

SUBSTANTIATION FOR OXYWATER ZWITTERIONS AND SINGLET OXYGEN ATOMS GENERATION FROM HYDROGEN PEROXIDE MOLECULES IN AQUEOUS SOLUTIONS

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Hydrogen peroxide is widely used as an oxidant. The results of thermodynamic calculations indicate the impossibility of spontaneous generation of hydroxyl and hydroperoxyl radicals from hydrogen peroxide in aqueous solutions. Hydrogen peroxide spontaneously decomposes in ferrous, ferric, and cupric Fenton reaction systems. Ferric xylenol orange and ferric pyridoxine complexes are oxidized rapidly and spontaneously by this oxidant. Hydrogen peroxide in aqueous solutions spontaneously oxidizes the sulfur atoms of hyposulfite anions and benzylpenicillin molecules. Thus, a hydrogen peroxide molecule generates another intermediate that differs from hydroxyl and hydroperoxyl radicals. Theoretical modeling shows that hydrogen peroxide can participate in the proton transfer reactions. Its isomerization to oxywater zwitterion with subsequent oxywater intramolecular disproportionation is a process that is very suitable for explaining all events of hydrogen peroxide decomposition and oxidative reactivity in aqueous systems. The oxywater zwitterion is a bipolar ion in which the opposite charges are localized on neighboring oxygen atoms. This determines the displacement of electron density from the negatively charged atom to the positively charged atom. As a result, the interoxygen bond heterolytically dissociates with liberation of a water molecule and formation of an oxygen atom (oxene) in a singlet quantum state. This atom has a vacant atomic orbital. The S-oxidation of benzylpenicillin and hyposulfite occurs via targeting of electron pairs of the sulfur atoms by the vacant atomic orbitals of the singlet oxygen atoms. We substantiate an oxene-mediated pathway of hydrogen peroxide disproportionation. A singlet oxygen atom interacts with a second hydrogen peroxide molecule through targeting the unshared electron pair of the oxygen atom by a vacant atomic orbital. The process may be called O-oxidation of hydrogen peroxide; it results in trioxidane (dihydrogen trioxide) formation. Hydrogen trioxide rapidly decomposes and produces water and singlet dioxygen. We have suggested a mechanism of the electron spin rotation during the singlet dioxygen quenching into the triplet quantum state. We have assumed the formation of a dimeric associate from singlet dioxygen antipodes by orbital parameter. Two simultaneous redox reactions (the electron exchange interaction) result in generation of two triplet dioxygen molecules. The first triplet molecule has +1 total electron spin, and the second one has -1 total electron spin. For Fenton reaction systems, the zwitterionization of hydrogen peroxide in Lewis acid-base complexes with metal ions is followed by intramolecular disproportionation of oxywater. The singlet oxene remains in complex with a metal ion. Ferrous iron ion changes its oxidation state to ferric due to rapid and inevitable one-electron transfer within the iron(II)-oxene complex. The ferric-oxyl complex is known as alpha-oxygen complex. In our opinion, the classic Fenton reaction occurs through alpha-complex formation. We maintain such view that is alternative to widespread conceptions of the hydroxyl radical generation or oxoferryl(IV) formation. We have reproduced electro-Fenton reactions of transition metal ions with electrogenerated hydrogen peroxide and presumably observed voltammetric signals for the singlet oxene atoms and oxyl radical anions (alpha-oxygen particles). The oxywater-oxene concept is successfully applicable to explain the catalytic activity of redox-inactive substances. We have used our oxywater-oxene concept for explanation of hydroperoxide monooxygen and dioxygen oxidative functionalization mechanisms in organic synthesis.

Keywords: hydrogen peroxide molecule, oxywater zwitterion, singlet oxene atom, Fenton reaction, oxyl radical anion, ferric-oxyl alpha-complex, electro-Fenton reaction.

Introduction

Hydrogen peroxide HOOH is widely used as an oxidant for medical disinfection, in advanced oxidation processes [1], in delignification processes [2], in organic synthesis for monooxygen and dioxygen

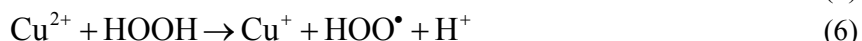
functionalization of substrates [3]. Hydrogen peroxide is a redox-signaling molecule in biological systems [4], and it is a facilitator of pathological oxidative stress via endogenous Fenton reactions [5]. There is a widespread opinion that hydrogen peroxide directly generates free radicals (hydroxyl HO• and hydroperoxyl HOO•) through one-electron redox reactions [1, 3, 5]:



Equation (1) is used for explanation of divalent (ferrous) iron and monovalent (cuprous) copper interaction with hydrogen peroxide [1, 3, 5]:



Equation (2) is used for explanation of trivalent (ferric) iron and divalent (cupric) copper interaction with hydrogen peroxide [1, 3, 5]:



Equations (3)–(6) are widespread interpretations of Fenton reactions [1, 3, 5], but these schemes are not proved [3, 6–8]. The summation 1+2 or 3+5 or 4+6 gives Equation (7) of one-electron hydrogen peroxide dismutation with simultaneous generation of hydroxyl and hydroperoxyl radicals:



Earlier, Chumakov A.A. et al. [9] used Equation (7) as the probable first step of non-catalytic (thermal or photochemical) hydrogen peroxide decomposition. It was shown that one hydrogen atom transfer led to increase in Gibbs free energy +39.9 kJ/mol in the gas phase. There was an assumption for endergonic activation of two hydrogen peroxide molecules associate (Fig. 1).

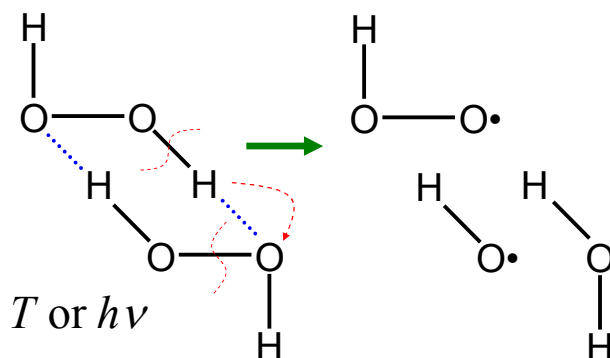


Fig. 1. Previously proposed thermal or photonic hydrogen peroxide one-electron with one-proton disproportionation within dimeric associate

The purpose of our present study is argumentation against the widespread view that hydrogen peroxide is a direct precursor of hydroxyl and hydroperoxyl radicals, as well as presentation of an oxywater-oxene conception for hydrogen peroxide decomposition kinetics and oxidative reactivity in aqueous systems.

I. Results

We carried out a complex study using thermodynamic calculations, performing reactions such as hydrogen peroxide decomposition in Fenton systems, model substrates oxidation (hyposulfite, benzylpenicillin, ferric xylenol orange chelates, ferric pyridoxine chelates), and electro-Fenton reactions. Besides, we used theoretical modeling.

