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Kinetics and Mechanism of Oxidation with Peroxides of Ferrocenylacetic Acid and Methyl Ferrocenylacetate

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Abstract—The reaction of ferrocenylacetic acid and its methyl ester with peroxides ROOR (R = H, *t*-Bu) in organic solvents was studied. It is shown that direct involvement of the substituent in this process leads to abnormally high reactivity of the acid toward H_2O_2 and *t*-BuOOH as compared with both the ester and ferrocene in a model system of Cp_2Fe + PhCOOH. An unusual shift of the absorption maximum of the ferrocenyl cation formed in the reaction course to longer wavelengths reaching up to several tens of nanometers was discovered.

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Earlier [1, 2] it was shown that ferrocenylacetic acid **I** has a much higher reactivity towards oxygen than ferrocene and can be oxidized in organic solvents to the corresponding ferricinium cation in the absence of strong Brønsted acids at 30–50ºC. In the model system $Cp_2Fe–O_2–HX$, where HX is a carboxylic acid equal or close by strength to acid **I**, under identical conditions the ferricinium cation is not formed. According to [3] the reason of such large differences in the reactivity between compound **I** and Cp_2Fe lies in the fact that the former reacts with O_2 as a bifunctional reagent, as illustrates Scheme 1.

This leads to a significant gain in the activation entropy due to the effect of approach and orientation ($T\Delta S^{\#} \approx 40–50$ kJ mol^{-1} [4]) compared with the above model system assuming that similar reaction sites are located in different molecules. The presumed reaction in this system can be represented by Eq. (1).

$$Cp_2Fe + O_2 + HX \rightleftarrows Cp_2Fe{\cdot}O_2{\cdots}HX \rightarrow Cp_2Fe^{+}X^{-} + HO_2^{\bullet}. \quad (1)$$

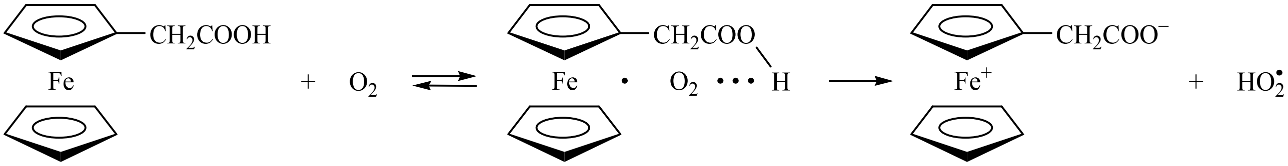
In this regard, it was of interest to study the general and specific features of the reaction of compound **I** and its methyl ester (**II**) with peroxides H_2O_2, t-C_4H_9OOH, and (t-$C_4H_9O)_2$, differing in their oxidizing properties and the size of the radical associated with the peroxide group. In the literature there are no data on the oxidation of ferrocene derivatives with peroxides.

We found that compound **I** is oxidized easily enough with H_2O_2 in ethanol at T = 20–23ºC to ferricinium cation. The formation of the latter is indicated by the appearance of absorption bands with λ_{max} = 629 nm in the electronic spectrum of the reaction mixture (Fig. 1).

Under similar conditions, the formation of the ferricinium cation in the model system $Cp_2Fe–H_2O_2–PhCOOH$ is not observed not only at the ratio of the concentrations $c_{HX}/c(Cp_2Fe)$ = 1 as occurs with compound **I**, but also at a tenfold excess of benzoic acid (pK_a = 4.2) over Cp_2Fe.

This result strongly suggests that the role of the carboxy group in compound **I** in stimulating its

Scheme 1.



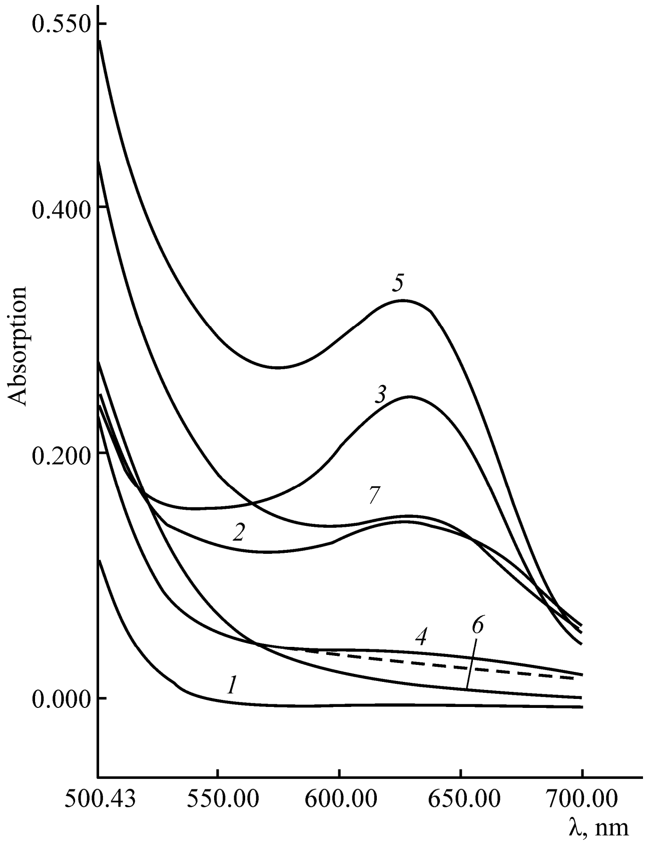


Fig. 1. Electronic spectra of reaction mixtures in ethanol (*1*) [Cp_2Fe + H_2O_2 + PhCOOH], (*2*) [**I** + H_2O_2], (*3*) [**I** + H_2O_2 + **III**], (*4*) [**I** + *t*-BuOOH], (*5*) [**I** + (*t*-BuO)$_2$ + **III**], (*6*) [**II** + H_2O_2 + PhCOOH], (*7*) [**II** + H_2O_2 + **III**]. Reaction time: 10 min (*1, 2, 4, 6, 7*), 90 s (*3*), 20 min (*5*); c^0(Cp_2Fe,**I**,**II**) 0.005 M; c^0_{peroxide} 0.15 (*1–3, 5*), 0.015 (*4, 6, 7*); [PhCOOH] = 0.05 (*1*), 0.025 M (*6*); [**III**] = 0.0025 (*3*), 0.015 (*5*), 0.025 M (*7*).

