

# The influence of solvent on the reaction between iron(II), (III) and hydrogen peroxide

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## Abstract

It has been found that in acetonitrile, in contrast to water, iron(III) is reduced by hydrogen peroxide, according to 2:1 stoichiometry. The reaction when performed by cyclic-voltammetry is an example of electrochemical catalytic processes of reductants. For the [Fe(III)]/[HOOH] ratios greater than 1, 1 mol of dioxygen is produced from 1 mol of hydrogen peroxide. The non-radical versus radical mechanism of the process has been discussed.

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## 1. Introduction

The activation of dioxygen, hydrogen peroxide and hydroperoxides is one of the most challenging problems in chemistry and biology. An understanding of the molecular details and mechanisms of the activation process will lead to new opportunities in the chemical process industries, pharmaceutical industry [1–3] and waste products management [2,4]. On the other hand dioxygen, although essential for aerobic life, can cause a lot of damages to living organisms, vide oxygen toxicity [5]. The processes include a partial reduction of dioxygen species, which among others includes hydrogen peroxide.

Fenton reagent, originally the mixture of iron(II) and hydrogen peroxide has long been known [6].

However, there is a considerable discussion about the nature of the reactive species formed in the system. Some groups advocate the free radical mechanism of the reactions occurred in the system [7]. The mechanism originated from Haber and Weiss [8] includes free hydroxyl radicals ( $\text{OH}^\bullet$ ) as reactive species. Others postulate that a high-valent iron complex is responsible for the oxidative properties of the reagent. This approach is represented by the oxygenated Fenton reagent [9] and the GIF family of systems [10]. The controversy arose at the very beginning of the use of Fenton reagent. As a matter of fact, the non-radical – “complex” mechanism was postulated first [11] and then further developed on the basis of mainly kinetic arguments [12].

A comparison of radical and non-radical approaches have been recently published [13,14]. However, the vast amount of results collected by independent authors come from experiments, which usually were performed in different conditions. The results published

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indicate that the system is very sensitive towards solvent, ligand, and catalyst to hydrogen peroxide ratio. Therefore, to systemize the reactions occurred in the system, we have started with the investigation of reactivity of iron(II) and (III) ions with hydrogen peroxide in water and acetonitrile.

## 2. Experimental

### 2.1. Equipment

A three-electrode potentiostat (Princeton Applied Research Model 273A) was used to record the voltammograms. The experiments were conducted in a 15 ml electrochemical cell with provision to control the presence of dioxygen with an argon-purge system. The working electrode was either a Bioanalytical Systems glassy-carbon (area, 0.09 cm<sup>2</sup>) or platinum (area, 0.023 cm<sup>2</sup>) inlay, the auxiliary electrode – a platinum wire, and the reference electrode – an Ag/AgCl wire in an aqueous tetramethylammonium chloride solution that was adjusted to give a potential of 0.00 V versus SCE. The latter was contained in a Pyrex tube with a cracked soft-glass tip, which was placed inside a Luggin capillary [15].

### 2.2. Chemicals and reagents

The reagents for the investigations and syntheses were of the highest purity commercially available and were used without further purification. The solvent for the experiments was either redistilled water or Burdick and Jackson “distilled in glass” grade acetonitrile (MeCN, 0.002% H<sub>2</sub>O). High-purity argon gas was used to deareate the solutions. All compounds were dried in vacuo over CaSO<sub>4</sub> for 24 h prior to use. Fe<sup>II</sup>(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (99+%) and Fe<sup>III</sup>(ClO<sub>4</sub>)<sub>3</sub>·9H<sub>2</sub>O (99+%) were obtained from GFS, perchloric acid (HClO<sub>4</sub>, 70%) from Laborchemie Apolda GmbH and hydrogen peroxide (30% in water) from Chempur. The [Fe<sup>II</sup>(MeCN)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> complex was prepared by multiple recrystallizations of [Fe<sup>II</sup>(H<sub>2</sub>O)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> from MeCN [16]. Almost-dry HOOH (94%) was prepared from reagent-grade HOOH (50%, Fisher Scientific via vacuum distillation) [17]. This solution was dissolved in acetonitrile and the concentration of HOOH was determined iodometrically [18].

### 2.3. Methods

#### 2.3.1. Determination of the amount of dioxygen evolved

The reaction system was gastight and connected to a manometric burette filled with brine, which was saturated with oxygen (air) prior to use. During the readings, the pressure was always equilibrated using a separatory funnel by adjusting brine levels to the same heights. The appropriate temperature and atmospheric pressure were taken into account in the calculations, which used the ideal gas law.

#### 2.3.2. Oxidation of cyclohexane by aqueous Fenton reagent

The substrate (1 M) and the appropriate amount of Fe<sup>II</sup>(ClO<sub>4</sub>)<sub>2</sub> or Fe<sup>III</sup>(ClO<sub>4</sub>)<sub>3</sub> were combined with 0.1 M HClO<sub>4</sub> in water (total volume = 5 ml) followed by the addition of dioxygen (O<sub>2</sub>, 1 atm) or high-purity argon gas (O<sub>2</sub>, 0 atm). The reaction cell (25 cm<sup>3</sup> vial with cut-out cap and Teflon-faced septum) had a 20 ml head space, which provided a reservoir to maintain a constant solution concentration of dioxygen. To the reaction mixture HOOH (30% solution in water, its analytical concentration was determined iodometrically [18]) was injected to give a proper concentration. The reactions were allowed to proceed for 24 h, with constant stirring to maintain an emulsion of cyclohexane in water at room temperature. After the experiment, the reaction mixture was extracted with diethyl ether. The aliquots (0.2 μl) were injected into a capillary-column gas chromatograph, with FID detector, for analysis. Authentic samples were always used to confirm product identifications and to produce standard curves for quantitative assays of the product species. Biphenyl (10 mM) was used as an internal standard.