I-1. Thermodynamic analysis. We carried out thermodynamic analysis of radical-generating reactions (Equations (3)–(7) for aqueous phase, using reference values [10] of standard thermodynamic functions of reagents (*rg*) and products (*prd*) of reactions (Table 1) and the known laws and equations of thermochemistry:

$$\Delta_r H_{298}^0 = \sum v \Delta_f H_{298}^0 \text{prd} - \sum v \Delta_f H_{298}^0 \text{rg}$$

$$\Delta_r S_{298}^0 = \sum v S_{298}^0 prd - \sum v S_{298}^0 rg$$

$$\Delta_r G_{298}^0 = \Delta_r H_{298}^0 - 298 \Delta_r S_{298}^0 \quad (\text{A})$$

$$\Delta_r G_{298}^0 = \sum v \Delta_f G_{298}^0 prd - \sum v \Delta_f G_{298}^0 rg \quad (\text{B})$$

Table 1

Reference values of standard thermodynamic functions of reagents and products of reactions

Rg and Prd	Phase	$\Delta_f H_{298}^0$ kJ/mol	S_{298}^0 J/(mol·K)	$\Delta_f G_{298}^0$ kJ/mol
HOOH	aqueous	-191.2	+143.9	-134.0
HOH	liquid	-285.8	+69.9	-237.1
HO [•]	gaseous	+39.0	+183.7	+34.2
HOO [•]	gaseous	+10.5	+229.0	+22.6
H ⁺	aqueous	0	0	0
HO ⁻	aqueous	-230.0	-10.8	-157.2
Fe ²⁺	aqueous	-89.1	-137.7	-78.9
Fe ³⁺	aqueous	-48.5	-315.9	-4.7
Cu ⁺	aqueous	+71.7	+40.6	+50.0
Cu ²⁺	aqueous	+64.8	-99.6	+65.5

The calculated standard thermodynamic functions of reactions 3–7 are presented in Table 2.

Table 2

Calculated standard thermodynamic functions (kJ/mol) of radical-generating reactions

Reaction	$\Delta_r H_{298}^0$	$298 \Delta_r S_{298}^0$	$\Delta_r G_{298}^0$ (A)	$\Delta_r G_{298}^0$ (B)
Fe ²⁺ + HOOH → Fe ³⁺ + HO [•] + ⁻ OH	+40.8	-44.5	+85.3	+85.2
Cu ⁺ + HOOH → Cu ²⁺ + HO [•] + ⁻ OH	-6.7	-33.2	+26.5	+26.5
Fe ³⁺ + HOOH → Fe ²⁺ + HOO [•] + H ⁺	+161.1	+78.5	+82.6	+82.4
Cu ²⁺ + HOOH → Cu ⁺ + HOO [•] + H ⁺	+208.6	+67.2	+141.4	+141.1
2HOOH → HOO [•] + HO [•] + HOH	+146.1	+58.1	+88.0	+87.7

I-2. Hydrogen peroxide decomposition in Fenton systems. We used a digital gas volume and temperature USB-detector for recording molecular dioxygen, produced during hydrogen peroxide decomposition in ferrous, ferric, and cupric Fenton reaction systems (Fig. 2). The reagents used were H₂O₂, FeSO₄·7H₂O, FeCl₃·6H₂O, and CuCl₂·2H₂O.

Decomposition of hydrogen peroxide was complete because of respective dioxygen volume. In accordance with Equation (8), the dismutation of two mol H₂O₂ gives one mol O₂:



At room temperature and standard atmospheric pressure (conditions of our experiments) one mmol H₂O₂ gives approximately 12 mL O₂ by the ideal gas Clapeyron–Mendeleev law calculation. We obtained approximately 42, 53, 64, and 75 mL O₂ from, respectively, 3.5, 4.4, 5.3, and 6.2 mmol H₂O₂ (Fig. 2).

The ferric and cupric systems had no changes in catalyst condition after the completion of hydrogen peroxide decomposition, that is, the ferric system looked like the initial yellow ferric chloride aqueous solution and the cupric system looked like the initial blue-green cupric chloride aqueous solution. In contrast, ferrous catalyst obviously changed its condition. The initial ferrous sulfate aqueous solution was transparent and colorless. Its interaction with hydrogen peroxide resulted in precipitation of iron(III) oxide-hydroxide with rusty color.

I-3. Oxidation of hyposulfite (thiosulfate). We used aqueous solutions of Na₂S₂O₃ 1.90 mol/L and H₂O₂ 0.88 mol/L. The mixtures of 1–2 mL hyposulfite with 3–4 mL hydrogen peroxide rapidly and spontaneously heated up to 50–55 Celsius degrees.

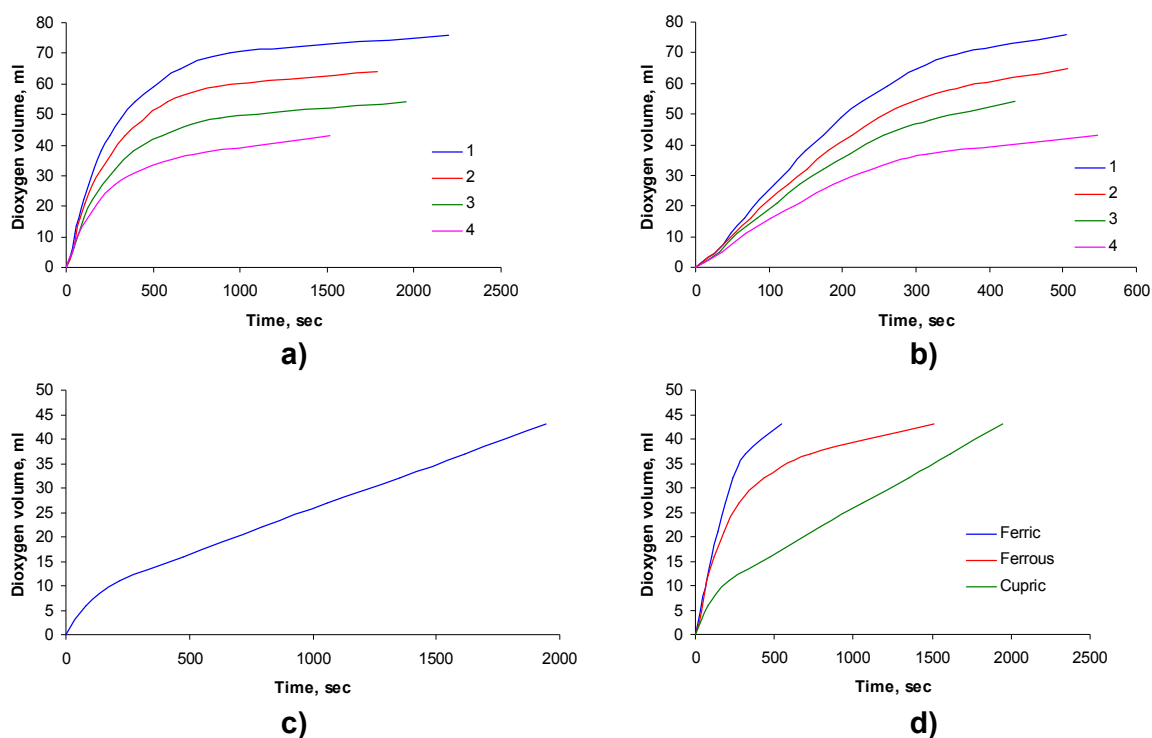


Fig. 2. The kinetics of dioxygen accumulation in Fenton systems (0.025 mol/L Fe^{2+} , 0.025 mol/L Fe^{3+} , 0.25 mol/L Cu^{2+} , 0.77 mol/L H_2O_2 , 1 – 6.2, 2 – 5.3, 3 – 4.4, 4 – 3.5 mmol H_2O_2): a) $\text{Fe}^{2+}/\text{H}_2\text{O}_2$; b) $\text{Fe}^{3+}/\text{H}_2\text{O}_2$; c) $\text{Cu}^{2+}/\text{H}_2\text{O}_2$ (3.5 mmol H_2O_2); d) the comparison of ferric, ferrous and cupric systems (3.5 mmol H_2O_2)

