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Specific Features of Formyl- and Acetylferrocene Oxidation with Peroxides in Water and Organic Solvents

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Abstract—Specific features of formyl- and acetylferrocene oxidation with peroxides ROOR (R = H, *tert*-C_4H_9) in different solvents are studied. It is shown that despite of the presence in complexes of strong electron-acceptor substituents they can be oxidized with hydrogen peroxide in the absence of strong Brønsted acids. Dilution of water with organic solvent leads to deceleration and complete standstill of the reaction. In the absence of acids the second order of the process with respect to peroxide and first one with respect to the metal complex was evaluated. In the presence of perchloric or trifluoroacetic acid the order with respect to peroxide decreases to the first one. The dependence of the reaction rate on the concentration of acid has an extremum point. The activity of other peroxides in the reaction with the above-mentioned compounds is significantly lower than the activity of hydrogen peroxide. Probable alternative mechanisms of oxidation of the above-mentioned ferrocenes with hydrogen peroxide in the presence and in the absence of acids differing in the way of coordination of reagents with one another and considering direct participation of substituent in the oxidation is suggested.

Keywords: ferrocenes, peroxides, reaction rate, oxidation

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It was shown previously that formyl- and acetylferrocene (compounds **I** and **II** respectively) can be oxidized with molecular oxygen in the presence of strong Brønsted acids HX like perchloric and trifluoroacetic acids [1]. The reaction proceeds through sequence of two macrostages. First the molecular oxidation of metal complex occurs leading to generation of peroxide radicals. The second stage is the chain-radical oxidation involving the substituent. The peculiar feature of the molecular oxidation is the participation in it of the substituent. The latter is a strong acceptor of electrons and possesses an electrophilic center (carbon atom of the carbonyl group) exhibiting the affinity to the molecule of oxygen in neutral as well as in the reduced state. In the suggested reaction mechanisms it is proposed that the reaction proceeds through the stage of formation of complex **I**(**II**)$\cdot O_2\cdot$HX in which the molecule of oxygen occupies the bridging position between the atom of metal and carbon atom of the carbonyl group. It initiates electron transfer from the metal atom to the molecule of oxidant.

The acid coordination of may occur through the molecule of coordinated oxygen as well as through the carbonyl group of the substituent in the metal complex. The chain radical oxidation of metal complexes at the C–H bonds of substituent leads to the formation of the corresponding hydroperoxides which are not only the sources of formation of new ferrocene derivatives, but may also play the role of oxidants of the starting metal complex and the reaction products. In this connection it was interesting to study the peculiarities of oxidation of formyl- and acetylferrocene with peroxides of different nature likes hydrogen peroxide **III**, *tert*-butyl hydroperoxide **IV**, and *tert*-butyl peroxide **V** in the presence and in the absence of $HClO_4$ and CF_3COOH.

It was found that compounds **I** and **II** are oxidized with peroxide **III** in water at 23°C in the absence of strong Brønsted acids. It was confirmed by the appearance of absorption band with λ_{max} 618 nm belonging to the ferricinium ion in electron absorption spectrum of the reaction mixture (Fig. 1).

This result was rather unexpected considering strong electron-acceptor properties of formyl and acetyl substituents {σ_I(CHO) 0.33, σ_R(CHO) 0.09; $\sigma_I(COCH_3)$ 0.33, $\sigma_R(COCH_3)$ = 0.17 [2]}. For

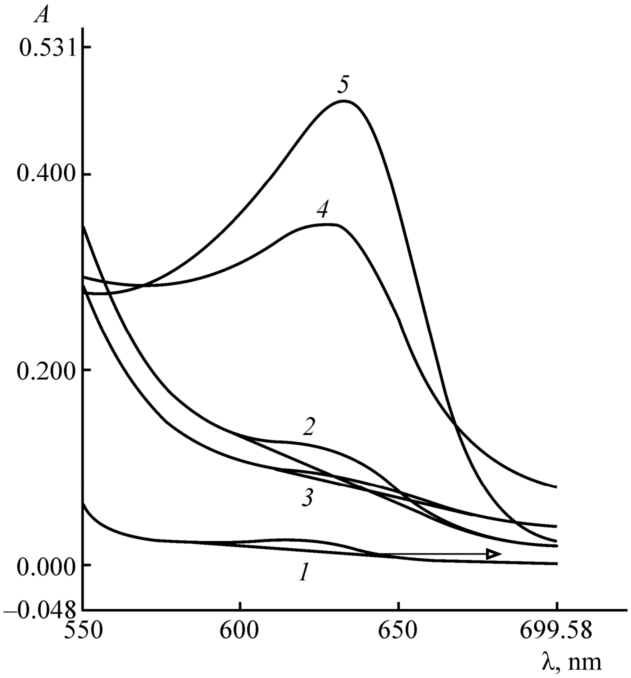


Fig. 1. Electron absorption spectra of ferricinium cation formed at the oxidation of ferrocene in model (*1*) acetone–water system, (*2*) of compounds **I** and (*3*) **II** in water with peroxide **III** in the absence of acids, (*4, 5*) the same for the case of oxidation of ferrocenes **I** and **II** in the presence of perchloric acid. $c^0_{\mathrm{I,II,VI}}$ 0.003 mol/L, c^0_{III} 0.15 mol/L, $c^0[(CH_3)_2CO]$ 9.0 mol/L, $c^0(HClO_4)$ 0.1 mol/L. T = 23°C. Reaction time (*1*) 30 min, (*2–5*) 25 s.