All experiments were done in triplicate. The presented values of concentration are the mean values of three independent experiments.

## 3. Results and discussion

Figs. 1 and 2 present cyclic-voltammograms of Fe<sup>II</sup>(ClO<sub>4</sub>)<sub>2</sub> (Fig. 1a and c) and Fe<sup>III</sup>(ClO<sub>4</sub>)<sub>3</sub> (Fig. 2a and c) in aqueous HClO<sub>4</sub> solutions registered at a glassy carbon electrode. The electrochemical behavior of Fe(III)/Fe(II) couple is irreversible. At a

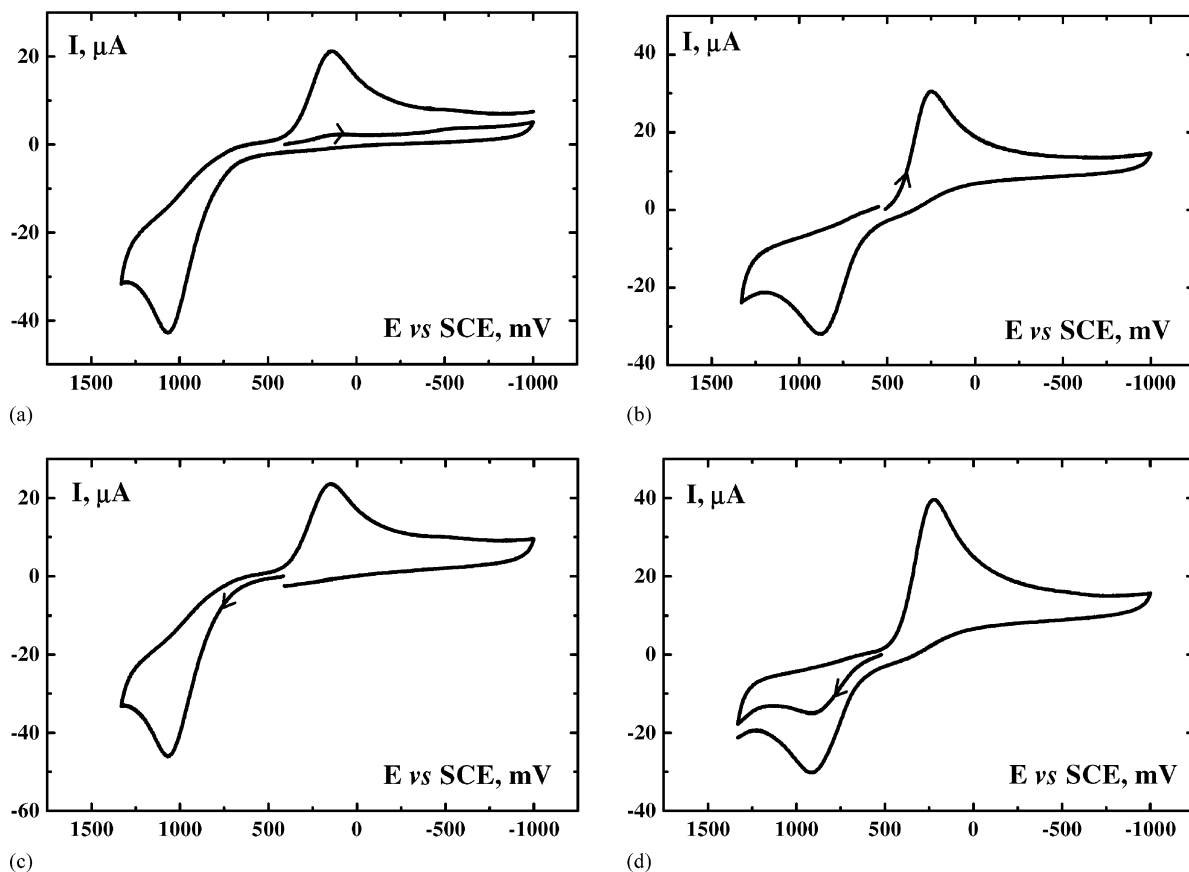


Fig. 1. Cyclic-voltammograms in water [0.1 M  $\text{HClO}_4$ ] for (a and c) 5 mM  $\text{Fe}^{\text{II}}(\text{ClO}_4)_2$  and (b and d) in the presence of 2.5 mM  $\text{HOOH}$ . Scan rate,  $0.1 \text{ V s}^{-1}$ , GCE ( $0.09 \text{ cm}^2$ ); SCE vs. NHE,  $+0.242 \text{ V}$ .

