SCIENTIFIC DISCUSSIONS

The Nature of Intermediates in Fenton Reaction Systems

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Abstract

Fenton reaction systems are widely used for oxidative activation of hydroperoxides in monooxygen oxidative functionalisation of organic compounds, *i.e.* the introduction of an oxygen atom into the composition of organic substrates. The nature of intermediates that are direct oxidants until now remains a subject of hypotheses and discussions. Catalysts for Fenton oxidation are diverse, differing by the nature of elements (*d*-, *f*-, *p*-elements) directly reacting with hydrogen peroxide species, its ligand surroundings, and the phase state. The literature explains the classic Fenton reaction in Fe^{2+}/H_2O_2 systems by generating either a free hydroxyl radical, or iron (IV)-oxo cation, however, both concepts were not verified. A common representation of hydrogen peroxide oxidation in Fe^{3+}/H_2O_2 systems is not supported due to electrochemical criteria. The formation idea of oxoiron (IV) species in Fe^{3+}/H_2O_2 systems assumes the active participation of the ligand surroundings of Fe^{3+} ion as a second electron donor, therefore, it is limited by the nature of ligands, however, having obtained the widest spread in biochemistry when interpreting fermentative activity of Fe^{3+} hemoproteins, in which protoporphyrin IX species are Fe^{3+} ion ligands. The key idea in copper Fenton chemistry that is hydrogen peroxide oxidation in Cu^{2+}/H_2O_2 systems is even more unsupported from the standpoint of electrochemistry. Pathways for free hydroxyl radical generation are most often substantiated for systems based on other metals with variable valences. Interaction mechanisms of *p*-elements with hydroperoxides are absolutely unclear.

The concept of universal priorities of polarization and dissociation of hydroperoxides during their oxidative activation and decomposition by Fenton catalysts is proposed to the scientific community as a hypothesis. The initial transformation of Fe(II) dihydroperoxo species into a complex of Fe^{2+} ion with a molecule of oxywater ($^-O-^+OH_2$) that dissociates to form a complex of Fe^{2+} ion with the oxygen atom (iron (II)-oxene) in ^1D-singlet quantum state is assumed for the classic Fenton reaction. Afterwards, α-oxygen complex $[Fe^{3+}O^{\bullet-}]^{2+}$ that is argumented as the major intermediate in Fe^{2+}/H_2O_2 systems is formed resulting from the fast and inevitable intracomplex electron transfer. An opportunity for transformation of α-oxygen complex into intermediates for subsequent intermediates, such as oxoiron (IV) species, cryptohydroxyl, and free hydroxyl radicals is demonstrated. A high probability for the invariability of oxidation degree of Fe^{3+} with the prevalence of $[Fe^{3+}O^0(^1D)]^{3+}$ intermediate is substantiated for Fe^{3+}/H_2O_2 systems, among other things, biochemical. The successful use of interpretation towards various catalysts, among other things, based on *p*-elements is illustrated.

Molecular oxygen (dioxygen) in the $^1\Delta_g$-singlet quantum state ($^1O_2$) that differs from the main ($^3\Sigma_g^-$, $^3O_2$) triplet state is produced in Fenton degradation (disproportionation) of hydrogen peroxide. Singlet dioxygen is of preparative value in dioxygen alkene and alkadiene functionalisation processes, such as synthesis of hydroperoxides and cyclic peroxides. The life time of $^1O_2$ generated in aqueous solutions of H_2O_2 is several microseconds. The $^1O_2 \rightarrow ^3O_2$ quenching overcomes a ban for electron spin reversal *via* a yet unknown mechanism. The $(^1O_2)_2$ associate is formed from antipodes on the orbital moment, as supposed by us. Resulting from

two simultaneous redox reactions, two $^3O_2$ species are formed. They are antipodes on spin moments of the unpaired electrons, the total spin of which is $+1$ and -1.

Contents

1. INTRODUCTION

Hydroperoxides (hydrogen peroxide, tert-butyl hydroperoxide, peroxy acids, *etc.*) are used in organic synthesis as oxidants (Fig. 1) for hydroxylation of alkanes and arenes [1−9], epoxidation of alkenes [10−25], the Baeyer−Villiger oxidation of ketones to esters [26, 27] and heteroatom oxidation in organonitrogen and organosulphur compounds [28, 29]. Oxidative activation of hydroperoxides is carried out in Fenton reaction systems (FRS) by the generation of intermediates directly oxidizing organic substrates. The nature of the formed particles of intermediate oxidants (reactive oxygen species) remains a matter of hypotheses and debate [30], although more than 100 years have passed since the Fenton's discovery of the oxidizing ability of the Fe^{2+}/H_2O_2 system [31].

A work objective is literature data review and analysis of the nature of intermediates in FRS with the formulation of problems and suggestion of options for their solution to the scientific community.

2. CATALYSTS FOR FENTON OXIDATION

Free water-soluble Fe^{2+} ions are a classic catalyst in Fenton reaction systems [31−41]. In reality, hexaaqua $[Fe^{2+}(H_2O)_6]^{2+}$ complexes [36] should be regarded as free Fe^{2+} ions, and in the context of the interaction of $Fe^{2+}+H_2O_2$, one should bear in mind the need of preliminary replacement of one of ligand water species with hydrogen peroxide species. In other words, the classic Fenton reaction is carried out in iron (II)-dihydroperoxy pentaaqua species $([(H_2O)_5Fe^{2+}(H_2O_2)]^{2+})$ [38].

Modified reaction schemes are called analogous Fenton-like systems [41]. As applied to divalent iron, modifications of the ligand surroundings are possible through the use of organic chelating compounds [1, 35, 40]. Both
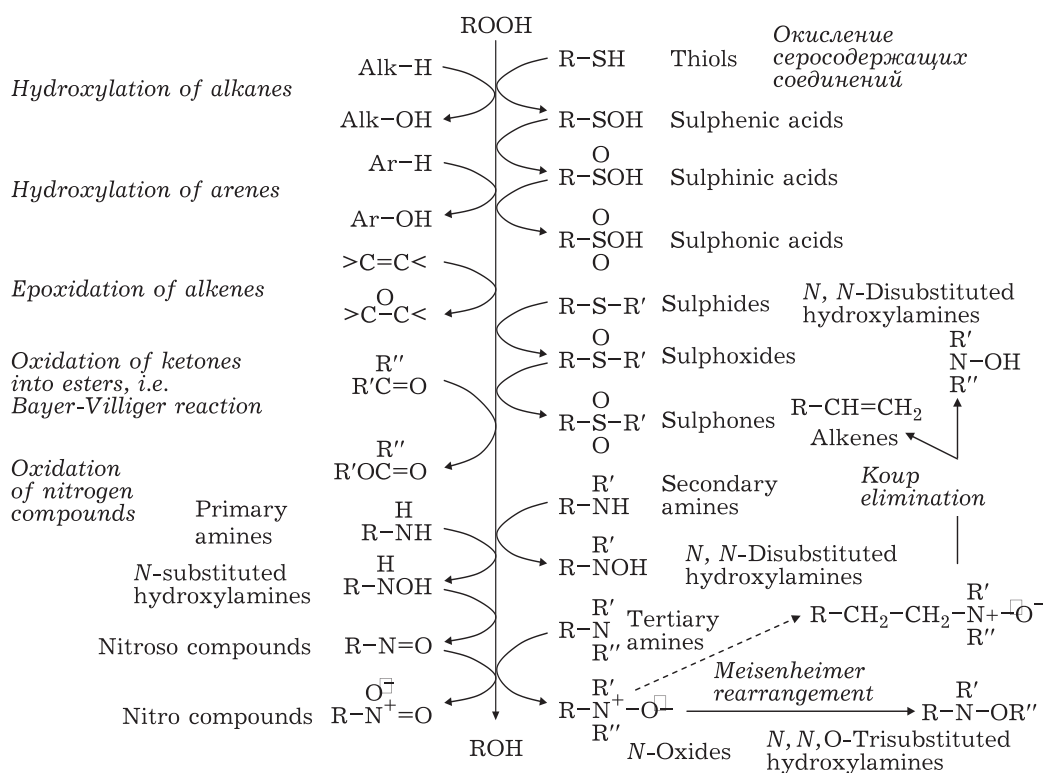
Fig. 1. Opportunities of using hydroperoxides in organic synthesis.

early and modern studies [3, 4, 15, 18, 24, 36, 37, 41−48, 54] proved catalytic activity of different forms of trivalent iron, such as water-dissolved Fe^{3+} ions (aquacomplexes) [36, 41, 54], chelate complexes with different organic ligands [3, 4, 15, 18, 36, 41, 44−47], heterogeneous catalysts, *i.e.* magnetite (Fe_3O_4) [24, 41], Fe^{3+} zeolites [37, 41], hematite (Fe_2O_3) [41], anhydrous crystalline iron (III) chloride [48].

A great deal of experimental data was accumulated regarding the activity of homogeneous and heterogeneous catalysts based on other metals of variable valency in different oxidation states. Copper mainly in +2 oxidation state may be used as aquacomplexes [39, 41, 50, 52], chelate complexes with organic ligands [2, 5, 20, 41, 49] and heterogeneous catalysts [41, 51, 53]. Similar liquid-phase and solid-phase forms are also being studied for cobalt, mainly in the bivalent oxidation state [19, 22, 41], manganese in +2, +3, and +4 oxidation states [2, 11, 22, 41], tetravalent titanium [14, 23, 29], vanadium in different oxidation states [10, 26], three- and hexavalent chromium [41]. Research also covers the transition metals in periods 5 and 6 of the

element system: molybdenum and tungsten as polyoxometallates [17, 41], ruthenium in +2, +3 and +4 oxidation states [41], tetravalent cerium as oxide [41], and monovalent rhenium [16].

Observations of activities of unusual hydroperoxide catalysts based on p-elements for oxidation with hydrogen peroxide could not be overlooked. George A. Olah's research group studied hydrocarbon oxidative functionalisation processes in 1970s−1990s and a part of their work was devoted to successful alkane and arene oxidation with hydrogen peroxide [6−8] using so-called superacids based on boron and antimony: HF/BF_3; HF/SbF_5; FSO_3H/SbF_5. The results of the international composite authors [13] demonstrated the efficiency of the simplest two non-transition metal salts, aluminium and gallium nitrates as catalysts for epoxidation of alkenes. Herewith, the catalytic activity of gallium is higher than that of aluminium. Paper [41] discusses opportunities of the Fenton-like activity in zero-valent aluminium. Another recently published paper [27] demonstrates the activity of the tin zeolite (stannosilicate) as a catalyst for the Bayer−Villigr reaction

using hydrogen peroxide and *tert*-butyl hydroperoxide.

Finally, the recent results by Russian researchers [12] who demonstrated the ability of 2,2,2-trifluoroacetophenone as a heterogeneous organic catalyst immobilised on the silicate substrate to activate hydrogen peroxide for epoxidation of alkenes.

One can confidently expect a further increase in papers on Fenton oxidation including using various unusual catalysts.

