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# Features of Autoxidation of Ferrocenylcarboxylic Acid and Its Methyl Ester in Organic Solvents in the Presence of Brønsted Acids

**V. M. Fomin and A. E. Shirokov**

*Lobachevskii Nizhny Novgorod State University, pr. Gagarina 23; Nizhny Novgorod, 603950 Russia*
*e-mail: niih325@bk.ru*

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**Abstract**—We have studied the autoxidation of ferrocenecarboxylic acid and its methyl ester in organic solvents in the presence of perchloric and trifluoroacetic acids. Based on the results of kinetic studies and data on the composition of the reaction products, we suggested the possible reaction mechanisms, including those of molecular and radical-chain macrostages of the process. The features of the solvent influence on the rate of oxidation of metallocomplexes and the reasons for its extreme dependence with increasing concentration of perchloric acid are discussed.

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We have previously shown that the oxidation of ferrocenylacetic acid and methyl ferrocenylacetate by molecular oxygen in organic solvents in the absence and the presence of Brønsted acids occurs as a sequence of two macrostages, the first of which consists in the molecular oxidation of the metal complex leading to the generation of peroxide radical, and the second is the radical-chain oxidation of the complex, initiated by this radical, therewith the second macrostage makes a decisive contribution to the overall process. [1, 2]. Continuing the investigation of peculiarities characteristic of the oxidation of the ferrocene series carboxylic acid we examined the autoxidation of ferrocenecarboxylic acid (**I**) and its methyl ester (**II**). This pair of the metallocomplexes differs from a pair of ferrocenylacetic acid–methyl ferrocenylacetate by the absence of methylene fragment between the carboxy group and the Cp-ligand and therefore the substituents show pronounced electron-withdrawing properties, as indicated by the values of their induction ($\sigma_I$) and resonance ($\sigma_R$) constants: –COOH, $\sigma_I = 0.34$, $\sigma_R = 0.29$; –$COOCH_3$, $\sigma_I = 0.34$, $\sigma_R = 0.16$ [3]. This should lead to a significantly decreased reactivity of the ferrocenylcarboxylic acid and methyl ferrocenylcarboxylate compared with a pair of ferrocenylacetic acid–methyl ferrocenylacetate, first of all in the first stage of their molecular interaction with oxygen leading to the generation of peroxide radicals, which should affect also the rate of radical-chain oxidation of the metallocomplexes.

An interest in ferrocenylcarboxylic acid oxidation is caused by the fact that carboxylic acids are the end organic products of the radical-chain oxidation of organic compounds, and further oxidative transformation can be associated only with the decarboxylation of the carboxy group under the influence of peroxide radicals [4], in accordance with Eqs. (1), (2):

$$R^1COOH + R^2O_2 \rightarrow R^2OOH + R^1COO^{\cdot}, \quad (1)$$

$$R^1COO^{\cdot} \xrightarrow{k} R^{1\cdot} + CO_2. \quad (2)$$

Reaction (1) is endothermic ($\Delta_r H^0 \approx 75$ kJ mol$^{-1}$), since the average energies of the O–H bond in the acid and the hydroperoxide are 440 kJ mol$^{-1}$ and 365 kJ mol$^{-1}$, respectively [5]. Therefore, it is unclear whether the radical-chain oxidation of ferrocenylcarboxylic acid under mild conditions at the temperature of 40–60°C will develop at all when its molecular oxidation is stimulated by a strong acid. The high reactivity of ferrocenylacetic acid with respect to oxygen is due to the fact that its oxidation easily occurs in the absence of strong acids, and the radical-chain oxidation is ensured by the participation in this process of two

