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Mechanism of the Reaction of 1,1'-Diethylferrocene and Decamethylferrocene with Peroxides in Organic Solvents

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Abstract—Kinetic relationships of oxidation of 1,1'-diethylferrocene and decamethylferrocene with peroxides ROOR (R = H, *t*-C_4H_9) in organic solvents were studied and the composition of oxidation products was established. It is shown that reactivity of $(C_5H_4C_2H_5)_2Fe$ is significantly lower than that of Cp^*_2Fe [Cp^* = η^5-$C_5(CH_3)_5$] which is seen from the ability of the first metal complex to undergo oxidation with a notable rate only in the presence of Brønsted acids, whereas the second substance is oxidized both in the presence and in the absence of these acids. Two possible mechanisms of oxidation of metal complexes in the presence of strong acids are discussed. One of them is based on the ability of ferrocene to fast and equilibrium protonation with the formation of $Cp_2Fe\overset{+}{—}H$ structure. Another one considers the ability of metal complexes to coordinate peroxides with the formation of weakly bound charge transfer complexes of the composition $Cp_2Fe^{\delta+}\cdot ROOR^{\delta-}$. The possibility of their formation is confirmed by the oxidation of Cp_2Fe with hydroperoxides in the absence of acids.

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The oxidation of ferrocene Cp_2Fe and its derivatives with peroxides practically is not studied. Among the data known up till now the composition should be mentioned of the oxidation products of this compound obtained in the reaction with benzoyl peroxide [1] and the fact of the formation of ferricinium ion at the oxidation of Cp_2Fe with hydrogen peroxide in the presence of strong Brønsted acids [2] or under the conditions of enzyme catalysis [3]. The oxidation of Cp_2Fe with hydrogen peroxide was compared in [4] with the mechanism of its oxidation with oxygen in the presence of perchloric acid. It was suggested that the oxidation of complex proceeds through the stage of formation of hydrogen peroxide, yet the latter was not found in the reaction products. This fact was explained by the consumption of peroxide for the oxidation of Cp_2Fe in the acidic medium. Later it was confirmed experimentally. The probable mechanism of this reaction was *a priori* assumed in [5] where the oxidation of Cp_2Fe with oxygen was studied. The aim of this work is the investigation of the reactivity and the mechanism of oxidation of diethylferrocene $(EtCp)_2Fe$ (compound **I**) and decamethylferrocene Cp^*_2Fe (compound **II**) with hydrogen peroxide **III**, *tert*-butyl hydroperoxide **IV**, and *tert*-butyl peroxide **V**. Reactions under study were carried out in the presence of benzoic **VI**, trifluoroacetic **VII**, and perchloric **VIII** acids respectively.

In the absence of acids diethylferrocene oxidizes with peroxide **III** at room temperature so slowly that it does not permit to trace spectrophotometrically the formation of ferricinium ion. Ferrocene behaves analogously even in the presence of the additive of acid **VI** in the reaction mixture. Under the same conditions compound **I** undergoes oxidation, as proved by the appearance of an absorption band of $(EtCp)_2Fe^+$ with λ_{max} at 642 nm (Fig. 1) in the electron absorption spectrum of the reaction mixture. At the introduction of strong acids **VII**, **VIII** in the reaction mixture the process proceeds with a high rate, and the maximum of the absorption band suffers a red shift[1] (Fig. 1).

The reason of the observed acceleration of the reaction under study is evident. Standard redox potential of oxidative system (H_2O_2 + H^+) is 0.72 V [6]. It is higher than the standard redox potential of diethylferrocene (in the case of ferrocene it is 0.59 V [7]) which makes the process thermodynamically favorable. Though in non-aqueous solvents the values

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[1] At present this effect is under study.