3. COMMON VIEWS OF FENTON OXIDATION MECHANISMS
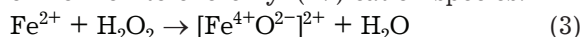
3.1. Classic Fenton reaction system

Hydroxyl radical concept. In 1932, Haber and Weiss [32] proposed the known scheme that has gained significant ground [34, 54]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^{\cdot} \qquad (1)$$

Proceeding from the foregoing in the previous section, one should imply electron transfer in a complex of iron (II)- hydroperoxo pentaaqua with the formation of iron (III)-hydroxo pentaaqua and a free hydroxyl radical [38]:

$$[(H_2O)_5Fe^{2+}\overset{H}{O}OH]^{2+} \rightarrow [(H_2O)_5Fe^{3+}(^-OH)]^{2+} + HO^{\bullet} \quad (2)$$
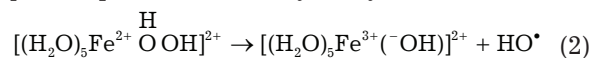
Oxoiron (IV) cation concept. At the same time in 1932, Bray and Gorin [33] suggested oxidation of iron ion to oxoferryl (IV) cation species:

$$Fe^{2+} + H_2O_2 \rightarrow [Fe^{4+}O^{2-}]^{2+} + H_2O \qquad (3)$$

The transfer of two electrons and a proton proceeds in the initial complex [38]:

$$[(H_2O)_5Fe^{2+}\overset{H}{O}OH]^{2+} \rightarrow [(H_2O)_5Fe^{4+}O^{2-}]^{2+} + H_2O \qquad (4)$$
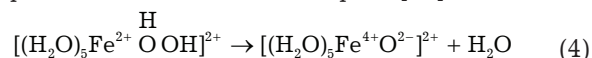
Ideas on competition of the two mechanisms. Seventy years later, Canadian author Dunford H. Brian [36] noted the pendency of the problem of the classic Fenton reaction. The debatability of the issue currently remains [30, 55]. The idea that allows the progression of both reactions (1) and (3) is common, and the prevalence of one of them is defined by specific conditions: medium acidity, ligand surroundings, oxidant type. Thus, according to [35, 39, 41], the hydroxyl radical prevails in acid media, while oxoferryl (IV) species are the oxidant at neutral and basic pH values when binding Fe^{2+} into chelated complexes. The authors of [1] demonstrate that an intermediate oxidant depends on the nature

of hydroperoxides in the oxidation of alkanes catalyzed by chelate complexes of iron (II): $HO^{\cdot}$ is generated when using H_2O_2, and the use of peracetic acid and *meta*-chloroperoxybenzoic acid is accompanied by the formation of $[Fe^{4+}O^{2-}]^{2+}$.

From the standpoint of thermodynamics [38], the transformation of iron (II)-hydroperoxo pentaaqua species to iron(IV)-oxo pentaaqua complex by equation (4) is more energetically preferable, however, this process is stepwise and the first stage, according to the authors, is the generation of the hydroxyl radical (equation (2). Herewith, strictly speaking, oxoferryl (IV) cation act as, the secondary intermediate, not alternative.

3.2. Systems based on trivalent iron

Without referring to literature data, any research chemist either already knows, or can readily experience that even the simplest compounds of divalent iron (*e.g.* green vitriol ($FeSO_4 \cdot 7H_2O$), Mohr's salt ($FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$), but also trivalent (iron (III) chloride ($FeCl_3 \cdot 6H_2O$) and iron (III) oxide (Fe_2O_3) provoke quite an intense decomposition (disproportionation) of hydrogen peroxide visible by gas release:

$$2H_2O_2 \xrightarrow{\ Fe^{2(3)+}\ } 2H_2O + O_2 \qquad (5)$$
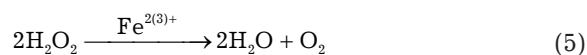
Evidently, dismutation of the oxidant (H_2O_2) itself proceeds *via* the generation of the same intermediates that are formed during the transformation of organic substrates in $Fe^{2(3)+}/H_2O_2$ systems.

Oxidation of hydrogen peroxide by iron (III). Yet the early authors [34, 54] began widely using the idea of direct oxidation of hydrogen peroxide by trivalent iron ions with the formation of the hydroperoxyl radical:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \qquad (6)$$
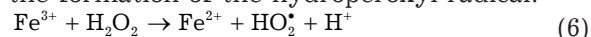
This scheme is accepted up to date [41]. The Fenton-like catalytic activity of Fe^{3+} zeolites [37] is explained by the preliminary reduction of iron (III) by equation (6) followed by generation of both $HO^{\cdot}$, and $[Fe^{4+}O^{2-}]^{2+}$ by equations (1) and (3). The authors of [44−47] explored interaction mechanisms of Fe^{3+} ions chelated by nitrilotriacetate (NTA) with hydrogen peroxide and proved the generation of the hydroxyl radical in the system. Fundamentally the same

idea [45] is adapted as an explanation:

$$HTA\text{-}Fe^{3+} + H_2O_2 \rightarrow HTA\text{-}Fe^{2+} + O_2^{\bullet-} + 2H^+ \qquad (7)$$
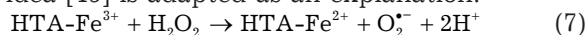
The superoxide radical anion (deprotonated form of the hydroperoxyl radical) is also regarded [45] as iron reductant (the Haber−Weiss reaction):

$$HTA\text{-}Fe^{3+} + O_2^{\bullet-} \rightarrow HTA\text{-}Fe^{2+} + O_2 \qquad (8)$$
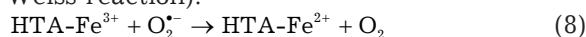
Afterwards, HTA-Fe^{2+} generates HO$^{\bullet}$ by equation (1). However, there is an objective cause casting doubt in the possibility of direct oxidation of hydrogen peroxide by trivalent iron ions (with the obviousness of the fact of their interaction). Compare standard electrode potentials of two half-reactions of reduction:
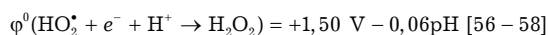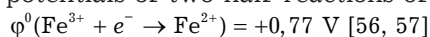
$$\varphi^0(Fe^{3+} + e^- \rightarrow Fe^{2+}) = +0,77 \text{ V } [56, 57]$$

$$\varphi^0(HO_2^{\bullet} + e^- + H^+ \rightarrow H_2O_2) = +1,50 \text{ V} - 0,06pH \, [56-58]$$

The reduction potential of the hydroperoxyl radical exceeds that of Fe^{3+} ions even with an increase in pH, therefore, reaction (6) proceeds in the reverse direction on electrochemical criteria.

Oxoiron (IV) formation. If the formation scheme of $[Fe^{4+}O^{2-}]^{2+}$ in Fe^{2+}/H_2O_2 systems does not have the problem of compliance with the electron balance (equation (3)); the generation of iron(IV)-oxo in Fe^{3+}/H_2O_2 systems requires a second electron donor:

$$Fe^{3+} + H_2O_2 + e^- \rightarrow [Fe^{4+}O^{2-}]^{2+} + H_2O \qquad (9)$$
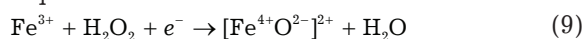
This scheme has become most widespread in biological chemistry [59] to explain the fermentation activity of iron (III) hemoproteins of catalase-peroxidase and monooxygenase groups. Iron (III) ion in the active centres of these enzymes is found in the centre of the aromatic ring of protoporphyrin IX.

Catalase-peroxidase enzymes react directly with endogenous hydrogen peroxide continuously generated in biological systems from oxygen *via* the intermediate formation of the superoxide radical anion [60, 61]:

$$O_2 + e^- \rightarrow O_2^{\bullet-} \qquad (10)$$

$$2O_2^{\bullet-} + 2H^+ \xrightarrow{\text{SOD}} O_2 + H_2O_2 \qquad (11)$$
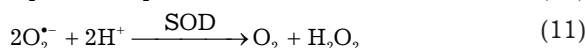
where SOD is the enzyme superoxide dismutase. Hydrogen peroxide in cells at low concentrations (oxidative *eustress* as the norm) acts as a physiological oxidant for sulfhydryl groups of polypeptides, which is required to form disulphide bonds of proteins, and peptides and cell signaling [62−64]. The enzyme system of antioxidant protection [65−67], with insufficiency of which pathological

oxidative distress develops [62], prevents the accumulation of high concentrations of H_2O_2. It is noteworthy that destruction of biolipids (nucleic acids, proteins and lipids) proceeds upon distress resulting from the same metal-induced Fenton oxidative activation of excess amounts of endogenic hydrogen peroxide [68, 69]. It has been accepted [59] that the protoporphyrin nucleus acts as the above donor of the second electron (equation (9)) oxidizing into the π-cation radical:

$$P[Fe^{3+}] + H_2O_2 \rightarrow P^{\bullet+}[Fe^{4+}O^{2-}]^{2+} + H_2O \qquad (12)$$
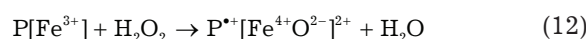
Catalase [67], myeloperoxidase [70], horseradish peroxidase [71], plant ascorbate peroxidase [72], and fungal basidiomycete peroxygenase [73] are patterns of catalase-peroxidase enzymes. Even more enzymes can be found in the ExplorEnz network database [74].

Active intermediate $P^{\bullet+}[Fe^{4+}O^{2-}]^{2+}$ oxidizes substrates specific for particular enzymes. For catalase, it is the second molecule of H_2O_2:

$$P^{\bullet+}[Fe^{4+}O^{2-}]^{2+} + H_2O_2 \rightarrow P[Fe^{3+}] + H_2O + O_2 \qquad (13)$$

Decomposition of hydrogen peroxide by equation (5) proceeds summarily (one of the mechanisms of antioxidant protection of cells).

Myeloperoxidase in neutrophil leukocytes of human blood oxidizes chloride into bactericidal hypochlorous acid (or hypochlorite anion):

$$P^{\bullet+}[Fe^{4+}O^{2-}]^{2+} + Cl^-(+H^+) \rightarrow P[Fe^{3+}] + ClO^-(H^+) \quad (14)$$
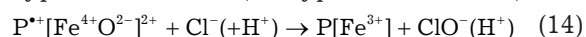
Horseradish peroxidase and L-ascorbate peroxidase are enzymes of antioxidant protection of plants reducing H_2O_2 to two water molecules due to donors of two hydrogen atoms that are diatomic phenols (pyrocatechin and hydroquinone) and ascorbic acid, respectively:

$$P^{\bullet+}[Fe^{4+}O^{2-}]^{2+} + 2e^- + 2H^+ \rightarrow P[Fe^{3+}] + H_2O \qquad (15)$$
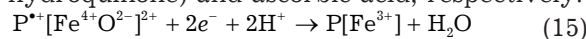
Herewith, diatomic phenols are oxidized to appropriate benzoquinones, ascorbic acid − to dehydroascorbic acid.

