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Review

Metal Complexes Containing Redox-Active Ligands in Oxidation of Hydrocarbons and Alcohols: A Review

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Received: 14 November 2019; Accepted: 6 December 2019; Published: 9 December 2019

Abstract: Ligands are innocent when they allow oxidation states of the central atoms to be defined. A noninnocent (or redox) ligand is a ligand in a metal complex where the oxidation state is not clear. Dioxygen can be a noninnocent species, since it exists in two oxidation states, i.e., superoxide (O_2^-) and peroxide (O_2^{2-}). This review is devoted to oxidations of C–H compounds (saturated and aromatic hydrocarbons) and alcohols with peroxides (hydrogen peroxide, *tert*-butyl hydroperoxide) catalyzed by complexes of transition and nontransition metals containing innocent and noninnocent ligands. In many cases, the oxidation is induced by hydroxyl radicals. The mechanisms of the formation of hydroxyl radicals from H_2O_2 under the action of transition (iron, copper, vanadium, rhenium, etc.) and nontransition (aluminum, gallium, bismuth, etc.) metal ions are discussed. It has been demonstrated that the participation of the second hydrogen peroxide molecule leads to the rapture of O–O bond, and, as a result, to the facilitation of hydroxyl radical generation. The oxidation of alkanes induced by hydroxyl radicals leads to the formation of relatively unstable alkyl hydroperoxides. The data on regioselectivity in alkane oxidation allowed us to identify an oxidizing species generated in the decomposition of hydrogen peroxide: (hydroxyl radical or another species). The values of the ratio-of-rate constants of the interaction between an oxidizing species and solvent acetonitrile or alkane gives either the kinetic support for the nature of the oxidizing species or establishes the mechanism of the induction of oxidation catalyzed by a concrete compound. In the case of a bulky catalyst molecule, the ratio of hydroxyl radical attack rates upon the acetonitrile molecule and alkane becomes higher. This can be expanded if we assume that the reactions of hydroxyl radicals occur in a cavity inside a voluminous catalyst molecule, where the ratio of the local concentrations of acetonitrile and alkane is higher than in the whole reaction volume. The works of the authors of this review in this field are described in more detail herein.

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

1. Introduction

"Oil is not a fuel. You can stoke with banknotes … " Mendeleev wrote these words more than one hundred years ago. Indeed, much cheaper energy sources can be found, while petroleum hydrocarbons must be used to produce valuable chemical compounds.

Hydrocarbons of oil and natural gas play a huge role in modern civilization, being, on the one hand, the most important source of energy, and on the other, raw materials for the chemical industry. Oil includes a significant amount of saturated hydrocarbons (alkanes), as well as arenes and other unsaturated hydrocarbons. Natural gas, as a rule, includes methane, ethane, and propane as the main components. At present, in industry, the chemical processing of hydrocarbons is carried out in most cases with the participation of heterogeneous catalysts, and requires elevated (more than 300 °C) temperatures. However, some low-temperature processes are known, e.g., the radical chain and microbiological oxidation of alkanes and benzene derivatives. In recent decades, alkanes that could not be introduced into such transformations have been added to compounds capable of being activated by metal complexes (olefins, hydrogen, carbon monoxide, oxygen, and nitrogen). In these processes, a molecule or its fragment, entering as a ligand in the coordination sphere of a metal complex, is chemically activated, i.e., it acquires the ability to enter into reactions that proceed very slowly in the absence of a complex.

In connection with the depletion of natural reserves of hydrocarbon raw materials, the need to implement intensive technologies and solve environmental problems, and the urgency of the problem of more complete and effective chemical processing of oil and gas components, sharply increases. Of particular importance are the searches for fundamentally new ways of involving hydrocarbons in chemical transformations. There is growing interest in new catalytic systems which are capable of efficiently and selectively functionalizing hydrocarbons, especially saturated ones, under mild conditions. Compounds of iron, copper, manganese, chromium, vanadium, and some other transition metals showed high catalytic activity in the oxidation of hydrocarbons with peroxides. The saturated nature and high chemical inertness of alkanes create noticeable difficulties in their activation; therefore, the interaction of both saturated and unsaturated C–H compounds with metal complexes is an extremely interesting theoretical problem [1–10].

2. Metal Complexes Containing Redox-Active Ligands

Redox-active, or 'noninnocent', ligands have more energetically-accessible levels that allow redox reactions to change their charge state [11]. In recent decades, noninnocent (or redox) ligands have been intensively studied for their unusual chemical behavior [12–23]. "Introduced in the late sixties, noninnocent (or redox) ligands have been extensively studied for their unusual and intriguing chemical behavior. Their ability to delocalize and/or provide electrons to the metal center of organometallic complexes confers them undisputable chemical interest and has proved valuable in the development of novel synthetic methodologies." [12]. Redox-noninnocent ligands are often found to play crucial roles in important natural processes mediated by metalloenzymes [16,17].

Redox-active ligands range from the small archetypical $NO^{+/\bullet/-}$ and $O_2^{0/\bullet-/2-}$systems via the classical 1,4-dihetero-1,3-diene chelates (e.g., α-diimine, dithiolene, or *o*-quinone redox series) to π-conjugated macrocycles. [15,22,23]. Currently, catalytic systems based on transition metal complexes (Rh, Ru, Pt, Pd, etc.) are widely used. Many catalytic reactions involving the compounds of these metals comprise processes in which metal atoms change their oxidation state and coordinate molecules of unsaturated organic compounds. Despite the effectiveness of such catalytic systems, the high cost of these metals, as well as their toxicity, necessitate the development of catalytic systems based on accessible and less harmful metals, for example, magnesium, calcium, aluminum, and gallium. Unlike transition metals, which can be present in compounds in various oxidation states, nontransition metals, as a rule, have one oxidation state (although, surely, nontransition metals can have a few different oxidation states). Recently, more and more examples of nontransition-metal complexes based on redox active ligands have appeared, having reactivities similar to those of transition metal compounds [23].

In this regard, the attention of researchers is drawn to o-quinone and α-diimine ligands. Their unique property is the ability to reversibly transform into anion-radical or dianionic forms while being bound to a metal atom. A specific feature of acenaphthene-1,2-diimine (bian) ligands is the ability to accept up to four electrons due to the reduction of both the diimine and naphthalene moieties. Of particular value is the redox activity of complexes of intransitive elements, which themselves are inactive. On complexes of nontransition metals with redox active ligands, oxidative addition and reductive elimination reactions become possible. This property makes such complexes similar, catalytically-active compounds of transition metals, and opens the possibility for their use in catalysis.

3. New Methods of Study of Alkane Oxidation Reactions

Di Stefano and co-workers [24] published a list of the following tools to distinguish between metal-based and free-radical oxidation mechanisms: (1) alcohol/ketone ratio (A/K); (2) kinetic isotope effects (KIE); (3) reaction under argon/air; (4) the Shul'pin test for alkyl hydroperoxides; (5) regioselectivity; (6) epimerization; (7) chirality transfer; (8) labeling studies; (9) use of radical traps; and (10) cyclohexene oxidation.

3.1. Detection of Alkyl Hydroperoxide by the Chromatography (GC) Before and After Treatment with PPh_3 (the Shul'pin Method)

A method was developed and used by Shul'pin (see Figure 1) [25–31]. In this method, the samples of reaction solutions obtained in the alkane oxidation with a peroxide are analyzed twice, i.e., before and after the addition of the excess of solid PPh_3. In recent years, the Shul'pin method has been employed by other chemists [32–35].