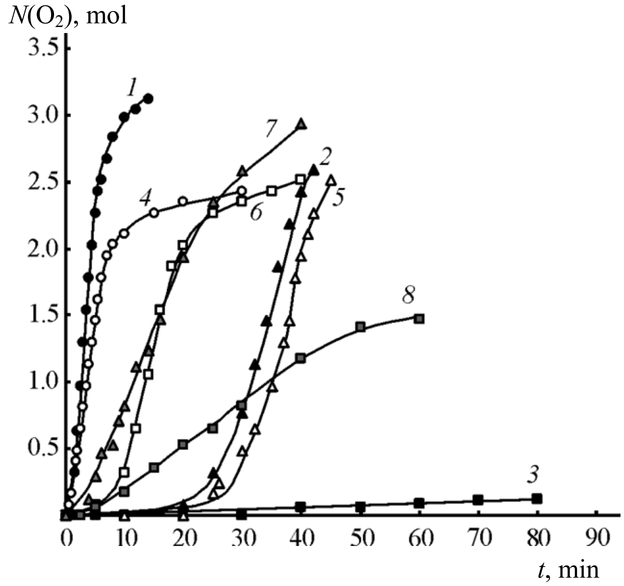


**Fig. 1.** Effect of solvent nature on the oxidation of compound **I** by molecular oxygen in the presence of acids **III** (*1–6*) and **IV** (*7, 8*): (*1*) DMF, (*2, 7*) ethanol, (*3, 8*) dioxane, (*4*) DMF–water (1:1), (*5*) ethanol–water (1:1), (*6*) dioxane–water (1:1). $T$ = 50°C, $c_{\mathrm{I}}^0$ = 0.01 M, $c_{\mathrm{HX}}$ = 0.214 M, $p(O_2) = 0.67\times10^5$ Pa.

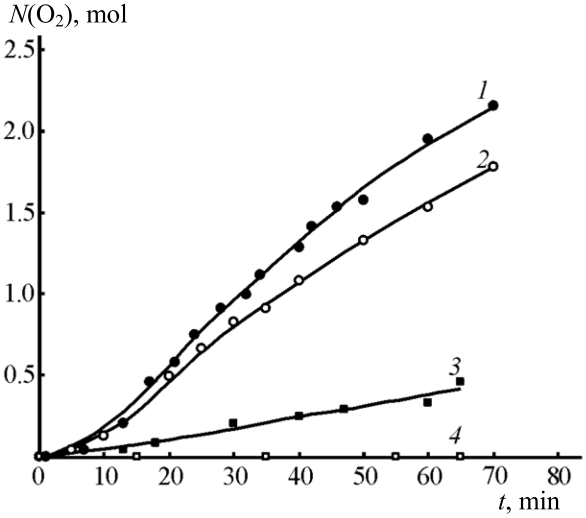


**Fig. 2.** Effect of solvent nature on the oxidation of compound **II** by molecular oxygen in the presence of acids **IV** (*1, 2*) and **III** (*3, 4*): (*1, 3*) ethanol, (*2, 4*) dioxane. $c_{\mathrm{II}}^0$ = 0.01 M, $c_{\mathrm{HX}}$ = 0.2 M, $p(O_2) = 0.47\times10^5$ Pa, $T$ = 50°C.

reaction centers, $–CH_2$ and –COOH, and reaction (2) for this complex should be very fast, by analogy with the decompopsition of the radical $C_6H_5CH_2COO^\bullet$ whose $k > 10^9$ $s^{-1}$, and should proceed with a significant gain in Gibbs free energy [1], which makes the process of decarboxylation of the ferrocenylacetic acid leading to the formation of radicals $C_5H_5Fe\cdot C_5H_4CH_2^\bullet$ generally thermodynamically favorable.