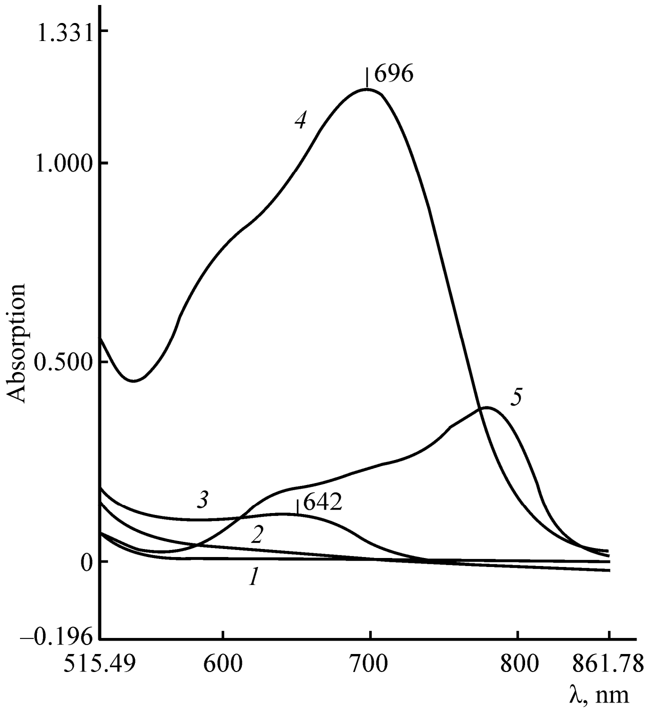


Fig. 1. Electron absorption spectra of the systems: (*1*) [Cp$_2$Fe + **III** + **VI**], (*2*) [**I** + **III**], (*3*) [**I** + **III** + **VI**], (*4*) [**I** + **III** + **VIII**], and (*5*) [**II** + **III** + **VI**] in ethanol. $c^0_{\text{I,II}}$ 0.005 mol/L, c^0_{III} 0.15 mol/L, c^0_{VI} 0.05 mol/L, c^0_{VIII} 0.05 mol/L; $T = 23$°C. Reaction time (*1*–*3*) 8 min, (*4*) 1.5 min, and (*5*) 1 min.

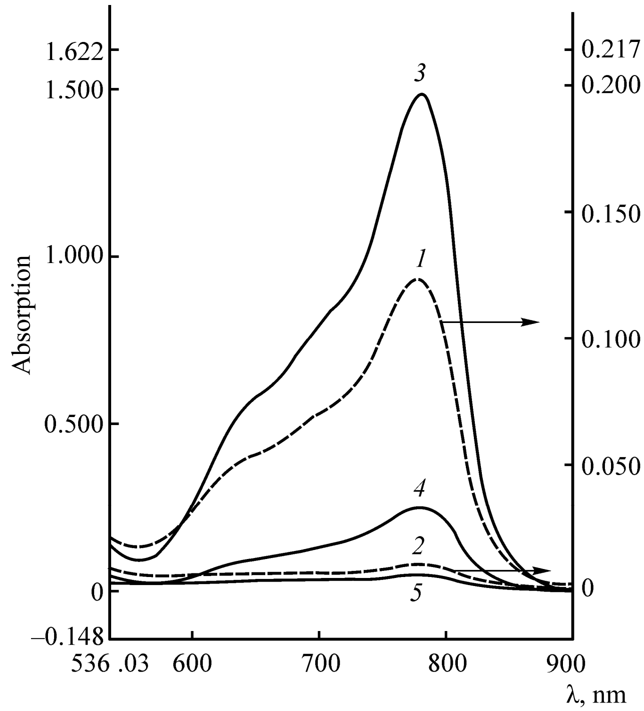


Fig. 2. Electron absorption spectra of the systems: (*1*) [**II** + **III**], (*2*) [**II** + **IV**], (*3*) [**II** + **III** + **VIII**], (*4*) [**II** + **IV** + **VIII**], and (*5*) [**II** + **V** + **VIII**] in (*1*–*4*) dioxane and (*5*) ethanol. c^0_{II} 0.005 mol/L, $c^0_{\text{III–V}}$ 0.15 mol/L, c^0_{VIII} 0.005 mol/L, $T = 23$°C. Reaction time 1 min.

of standard redox potentials of reacting substances, i.e., of metal complexes and peroxides, differ from those in water solutions, their difference determining the change in the standard Gibbs function of the reaction may alter insignificantly at the transfer from one solvent to another [6].

Unlike ferrocene and compound **I,** substance **II** is capable of oxidation with hydrogen peroxide in the absence of acids (Fig. 1) which is confirmed by the appearance of an absorption band at 780 nm in the electron absorption spectrum of the reaction mixture. According to [8] it can be attributed to Cp_2^*Fe^+ cation. It is caused by a significant decrease in the redox potential of compound **II** as compared to ferrocene and compound **I** due to the strong electron-donor effect of ten methyl substituents. The data on the value of redox potential of Cp_2^*Fe are regretfully absent.