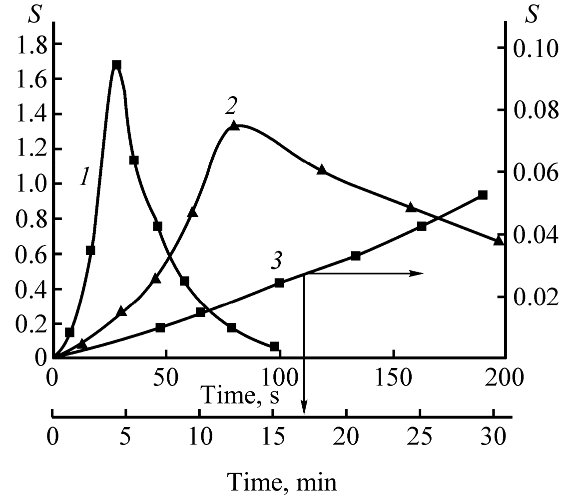


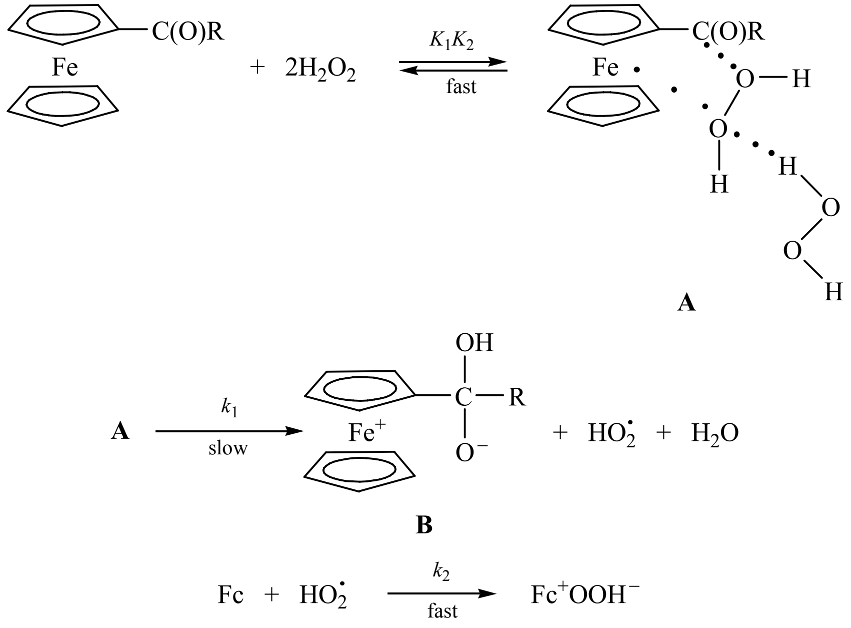
Fig. 2. Kinetic curves of accumulation of ferricinium cation at the oxidation of (*1*) compounds **I** and (*2*) **II** with hydrogen peroxide in water and ferrocene in model acetone–water system (*3*). $c^0_{\mathrm{I,II,VI}}$ 0.003 mol/L, c^0_{III} 0.15 mol/L, $c^0[(CH_3)_2CO]$ 9.0 mol/L, T = 23°C.

comparison note that unsubstituted ferrocene **VIII** is oxidized with peroxide **III** in water-ethanol mixtures only in the presence of strong Brønsted acids. The result permits a suggestion that the oxidation of compounds **I** and **II** in the absence of acids is caused by the direct participation of substituents in this process. For the confirmation of this assumption the oxidation of ferrocene with peroxide **III** in the absence of acid in mixed acetone-water system was carried out. In this case acetone was regarded as an analog of the substituted Cp-ligand. The concentration of acetone in water was chosen to be sufficient for dissolution of ferrocene. It turned out to be 9 mol/L. It was found that under these conditions ferrocene oxidizes to give ferricinium cation, but the rate of this process evaluated from S_{abs}/c value (here S_{abs} is the integral intensity of absorption band of the obtained ferricinium cation) is 276 times slower than the rate of oxidation of compound **II** in water (S_{abs}/c) at the same concentrations of metal complex and peroxide **III** though the concentration of acetone is 3000 times higher than the concentration of ferrocene (0.003 mol/L) (Fig. 2).

If the rate of oxidation in model system is extrapolated to the concentration of acetone equal to the concentration of metal complex analogously to the concentrations of iron and acetyl group in compound **II**, the ratio of rate of oxidation of compound **II** in water and the rate of oxidation of ferrocene in model system $w_{\mathrm{II}}/w_{\mathrm{VIII}}$ will be equal to 8.28×10^5. This result confirms the above assumption that the substituents in compounds **I** and **II** directly participate in the oxidation. Note that use of acetophenone as the analog of substituted Cp-ligand in the compound **II** seems to be more logical, but the latter is practically insoluble in water.

The results of experiments show that the reactivity of compound **II** toward peroxide **III** is lower than that of compound **I**. It arises evidently from the lower value of $\sigma_R(CHO)$ as compared to $\sigma_R(COCH_3)$ and the effect of steric factor in the reaction of these substituents with peroxide **III** (Figs. 1, 2). The dilution of water with dioxane or ethanol leads to deceleration of the reaction. It shows the significant effect of permittivity on the rate of the process under study in agreement with the known fact of the increase in the rate of the electron transfer reactions with the increase in permittivity of the solvent [3]. In pure dioxane and ethanol oxidation of compounds **I** and **II** does not take place. Proceeding of the reaction in the above-

Scheme 1.



mentioned solvents becomes possible only after introduction of strong acid to the reaction mixture.

For obtaining more complete picture of the reaction under study it was interesting to compare reactivity of peroxide **III** with peroxides **IV** and **V**.

It was found that in contrast to peroxide **III** the metal complexes under study were oxidized with peroxide **IV** only in the presence of acid, while with peroxide **V** no reaction occurred even in the acidic medium. Low reactivity of the last two peroxides as compared to peroxide **III** may be due to the fact that at the substitution of hydrogen atom in H_2O_2 with *tert*-butyl radical the oxidative properties of peroxides decrease while sterical hindrances to their reactions with metal complexes considerably increase. Note that if instead of compounds **I** and **II** diacetylferrocene is used, the rate of its oxidation is approximately by an order of magnitude slower than that of compounds **I** and **II**.