platinum electrode the reduction/oxidation process for the  $\text{Fe}(\text{III})/\text{Fe}(\text{II})$  couple is reversible regardless of the kind of iron salt used as a starting material. We have chosen however, the glassy carbon electrode for further investigations to avoid a catalytic decomposition of hydrogen peroxide, that can occur on platinum. The electrochemical reversibility of the  $\text{Fe}(\text{III})/\text{Fe}(\text{II})$  couple is not important for the problems discussed in the paper. Note, that the CV method is the very convenient one to determine the oxidation state of a metal ion in the solution. If we start with a reduced form [ $\text{Fe}(\text{II})$ ] no reduction peaks are observed if the cathodic scan was performed first (Fig. 1a). Likewise, if a metal ion is in the highest oxidation state, [ $\text{Fe}(\text{III})$ ], there are no oxidation peaks during the first anodic scan (Fig. 2c).

The addition of 0.5 eq. of  $\text{HOOH}$  to the solution of  $\text{Fe}^{\text{II}}(\text{ClO}_4)_2$  causes the oxidation peak of  $\text{Fe}(\text{II})$  almost to disappear (compare Fig. 1c and d) in the first anodic scan (it disappears completely when higher concentrations of  $\text{Fe}^{\text{II}}(\text{ClO}_4)_2$  and  $\text{HOOH}$  at the same ratio are used) and the reduction of  $\text{Fe}(\text{III})$  is observed in the first negative scan (Fig. 1b). There is no indication on the cyclic-voltammogram that dioxygen is evolved in the experiment. In the aqueous solution of  $\text{HClO}_4$ , dioxygen is reduced at  $-0.8 \text{ V}$  (versus SCE), and hydrogen peroxide is not reduced nor oxidized in the potentials window used.

When  $\text{Fe}^{\text{III}}(\text{ClO}_4)_3$  is used instead of  $\text{Fe}^{\text{II}}(\text{ClO}_4)_2$  there are no changes in the anodic part of cyclic-voltammogram after addition of  $\text{HOOH}$  (compare Fig. 2c and d). However, the increase of the cathodic peak's