A fungal peroxygenase performs stereoselective oxidative biotransformation of various organic substrates, such as hydroxylation of alkanes and arenes and N- and S-oxidation:

$$P^{\bullet+}[Fe^{4+}O^{2-}]^{2+} + X \rightarrow P[Fe^{3+}] + XO \qquad (16)$$
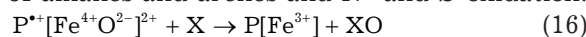
where X is an organic substrate, XO is its oxidative functionalization product. A clear analogy with organic synthesis processes (Fig. 1) is obvious; therefore, this enzyme can be safely referred to biochemical prototypes of catalysts for so-called bioinspired oxidation [75].

The cytochrome P-450 monooxygenase

system functioning in human liver cells and responsible for brand similar reactions of biotransformation of xenobiotics is another prototype [76–82]. Accepted oxidation mechanisms correspond to equation (16). The difference from catalase-peroxidase enzymes consists in the use of molecular oxygen O_2 that is preliminarily reduced to the peroxide group:

$$P[Fe^{3+}] + e^- \rightarrow P[Fe^{2+}] \tag{17}$$

$$P[Fe^{2+}] + O_2 \rightarrow P[Fe^{3+}(O_2^{\bullet-})]^{2+} \tag{18}$$

$$P[Fe^{3+}(O_2^{\bullet-})]^{2+} + e^- \rightarrow P[Fe^{3+}(O_2^{2-})]^+ \tag{19}$$
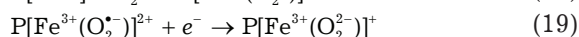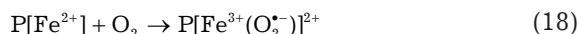
Afterwards, the complex accepts a proton:

$$P[Fe^{3+}(O_2^{2-})]^+ + H^+ \rightarrow P[Fe^{3+}(^-OOH)]^{2+} \tag{20}$$

Intermediate complexes, such as peroxoiron (III) $[Fe^{3+}(O_2^{2-})]^+$ (equation (19)) and hydroperoxoiron (III) $[Fe^{3+}(^-OOH)]^{2+}$ (equation (20)) are also regarded as intermediate oxidants [80, 81]. However, complex $P^{\bullet+}[Fe^{4+}O^{2-}]^{2+}$ generated resulting from the second protonation is regarded as major, sometimes, sole [82]:

$$P[Fe^{3+}(^-OOH)]^{2+} + H^+ \rightarrow P^{\bullet+}[Fe^{4+}O^{2-}]^{2+} + H_2O \tag{21}$$

It must be noted that early papers [76–78] discussed only the intermediate formed resulting from addition of both protons (equations (20) and (21)) and represented it in the $P[FeO]^{3+}$ format without specifying the oxidation states of iron and oxygen and without the use of the idea of oxidation of protoporphyrin IX into the π-radical cation. This intermediate received then such a designation as Fe (III) oxene. The strict meaning of the term oxene is the oxygen atom in the zero oxidation state. Not knowing precisely nature of the electron di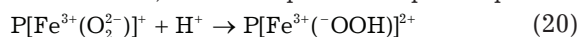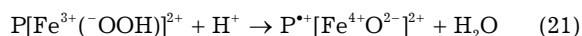stribution within the complex $P\cdot+[Fe^{4+}O^{2-}]^{2+}$, the early authors accepted the name Fe (III) oxene and noted this formality in their publications. Although the synonym of cytochrome P-450 oxene transferase was in fact correct, since the active $P[FeO]^{3+}$ complex indeed performed the transfer of the oxygen atom (oxene) onto oxidizable substrates (see equation (16)). Later works [79–82] that already confidently talked about the formation of $P^{\bullet+}[Fe^{4+}O^{2-}]^{2+}$ traditionally called the complex oxenoid. Currently, with regard to iron (III)-heme proteins, this term is not used.
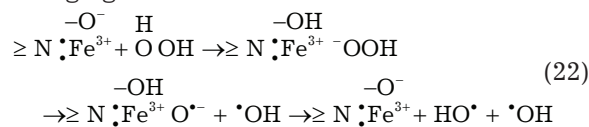
This is not a coincidence that discussion of the details of the early conception of oxenoid oxidation and the use of the term oxene was

begun by us. The reason for this will become clear to readers after reading subsection 3.2 of section 4.

In conclusion, the following should be said. With the widest distribution of the concept of $Fe^{3+} \rightarrow Fe^{4+}$ for systems where the protoporphyrin nucleus giving the second electron is Fe^{3+} ion ligands (equation (12)), the idea is not always acceptable, if Fe^{3+} ion ligands are different in nature, as it is obvious that not any ligands that can be donors of the second electron (equation (9)).

Exclusive ideas. Prior to the completion of section 3.2, let us present two unusual interpretations of H_2O_2 activation by trivalent iron.

Paper [4] demonstrates the oxidation of organic compounds by hydrogen peroxide when using catalysts of Fe^{3+} complexes with chlorinated derivatives of 8-hydroxyquinoline. The authors regard the hydroxyl radical as the oxidizing particle. Their idea of the direct generation of two $HO^\bullet$ radicals from the water molecule without changing iron oxidation state is unusual:

$$
\begin{aligned}
&\overset{-O^-}{\geq N \overset{\bullet}{\bullet} Fe^{3+}} + \overset{H}{O}OH \rightarrow \overset{-OH}{\geq N \overset{\bullet}{\bullet} Fe^{3+}} {}^-OOH \\
&\overset{-OH}{\rightarrow \geq N \overset{\bullet}{\bullet} Fe^{3+}} O^{\bullet-} + {}^\bullet OH \rightarrow \overset{-O^-}{\geq N \overset{\bullet}{\bullet} Fe^{3+}} + HO^\bullet + {}^\bullet OH
\end{aligned}
\tag{22}
$$

where $-O-$ is phenolate oxygen, $\geq N$: is pyridine nitrogen atom. According to the authors, the oxygen atom of the organic ligand accepts one electron of the hydrogen peroxide molecule. The resulting hydroperoxide group ($HOO-$) binds to Fe^{3+}, and then the interoxygen bond is broken homolytically. The return of the previously accepted proton onto $O^{\bullet-}$ releases the second hydroxyl radical.

Note that the authors having demonstrated an opportunity for the formation of the interesting $Fe^{3+}O^{\bullet-}$ that will be discussed further, did not discuss an opportunity for its functioning as active oxidant species.

Paper [48] studied oxidative activation of hydrogen peroxide over anhydrous iron (III) chloride:

$$(Cl^-)_3Fe^{3+} + H_2O_2 \rightarrow [Cl_3FeO]^0 + H_2O \tag{23}$$

The authors represented four possible options for electron distribution within a $[Cl_3FeO]^0$ complex:

$$(Cl^-)_3Fe^{3+}O^0 \tag{I}$$

$$(Cl^-)_3Fe^{4+}O^{\bullet-} \tag{II}$$

$$(Cl^-)_2(Cl^\bullet)Fe^{4+}O^{2-} \tag{III}$$

$(Cl^-)_3 Fe^{5+}O^{2-}$ (IV)
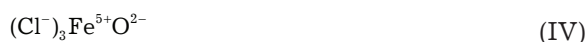
Complex (III) corresponds to iron(IV)-oxo concept for Fe^{3+}/H_2O_2 systems (subsection 3.2.). The Cl^- ion acts as a second electron donor (equation (9)). Complexes (II) and (IV), accordingly, iron (IV) oxyl and iron(V)-oxo are unusual and interesting. However, the authors exclude all the options, where iron acquires the hypervalent oxidation degree +4 or +5, that is complexes (II), (III) and (IV) and argue in favour of the invariability of the oxidation state of +3 during catalysis. In other words, they substantiate generating Fe(III)-oxene or complex (I). Their use of the term oxene is characterised in this case by the semantic accuracy.

3.3. Iron-free Fenton systems

Numerous examples of Fenton-like systems not containing iron were given by us in Section 2. Authors who demonstrate in their papers the catalytic activity itself (by the yield of oxidation products) pay attention to the discussion of fundamental mechanisms of catalysis.

Nevertheless, there is an opportunity to form an impression of the most used concepts for these systems. It should be noted right away that the main tendency is an adaptation (with its peculiarities for specific catalysts) of mechanisms that are used for iron-containing reaction systems.
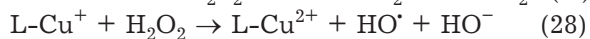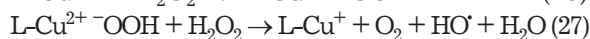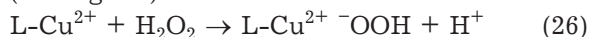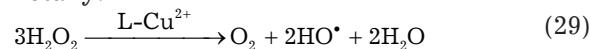
Fenton activity of copper. Beyond iron, copper is one of the most common Fenton catalysts and representations of Fenton chemistry of iron are most adapted for it compared to other elements. Interaction mechanisms of in Cu^+/H_2O_2 and Cu^{2+}/H_2O_2 systems are accepted as identical to mechanisms in Fe^{2+}/H_2O_2 and Fe^{3+}/H_2O_2 systems, respectively [41]:

$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + HO^- + HO^{\bullet}$ (24)

$Cu^{2+} + H_2O_2 \rightarrow Cu^+ + HO_2^{\bullet} + H^+$ (25)
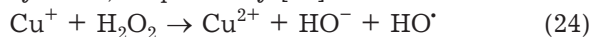
The authors of [51] present the following reaction sequence for the Cu-containing catalyst (L is ligand):

$L-Cu^{2+} + H_2O_2 \rightarrow L-Cu^{2+} \, ^-OOH + H^+$ (26)

$L-Cu^{2+} \, ^-OOH + H_2O_2 \rightarrow L-Cu^+ + O_2 + HO^{\bullet} + H_2O$ (27)

$L-Cu^+ + H_2O_2 \rightarrow L-Cu^{2+} + HO^{\bullet} + HO^-$ (28)

Totally:

$$3H_2O_2 \xrightarrow{\text{L-Cu}^{2+}} O_2 + 2HO^{\bullet} + 2H_2O$$ (29)

The authors examine as possible (equation (27)) simultaneous hydrogen atom transfer (an electron with proton) onto H_2O_2 molecule and intracomplex electron transfer onto Cu^{2+} ion.

Schemes [52] similar to the Haber–Weiss reaction (equations (7) and (8)), *i.e.* those with the generation and participation of the superoxide radical anion are also used:

$Cu^{2+} + H_2O_2 \rightarrow Cu^+ + O_2^{\bullet-} + 2H^+$ (30)

$Cu^{2+} + O_2^{\bullet-} \rightarrow Cu^+ + O_2$ (31)

At last, by analogy with the formation of tetravalent iron (equation (3)), an opportunity to generate copper-oxo (III) cation or oxocopryl (III) is regarded:

$Cu+ + H_2O_2 \rightarrow [Cu^{3+}O^{2-}] + H_2O$ (32)
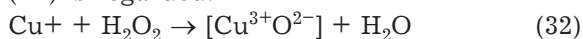
Competitive reactions (24) and (32) with the prevalence of $HO^{\bullet}$ in low values of pH and $[Cu^{3+}O^{2-}]^+$ in neutral and alkaline media are also discussed [39] for Fe^{2+} (subsection 3.1).