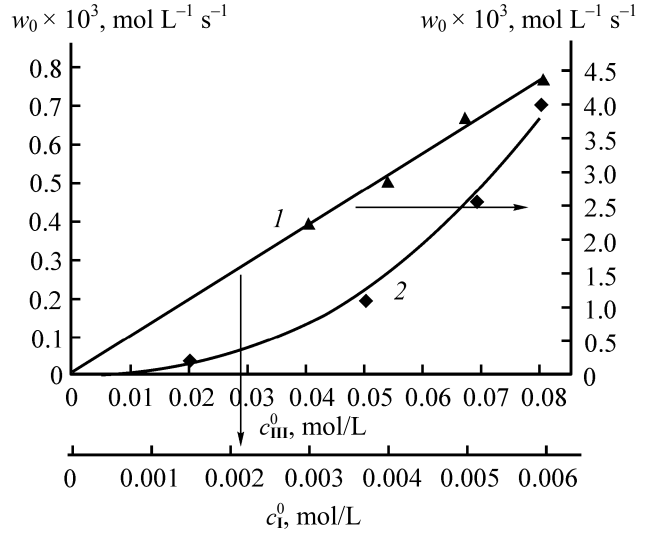


Fig. 3. Effect of starting concentration of compound (*1*) **I** and (*2*) peroxide **III** on the rate of oxidation of metal complex in water. (*1*) c^0_{III} 0.15 mol/L, (*2*) c^0_{I} 0.0003 mol/L, $T = 23$°C.

Results of investigation of kinetics of oxidation of chosen compounds with peroxide **III** in water in the absence of acid show that the process is described by the equation of the first order reaction with respect to starting concentration of compounds **I** and **II** which follows from the fact of linear increase in the initial reaction rate w_0 with the increase of concentration of metal complex, and second order kinetic equation with respect to the starting concentration of peroxide which is confirmed by the character of the kinetic curve of the dependence of reaction rate on the concentration of the latter (Fig. 3). Its logarithmic anamorphose has the slope $\log w = f[\log c^0(H_2O_2)]$ approximately equal to 2 corresponding to the reaction order with respect to hydrogen peroxide.

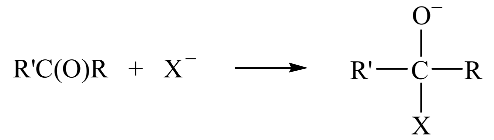
Hence, the kinetic equation of the reaction can be written as:

$$w_0 = k_{\text{eff}}[\text{Fc}]_0[H_2O_2]_0^2, \qquad (1)$$

where Fc = **I**, **II**; w_0[1] = A s^{-1}.

Note that the conversion of compounds **I** and **II** during the establishing of kinetic rules did not exceed 1–2% that permitted considering the current concentrations of reagents which determine the observed reaction rate equal to starting ones. From the above-demonstrated data and considering the properties of starting reagents it is possible to suggest the following mechanism of the reaction under study (Scheme 1). In Scheme 1 K_1 and K_2 are the equilibrium constants of successive addition of peroxide **III** to metal complex.

The formation of the product **B** reflects the ability of carbonyl compounds, aldehydes and ketones, to add nucleophilic reagents according to reaction (2) [4]:



$$\text{R'C(O)R} + X^- \longrightarrow \text{R'}-\overset{O^-}{\underset{X}{C}}-\text{R} \qquad (2)$$

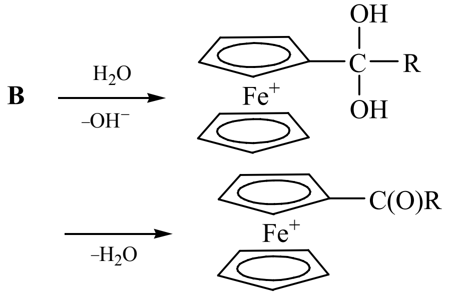
where R = H, alkyl.

In the oxidation of compounds **I** and **II** this agent is the OH^- anion whose formation during the transfer of an electron from the iron atom to the σ*-orbital of the O–O bond of hydrogen peroxide and subsequent addition to carbonyl group proceed synchronically in one act. In the case of aldehydes the addition of X^- proceeds with higher rate than in the case of ketones. It is caused firstly by higher electrophilicity of carbon atom in aldehydes, and also by steric hindrances which in aldehydes are much lower than in ketones [4]. Just by this fact it can be explained that the oxidation of compound **I** with peroxide **III** in water proceeds faster than of compound **II** (Fig. 2). It cannot be excluded that the reactivity of the carbonyl group of substituent toward OH^- in ferriciniun cation may be significantly higher than in neutral complex. The latter can coordinate only this nucleophile.

From the structure of complex **A** in scheme (1) it is seen that optimal for the participation of substituent in oxidation such coordination of molecules of metal complex and hydrogen peroxide must be achieved where the first molecule of oxidant occupies bridging position between the metal atom, the electron donor, and the carbonyl group of the substituent actings as Lewis acid. In this way the conjugation of reaction centers of metal complex is provided which stimulates the oxidation of metal. The coordination of the second hydrogen peroxide molecule improves the oxidative properties of the first molecule and makes the process thermodynamically more favorable. The process of electron transfer from metal atom to peroxide bond and the addition of obtained OH^- ion to the carbon atom of carbonyl group proceeds synchronically due to the conjugation chain between the metal atom and the carbonyl group of the substituent, which was provided by H_2O_2 molecule. In this case the state of hydrogen peroxide molecule bound with metal atom and the substituent in the transition complex may be described by the critical structure $[HO\cdots OH]^{-\delta}$ ($\delta \leq 1$).

When such coordination takes place the formation of each bond of metal complex with peroxide strengthens another one. Due to that the enthalpy of coordination must be higher than the sum of bond energies of peroxide with each of the reaction centers separately. The evolving energy will partially compensate the consumption of energy for electron transfer from the iron atom to H_2O_2 which will decrease the activation energy of the process of complex oxidation. The coordination of H_2O_2 with the iron atom may occur by the interaction of higher occupied molecular orbitals $d_{x^2-y^2}$ and d_{xy} of metal complexes localized on the iron atom [5] with the vacant σ*-orbital of peroxide bond.