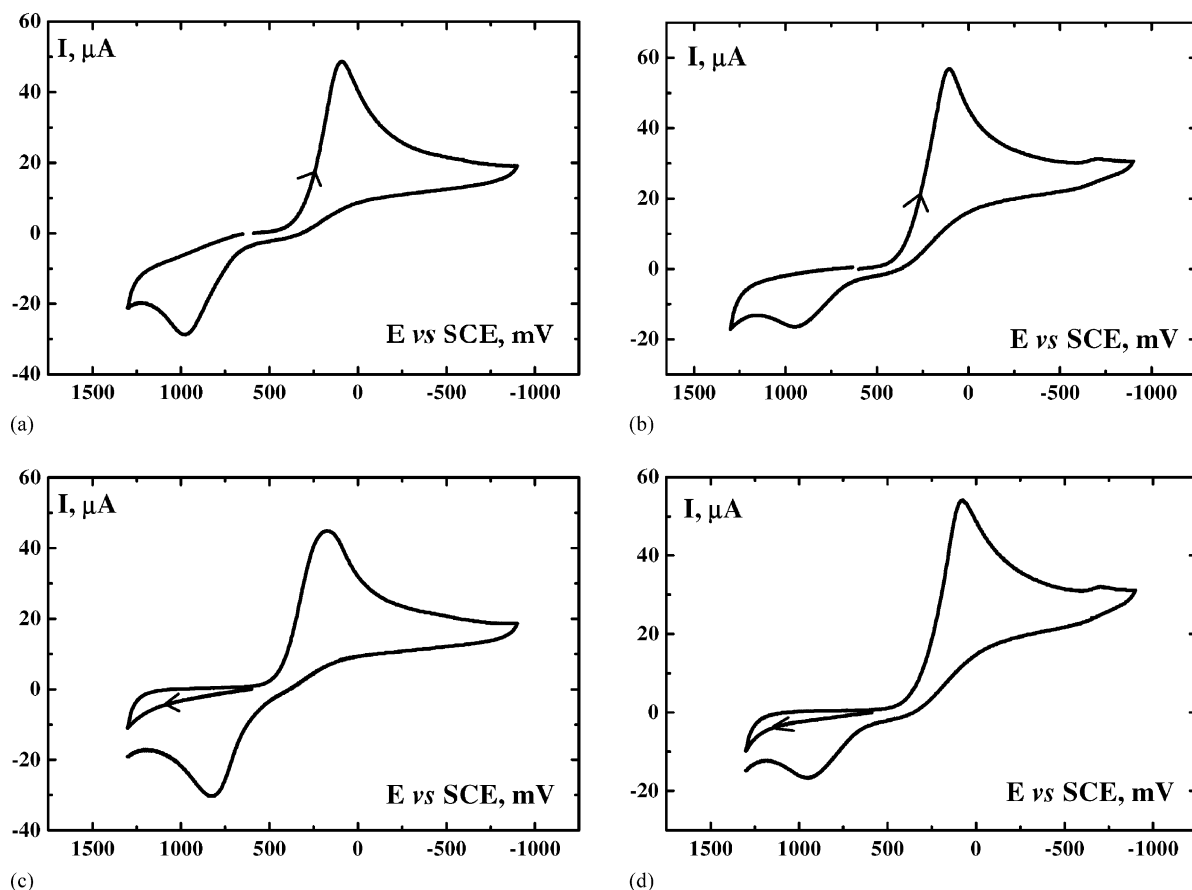


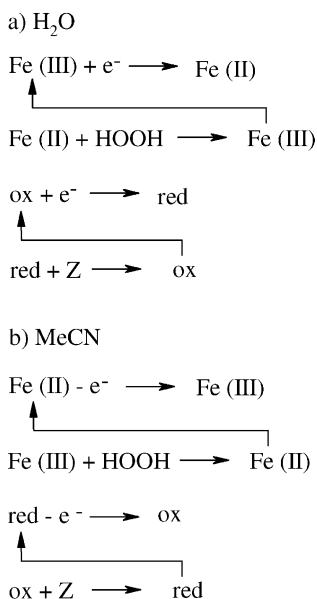
Fig. 2. Cyclic-voltammograms in water [0.1 M  $\text{HClO}_4$ ] for (a and c) 5 mM  $\text{Fe}^{\text{III}}(\text{ClO}_4)_3$  and (b and d) in the presence of 2.5 mM HOOH. Scan rate,  $0.1 \text{ V s}^{-1}$ , GCE ( $0.09 \text{ cm}^2$ ); SCE vs. NHE,  $+0.242 \text{ V}$ .

height indicates that an electrochemical catalytic current is formed. When  $\text{Fe}(\text{III})$  is electrochemically reduced in the presence of HOOH, the electrogenerated  $\text{Fe}(\text{II})$  reacts with HOOH to produce  $\text{Fe}(\text{III})$ , and since the current is proportional to the concentration of electroactive species, the height of the reduction peak increases. It can be visualized in the Scheme 1a. The cathodic current increase however is not large due to small  $[\text{HOOH}]/[\text{Fe}(\text{III})]$  ratio used and to a relatively small reaction rate constants between  $\text{Fe}(\text{II})$  and HOOH [20]. The same effect causes the height of the corresponding anodic peak of  $\text{Fe}(\text{II})$  oxidation to decrease due to the consumption of  $\text{Fe}(\text{II})$  in the chemical process. It is worth to notice that the catalytic current is stable; the height of the  $\text{Fe}(\text{III})$  reduction peak even in the presence

of large HOOH excess remains unchanged at least within 3 h.

In the case of  $\text{Fe}(\text{III})$  – introduced into solution or produced by oxidation of  $\text{Fe}(\text{II})$  by HOOH – a shift of  $\text{Fe}(\text{II})$  oxidation peak, after electro-reduction of  $\text{Fe}(\text{III})$ , towards negative potentials is observed. This is probably caused by the formation of hydroxo-complexes of  $\text{Fe}(\text{II})$  during the reduction of  $[(\text{H}_2\text{O})_5\text{Fe}^{\text{III}}-\text{OH}]^{2+}$ , which is formed when iron(III) salts are dissolved in water [19].

In contrast, in MeCN on cyclic-voltammograms registered from  $\text{Fe}^{\text{II}}(\text{ClO}_4)_2$  solutions there was no indication of  $\text{Fe}(\text{II})$  oxidation by HOOH (Fig. 3).  $\text{Fe}(\text{III})$  is however, reduced by HOOH to  $\text{Fe}(\text{II})$  (Fig. 4). The voltammogram obtained after addition of HOOH to  $\text{Fe}^{\text{III}}(\text{ClO}_4)_3$  solution closely resembles that



Scheme 1. Formation of the electrochemical catalytic current of an (a) oxidant, and (b) reductant.

registered from Fe<sup>II</sup>(ClO<sub>4</sub>)<sub>2</sub> solution. This indicates, that Fe(III) is completely reduced by HOOH. Again, the reaction between Fe(III) and HOOH shows 2:1 stoichiometry—the reduction peak of Fe(III) disappears after addition of 0.5 eq. of HOOH. In acetonitrile the potential of the Fe(III)/Fe(II) couple is shifted about 0.5 V (in comparison to water) towards more positive potentials, which means that in acetonitrile Fe(III) is a stronger oxidant and Fe(II) is a weaker reductant than in water. Such effect is observed up to 1.1% concentration of water in acetonitrile. Above this limit, the observed phenomena are the same as in water. Since HOOH in MeCN is not oxidized prior to +2.0 V (versus SCE), we can expect that a catalytic

current can occur when Fe(II) is electrochemically oxidized in the presence of HOOH. Indeed, the increase of the height of Fe(II) oxidation peak in the presence of HOOH is observed (Fig. 4c and d). And this is, with the best of our knowledge, the first case when HOOH is acting as a reductant in an electrochemical catalytic system (Scheme 1b). This reaction opens a new perspective in the electrochemical catalytic processes. The known examples of catalytic currents involving metal ions have included so far only the metal reduction processes. This means that the metal ions have to be reoxidized to accommodate the catalytic current [20]. In the presented case (Scheme 1b) iron(II) is oxidized and needs to be reduced.