One important point should be taken into account: almost all used copper catalysts contained this element in the +2 oxidation state.

The fact itself of the interaction of Cu^{2+} with H_2O_2 is obvious, as even without the literature data, it is easy to experience that copper sulphate ($CuSO_4 \cdot 5H_2O$) provokes intense decomposition of hydrogen peroxide with oxygen release:

$$2H_2O_2 \xrightarrow{\text{Cu}^{2+}} 2H_2O + O_2$$ (33)

At the same time, as for Fe^{3+} (subsection 3.2), from the standpoint of electrochemistry, there is no opportunity for direct oxidation of hydrogen peroxide with divalent copper by equation (25):

$\varphi^0(Cu^{2+} + e^- \rightarrow Cu^+) = +0.15 \ V \ [56, 57]$

$\varphi^0(HO_2^{\bullet} + e^- + H^+ \rightarrow H_2O_2) = +1.50 \ V - 0.06pH \ [56-58]$
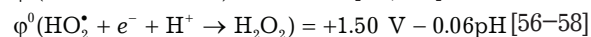
Herewith, divalent copper ($\varphi^0 = +0.15$ V) compared to trivalent iron (($\varphi^0 = +0.77$ V) is characterised by an even smaller ability to oxidize H_2O_2. In other words, the key reaction (25) used by researchers when interpreting Fenton chemistry of copper (II) is called into question. The doubt in an opportunity of preliminary $Cu^{2+} \rightarrow Cu^+$ reduction thus does not allow safely using schemes (24) and (32) (Cu^+/H_2O_2) for Fenton catalysts based on Cu^{2+} that are, however, really active and basic among copper catalysts.

It is obvious that the solution of this problem consists in substantiation of another interaction mechanism in the Cu^{2+}/H_2O_2 system.

Other transition d- and f-elements. Attempts have been made for the rest of metals with

variable valencies to mainly use the concept of generating the traditional hydroxyl radical that both in the past and often presently is associated for most chemists with the notion of Fenton reaction systems before other possible intermediates.

As indicated in Section 2, *cobalt* is present in catalysts in the bivalent oxidation state. Fenton activity of Co^{2+} ion is interpreted in some cases *via* reduction of Co^{2+} to Co^+ [41]:

$$Co^{2+} + H_2O_2 \rightarrow Co^{2+-}OOH + H^+ \qquad (34)$$
$$Co^{2+-}OOH \rightarrow Co^+ + 1/2O_2 + HO^{\bullet} \qquad (35)$$
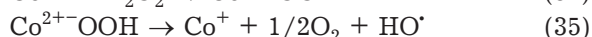
The physical nature of SO_2 is unclear. Reversible oxidation of Co^{2+} to Co^{3+} is discussed in other cases [83, 84]:

$$Co^{2+} + H_2O_2 \rightarrow Co^{3+} + HO^- + HO^{\bullet} \qquad (36)$$
$$Co^{3+} + H_2O_2 \rightarrow Co^{2+} \ HO_2^{\bullet} + H^+ \qquad (37)$$

Here is a complete analogy with (1), (6), (24) and (25).

The authors of [19] studied epoxidation of various alkenes with the general formula $R_1R_2C=CR_3R_4$ by hydrogen peroxide in the presence of a cobalt catalyst over Fe_3O_4 substrate and suggested the formation of the transition state without the generation of free radicals in the catalytic cycle:

The interpretation of Fenton chemistry of manganese is a complicated task for researchers compared to iron, cobalt, and copper due to a wide range of possible oxidation states, *i.e.* up to +7. The used catalysts mainly contain Mn^{2+} and Mn^{4+}, and the intermediate formation of Mn^{3+} [41] and Mn^{5+} [11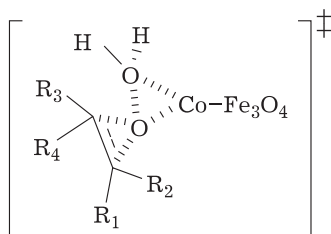] is suggested for catalytic cycles. $HO^{\bullet}$, $HO_2^{\bullet}$, and $O_2^{\bullet-}$ radicals [41] and pentavalent manganese oxocomplexes ($LMn^V=O$ [11]) chelated with organic ligands L are regarded as intermediates.

The catalytic cycle of $Cr(III) \leftrightarrow Cr(VI)$ with the intermediate formation of $Cr(IV)$ and $Cr(V)$ and the generation of $HO^{\bullet}$ at each of three oxidation stages of trivalent chromium to the hexavalent state is suggested for chromium [41]:

$$Cr(III) + H_2O_2 \rightarrow Cr(IV) + HO^- + HO^{\bullet} \qquad (38)$$
$$Cr(IV) + H_2O_2 \rightarrow Cr(V) + HO^- + HO^{\bullet} \qquad (39)$$

$$Cr(V) + H_2O_2 \rightarrow Cr(VI) + HO^- + HO^{\bullet} \qquad (40)$$
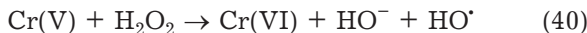
The regeneration of $Cr(VI)$ to $Cr(III)$ is possible with the participation of hydrogen peroxide itself, according to the opinion of researches of [41]. And although specific equations are not given, apparently, mechanisms similar to reactions (6)− (8), (25), (30), (31), and (37) are implied.

At last, the mechanism of Fenton activity absolutely identical to the traditional view is adopted for the f-element cerium [85]:

$$Ce^{3+} + H_2O_2 \rightarrow Ce^{4+} + HO^- + HO^{\bullet} \qquad (41)$$
$$Ce^{4+} + H_2O_2 \rightarrow Ce^{3+} + HO_2^{\bullet} + H^+ \qquad (42)$$

p-**Element activity.** As noted above, authors do not always discuss mechanisms of activity for catalysts studied by them. For example, the nature of the intermediates in the Al^{3+}/H_2O_2 and Ga^{3+}/H_2O_2 systems remains unclear [13].

Zero-valent aluminium (*i.e.* simply aluminium metal) was referred to as Fenton-like catalysts in $Al^0/O_2/H^+$ systems at $pH \leq 4$ [41]:

$$Al^0 \rightarrow Al^{3+} + 3e^- \qquad (43)$$
$$2O_2 + 2e^- \rightarrow 2O_2^{\bullet-} \qquad (44)$$
$$2O_2^{\bullet-} + 2H+ \rightarrow H_2O_2 + O_2 \qquad (45)$$
$$H_2O_2 + e^- \rightarrow HO^- + HO^{\bullet} \qquad (46)$$

Totally:

$$Al^0 + O_2 + 2H+ \rightarrow Al^{3+} \ HO^- + HO^{\bullet} \qquad (47)$$
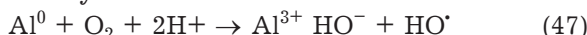
In conclusion of subsection 3.3, H_2O_2 activation under the action of the superacids already mentioned in Section 2 will be addressed by us. Researchers of [6−9] substantiate protonation of hydrogen peroxide with the formation of hydroperoxonium ion ($H_3O_2^+$) that is considered by the authors as the intermediate of electrophilic hydroxylation of hydrocarbons. Papers of George A. Olah and his colleagues [6−8] do not exclude proteolytic cleavage of hydrogen peroxide with the generation of the hydronium ion (HO^+):

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \rightarrow H_2O + HO^+ \qquad (48)$$
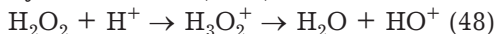
The authors of [9] interpret the oxidative activity of $H_3O_2^+$ towards C−H bonds of alkanes otherwise, substantiating the hydride transfer with the formation of the carbocation:

$$R_3C-H + H_3O_2^+ \rightarrow R_3C+ + 2H_2O \qquad (49)$$
$$R_3C^+ + H_2O \rightarrow R_3C-^+OH_2 \rightarrow R_3C-OH + H^+ \qquad (50)$$
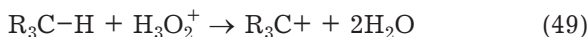
3.4. The problems formulation

Analysing the literature data regarding the nature of intermediates, the following problems may be formulated.

The mechanism even for the classic Fenton reaction has not been verified; two alternative interaction concepts in Fe^{2+}/H_2O_2 systems are competing.

Common views about the kinetics of interactions in Fe^{3+}/H_2O_2 systems are either not supported from the standpoint of electrochemistry (H_2O_2 oxidation with reduction of Fe^{3+} to Fe^{2+}), or applicable to a limited number of ligands for Fe^{3+} (particularly, to protoporphyrin ligands).

Prereduction of Cu^{2+} to Cu^+ with H_2O_2 oxidation that is the key idea of Fenton chemistry of copper (II) is even more unsupported from the standpoint of electrochemistry.

Unverifiable concepts of Fenton chemistry of iron have mainly been adapted for the rest of metals with variable valencies.

Activation mechanisms of hydroperoxides *via* catalysts based on *p*-elements are absolutely unclear. The concepts of generating free radicals or oxo complexes of hypervalent forms of elements are almost inapplicable to these systems, as they are based on the ideas about active electron transitions between elements and hydroperoxides.

The next section of our article gives a presentation of our own solution option of the problems formulated here. Our hypothesis is offered for consideration to the scientific community as a possible universal concept of oxidation mechanisms in Fenton reaction systems.

4. THE HYPOTHESIS OF THE PRIMACY OF INTRAMOLECULAR REARRANGEMENTS OF HYDROPEROXIDES IN FENTON REACTION SYSTEMS

4.1. Opportunity to the polarization of hydroperoxides in Fenton systems

Binding of Me^{n+} ion as a Lewis acid with hydroperoxide (ROOH) molecule as a Lewis base precedes the generation of active intermediates in Fenton systems ($Me^{n+}/ROOH$):

$$Me^{n+} + \overset{H}{O}OR \rightarrow Me^{n+}\overset{H}{O}OR \qquad (51)$$

The electrostatic field of the positively-charged metal ion may cause polarization − zwitter-ionization of the hydrogen peroxide molecule resulting from intramolecular proton transfer, as assumed by us:

$$Me^{n+}\overset{H}{O}OR \rightarrow Me^{n+\,-}OO\underset{R}{\overset{H}{O^+}} \qquad (52)$$
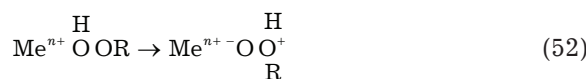
A literature search was carried out by us and several publications proving an opportunity for polarization of hydroperoxides in Lewis complexes with metal ions of Fenton catalysts were found. H. F. Schaefer III and his colleagues [86, 87] discussed an opportunity of hydrogen peroxide isomerization in the 90-th of the last century:

$$\overset{H}{O}OH \rightarrow {}^-OO\underset{H}{\overset{H}{O^+}} \qquad (53)$$

The isomer was called oxywater. Both early [88] and modern [89] works devoted to quantum-chemical calculations of isomerization are found. Oxywater is formed in active centres of catalase peroxidase enzymes prior to the generation of iron (IV)-oxo, as assumed by the authors of [90−93]:

$$P[Fe^{3+}\overset{H}{O}OH]^{3+} \rightarrow P[Fe^{3+\,-}OO\underset{H}{\overset{H}{O^+}}]^{3+}$$
$$\rightarrow P^{\bullet+}[Fe^{4+}O^{2-}]^{2+} + H_2O \qquad (54)$$
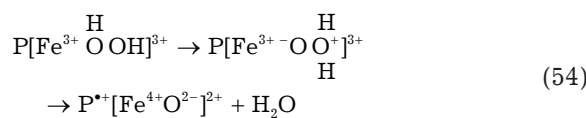
According to quantum chemical calculations of the authors of [90], oxywater in complexes with metal cations is stabilized in a degree directly proportional to the charge on the metal ion. These results support polarization (zwitter-ionization) of hydroperoxides in Lewis complexes with metal ions of Fenton catalysts.

