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The Influence of Solvent on the Reaction Between Iron (II), (III) and *tert*-Butyl Hydroperoxide – Electrochemical Catalytic Processes of Reductants[*]

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It has been found that *tert*-butyl hydroperoxide is analogous to hydrogen peroxide with respect to their reactivity towards iron(II) and iron(III). In water iron(II) is oxidized by *tert*-butyl hydroperoxide, whereas in acetonitrile iron(III) is reduced by *tert*-butyl hydroperoxide. The last reaction when performed by cyclic-voltammetry is an example of electrochemical catalytic processes of reductants.

Key words: Fenton reagent, *tert*-butyl hydroperoxide activation, electrochemical catalytic current

Electrochemical catalytic processes, in which a substrate of an electrochemical reaction is regenerated by a chemical reaction occurring in the solution constantly attract much attention [1–3]. This is not only due to the possibility of increasing the sensitivity of an analytical method or the possibility to determine a concentration of electrochemically inactive substances. Many current challenging and technologically important processes like activation of dioxygen and hydroperoxides for the selective fuctionalization of hydrocarbons [4–7], waste products management [8–10] as well as biomimetics of enzyme actions, and other processes important to life are also of catalytic nature [11–13]. Therefore, new possibilities of employments of electrochemical methods can add an impact to investigations of these processes.

The electrochemical catalytic processes [1–3] have been known from the beginning of polarography. When a depolarizer is reduced on the electrode in the presence of electrochemically inactive substance "Z" the catalytic process is described by equations:

$$\text{ox} + \text{ne}^- \rightleftarrows \text{red} \tag{1}$$

$$\text{red} + \text{Z} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{ox} + \text{Y} \tag{2}$$

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[*] Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.
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The reduced form of the depolarizer is oxidized and this causes the observed current to increase with comparison to that registered in the absence of substance "Z". Since the vast number of examples of catalytic currents were found using polarographic method, in which a metal ion was reduced and then reoxidized by an "oxidant" present in solution; this class of catalytic current was named as "catalytic currents of oxidants" [14]. The theory of electrochemical catalytic currents has been fully developed, and basically the increase of current is proportional to square root of the concentration of substance "Z "and also to the square root of the rate constant of its reaction with the reduced form of depolarizer [1–3]. The classical example of catalytic current of oxidants is the electroreduction of iron(III) to iron(II) in the presence of hydrogen peroxide in water solution [15]. Electrogenerated iron(II) reacts with hydrogen peroxide in a sequence of steps known as Fenton reactions, in which iron(III) is formed causing the increase of the observed current. The mechanism of Fenton reagent has attracted much attention lately, and several reviews have discussed the nature of the reactive species formed in the system [4,16–18]. However, for the catalytic currents theory it is important, that in the Fenton system iron(II) is oxidized by hydrogen peroxide.

We have found however, that in acetonitrile, in contrast to water, iron(II) is not oxidized by hydrogen peroxide but hydrogen peroxide reduces iron(III) [19]. The reaction when performed by cyclic-voltammetry is an example of electrochemical catalytic processes of reductants.

$$\text{red} - \text{ne}^- \rightleftarrows \text{ox} \qquad (3)$$

$$\text{ox} + \text{Z} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{red} + \text{Y} \qquad (4)$$

In metal ions activation of hydroperoxides for oxidation of organic substrates *tert*-butyl hydroperoxide is an alternative oxidant to hydrogen peroxide. Some authors suggested that application of *tert*-butyl hydroperoxide instead of hydrogen peroxide changes the mechanism of the oxidation processes [20–23]. Therefore, we have performed a study on the influence of solvent on the reaction between iron(II), (III) and *tert*-butyl hydroperoxide.

EXPERIMENTAL

A three-electrode potentiostat (Princeton Applied Research Model 273A) was used to record the voltammograms. The experiments were conducted in a 15 cm^3 electrochemical cell with provision to control the presence of dioxygen with an argon-purge system. The working electrode was a Bioanalytical Systems glassy-carbon (area, 0.09 cm^2) 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 *vs* SCE. The latter was contained in a Pyrex tube with a cracked soft-glass tip, which was placed inside a Luggin capillary [2].