The system however, is not stable, with 5 mM Fe(II) and 20 mM HOOH, the catalytic effect disappears after approximately 30 min, which means that HOOH is completely decomposed. This indicates that although HOOH does not oxidize Fe(II) to Fe(III), it is decomposed in the mixture. Therefore, we have investigated dioxygen evolution for different combinations of iron, hydrogen peroxide, and solvent. The results are presented in Table 1.

The results obtained indicate that in water for the ratios [Fe]/[HOOH] > 1 dioxygen is practically not evolved in the presence of Fe(II), whereas in the presence of Fe(III) the amount of dioxygen formed is equal to 0.5 mol of hydrogen peroxide. The same stoichiometry of dioxygen evolution is observed for both iron ions in water when [Fe]/[HOOH] ≤ 1. It is characteristic that in MeCN for [Fe(III)]/[HOOH] > 1, 1 mol of HOOH is decomposed to form 1 mol of dioxygen, and the number decreases with the decrease of the ratio. Fe(II) in MeCN catalyses the decomposition of HOOH with the formation of less than 0.5 mol dioxygen per 1 mol HOOH. The oxidation state of iron after dioxygen evolution is in the agreement with the CV

Table 1  
Dioxygen evolution for different iron(II)/(III) to hydrogen peroxide ratios in water and in acetonitrile

[Fe]/[HOOH]		Number of dioxygen moles found per mol of HOOH ( $n_{\text{O}_2}/n_{\text{HOOH}}$ )			
Solvent	Iron source	4/1	2/1	1/1	1/10
H <sub>2</sub> O	Fe <sup>II</sup> (ClO <sub>4</sub> ) <sub>2</sub>	0.04	0.04	0.34	0.46
	Fe <sup>III</sup> (ClO <sub>4</sub> ) <sub>3</sub>	0.44	0.50	0.50	0.49
MeCN	Fe <sup>II</sup> (ClO <sub>4</sub> ) <sub>2</sub>	0.28	0.36	0.38	0.17
	Fe <sup>III</sup> (ClO <sub>4</sub> ) <sub>3</sub>	0.92	0.92	0.61	0.14

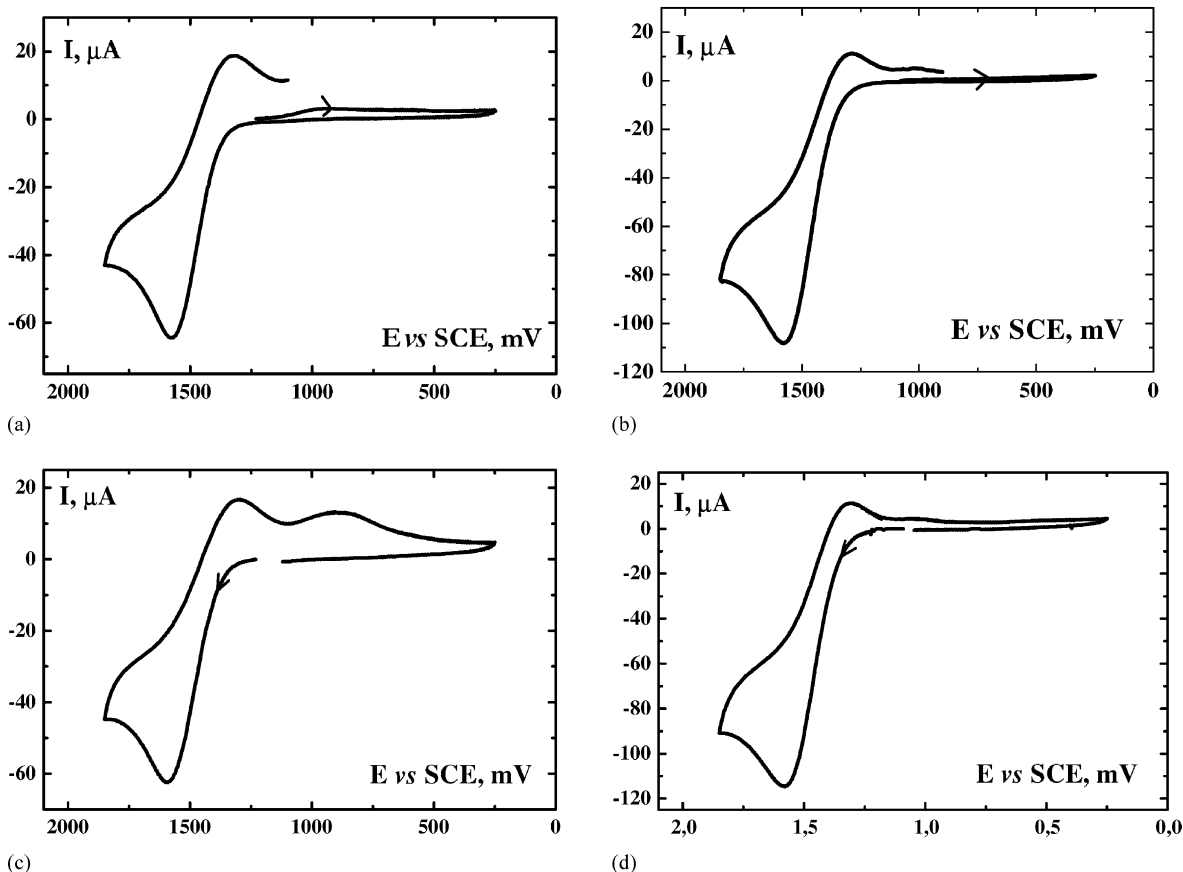
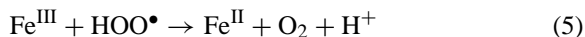
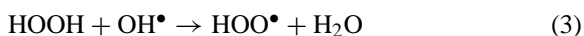