The reactivity of compounds **I**, **II** with respect to another peroxides also differ significantly. The reaction of substance **I** with peroxides **IV**, **V** proceeds only in the presence of acids. At the same time peroxide **IV** can oxidize compound **II** to ferricinium ion (Fig. 2). With respect to peroxide **V** the complex is relatively inert at room temperature and undergoes oxidation only in the presence of strong acids.

The rates of accumulation of $(\text{EtCp})_2\text{Fe}^+$ and Cp_2^*Fe^+ cations at the oxidation of compounds **I,II** depend on the nature of solvent and the reaction time. They increase in the series dioxane < ethanol < DMF which is illustrated by an example of the first metal complex (Fig. 3).

In ethanol the process is characterized by the presence of small induction period caused evidently by the processes of association of reagents and solvents with one another through hydrogen bonds. The deceleration effect of water additives to the above-mentioned solvents (Fig. 3) confirms this fact despite of the higher value of permittivity of mixed solvents as compared to individual ones. This means that on the whole the rules of variation of the rate of oxidation of metal complex and of the value of permittivity of the medium may not correspond to one another due to the

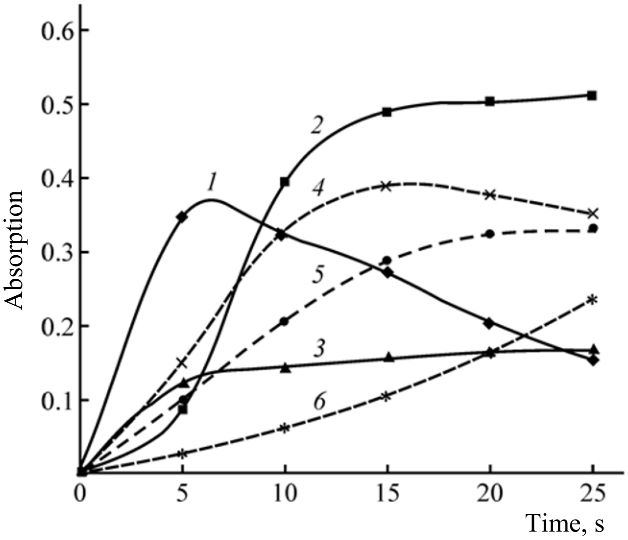


Fig. 3. Kinetic curves of accumulation of ferricinium ion at the oxidation of compound **I** with peroxide **III** in the presence of the acid **VIII** in (*1*) DMF, (*2*) ethanol, (*3*) dioxane, in the systems (*4*) DMF–water and (*5*) dioxane–water, (*6*) ethanol–water (components ratio 2 : 1). c_{I}^0 0.002 mol/L, c_{III}^0 0.006 mol/L, c_{VIII}^0 0.1 mol/L, $T = 23°\mathrm{C}$.

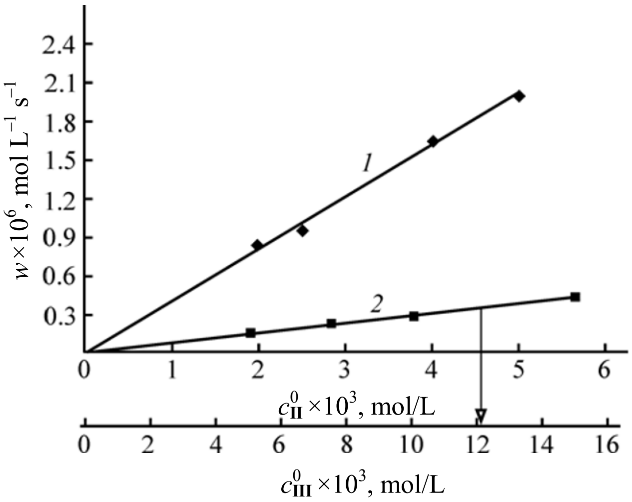


Fig. 4. Effect of initial concentration of compounds (*1*) **II** and (*2*) **III** on the rate of oxidation of metal complex in dioxane in the absence of acid at 23°C; c_{III}^0 0.15 mol/L, c_{II}^0 0.01 mol/L.

effect of specific solvation of reagents with the solvent.

