and high catalytic activity. *RSC Adv.* **2016**, *6*, 48165–48180. [\[CrossRef\]](#)
40. Bilyachenko, A.N.; Levitsky, M.M.; Yalymov, A.I.; Korlyukov, A.A.; Khrustalev, V.N.; Vologzhanina, A.V.; Shul'pina, L.S.; Ikonnikov, N.S.; Trigub, A.E.; Dorovatovsky, P.V.; et al. Cage-like Fe₆Na₈-Germesquioxanes: Structure, Magnetism, and Catalytic Activity, English Version. *Angew. Chem. Int. Ed.* **2016**, *55*, 15360–15363. [\[CrossRef\]](#) [\[PubMed\]](#)
41. Yalymov, A.I.; Bilyachenko, A.N.; Levitsky, M.M.; Korlyukov, A.A.; Khrustalev, V.N.; Shul'pina, L.S.; Dorovatovskii, P.V.; Es'kova, M.A.; Lamaty, F.; Bantreil, X.; et al. High Catalytic Activity of Heterometallic (Fe₆Na₇ and Fe₆Na₆) Cage Silsesquioxanes in Oxidations with Peroxides. *Catalysts* **2017**, *7*, 101. [\[CrossRef\]](#)
42. Collins, T.J.; Ryabov, A.D. Targeting of High-Valent Iron-TAML Activators at Hydrocarbons and Beyond. *Chem. Rev.* **2017**, *117*, 9140–9162. [\[CrossRef\]](#)
43. Fürstner, A. Iron Catalysis in Organic Synthesis: A Critical Assessment of What It Takes to Make This Base Metal a Multitasking Champion. *ACS Cent. Sci.* **2016**, *2*, 778–789. [\[CrossRef\]](#) [\[PubMed\]](#)
44. Sun, X.; Li, J.; Huang, X.; Sun, C. Recent Advances in Iron-Catalyzed C–H Bond Activation Reactions. *Curr. Inorg. Chem.* **2012**, *2*. [\[CrossRef\]](#)
45. Schreder, K.; Junge, K.; Bitterlich, B.; Beller, M. Fe-Catalyzed Oxidation Reactions of Olefins, Alkanes, and Alcohols: Involvement of Oxo- and Peroxo Complexes. In *a Book Iron Catalysis*; Plietker, B., Ed.; Springer: Berlin/Heidelberg, Germany, 2011; Volume 33, pp. 83–109. ISBN 978-3-642-14670-1. [\[CrossRef\]](#)
46. Sun, C.-L.; Li, B.-J.; Shi, Z.-J. Direct C–H transformation via iron catalysis. *Chem. Rev.* **2011**, *111*, 1293–1314. [\[CrossRef\]](#)
47. Lee, C.; Sedlak, D.L. A novel homogeneous Fenton-like system with Fe(III)–phosphotungstate for oxidation of organic compounds at neutral pH values. *J. Mol. Catal. A Chem.* **2009**, *311*, 1–6. [\[CrossRef\]](#)
48. Mitra, M.; Nimir, H.; Hrovat, D.A.; Shteinman, A.A.; Richmond, M.G.; Costas, M.; Nordlander, E. Catalytic C–H Oxidations by Nonheme Mononuclear Fe(II) Complexes of Two Pentadentate Ligands: Evidence for an Fe(IV) Oxo Intermediate. *J. Mol. Catal.* **2016**, *426*, 350–356. [\[CrossRef\]](#)

49. Schreder, K.; Join, B.; Amali, A.J.; Junge, K.; Ribas, X.; Costas, M.; Beller, M. A Biomimetic Iron Catalyst for the Epoxidation of Olefins with Molecular Oxygen at Room Temperature. *Angew. Chem. Int. Ed.* **2011**, *50*, 1425–1429. [CrossRef] [PubMed]
50. Retcher, B.; Costa, J.S.; Tanga, J.; Hage, R.; Gamez, P.; Reedijk, J. Unexpected high oxidation of cyclohexane by Fe salts and dihydrogen peroxide in acetonitrile. *J. Mol. Catal. A Chem.* **2008**, *286*, 1–5. [CrossRef]
51. Nam, W.; Lee, Y.-M.; Fukuzumi, S. Tuning Reactivity and Mechanism in Oxidation Reactions by Mononuclear Nonheme Iron(IV)-Oxo Complexes. *Acc. Chem. Res.* **2014**, *47*, 1146–1154. [CrossRef] [PubMed]
52. Bilis, G.; Louloudi, M. The Catalytic Function of Nonheme Iron (III) Complex for Hydrocarbon Oxidation. *Bioinorg. Chem. Appl.* **2010**, *2010*, 861892. [CrossRef]
53. Gomez, L.; Garcia-Bosch, I.; Company, A.; Benet-Buchholz, J.; Polo, A.; Sala, X.; Ribas, X.; Costas, M. Stereospecific C–H Oxidation with H₂O₂ Catalyzed by a Chemically Robust Site-Isolated Iron Catalyst. *Angew. Chem. Int. Ed.* **2009**, *48*, 5720–5723. [CrossRef]
54. England, J.; Gondhia, R.; Bigorra-Lopez, L.; Petersen, A.R.; White, A.J.P.; Britovsek, G.J.P. Towards robust alkane oxidation catalysts: Electronic variations in non-heme iron(II) complexes and their effect in catalytic alkane oxidation. *Dalton Trans.* **2009**, 5319–5334. [CrossRef]
55. Stanje, B.; Traar, P.; Schachner, J.; Belaj, F.; Mösch-Zanetti, N.C. Iron catalyzed oxidation of benzylic alcohols to benzoic acids. *Dalt. Trans.* **2018**, *47*, 6412–6420. [CrossRef]
56. Jaafar, H.; Vileno, B.; Thibon, A.; Mandon, D. Tuning the conversion of cyclohexane into cyclohexanol/one by molecular dioxygen, protons and reducing agents at a single non-porphyrinic iron centre and chemical versatility of the tris(2-pyridylmethyl)amine TPAFeIIICl₂ complex in mild oxidation chemistry. *Dalton Trans.* **2011**, *40*, 92–106. [CrossRef]
57. Bitterlich, B.; Anilkumar, G.; Gelalcha, G.F.; Spilker, B.; Grotevendt, A.; Jackstell, R.; Kin Tse, M.; Beller, M. Development of a General and Efficient Iron-Catalyzed Epoxidation with Hydrogen Peroxide as Oxidant. *Chem. Asian J.* **2007**, *2*, 521–529. [CrossRef]
58. Garcia-Bosch, I.; Codol, Z.; Prat, I.; Ribas, X.; Lloret-Fillol, J.; Costas, M. Iron-Catalyzed C–H Hydroxylation and Olefin cis-Dihydroxylation Using a Single-Electron Oxidant and Water as the Oxygen-Atom Source. *Chem. Eur. J.* **2012**, *18*. [CrossRef]