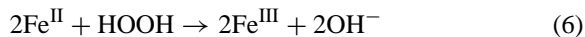
Fig. 3. Cyclic-voltammograms in MeCN [0.1 M (Et<sub>4</sub>N)ClO<sub>4</sub>] for (a and c) 5 mM Fe<sup>II</sup>(ClO<sub>4</sub>)<sub>2</sub> and (b and d) in the presence of 2.5 mM HOOH. Scan rate, 0.1 V s<sup>-1</sup>, GCE (0.09 cm<sup>2</sup>); SCE vs. NHE, +0.242 V.

measurements presented, e.g. in water Fe(II) is oxidized to Fe(III), and Fe(III) does not change the oxidation state, in contrast, in MeCN, Fe(II) stays at this oxidation state and Fe(III) is reduced to Fe(II). Blank experiments (with HOOH and without iron) show that the uncatalysed decomposition of HOOH does not occur within a time framework of the experiments.

The results presented allow to discuss the mechanism of reactions occurring in the Fenton system. The radical mechanism [21] for Fe(II)/HOOH system in water is as follows:



For the [Fe<sup>II</sup>]/[HOOH] > 1 only reactions (1) and (2) should be considered, which gives an overall reaction:



The process is in accordance with the observed reaction stoichiometry and dioxygen is not evolved. For the [Fe<sup>II</sup>]/[HOOH] > 1 the reactions (1), (3) and (5) are dominant and the overall process is:



This is also in agreement with observed stoichiometry of dioxygen evolution, however the reaction

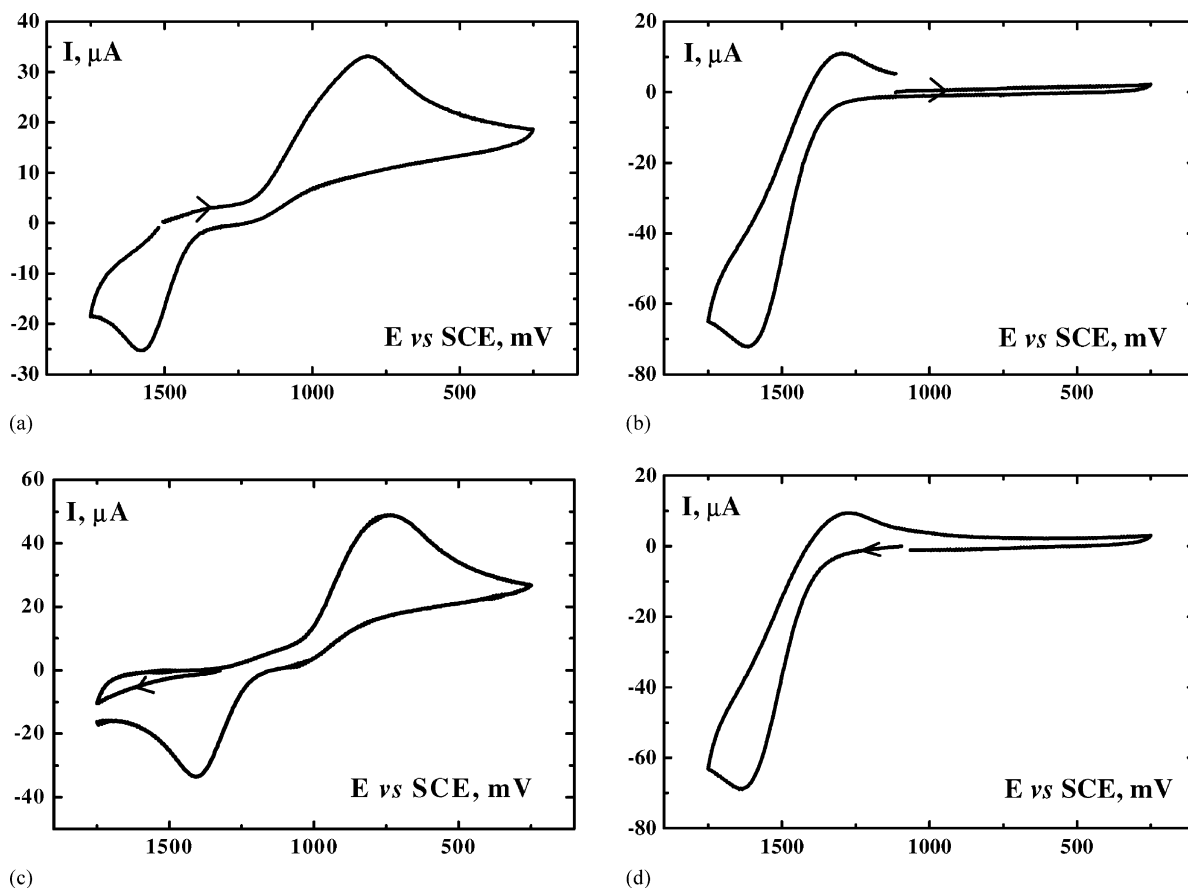
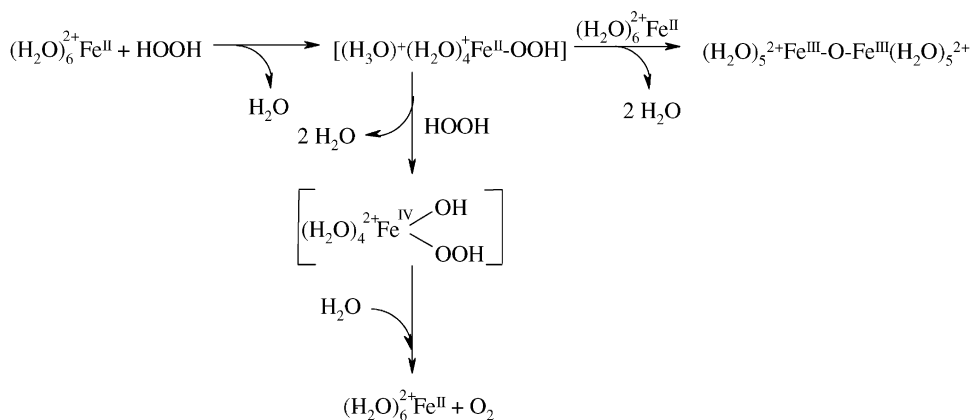