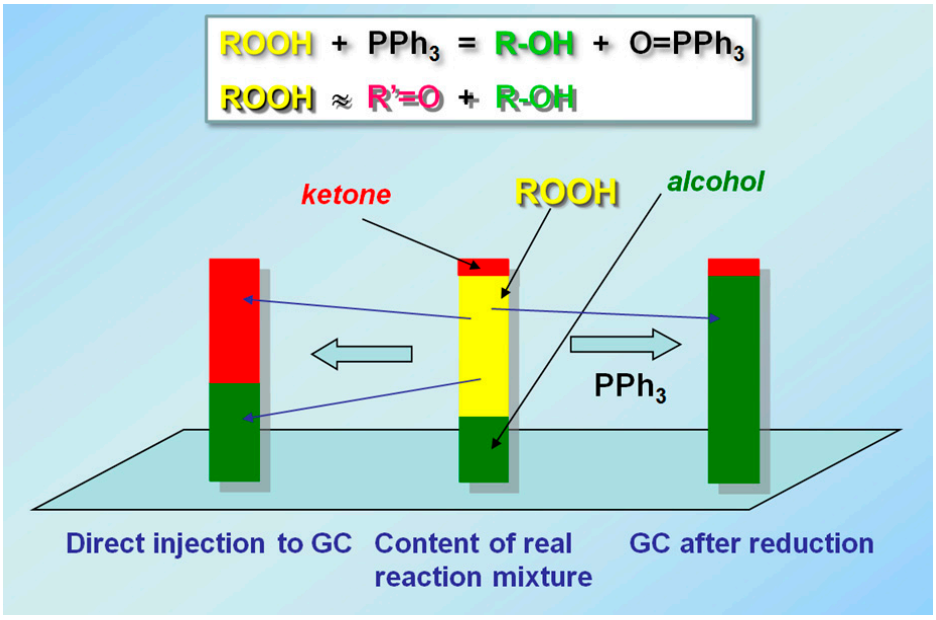


Figure 1. A schematic of the method of determination of the real concentrations of products in alkane RH oxidation with peroxides to afford ROOH.

Alkyl hydroperoxides are transformed in the GC injector into a mixture of the corresponding ketone and alcohol (see Figure 1). After the addition of PPh_3 to the reaction sample, the concentration of cyclohexanone decreases while that of cyclohexanol noticeably rises after the same time period. This may be explained by the reduction of the formed cyclohexyl hydroperoxide to give the corresponding alcohol. An example is presented in Figure 2 [30,31]. This method (i.e., a comparison of the cyclohexanol and cyclohexanone concentrations before and after treating with PPh_3) allows us to calculate the real concentrations, not only of the alkyl hydroperoxide, but also of the alcohols and ketones present in the solution at a given moment.

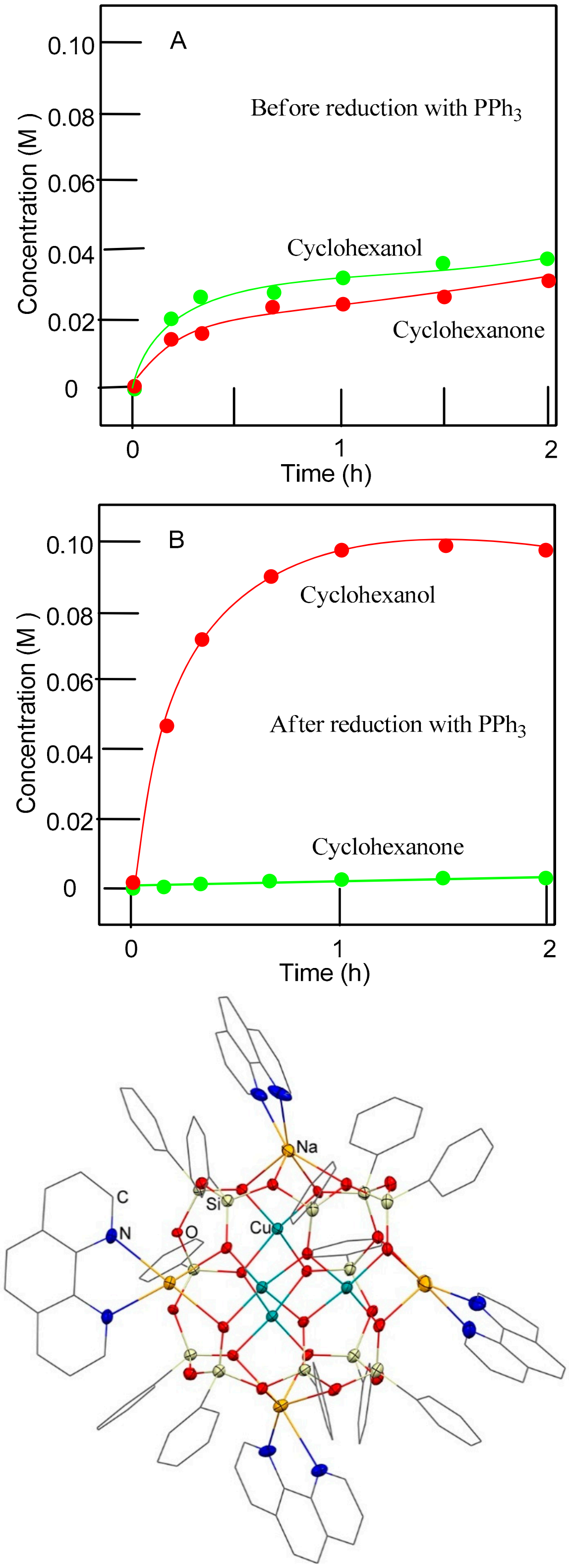


Figure 2. Accumulation of cyclohexanol and cyclohexanone in oxidation of cyclohexane (0.46 M) with hydrogen peroxide (2.0 M, 50% aqueous) catalyzed by compound $(PhSiO_{1,5})_{12}(CuO)_4(NaO_{0.5})_4(phen)_4$ (5×10^{-4} M; its structure is shown in the bottom of this Figure) in MeCN at 50 °C. The concentrations of cyclohexanone and cyclohexanol were determined before (graph A) and (graph B) after reduction of the aliquots with solid PPh_3 (according to the Shul'pin method [26–31]). The Figure 2 is adapted from Ref. [31].

3.2. A Competitive Oxidation of Cyclohexane and Acetonitrile as a Method for Detection of Hydroxyl Radicals

Most often, when oxidized with hydrogen peroxide, the oxidizing particle is a hydroxyl radical. It can be assumed that in oxidations by hydrogen peroxide, the oxidizing species is a hydroxyl radical. This conclusion has received kinetic confirmation [36].