Zwitterion **B** is stabilized by an intramolecular electrostatic interaction, but in water solution it is most probably protonated with the molecule of solvent according to the equation:



(3)

The ability of metal complexes under study to enter the reaction with hydrogen peroxide as bifunctional reagents permits the understanding of their high reactivity as compared to ferrocene in model system $Cp_2Fe + CH_3C(O)CH_3 + H_2O_2$ where the same reaction centers are included in the composition of different molecules, as the result of approaching and orientation

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[1] Use of this dimensionality of the reaction rate is connected with some complications at the evaluation of absolute concentrations of ferricinium cation.

Scheme 2.

$$\mathrm{Fc + 2H_2O_2 \xrightleftharpoons{K_1,K_2} \underset{\mathbf{C}}{Fc{\cdot}2H_2O_2}}$$

$$\mathrm{\mathbf{C} + CH_3C(O)CH_3 \xrightleftharpoons{K_3} \underset{\mathbf{D}}{Fc{\cdot}2H_2O_2{\cdot}CH_3C(O)CH_3}}$$

$$\mathrm{\mathbf{D} \rightarrow Fc^+ + CH_3C(OH)(O^-)CH_3 + H_2O + HO_2^{\cdot}}$$

leading to a definite gain in activation enthalpy of the reaction under study compared to the model one which has a higher order [6]. The assumed mechanism of the model reaction can be described by Scheme 2.

In the enzymatic polyfunctional catalysis the effect of the approach and orientation is evaluated by the gain in activation free energy value which can be designated as $\Delta G^{\#}_{\mathrm{a,o}}$ equal to 10–11 kcal/mol due to the contribution of $T\Delta S^{\#}$ [6].

The gain in energy from the participation of the second molecule of hydrogen peroxide in the process of oxidation may be evaluated suggesting that the complex may be oxidized with the participation of one H_2O_2 molecule, though this process is very slow (Scheme 3).

Summary reactions corresponding to Schemes 1 and 3 are described by Eqs. (4) and (5):

$$\mathrm{Fc + 2H_2O_2 \rightarrow P + HO_2^{\cdot} + H_2O}, \quad \Delta_r H^0_3, \tag{4}$$

$$\mathrm{Fc + H_2O_2 \rightarrow P + HO^{\cdot}}, \quad \Delta_r H^0_4. \tag{5}$$

Subtraction of Eq. (5) from the Eq. (4) gives resulting Eq. (6):

$$\mathrm{H_2O_2 + HO^{\cdot} \rightarrow HO_2^{\cdot} + H_2O}, \quad \Delta_r H^0_5, \tag{6}$$

where $\Delta_r H^0_5 = \Delta_r H^0_4 - \Delta_r H^0_3$. The value and sign of $\Delta_r H^0_5$ permit comparative evaluation of $\Delta_r H^0_3$ and $\Delta_r H^0_4$.

If $\Delta_r H^0_5 < 0$ meaning that $\Delta_r H^0_3$ is more negative than $\Delta_r H^0_4$. Hence the process (3) and the mechanism (1) are more favorable by energy than the process (4) and the mechanism (3). If $\Delta_r H^0_5 > 0$ the opposite situation is observed.

$\Delta_r H^0_5$ can be calculated from the energies of bonds breaking and forming D:

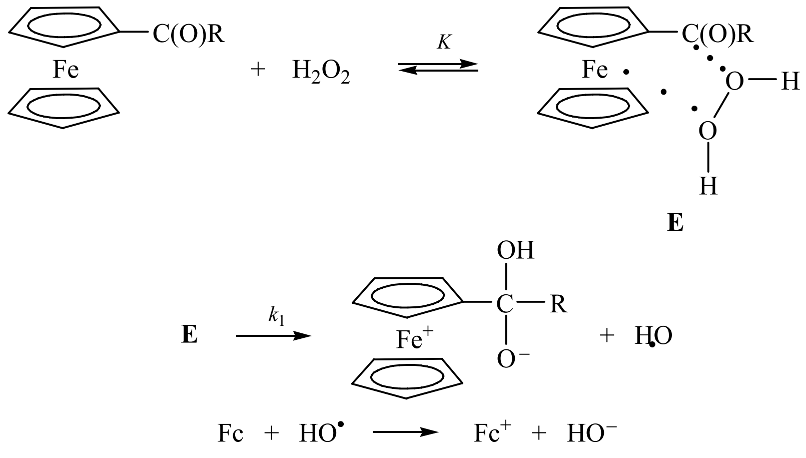
$$\Delta_r H^0_5 = D_{\mathrm{H{-}OOH}} - D_{\mathrm{H{-}OH}} = 89.5\ \mathrm{kcal/mol} - 119.2\ \mathrm{kcal/mol} = -29.2\ \mathrm{kcal/mol}. \tag{7}$$

$D_{\mathrm{H{-}OOH}}$ and $D_{\mathrm{H{-}OH}}$ values are taken from [7].

Then according to Eq. (7) $\Delta_r H^0_5$ will be equal to –29.2 kcal/mol proving that the mechanism described by the Scheme 1 is favorable. Final conclusion can be made after consideration of $\Delta_r S^0_5$ value and evaluation of $\Delta_r G^0{}_5 = \Delta H^0_5 - T\Delta_r S^0_5$. For reaction (6) $\Delta_r S^0_5 = S^0(\mathrm{HO_2}) + S^0(\mathrm{H_2O}) - S^0(\mathrm{H_2O_2}) - S^0(\mathrm{HO}) = 54.7 + 45.1 - 55.4 - 49.3 \sim 0.5$ e.u. (cal mol^{-1} K^{-1}). Then $\Delta_r G^0_5 = -29200 - 298 \times 0.5 = -29349$ cal/mol. $S^0_i(298, i)$ values are taken from [9].

Hence, just the participation of two molecules of peroxide **III** having higher redox potential than one molecule makes the process of oxidation of compounds **I** and **II** with peroxide **III** quite real. At the same time the formal equilibrium in the reaction (3) is absolutely shifted to the left. It is confirmed by the low yield of obtained ferricinium cation if it is compared with the yield of this product in the oxidation of compounds **I** and **II** in the presence of strong acids at

Scheme 3.



the same concentrations of metal complex and peroxide **III**.