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 acetonitrile, 99.93+%, HPLC grade purchased from Aldrich. High-purity argon gas was used to deareate the solutions. $Fe(ClO_4)_2 \cdot 6H_2O$, $Fe(ClO_4)_3 \cdot 6H_2O$, and $Fe(ClO_4)_3$ were obtained from GFS, perchloric acid ($HClO_4$, 70%) from Laborchemie Apolda GmbH, and *tert*-butyl hydroperoxide, *t*-BuOOH, (70 % solution in water or 5.0–8.0 M solution in decane) was produced by Aldrich. The concentration of *tert*-butyl hydroperoxide was determined iodometrically [24].

The amount of dioxygen evolved was determined in a gastight reaction system, connected to a manometric burette filled with brine, which was saturated with oxygen 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.

RESULTS AND DISCUSSION

Fig. 1 presents the behavior of iron(II) on a glassy carbon electrode in water solution in the presence of *tert*-butyl hydroperoxide. The electrochemical behavior of Fe(III)/Fe(II) couple is irreversible. We have chosen however, the glassy carbon electrode for investigations to avoid a catalytic decomposition of *tert*-butyl hydroperoxide that can occur on a platinum electrode. The electrochemical reversibility of the Fe(III)/Fe(II) couple is not important for the problems discussed in the paper.

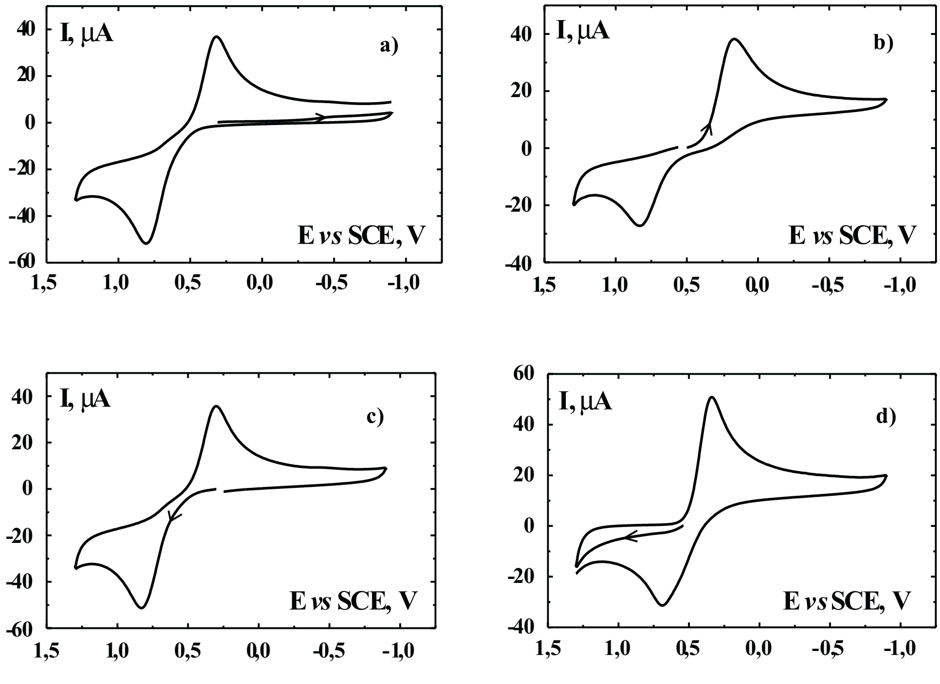


Figure 1. Cyclic voltammograms in water [0.1 M $HClO_4$] for (a, c) 5 mM $Fe(ClO_4)_2$ and (b, d) in the presence of 5 mM *t*-BuOOH. Scan rate, 0.1 V s^{-1}, GCE (0.09 cm^2); SCE *vs* NHE, +0.242 V.