In order to determine the kinetic characteristics of the oxidizing species X generated by the catalytic system studied in this work, the dependence of the alkane oxidation rate on its initial concentration was studied (see, for example, Figure 2) [30,31]. The nature of the dependence corresponds to the assumption of the competitive interaction of the oxidizing species X with acetonitrile and cyclohexane (RH):

$$\mathrm{H_2O_2} + \text{compound } \mathbf{1} \rightarrow \mathrm{X} \tag{1}$$

$$\mathrm{X} + \mathrm{CH_3CN} \rightarrow \ldots \rightarrow \text{products} \tag{2}$$

$$\mathrm{X} + \mathrm{RH} \rightarrow \ldots \rightarrow \mathrm{ROOH} \tag{3}$$

Here, stage (1) is the effective reaction of generating oxidizing species X at rate W_1, and stages (2) and (3) are the transformations of CH_3CN and RH with the formation, in particular, of alkyl hydroperoxide ROOH, induced by interactions that limit their speed with X. The rate constants of these interactions are k_2 and k_3, respectively. Assuming that the concentration of species X is quasistationary, we obtain the following expression for the initial rate of formation of ROOH:

$$\mathrm{d[ROOH]/d}t)_0 = k_3[\mathrm{RH}]_0\{W_1/(k_2[\mathrm{CH_3CN}]_0 + k_3[\mathrm{RH}]_0\} \tag{4}$$

Equation (4) can be presented in the form of Expression (5), which is convenient for the analysis of experimental data:

$$\mathrm{d[ROOH]/d}t)_0{}^{-1} = \{(1 + k_2[\mathrm{CH_3CN}]_0/k_3[\mathrm{RH}]_0\}/W_1 \tag{5}$$

An analysis of the experimental data in accordance with Equation (5), assuming that the concentrations of acetonitrile and alkane correspond to their uniform distribution over the reaction volume, allows us to determine the ratio of the rate constants of the interaction of the oxidizing particle with CH_3CN and alkane—$k_2[CH_3CN]_0/k_3$. If this assumption is true, then, in the case of the induction of oxidation by a hydroxyl radical, for example, the obtained ratio corresponds to that calculated from the data of radiation-chemical measurements. These ratios also were close to the value determined during the oxidation of cyclohexane in acetonitrile, when the oxidation-inducing species was certainly a hydroxyl radical, arising from the photodissociation of H_2O_2 as the primary product [36].

This is observed, in particular, in the case of the simplest vanadium catalysts, for which the data on regioselectivity also indicate the induction of the process by hydroxyl radicals. If, however, near the reaction center of the catalyst, where OH radicals appear, as evidenced by the data on regioselectivity, the concentrations of acetonitrile and alkane are different from the expected ones, then the obtained ratio of constants will differ from the expected one, which is observed in the case of complicated catalytic systems.

4. Activation of Hydrocarbons in the Presence of Chloride Platinum Complexes

At the turn of the 1960s and 70s, Shilov, Shteinman, et al. (see Refs. [2,10]) described the first example of alkane activation by a metal complex. It was found that when methane is heated in a solution of deuterated water or acetic acid with the Na_2PtCl_4 salt, an H–D exchange occurs in the methane molecule. If the tetravalent platinum derivative $PtCl_6{}^{2-}$ is also present in the reaction solution, methane is oxidized to form methanol and methyl chloride. An investigation of the reaction by indirect methods (in particular, kinetic) suggested that the processes of deutero exchange and oxidation proceed through intermediate σ-methyl complexes of platinum: $CH_3PtCl_4(H_2O)$.

In 1979, Shul'pin found that the interaction of platinum chloride with aromatic compounds in an acidic medium [37,38] leads to the formation of σ-aryl complexes of platinum(IV). The synthesis of such compounds was carried out in an aqueous trifluoroacetic acid medium. The reaction takes place in a few minutes or hours by heating a homogeneous reaction solution. After trifluoroacetic acid and water are removed in vacuo, the residue is chromatographed on silica gel, which contains ammonia. The acetone-hexane mixture elutes the yellow or orange strip of the complex, and the yellow strip of the original platinum chloride hydrochloric acid remaining on the column is then easily washed out with water. The resulting aromatic derivatives of platinum are yellow or orange crystalline substances, which were characterized by elemental analysis, IR and NMR spectra (see, for example, Figure 3).

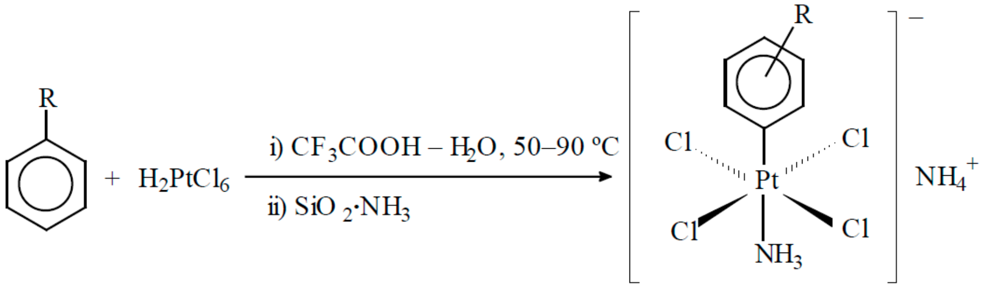


Figure 3. The reaction of arenes with hexachloroplatinate anion to afford σ-aryl complexes of platinum(IV).

The complexes include two ammonia molecules. X-Ray diffraction analysis showed that there are one ammonia ligand and one ammonium cation [37,38]. The anion particle is octahedral, with a platinum atom in the center. Four chlorine atoms are located in equatorial positions, and the positions of σ-aryl ligand and the ammonia molecule occupy axial positions. As aromatic substrates, benzene, its monosubstituted derivatives (toluene, ethylbenzene, anisole, chlorobenzene, fluorobenzene, nitrobenzene, benzoic acid, acetophenone, diphenyl), disubstitkuted benzenes (*o*- and *m*-xylenes, *m*-chlorotoluene, *o*-nitrotoluene, were used) *o*- and *m*-fluorochloro,benzenes), naphthalene.

It is important to emphasize that in the case of naphthalene, the platinum ion only enters the β position and the formation of *ortho*-platinized derivatives o nbqwasf monosubstituted benzenes is not observed in this reaction. It was not possible to isolate a significant amount of the σ-aryl complex from reaction products with aromatic compounds having only ortho-hydrogens (*p*-xylene, *p*-dimethoxybenzene, *p*-dichlorobenzene, mesitylene, pentamethylbenzene, and pentafluorobenzene). The reason for this pronounced steric deactivation of the ortho positions is apparently the large volume of the group containing platinum entering the ring. By the method of competing reactions, the relative reactivity of various aromatic compounds was determined. The composition of the mixture of complexes after chromatography was determined by PMR. The logarithms of relative rates satisfactorily correlate with Hammett σ and Brown σ^+ electrophilic constants. For most substituents, the best correlation was obtained using the constants σ and σ^+ (parameters $\rho = -3.0$ and $\rho^+ = -1.5$). The observed change in the ratio of isomers is due to the process of *para-meta*-isomerization of the complex, which takes place simultaneously with its accumulation, as shown in Figure 4:

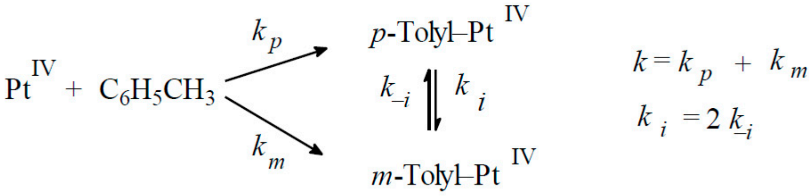


Figure 4. Accumulation and isomerization of Pt(IV) σ-complexes with toluene.

The formation of Pt (IV) σ-aryl complexes apparently occurs with the intermediate occurrence of π-complexes and Wheland intermediates, as shown in Figure 5 [37,38]. Isomerization proceeds through a transition state.