4.2. Molecular kinetics of dissociation of polarized hydroperoxides

The appearance of opposite signs on oxygen atoms directly bound to each other creates the conditions for heterolytic dissociation of the interoxygen bond of polarized hydroperoxides resulting from electron density shift from the negatively charged atom to positively charged:

$$Me^{n+\,-}OO\underset{R}{\overset{H}{O^+}} \rightarrow [Me^{n+}O^0]^{n+} + ROH \qquad (55)$$
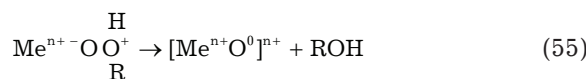
Thus, the generation of atomic hydrogen (oxene) remaining in the complex with a metal ion is substantiated. This approach is in agreement with the idea in the above-cited work [48] on the formation of oxene over anhydrous iron (III) chloride.

The question arises whether the quantum state of the generated oxygen atom is different from the main triplet state ($2p[\uparrow\downarrow][\uparrow][\uparrow]$ or $2p[\uparrow\downarrow][\downarrow][\downarrow]$). The same authors [48] depict oxene as •O•, *i.e.* imply exactly the main triplet state. However, according to [90, 94], the oxygen atom in the ^{1}D-singlet quantum state is formed during oxywater dissociation:

$$H_2\overset{+}{O}-\overset{-}{O} \rightarrow H_2O + O(^1D)\ (2p[\ \uparrow\downarrow\ ][\ \uparrow\downarrow\ ][\quad]) \quad (56)$$
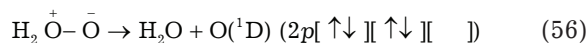
Modelling using the simplest quantum-chemical graphs and compliance with the law of conservation of electron spin [95] when depicting the molecular rearrangements testifies in favour of precisely the ^{1}D state:

$$
\begin{array}{l}
\quad\quad[\quad][\quad]\ V \\
\quad\quad[\quad]\ IV \quad\quad [\quad][\quad]III' \\
H_2O_2\,[\ \uparrow\downarrow\ ][\ \uparrow\downarrow\ ]III \rightarrow H_2O\ [\ \uparrow\downarrow\ ]\quad II' \\
\quad\quad[\ \uparrow\downarrow\ ]\ II \quad\quad\quad [\ \uparrow\downarrow\ ][\ \uparrow\downarrow\ ]\ I' \\
\quad\quad[\ \uparrow\downarrow\ ][\ \uparrow\downarrow\ ]\ I \\
\\
\quad + O[\ \uparrow\downarrow\ ][\ \uparrow\downarrow\ ][\quad]
\end{array}
\quad (57)
$$

Roman numerals indicate the energy levels (molecular orbitals (MO)) of H_2O_2 and H_2O molecules.

For H_2O_2 (both HOOH and $H_2O^+-O^-$): I − two bonding σ_{py}-MO and σ_{pz}-MO (O−H bonds), II − bonding σ_{px}-MO (the relationship O−O), III − two non-bonding π_{py}^0-MO and π_{pz}^0-MO (lone electron pairs − by one at two oxygen atoms in HOOH or both − at one negatively charged atom in the oxywater molecule), IV − antibonding σ_{px}^*-MO (the relationship O−O), V − two antibonding σ_{py}^*-MO and a σ_{pz}^*-MO (O−H bonds).

For H_2O: I' − two bonding σ_{px}-MO and σ_{py}-MO (O−H bonds), II' − non-bonding π_{pz}^0-MO (lone electron pair of the oxygen atom), III' − two antibonding σ_{px}^*-MO and a σ_{py}^*-MO (O−H bonds).

Thus, ion metal species (in the previous oxidation state) with the oxygen atom (oxene) in the ^{1}D-singlet quantum state may be generated resulting from polarization and dissociation of hydroperoxides in Lewis complexes with Fenton catalysts (equation (52) and (55)), such as $[Me^{n+}O^0(^1D)]^{n+}$.
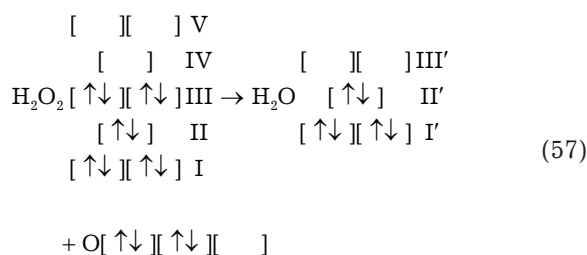
4.3. The hypothesis of the universal primacy of polarization and dissociation of hydroperoxides in Fenton systems

Let us formulate some general provisions as a hypothesis:

1. Polarization (zwitter-ionization) of hydroperoxides followed by dissociation generating the oxygen atom (oxene) in the ^{1}D-singlet quantum state, regardless of the nature of catalysts in Fenton systems occurs in the initial stages of oxidative activation and decomposition of hydroperoxides; the oxidation state of the Me^{n+} cation does not change at this stage.

2. ^{1}D-oxene may be an oxidizer of organic substrates.

3. Electron transitions in $[Me^{n+}O^0(^1D)]^{n+}$ complexes with the formation of monooxygen intermediates of subsequent orders are possible: $[Me^{(n+1)+}O^{\bullet-}]^{n+}$ and $[Me^{(n+2)+}O^{2-}]^{n+}$ depending on the specific nature of catalysts (mainly on the ability of the Me^{n+} ion to transfer 1 or 2 electrons to oxene). These intermediates may also become oxidizers of organic substrates.

4. Formation reactions of protonated forms of the indicated intermediates in the reaction systems, *e.g.* $[Me^{(n+1)+}(^{\bullet}OH)]^{(n+1)+}$ are probable at acidic pH values. The hydroxyl radical may be released from the complex; $HO^{\bullet}$ radical may also oxidize organic substrates in both bound and free states.

5. Dioxygen intermediates ($HO_2^{\bullet}$, $O_2^{\bullet-}$, $O_2(^1\Delta_g)$ from H_2O_2) and final decomposition products (H_2O and $O_2(^3\Sigma_g^-)$ from H_2O_2) are formed resulting from interactions of monooxygen intermediates with hydroperoxides molecules and between each other.

4.4. Hypothesis adaptation towards the classic Fenton system

The polarization of hydrogen peroxide followed by dissociation of oxywater during the initial phase leads to the generation of iron (II)-^{1}D-oxene species:

$$
\begin{array}{c}
\ \ \ H \quad\quad\quad\quad\quad H \\
Fe^{2+}\,O\,OH \rightarrow Fe^{2+\ -}O\,O^+ \rightarrow [Fe^{2+}O^0(^1D)]^{2+} + HOH \quad (58)\\
\quad\quad\quad\quad\quad\quad\quad H
\end{array}
$$
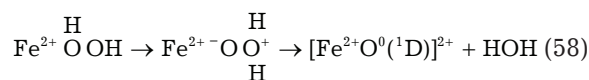
An opportunity for the formation of these complexes in Fe^{2+}/H_2O_2 systems has been never discussed in the literature. Moreover, the idea

of the participation of singlet oxygen atoms in any natural or anthropogenic oxidative systems is represented to date only by individual works. We have managed to find a publication [96], the authors of which substantiated the generation of singlet oxene during oxidation with O_2 of C–C and C–H bonds in the presence of trinuclear copper complexes.

There is no doubt that ^{1}D-oxene has the highest oxidation potential. However, oxene is likely to have no time to interact with organic substrates and other hydroperoxides molecules precisely in systems with bivalent iron readily giving away one electron, as it takes away an electron from Fe^{2+} ion coupled therefrom inevitably and very quickly:

$$[Fe^{2+}O^0(^1D)]^{2+}$$
$$Fe^{2+}3d[\uparrow][\uparrow][\uparrow][\uparrow][\uparrow\downarrow]\ O^02p[\quad][\uparrow\downarrow][\uparrow\downarrow]$$
$$[Fe^{3+}O^{\bullet-}]^{2+}$$
$$\rightarrow Fe^{3+}3d[\uparrow][\uparrow][\uparrow][\uparrow][\uparrow]\ O^{\bullet-}2p[\ \downarrow\ ][\uparrow\downarrow][\uparrow\downarrow] \quad (59)$$
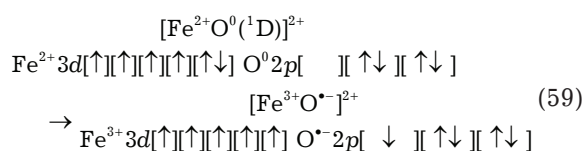
The idea of the formation of a complex of the oxyl anion radical with iron (III) ion or iron (III) oxide is a new interpretation of the classic Fenton reaction. At the same time, Russian scientists under the supervision of G. I. Panov (Boreskov Institute of Catalysis SB RAS, Novosibirsk) discovered original systems for selective oxidation of organic compounds including nitrogen (I) oxide (N_2O) as oxidant and iron zeolites ZSM-5 as catalysts [97]. These systems were reproduced as biomimetic, *i.e.* simulating oxidation of organic substrates of methane monooxygenase [98, 99]. The studies of the Novosibirsk research group have continued for more than 20 years now [100–103]. The study of Fe-ZSM-5/N_2O systems was also the subject matter of the work of the Swiss group under the leadership of Gerhard D. Pirngruber [104–106] and other authors [107]. The uniqueness of these systems lies in the generation of Fe(III)-oxyl complexes called α-oxygen:

$$ZSM-5[Fe^{2+}] + N_2O \rightarrow ZSM-5[Fe^{3+}O^{\bullet-}]^{2+} + N_2 \quad (60)$$

Even at room temperature, α-oxygen performs oxidative functionalization of hydrocarbons very actively and herewith selectively, particularly hydroxylation of alkanes and arenes and epoxidation of alkenes [97–103].
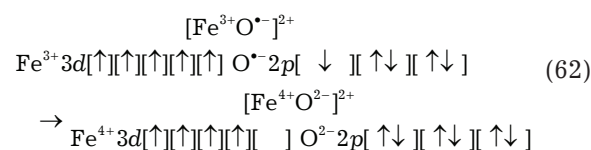
Thus, the existence of Fe(III)-oxyl complexes

has been proven. The prevalence of $[Fe^{3+}O^{\bullet-}]^{2+}$ in classic Fenton systems (Fe^{2+}/H_2O_2) was argumented by us just below after the demonstration of their possible additional transformations.