59. Yang, Z.; Qian, J.; Yu, A.; Pan, B. Singlet oxygen mediated iron-based Fenton-like catalysis under nanoconfinement. *Proc. Natl. Acad. Sci. USA* **2019**, *116*, 6659–6664. [CrossRef] [PubMed]
60. Lopes de Araújo, M.; Correia, G.A.; Carvalho, W.A.; Shul'pina, L.S.; Kozlov, Y.N.; Shul'pin, G.B.; Mandelli, D. The effect of additives (pyrazine, pyrazole and their derivatives) in the oxidation with FeCl₃–H₂O₂ in aqueous solutions. *Catal. Today* **2020**. [CrossRef]
61. Kirillov, A.M.; Kirillova, M.V.; Pombeiro, A.J.L. Multicopper complexes and coordination polymers for mild oxidative functionalization of alkanes. *Coord. Chem. Rev.* **2012**, *256*, 2741–2759. [CrossRef]
62. Calero, R.; Vega, A.; María García, A.; Spodine, E.; Manzur, J. Oxidation and Catalytic Properties of a Binuclear Copper(I) Complex with a Meta-Xylyl Spacer Ligand. *J. Chil. Chem. Soc.* **2003**, *48*. [CrossRef]
63. Wurtele, C.; Sander, O.; Lutz, V.; Waitz, T.; Tuzek, F.; Schindler, S. Aliphatic C–H Bond Oxidation of Toluene Using Copper Peroxo Complexes That Are Stable at Room Temperature. *J. Am. Chem. Soc.* **2009**, *131*, 7544–7545. [CrossRef] [PubMed]
64. Kirillov, A.M.; Kirillova, M.V.; Shul'pina, L.S.; Figiel, P.J.; Gruenwald, K.R.; Guedes da Silva, M.F.C.; Haukka, M.; Pombeiro, A.J.L.; Shul'pin, G.B. Mild oxidative functionalization of alkanes and alcohols catalyzed by new mono- and dicopper(II) aminopolyalcoholates. *J. Mol. Catal. A Chem.* **2011**, *350*, 26–34. [CrossRef]
65. Song, X.; Yan, Y.; Wang, Y.; Hu, D.; Xiao, L.; Yu, J.; Zhang, W.; Jia, M. Hybrid compounds assembled from copper-triazole complexes and phosphomolybdic acid as advanced catalysts for the oxidation of olefins with oxygen. *Dalton Trans.* **2017**, *47*, 16655–16662. [CrossRef]
66. Kirillov, A.M.; Karabach, Y.Y.; Kirillova, M.V.; Haukka, M.; Pombeiro, A.J.L. New diamondoid-like [Cu₃B(l-O)₆] core self-assembled from Bis-Tris biobuffer for mild hydrocarboxylation of alkanes to carboxylic acids. *Dalton Trans.* **2011**, *40*, 6378. [CrossRef]
67. Sutradhar, M.; Alegria, C.B.A.E.; Guedes da Silva, M.F.C.; Liu, C.-M.; Pombeiro, A.J.L. Peroxidative Oxidation of Alkanes and Alcohols under Mild Conditions by Di- and Tetranuclear Copper (II) Complexes of Bis (2-Hydroxybenzylidene) Isophthalohydrazide. *Molecules* **2018**, *23*, 2699. [CrossRef]
68. Nandi, M.; Roy, P. Peroxidative oxidation of cycloalkane by di-, tetra- and polynuclear copper (II) complexes. *Indian J. Chem.* **2013**, *52*, 1263–1268. Available online: <http://hdl.handle.net/123456789/21507>.
69. Saha, M.; Vyas, M.K.; Martins, L.M.D.R.S.; Martins, N.M.R.; Pombeiro, A.J.L.; Mobin, S.M.; Bhattacharjee, D.; Bhabak, K.P.; Mukhopadhyay, S. Copper(II) tetrazolato complexes: Role in oxidation catalysis and protein binding. *Polyhedron* **2017**, *132*, 53–63. [CrossRef]
70. Sutradhar, M.; Roy Barman, T.; Pombeiro, A.J.L.; Martins, L.M.D.R.S. Aroylhydrazone Schiff Base Derived Cu(II) and V(V) Complexes: Efficient Catalysts towards Neat Microwave-Assisted Oxidation of Alcohols. *Int. J. Mol. Sci.* **2020**, *21*, 2832. [CrossRef] [PubMed]
71. Shiota, Y.; Yoshizawa, K. Comparison of the Reactivity of Bis(μ -oxo)CuIICuIII and CuIIICuIII Species to Methane. *Inorg. Chem.* **2009**, *48*. [CrossRef] [PubMed]
72. Shul'pina, L.S.; Vinogradov, M.M.; Kozlov, Y.N.; Nelyubina, Y.V.; Ikonnikov, N.S.; Shul'pin, G.B. Copper complexes with 1,10-phenanthrolines as efficient catalysts for oxidation of alkanes by hydrogen peroxide. *Inorg. Chem. Acta* **2020**, *512*, 119889. [CrossRef]

73. Bilyachenko, A.N.; Dronova, M.S.; Yalymov, A.I.; Korlyukov, A.A.; Shul'pina, L.S.; Arkhipov, D.E.; Shubina, E.S.; Levitsky, M.M.; Kirilin, A.D.; Shul'pin, G.B. New binuclear cage-like copper(II) silsesquioxane ("cooling tower"); its high catalytic activity in oxidation of benzene and alcohols. *Eur. J. Inorg. Chem.* **2013**, *30*, 5240–5246. [CrossRef]
74. Dronova, M.S.; Bilyachenko, A.N.; Yalymov, A.I.; Kozlov, Y.N.; Shul'pina, L.S.; Korlyukov, A.A.; Arkhipov, D.E.; Levitsky, M.M.; Shubina, E.S.; Shul'pin, G.B. Solvent-controlled synthesis of tetranuclear cage-like copper(II) silsesquioxanes. Remarkable features of the cage structures and their high catalytic activity in oxidation with peroxides. *Dalton Trans.* **2014**, *43*, 872–882. [CrossRef]
75. Vinogradov, M.M.; Kozlov, Y.N.; Bilyachenko, A.N.; Nesterov, D.S.; Shul'pina, L.S.; Zubavichus, Y.V.; Pombeiro, A.J.L.; Levitsky, M.M.; Yalymov, A.I.; Shul'pin, G.B. Alkane oxidation with peroxides catalyzed by cage-like copper(II) silsesquioxanes. *New J. Chem.* **2015**, *39*, 187–199. [CrossRef]
76. Bilyachenko, A.N.; Dronova, M.S.; Yalymov, A.I.; Lamaty, F.; Bantreil, X.; Martinez, J.; Bizet, C.; Shul'pina, L.S.; Korlyukov, A.A.; Arkhipov, D.E.; et al. Cage-like Copper(II) Silsesquioxanes: Transmetalation Reactions, Structural, Quantum Chemical and Catalytic Studies. *Chem. Eur. J.* **2015**, *21*, 8758–8770. [CrossRef]