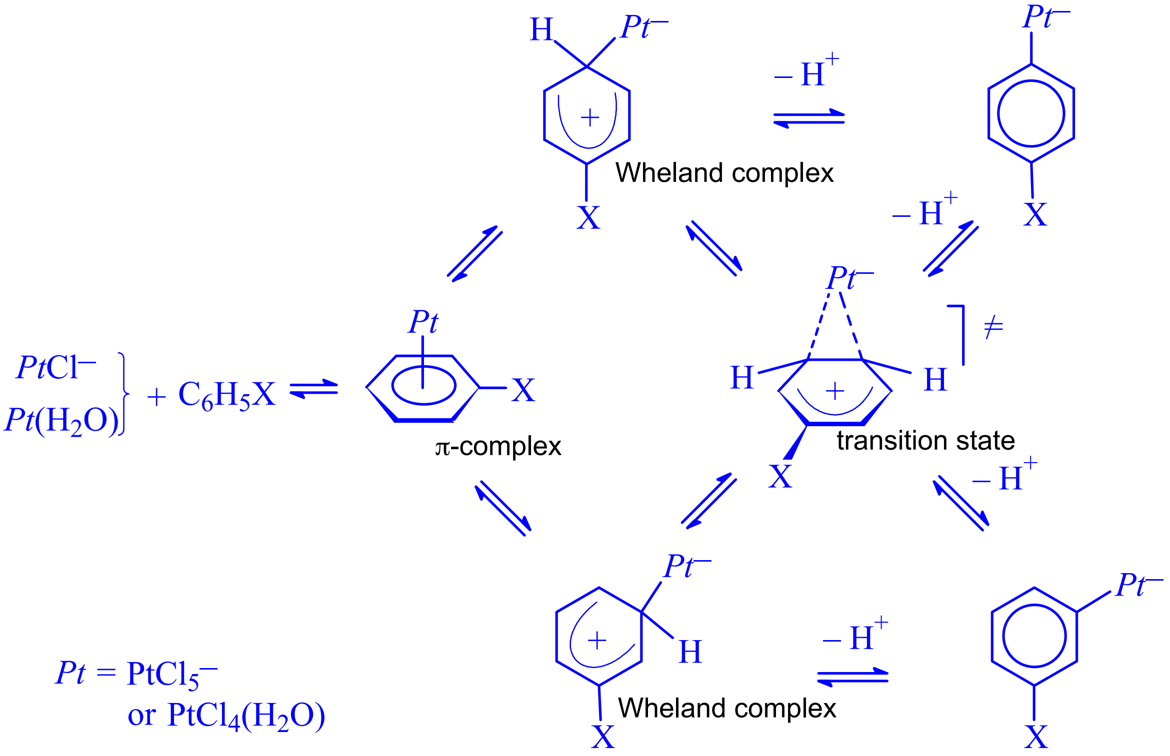


Figure 5. The proposed electrophilic mechanism for the replacement of hydrogen by Pt(IV) in toluene.

The first example of photoelectrophilic substitution in the aromatic series [38]. It turned out that the σ-aryl complexes of platinum(4+) can be easily obtained by irradiating solutions of $PtCl_6^{2-}$ and arenes in acetic or aqueous trifluoroacetic acid at 20 °C with full light from a high-pressure mercury lamp (the main emission maxima at 365, 405, and 436 nm). The yields of the resulting complexes are 10–45%. The rate of formation of the complex with anisole does not depend on the nature of the solvent, and the yield of the complex weakly depends on the concentration of anisole taken in excess. A change in the initial reaction rate in the temperature range 21–56.5 °C corresponds to Ea = 5 ± 1 kcal/mol. The activation energy for the thermal reaction is much higher.

A simplified scheme was proposed for the formation of the $[ArPtCl_4NH_3]^-$ (Figure 6) in the photochemical reaction with arenes, which takes into account the registration of Pt(3+) signals in the EPR spectra and the order of reaction close to zero in the arene, as well as the independence of the reaction rate from light intensity at a sufficiently high intensity.

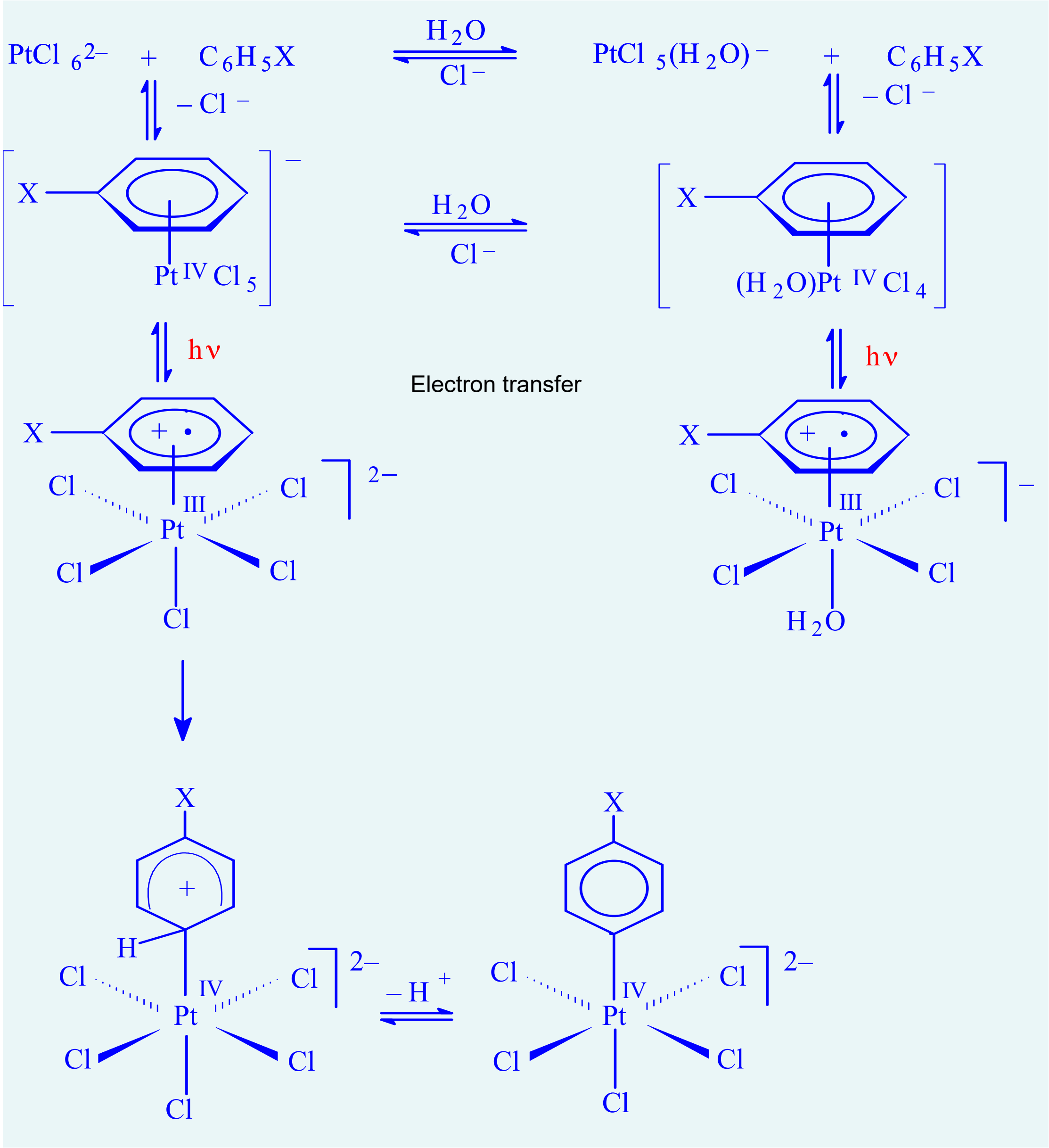


Figure 6. Scheme of photo-electrophilic metallization of arenes.