As mentioned above, the main product of oxidation of both ferrocenes with hydrogen peroxide is the corresponding ferricinium cation. $(\mathrm{EtCp})_2\mathrm{Fe}^+$ cation is significantly more stable than $\mathrm{Cp_2Fe}^+$ one, but in the course of time it also suffers an oxidative destruction. $\mathrm{Cp}_2^*\mathrm{Fe}^+$ cation is exceptionally stable even in the absence of acid and can exist unchanged in ethanol solution for many weeks at room temperature and at 50°C. Its transformation leads to the formation of brown precipitate. According to IR spectroscopy it is a hydrated oxohydroxoderivative of trivalent iron Fe(O)OH (absorption bands with $\lambda_{\max}$ 505, 872, 3392 cm^{-1} correspond to Fe–O, Fe=O, and O–H bond vibrations, and the bands with $\lambda_{\max}$ 1045 and 1653 cm^{-1} are attributed to the bending vibrations of Fe–O–H and coordinationally bound water respectively [9]).

Note also that the oxidation of metal complex **I** with hydrogen peroxide in the later stages of the process may be accompanied by liberation of oxygen. Its formation is explained by the decomposition of hydrogen peroxide catalyzed by the formed Fe(III) derivatives. It is especially clearly seen at the use of DMF as a solvent.

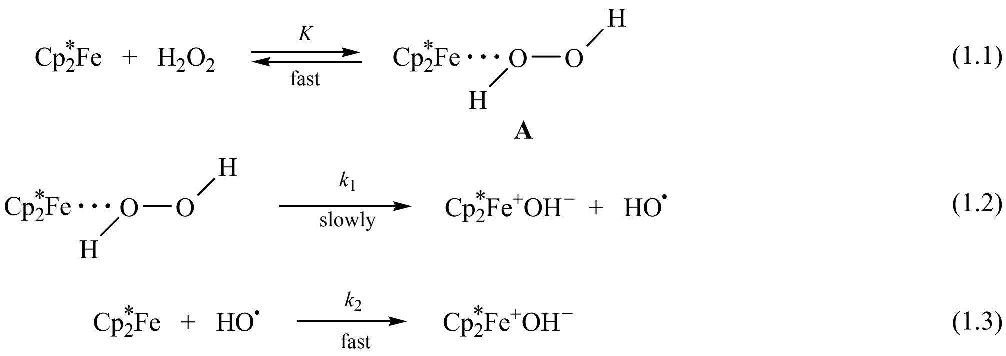
Results of studies of kinetic relationships of compound **II** oxidation with peroxide **III** in dioxane and ethanol in the absence of acid show that the process is described by the kinetic equation of the first order reaction with respect to the starting concentration of each reagent. If follows from the fact of linear increase in the initial reaction rate w_0 at the increase in concentration of metal complex and peroxide (Fig. 4).

$$w_0 = k_{\mathrm{eff}}[\mathrm{Cp}_2^*\mathrm{Fe}][\mathrm{H_2O_2}]. \qquad (1)$$

Bimolecular character of the main reaction together with the consideration of properties of starting reagents and the nature of main product permits to assume the mechanism shown in Scheme 1.

This mechanism is based on the assumption that between $\mathrm{Cp}_2^*\mathrm{Fe}$ and $\mathrm{H_2O_2}$ the primary coordination is possible with the formation of weakly bound charge transfer complex (A) due to the interaction of HOMO d_{xy} or $d_{x^2-y^2}$ orbitals of metal complex localized on metal atom [10] with the vacant σ* orbital of the peroxide bond. The formation of such adducts between the transition metal complexes and hydroperoxides was previously mentioned in [11]. The necessity to take reaction (1.3) into the consideration is caused by the high activity of $\mathrm{HO}^\bullet$ radical as one-electron oxidant [$\varphi^0(\mathrm{OH^-/HO^\bullet}) = 2.0$ V] in neutral and alkaline medium [6]. It should be noted that the reaction of ferrocene with alkylperoxide radical $\mathrm{RO}_2^\bullet$ is characterized by the rate constant having the order of magnitude of 10^5 L mol^{-1} s^{-1} [12]. $\mathrm{HO}^\bullet$ radical is by all parameters

Scheme 1.