77. Bilyachenko, A.N.; Kulakova, A.N.; Levitsky, M.M.; Petrov, A.A.; Korlyukov, A.A.; Shul'pina, L.S.; Khrustalev, V.N.; Dorovatovskii, P.V.; Vologzhanina, A.V.; Tsareva, U.S.; et al. Unusual Tri-, Hexa- and Nonanuclear Organosilicon Copper Clusters: Synthesis, Structures and Catalytic Activity in Oxidations with Peroxides. *Inorg. Chem.* **2017**, *56*, 4093–4103. [CrossRef]
78. Bilyachenko, A.N.; Kulakova, A.N.; Levitsky, M.M.; Korlyukov, A.A.; Khrustalev, V.N.; Vologzhanina, A.V.; Titov, A.A.; Dorovatovskii, P.V.; Shul'pina, L.S.; Lamaty, F.; et al. Ionic Complexes of Tetra- and Nonanuclear Cage Copper(II) Phenylsilsesquioxanes: Synthesis and High Activity in Oxidative Catalysis. *ChemCatChem* **2017**, *9*, 4437–4447. [CrossRef]
79. Kulakova, A.N.; Bilyachenko, A.N.; Levitsky, M.M.; Khrustalev, V.N.; Korlyukov, A.A.; Zubavichus, Y.V.; Dorovatovskii, P.V.; Lamaty, F.; Bantreil, X.; Villemejeanne, B.; et al. Si₁₀Cu₆N₄ Cage Hexacoppersilsesquioxanes Containing N-Ligands: Synthesis, Structure, and High Catalytic Activity in Peroxide Oxidations. *Inorg. Chem.* **2017**, *56*, 15026–15040. [CrossRef] [PubMed]
80. Bilyachenko, A.N.; Levitsky, M.M.; Khrustalev, V.N.; Zubavichus, Y.V.; Shul'pina, L.S.; Shubina, E.S.; Shul'pin, G.B. Mild and Regioselective Hydroxylation of Methyl Group in Neocuproine: Approach to an N,O-Ligated Cu₆ Cage Phenylsilsesquioxane". *Organometallics* **2018**, *37*, 168–171. [CrossRef]
81. Bilyachenko, A.N.; Levitsky, M.M.; Korlyukov, A.A.; Khrustalev, V.N.; Zubavichus, Y.V.; Shul'pina, L.S.; Shubina, E.S.; Vologzhanina, A.V.; Shul'pin, G.B. Heptanuclear Cage Cu^{II}-Silsesquioxanes: Synthesis, Structure and Catalytic Activity. *Eur. J. Inorg. Chem.* **2018**, *22*, 2505–2511. [CrossRef]
82. Bilyachenko, A.N.; Kulakova, A.N.; Shul'pina, L.S.; Levitsky, M.M.; Korlyukov, A.A.; Khrustalev, V.N.; Zubavichus, Y.V.; Dorovatovskii, P.V.; Tsareva, U.S.; Shubina, E.S.; et al. Family of penta- and hexanuclear metallasilsesquioxanes: Synthesis, structure and catalytic properties in oxidations. *J. Organometal. Chem.* **2018**, *867*, 133–141. [CrossRef]
83. Astakhov, G.S.; Bilyachenko, A.N.; Korlyukov, A.A.; Levitsky, M.M.; Shul'pina, L.S.; Bantreil, X.; Lamaty, F.; Vologzhanina, A.V.; Shubina, E.S.; Dorovatovskii, P.V.; et al. High cluster (Cu₉) cage silsesquioxanes. Synthesis, structure and catalytic activity. *Inorg. Chem.* **2018**, *57*, 11524–11529. [CrossRef]
84. Kulakova, A.N.; Bilyachenko, A.N.; Korlyukov, A.A.; Shul'pina, L.S.; Bantreil, X.; Lamaty, F.; Shubina, E.S.; Levitsky, M.M.; Ikonnikov, N.S.; Shul'pin, G.B. A new "bicycle helmet"-like copper(II),sodiumphenylsilsesquioxane. Synthesis, structure and catalytic activity. *Dalton Trans.* **2018**, *47*, 15666–15669. [CrossRef]
85. Astakhov, G.S.; Bilyachenko, A.N.; Levitsky, M.M.; Shul'pina, L.S.; Korlyukov, A.A.; Zubavichus, Y.V.; Khrustalev, V.N.; Vologzhanina, A.V.; Shubina, E.S.; Dorovatovskii, P.V.; et al. Coordination Affinity of Cu(II)-Based Silsesquioxanes toward N,N-Ligands and Associated Skeletal Rearrangements: Cage and Ionic Products Exhibiting a High Catalytic Activity in Oxidation Reactions. *Inorg. Chem.* **2020**, *59*, 4536–4545. [CrossRef]
86. Kulakova, A.N.; Khrustalev, V.N.; Zubavichus, Y.V.; Shul'pina, L.S.; Shubina, E.S.; Levitsky, M.M.; Ikonnikov, N.S.; Bilyachenko, A.N.; Kozlov, Y.N.; Shul'pin, G.B. Palanquin-like Cu₄Na₄ Silsesquioxane. Synthesis (via oxidation of 1,1-bis(diphenylphosphino)methane), structure and catalytic activity in alkane or alcohol oxidation with peroxides. *Catalysts* **2019**, *9*, 154. [CrossRef]
87. Kulakova, A.N.; Bilyachenko, A.N.; Khrustalev, V.N.; Zubavichus, Y.V.; Dorovatovskii, P.V.; Shul'pina, L.S.; Bantreil, X.; Lamaty, F.; Shubina, E.S.; Levitsky, M.M.; et al. Cu₄₂Ge₂₄Na₄—A Giant Trimetallic Sesquioxane Cage: Synthesis, Structure, and Catalytic Activity. *Catalysts* **2018**, *8*, 484. [CrossRef]
88. Kulakova, A.N.; Korlyukov, A.A.; Zubavichus, Y.V.; Khrustalev, V.N.; Bantreil, X.; Shul'pina, L.S.; Levitsky, M.M.; Ikonnikov, N.S.; Shubina, E.S.; Lamaty, F.; et al. Hexacoppergermsesquioxanes as complexes with N-ligands: Synthesis, structure and catalytic properties. *J. Organometal. Chem.* **2019**, *884*, 17–28. [CrossRef]
89. Kulakova, A.N.; Sedykh, E.E.; Levitsky, M.M.; Dorovatovskii, P.V.; Khrustalev, V.N.; Shul'pina, L.S.; Shubina, E.S.; Kozlov, Y.N.; Ikonnikov, N.S.; Bilyachenko, A.N.; et al. The first tris-heteroleptic copper cage, ligated by germsesquioxanes, 2,2'-bipyridines and 3,5-dimethylpyrazolates. Synthesis, structure and unique catalytic activity in oxidation of alkanes and alcohols with peroxides. *J. Organometal. Chem.* **2019**, *899*, 120911. [CrossRef]