I-4. Oxidation of benzylpenicillin. The benzylpenicillin sodium salt was dissolved in aqueous hydrogen peroxide solution without any Fenton catalyst addition. The system was protected from thermal and photochemical activation. As a result, we observed the colloid solution formation, and hydrogen peroxide disproportionation with the gas-phase molecular oxygen liberation.

The NMR-spectroscopy data (Section I-7) was indicative of S-oxidation of the sulfide fragment.

I-5. Oxidation of ferric xylenol orange chelates. The xylenol orange aqueous solution $5 \cdot 10^{-5}$ mol/L has yellow color and absorbs visible light with $\lambda_{\text{max}}=430$ nm. When the equimolar amount of iron(III) chloride was added, violet color with $\lambda_{\text{max}}=575$ nm appeared. The violet color was stable for many months. When hydrogen peroxide was added, the discoloration of solution occurred very quickly within a few minutes. The final solution had no absorption maximums in visible region and it looked like pale yellow ferric chloride aqueous solution.

The NMR-spectroscopy data (Section I-7) were an evidence in favor of N-oxidation with subsequent Cope elimination.

When iron(II) sulfate was added into the xylenol orange aqueous solution, the yellow color and absorption maximum on 430 nm were not changed. Further addition of hydrogen peroxide led to violet coloring with maximal absorption at 575 nm.

I-6. Oxidation of ferric pyridoxine chelates. The ferric pyridoxine chelates determine the red color of aqueous solution with absorption maximum of visible light at 449 nm. The hydrogen peroxide adding resulted in solution discoloration. The final solution had no absorption maximums in visible region and it looked like pale yellow ferric chloride aqueous solution.

Based on NMR-spectroscopy results (Section I-7) we concluded that the primary alcohol group at pyridine nucleus 4 carbon atom oxidized into carboxyl group as the main reaction path.

When iron(II) sulfate was added into the pyridoxine aqueous solution, the latter remained colorless. Further addition of hydrogen peroxide led to red coloring with maximal absorption at 449 nm.

I-7. The NMR-spectroscopy. We used a Bruker Avance III HD NMR-spectrometer for determining the products of benzylpenicillin and two chelate complexes oxidation. The initial structures of organic molecules are presented on Fig. 3.

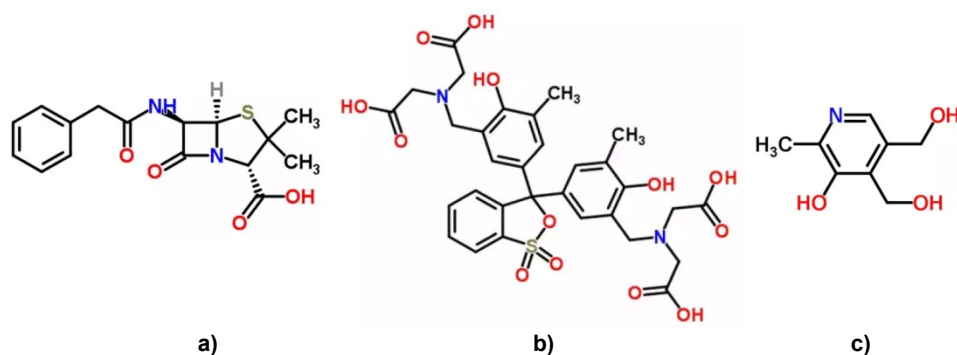
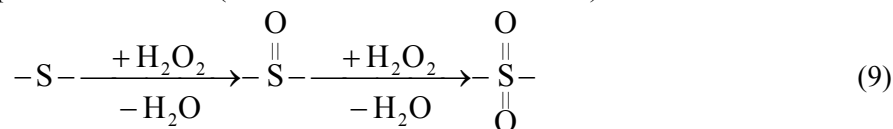


Fig. 3. The structures of organic model substrates of oxidation (received from ChemSpider database, www.chemspider.com): a) benzylpenicillin (ChemSpider ID 5693), b) xylenol orange (ChemSpider ID 65838), c) pyridoxine (ChemSpider ID 1025)

I-7-a. Oxidation of benzylpenicillin. For benzylpenicillin sodium salt aqueous solution, two methyl groups gave 1.37 and 1.43 ppm signals in $^1\text{H-NMR}$ spectrum and 26.42 and 30.61 ppm signals in $^{13}\text{C-NMR}$ spectrum (positive in DEPT-135 spectrum). The neighboring quaternary carbon atom gave 64.33 ppm signal in $^{13}\text{C-NMR}$ spectrum (absent in DEPT-135 spectrum). For the colloid solution (formed soon after benzylpenicillin sodium salt dissolved in aqueous hydrogen peroxide solution), there were six methyl-group signals in the range 1.08–1.47 ppm of $^1\text{H-NMR}$ spectrum and in the range 16.83–26.85 ppm of $^{13}\text{C-NMR}$ spectrum (positive in DEPT-135 spectrum). There were two quaternary carbon atoms signals 50.04 and 56.01 ppm in $^{13}\text{C-NMR}$ spectrum (absent in DEPT-135 spectrum). There were no conditions for new methyl groups and quaternary carbon atoms generation during benzylpenicillin oxidation by hydrogen peroxide. Thus, the increasing of their number was determined by surrounding modification that was the stepwise S-oxidation (sulfide \rightarrow sulfoxide \rightarrow sulfone):



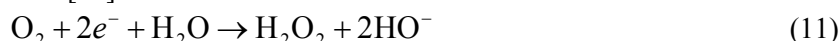
I-7-b. Oxidation of ferric xylenol orange chelates. The NMR-spectroscopy data are available in our previous paper [11] where the N-oxidation of tertiary amine fragments is argued:



The scheme of proposed subsequent N-oxide Cope elimination and some rearrangements with possible oligomerization of intermediates is in the article [11].