The validity of the above scheme is confirmed by deceleration of the process under study with the additives of OH^- ions introduced in solution with NaOH (Fig. 4) which can occupy a coordination vacancy at the electrophilic carbon atom in the transition metal complex and to block the access of hydrogen peroxide to the latter.

It is known that in alkaline medium the ferricinium cation is significantly less stable than in the acidic one [5]. Therefore the decelerating effect of OH^- on the reaction rate may be explained alternatively. The oxidation of the metal complex takes place because in the alkaline medium hydrogen peroxide is also a sufficiently strong oxidant, but due to the extremely low stability of ferricinium cation and its low stationary concentration the absorption band of this product cannot be detected. If in this case NaOH is neutralized with the excess of acid, the formation of ferricinium ion is hardly probable due to the exhaustion of compound **I** and **II** in alkaline medium. Actually, we observe the appearance of the absorption band of ferricinium ion having high intensity at the introduction of acid neutralizing NaOH in the reaction mixture. Note that if oxidation of compounds **I** and **II** is carried out in the presence of acid of the same concentration without the preliminary addition of NaOH, the intensity of the absorption band of ferricinium cation will be the same as in the above-described case. It shows that no oxidation of metal complex takes place in the presence of NaOH confirming our point of view on the mechanism of the influence of OH^- ions on the process under study and on the mechanism of this process.

Kinetic analysis of Scheme 1 based on quasi-equilibrium approach gives the following equation of the reaction rate:

$$w = k_1[\mathbf{A}] = k_1K_1K_2[\mathrm{Fc}][\mathrm{H_2O_2}]^2,$$

$$\mathrm{Fc} = \mathbf{I}, \mathbf{II}. \qquad (8)$$

It is identical to the experimental one. Therefore $k_{\mathrm{ef}} = k_1K_1K_2$.

The oxidation of compounds **I** and **II** with peroxide **III** has a certain resemblance to the process of oxidation of cyclopentadienyl derivatives of molybdenum and tungsten of the composition Cp_2MX_2 (M = Mo, W; X = Cl, Br, I) with hydroperoxide **IV** which is also described by kinetic equation of the first order reaction with respect to the metal complex and by the second order equation with respect to peroxide [8]. At the same time the composition of products of reduction of two molecules of hydroperoxide **IV** (Scheme 4) differs from that presented in the Scheme 1.

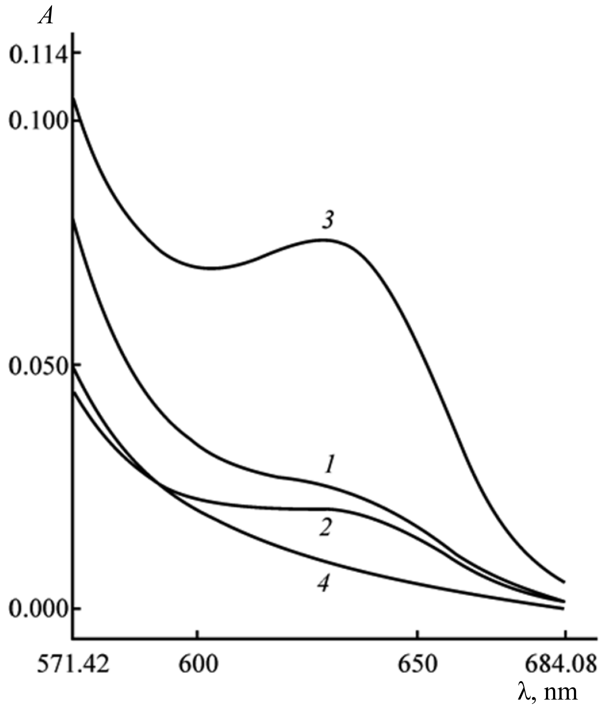


Fig. 4. Effect of additives of (*4*) NaOH and (*2*, *3*) $NaClO_4$ on the oxidation of compound **II** with peroxide **III**; (*1*) without the additives. c^0_{II} 0.003 mol/L, c^0_{III} 0.15 mol/L, (*2*) c^0_{I} 0.003 mol/L, c^0(NaOH) 0.1 mol/L, $c^0(NaClO_4)_2$ 0.05 mol/L, $c^0(NaClO_4)_3$ 0.5 mol/L, *T* = 23°C. Reaction time 25 s.

$$\mathrm{Cp_2MX_2 + 2ROOH \rightleftarrows Cp_2MX_2{\cdot}2ROOH}$$

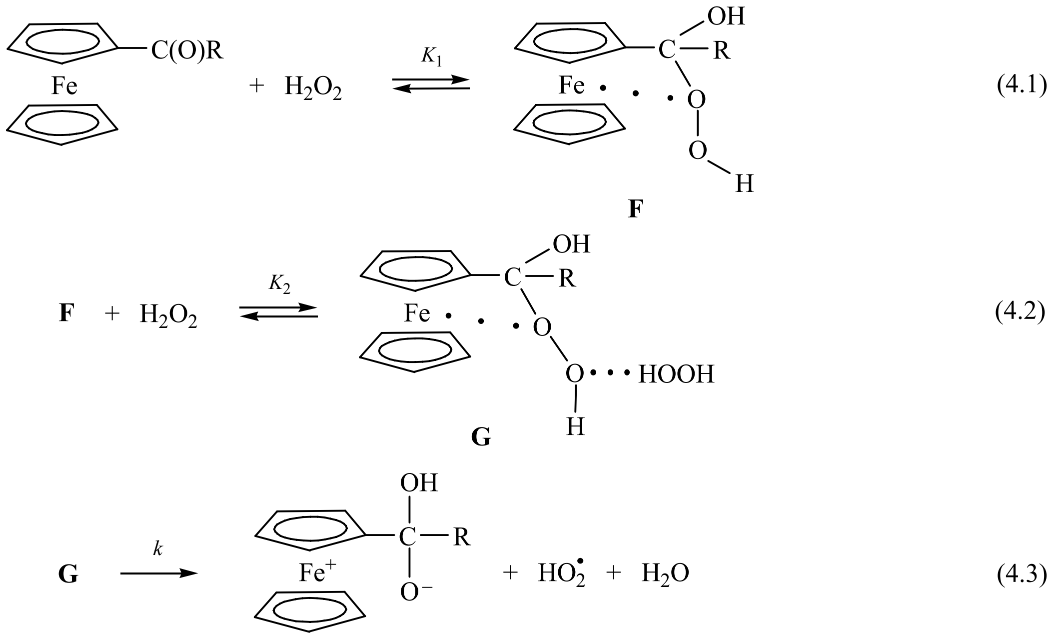
$$\rightarrow \mathrm{[Cp_2MX_2]^{+}OOR^{-} + H_2O + RO^{\boldsymbol{\cdot}}}.$$

The reason of this difference is most probably the absence of substituents capable of interaction with peroxide molecules in the above-mentioned derivatives of Mo and W.