90. Punniyamurthy, T.; Rout, L. Recent advances in copper-catalyzed oxidation of organic compounds. *Coord. Chem. Rev.* **2008**, *252*, 134–154. [CrossRef]
91. Sabbatini, A.; Martins, L.M.D.R.S.; Mahmudov, K.T.; Kopylovich, M.N.; Drew, M.G.B.; Pettinari, C.; Pombeiro, A.J.L. Microwave-assisted and solvent-free peroxidative oxidation of 1-phenylethanol to acetophenone with a Cu^{II}-TEMPO catalytic system. *Catal. Com.* **2014**, *48*, 69–72. [CrossRef]

92. Perraud, O.; Sorokin, A.B.; Dutasta, J.-P.; Martinez, A. Oxidation of cycloalkanes by H_2O_2 using a copper-hemicryptophane complex as a catalyst. *Chem. Commun.* **2013**, 49, 1288–1290. [CrossRef] [PubMed]
93. Ünver, H.; Kani, I. Homogeneous oxidation of alcohols in water catalyzed with Cu(II)-triphenyl acetate/bipyridyl complex. *Polyhedron* **2017**, 134, 257–262. [CrossRef]
94. Czerwińska, K.; Machura, B.; Kula, S.; Krompiec, S.; Erfurt, K.; Roma-Rodrigues, C.; Fernandes, A.R.; Shul'pina, L.S.; Ikonnikov, N.S.; Shul'pin, G.B. Copper(II) complexes of functionalized 2,2':6',2''-terpyridines and 2,6-di(thiazol-2-yl)pyridine: Structure, spectroscopy, cytotoxicity and catalytic activity. *Dalton Trans.* **2017**, 46, 9591–9604. [CrossRef]
95. Gurbanov, A.V.; Martins, L.M.D.R.S.; Kopylovich, M.N.; Sutradhar, M.; Zubkov, F.I.; Mahmudov, K.T.; Pombeiro, A.J.L. Mechanochemical and Conventional Synthesis of Copper(II)Coordination Polymers Bearing Arylhydrazone of Acetoacetanilide and Their Catalytic Activity in Conversion of Acetone to Acetic Acid. *ChemistrySelect* **2020**, 5, 923–7927. [CrossRef]
96. Choroba, K.; Machura, B.; Kula, S.; Raposo, L.R.; Fernandes, A.R.; Kruszynski, R.; Erfurt, K.; Shul'pina, L.S.; Kozlov, Y.N.; Shul'pin, G.B. Copper(II) complexes with 2,2':6',2''-terpyridine, 2,6-di(thiazol-2-yl)pyridine and 2,6-di(pyrazin-2-yl)pyridine substituted with quinolines. Synthesis, structure, antiproliferative activity, and catalytic activity in oxidation of alkanes and alcohols with peroxides. *Dalton Trans.* **2019**, 48, 12656–12673. [CrossRef]
97. Brinksma, J.; Rispens, M.T.; Hage, R.; Feringa, B.L. New manganese catalysts for alcohol oxidation. *Inorg. Chim. Acta* **2002**, 337, 75–82. [CrossRef]
98. Steen, J.D.; Stepanovic, S.; Parvizian, M.; de Boer, J.W.; Hage, R.; Chen, J.; Swart, M.; Gruden, M.; Browne, W.R. Lewis versus Brønsted Acid Activation of a Mn(IV) Catalyst for Alkene Oxidation. *Inorg. Chem.* **2019**, 58, 14924–14930. [CrossRef]
99. Pinto, M.F.; Olivares, M.; Vivancos, A.; Guisado-Barrios, G.; Albrecht, M.; Royo, B. (Di)Triazolylidene Manganese Complexes in Catalytic Oxidation of Alcohols to Ketones and Aldehydes. *Catal. Sci. Technol.* **2019**, 9, 2421–2425. [CrossRef]
100. Shul'pin, G.B.; Lindsay-Smith, J.R. Oxidations by the reagent ' H_2O_2 -manganese(IV) complex-carboxylic acid'. Part 1. Oxidation of saturated hydrocarbons with peroxy acids and hydrogen peroxide. *Russ. Chem. Bull.* **1998**, 47, 2379–2386. [CrossRef]
101. Lindsay Smith, J.R.; Shul'pin, G.B. Efficient stereoselective oxygenation of alkanes by peroxyacetic acid or hydrogen peroxide and acetic acid catalysed by a manganese(IV) 1,4,7-trimethyl-1,4,7-triazacyclononane complex. *Tetrahedron Lett.* **1998**, 39, 4909–4912. [CrossRef]
102. Shul'pin, G.B.; Süß-Fink, G.; Lindsay Smith, J.R. Oxidations by the system "Hydrogen Peroxide–Manganese(IV) Complex–Acetic Acid", Part II. Hydroperoxidation and hydroxylation of alkanes in acetonitrile. *Tetrahedron* **1999**, 55, 5345–5358. [CrossRef]
103. Shul'pin, G.B.; Süß-Fink, G.; Shul'pina, L.S. Oxidations by the system "hydrogen peroxide–manganese(IV) complex–carboxylic acid". Part 3. Oxygenation of ethane, higher alkanes, alcohols, olefins and sulfides. *J. Mol. Catal. A Chem.* **2001**, 170, 17–34. [CrossRef]
104. Mandelli, D.; Woitiski, C.B.; Schuchardt, U.; Shul'pin, G.B. Hydrogen-peroxide epoxidation of natural olefins catalyzed by a dinuclear manganese complex. *Chem. Natur. Comp.* **2002**, 38, 243–245. [CrossRef]
105. Shul'pin, G.B.; Nizova, G.V.; Kozlov, Y.N.; Pechenkina, I.G. Oxidations by the "hydrogen peroxide–manganese(IV) complex–carboxylic acid" system. Part 4. Efficient acid-base switching between catalase and oxygenase activities of a dinuclear manganese(IV) complex in the reaction with H_2O_2 and an alkane. *New J. Chem.* **2002**, 26, 1238–1245. [CrossRef]
106. Nizova, G.V.; Bolm, C.; Ceccarelli, S.; Pavan, C.; Shul'pin, G.B. Hydrocarbon oxidations with hydrogen peroxide catalyzed by a soluble polymer-bound manganese(IV) complex with 1,4,7-triazacyclononane. *Adv. Synth. Catal.* **2002**, 344, 899–905. [CrossRef]
107. Kozlov, Y.N.; Mandelli, D.; Woitiski, C.B.; Shul'pin, G.B. Mechanism of the oxidation of olefins and alkanes with a H_2O_2 -dimeric Mn(IV) complex–acetic acid system. *Russ. J. Phys. Chem.* **2004**, 78, 370–374.