I-7-c. Oxidation of ferric pyridoxine chelates. The detailed NMR-spectroscopy data are available in our previous paper [12]. Partially, for pyridoxine aqueous solution, two methylene fragments of primary alcohol groups gave 4.60 and 4.79 ppm signals in $^1\text{H-NMR}$ spectrum and 56.63 and 58.02 ppm signals in $^{13}\text{C-NMR}$ spectrum (negative in DEPT-135 spectrum). For final solution, formed after hydrogen peroxide adding to the red aqueous solution of ferric pyridoxine chelates, there were signals 3.97 ppm in $^1\text{H-NMR}$ spectrum and 59.04 ppm in $^{13}\text{C-NMR}$ spectrum (negative in DEPT-135 spectrum) that were for only one methylene group. We concluded that the primary alcohol group at *para*-position relative to pyridine nitrogen atom was oxidized into carboxyl group. The acylation of hydroxyl group at nearby molecule 3 carbon atom resulted in intermolecular ester bond formation. That was the main reaction pathway (Fig. 4). The additional oxidative modifications were the oxidation of another primary alcohol group at pyridine nucleus 5 carbon atom and the N-oxidation of pyridine nitrogen atom [12].

I-8. Electro-Fenton reactions. Earlier, Chumakov A.A. et al. [13] reproduced electro-Fenton-like reactions of metal ions Cr^{3+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , La^{3+} , and Ce^{4+} with electrogenerated hydrogen peroxide. The voltammetry with mercury film working electrode was used. The molecular dioxygen was electrochemically reduced on the mercury film electrode. The voltammogram of oxygen reduction was a two-wave curve (Fig. 5a). The first wave in the voltage ranging from zero to -1 V corresponded to hydrogen peroxide generation reaction [13]:



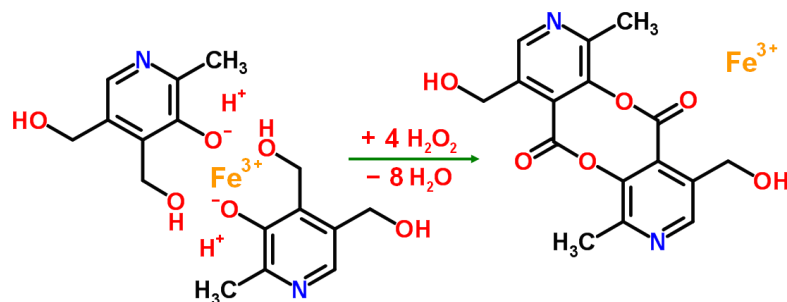


Fig. 4. Suggested scheme of main reaction pathway during ferric pyridoxine chelate oxidation by hydrogen peroxide in aqueous solution

The second wave between -1 and -2 V was the electric current of two-electron hydrogen peroxide reduction:



When hydrogen peroxide was added into an electrochemical cell, we watched amperage increasing between -1 and -2 V. The electric current was proportional to hydrogen peroxide concentration in the cell, and there were no changes in the shape of the second wave of voltammetric curve (Fig. 5b). In the presence of Cr^{3+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , La^{3+} , or Ce^{4+} ions, there was appearance of a new wave in the voltage range between -1.4 and -1.8 V with current maximum near -1.6 V (Fig. 5c).

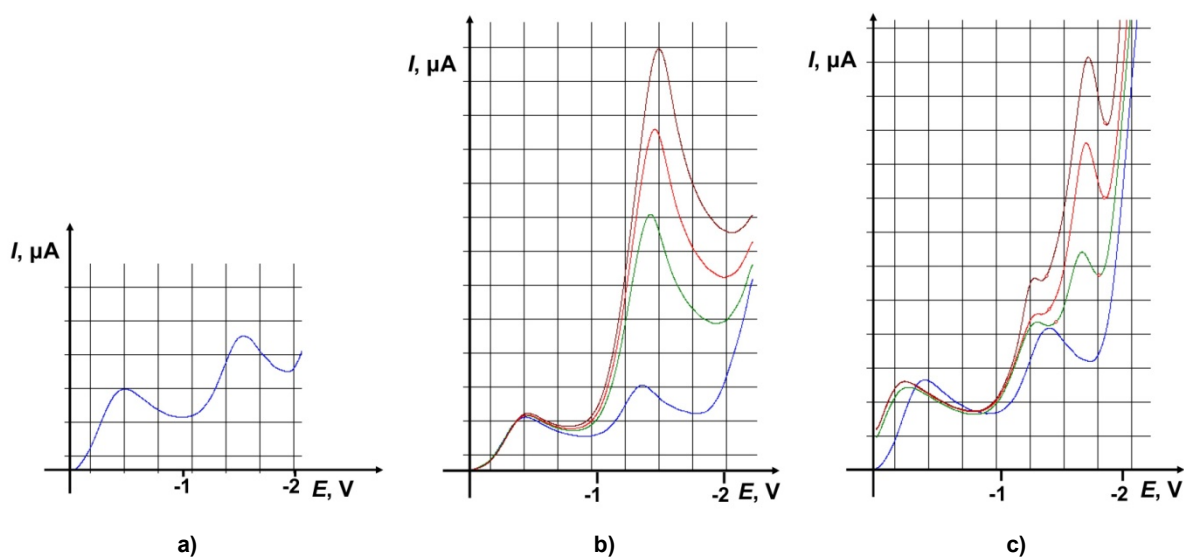


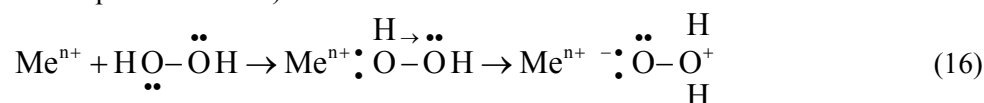
Fig. 5. Voltammograms: a) oxygen reduction on the mercury film electrode, b) changing when hydrogen peroxide is added, c) changing in the presence of transition metal ions

The voltammogram changing in the presence of transition metal ions (Fig. 5c) was interpreted as hydroxyl radical generation and its one-electron cathodic reduction [13]. However, at the present time we outline another explanation presented in the discussion section of this paper.

I-9. Theoretical foundation. Theoretically, hydrogen peroxide molecule can participate not only in one-electron redox reactions (Equations (1) and (2)) but also in proton transfer reactions with generation of hydroperoxide anion [14], hydroperoxonium cation [15] and oxywater zwitterion [16]:



Earlier, Chumakov A.A. et al. [3] argued the zwitterionization of hydrogen peroxide in Fenton reaction systems due to positively charged electrostatic field of the metal ion Me^{n+} catalyst (polarization of H_2O_2 in Lewis acid-base complex with Me^{n+}):



Noncatalytically, the oxywater generation can take place in an associate of two hydrogen peroxide molecules, due to simultaneous intermolecular proton transfers (Fig. 6).