significantly more active than $RO_2^{\bullet}$, and the rate constant of its reaction with compounds **I** and **II** must be significantly larger. Using the quasiequilibrium approximation for the evaluation of complex A concentration and assuming that the concentration of $HO^{\bullet}$ radicals is stationary it is possible to show that the rate of accumulation of $Cp_2^*Fe^+$ cation which is established spectrophotometrically according to the scheme presented will be described by Eq. (2).

$$w_0' = k_1K[Cp_2^*Fe][H_2O_2] + k_2[Cp_2^*Fe][HO] = 2k_1K[Cp_2^*Fe][H_2O_2]. \quad (2)$$

It is identical to the experimentally established one ($2k_1K = k_{eff}$). If $HO^{\cdot}$ radical is consumed not only in the reaction (1.3), but also in the reactions of abstraction of hydrogen atoms from different substrates, the coefficient in the Eq. (2) must be less than two.

As it was mentioned above, the addition of acids led to a significant increase in the rate of oxidation of compounds **I** and **II**. In connection with this it was interesting to study the kinetics of their oxidation with hydrogen peroxide in the presence of strong acids. The obtained results show that both processes are described by the kinetic equation of the first order reaction with respect to the initial concentration of metal complex, of peroxide, and of acid (Fig. 5).

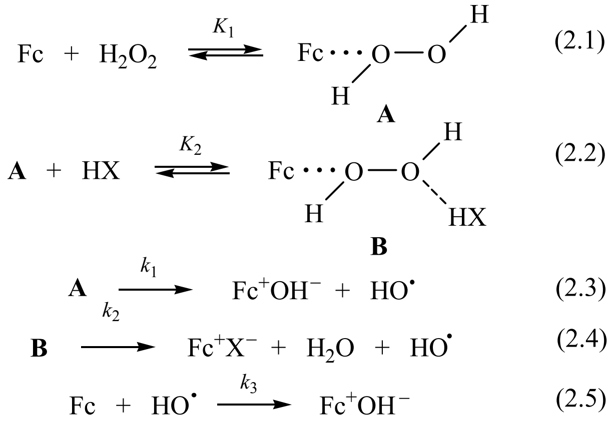
Thus it follows that the kinetic equation of the reaction for these processes will look as follows.

$$w_{0,HX} = k'_{eff}\,[Fc][HX][H_2O_2], \quad (3)$$

$$Fc = Cp_2^*Fe,\ (EtCp)_2Fe.$$

On the basis of these and the above-presented data two alternative mechanisms of oxidation of complexes under consideration which are not complicated by secondary processes may be suggested. They are described by Schemes 2 and 3 respectively. Scheme 2 is based on Scheme 1, according to which the presence of acid does not influence the ability of metal complex to coordinate the molecule of peroxide.

Scheme 2.



$$Fc = Cp_2^*Fe,\ (EtCp)_2Fe.$$

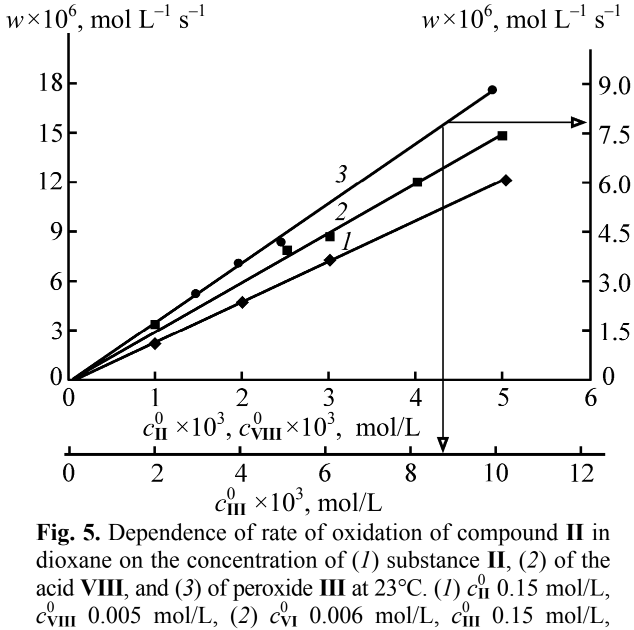


Fig. 5. Dependence of rate of oxidation of compound **II** in dioxane on the concentration of (*1*) substance **II**, (*2*) of the acid **VIII**, and (*3*) of peroxide **III** at 23°C. (*1*) c^0_{II} 0.15 mol/L, c^0_{VIII} 0.005 mol/L, (*2*) c^0_{VI} 0.006 mol/L, c^0_{III} 0.15 mol/L, (*3*) c^0_{II} 0.005 mol/L, c^0_{VIII} 0.005 mol/L.