Fig. 4. Cyclic-voltammograms in MeCN [0.1 M (Et<sub>4</sub>N)ClO<sub>4</sub>] for (a and c) 5 mM Fe<sup>III</sup>(ClO<sub>4</sub>)<sub>3</sub> and (b and d) in the presence of 2.5 mM HOOH. Scan rate, 0.1 V s<sup>-1</sup>, GCE (0.09 cm<sup>2</sup>); SCE vs. NHE, +0.242 V.

implies a catalytic nature of the process, which is somewhat misleading, since the initiation reaction is the stoichiometric one. The observed results however can also be explained taking into account a non-radical mechanism. Based on our previous work [9], and taking into account properties of iron(II) and iron(III) aqua-complexes [22] the mechanism presented in the Scheme 2 is consistent with the observed behavior of Fe(II)/HOOH system in water. The formation of an iron–hydroperoxo intermediate is proposed in the first step. The presence of such intermediate however, is also postulated in the radical mechanism [13]. We cannot prove the existence of such structure, but the proposition is based on the nucleophilic properties of hydrogen peroxide and on the fact that several hydroperoxo complexes of iron have been recently

isolated and characterized [23]. It is also known that  $\mu$ -oxo diiron(III) species are the final products of Fe(II) oxidation.

The mechanism proposed explains the observed increase of dioxygen evolved with the increase of amount of HOOH versus Fe. For [Fe]/[HOOH] > 1 ratios the formation of (H<sub>2</sub>O)<sub>5</sub><sup>2+</sup>Fe<sup>III</sup>OH only takes place and dioxygen is not formed. The presence of higher concentrations of HOOH causes the occurrence of its reaction with the iron–hydroperoxo intermediate formed in the first step and the amount of dioxygen reaches the 0.5:1 ( $n_{O_2}/n_{HOOH}$  – number of mole dioxygen evolved per 1 mol of HOOH) stoichiometry. The second reactive intermediate, which appears in this step is also the hypothetical one and was proposed by Sawyer based on the results obtained



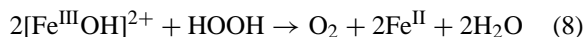
Scheme 2. Proposed mechanism for Fe(II) activation of HOOH in aqueous solution.

for the metal-induced oxygenation of organic substrates in basic, non-aqueous media. Several cases were reported, in which the reactivity patterns of oxidations of alkanes suggest the involvement of other oxidant than hydroxyl radical. They include a formation of larger quantities of ketone versus alcohol [14], relatively high kinetic isotope effect [13,14], and the most remarkable – enantioselective catalytic hydroxylation by HOOH using a non-heme iron complexes with chiral ligands as catalysts [24]. Based on above presented arguments, Que and co-workers proposed similar reactive intermediate in the models of HOOH activation [25].

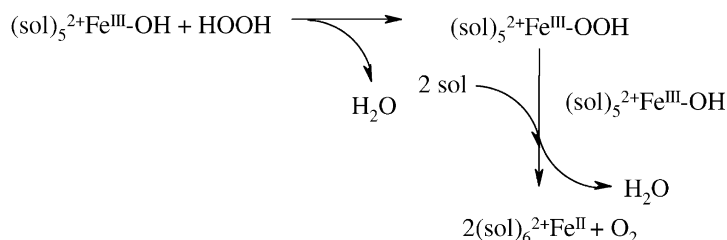
In water, Fe(III) causes the catalytic decomposition of HOOH. Although, the process is slow, the evolution of 0.5 mol of dioxygen from 1 mol of HOOH, regardless of the  $[\text{Fe}(\text{III})]/[\text{HOOH}]$  ratio confirms the statement. It is known that simple iron(III) salts can mimic catalase action [26] in water.