If Fenton reaction proceeds in acid medium, then Bronsted acids (proton donors) may transfer a proton of an α-oxygen complex:

$$[Fe^{3+}O^{\bullet-}]^{2+} + H^+ \rightarrow [Fe^{3+}(^{\bullet}OH)]^{3+} \rightarrow Fe^{3+} + HO^{\bullet} \quad (61)$$

An opinion of a number of researches about the prevalence of free hydroxyl radical in acid media was given by us in subsection 3.1. Our interpretation (equation (61)) can be viewed as a substantiation of this standpoint. It should be noted that the bound form of $[Fe^{3+}(^{\bullet}OH)]^{3+}$ species is not ignored in literary discussions and also suggested as a possible active intermediate called crypto-$^{\bullet}$OH [30, 35].

Finally, the generation of oxoiron (IV) is possible within the framework of our interpretation resulting from the transfer of the second electron from Fe^{3+} ion in an α-oxygen complex:

$$[Fe^{3+}O^{\bullet-}]^{2+}$$
$$Fe^{3+}3d[\uparrow][\uparrow][\uparrow][\uparrow][\uparrow]\ O^{\bullet-}2p[\ \downarrow\ ][\uparrow\downarrow][\uparrow\downarrow] \quad (62)$$
$$[Fe^{4+}O^{2-}]^{2+}$$
$$\rightarrow Fe^{4+}3d[\uparrow][\uparrow][\uparrow][\uparrow][\quad]\ O^{2-}2p[\uparrow\downarrow][\uparrow\downarrow][\uparrow\downarrow]$$

The profile of all possible monoxygen intermediates in the classic Fenton system is presented in Fig. 2.

Let us give some arguments in favour of the prevalence of α-oxygen $[Fe^{3+}O^{\bullet-}]^{2+}$ complexes in Fe^{2+}/H_2O_2 systems:

Iron (III)-oxyl is quickly and inevitably generated from the preceding iron (II)-^{1}D-oxene resulting from an internal electron transition (equation (59));

The formation of bound and free hydroxyl radicals is limited by acidic pH values (equation (61)); even where oxidizable organic substrates compete with Bronsted acids in the reactions with α-oxygen $O^{\bullet-}$ (*i.e.*, oxidation reactions with oxyl compete with protonation processes therefrom);
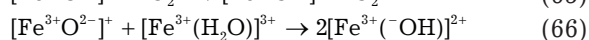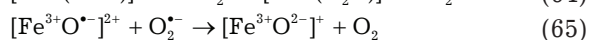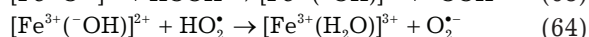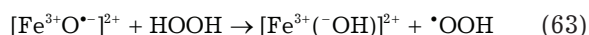
The formation of oxoferryl (IV) involves a violation of the energetically favorable state of the stable state of a half-filled $3d$-sublevel of Fe^{3+} ion (equation (62)).

In addition to argument 2): α-oxygen ($[Fe^{3+}O^{\bullet-}]^{2+}$), cryptohydroxyl ($[Fe^{3+}(^{\bullet}OH)]^{3+}$) and free hydroxyl (HO$^{\bullet}$), differing degrees of cou-

pling and protonation (equation (61)), should not vary considerably on the specifics of oxidizing abilities, as all of them are based on the same $2p^5$-radical monooxygen form ($O^{\bullet-}$ ($[\uparrow\downarrow][\uparrow\downarrow][\uparrow]$ or $[\uparrow\downarrow][\uparrow\downarrow][\downarrow]$)). This has been said due to the fact that the concept of free hydroxyl radical still currently occupies the leading positions in the chemistry of Fenton oxidation, which arises, apparently, from research results of oxidation product profiles. In other words, our interpretation simply argues that not the free and protonated form ($O^{\bullet}$) (*i.e.*, $HO^{\bullet}$) but the bound deprotonated form ($[Fe^{3+}O^{\bullet-}]^{2+}$) ($\alpha$-oxygen complex) is formed with a greater likelihood in Fe^{2+}/H_2O_2 systems.

In addition to argument 3): iron ion in ZSM-5$[Fe^{3+}O^{\bullet-}]^{2+}$ species retains a configuration of $3d^5$, as demonstrated in the paper [106] by resonant inelastic X-ray scattering (RIXS). In other words, oxoiron(IV) is not formed by equation (62).

In accordance with provision 5 of our general interpretation (subsection 4.3), dioxygen intermediates and molecular oxygen (O_2) are formed in the Fe^{2+}/H_2O_2 system resulting from oxidation of native molecules of H_2O_2 by α-oxygen and subsequent reactions, for example:

$$[Fe^{3+}O^{\bullet-}]^{2+} + HOOH \rightarrow [Fe^{3+}(^-OH)]^{2+} + {}^{\bullet}OOH \quad (63)$$
$$[Fe^{3+}(^-OH)]^{2+} + HO_2^{\bullet} \rightarrow [Fe^{3+}(H_2O)]^{3+} + O_2^{\bullet-} \quad (64)$$
$$[Fe^{3+}O^{\bullet-}]^{2+} + O_2^{\bullet-} \rightarrow [Fe^{3+}O^{2-}]^+ + O_2 \quad (65)$$
$$[Fe^{3+}O^{2-}]^+ + [Fe^{3+}(H_2O)]^{3+} \rightarrow 2[Fe^{3+}(^-OH)]^{2+} \quad (66)$$

Alternatively, hydroperoxyl radical (equation (63)) is oxidized at once by the second α-oxygen:

$$[Fe^{3+}O^{\bullet-}]^{2+} + HO_2^{\bullet} \rightarrow [Fe^{3+}(^-OH)]^{2+} + O_2 \quad (67)$$
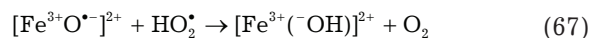
Totally, hydrogen peroxide disproportionation in the Fe^{2+}/H_2O_2 system is described by the following equation (simplistically):

$$2Fe^{2+} + 3H_2O_2 \rightarrow 2Fe^{3+} + 2HO^- + 2H_2O + O_2 \quad (68)$$
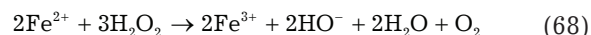
And another two points for the Fe^{2+}/H_2O_2 system are given:

1) the resulting molecular oxygen (equations (65), (67), and (68)) can be present in singlet quantum state, and that will be discussed below;

2) the generated trivalent form of iron is able to continue catalysis in the system, therefore, arguments from the following section are also applicable to Fe^{2+}/H_2O_2 systems.

4.5. Use of the interpretation to trivalent iron-based systems

Iron(III)-^{1}D-oxene is generated in Fe(III)-dihydroperoxo species is generated resulting from polarization and dissociation of the H_2O_2 molecule:

$$Fe^{3+}\overset{H}{O}OH \rightarrow Fe^{3+}{}^-O\overset{H}{\underset{H}{O}}{}^+ \rightarrow [Fe^{3+}O^0(^1D)]^{3+} + HOH \quad (69)$$
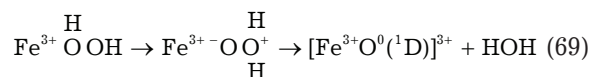
Note again paper [48] cited in subsection 3.2 also justifying the formation of oxene in the

Fig. 2. Profiles of probable monooxygen intermediates in the Fe^{2+}/H_2O_2 system: I − Fe(II) dihydroperoxo species, II − complex of iron (II) with oxywater; III − iron (II)-^{1}D-oxene; IV − Fe (III)-oxyl species (α-oxygen); V − oxoferryl (IV); VI − iron(III) hydroxyl (crypto-hydroxyl); VII − free hydroxyl radical.

Fe^{3+}/H_2O_2 system. Let us repeat that according to the authors, internal electron transitions do not occur in the complex and hypervalent states of iron are not formed. The authors of the prese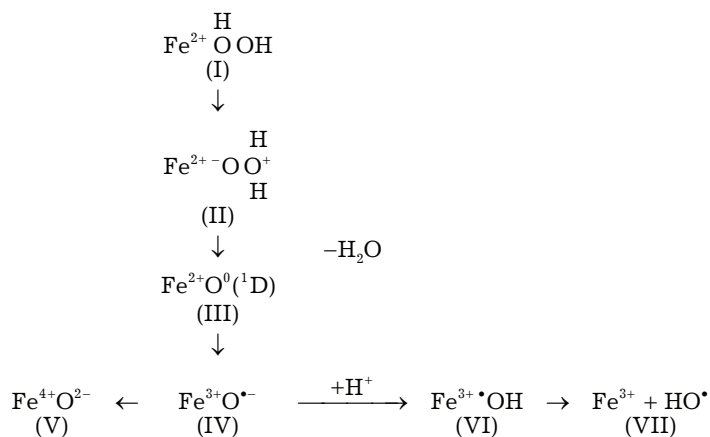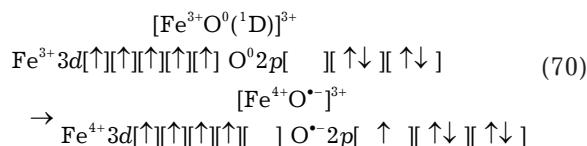nt work are leaning to the same standpoint. The generation of both iron(IV)-oxyl $[Fe^{4+}O^{\bullet-}]^{3+}$ and oxoferryl (IV) is associated with the violation of a configuration of $3d^5$ of Fe^{3+} ion:

$$[Fe^{3+}O^0(^1D)]^{3+}$$
$$Fe^{3+}3d[\uparrow][\uparrow][\uparrow][\uparrow][\uparrow]\ O^02p[\quad][\uparrow\downarrow][\uparrow\downarrow] \quad (70)$$
$$\rightarrow {}^{[Fe^{4+}O^{\bullet-}]^{3+}}_{Fe^{4+}3d[\uparrow][\uparrow][\uparrow][\uparrow][\quad]\ O^{\bullet-}2p[\ \uparrow\ ][\uparrow\downarrow][\uparrow\downarrow]}$$

Although this option should not be excluded. However, as can be seen (equation (70)), the formation of oxoiron(V) ($[Fe^{5+}O^{2-}]^{3+}$) is definitely eliminated. According to the well-known Pauli principle and the law of conservation of the electron spin [95], none of the electrons of Fe^{4+} can mate with a single electron ($O^{\bullet-}$). This spin ban is in agreement with the requirement of the presence of second electron donors in Fe^{3+}/H_2O_2 systems to generate $[Fe^{4+}O^{2-}]^{2+}$ (equations (9) and (12)).