The para-meta isomerization reaction requires a high activation energy (25 kcal/mol); therefore, under the conditions of photoinduced metalation (15–20 °C), the reversible migration of the $PtCl_5^-$ fragment to the meta position is impossible. In the case of photo-stimulated reactions, the process apparently proceeds with the participation of free radicals, for example, for *n*-hexane:

$$Pt^{IV}Cl_6^{2-} \xrightarrow{h\nu} \{Pt^{III}Cl_5^{2-} + Cl^{\bullet}\};$$

$$n\text{-}C_6H_{14} + Cl^{\bullet} \rightarrow n\text{-}C_6H_{13} + HCl;$$

$$n\text{-}C_6H_{13}^{\bullet} + Pt(IV) \rightarrow n\text{-}C_6H_{13}^{+} + Pt(III);$$

$$n\text{-}C_6H_{13}^{+} \rightarrow n\text{-}C_4H_9CH = CH_2 + H^+;$$

$$n\text{-}C_4H_9CH = CH_2 + Pt(II) \rightarrow \pi\text{-}(n\text{-}C_4H_9CH = CH_2)Pt(II);$$

$$n\text{-}C_6H_{13}^{\bullet} + Pt(III) \rightarrow \sigma\text{-}(n\text{-}C_6H_{13})\text{-}Pt(IV);$$

$$\sigma\text{-}(n\text{-}C_6H_{13})\text{-}Pt(IV) \rightarrow \pi\text{-}(n\text{-}C_4H_9CH = CH_2)Pt(II) + H^+.$$

5. A Hydrogen Peroxide Molecule Can Act Both as Oxidizing and as Reducing Reagent

5.1. Oxidation and Reduction with H_2O_2

An old fable tells that once a peasant and a satyr dined on a cold winter day. The peasant began to breathe in his arms, bringing them to his lips. The satyr asked him why he was doing this. The peasant answered that this is the way in which he warms his hands in cold weather. The food was very hot; and the peasant began to take it little by little, bring it to his lips and blow (see Figure 7). The satyr again asked what he was doing, and the peasant replied that he was cooling the food, because it was too hot.

Figure 7. Jacob Jordaens, Satyr and the peasant (1622), The Pushkin State Museum of Fine Arts, Moscow.

The behavior of the peasant from Aesop's fable is reminiscent of the behavior of a hydrogen peroxide molecule. So, for example, hydrogen peroxide can oxidize an iron(II) compound in Fenton's reagent [39–44]. But hydrogen peroxide can reduce iron(III) derivatives and tetranitromethane (see below).

An interesting result was obtained by Skurlatov, Travin, Duca et al. [45–47] in the study of catalysis by copper ions of the decomposition of H_2O_2 in the presence of ascorbic acid (DH). The authors showed that at high concentrations of H_2O_2, the rate of initiation of active intermediate particles in the dark chain process of decomposition of H_2O_2 coincided with the rate of nonchain oxidation of DH_2 in this process. It was found that the rate of nonchain oxidation of oxidation of DH_2 was proportional to $[Cu^{2+}]$, $[DH_2]$ and $[H_2O_2]$, i.e., oxidation occurs as a result of the effectively trimolecular interaction of Cu^{2+}, DH_2, and H_2O_2. A detailed kinetic analysis led the authors to conclude that the most likely reaction is the interaction of the Cu^{2+} complex with the ascorbate ion and hydrogen peroxide. The authors also noted the peculiarity of this reaction, i.e., that the valency of the metal ion in this transformation is not changed:

$$CuDH^{+} + H_2O_2 \rightarrow Cu^{2+} + D^{-\cdot} + {}^{\cdot}OH + H_2O.$$

The Cu^{+} ions observed during this process appear to be secondary species formed in the course of the decomposition of H_2O_2 as a result of a sequence of reactions:

$$\dot{O}H + H_2O_2 \rightarrow H_2O + H\dot{O}_2;$$

$$H\dot{O}_2 + Cu_2{}^{+} \rightarrow H^{+} + O_2 + Cu^{+}.$$

The role of Cu^{2+} as a catalyst is to facilitate electron transfer from the molecule of the reducing agent, DH_2, bound to the copper ion to the oxidizing agent, H_2O_2. Direct interaction of the reducing and oxidizing agents under the conditions studied by the authors was not observed, and Cu^{2+} ions did not catalyze the decomposition of H_2O_2.

5.2. Decomposition of H_2O_2 to Afford Hydroxyl Radicals Occurs with the Simultaneous Participation of Two Molecules H_2O_2

Kozlov and co-workers studied the initiation process in the system $Fe^{3+} + H_2O_2$ [48] (see also [49]). It was accepted that hydrogen peroxide in the form of H_2O_2 exhibits oxidizing properties

$$2Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + 2\,OH^{-},$$

more often in the presence of a catalyst

$$RH + 2H_2O_2 \rightarrow ROOH + 2H_2O.$$

In the form of an anion, $HO_2{}^{-}$ hydrogen peroxide is a reducing agent

$$HO_2{}^{-} + 2Fe(CN)_6{}^{3-} \rightarrow H^{+} + O_2 + 2Fe(CN)_6{}^{4-}$$

$$HO_2{}^{-} + C(NO_2)_4 \rightarrow H^{+} + O_2 + C(NO_2)_3{}^{-} + NO_2{}^{-}.$$

In this regard, in the presence of catalysts, the transformation

$$HO_2{}^{-} + H_2O_2 \rightarrow H_2O + OH^{-} + O_2,$$

can occur in which one molecule of hydrogen peroxide is a reducing agent and the other is an oxidizing agent.

The authors of [48], using the inhibitor method to study the initiation mechanism of the ion-radical chain decomposition of H_2O_2 with iron(3+) perchlorate in aqueous solutions acidified with $HClO_4$, found that with an increase in both the Fe^{3+} and H_2O_2 concentrations, orders of magnitude of the initiation reaction rate (W_i) by [Fe^{3+}] and [H_2O_2], respectively, become higher than the first order. A detailed kinetic study led the authors to conclude that at elevated concentrations of Fe^{3+} and H_2O_2, along with the mechanism for generating active particles, reactions I, II, i3 (see Scheme 1) and the reactions i2, i3 (see Scheme 1) occurred. The two latter reactions indicate the reducing properties of the $FeHO_2{}^{2+}$ complex when it interacts with $FeOH_2{}^{+}$ and H_2O_2 oxidants, respectively. Reaction (i3) is an example of catalysis of the interaction between a $HO_2{}^{-}$ reductant and an oxidizing agent, H_2O_2, in the presence of Fe^{3+} ions. In acidified solutions, the interaction of these species is not observed.