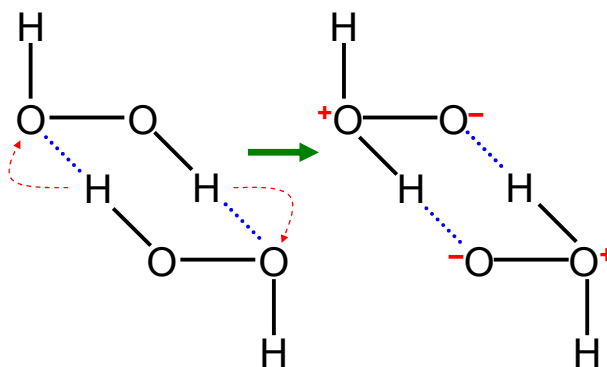
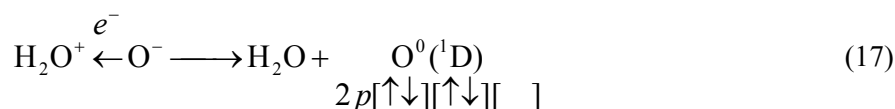


Fig. 6. Suggested scheme of oxywater generation within hydrogen peroxide dimeric associate

The oxywater is a bipolar ion, in which the opposite charges are localized on neighboring oxygen atoms. This determines the displacement of electron density from the negatively charged atom to the positively charged atom. As a result, interoxygen bond heterolytically dissociates (intramolecular disproportionation) with liberation of a water molecule and formation of an oxygen atom (oxene) in a 1D -singlet quantum state. This atom has a vacant atomic orbital [3]:



II. Discussion

II-1. Common basis for oxywater-oxene conception. The results of thermodynamic calculations are the evidence for impossibility of spontaneous hydroxyl and hydroperoxyl radicals generation from hydrogen peroxide in aqueous solution, even in the presence of iron and copper ions, because radical-generating reactions are endergonic (Table 2). However, the facts of iron and copper ions interactions with hydrogen peroxide are undoubted. Firstly, there is a great number of the literature data, for example, referenced in papers [1, 3]. Secondly, we have shown that hydrogen peroxide spontaneously decomposes in ferrous, ferric, and cupric Fenton reaction systems (Fig. 2). Thirdly, ferric xylenol orange and ferric pyridoxine complexes are oxidized rapidly and spontaneously by hydrogen peroxide, due to interaction of chelated iron(III) ions with oxidant molecules (Sections I-5 and I-6). Lastly, hydrogen peroxide in aqueous solutions spontaneously (without thermal, photonic or catalytic activation) oxidizes the sulfur atoms of hyposulfite and benzylpenicillin molecules (Sections I-3 and I-4). Thus, a hydrogen peroxide molecule generates another intermediate that differs from hydroxyl and hydroperoxyl radicals. In our opinion, the hydrogen peroxide molecule isomerization to oxywater zwitterion (Equation (15)) with subsequent oxywater intramolecular disproportionation (Equation (17)) is a process that is very suitable for explaining all events of hydrogen peroxide reactivity in aqueous systems.

II-2. Hydrogen peroxide decomposition. In contrast to widespread schemes of one-electron redox reactions (Equations (1) and (2)), we postulate the priority of proton transfer reactions in hydrogen peroxide aqueous solutions (Equations (13)–(15)). In contrast to our previous assumption for thermal or photonic one-electron with one-proton transfer in the associate of two hydrogen peroxide molecules with simultaneous hydroxyl and hydroperoxyl radicals generation (Fig. 1), we now argue the oxywater

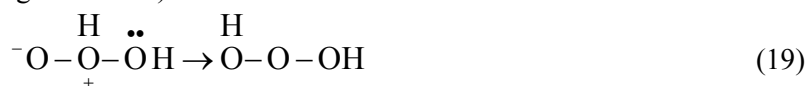
zwitterions generation in hydrogen peroxide dimer, due to simultaneous intermolecular proton transfers (Fig. 6). Further, the oxygen atoms in ¹D-singlet quantum state are generated (Equation (17)).

For Fenton reaction systems, the zwitterionization of hydrogen peroxide in Lewis acid-base complex with Meⁿ⁺ (Equation (16)) is also followed by intramolecular disproportionation of oxywater (Equation (17)). The ¹D-oxene remains in a complex with the metal ion. Thus, the complexes [Fe²⁺O⁰(¹D)]²⁺, [Fe³⁺O⁰(¹D)]³⁺, and [Cu²⁺O⁰(¹D)]²⁺ are primary intermediates in ferrous, ferric, and cupric Fenton reaction systems (Section I-2).

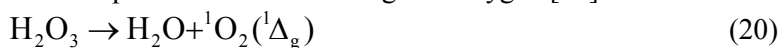
The singlet oxygen atom has a vacant atomic orbital (2p[↑↓][↑↓][]). In contrast to our previous argumentation for the free radical chain mechanism of hydrogen peroxide decomposition [9], we now substantiate a ¹D-oxene-mediated pathway of hydrogen peroxide disproportionation in aqueous solutions. A singlet oxygen atom interacts with another hydrogen peroxide molecule through targeting the unshared electron pair of oxygen atom by the vacant atomic orbital:



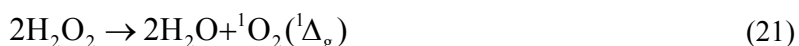
The process may be called O-oxidation of hydrogen peroxide. The proton transfer follows this reaction and results in trioxidane (dihydrogen trioxide) formation:



Hydrogen trioxide rapidly decomposes and produces water and singlet dioxygen [17]:

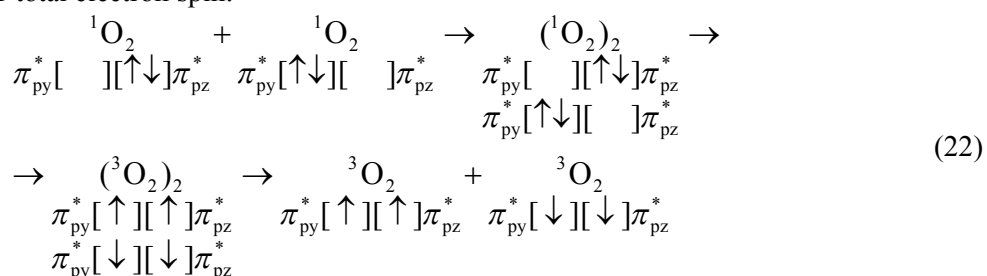


Thus, dismutation of hydrogen peroxide (Equation (8)) results in singlet molecular oxygen generation via Equations (15), (17)–(20):

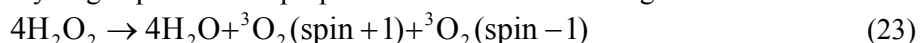


The decomposition of hydrogen peroxide in ferric (Fig. 2b) and cupric (Fig. 2c) systems occurs via Equations (16)–(20).

Previously, Chumakov A.A. et al. [3] carried out the substantiation of the singlet quantum state of molecular oxygen generated during hydrogen peroxide decomposition (Equation (21)), using simple quantum chemical graphical modeling. Besides, we have suggested a mechanism of electron spin rotation during the quenching process ¹O₂ → ³O₂. We have assumed the formation of an associate (¹O₂)₂ from antipodes of orbital parameter. Two simultaneous redox reactions (the electron exchange interaction) result in two triplet dioxygen molecules generation. The first molecule ³O₂ has +1 total electron spin and the second one has –1 total electron spin:



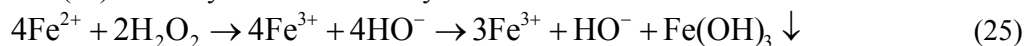
The overall equation of hydrogen peroxide disproportionation is the following:



II-3. Classic Fenton reaction mechanism. The trivalent iron and divalent copper ions serve as catalysts of oxywater formation and singlet ¹D-oxygen atom generation. The ferric ions are more active than cupric ions (Fig. 2d). The ferric and cupric ions are true catalysts because their oxidation states do not change after the completion of hydrogen peroxide decomposition. In contrast, ferrous iron ions are not true catalysts of hydrogen peroxide dismutation because of change of their oxidation state to ferric. Ferrous sulfate is a reagent oxidized by hydrogen peroxide:



The process of hydrogen peroxide decomposition in ferrous Fenton system (Fig. 2a) is accompanied by precipitation of iron(III) oxide-hydroxide with rusty color:

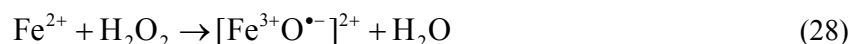


The oxidation of divalent iron to trivalent one by hydrogen peroxide is proved by violet coloration ($\lambda_{\text{max}}=575$ nm) of yellow ferrous xylenol orange aqueous solution (Section I-5) and red coloration ($\lambda_{\text{max}}=449$ nm) of colorless ferrous pyridoxine aqueous solution (Section I-6), when hydrogen peroxide is added.