One can safely allow the invariability of the oxidation state of trivalent iron and the prevalence of iron (III)-^{1}D-oxene species among possible intermediates within our interpretation. Let us interpret the enzymatic activity of iron(III) hemoproteins from this standpoint. The mechanism of activation of H_2O_2 for catalase-peroxidase enzymes corresponds to equation (69) (with a specification of ligand nature):

$$P[Fe^{3+}\overset{H}{O}OH] \rightarrow P[Fe^{3+}{}^-O\overset{H}{\underset{H}{O}}{}^+]$$
$$\rightarrow P[Fe^{3+}O^0(^1D)]^{3+} + HOH \quad (71)$$
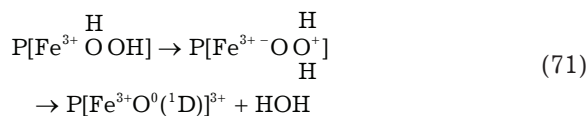
Of course, one cannot deny internal electron transitions in $P[Fe^{3+}O^0(^1D)]^{3+}$ species using the common (see subsection 3.2) form ($P^{\bullet+}[Fe^{4+}O^{2-}]^{2+}$):

$$P[Fe^{3+}O^0(^1D)]^{3+} \rightarrow P[Fe^{4+}O^{\bullet-}]^{3+} \rightarrow P^{\bullet+}[Fe^{4+}O^{2-}]^{2+} \quad (72)$$
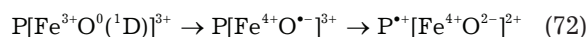
At least, the non-requirement of generating forms with tetravalent iron is accepted by us.

Proceeding from this argumentation, ^{1}D-oxene bound with Fe^{3+} ion is an oxidizer of substrates of catalase-peroxidase enzymes. The same species are also formed in the enzyme active centres of the P-450 monooxygenase
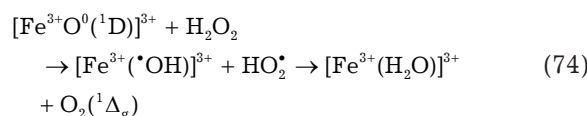
system resulting from protonation of Fe(III)-dihydroperoxo:

$$P[Fe^{3+}(^-OOH)]^{2+} + H^+ \rightarrow P[Fe^{3+}{}^-O\overset{H}{\underset{H}{O}}{}^+]$$
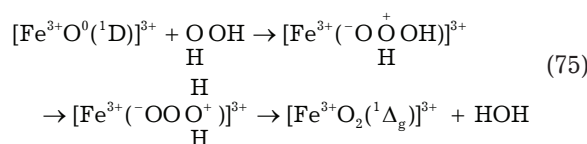$$\rightarrow P[Fe^{3+}O^0(^1D)]^{3+} + HOH \quad (73)$$
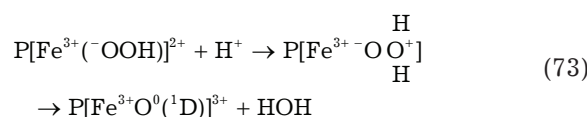
(See equation (21) for comparison). Thus, our interpretation allows resuming the use of the concepts, such as oxene-transferase and oxenoid oxidation towards the system of the cytochrome P-450 on the rights of semantically correct terms.

^{1}D-oxene is argumented as a prevailing oxidizer of organic substrates in biochemical peroxigenase and monoxigenase Fe(III)-heme systems, and also in anthropogenic systems of organic synthesis based on Fe^{3+}/H_2O_2, as once again stressed by us. Additionally, a singlet oxygen atom, together with α-oxygen will be an active intermediate of the classic Fenton oxidation due to the formation of a trivalent iron forms in Fe^{2+}/H_2O_2 systems (subsection 4.4).

Let us dwell on catalase enzymatic activity and the total mechanism of hydrogen peroxide disproportionation in Fe^{3+}/H_2O_2 systems. The first water molecule is formed resulting from oxywater dissociation (equations (69) and (71)). Afterwards, the complex $[Fe^{3+}O^0(^1D)]^{3+}$ ($P[Fe^{3+}O^0(^1D)]^{3+}$ for catalase) oxidizes the second molecule of hydrogen peroxide. Herewith, one can assume several kinetic options. The intermediate formation of crypto-hydroxyl species is also probable:

$$[Fe^{3+}O^0(^1D)]^{3+} + H_2O_2$$
$$\rightarrow [Fe^{3+}(^\bullet OH)]^{3+} + HO_2^\bullet \rightarrow [Fe^{3+}(H_2O)]^{3+} \quad (74)$$
$$+ O_2(^1\Delta_g)$$

Considering the presence of a vacant orbital for an atom of ^{1}D-oxene (see equation (56)) and lone electron pairs in the hydrogen peroxide molecule, one can allow the formation of decomposition products without the intermediate generation of free radicals but with the formation of the trioxide group:

$$[Fe^{3+}O^0(^1D)]^{3+} + \underset{H}{O}OH \rightarrow [Fe^{3+}(^-O\overset{+}{O}\underset{H}{OH})]^{3+}$$
$$\rightarrow [Fe^{3+}(^-O\overset{H}{\underset{H}{O}}O^+)]^{3+} \rightarrow [Fe^{3+}O_2(^1\Delta_g)]^{3+} + HOH \quad (75)$$

At last, there is the probability for the formation of $O_2(^1\Delta_g)$ resulting from the

recombination of two atoms of oxene:

$$2[Fe^{3+}O^0(^1D)]^{3+} \rightarrow 2Fe^{3+} + O_2(^1\Delta_g)) \tag{76}$$
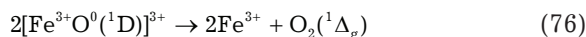
Dioxygen molecule is formed in the singlet quantum $^1\Delta_g$ state that differs from the main triplet state ($^3\Sigma_g^-$) in spin and orbital parameters of two external electrons at two antibonding π_{py}^*--MO and π_{pz}^*-MO [108]:

$$
O_2(^1\Delta_g) \begin{matrix} [\quad] & IV \\ [\ ][\uparrow\downarrow] & III \\ [\uparrow\downarrow][\uparrow\downarrow] & II \\ [\uparrow\downarrow] & I \end{matrix} \quad \bigg| \quad O_2(^3\Sigma_g^-) \begin{matrix} [\quad] & IV \\ [\ \uparrow\ ][\ \uparrow\ ] & III \\ [\uparrow\downarrow][\uparrow\downarrow] & II \\ [\uparrow\downarrow] & I \end{matrix} \tag{77}
$$

Designations: I − bonding σ_{px}-MO; II − two bonding π_{py}-MO and π_{pz}-MO; III − two antibonding π_{py}^*-MO and the π_{pz}^*-MO; IV − antibonding σ_{px}^*-MO.

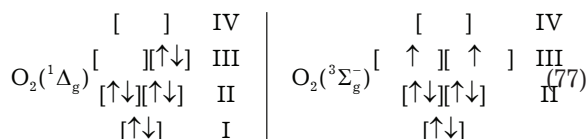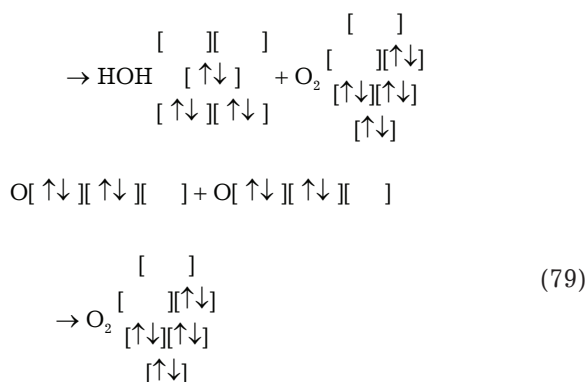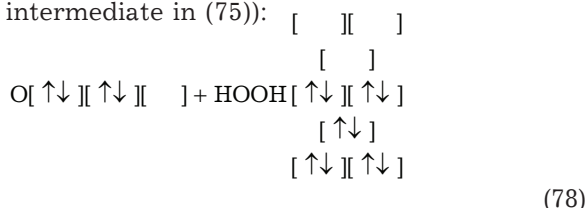The proof of precisely the $^1\Delta_g$ state of O_2 can be obtained by modeling the simplest quantum-chemical graphs and the observance of the law of conservation of the electronic spin. Let us refer to equations (74)−(76) (omit iron ions and intermediate radicals in (74) and trioxide intermediate in (75)):

$$
O[\uparrow\downarrow][\uparrow\downarrow][\quad] + HOOH \begin{matrix} [\quad][\quad] \\ [\quad] \\ [\uparrow\downarrow][\uparrow\downarrow] \\ [\uparrow\downarrow] \\ [\uparrow\downarrow][\uparrow\downarrow] \end{matrix} \tag{78}
$$

$$
\rightarrow HOH \begin{matrix} [\quad][\quad] \\ [\uparrow\downarrow] \\ [\uparrow\downarrow][\uparrow\downarrow] \end{matrix} + O_2 \begin{matrix} [\quad] \\ [\quad][\uparrow\downarrow] \\ [\uparrow\downarrow][\uparrow\downarrow] \\ [\uparrow\downarrow] \end{matrix}
$$

$$
O[\uparrow\downarrow][\uparrow\downarrow][\quad] + O[\uparrow\downarrow][\uparrow\downarrow][\quad]
$$

$$
\rightarrow O_2 \begin{matrix} [\quad] \\ [\quad][\uparrow\downarrow] \\ [\uparrow\downarrow][\uparrow\downarrow] \\ [\uparrow\downarrow] \end{matrix} \tag{79}
$$

The nature of orbitals for all reagents and products is characterised in text comments for Schemes (57) and (77).
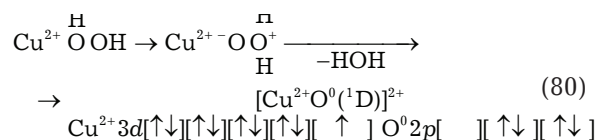
Experimental verifications of the $^1\Delta_g$ state of dioxygen formed in Fe^{3+}/H_2O_2 systems have been obtained when studying the decomposition of H_2O_2 by Fe(III)-heme peroxides using chemiluminescence analysis [109−111]. It is noteworthy that singlet dioxygen is of the real preparative value in organic synthesis

of hydroperoxides and cyclic peroxides by cycloaddition reactions with the participation of alkenes and conjugated alkadienes [112−114]. In other words, opportunities of Fenton systems include not only monooxygen oxidative functionalisation (see Fig. 1) but also the introduction of the dioxygen group into substrate molecules.

4.6. Iron-free catalysts: eliminating ambiguities

The advantage of the concept of the universal primacy for intramolecular rearrangements of hydroperoxides is its independence on redox properties of the element that directly interacts with the hydroperoxide molecule. The presence of positive charge $n+$ at the atom of element E, *i.e.* the polarizing factor becomes the main determinant of Fenton activity. Of course already after the formation of the $[E^{n+}O^0(^1D)]^{n+}$ complex, the redox activity of E^{n+} ion will define the principal nature of oxygen intermediates in a specific Fenton system: actually $[E^{n+}O^0(^1D)]^{n+}$ in the absence of the electron-donor potential of E^{n+} ion, $[E^{(n+1)+}O^-]^{n+}$ or $[E^{(n+2)+}O^{2-}]^{(n+1)+}$ with the possibility of $E^{(n+1)+}$ ion to donate one or two electrons for ^1D oxygen atom.