In the case of oxidation of compound **I** the formation of triple complex of the type **B** is a necessary condition of proceeding of the metal complex oxidation with the noticeable rate, and the reaction (2.3) does not play significant role in it. The oxidation of compound **II** may proceed also without the participation of acid. Therefore the role of the latter in the process of oxidation consists in the opening of energetically more favorable pathway of oxidation of metal complex connected with the formation of highly reactive complex **B**.

In agreement with the scheme presented the rate of accumulation of ferricinium ion at the oxidation of compound **II** will be equal to:

$$w = \frac{d[Cp^*_2Fe^+]}{dt} = w_1 + w_2 + w_3,$$

$$= k_1[A] + k_2[C] + k_3[Fc][HO]. \qquad (4)$$

Applying the approximations which were considered in the analysis of Scheme 1 to Scheme 2 Eq. (5) for the reaction rate is easily obtained.

$$w = 2K_1[Cp^*_2Fe][H_2O_2](k_1 + k_2K_2[HX]). \qquad (5)$$

When the concentrations of decamethylferrocene and hydrogen peroxide are constant Eq. (5) is the equation of a straight line $w = a + b[HX]$. When $[HX]^0 = 0$ the equation for the reaction rate is reduced to Eq. (2), and at high HX concentrations, to Eq. (6).

$$w'_{0,HX} = 2k_2K_1K_2[Cp^*_2Fe][H_2O_2][HX]. \qquad (6)$$

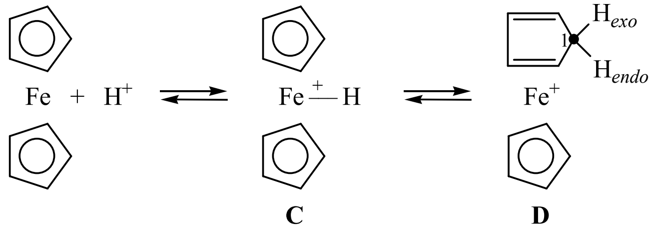
We failed to establish experimentally the dependence $w = a + b[HX]$ because a value equal to the reaction rate in the absence of acid w_0 is much smaller than the reaction rate in its presence. The knowledge of w'_0 and $w'_{0,HX}$ permits to evaluate relative reactivity of complexes **A** and **B** as k_2/k_1 ratio at [HX] = 1 by means of Eq. (7) resulting from the comparison of Eqs. (2) and (6).

$$\frac{k_2}{k_1} = \frac{w_2}{w_1} \cdot \frac{1}{K_2[HX]}. \qquad (7)$$

As is known, the equilibrium constants of hydrogen complexes with the participation of alkyl hydroperoxides are equal to 1.5–2 [13]. Hydrogen peroxide is less basic than the alkyl hydroperoxides. Due to that we can assume the K_2 value equal to unity without a significant error. It leads to $k_2/k_1 \approx 1.2\times10^4$ which shows that reactivity of triple complex **B** is significantly higher than the reactivity of complex **A**, and the pathway described by the Eq. (6) brings main contribution in the total process of oxidation of compound **II**.

Mechanism (3) is based on the well known data on the ability of ferrocene to undergo fast and equilibrium protonation with strong acids according to the Eq. (8) [14–16].