oxidation is significantly higher than the role of free benzoic acid in the model system in the oxidation of ferrocene. This strongly evidences that the high reactivity of compound **I** compared with ferrocene with respect to H_2O_2 and O_2 is due to the participation of the substituents in the oxidation process affecting mutual approach and orientation of the reagents.

Another proof of this conclusion is the lack of effect of addition of benzoic acid on the rate of oxidation of compound **I**.

The rate of reaction of **I** with H_2O_2 is sensitive to the nature of the solvent and increases in the series of toluene << dioxane << ethanol < DMF < acetonitrile, which corresponds to an increase in the solvating power of these solvents and their dielectric constant in the same series. In DMF ferricinium cation is unstable and is detected only at the beginning of the reaction. The formation of the ferricinium cation in dioxane and toluene at the oxidation of compound **I** with hydrogen peroxide is observed at $T > 30°C$ and occurs only in the presence of a strong acid, CF_3COOH (**III**) or $HClO_4$ (**IV**).

Figure 1 shows the influence of peroxide nature on the rate of oxidation of compound **I**. While *tert*-butyl hydroperoxide oxidizes compound **I** in ethanol slowly, the *tert*-butyl peroxide is not able to oxidize this metal complex. The oxidation of the metal complex with these peroxides in ethanol becomes possible only in the presence of a strong acid.

The ferricinium cation formed at the oxidation of compound **I** is unstable under the reaction conditions and its concentration is changed with time passing a maximum. This results in a low yield of the cation per mole of the starting metal complex at the moment of attaining its maximum content in the reaction mixture. This is clearly seen at comparing the intensity of the absorption bands of the cation formed by oxidation of compound **I** in the absence and the presence of acid **III** (Fig. 1). The product of oxidative decomposition of the ferricinium cation is a brown residue, which, according to IR spectroscopy (the bands 470, 966, 3340 cm^{-1} corresponding to the stertching vibrations (υ) of Fe–O, Fe=O and OH bonds, respectively [5]) can be regarded as the iron(III) oxohydroxo derivative Fe(O)OH. In the final reaction products cyclopentadiene, a small amount of CO_2 and a very large amount of O_2 were found; the formation of the latter occurs in the later stages of the studied process due, most likely, to the decomposition of the unused peroxide. At a ratio $c^0(H_2O_2)/c^0_{\mathbf{I}} = 3$ the formation of O_2 can reach ~50% of the theoretically possible.

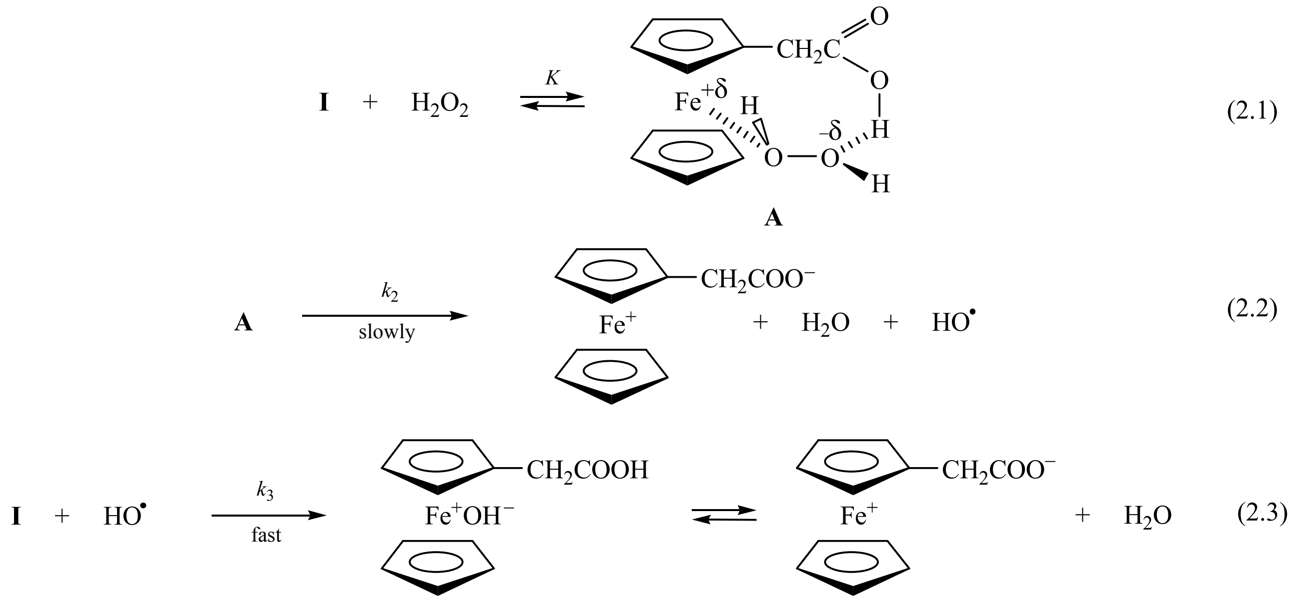
The results of the study of kinetics of the compound **I** oxidation with H_2O_2 in ethanol suggests that the process is described by a first order kinetic equation with respect to the initial concentration of each reactant, that is,

$$W_{\text{exp}} = k_{\text{eff}}[\mathrm{I}]_0[H_2O_2]_0. \qquad (2)$$

This follows from the fact of the linear increase of the initial reaction rate (W_0) with increasing concentration (Fig. 2).