Equilibrium transformations

I. $Fe^{3+} \rightleftarrows FeOH^{2+} + H^+$ K_I

II $Fe^{3+} + H_2O_2 \rightleftarrows FeHO_2^{2+} + H^+$ K_{II}

III. $H\dot{O}_2 \rightleftarrows H^+ + \dot{O}_2^-$ K_{III}

Initiation reactions

i1. $FeHO_2^{2+} \rightarrow Fe^{2+} + H\dot{O}_2$ k_{i1}

i2. $FeHO_2^{2+} + FeOH^{2+} \rightarrow 2\,Fe^{2+} + H_2O + O_2$ k_{i2}

i3. $FeHO_2^{2+} + H_2O_2 \rightarrow Fe^{2+} + H_2O + O_2 + \dot{O}H$ k_{i3}

Chain extension reactions

1. $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \dot{O}H$ k_1

2. $\dot{O}H + H_2O_2 \rightarrow H_2O + H\dot{O}_2$ k_2

3. $Fe^{3+} + \dot{O}_2^- \rightarrow Fe^{2+} + O_2$ k_3

Chain termination reactions

4. $Fe^{2+} + H\dot{O}_2 \rightarrow Fe^{3+} + HO_2^-$ k_4

5. $Fe^{2+} + \dot{O}H \rightarrow Fe^{3+} + OH^-$ k_5

6. $H\dot{O}_2 + H\dot{O}_2 \rightarrow H_2O_2 + O_2$ k_6

6′ $H\dot{O}_2 + \dot{O}_2^- \rightarrow HO_2^- + O_2$ $k_{6'}$

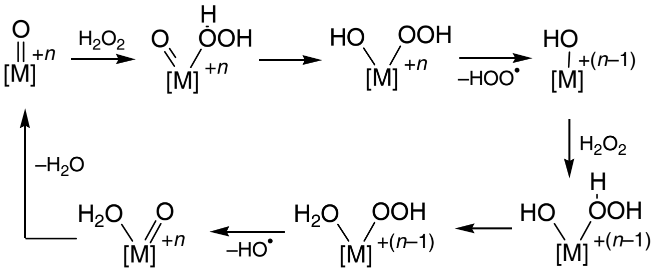
Scheme 1. The mechanism of catalytic decomposition of hydrogen peroxide by iron ions.

Considering the generation reactions of active particles (i1) and (i2), the equilibrium transformations (I), (II), and (IV), the chain extension reactions (1), (2), (3), and the termination reactions (4), (5), (6) (see Scheme 1), the authors of [48] quantitatively described the experimental data available in the literature on the decomposition of H_2O_2 at $[H^+] < 10^{-2}$ M and $[H_2O_2] < 1$ M. Unfortunately, typos were made in the kinetic expression for the decomposition rate of H_2O_2 in [48], and the reaction of generation of active particles (i3) and the interaction of $H\dot{O}_2$ with O_2^- (reaction 6′) in the open circuit were not taken into account. In this regard, the authors considered that it is necessary to give here a corrected expression for the decomposition rate of hydrogen peroxide, taking into account both reactions (i3) and (6′).

The analysis of the reaction mechanism presented in Scheme 1 in the quasistationary approximation with respect to the concentration of chain carriers Fe^{2+}, OH, and HO_2 ($O_2^{-\bullet}$) led to Expression (A) for the rate of decomposition of H_2O_2.

$$\frac{d[H_2O_2]}{dt} = 2W_{O_2} = \left(\frac{2W_i}{\frac{k_4}{k_1k_3}\frac{([H^+]+K_I+K_{II}[H_2O_2])}{K_{III}[H_2O_2][Fe^{3+}]_0} + \frac{k_5}{k_1k_2[H_2O_2]^2} + \frac{([H^+]+K_I+K_{II}[H_2O_2])^2}{k_3{}^2K_{III}{}^2[Fe^{3+}]_0{}^2}\left(k_6 + k_{6'}\frac{K_{III}}{[H^+]}\right)} \right) \quad \text{(A)}$$

A proposed mechanism for the generation of species $HOO^\bullet$ and $HO^\bullet$ formation in the transition-metal complex/H_2O_2 systems is shown in Scheme 2 (the oxidation state of the metal is indicated).



Scheme 2. Simplified mechanism of formation of radicals HOO• and HO•.

The mechanism of the radical formation catalyzed by the nontransition-metal complex should be of a fundamentally different type, because the unique, stable, nonzero oxidation state of Al is +III, and the formation of Al(II) or Al(IV) species is highly unfavorable. A radical mechanism of hydrocarbon oxidations with the environmentally-friendly and cheap homogenous nontransition metal system $[Al(H_2O)_6]^{3+}/H_2O_2/MeCN–H_2O$ [50] and similar species [51–53] was proposed on the basis of DFT calculations. The dramatic activation of H_2O_2 toward homolysis in the key intermediate $[Al(H_2O)_4(OOH)(H_2O_2)]^{2+}$ due to the presence of the easily oxidizable OOH coligand provides, without change of metal oxidation state, the generation of HO• radicals which then oxidize hydrocarbons. The mechanism of the generation of HO• and HOO• radicals—the former is able to directly oxidize even very inert saturated hydrocarbons—includes: (i) the substitution of a H_2O molecule for H_2O_2 in the starting complex $[Al(H_2O)_6]^{3+}$, (ii) the H-transfer from the coordinated H_2O_2 to water (protolysis), and (iii) the second substitution of the ligated H_2O for H_2O_2 to give the hydroperoxo-complex $[Al(H_2O)_4(OOH)(H_2O_2)]^{2+}$. This complex plays a crucial role in the mechanism due to unusual weakness of the HO–OH and Al–OOH bonds (the homolytic O–O bond energy of H_2O_2 ligated in $[Al(H_2O)_4(OOH)(H_2O_2)]^{2+}$ is 6.1 kcal/mol vs. 39.4 kcal/mol in free H_2O_2. A simplified analogy of Fenton reagent and oxidation catalyzed by a nontransition aluminum derivative is demonstrated in the Graphical Abstract.

6. Oxidation of Hydrocarbons and Alcohols with Peroxides in the Presence of Metal Complexes Bearing Nitrogen-Containing Ligands

6.1. Pyrazinecarboxylic Acid (PCA) is a Unique Powerful Cocatalyst in the Oxidation of Organic Compounds with Hydrogen Peroxide. Reagent "H_2O_2—Derivative of Vanadium—Pyrazinecarboxylic Acid"

Simple salts of transition metals very seldom exhibit high activity in oxidation processes. However, it was discovered that some additives lead to a dramatic increase in the effectiveness of the oxidizing system. The vanadate anion, VO_3^-, is itself not active as a catalyst in the oxidation of alkanes and other organic compounds with hydrogen peroxide. In 1993, Shul'pin et al. found [54,55] that in a solution of acetonitrile, this compound catalyzes the effective oxidation of saturated and aromatic hydrocarbons, as well as alcohols and olefins, with hydrogen peroxide in air at temperatures of 20–60 °C if pyrazinecarboxylic acid is present as a cocatalyst (further, we will use the abbreviations PCA or pcaH, where PCA is the anion of pyrazinic acid) at concentrations several times higher than the concentration of the vanadium complex. Other (similar in structure) amino acids turned out to be less active cocatalysts [56]. Later, the vanadate–PCA–H_2O_2 system was carefully studied in various oxidations [57–75]. The primary product of the alkane oxidation reaction of the reagent under discussion is alkyl hydroperoxide, which decomposes during the process with the formation of the corresponding carbonyl compound (ketone or aldehyde) and alcohol. In the initial period of the reaction, especially at low temperatures, only alkyl hydroperoxide is found in the solution. Benzene is converted to phenol.