Another mechanism of oxidation of compounds **I**, **II** according to Scheme 4 takes into account the ability of carbonyl compounds to add hydrogen peroxide with the formation of organic hydroperoxide.

This mechanism seems quite attractive from the point of view of reducing steric hindrances in the reaction of compounds **I** and **II** with peroxides which can be rather significant. But the reaction (4.1) proceeds really only under the action of strong acids [10]. There-

Scheme 4.



fore the contribution from the mechanism described by the scheme 4 in the overall process of oxidation of chosen compounds may occur to be quite insignificant.

As it can be expected, the addition of a strong acid, for example, $HClO_4$ or CF_3COOH, leads to significant acceleration of oxidation of compounds with hydrogen peroxide which is due to the increase in the redox potential of hydrogen peroxide in the presence of acid [$\varphi^0(H_2O_2, H^+) = 0.72$ V] [11].

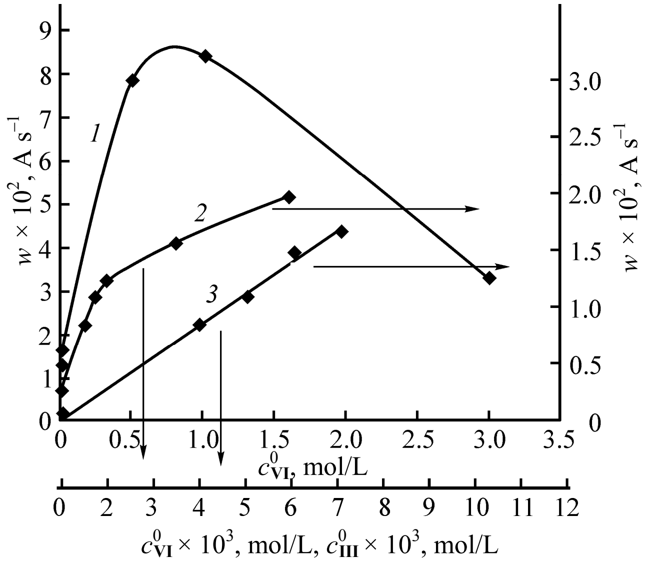


Fig. 5. Dependence of the rate of oxidation of compound **I** on the initial concentration of (*1, 2*) CF_3COOH and (*3*) peroxide **III** in water. (*2*) Initial plot of the curve (*1*). (*1, 2*) c^0_I 0.003 mol/L, c^0_{III} 0.15 mol/L, (*3*) c^0_I 0.003 mol/L, c^0_{VI} 0.5 mol/L, $T = 23$°C.

It is established that the process of oxidation of metal complexes with peroxide **III** in water in the presence of strong acid is described by the kinetic equation of the first order with respect to the initial concentration of metal complex and with respect to the concentration of strong acid when it is small. In the broad interval of changes in the concentration of acid the dependence $w = f(c_{HX})$ has a clearly expressed maximum. The reaction order with respect to starting concentration of peroxide becomes equal to unity (Fig. 5). It distinguishes the process of oxidation of compounds **I** and **II** in the presence of acid from the process without its participation.

The peculiarity of the dependence of the rate of oxidation on the acid concentration in the initial plot is that it starts not from zero, but from some point on the ordinate axis corresponding to the rate of oxidation of complex with peroxide in the absence of acid (w_0). The kinetic equation in this case is as follows:

$$w = w_0 + k'_{eff}[Fc][H_2O_2][HX], \quad (8)$$

$$\text{or } w = w_0 + k''_{eff}[HX], \quad (9)$$

$$[Fc] = \text{const and } [H_2O_2] = \text{const}, \ k''_{eff} = k'_{eff}[Fc][H_2O_2].$$

When $c_{HX} = 0$, $w = w_0$, at the sufficiently high concentrations of acids equation (8) transforms to Eq. (10).

$$w = k'_{\mathrm{eff}}\,[\mathrm{Fc}][\mathrm{H_2O_2}][\mathrm{HX}]. \qquad (10)$$

Starting from the above mentioned data several alternative mechanisms of oxidation of compounds **I** and **II** in the presence of acids differing in the way of coordination of reagents (Schemes 5–7) can be assumed.

Scheme 6 considers that the substituent –C(O)R in the Cp-ligand of metal complex only indirectly participates in the oxidation of the latter favoring the coordination of hydrogen peroxide with it. Therefore it does not take part in transformations. It is caused by the fact that proton transfer from HX to $\mathrm{OH^-}$ anion will proceed undoubtedly much faster than the reaction of anion with carbonyl group [12].

The mechanism described by Scheme 6 considers the possibility of another way of coordination of acid with metal complex through the oxygen atom of substituent leading to the increase in electrophilicity of carbon atom of the carbonyl group and its direct participation in the process of oxidation of the latter.

The mechanism in Scheme 7 is analogous to the mechanism described by Scheme 4. In particular, it considers the possibility of H_2O_2 addition to the carbonyl group. But in this case the reaction is catalyzed by the acid [10], and the process on the whole becomes quite real.

Analysis of any of the above-presented schemes using quasiequilibrium approximation leads to kinetic equation of the reaction which is identical to the experimentally found one. For example, for Scheme 5 the reaction rate will be expressed as follows:

$$w = kK_1K_2[\mathrm{Fc}][\mathrm{H^+}][\mathrm{H_2O_2}].$$

For Scheme 6 the reaction rate expression must contain K'_1 and K'_2 instead of K_1 and K_2.