Based on the above, it is possible to suggest the following probable mechanism of the oxidation of compound **I** with hydrogen peroxide if not complicated by secondary processes (Scheme 2).

Scheme 2.



The scheme takes into account the ability of HO• radicals to act as an effective one-electron oxidant (φ^0 = 2.0 V in alkaline medium or 2.8 V in acidic medium [6]), and is more effective than alkylperoxide radical, whose rate constant at the oxidation of ferrocene and some of its derivatives is of the order of 10^5 l mol^{-1} s^{-1} [7].

The formation of CO_2 in the reaction products can be ascribed to the decarboxylation of compound **I** under the action of the same HO• radical.

$$\mathrm{I} + \mathrm{HO}^{\cdot} \rightarrow H_2O + C_5H_5FeC_5H_4CH_2COO^{\cdot}$$
$$\rightarrow CO_2 + C_5H_5FeC_5H_4CH_2^{\cdot}.$$

This scheme can be extended to the reaction of compound **I** with t-C_4H_9OOH.

The low reactivity of the t-C_4H_9OOH compared with H_2O_2 and the lack of reaction of compound **I** with the $(t\text{-}C_4H_9O)_2$ may be due to the reduction of the oxidative properties of peroxides at the replacement of one or two hydrogen atoms in hydrogen peroxide by more electron-donor *tert*-butyl radical, as well as by a significant increase in the steric hindrances to their coordination with iron.

For comparison, below is given the presumed scheme of oxidation of ferrocene in a model system, assuming that the metal complex, yet slowly, is still oxidized (Scheme 3).

In terms of the thermodynamic characteristics (Δ_rG^0), this process is even more favorable by energy than the above, because the standard redox potential of ferrocene and the pK_a of benzoic acid are slightly, but still less than similar properties of compound **I** [8]. At the same time, the oxidation of ferrocene in a model system, if occurs, is immeasurably slower than the oxidation of compound **I**, despite the fact that complex **B** has the same conjugation chain of the elements involved in the transformation of the reactants as in the complex **A**. The reason for this, as is clear, originates from the fact that the free activation energy of the oxidation of compound **I** is less by the value of

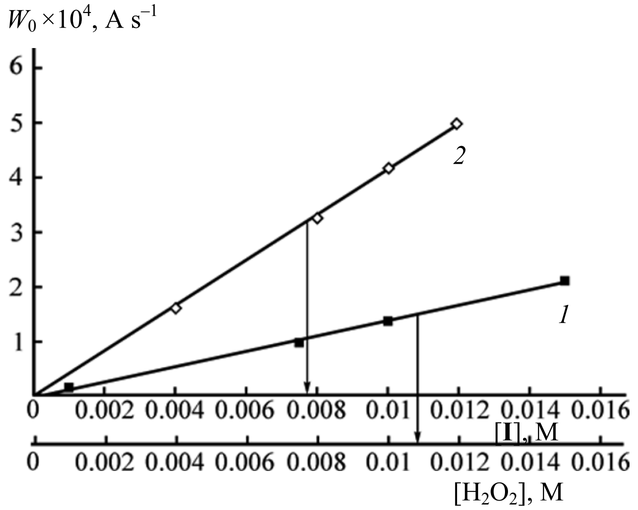
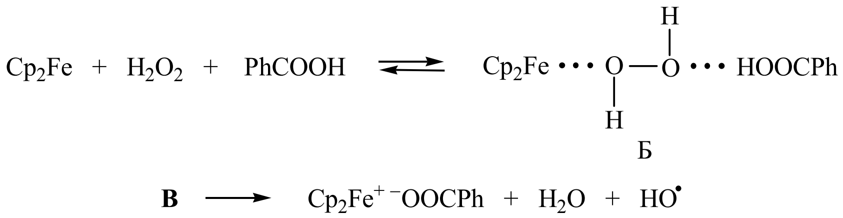


Fig. 2. Influence of the initial concentration of H_2O_2 (*1*) and compound **I** (*2*) on the rate of oxidation in ethanol at 23°C. c_{I}^0 0.01 M (*1*), $c^0(H_2O_2)$ 0.03 M (*2*).

Scheme 3.



$$\mathrm{Cp_2Fe + H_2O_2 + PhCOOH \rightleftharpoons Cp_2Fe\cdots O(H){-}O(H)\cdots HOOCPh}\quad \text{Б} \qquad (3.1)$$

$$\mathrm{B \longrightarrow Cp_2Fe^{+}\,{}^{-}OOCPh + H_2O + HO^{\bullet}} \qquad (3.2)$$

$\Delta G^{\#}_{\text{approach+orientation}}$ than that of the oxidation of ferrocene in the model system.

From the structure of complex **A** in the Scheme 2 it is seen that for the optimal manifestation of the effect of approach and orientation the coordination of compound **I** and H_2O_2 should provide a bridging position of the oxidant molecule between the metal atom and the carboxy group of the substituent, thus providing the conjugation of the electron-acceptor (–COOH) and electron donor (Fe) sites of the metal complex to stimulate the oxidation of the metal.