In 2005, Bell et al. [76] published a paper in which they examined the discussed oxidizing system (and the "robot arm" mechanism) using the density functional method (DFT), and showed that, in fact, the direct proton transfer from the H_2O_2 molecule to the oxygen atom of the vanadium-containing particle is noticeably-higher compared with proton migration; the barrier is first from hydrogen peroxide to the carboxyl group of the PCA anion (coordinated with the vanadium ion at the nitrogen atom), and only then to the V=O fragment (Figure 8). American chemists concluded that “the hydrogen transfer step can also become a speed-determining step for the whole process. This is in agreement with the hypothesis of Shul’pin and others that the catalytic activity of the catalyst is determined by the ability to transfer the proton from hydrogen peroxide to the vanadyl group.” The effective activation energy of the process experimentally determined by the author of the dissertation (63–80 kJ mol^{-1}) also agrees well with the value of Ea calculated by Bell et al. (67–81 kJ mol^{-1}). It is interesting to note that, based on the calculations, American chemists suggested that “it is impossible to find a cocatalyst better than PCA” [76].

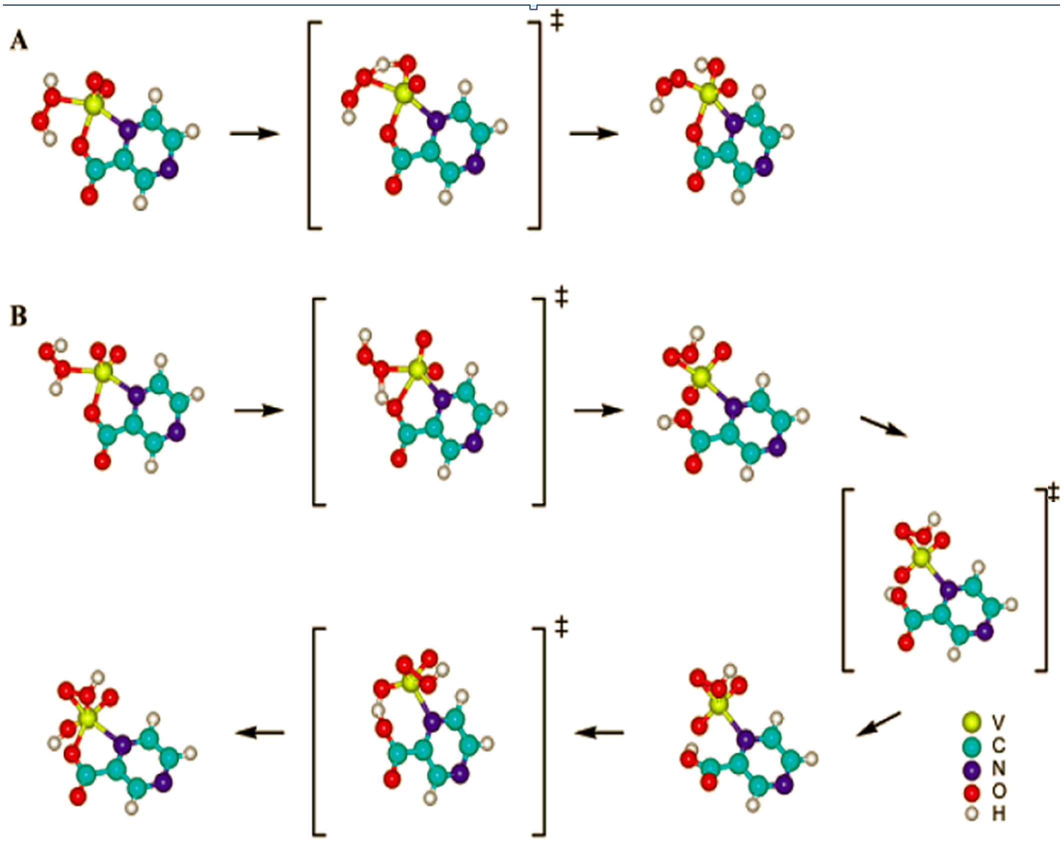


Figure 8. Hydrogen migration via direct (**A**) and “robot’s arm” (**B**) mechanisms. Adapted from Ref. [76].

Kuznetsov [57], in collaboration with the authors of this review, proposed a “water-assisted mechanism” in which the transfer of hydrogen is carried out using a water molecule (Figure 9). This mechanism, according to calculations, with a speed-limiting stage of proton transfer, turned out to be very beneficial. The PCA ligand in the complex, whose role is to stabilize the transition state for the V(IV) particle involved in the limiting stage, greatly accelerates the reaction. The activation barrier for the formation of a hydroxyl radical in the presence of PCA was 9.6 kcal mol^{-1} lower than the barrier for the reaction in the absence of PCA, which is consistent with experimental observations.

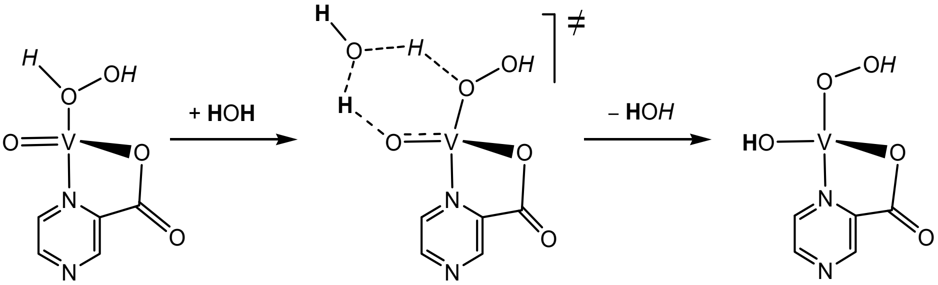
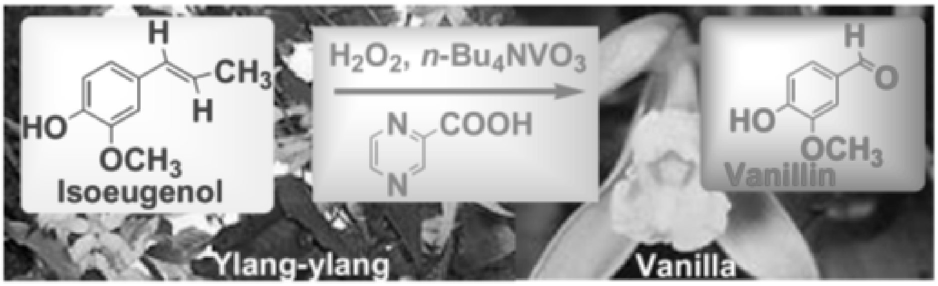


Figure 9. Scheme of a water-assisted mechanism for the transfer of hydrogen with a six-membered transition state.

Gusevskaya [74] applied the H_2O_2–vanadate–PCA reagent to the very important oxidation of isoeugenol into vanillin (see Scheme 3). The mechanism of this oxidation has been studied.

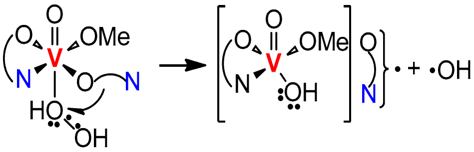


Scheme 3. The oxidation of isoeugenol to vanillin [74].