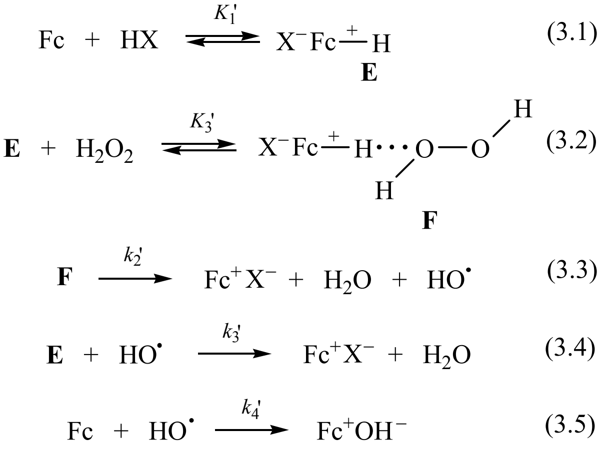
The protonation of compound **II** unambiguously leads only to the structure **C**. The protonation of compound **I** as well as the protonation of ferrocene is possible at the metal atom as well as at the Cp-ligand. According to [15] the protonation of ferrocene at the metal atom is by 5 kcal more favorable than at the Cp-ligand. Besides, in the same work it was established that Fe–H bond energy in the structure **C** is equal to 50 kcal mol^{-1}, which is significantly smaller than C–H bond energy in the organic compounds. It permits to consider structure **C** as an effective donor of hydrogen atom in the reactions with oxidants. Just this structure must be considered as located on the coordinate of the reaction of oxidation of metal complex. This conclusion is confirmed by the results of quantum-chemical calculations of structures **C** and **D** [16]. These calculations show that the energies of these structures differ by 1.9 kcal mol^{-1}, and bond lengths of $C^{(1)}$–H_{exo}, $C^{(1)}$–H_{endo}, and Fe–H bonds are 1.100 Å, 1.193 Å, and 1.516 Å respectively. From the comparison of data presented it follows that Fe–H bond is significantly less strong than two $C^{(1)}$–H bonds, and hence, more reactive. On the basis of the above considerations alternative mechanism of the oxidation



C **D** (8)

of complexes under study in the presence of acids can be described by Scheme 3.

Scheme 3.



Fc = Cp_2^*Fe, $(EtCp)_2Fe$.

The calculations presented in [5] show that the reactions of protonated complexes with H_2O_2 and $HO^\bullet$ according to Eqs. (3.2)–(3.3) and (3.4) respectively are thermodynamically favorable as follows from the values of the standard Gibbs free energies of these reactions $\Delta_rG^0_{3.2+3.3} = -115.7$ kJ mol^{-1} and $\Delta_rG^0_{3.4} = -290.3$ kJ mol^{-1}.

It is possible to show that the expression for the rate of oxidation of both complexes according to the Scheme 3 will be as follows.

$$w = 2k_2'K_1'K_2'[Fc][H_2O_2][HX]. \qquad (9)$$

Considering the possibility of oxidation of compound **II** with hydrogen peroxide in the absence of acid the general dependence of the rate of oxidation of metal complex according to the mechanism (3) on the concentration of acid will be also described by the equation $w = a + b[HX]$ at $[H_2O_2]$ = const and $[Cp_2^*Fe]$ = const.

Mechanisms 2 and 3 cannot be distinguished kinetically or thermodynamically because they are described by the same kinetic equations and lead to the same composition of the reaction products if only the main stages are taken into consideration.

$$Cp_2^*Fe + H_2O_2 + HX \rightarrow Cp_2^*Fe^+X^- + H_2O + HO^\bullet. \qquad (10)$$

At the same time the difference in the structure of activated complexes corresponding to the limiting stages (2.4) and (3.3) will specify the difference in the values of activation energies of the oxidation processes of the metal complexes described by the above-mentioned schemes. Note that making the choice in favor of the mechanism 2 or 3 is a rather complicated task. The fact of oxidation of Cp_2^*Fe with hydrogen peroxide in the absence of acid indicates that the necessary condition for the proceeding of this reaction is the coordination of metal complex and peroxide as it is shown in Scheme 1. The participation of acid in this process according to Scheme 2 only improves the oxidative properties of the peroxide. On the other hand, Cp_2^*Fe and $(EtCp)_2Fe$ complexes regarded as strong bases due to the presence of electron-donating substituents in them will exhibit higher affinity to proton as compared to unsubstituted ferrocene, and hence they must be protonated more easily. It will favor oxidation of both metal complexes with the participation of acid according to the mechanism 3. Nevertheless, Scheme 3 seems to be preferred if the effect of sterical hindrances created by the substituents in Cp-ligand for the proceeding of the reaction are considered. Effect of these hindrances becomes still more pronounced if instead of peroxide **III** compound **IV** and especially **V** having bulky alkyl groups are used as oxidants.