Coordination of H_2O_2 with an iron atom may be due to the interaction of higher occupied orbitals of the metal complex d_{x2-y2} and d_{xy} localized at the metal atom [9] with the vacant σ*-orbital of the peroxide bond providing a loosely bound charge-transfer complex $\mathbf{I}^{\delta+}\cdot HOOH^{\delta-}$. In such coordination, the formation of each bond between compound **I** and H_2O_2 will help to strengthen the other one, with the result that the enthalpy of coordination will be higher than the sum of the binding energies of hydrogen peroxide to each of the sites of compound **I** separately. The energy released will compensate partly the energy consumption for electron transfer from the iron atom to the H_2O_2 and thereby reduce the activation energy for the transformation of the complex **A** into the reaction products. Another source of compensation for these expenditures is the high electron affinity of the substituent carboxy group with respect to the reduced form of hydrogen peroxide, which can be roughly described as $[HO\cdots OH]^{-\delta}$ ($\delta \le 1$) and that finally corresponds to the OH^- anion. The proton transfer from the substituent carboxy group to the OH^- is undoubtly favorable by energy, and occurs at a high rate ($k \sim 10^{11}$ l mol^{-1} s^{-1} [10]) in the reactions of this type. A simple calculation shows that the enthalpy of reaction with $OH^-$of phenylacetic acid

$$\mathrm{PhCH_2COOH + OH^- \rightarrow PhCH_2COO^- + H_2O},\ \Delta_r H^0,$$

which can be regarded as a model of the substituted Cp-ligand in the compound **I**, is –208.4 kJ mol^{-1}. The data on the standard enthalpy of formation of reactants involved in this reaction, required for the calculation of the $\Delta_r H^0$, is taken from [11, 12]. In fact, the oxidation of compound **I** would be kinetically favorable, that is, has a low value of activation energy, if the stage of electron transfer on H_2O_2 and proton transfer on the $[HO\cdots OH]^{-\delta}$ should not be separated in time, and should proceed as a single synchronous process, and proton transfer may start already at a certain critical value of $\delta < 1$, being aided by the presence of the conjugation chain in the complex **A.**

The decisive role of the acid substituent, introduced into the Cp-ligand, at the oxidation of compound **I** follows not only from a comparison of its reactivity and that of ferrocene in the model system, but from the inertness of the methyl ester of compound **I** with respect to H_2O_2, despite the fact that inductive and resonance constants of the substituents $–CH_2COOH$ and $–CH_2COOCH_3$ should be close to each other [13] (Fig. 1).

Figure 1 shows that while compound **I** is relatively easily oxidized by hydrogen peroxide, compound **II** is stable toward it, and is oxidized in the presence of strong acids and does not oxidize in the presence of benzoic acid.

Kinetic analysis of Scheme (2) leads to Eq. (2).

In accordance with the scheme the rate of oxidation of **I** with hydrogen peroxide (W) is described by Eq. (3) and the rate of accumulation of ferricinium ion, which takes into account the reaction (2.3), is described by Eq. (4):

$$W = k_2[\mathbf{A}], \qquad (3)$$

$$W_1 = k_2[\mathbf{A}] + k_3[\mathrm{I}][\mathrm{HO^{\cdot}}]. \qquad (4)$$

Assuming that the equilibrium (2.1) is reached quickly and the transformation of the complex **A** according to Eq. (2.2) does not violate it, that is, when $k_2 \ll k_1$ and $k_2 \ll k_{-1}$, it can be shown that the expression for W takes the form:

$$W = k_2K[\mathbf{I}][\mathrm{H_2O_2}], \qquad (5)$$

$$K = k_1/k_{-1}$$

Here $K = k_1/k_{-1}$.

If we apply the stationarity principle to the concentration of $HO^\bullet$ radicals, which is acceptable when $k_3 >> k_2$, then the equation for the rate of accumulation of the ferricinium cation (W_1) is transformed into Eq. (6):

$$W = 2k_2K[I][H_2O_2], \quad (6)$$

which is identical to the experimentally found Eq. (2) while we consider the initial reaction rate. From the comparison of these equations follows that $k_{eff} = 2k_2K$.

The numerical value of the coefficient in Eq. (6) is less than two, if the radical $HO^\bullet$ is consumed not only in the reaction (2.3), but also in other processes, turning into the water.

As noted above, the reaction of compounds **I** and **II** with peroxides is greatly accelerated in the presence of a strong Brønsted acid due to a sufficiently high standard redox potential of oxidizing systems $\{H^+ + ROOR\}$, which at ROOR = H_2O_2 is 0.72 [6]. In this connection we studied the kinetics of oxidation of compound **I** by hydrogen peroxide in ethanol in the presence of acid **III**. The results indicate that the order of reaction with respect to the initial concentration of metal complex and the peroxide remains unchanged, i.e., is the first. The dependence of reaction rate W^0 on the acid concentration is more complicated: at low acid concentrations the rate increases linearly with increasing concentration, in a wider range of concentrations of acid it passes through a maximum (Fig. 3).

It is noteworthy that the initial part of the dependence $W = f(c_{HX})$ starts not from the origin but from some point on the vertical axis, cutting off a segment corresponding to the rate of oxidation of compound **I** in the absence of acid. Thus, at low concentrations of acid **III** the the kinetic equation of the reaction is described in general form by Eq. (7).

$$W'_{exp} = W + k'_{eff}[\mathbf{I}][H_2O_2][HX]. \quad (7)$$

At constant concentrations of compound **I** and H_2O_2 Eq. (7) reduces to equation of a straight line (7.1), and at a constant concentration of acid it is transformed into relation (7.2)

$$W'_{exp} = a + b[HX], \quad (7.1)$$

$$W'_{exp} = (k_{eff} + k'_{eff}[HX])[\mathbf{I}][H_2O_2]. \quad (7.2)$$

It should also be noted that the compositions of the oxidation products of **I** in the absence and presence of acid do not much differ from each other.