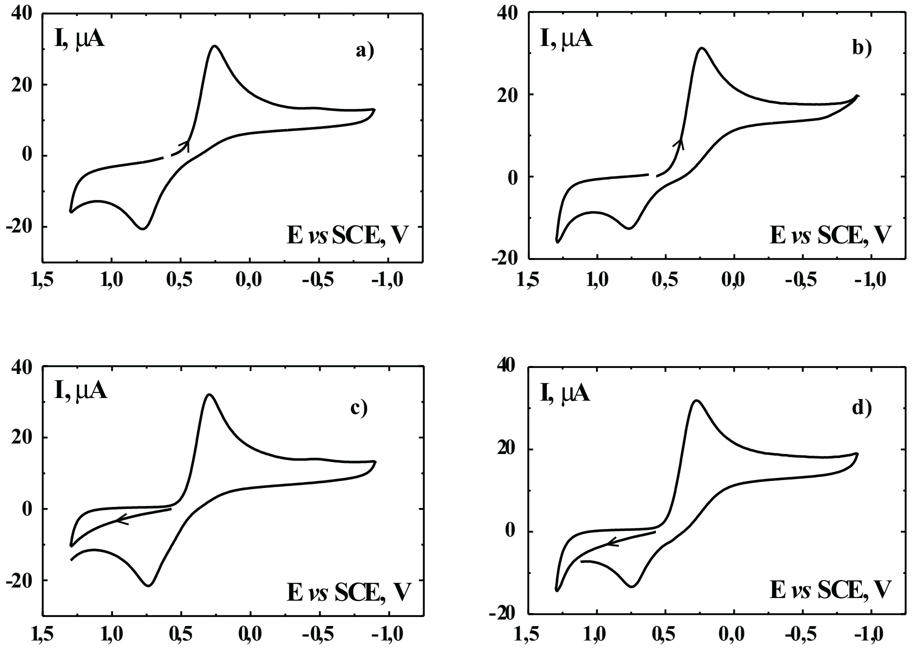


Figure 2. Cyclic voltammograms in water [0.1 M $HClO_4$] for (a, c) 5 mM $Fe(ClO_4)_3$ and (b, d) in the presence of 5 mM *t*-BuOOH. Scan rate, 0.1 V s^{-1}, GCE (0.09 cm^2); SCE *vs* NHE, +0.242 V.

The cyclic voltammograms show that iron(II) is oxidized by *tert*-butyl hydroperoxide – after addition of the latter to the solution the peak corresponding to reduction of iron(III) is present in the first cathodic scan. In contrast, iron(III) remains unchanged in the presence of *tert*-butyl hydroperoxide (Fig. 2). However, the small increase of the height of iron(III) reduction peak in the cathodic scan and the decrease of the height of reverse anodic peak of the oxidation of electroreduced iron(II) with comparison to those registered in the solution without *tert*-butyl hydroperoxide indicates that the catalytic effect occurs. The dependence of i_c/i_d (where i_c and i_d are the heights of iron(III) reduction peaks in the presence and in the absence of *tert*-butyl hydroperoxide, respectively) on the square root of *tert*-butyl hydroperoxide concentration is typical for catalytic currents [1] (Fig. 3).

In acetonitrile, analogously to hydrogen peroxide [19], *tert*-butyl hydroperoxide causes the reduction of iron(III) to iron(II) (Fig. 4). The addition of *tert*-butyl hydroperoxide to the solution containing iron(III) in acetonitrile causes the appearance of iron(II) oxidation peak in the first anodic scan. Therefore, in acetonitrile solution containing iron(II) and *tert*-butyl hydroperoxide catalytic effect corresponding to the reduction of electrochemically oxidized iron(III) occur (Fig. 5).

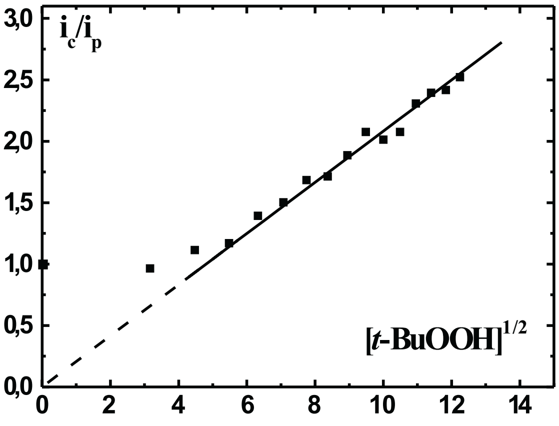


Figure 3. The dependence of i_c/i_d (where i_c and i_d are the heights of iron(III) reduction peaks in the presence and in the absence of *tert*-butyl hydroperoxide, respectively) on square root from *tert*-butyl hydroperoxide concentration.