108. Woitiski, C.B.; Kozlov, Y.N.; Mandelli, D.; Nizova, G.V.; Schuchardt, U.; Shul'pin, G.B. Oxidations by the system "hydrogen peroxide–dinuclear manganese(IV) complex–carboxylic acid". Part 5. Epoxidation of olefins including natural terpenes. *J. Mol. Catal. A Chem.* **2004**, 222, 103–119. [CrossRef]
109. Shul'pin, G.B.; Nizova, G.V.; Kozlov, Y.N.; Arutyunov, V.S.; dos Santos, A.C.M.; Ferreira, A.C.T.; Mandelli, D. Oxidations by the system "hydrogen peroxide– $[\text{Mn}_2\text{L}_2\text{O}_3][\text{PF}_6]_2$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane)–oxalic acid". Part 6. Oxidation of methane and other alkanes and olefins in water. *J. Organometal. Chem.* **2005**, 690, 4498–4504. [CrossRef]
110. Mandelli, D.; Steffen, R.A.; Shul'pin, G.B. Carvone epoxidation by the system "Hydrogen peroxide– $[\text{Mn}_2\text{L}_2\text{O}_3][\text{PF}_6]_2$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane)–carboxylic acid": A combinatorial approach to the process optimization" <Part 7 from the series "Oxidations by the system hydrogen peroxide– $[\text{Mn}_2\text{L}_2\text{O}_3][\text{PF}_6]_2$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane)–carboxylic acid. *React. Kinet. Catal. Lett.* **2006**, 88, 165–174.
111. Romakh, V.B.; Therrien, B.; Karmazin-Brelot, L.; Labat, G.; Stoeckli-Evans, H.; Shul'pin, G.B.; Süß-Fink, G. Dinuclear manganese complexes containing 1,4-dimethyl-1,4,7-triazacyclononane ligands as well as carboxylato and oxo bridges. *Inorg. Chim. Acta* **2006**, 359, 1619–1626. [CrossRef]
112. Romakh, V.B.; Therrien, B.; Süß-Fink, G.; Shul'pin, G.B. Dinuclear manganese complexes containing chiral 1,4,7-triazacyclononane-derived ligands and their catalytic potential for the oxidation of olefins, alkanes, and alcohols. *Inorg. Chem.* **2007**, 46, 1315–1331. [CrossRef] [PubMed]
113. Nizova, G.V.; Shul'pin, G.B. A unique rate-accelerating effect of certain amino acids in the H_2O_2 oxidation of alkanes catalyzed by a dinuclear manganese complex containing 1,4,7-trimethyl-1,4,7-triazacyclononane" <Part 9 from the series "Oxidations by the system hydrogen peroxide– $[\text{Mn}_2\text{L}_2\text{O}_3][\text{PF}_6]_2$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane)–carboxylic acid">. *Tetrahedron* **2007**, 63, 7997–8001. [CrossRef]

114. Kozlov, Y.N.; Nizova, G.V.; Shul'pin, G.B. Alkane oxidation by the system 'tert-butyl hydroperoxide-[Mn₂L₂O₃][PF₆]₂ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane)-carboxylic acid'. *J. Phys. Org. Chem.* **2008**, *21*, 119–126. [\[CrossRef\]](#)
115. Shul'pin, G.B.; Matthes, M.G.; Romakh, V.B.; Barbosa, M.I.F.; Aoyagi, J.L.T.; Mandelli, D. Oxidations by the system 'hydrogen peroxide-[Mn₂L₂O₃][PF₆]₂ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane)-carboxylic acid'. Part 10: Co-catalytic effect of different carboxylic acids in the oxidation of cyclohexane, cyclohexanol, and acetone. *Tetrahedron* **2008**, *64*, 2143–2152. [\[CrossRef\]](#)
116. Shul'pin, G.B.; Kozlov, Y.N.; Kholuiskaya, S.N.; Plieva, M.I. Oxidations by the system 'hydrogen peroxide-[Mn₂L₂O₃]²⁺ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane)-oxalic acid'. Part 11. Degradation of dye Rhodamine 6G and oxygenation of cyclohexene. *J. Mol. Catal. A Chem.* **2009**, *299*, 77–87. [\[CrossRef\]](#)
117. Shul'pin, G.B.; Kozlov, Y.N.; Shul'pina, L.S.; Strelkova, T.V.; Mandelli, D. Oxidation of Reactive Alcohols with Hydrogen Peroxide Catalyzed by Manganese Complexes" <Part 12 from the series "Oxidations by the system hydrogen peroxide-[Mn₂L₂O₃]²⁺ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane)-carboxylic acid">. *Catal. Lett.* **2010**, *138*, 193–204. [\[CrossRef\]](#)
118. Kozlov, Y.N.; Shul'pina, L.S.; Strelkova, T.V.; Shul'pin, G.B. Kinetics and Mechanism of 1-Phenylethanol Oxidation by the System Hydrogen Peroxide-Manganese(IV) Binuclear Complex-Oxalic Acid. *Russ. J. Phys. Chem. A* **2010**, *84*, 1502–1505. [\[CrossRef\]](#)
119. Mandelli, D.; Kozlov, Y.N.; Carvalho, W.A.; Shul'pin, G.B. Oxidations by the system 'hydrogen peroxide-[Mn₂L₂O₃]²⁺ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane)-carboxylic acid'. Part 13. Epoxidation of methyl oleate in acetonitrile solution. *Catal. Commun.* **2012**, *26*, 93–97. [\[CrossRef\]](#)
120. Shul'pin, G.B.; Nesterov, D.S.; Shul'pina, L.S.; Pombeiro, A.J.L. A hydroperoxo-rebound mechanism of alkane oxidation with hydrogen peroxide catalyzed by binuclear manganese(IV) complex in the presence of an acid with involvement of atmospheric dioxygen <Part 14 from the series "Oxidations by the system hydrogen peroxide-[Mn₂L₂O₃]²⁺ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane)-carboxylic acid">. *Inorg. Chim. Acta* **2017**, *455*, 666–676. [\[CrossRef\]](#)
121. Conte, V.; Coletti, A.; Floris, B.; Licini, G.; Zonta, C. Mechanistic aspects of vanadium catalysed oxidations with peroxides. *Coord. Chem. Rev.* **2011**, *255*, 2165–2177. [\[CrossRef\]](#)
122. Shul'pin, G.B.; Attanasio, D.; Suber, L. Efficient H₂O₂ oxidation of alkanes and arenes to alkyl peroxides and phenols catalyzed by the system vanadate-pyrazine-2-carboxylic acid. *J. Catal.* **1993**, *142*, 147–152. [\[CrossRef\]](#)
123. Shul'pin, G.B.; Attanasio, D.; Suber, L. Oxidations by a H₂O₂-VO₃⁻-pyrazine-2-carboxylic acid reagent. 1. Oxidations of alkanes in CH₃CN to produce alkyl peroxides. *Russ. Chem. Bull.* **1993**, *42*, 55–59.