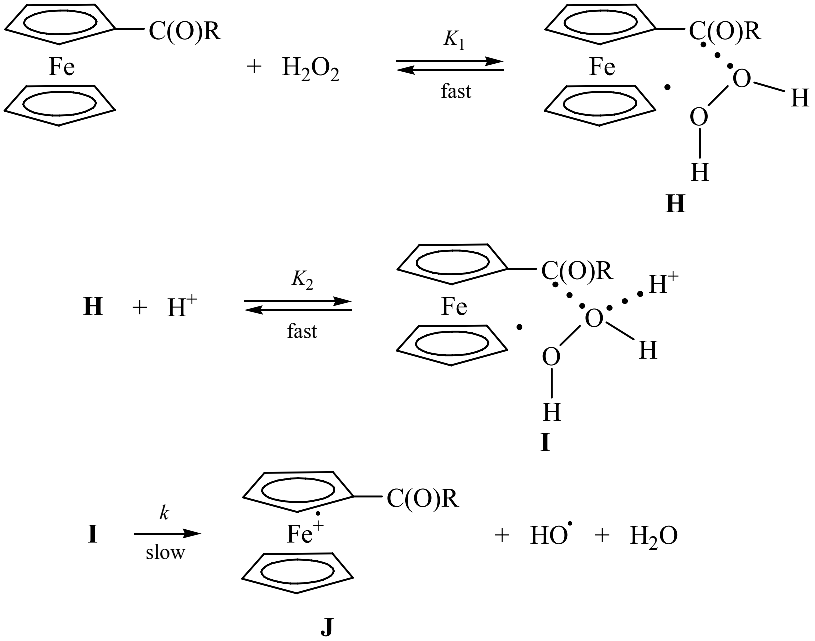
$$w = kK'_1K'_2[\mathrm{Fc}][\mathrm{H^+}][\mathrm{H_2O_2}].$$

For Scheme 7 the reaction rate expression is practically identical.

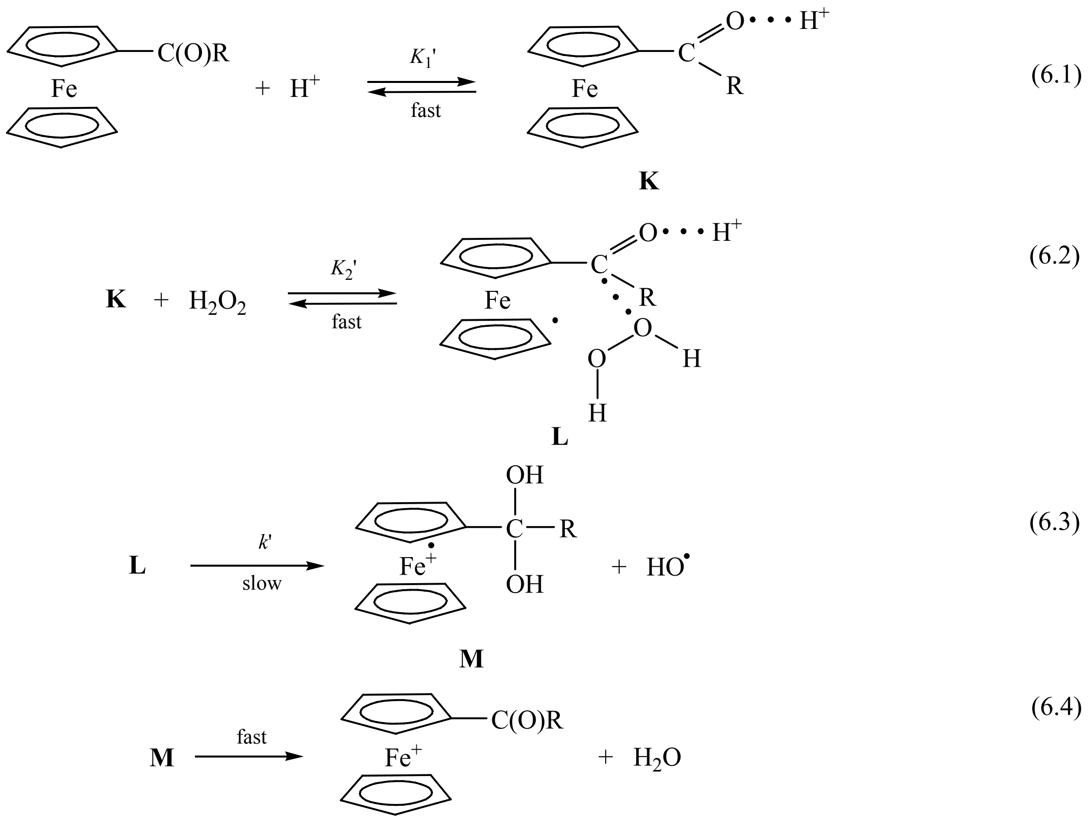
$$w = k''K'_1K_2''\mathrm{K}_3''[\mathrm{Fc}][\mathrm{H^+}]\mathrm{H_2O_2}],$$

All the mechanisms are described by the same summary reaction. They lead to the same composition of products. From that it follows that $\Delta_\mathrm{r}G^0_6 = \Delta_\mathrm{r}G^0_7 = \Delta_\mathrm{r}G^0_8$. At the first glance Scheme 5 seems more probable due to the following reason. The formation of final products at the transformation of the triple complex **F** proceeds avoiding the intermediate stage, that is, by the shorter and more favorable by energy pathway, than in Scheme 6 where the reaction (6.3) is the intermediate stage. Intermediate **L** is unambiguously characterized by higher energy than the final product. It shows that the transition state, corresponding to the transformation of complex **L** will have more complex structure and higher energy than the transition state in the transformation of complex **I**,