It is one of the main reasons causing their lower reactivity as compared to hydrogen peroxide. At the protonation of metal complexes by the metal atom it acquires configuration with the inclined Cp ligands. The angle between them may be significantly smaller than 180° [17]. It significantly facilitates the attack of Fe–H bond in them from the side of peroxides. At the comparison of the reactivity of peroxides it is necessary also to consider the decrease in their oxidative potential at the substitution of one or two hydroden atoms in peroxide **III** with a *tert*-butyl group. As compared to hydrogen it is a stronger electron donor to the side of peroxide bond.

On the whole it can be expected that the processes 2 and 3 proceed in parallel.

EXPERIMENTAL

Electron absorption spectra and kinetics of oxidation of metal complexes were measured on a IR SHIMADZU UV-1700 spectrophotometer in quartz cells. The working solutions were prepared and the spectra were taken under argon. IR spectra of the solid product of oxidation of compound **I** were recorded on a Prestige-21 SHIMADZU spectrometer (KBr, mineral oil). $Cp_2^*Fe^+$ concentration was determined with the help of a calibration curve obtained at the oxidation of compound **II** with a large excess of hydrogen peroxide in the presence of a significant concentration of acid (0.5 mol/L). For the evaluation of concentration of $(EtCp)_2Fe^+$ this procedure is non-applicable because of the red shift of λ_{max} of its absorption band.

Commercial hydrogen peroxide was of "pure for analysis" grade. In the samples of *tert*-butyl hydroperoxide and *tert*-butyl peroxide the main substance content was no less than 99%. All solvents used were of "pure for analysis" grade and were additionally purified by known procedures.

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REFERENCES

1. Beckwitt, A.J. and Leydon, R.J., *Tetrahedron*, 1964, vol. 20, p. 791.
2. Claude, F., These doct. Ing. Univ. Paris, 1973, p.130.
3. Epton, R., Hobson, M.E., and Marr, G., *J. Organomet. Chem*., 1973, vol. 134, p. 23.
4. Lubach, J. and Drenth, W., *Rec. Trav. Chim*., 1973, vol. 92, no. 4, p. 596.
5. Fomin, V.M., *Russ. J. Gen. Chem*., 2007, vol. 77, no. 5, p. 954.
6. Dey, K. and Selbin, D., *Theoretical Inorganic Chemistry*, ACS Publication, 1962
7. Castanola, M., Floris, B., Illuminaty, G., and Ortaggi, G., *J. Organomet. Chem*., 1973, vol. 60, no. 1, p. 23.
8. Su, B., Hatay, I., Ge, P.Y., Mendez, M., Corminbouef, C., Samec, Z., Ersoz, M., and Girault, H.H., *Chem. Commun*., 2010, vol. 46, p. 2918.
9. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, 1978.
10. *Metody elementoorganicheskoi khimii. Zhelezoorganicheskie soedineniya.* (Methods of Organoelement Chemistry. Organoiron Compounds), Nesmeyanov, A.N. and Kochetkov, K.A., Eds., Moscow: Nauka, 1983.
11. Emmanuel, O.N. and Skibida, I.P., Abstracts of Papers, *VI All-Union Conf. on the Chemistry of Organic Peroxide Compounds*, Donetsk, 1976, p. 16.
12. Postnikov, L.M., Toshina, E.M., and Shlyapintoh, V.Ya., *Dokl. Akad. Nauk SSSR*, 1967, vol. 172, no. 3, p. 651.
13. *Khimiya organicheskikh peroksidov* (Chemistry of Organic Peroxides), Emmanuel, N.M., Ed., Volgograd, VPI edition, 1982, p. 93.
14. Ikonomou, M.G., Sunner, J., and Kerrable, P., *J. Phys. Chem*., 1988, vol. 92, p. 6308.
15. Meot-Ner, M. (Mautner), *J. Am. Chem. Soc.,* 1989, vol. 111, no. 8, p. 2830.
16. Borisov, Yu.A. and Ustynyuk, N.A., *Russ. Chem. Bull*., 2002, vol. 51, no. 10, p. 1900.
17. Green M., *Organometal Compounds of Transition Metals,* London: Methuen, 1968. Translated under the title *Metallorganicheskie soedineniya perekhodnykh metallov*, Moscow: Mir, 1972, p. 172.