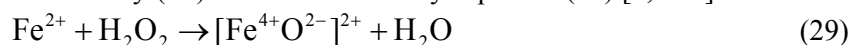
We argued [3] the rapid and inevitable one-electron transfer within the iron(II)-oxene complex:



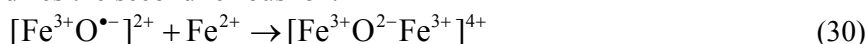
The ferric-oxyl radical-anion complex is known to be generated from nitrous oxide on the surface of FeZSM-5 zeolite and is considered as α -oxygen complex [18]. In our opinion, the classic Fenton reaction occurs through this complex formation:



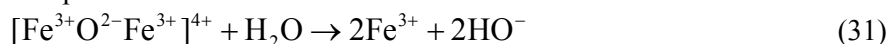
Such view is alternative to the widespread classic Fenton reaction conceptions of hydroxyl-free radical generation (Equation (3)) or the oxoferryl(IV) cation formation by Equation (29) [3, 6–8]:



The α -oxygen complex oxidizes the second ferrous ion:

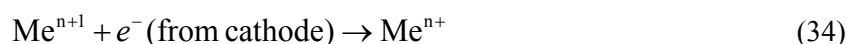


Further, the hydrolysis of complex cation occurs:

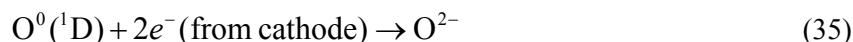


The sequence of reactions by Equations (16), (17), (27), (30), and (31) is the mechanism of reaction by Equation (24). The generated ferric ions decompose hydrogen peroxide by the mechanism including consequent formation of oxywater, ^1D -oxene, dihydrogen trioxide, singlet dioxygen and quenching of singlet dioxygen to triplet quantum state (Equations (16)–(20), and (22)). The rate of hydrogen peroxide decomposition in ferrous system decreases compared to ferric system, because of removal of Fe^{3+} ions in the first one by precipitation of iron(III) oxide-hydroxide (Fig. 2).

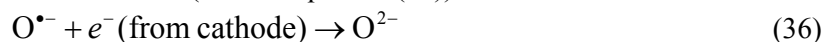
II-4. Electro-Fenton reactions. Earlier [13], we interpreted changes of the second voltammogram wave (Fig. 5c) as hydroxyl radical generation and its one-electron cathodic reduction including redox cycling of metal ion oxidation state:



At the present time, we maintain another explanation. The second wave is the electric current of two-electron hydrogen peroxide reduction (Equation (12)), but the detailed mechanism includes hydrogen peroxide isomerization to oxywater (Equation (15)) and ^1D -oxene generation (Equation (17)). The polarization of hydrogen peroxide occurs in an electrochemical cell under the electric field between electrodes. Thus, the second wave is in truth the current of ^1D -oxene two-electron reduction:



In the presence of transition metal ions, there is Lewis acid-base complexation between a Me^{n+} ion and the $\text{O}^0(^1\text{D})$ atom. The one-electron transfer within the complex $[\text{Me}^{n+}\text{O}^0(^1\text{D})]^{n+}$ results in α -oxygen (oxyl radical-anion) $\text{O}^{\bullet-}$ generation in the $[\text{Me}^{n+1}\text{O}^{\bullet-}]^{n+}$ form (versus Equation (32)) Thus, the wave in the voltage range between -1.4 and -1.8 V with current maximum near -1.6 V (Fig. 5c) is the current of oxyl radical-anion one-electron cathodic reduction (versus Equation (33)):

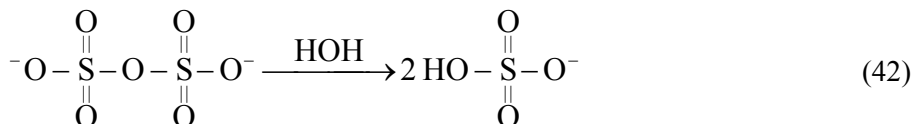
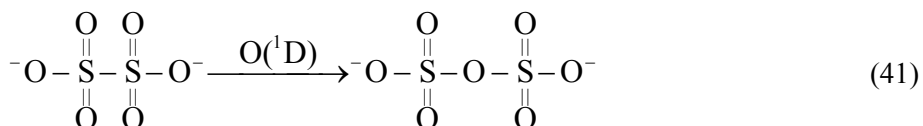
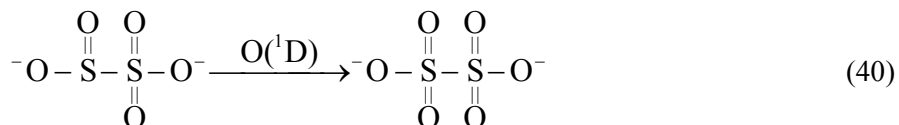
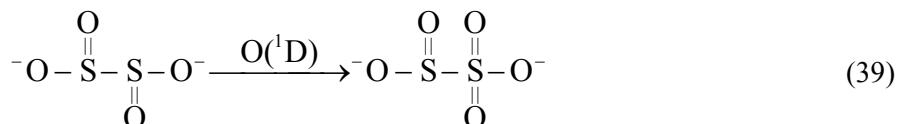
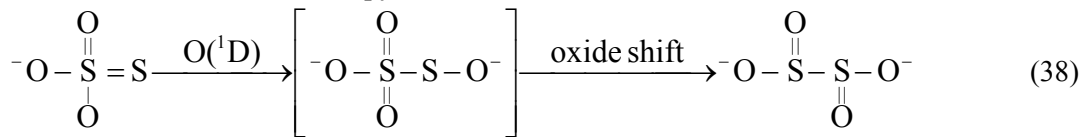


The hydrolysis of oxide anion occurs:

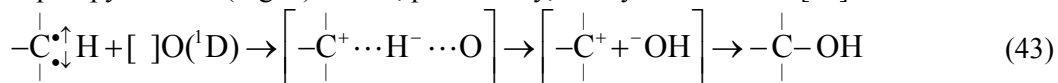


The redox cycling of metal ion oxidation state occurs as $\text{Me}^{n+} \leftrightarrow \text{Me}^{n+1}$. For the used salts [13], there are cycles $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$, $\text{Cu}^+ \leftrightarrow \text{Cu}^{2+}$, $\text{La}^{2+} \leftrightarrow \text{La}^{3+}$, $\text{Ce}^{3+} \leftrightarrow \text{Ce}^{4+}$, and others.