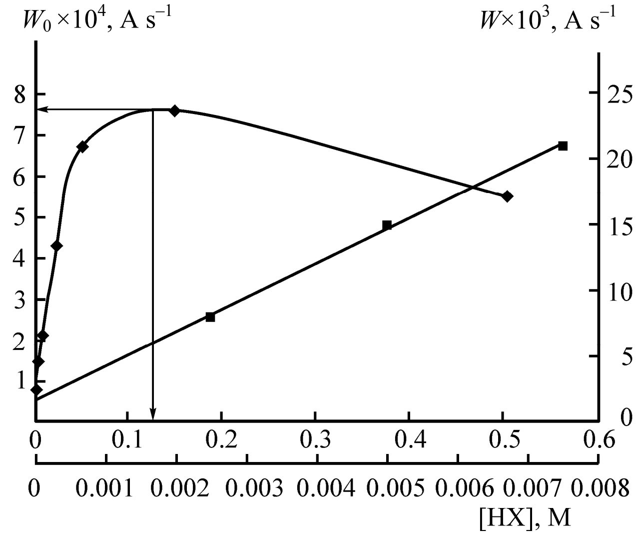


Fig. 3. The dependence of the oxidation rate of compound **I** in ethanol on concentration of acid **III**. T 23°C, $c_{\mathbf{I}}^0$ 0.005 M, $c^0(H_2O_2)$ 0.15 M.

The data obtained taking into account the known properties of the reactants allow us to suggest two alternative mechanisms of oxidation of compound **I** in the presence of acid differing by its coordination with other reagents (Schemes 4 and 5).

Scheme 4 takes into account firstly that the presence of a strong acid may not affect the way of coordination of compound **I** with H_2O_2, and secondly, the proton donor for the reduced form of peroxide $[HO\cdots OH]^{-\delta}$ is the strong acid which is more favorable kinetically and thermodynamically than the proton transfer from the carboxy group of substituent, whose role in this case is reduced to the retention of peroxide in the coordination sphere of the metal increasing the equilibrium concentration of the complex **C** and hence the process rate.

From the Scheme 4 follows that the rate of oxidation of compound **I** by hydrogen peroxide, taking stage (4.5) into account, obeys the Eq. (8).

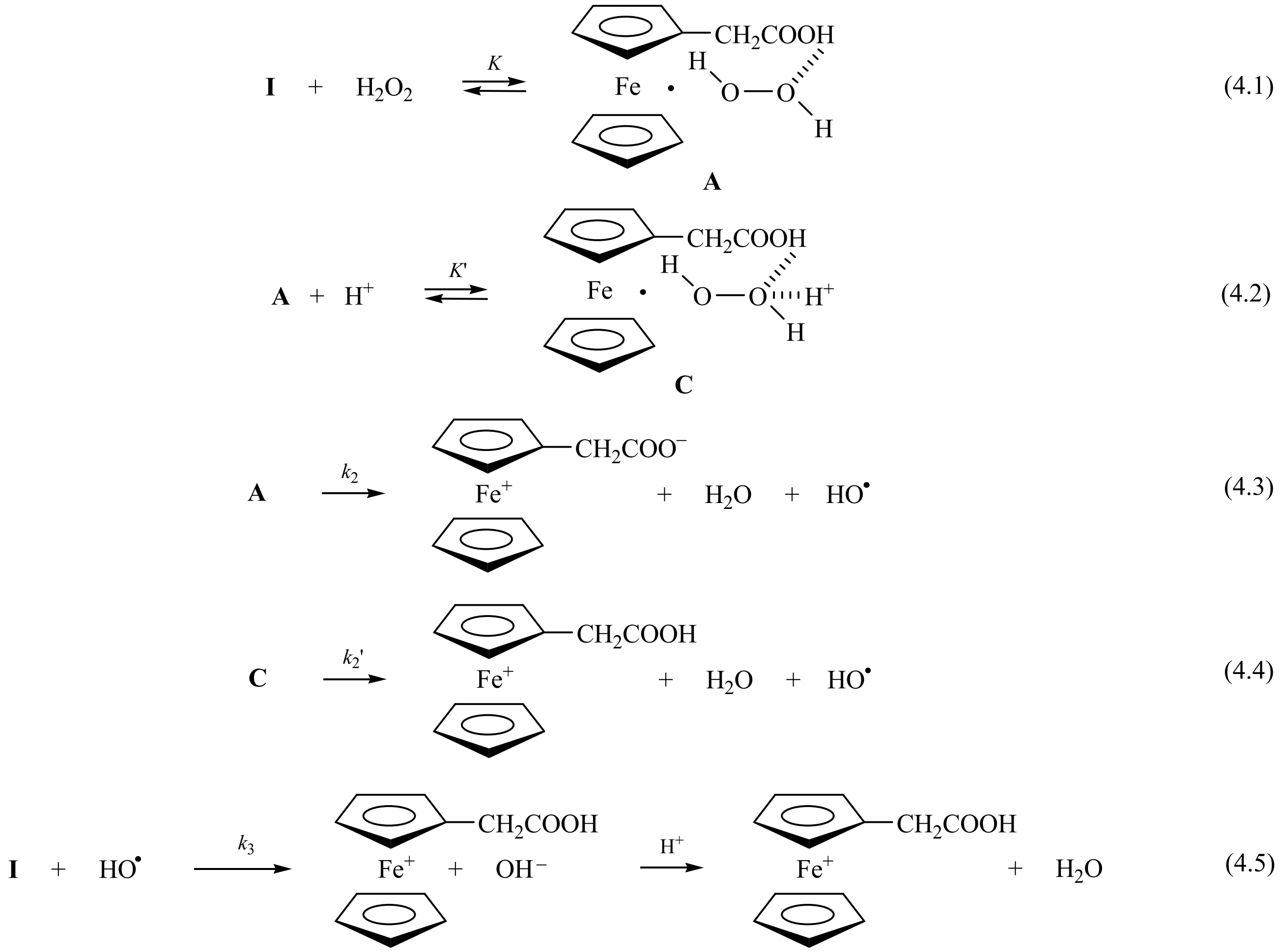
$$W_2 = k_2[\mathbf{A}] + k'_2[\mathbf{C}] + k_3[\mathbf{I}][HO^\bullet]. \quad (8)$$

Using the principle of quasi-equilibrium to find the concentration of complexes **A** and **C** and the stationarity principle for finding the concentration of radicals $HO^\bullet$, we obtain the following dependence of reaction rate on the concentration of the reactants:

$$W_2 = 2k_2K[\mathbf{I}][H_2O_2] + 2k'_2KK'[\mathbf{I}][H_2O_2][HX]. \quad (9)$$

At constant concentrations of the compound **I** and H_2O_2 this is the equation of a straight line identical to

Scheme 4.