In acetonitrile, the redox potential of Fe(III)/Fe(II) couple is shifted towards positive potentials and this

causes that Fe(III) oxidizes hydrogen peroxide. The overall reaction is:



and two plausible mechanisms of the process are presented in Scheme 3. The first one (Scheme 3a) is based on the analogy to the  $\text{M}_2(\mu\text{-O})_2$  diamond core complexes. Complexes with such cores have been well characterized for Mn [27], Cu [28], and Fe [29]. In the case of manganese these complexes can catalyze O–O bond formation that results in dioxygen evolution and therefore they are functional models for the  $\text{O}_2$ -evolving complex in Photosystem II. The main drawback of the mechanism is the assumption that O–O bond is broken first and then remade. Therefore, an alternative mechanism, based on the nucleophilic properties of HOOH is proposed. Although,  $\text{HOO}^-$  is a weaker Brønsted base [ $pK_{\text{a}}(\text{HOOH}) = 11.8$ ] than  $\text{HO}^-$  [ $pK_{\text{a}}(\text{H}_2\text{O}) = 15.7$ ], it is a much stronger Lewis base [ $(E_{\text{ox}})_{\text{HOO}^-} = +0.20\text{ V}$  (versus NHE) versus  $(E_{\text{ox}})_{\text{OH}^-} = +1.89\text{ V}$ ]. The more negative, or less



Scheme 3. Proposed mechanism for Fe(III) catalyzed decomposition of HOOH in acetonitrile.



positive, the potential the more basic is a species; with the electron ( $e^-$ ) at the reduction potential of the solvent, which can be considered as an ultimate Lewis base ( $-2.93$  V versus NHE for  $H_2O$ ). Relative to the Lewis basicity of  $H_2O$  [ $(E_{ox})_{H_2O, pH 5} = +2.43$  V], that for  $HOOH$  [ $(E_{ox})_{HOOH, pH 5} = +1.01$  V] also is also much greater [30]. Therefore, the formation of iron–hydroperoxo complex from hydroxo one (which exists in acetonitrile due to the presence of traces of water) is favorable, and then interaction of the two gives dioxygen. Both of the mechanisms account for the observed  $Fe/HOOH$  and  $O_2/HOOH$  stoichiometries.

It is rather difficult to explain the irregular stoichiometry observed during dioxygen evolution in the  $Fe(II)/HOOH$  system in  $MeCN$ . The ratios of  $O_2/HOOH$  are below 0.5,  $Fe(II)$  is not oxidized, but the disappearance of the electrochemical catalytic effect in time suggests that hydrogen peroxide is consumed. This can be explained by an assumption that polyhydroxy adducts of iron are formed in the system or that the solvent is partially oxidized.

The early investigations on Fenton system, which proposed hydroxyl radical as a reactive species were mainly based on kinetic measurements and not product analysis. Therefore, we have tried to oxidize cyclohexane in the system for different  $[Fe(II,III)]/[HOOH]$  ratios (2/0.1) in dioxygen and argon atmosphere. The concentration of cyclohexane was always equal to 1 M. The high concentration of cyclohexane was used to favor the formation of the dimer-dicyclohexyl. The process was performed in the heterogeneous system, but the oxidation of benzene in similar system affords good yields of the products [31]. When  $Fe(III)$  was used, no products were detected for all applied combinations of  $[Fe(III)]/[HOOH]$  ratios. As we have indicated, in water solution,  $Fe(III)$  causes the decomposition of  $HOOH$  without changing metal oxidation state. Obviously, the transition species formed in the process cannot oxidize cyclohexane. The results for  $Fe(II)/HOOH$  system are presented in Table 2. The low yield of products in the case of higher  $[HOOH]/[Fe(II)]$  ratio is probably caused by dioxygen evolution from hydrogen peroxide as a parallel process. The almost total absence of the dimer in the presence of the large excess of substrate (1 M) indicates that the observed process cannot be considered as a purely radical one. Further conformation of the

Table 2

Oxidation of cyclohexane ( $c-C_6H_{12}$ , 1 M) by Fenton reagent in 0.1 M  $HClO_4$  in water<sup>a</sup>

Concentration (mM)		Atmosphere	Products (mM $\pm$ 10%)		
Fe(II)	HOOH		Ketone	Alcohol	Dimer
2	1	Ar	0.07	0.21	0.01
2	1	O <sub>2</sub>	0.29	ND	ND
1	1	Ar	0.10	0.22	0.01
1	1	O <sub>2</sub>	0.18	ND	ND
1	10	Ar	0.20	0.20	0.01
1	10	O <sub>2</sub>	0.33	0.21	ND

ND: not detected.

<sup>a</sup> Emulsion of  $c-C_6H_{12}$  was maintained during the experiment. Products were analyzed after 24 h.

assumption is the fact that cyclohexanone is a sole product in the presence of dioxygen for  $[Fe(II)]/[HOOH] > 1$ . The observed results are in a good agreement with experiments performed earlier [32].

We do not claim that radical mechanism cannot occur in the Fenton systems, however, the assumption that in the system containing metal ions only free hydroxyl radicals are present seems to be unjustified. The results presented show that the system is very sensitive towards almost any experimental variables, i.e. solvent, ligand, water content in organic solvent, and the oxidation state of metal ion, which can be rapidly changed at the beginning of the experiment.

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