124. Kirillov, A.M.; Shul'pin, G.B. Pyrazinecarboxylic acid and analogs: Highly efficient co-catalysts in the metal-complex-catalyzed oxidation of organic compounds. *Coord. Chem. Rev.* **2013**, *257*, 732–754. [\[CrossRef\]](#)
125. Shul'pin, G.B.; Druzhinina, A.N.; Nizova, G.V. Oxidation with the H₂O₂-VO₃⁻-pyrazine-2-carboxylic acid reagent. 2. Oxidation of alcohols and aromatic hydrocarbons. *Russ. Chem. Bull.* **1993**, *42*, 1327–1329.
126. Nizova, G.V.; Shul'pin, G.B. Oxidation by a H₂O₂-vanadium complex-2-pyrazinecarboxylic acid reagent. 3. Evidence for hydroxyl radical formation. *Russ. Chem. Bull.* **1994**, *43*, 1146–1148. [\[CrossRef\]](#)
127. Shul'pin, G.B.; Süß-Fink, G. Oxidations by the reagent "H₂O₂-vanadium complex-pyrazine-2-carboxylic acid". Part 4. Oxidation of alkanes, benzene and alcohols by an adduct of H₂O₂ with urea. *J. Chem. Soc. Perkin Trans. 2* **1995**, *7*, 1459–1463. [\[CrossRef\]](#)
128. Shul'pin, G.B.; Drago, R.S.; Gonzalez, M. Oxidations by a "H₂O₂-vanadium complex-pyrazine-2-carboxylic acid" reagent. 5. Oxidation of lower alkanes with the formation of carbonyl compounds. *Russ. Chem. Bull.* **1996**, *45*, 2386–2388. [\[CrossRef\]](#)
129. Guerreiro, M.C.; Schuchardt, U.; Shul'pin, G.B. Oxidation with the "O₂-VO₃⁻-pyrazine-2-carboxylic acid" reagent. Part 6. Oxidation of n-heptane and cyclohexane. Direct determination of alkyl hydroperoxides by gas-liquid chromatography. *Russ. Chem. Bull.* **1997**, *46*, 749–754. [\[CrossRef\]](#)
130. Shul'pin, G.B.; Guerreiro, M.C.; Schuchardt, U. Oxidations by the reagent O₂-H₂O₂-vanadium complex-pyrazine-2-carboxylic acid. Part 7. Hydroperoxidation of higher alkanes. *Tetrahedron* **1996**, *52*, 13051–13062. [\[CrossRef\]](#)
131. Nizova, G.V.; Süß-Fink, G.; Shul'pin, G.B. Oxidations by the reagent «O₂-H₂O₂-vanadium complex-pyrazine-2-carboxylic acid»-8. Efficient oxygenation of methane and other lower alkanes in acetonitrile. *Tetrahedron* **1997**, *53*, 3603–3614. [\[CrossRef\]](#)
132. Schuchardt, U.; Guerreiro, M.C.; Shul'pin, G.B. Oxidation with the 'O₂-H₂O₂-vanadium complex-pyrazine-2-carboxylic acid' reagent. 9. Oxidation of cyclohexene and decalin. *Russ. Chem. Bull.* **1998**, *47*, 247–252. [\[CrossRef\]](#)
133. Süß-Fink, G.; Nizova, G.V.; Stanislas, S.; Shul'pin, G.B. Oxidations by the reagent 'O₂-H₂O₂-vanadate anion-pyrazine-2-carboxylic acid'. Part 10. Oxygenation of methane in acetonitrile and water. *J. Mol. Catal. A Chem.* **1998**, *13*, 163–170. [\[CrossRef\]](#)
134. Shul'pin, G.B.; Ishii, Y.; Sakaguchi, S.; Iwahama, T. Oxidations with the "O₂-H₂O₂-vanadium complex-pyrazine-2-carboxylic acid" reagent. 11. Oxidation of styrene, phenylacetylene, and their derivatives with the formation of benzaldehyde and benzoic acid. *Russ. Chem. Bull.* **1999**, *48*, 887–890.
135. Süß-Fink, G.; Stanislas, S.; Shul'pin, G.B.; Nizova, G.V.; Stoeckli-Evans, H.; Neels, A.; Bobillier, C.; Claude, S. Oxidative functionalisation of alkanes: Synthesis, molecular structure and catalytic implications of anionic vanadium(V) oxo and peroxo complexes containing bidentate N,O ligands. *J. Chem. Soc. Dalton Trans.* **1999**, *18*, 3169–3175. [\[CrossRef\]](#)
136. Shul'pin, G.B.; Kozlov, Y.N.; Nizova, G.V.; Süß-Fink, G.; Stanislas, S.; Kitaygorodskiy, A.; Kulikova, V.S. Oxidations by the reagent "O₂-H₂O₂-vanadium derivative-pyrazine-2-carboxylic acid" Part 12. Main features, kinetics and mechanism of alkane hydroperoxidation. *J. Chem. Soc. Perkin Trans. 2* **2001**, *2*, 1351–1371. [\[CrossRef\]](#)
137. Kozlov, Y.N.; Nizova, G.V.; Shul'pin, G.B. The mechanism of hydrogen peroxide-induced aerobic oxidation of alkanes in catalysis by a vanadium complex and pyrazine-2-carboxylic acid. *Russ. J. Phys. Chem.* **2001**, *75*, 770–774.