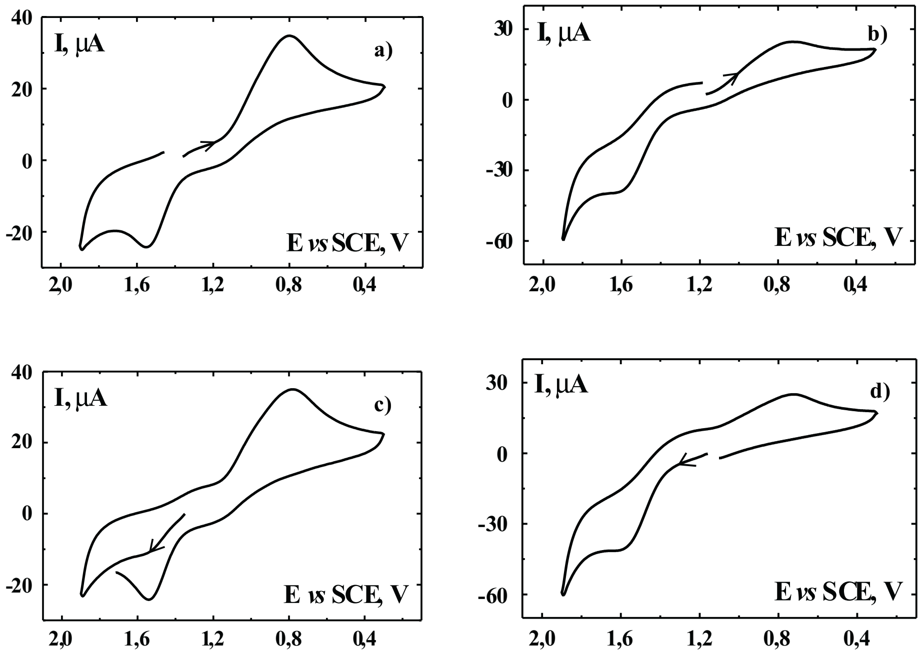


Figure 4. Cyclic voltammograms in MeCN [0.1 M $(Et_4N)ClO_4$] for (a, c) 5 mM $Fe(ClO_4)_3$ and (b, d) in the presence of 5 mM *t*-BuOOH. Scan rate, 0.1 V s^{-1}, GCE (0.09 cm^2); SCE *vs* NHE, +0.242 V.