II-5. Model substrates oxidation. The sulfur atom of benzylpenicillin molecule has two unshared electron pairs. Thus, the S-oxidation by Equation (9) occurs via targeting of sulfur atom electron pairs by vacant atomic orbitals of two singlet oxygen atoms generated from hydrogen peroxide molecules. The reaction of hyposulfite oxidation by hydrogen peroxide occurs rapidly and spontaneously. As supported by us, the reaction occurs via the non-radical stepwise S-oxidation by ^1D -oxene oxidant and results in dithionite, metabisulfite, dithionate, pyrosulfate, and bisulfate formation:



For ferric chelate oxidation, the direct oxidant is also a singlet ^1D -oxygen atom generated by the chelated Fe^{3+} ions. The N-oxidation of xylenol orange molecule (Equation (10)) occurs via targeting of the nitrogen atom unshared electron pair by ^1D -oxene vacant atomic orbital [11]. The oxidation of primary alcohol group of pyridoxine (Fig. 4) occurs, presumably, via hydride transfer [12]:



There is consequent formation of geminal diol, aldehyde, and carboxylic acid. Further, the acylation of hydroxyl group at nearby molecule 3 carbon atom results in intermolecular ester bond formation [12].

II-6. The application of oxywater-oxene conception. The oxywater-oxene concept is successfully applicable to explain the catalytic activity of redox-inactive substances, for which the free radical or high-valence species generation schemes are unusable. For instance, gallium(III) and aluminum(III) nitrates catalyze the epoxidation of some olefins with hydrogen peroxide [19]. The mechanism is unclear. We assume the formation of Lewis acid-base complexes $[\text{Al}^{3+}\text{O}(^1\text{D})]^{3+}$ and $[\text{Ga}^{3+}\text{O}(^1\text{D})]^{3+}$. The epoxidation occurs by singlet oxene. For another example, the hydrogen peroxide lanthanum(III) system (including $\text{La}(\text{NO}_3)_3$, or $\text{La}(\text{OH})_3$, or La_2O_3) is a generator of $^1\Delta_g$ -singlet dioxygen [20]. Although we maintain the redox cycling $\text{La}^{2+} \leftrightarrow \text{La}^{3+}$ in an electrochemical cell [13], it is unlikely that lanthanum(III) changes oxidation degree +3 when generating a singlet dioxygen $^1\text{O}_2$ from hydrogen peroxide [20]. We suggest the formation of a similar Lewis acid-base complex $[\text{La}^{3+}\text{O}(^1\text{D})]^{3+}$ and subsequent generation and decomposition of dihydrogen trioxide (Equations (18)–(20)).

Hydroperoxides, including the simplest hydrogen peroxide, are widely used in organic synthesis for oxygen functionalization processes, such as alkanes and arenes hydroxylation, alkenes epoxidation, Baeyer-Villiger ketones oxidation to esters, organonitrogen compounds N-oxidation and organosulfur compounds S-oxidation [3]. In addition to monooxygen oxidation, the dioxygen functionalization by $^1\Delta_g$ -singlet molecular oxygen also takes place in organic synthesis and includes synthesis of hydroperoxides from alkenes and cyclic peroxides from alkadienes [21–23].

We used our oxywater-oxene concept for explanation of the mechanisms of hydroperoxide monooxygen (Fig. 7) and dioxygen (Fig. 8) oxidative functionalization processes in organic synthesis.

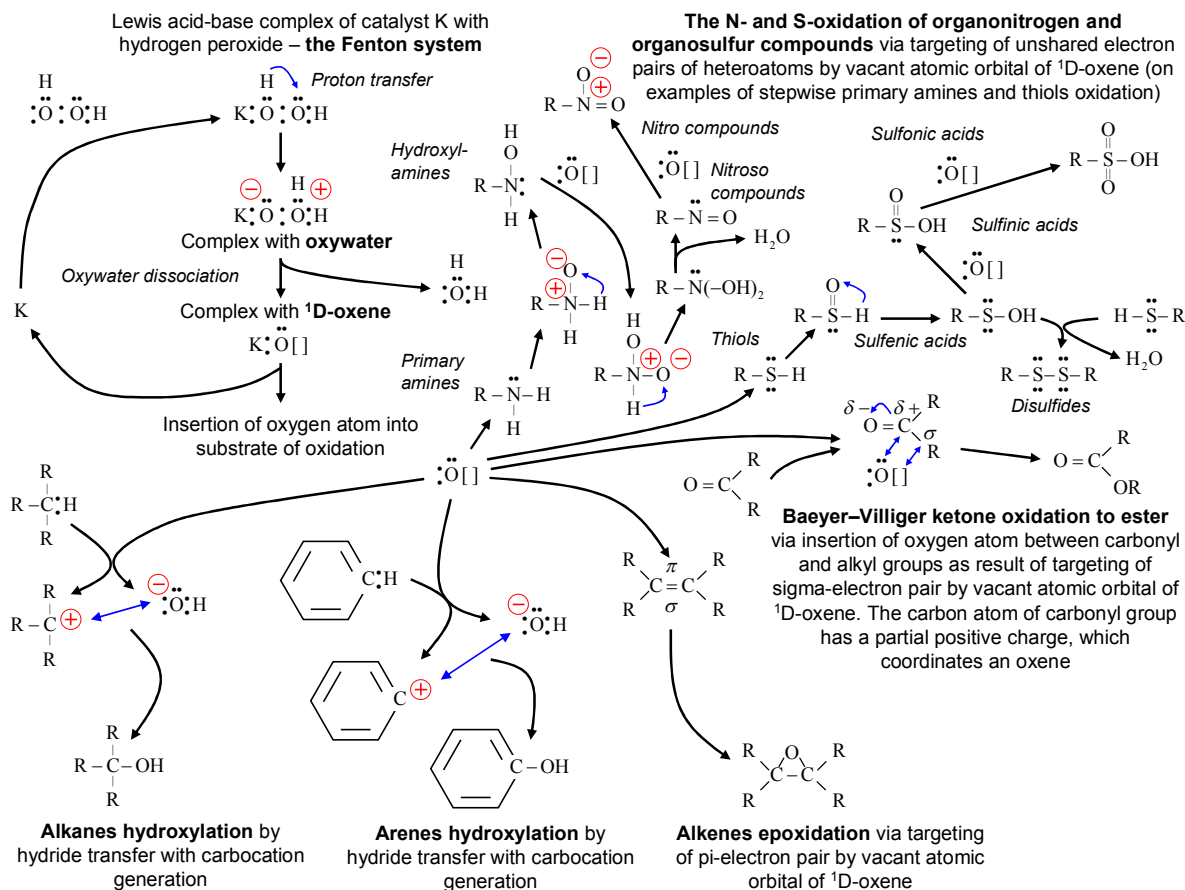


Fig. 7. Suggested mechanisms of oxygen atom insertion into molecules of organic substrates of monooxygen functionalization when using the Fenton catalytic systems