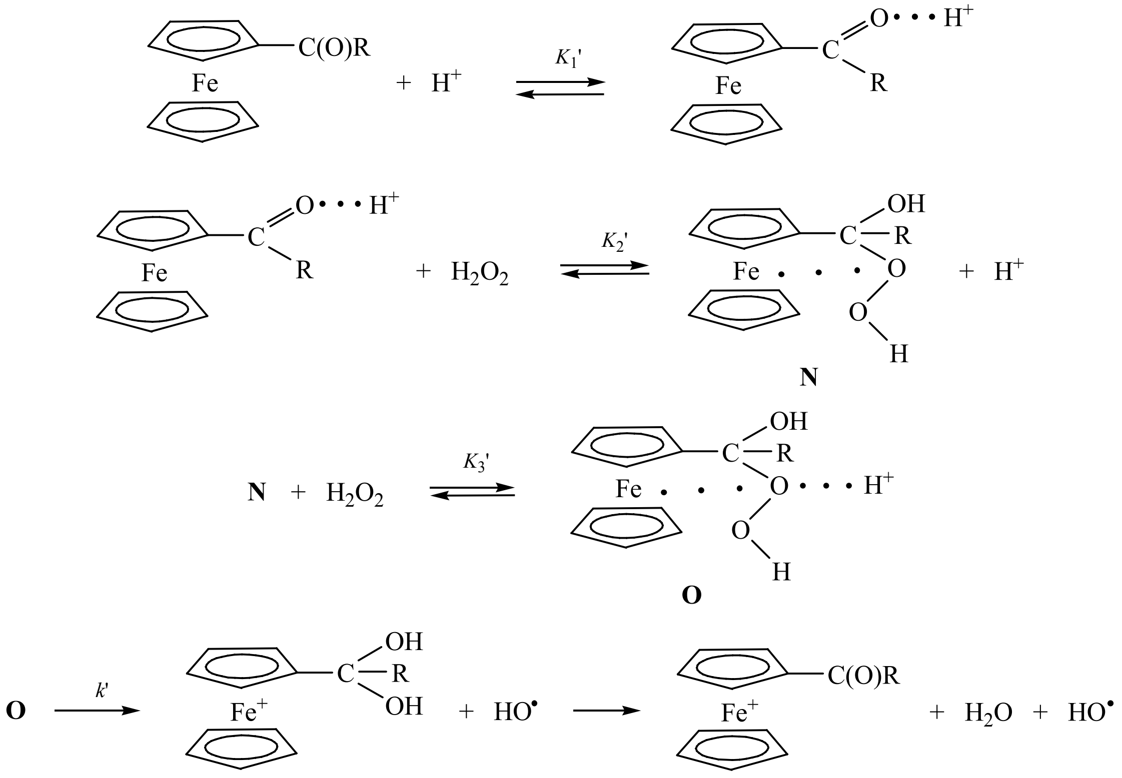
Scheme 5.



Scheme 6.



Scheme 7.



that is, $E_{7.3} > E_{6.3}$. Note that the reason due to which the shorter pathway of oxidation of the compound **I** or **II** to ferricinium ion may occur in this case to be also kinetically more favorable is caused most of all by the fact that oxidative system $H_2O_2 + H^+$ has sufficiently high oxidation potential (0.72 V [11]). At the same time starting from the properties of reagents it is possible to state with assurance that the concentration of intermediate **L** will be significantly higher that of intermediate **I** which will influence the rate of their transformation to the reaction products and equalize the contribution of these mechanism to the process on the whole.

Considering the effect of steric factors on the reaction of compounds **I** and **II** with peroxide **III** Scheme 7 seems more preferred compared to Scheme 5 because hydroperoxide fragment in the complex **O** seems more compact than the peroxide molecule. Therefore by steric reasons it is more convenient for the interaction with the iron atom. Besides, the mechanisms of the reactions presented in the Schemes 6 and 7 reflect the possibility of observing the effect of approach and orientation in the oxidation of compounds **I** and **II** if the complexes **K** and **O** are regarded as independent bifunctional reagents. It must lead to a decrease in free energy of activation of the process. Mechanism (5) excludes the possibility of observing this effect because complex **H** is not a bifunctional reagent.

The observed dependence $w = f(c_{\mathrm{HX}})$ with the clearly expressed maximum indicates the different states of metal complexes at low and high concentrations of acid. Firstly, strong acids, taken in high concentrations, protonate compounds **I** and **II** at the carbonyl group to form α-ferrocenylcarbenium ions [5] which are much more inert to oxidation than the intermediate structures of these complexes where carbon atom does not carry a high positive charge. Secondly, the process of hydration of compounds under study is possible which is catalyzed with acids. The subsequent protonation of the obtained product at high concentrations of acids leads to the formation of the same carbocation complex.

With the purpose to confirm the mechanism of acid participation in the process of oxidation of compounds **I** and **II** with peroxide **III** according to Scheme 6 the effect of sodium perchlorate on the rate of the reaction under study in the absence of acid was investigated (Fig. 4). From the figure presented it is seen that the addition of salt accelerates oxidation in water which may be seen from the increase in the integral intensity of the absorption band of ferricinium cation *S* corresponding to the amount of formed ferricinium cation.

$NaClO_4$ concentration (mol/L)	Peak area, *S*
0	0.142
0.05	0.328
0.5	1.387

The obtained result may be explained by the catalytic action of sodium ions on the process under study connected with the activation of carbonyl group with respect to the nucleophilic reagent in neutral and reduced state while their coordination.

The peculiarity of processes under investigation consists in their possible ability to can proceed according to different mechanisms simultaneously. For the reaction of peroxide **IV** with the compounds **I** and **II** considering steric factors mechanism (6) is the most suitable.

EXPERIMENTAL

Electron absorption spectra of metal complexes were registered on a SHIMADZU UV-1700 spectrophotometer in quartz cells in the range 500–800 nm. The preparation of operating solutions and recording of their spectra were carried out under argon.

The reaction progress was controlled by the appearance of the absorption band with $\lambda_{\max}$ 618–620 nm.

Commercial hydrogen peroxide of “pure for analysis” grade was used. The content of main substance in the samples of *tert*-butylhydroperoxide and *tert*-butylperoxide was no less than 99%. All solvents used were of “pure for analysis” grade. They were additionally purified according to reported procedures.

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