Eq. (7.1), which corresponds to the initial segment of the experimentally established dependence $W = f([\mathrm{HX}])$ (Fig. 3).

$$W_2 = a + b[\mathrm{HX}], \tag{9.1}$$

$$a = 2k_2K[\mathbf{I}][\mathrm{H_2O_2}],\ b = 2k_2'KK'[\mathbf{I}][\mathrm{H_2O_2}].$$

At [HX] = 0, Eq. (9) reduces to Eq. (6), and at high concentrations of HX, to the Eq. (10).

$$W_2 = 2k_2'KK'[\mathbf{I}][\mathrm{H_2O_2}][\mathrm{HX}]. \tag{10}$$

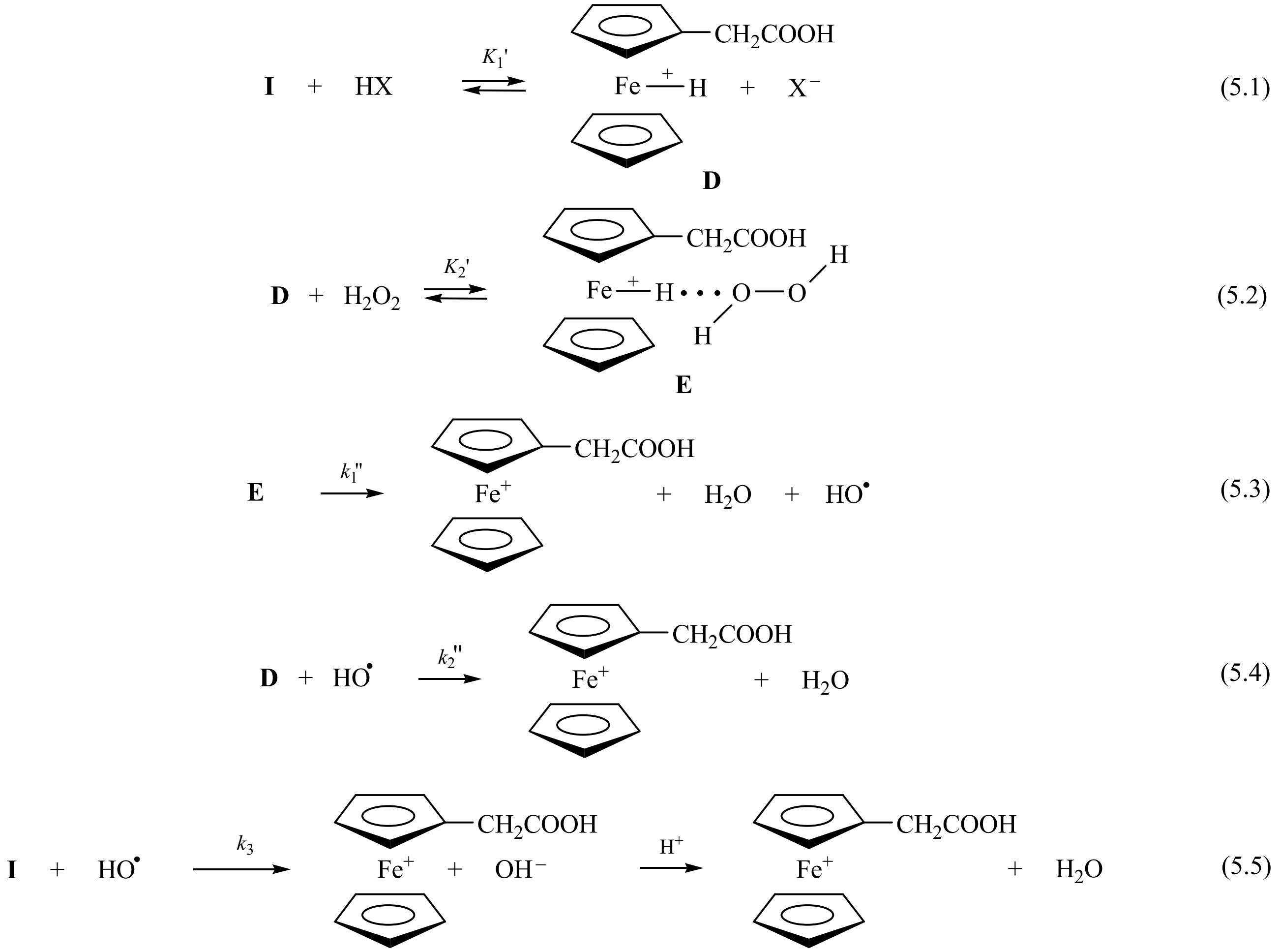
Using Eqs. (6) and (9) we can estimate the reactivity of the complexes **A** and **C** at their transformation into reaction products as the k_2/k_1 ratio at a concentration [HX] = 1 M. The reaction rates W_1 and W_2 can be found from the plot $W = f([\mathrm{HX}])$ on its linear segment.