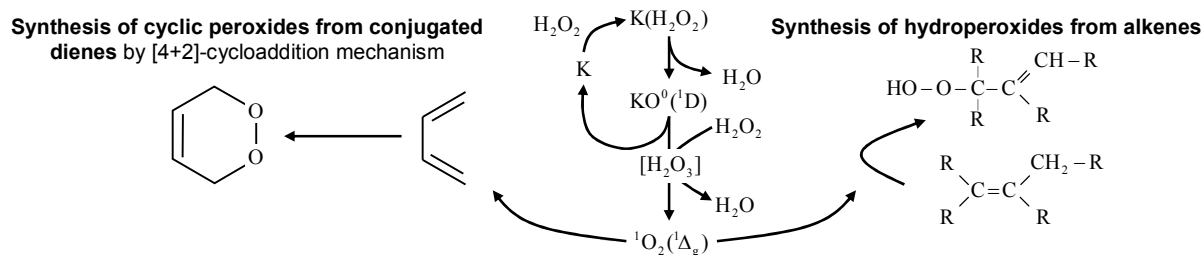


Fig. 8. Suggested mechanisms of peroxide group insertion into molecules of organic substrates of dioxygen functionalization when using the Fenton catalytic systems

Conclusion

Hydrogen peroxide isomerization to oxywater zwitterion with subsequent oxywater intramolecular disproportionation is a process that is very suitable for explaining all events of hydrogen peroxide decomposition and oxidative reactivity in aqueous systems.

An oxygen atom (oxene) in a singlet quantum state has a vacant atomic orbital. It mediates disproportionation of hydrogen peroxide in aqueous solutions via O-oxidation of the second hydrogen peroxide molecule. The formed trioxidane (dihydrogen trioxide) rapidly decomposes and produces water and singlet dioxygen. The quenching of the latter substance into triplet quantum state occurs via electron exchange interaction between two singlet dioxygen molecules.

For Fenton reaction systems, the complexes of singlet oxene with metal ions are primary intermediates. The classic Fenton reaction occurs through alpha-complex (ferric-oxyl radical anion) formation due to rapid and inevitable one-electron transfer within the iron(II)-oxene complex.

The singlet oxygen atoms are direct oxidants during alkanes and arenes hydroxylation, alkenes epoxidation, Baeyer-Villiger ketones oxidation to esters, organonitrogen compounds N-oxidation and organosulfur compounds S-oxidation. The most common mechanism is the targeting of shared or unshared electron pairs by a vacant atomic orbital.

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ОБОСНОВАНИЕ ГЕНЕРИРОВАНИЯ ЦВИТТЕРИОНОВ ОКСИВОДЫ И СИНГЛЕТНЫХ АТОМОВ КИСЛОРОДА ИЗ МОЛЕКУЛ ПЕРОКСИДА ВОДОРОДА В ВОДНЫХ РАСТВОРАХ

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Пероксид водорода широко используется в качестве окислителя. Результаты термодинамических расчётов свидетельствуют о невозможности самопроизвольного генерирования гидроксильного и гидропероксильного радикалов из пероксида водорода в водных растворах. Однако при этом пероксид водорода спонтанно разлагается в реакционных системах Фентона с двухвалентным и трёхвалентным железом и двухвалентной медью. Хелатные комплексы ксиленолового оранжевого и пиридоксина с железом(III) окисляются пероксидом водорода самопроизвольно и быстро. Наконец, пероксид водорода в водных растворах спонтанно окисляет атомы серы анионов тиосульфата (гипосульфита) и молекул бензилпенициллина. Таким образом, интермедиаты, генерируемые из молекул пероксида водорода, с большой вероятностью отличаются по природе от радикалов гидроксила и

гидропероксида. Теоретическое моделирование показывает, что молекула пероксид водорода может отдавать или акцептировать протон, а также изомеризоваться в биполярный ион (цвиттерион) оксидовы. Схема внутримолекулярной передачи протона с последующим внутримолекулярным диспропорционированием оксидовы способна универсально объяснять все случаи разложения и окислительной реактивности пероксида водорода в водных системах. Цвиттерион оксидовы (оксида воды) характеризуется локализацией разноименных зарядов на соседних непосредственно связанных кислородных атомах. Это обуславливает смещение электронной плотности в сторону положительно заряженного атома кислорода и, в итоге, диссоциацию межкислородной связи по гетеролитическому типу с высвобождением молекулы воды и образованием атома кислорода (оксена) в синглетном квантовом состоянии. Данный атом имеет вакантную атомную орбиталь. Процессы S-окисления бензилпенициллина и тиосульфата протекают через акцепцию неподеленных электронных пар атомов серы вакантными атомными орбиталями синглетных атомов кислорода. Нами аргументирована схема оксен-опосредованного диспропорционирования пероксида водорода. Синглетный атом кислорода реагирует со второй молекулой пероксида водорода, акцептируя вакантной атомной орбиталью неподеленную электронную пару одного из двух атомов кислорода. Процесс может быть назван O-окислением пероксида водорода, он приводит к образованию триоксида (триоксида диводорода), который быстро распадается на воду и синглетный молекулярный кислород (дискислород). Нами предположен механизм обращения электронного спина в ходе тушения синглетного состояния дискислорода и перехода в триплетное состояние. Допущено формирование димерного ассоциата из молекул синглетного дискислорода, являющихся антиподами по орбитальному моменту. Внутри ассоциата осуществляется электронообменное взаимодействие, приводящее к образованию двух молекул триплетного дискислорода, являющихся антиподами по спиновым моментам: одна молекула со спином +1, другая молекула со спином -1. Для любой реакционной системы Фентона, цвиттерионизация пероксида водорода и внутримолекулярное диспропорционирование оксидовы протекают в кислотно-основном комплексе Льюиса с ионом металла. Синглетный оксен остаётся в комплексе с ионом металла. Двухвалентный ион железа меняет свою степень окисления на трёхвалентную в результате быстрой и неизбежной передачи одного электрона внутри комплекса железа(II)-оксена. Формирование комплекса железа(III)-оксильного радикал-аниона (альфа-комплекса) в классической системе Фентона является представлением, альтернативным широко распространённым концепциям генерирования гидроксильного радикала или катиона оксожелеза(IV). Нами воспроизведены реакции электро-Фентона – взаимодействия ионов металлов переменной валентности с электрогенерированным пероксидом водорода. При этом, предположительно, получены вольтамперметрические сигналы атомов синглетного кислорода и оксильных радикал-анионов (альфа-кислородных частиц). Оксидно-оксеноидная концепция успешно применима для объяснения каталитической активности редокс-неактивных веществ, для которых в принципе исключаются схемы генерирования свободных радикалов или гипервалентных форм. Нами аргументируются механизмы гидропероксидной монокислородной и дискислородной окислительной функционализации в органическом синтезе.

Ключевые слова: молекула пероксида водорода, цвиттерион оксидовы, атом синглетного кислорода, реакция Фентона, оксильный радикал-анион, железоз(III)-оксильный альфа-комплекс, реакция электро-Фентона.

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