It is important that the concept enables the solution of problems formulated in sect. 3.4. Thus, the interpretation of Fenton activity for copper (II)-based catalysts comes from the scheme understood by readers in advance:
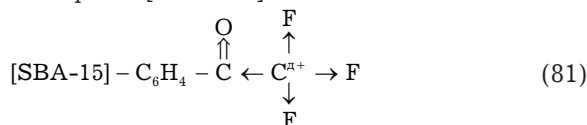
$$
Cu^{2+}\overset{H}{O}OH \rightarrow Cu^{2+}\ ^-O\overset{\Pi}{\underset{H}{O}}^+ \xrightarrow[-HOH]{} \tag{80}
$$

$$
\rightarrow \begin{matrix} [Cu^{2+}O^0(^1D)]^{2+} \\ Cu^{2+}3d[\uparrow\downarrow][\uparrow\downarrow][\uparrow\downarrow][\uparrow\downarrow][\ \uparrow\ ]\ O^0 2p[\quad][\uparrow\downarrow][\uparrow\downarrow] \end{matrix}
$$

The probability degree of the subsequent generation of $[Cu^{3+}O^{\bullet-}]^{2+}$ and $[Cu^{4+}O^{2-}]^{2+}$ intermediates will not be discussed by us now, let us only note that their formation is acceptable, in principle. The important thing is that the explanation of the mechanism of a primary step for oxidative activation of H_2O_2 by Cu^{2+} ion is provided.

The paper will not be overloaded by us with equations of the generation of probable intermediates in Fenton systems based on other metals with variable valencies on the reason of already sufficient demonstration of general and private schemes of our concept.

However, it will not yet be excessive to note that the concept quite successfully explains

catalytic activities of aluminium (III) and gallium (III) nitrates [13] *via* similar formation of $[Al^{3+}O^0(^1D)]^{3+}$ and $[Ga^{3+}O^0(^1D)]^{3+}$ complexes.

In our opinion, the ability of lanthanum (III) compounds to catalyse H_2O_2 disproportionation with the generation of $^1\Delta_g$-singlet dioxygen (or simply $^1O_2$) used with the purposes indicated above can be explained from the same standpoint [115−118]:

$$[SBA\text{-}15] - C_6H_4 - \overset{\overset{O}{\Uparrow}}{C} \leftarrow \overset{\overset{F}{\uparrow}}{\underset{\underset{F}{\downarrow}}{C^{\pi+}}} \rightarrow F \qquad (81)$$

Apparently, $[La^{3+}O^0(^1D)]^{3+}$ complex is initially formed in the La^{3+}/H_2O_2 system, and the formation of $^1O_2$ occurs *via* a mechanism similar to at least one of schemes (74)−(76) for the Fe^{3+}/H_2O_2 system.

At last, the concept is also applicable to polyfluoro superacids [6−8] indicated in section II and stannoacids [27], and even to 2,2,2-trifluoroacetophenone [12].

Tetrafluoroborate (BF_4^-) and hexafluoroantimonate (SbF_6^-) anions, where boron and antimony atoms become electron deficient and strongly electrophilic centres bearing at least a partial positive charge, the electrostatic field of which can polarize the H_2O_2 molecule with the generation of ^1D-oxene due to the enormous electronegativity of the neighboring fluorine atoms (as known, maximum among all the chemical elements). Such a reading even does not contradict the interpretation of the authors themselves [6−8], as the hydronium ion (HO^+) (equation (48)) suggested by them is the protonated form of the singlet oxygen atom.

Tin (IV) atoms are polarizing centres of stannosilicates [27], and the carbon atom of the trifluoromethyl group similarly to of B and Sb atoms in superacids experiencing significant electron withdrawing effects of both three fluorine atoms and the neighboring carbonyl group − in organic catalyst molecule [12]:

$$[SBA\text{-}15] - C_6H_4 - \overset{\overset{O}{\Uparrow}}{C} \leftarrow \overset{\overset{F}{\uparrow}}{\underset{\underset{F}{\downarrow}}{C^{\pi+}}} \rightarrow F$$
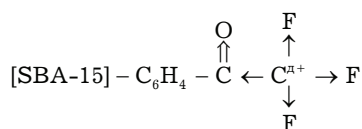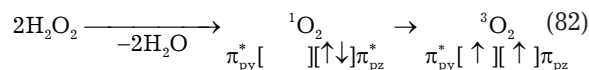
4.7. Hypothesis on the mechanism of a singlet-triplet transition of dioxygen

Prior to the final conclusion of the entire work, it was decided by us to include this small section discussing the issue of quantum states of dioxygen, formed in Fenton systems during disproportionation of hydroperoxides.

Atmospheric molecular oxygen or dioxygen (O_2) is a paramagnetic substance, as established long ago [108]. The parallel location of spins of two electrons (scheme (77)) at antibonding π_{py}^*-MO and π_{pz}^*-MO in the main triplet $(^3\Sigma_g^-$ or simply $^3O_2$) state with the lowest energy explains this fact. Singlet dioxygen $(^1O_2)$ (excited state) is characterized by the antiparallel location of spins of these two electrons. Herewith, the doubly degenerate $^1\Delta_g$-state where electrons are paired (scheme (77)) and are present either in π_{py}^*-MO, or π_{pz}^*-MO (therefore doubly degenerate) is distinguished [108].
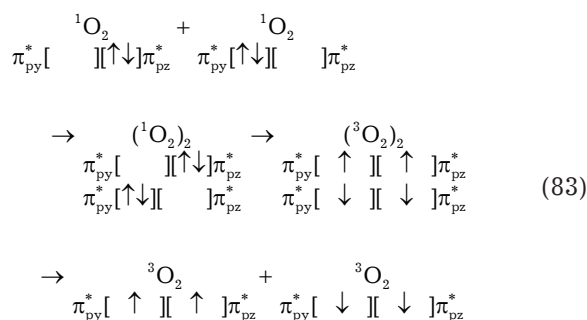
There is still the singlet state $(^1\Sigma_g^+)$ with the maximum energy [108], in which these two electrons with antiparallel spins are lone $(\pi_{py}^*$-MO$[\uparrow][\downarrow]\pi_{pz}^*$-MO$)$, however, singlet-singlet transitions $(^1\Delta_g\rightarrow^1\Sigma_g^+)$ are not spin-forbidden. And here singlet-triplet (S−T) and triplet-singlet (T−S) transitions, such as $^1O_2\rightarrow^3O_2$, being real, somehow overcome the exclusion on electron spin reversal [95, 108].

The lifetime of singlet dioxygen is measured in fractions of a second, herewith, in aqueous solutions − a few microseconds [108]. Therefore, suppression of oxygen $(^1O_2)$ formed during the Fenton disproportionation of H_2O_2 in aqueous solutions proceeds almost instantly:

$$2H_2O_2 \xrightarrow[-2H_2O]{} \underset{\pi_{py}^*[\quad][\uparrow\downarrow]\pi_{pz}^*}{^1O_2} \rightarrow \underset{\pi_{py}^*[\uparrow][\uparrow]\pi_{pz}}{^3O_2} \quad (82)$$

The mechanisms of forbidden transitions of dioxygen quantum states are, in principle, a separate big problem of chemical science, which has been unsolved and actively discussed until now [108]. For the S−T transition (quenching the singlet state), there is no definitive answer to two questions: 1) how to overcome the energy barrier of steaming two electrons $(^1\Delta_g\rightarrow^1\Sigma_g^+)$; 2) how to overcome the exclusion on electron spin reversal $(^1\Sigma_g^+\rightarrow^3\Sigma_g^-)$.

We want to argue for our proposed S−T transition mechanism. The following schema illustrates our hypothesis:

$$\pi_{py}^*[\quad][\uparrow\downarrow]\pi_{pz}^* \quad \overset{^1O_2}{\pi_{py}^*}[\uparrow\downarrow][\quad]\pi_{pz}^*$$

$$\rightarrow \quad \overset{(^1O_2)_2}{\pi_{py}^*[\quad][\uparrow\downarrow]\pi_{pz}^*} \quad \rightarrow \quad \overset{(^3O_2)_2}{\pi_{py}^*[\uparrow][\uparrow]\pi_{pz}^*} \quad (83)$$
$$\pi_{py}^*[\uparrow\downarrow][\quad]\pi_{pz}^* \qquad \pi_{py}^*[\downarrow][\downarrow]\pi_{pz}^*$$

$$\rightarrow \quad \overset{^3O_2}{\pi_{py}^*[\uparrow][\uparrow]\pi_{pz}^*} \quad + \quad \overset{^3O_2}{\pi_{py}^*[\downarrow][\downarrow]\pi_{pz}^*}$$

Two molecules of singlet dioxygen that are antipodes on the orbital momentum form a short-lived associate $(^1O_2)_2$ owing to two donor-acceptor interactions between an electron pair and a vacancy of MO of the same name. Two redox reactions with the formation of two molecules of triplet oxygen that are antipodes on spin moments of lone electrons proceed simultaneously in the associate. The total spin in the first $^3O_2$ molecule is +1, in the second one − (−1). It is most likely that the number of $^3O_2$ molecules of one spin sign in nature (in the scale of all the spheres of our plane, such as the atmosphere, hydrosphere, lithosphere, biosphere, and even the Universe) is equal to the number of $^3O_2$ molecules of the opposite spin sign. Furthermore, the total spin of all natural $^3O_2$ molecules including species generated photosynthetically in the biosphere and anthropogenically in artificial chemical systems is zero.

5. CONCLUSION

The concept suggested here and argumented as a hypothesis does not claim to be an alternative that excludes the nature of long-debated intermediates in Fenton systems, as emphasized by us.

Presuming the universal primary polarization (zwitter-ionization) and heterolytic dissociation of hydroperoxides in Fenton complexes with the initial generation of ^1D-oxene, our interpretation demonstrates opportunities for subsequent intramolecular electron transitions, reactions of protonation and decomposition of complexes to generate other species including commonly recognized monooxygen ones. Thus, Fe^{2+}/H_2O_2 for classic Fenton systems is substantiated as a required intermediate, *i.e.* $[Fe^{3+}O^{•−}]^{2+}$ α-oxygen species that may yield both oxoiron (IV) species and free hydroxyl radical resulting from subsequent transformations.

At the same time, one cannot but notice the successful application of the proposed interpretation in cases when existing ideas (H_2O_2 oxidation by Fe^{3+} or Cu^{2+} ions) are doubtful or mechanisms of interactions of catalysts with hydroperoxides (Al^{3+}/H_2O_2, Ga^{3+}/H_2O_2, La^{3+}/H_2O_2, HBF_4/H_2O_2, $HSbF_6/H_2O_2$, $Sn(IV)/H_2O_2$, and 2,2,2-trifluoroacetophenone/H_2O_2 systems) are not at all clear. A singlet oxygen atom for the listed systems is assumed as the predominant intermediate.

Our survey and analytical paper will be useful to researchers dealing with issues of substance oxidation in Fenton systems as hoped.

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