138. Süß-Fink, G.; Gonzalez, L.; Shul'pin, G.B. Alkane oxidation with hydrogen peroxide catalyzed homogeneously by vanadium-containing polyphosphomolybdates. *Appl. Catal. A General*. **2001**, *217*, 111–117. [\[CrossRef\]](#)
139. Shul'pin, G.B.; Kozlov, Y.N. Kinetics and mechanism of alkane hydroperoxidation with *tert*-butyl hydroperoxide catalysed by a vanadate ion. *Org. Biomol. Chem.* **2003**, *1*, 2303–2306. [\[CrossRef\]](#) [\[PubMed\]](#)
140. Süß-Fink, G.; Hong, Y.; Nizova, G.V.; Stanislas, S.; Shul'pin, G.B. Oxygenation of methane with atmospheric oxygen in aqueous solution promoted by H₂O₂ and catalyzed by a vanadate ion–pyrazine-2-carboxylic acid system. *Russ. Chem. Bull.* **1997**, *46*, 1801–1803. [\[CrossRef\]](#)
141. Nizova, G.V.; Kozlov, Y.N.; Shul'pin, G.B. Effect of acetonitrile on the catalytic decomposition of hydrogen peroxide by vanadium ions and conjugated oxidation of alkanes. *Russ. Chem. Bull.* **2004**, *53*, 2330–2333. [\[CrossRef\]](#)
142. Kozlov, Y.N.; Nizova, G.V.; Shul'pin, G.B. Oxidations by the reagent “O₂–H₂O₂–vanadium derivative–pyrazine-2-carboxylic acid”. Part 14. Competitive oxidation of alkanes and acetonitrile (solvent). *J. Mol. Catal. A Chem.* **2005**, *227*, 247–253. [\[CrossRef\]](#)
143. De la Cruz, M.H.C.; Kozlov, Y.N.; Lachter, E.R.; Shul'pin, G.B. Oxidations by the reagent “O₂–H₂O₂–vanadium derivative–pyrazine-2-carboxylic acid”. Part 13. Kinetics and mechanism of the benzene hydroxylation. *New J. Chem.* **2003**, *27*, 634–638. [\[CrossRef\]](#)
144. Jannini, M.J.D.M.; Shul'pina, L.S.; Schuchardt, U.; Shul'pin, G.B. Oxidation of alkanes with hydrogen peroxide catalyzed by the “vanadate-ion–pyrazine-2-carboxylic acid” system in the presence of pyridine (Part 15 of the series “Oxidations by the reagent O₂–H₂O₂–vanadium derivative–pyrazine-2-carboxylic acid”). *Petrol. Chem.* **2005**, *45*, 413–418.
145. Khaliullin, R.Z.; Bell, A.T.; Head-Gordon, M. A density functional theory study of the mechanism of free radical generation in the system vanadate/PKA/H₂O₂. *J. Phys. Chem. B* **2005**, *109*, 17984–17992. [\[CrossRef\]](#)
146. Kozlov, Y.N.; Romakh, V.B.; Kitaygorodskiy, A.; Buglyó, P.; Süß-Fink, G.; Shul'pin, G.B. Oxidation of 2-propanol and cyclohexane by the reagent “Hydrogen peroxide–vanadate anion–pyrazine-2-carboxylic acid”: Kinetics and mechanism. *J. Phys. Chem. A* **2007**, *111*, 7736–7752. [\[CrossRef\]](#)
147. Romakh, V.B.; Süß-Fink, G.; Shul'pin, G.B. Vanadate ion-catalyzed oxidation of methane with hydrogen peroxide in an aqueous solution. *Petrol. Chem.* **2008**, *48*, 440–443. [\[CrossRef\]](#)
148. Bolm, C. Vanadium-catalyzed asymmetric oxidations. *Coord. Chem. Rev.* **2003**, *237*, 245–256. [\[CrossRef\]](#)
149. Gusevskaya, E.V.; Menini, L.; Parreira, L.A.; Mesquita, R.A.; Kozlov, Y.N.; Shul'pin, G.B. Oxidation of isoeugenol to vanillin by the “H₂O₂–vanadate–pyrazine-2-carboxylic acid” reagent. *J. Mol. Catal. A* **2012**, *363–364*, 140–147. [\[CrossRef\]](#)
150. Sutradhar, M.; Shvydkiy, N.V.; Guedes da Silva, M.F.C.; Kirillova, M.V.; Kozlov, Y.N.; Pombeiro, A.J.L.; Shul'pin, G.B. New binuclear oxovanadium(V) complex as a catalyst in combination with pyrazinecarboxylic acid (PCA) for efficient alkane oxygenation by H₂O₂. *Dalton Trans.* **2013**, *42*, 11791–11803. [\[CrossRef\]](#) [\[PubMed\]](#)
151. Licini, G.; Conte, V.; Coletti, A.; Mba, M.; Zont, C. Recent advances in vanadium catalyzed oxygen transfer reactions. *Coord. Chem. Rev.* **2011**, *255*, 2345–2357. [\[CrossRef\]](#)
152. Sutradhar, M.; da Silva, J.A.L.; Pombeiro, A.J.L. (Eds.) *Vanadium Catalysis*; RSC: London, UK, 2020; Chapter 4; pp. 72–96. ISBN 978-1-83916-088-2. [\[CrossRef\]](#)
153. Bryliakov, K.P.; Talsi, E.P.; Stas'ko, S.N.; Kholdeeva, O.A.; Popov, S.A.; Tkachev, A.V. Stereoselective oxidation of linalool with *tert*-butyl hydroperoxide, catalyzed by a vanadium(V) complex with a chiral terpenoid ligand. *J. Mol. Catal. A Chem.* **2003**, *194*, 79–88. [\[CrossRef\]](#)
154. Fomenko, I.S.; Vincendeau, S.; Manoury, E.; Poli, R.; Abramov, P.A.; Nadolinny, V.A.; Sokolov, M.N.; Gushchin, A.L. An oxidovanadium(IV) complex with 4,4'-di-*tert*-butyl-2,2'-bipyridine ligand: Synthesis, structure and catalyzed cyclooctene epoxidation. *Polyhedron* **2020**, *177*, 114305. [\[CrossRef\]](#)