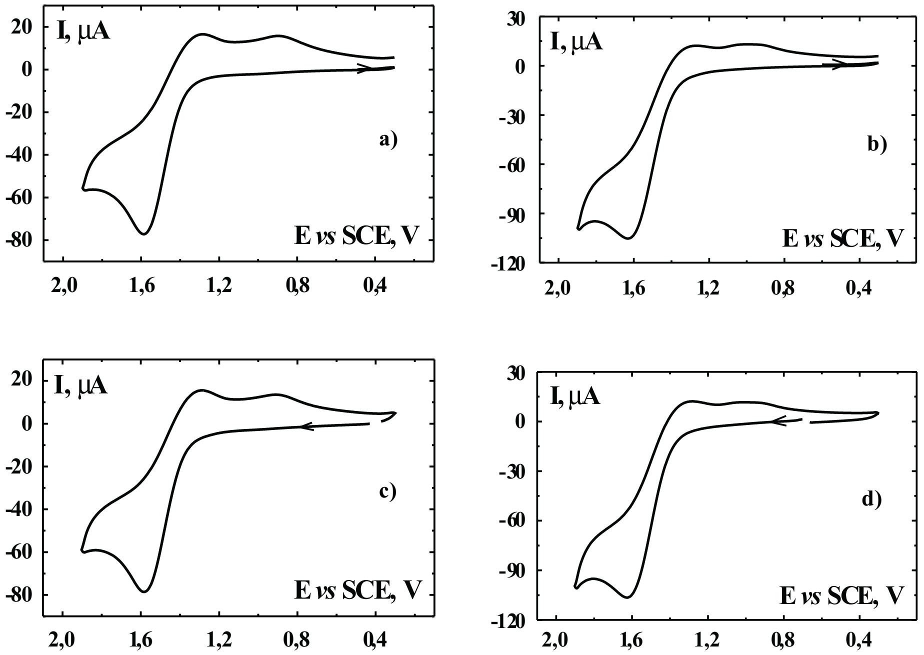


Figure 5. Cyclic voltammograms in MeCN [0.1 M (Et$_4$N)ClO$_4$] for (a, c) 5 mM Fe(ClO$_4$)$_2$ and (b, d) in the presence of 5 mM *t*-BuOOH. Scan rate, 0.1 V s^{-1}, GCE (0.09 cm^2); SCE *vs* NHE, +0.242 V.

Again the plot of i_c/i_d *vs* the square root of *tert*-butyl hydroperoxide concentration (Fig. 6) corresponds to the theory of catalytic processes. This type of catalytic processes can be described as catalytic current of reductants. Scheme 1 presents the formation of catalytic currents for iron(II) and iron(II) and *tert*-butyl hydroperoxide acting as an oxidant and as a reductant, respectively.

It is characteristic that in acetonitrile for the [Fe(III)]/[HOOH] ratios grater than 1 one mole of dioxygen is produced from one mole of hydrogen peroxide [19]. This behavior was not observed for *tert*-butyl hydroperoxide. The measurements of dioxygen evolution in Fe(III)/*t*-BuOOH system were performed for molar ratios 2 to 0.25. In all cases the number of moles of dioxygen evolved per one mole of *tert*-butyl hydroperoxide reaches a maximum (between 0.25 and 0.35) after approximately 5–10 min and then the consumption of dioxygen is observed. This is probably due to the reaction of *tert*-butyl alcohol with dioxygen, the fact however, needs to be confirmed by an independent experiment.

The results presented indicate that taking into account redox properties the systems Fe(II), Fe(III)/HOOH and Fe(II), Fe(III)/*t*-BuOOH are analogues. The experiments with dioxygen evolution confirm the statement [19] that the processes of dioxygen and hydroperoxides activation by transition metal complexes are very sensitive to almost any experimental variables and almost each system is unique.

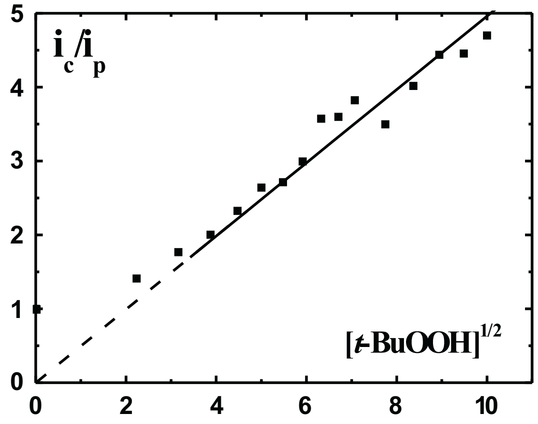
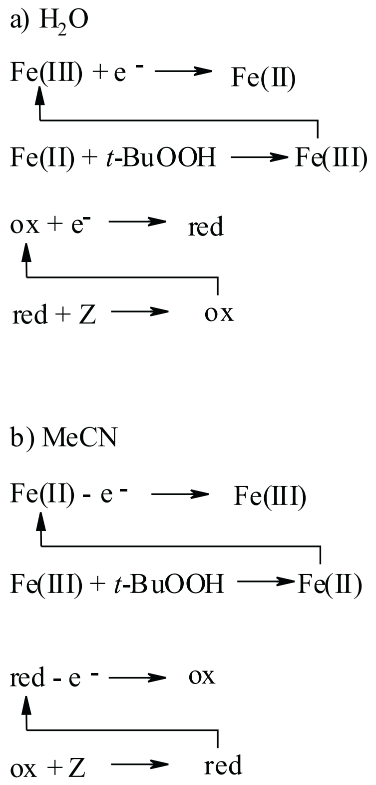


Figure 6. The dependence of i_c/i_d (where i_c and i_d are the heights of iron(II) oxidation peak in the presence and in the absence of *tert*-butyl hydroperoxide, respectively) on square root from *tert*-butyl hydroperoxide concentration.



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

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