6.2. Oxidation of Hydrocarbons and Alcohols with Peroxides Catalyzed by Various Amine-Containing Complexes

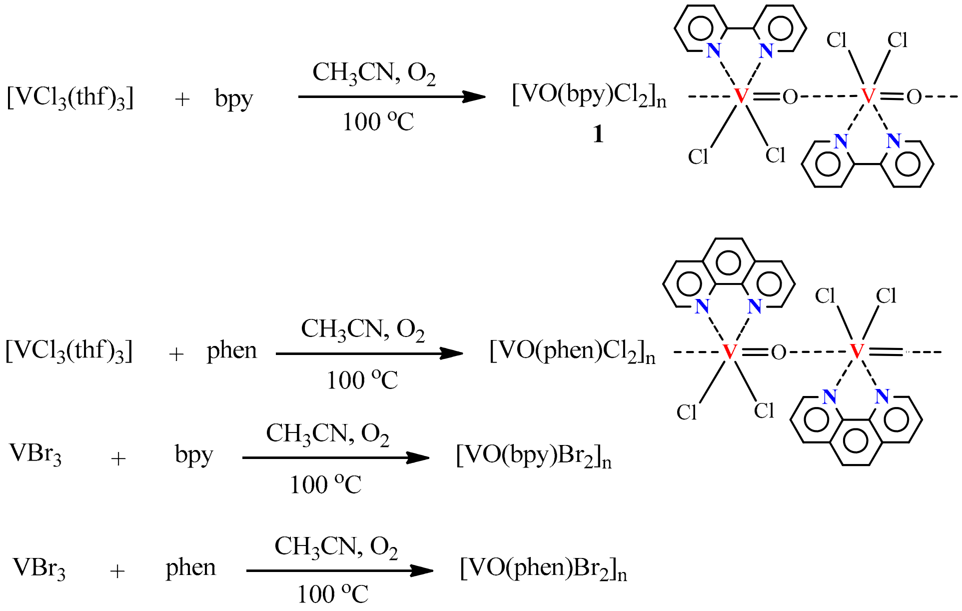
Constable and Housecroft described nonclassical coordination modes in complexes of oligopyridine ligands [77]. They wrote that these are "more Hydra than Janus". Hydra was a multi-headed water monster of Greek mythology. In contrast, the Roman God Janus is usually depicted as having (only) two faces. Oligopyridine ligands and the related compound 1,10-phenanthroline have played a critical role in the development of coordination chemistry. [77].

The importance of redox noninnocent ligands cannot be understated, since this area of research is an integral part of modern chemistry [78]. It should be noted that some vanadium derivatives with ligands containing nitrogen atoms are good catalysts for the oxidation of alkanes and alcohols with hydrogen peroxide, and do not require the presence of PCA. Machura et al. [79] described the oxidation of inert alkanes to alkyl hydroperoxides by H_2O_2 catalyzed with monomeric oxovanadium(V) complexes of 8-hydroxyquinoline derivatives as noninnocent ligands (Scheme 4). The analogous ligands in complexes with copper or rhenium were used in oxidations by peroxides [80–83]

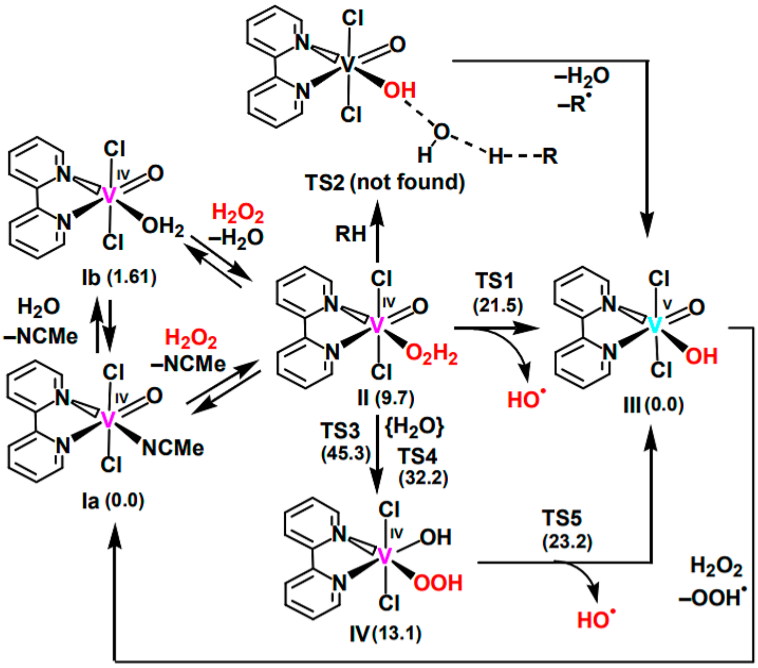


Scheme 4. Cleavage of the HO–OH bond and intramolecular electron transfer in a vanadium complex in the absence of PCA. Adapted from Ref. [79].

Gushchin, Kuznetsov, et al. recently [84,85] observed high activity among the vanadium complexes shown in Scheme 5 in the oxidation of hydrocarbons with peroxides. The mechanism for the generation of OH radicals is presented in Scheme 6. The dependence of the oxidation rate in the case of catalyst **1** is in a good agreement with the Arrhenius Equation (Ea = ca. 20 kcal/mol) and with the value calculated in accordance with the model shown in Scheme 6 (ΔH′ = 19.6 kcal/mol). The proposed model is also in agreement with the experimental data.



Scheme 5. The preparation of certain vanadium complexes [84,85].



Scheme 6. The mechanism for the generation of OH radicals. Adapted from Ref. [85].

Metal complexes containing a few atoms of silicon or germanium as well as ions of a transition metal often have higher catalytic activity in comparison with mononuclear compounds. In recent years, Bilyachenko and co-workers have proposed a new convenient route to metallasilsesquioxanes and synthesized a series of complexes containing various transition metal ions (iron, copper, cobalt, and nickel). These compounds have been used as efficient catalysts in hydrogen peroxide oxidations of hydrocarbons and alcohols [30,31,86–107] (see an example in Figure 2; see also Reviews [108,109]). The activity of such catalysts was especially high if their molecules contained amines and olygoamines (pyridine, dipyridyl, phenanthroline, etc.).

7. Conclusions

Only due to redox-active ligands are mechanisms of generation of free radicals from peroxides realized with the participation of metal ions, without changing their valence state. Both transition and nontransition metal ions can induce such reactions. The most efficient hydroxyl generation processes occur with the simultaneous participation of two H_2O_2 molecules.

Author Contributions: G.B.S., Y.N.K. and L.S.S. wrote the paper.

Funding: This research was funded by the RUDN University Program "5-100", the Russian Foundation for Basic Research (Grant Nos. 19-03-00142), the Ministry of Education and Science of the Russian Federation (project code RFMEFI61917X0007), as well as by the Initiative Program in the frames of the State Task 0082-2014-0007, "Fundamental regularities of heterogeneous and homogeneous catalysis."and also by the Program of Fundamental Research of the Russian Academy of Sciences for 2013–2020 on the research issue of IChP RAS No. 47.16. State registration number of Center of Information Technologies and Systems for Executive Power Authorities (CITIS): AAAA-A17-117040610283-3.

Acknowledgments: The publication has been prepared with the support of the «RUDN University Program 5-100» and funded by RFBR according to Research Projects Grant No. 19-03-00142, the Ministry of Education and Science of the Russian Federation (project code RFMEFI61917X0007), as well as by the Initiative Program in the frames of the State Tasks 0082-2014-0004 and 0082-2014-0007 "Fundamental regularities of heterogeneous and homogeneous catalysis". This work was also performed within the framework of the Program of Fundamental Research of the Russian Academy of Sciences for 2013–2020 on the research issue of IChP RAS No. 47.16. State registration number of Center of Information Technologies and Systems for Executive Power Authorities (CITIS): AAAA-A17-117040610283-3.

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

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