155. Süß-Fink, G.; Gonzalez Cuervo, L.; Therrien, B.; Stoeckli-Evans, H.; Shul'pin, G.B. Mono and oligonuclear vanadium complexes as catalysts for alkane oxidation: Synthesis, molecular structure and catalytic potential. *Inorg. Chim. Acta* **2004**, *357*, 475–484. [\[CrossRef\]](#)
156. Kirillova, M.V.; Kuznetsov, M.L.; Romakh, V.B.; Shul'pina, L.S.; Fraústo da Silva, J.J.R.; Pombeiro, A.J.L.; Shul'pin, G.B. Mechanism of oxidations with H₂O₂ catalyzed by vanadate anion or oxovanadium(V) triethanolamine (vanadatane) in combination with pyrazine-2-carboxylic acid (PCA): Kinetic and DFT studies. *J. Catal.* **2009**, *267*, 140–157. [\[CrossRef\]](#)
157. Shul'pina, L.S.; Kirillova, M.V.; Pombeiro, A.J.L.; Shul'pin, G.B. Alkane oxidation by the H₂O₂–NaVO₃–H₂SO₄ system in acetonitrile and water. *Tetrahedron* **2009**, *65*, 2424–2429. [\[CrossRef\]](#)
158. Kirillova, M.V.; Kuznetsov, M.L.; Kozlov, Y.N.; Shul'pina, L.S.; Kitaygorodskiy, A.; Pombeiro, A.J.L.; Shul'pin, G.B. Participation of Oligovanadates in Alkane Oxidation with H₂O₂ Catalyzed by Vanadate Anion in Acidified Acetonitrile: Kinetic and DFT Studies. *ACS Catal.* **2011**, *1*, 1511–1520. [\[CrossRef\]](#)
159. Sutradhar, M.; Martins, L.M.; Roy Barman, T.; Kuznetsov, M.L.; Guedes da Silva, M.F.C.; Pombeiro, A.J.L. Vanadium complexes of different nuclearities in the catalytic oxidation of cyclohexane and cyclohexanol—An experimental and theoretical investigation. *New J. Chem.* **2019**, *43*, 17557–17570. [\[CrossRef\]](#)
160. Maurya, M.R.; Tomar, R.; Avelilla, F.; Ribeiro, N.; Carvalho, M.F.N.N.; Kuznetsov, M.L.; Correia, I.; Pessoa, J.C. Trinuclear vanadium(IV) and vanadium(V) complexes derived from 2,4,6-triacetylphloroglucinol and study of their peroxidase mimicking activity. *Dalton Trans.* **2020**, *49*, 2589–2609. [\[CrossRef\]](#) [\[PubMed\]](#)
161. Nagataki, T.; Ishii, K.; Tachi, Y.; Itoh, S. Ligand effects on Ni^{II}-catalysed alkane-hydroxylation with *m*-CPBA. *Dalton Trans.* **2007**, 1120–1128. [\[CrossRef\]](#) [\[PubMed\]](#)

162. Itoh, S.; Bandoh, H.; Nagatomo, S.; Kitagawa, T.; Fukuzumi, S. Aliphatic hydroxylation by a bis(–oxo)dinickel(III) complex. *J. Am. Chem. Soc.* **1999**, *121*, 8945–8946. [[CrossRef](#)]
163. Kunishita, A.; Doi, Y.; Kubo, M.; Ogura, T.; Sugimoto, H.; Itoh, S. Ni(II)/H₂O₂ reactivity in bis[(pyridin-2-yl)methyl] amine tridentate ligand system. Aromatic hydroxylation reaction by bis(–oxo)dinickel(III) complex. *Inorg. Chem.* **2009**, *48*, 4997–5004. [[CrossRef](#)]
164. Bilyachenko, A.N.; Yalymov, A.I.; Shul'pina, L.S.; Mandelli, D.; Korlyukov, A.A.; Vologzhanina, A.V.; Es'kova, M.A.; Shubina, E.S.; Levitsky, M.M.; Shul'pin, G.B. Novel Cage-Like Hexanuclear Nickel(II) Silsesquioxane. Synthesis, Structure, and Catalytic Activity in Oxidations with Peroxides. *Molecules* **2016**, *21*, 665. [[CrossRef](#)]
165. Bilyachenko, A.N.; Yalymov, A.I.; Levitsky, M.M.; Korlyukov, A.A.; Es'kova, M.A.; Long, J.; Larionova, J.; Guari, Y.; Shul'pina, L.S.; Ikonnikov, N.S.; et al. First cage-like pentanuclear Co(II)-silsesquioxane. *Dalton Trans.* **2016**, *35*, 13663–13666. [[CrossRef](#)]
166. Paul, A.; Martins, L.M.D.R.S.; Karmakar, A.; Kuznetsov, M.L.; Novikov, A.S.; Guedes da Silva, M.F.C.; Pombeiro, A.J.L. Environmentally benign benzyl alcohol oxidation and C–C coupling catalysed by amide functionalized 3D Co(II) and Zn(II) metal organic frameworks. *J. Catal.* **2020**, *385*, 324–337. [[CrossRef](#)]
167. Shul'pin, G.B.; Kozlov, Y.N.; Shul'pina, L.S.; Petrovskiy, P.V. Oxidation of alkanes and alcohols with hydrogen peroxide catalyzed by complex Os₃(CO)₁₀(μ-H)₂. *Appl. Organometal. Chem.* **2010**, *24*, 464–472. [[CrossRef](#)]
168. Shul'pin, G.B.; Kozlov, Y.N.; Shul'pina, L.S.; Kudinov, A.R.; Mandelli, D. Extremely Efficient Alkane Oxidation by a New Catalytic Reagent H₂O₂/Os₃(CO)₁₂/Pyridine. *Inorg. Chem.* **2009**, *48*, 10480–10482. [[CrossRef](#)]
169. Shul'pin, G.B.; Kudinov, A.R.; Shul'pina, L.S.; Petrovskaya, E.A. Oxidations catalyzed by osmium compounds. Part 1: Efficient alkane oxidation with peroxides catalyzed by an olefin carbonyl osmium(0) complex. *J. Organometal. Chem.* **2006**, *691*, 837–845. [[CrossRef](#)]
170. Shul'pina, L.S.; Kudinov, A.R.; Petrovskaya, E.A.; Strelkova, T.V.; Shul'pin, G.B. Hydrogen peroxide oxidation of alkanes catalyzed by the osmium complex Os₃(CO)₁₁(η²-PhCOCH=CHCOPh). *Petrol. Chem.* **2006**, *46*, 164–166. [[CrossRef](#)]