$$\frac{k_2}{k_1} = \frac{W_2}{W_1} \cdot \frac{1}{K'[\mathrm{HX}]}. \tag{11}$$

It is known that basicity of H_2O_2 is rather low, so the energy of the hydrogen bond in the $H_2O_2\cdots H^+$ complex varies, apparently, in the normal range 9–14 kJ mol^{-1}. For the complexes with such energy of hydrogen bond the equilibrium constant of their formation is ~0.2–2.0 [14]. It is not a big mistake to equate K' to unity. With this in mind, it follows from Eq. (11) that the ratio of $k_2/k_1 \sim 1.75\times10^3$. This result suggests that the reactivity of complex **C** is much greater than that of complex **A**, and the route of oxidation of compounds **I** described by Eq. (10) makes a decisive contribution to the overall oxidation of the metal complex, although the concentration of the intermediate **C** is obviously lower compared with **A** $([\mathbf{C}]/[\mathbf{A}]=K'[\mathrm{HX}])$.

Scheme 5 for the oxidation of **I** is based on the known data about the ability of ferrocene to be protonated by strong acids both at the Cp-ligand and at the iron atom fast reaching the equilibrium [15–17].

Scheme 5.



Ferrocene derivatives with strong electron-withdrawing substituents usually are not protonated at the metal atom [9]. In compound **I**, the substituent is not a strong electron acceptor [8], and therefore we can expect the protonation of the complex by strong acids to occur both at the carboxy group and the metal. First pathway would result in α-ferrocenylcarbenium ion $C_5H_5FeC_5H_4C^+H_2$ [3]. At the protonation of the metal, a weak and therefore reactive Fe–H bond would form (in ferrocene, its energy is ~209 kJ mol^{-1} [16]), which can easily react with peroxide.

According to the calculations [18], the reaction of protonated ferrocene with H_2O_2 and $HO^{\bullet}$ radical is thermodynamically favorable, as indicated by the values of the standard Gibbs free energy, equal to –115.7 and –290.3 kJ mol^{-1}, respectively. For compactness, in the scheme (5) the pathway of compound **I** oxidation in the absence of acid is omitted.

If we consider the rate of oxidation of compounds **I** as a the rate of accumulation of the ferricinium cation (W_2'), that is

$$W_2' = k_1''[\mathbf{E}] + k_2''[\mathbf{D}][HO^{\bullet}] + k_3[\mathbf{I}][HO^{\bullet}], \tag{12}$$

then, using in the kinetic analysis of the Scheme 5 the same approaches as in the analysis of Scheme 4, we obtain the final equation for the reaction rate.

$$W_2' = 2k_1''K_1'K_2'[\mathbf{I}][H_2O_2][HX]. \tag{13}$$

Considering the rate of oxidation of **I** without the acid, the Eq. (13) can be reduced to an equation similar to Eq. (9).

It is not possible to assess the contribution of each of the routes described by Schemes 4 and 5 separately to the overall process of compound **I** oxidation. Kinetically and thermodynamically the two mechanisms are indistinguishable, since they are described by the same kinetic equations and lead to the same composition of reaction products. At the same time, the difference in the structure of activated complexes corresponding to the limiting stages (4.4) and (5.3), respectively, of these mechanisms determines the difference in their activation energies. In the oxidation of compound **I** with t-C_4H_9OOH and especially with $(t\text{-}C_4H_9O)_2$ a preference should be given to Scheme 5, because at the protonation of the metal complex the latter gets the configuration with inclined Cp-ligands, in which the angle between the centers of the rings and the iron atom can be significantly less than 180º [19]. This makes less significant the steric hindrance in the reaction of the protonated metal complex with the peroxides bearing bulky substituents.

The extreme dependence $W = f([HX])$ observed at the oxidation of compound **I** (Fig. 3) is not associated directly with the discussed mechanisms 4 and 5. The presence of such dependence may originate from two reasons:

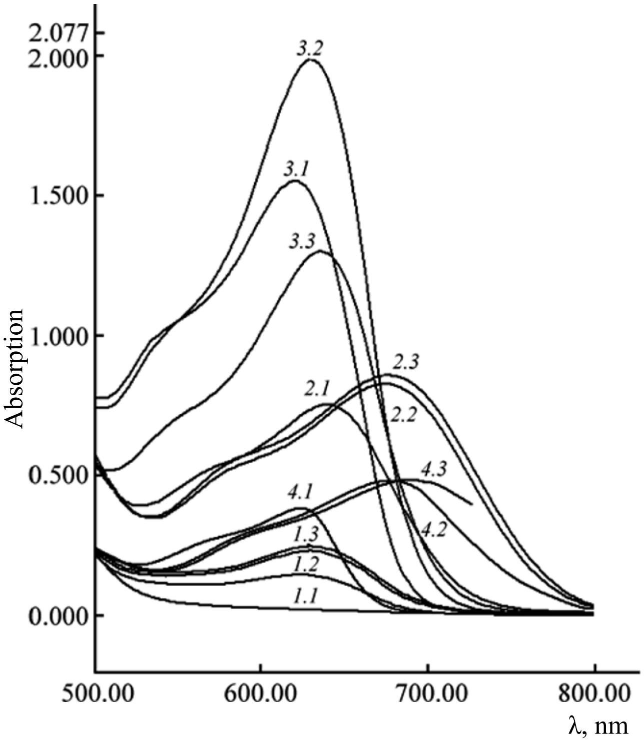


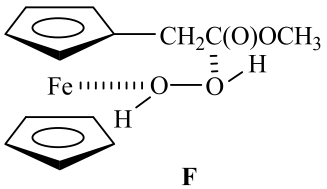
Fig. 4. Dynamics of changes of the electronic spectrum of the ferricinium cation at 23°C: (a, b) [**I** + **III**]; [ferricinium + **IV**]; in ethanol: (*1.1*) 10 s, (*1.2*) 20 s, (*1.3*) 2 min, (*2.1*) 10 s, (*2.2*) 20 s, (*2.3*) 4 min; in acetonitrile: (*3.1*) 10 s, (*3.2*) 20 s, (*3.3*) 130 s; in dioxane: (*4.1*) 20 s, (*4.2*) 1 min, (*4.3*) 2 min. $c_{\mathbf{I}}^0$ 0.005 M, $c^0(H_2O_2)$ 0.15 M, $c^0_{\mathbf{III}}$ 0.0025 M (*1*), 0.5 M (*2*, *3*); c_{Fc}^0 0.002 M, $c^0(H_2O_2)$ 0.04 M, $c_{\mathbf{IV}}^0$ 0.1 M.

(1) Increase in the degree of association with an increase in the acid concentration, which leads to the formation of dimeric hydrogen complexes of low reactivity in the oxidation of compound **I**.

(2) A possibility of protonation of the substituent's carboxy group at a significant concentrations of acid resulting in the formation of α-ferrocenylcarbenium ion possessing a strong electron acceptor at the Cp-ligand, which should be much more resistant to oxidation than the parent compound **I**.

As mentioned above, compound **II** is not very reactive with respect to H_2O_2, and in contrast to the compound **I** can be oxidized only in the presence of a strong acid.

The presence in compound **II** of electrophilic carbon atom of the carbonyl group capable of coordinating H_2O_2 due to donor–acceptor interaction, as shows complex **F**, does not lead to the initiation of the oxidation reaction.

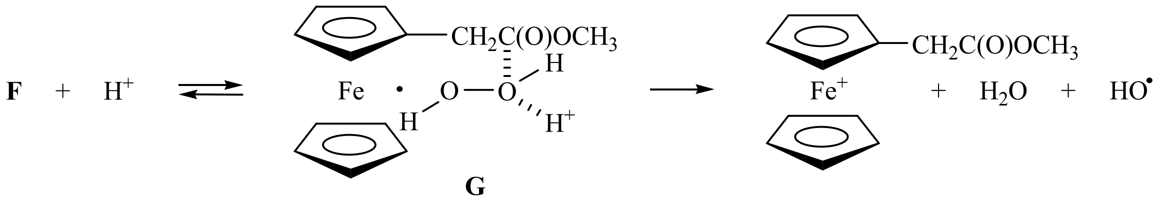


F

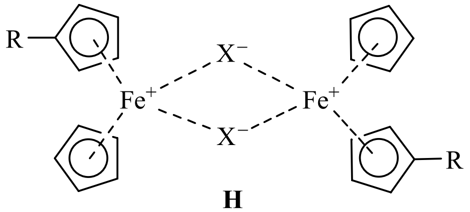
This is due to a low affinity and reactivity of the carbon atom of the carbonyl group of the substituent in compound **II** with respect to nucleophilic reagents, even to OH^- anion [20]. As a consequence, electron transfer from the iron atom to H_2O_2, accompanied by the rupture of peroxide bond and the formation of free OH^- anion, is disadvantageous by energy. In the presence of a strong acid the oxidation of compound **II** becomes possible not only through the stage of its protonation at the metal atom, as shows Scheme 5, but involving the complex **F**.

The role of the coordination of hydrogen peroxide with the carbonyl carbon atom is the same as the coordination of the peroxide with the carboxyl group of compound **I** in Scheme 4.

A very unusual phenomenon was found at the oxidation of compound **I** in the presence of acids, which consists in shift of the absorption band maximum of the formed ferricinium cation in the reaction course to longer wavelengths with respect to its initial position, which is observed in 8–10 s, the



least possible time after the reaction start (Fig. 4). Figure 4 shows that the shift value $\Delta\lambda_{max}$ depends on the nature of the solvent and is in some way related to the concentration of the reagents, and can reach several tens of nanometers. It could be assumed that the observed phenomenon is connected with a change in the nature of the substituent in the formed cation under the influence of the environment, since it is known that the position of the absorption maximum λ_{max} of the ferricinium cation depends on the nature of its substituent [9]. However, the discovery of the above phenomenon also at the oxidation of unsubstituted ferrocene (Fig. 4, curves *4.1–4.3*) indicates that its appearance is due to another cause. It is possible that it is caused by the formation of an associate of the form



H

transformation of which may lead eventually to the disproportionation of the ferricinium cation, as it is assumed in [21].

$$2Cp_2Fe^+X^- \rightleftarrows \mathbf{H} \rightarrow Cp_2Fe + 2Cp_2 + FeX_2$$

In line with this, the change in the spectrum of the ferricinium cation can presumably be regarded as the dynamics of this process. To prove this, it is necessary to carry out a more detailed study of the observed phenomenon.

EXPERIMENTAL

Electronic spectra and kinetics of oxidation of metal complexes were registered on a SHIMADZU UV-1700 spectrophotometer using a quartz cell. Preparation of working solutions and recording the spectra were carried out in an argon atmosphere. The IR spectra of the solid product of compound **I** oxidation were recorded on a IR Prestige-21 SHIMADZU spectrophotometer (KBr plates, mineral oil). Liquid and gaseous products of oxidation of metal complex were determined by GLC.

Synthesis of compound **I** was carried out by the procedure [1], purification was carried out by double recrystallization from diethyl ether.

Compound **II** was obtained by the reaction of compound **I** with diazomethane [22]. Commercial hydrogen peroxide used in the study was of analytical grade. The samples of t-C_4H_9OOH and $(t\text{-}C_4H_9O)_2$ contained at least 99% of the basic substance. All the used solvents of analytical grade were purified by known methods [23].

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