It was established that the ferrocenylcarboxylic acid unlike the ferrocenylacetic acid had significantly greater resistance to oxygen and was oxidized by it in organic solvents (dioxane, ethanol, DMF, and mixtures thereof) at a significant rate only in the presence of strong Brønsted acids $HClO_4$ (**III**) and $CF_3COOH$ (**IV**). The reactivity of compound **II** is even lower than that of **I**. The rate of oxidation of the metallocomplexes depends on the nature of the solvent and acid, as illustrates Fig. 1. The analysis of Figs. 1, 2 attracts attention to the following features: (1) A very low rate of oxidation of ferrocenylcarboxylic acid and methyl ferrocenylcarboxylate in dioxane in the presence of $HClO_4$ and its growth at the dilution of dioxane with water, accompanied by the appearance of an induction period on the kinetic curve; (2) the increase in the rate of oxidation of compounds **I** and **II** in dioxane at replacing the acid **III** by **IV** and a lower rate of oxidation in this solvent compared to ethanol; (3) the presence of the induction period on the kinetic curves of oxidation of metallocomplex in the proton-containing solvent and the appearance of the induction period at diluting DMF with water and its increase in the ethanol diluted with water; (4) a significant amount of the oxygen absorbed in the reaction mixture per mole of metallocomplex [$N(O_2)$], which can reach 2.5–3.5 (except for dioxane), that is significantly higher than the $N(O_2)$ value for the oxidation of ferrocene under similar conditions (~0.3) that proceeds along the molecular mechanism [6] .

Last fact indicates indirectly a significant contribution of radical-chain route to the overall oxidation of ferrocenylcarboxylic acid in DMF, ethanol, and mixed solvents. In dioxane the radical-chain oxidation of ferrocenylcarboxylic acid and methyl ferrocenylcarboxylate in the presence of $HClO_4$ does not develop within reaction time of 60–80 min characteristic of the oxidation of ferrocenylacetic acid under similar conditions.

Direct confirmation of the existence of radical-chain oxidation route of ferrocenylcarboxylic acid is the inhibition of the process at adding ionol or *o*-phenylenediamine, regardless of the nature of the acid and the solvent (Fig. 2).

Thus, the oxidation of compounds **I** and **II**, as well as the oxidation of ferrocenylacetic acid or methyl ferrocenylacetate, should be regarded as a sequence of two macrostages. The first stage takes place along the molecular mechanism and can be regarded as the chain initiation stage, the second step is a radical chain process, and it makes a decisive contribution to the overall oxidation of the metallocomplex. It should be emphasized that the development of radical-chain route in the oxidation of ferrocene derivatives is entirely due to the presence of a substituent in the metallocomplex and its involvement in this process.

The primary product of oxidation of the ferrocenylcarboxylic acid and methyl ferrocenylcarboxylate in ethanol and mixed solvent dioxane–water (1:1) is the corresponding ferricenium cation, whose formation is detected by an absorption band with $\lambda_{max}$ = 625–627 nm in the electronic spectra of the reaction mixture immediately after the start of bubbling oxygen through it at $T$ = 50°C. The formation of the cation is also confirmed by the change of the color of the oxidized solution from orange-yellow to green, which is typical for ferrocenium ion. Over time, the ferrocenium ion undergoes a transformation with destruction of its structure, as evidenced by further change in solution color from green to brown and the simultaneous disappearance of the absorption band at 625 nm. In DMF the ferrocenium cation is much less stable than in ethanol and the dioxane–water solvent, and the green color of the cation appears only on the boundary of contact of the solution with oxygen. At the oxidation the solution becomes of brownish-red color. The products of oxidative degradation of the ferrocenium cation are cyclopentadiene, cyclopentadienone dimer, and a brown sludge, which contains a derivative of trivalent iron. In addition, it was found that the development of the process of ferrocenylcarboxylic acid oxidation leads to the formation of carbon oxide (**IV**), whose yield [$N(CO_2)$] varies depending on the nature of the solvent used: 0.25–0.3 in ethanol and DMF, and 0.12–0.15 in dioxane–water (1:1) mixture. The appearance of this product should be considered as a result of oxidative decarboxylation of ferrocenylcarboxylic acid.

The absence of new ferrocene derivatives among the products of oxidation of compound **I**, unlike the case of the oxidation of ferrocenylacetic acid, seems quite logical, given the nature of the substituent in the oxidized complex. In the products of oxidation of compound **II**, along with the products of oxidative degradation of the ferrocenium ion, we found trace amounts of new ferrocene derivative $C_5H_4FeC_5H_4C(O)C(O)H$, as well as methanol, CO and $CO_2$. At the oxidation of compound **II** in a dioxane–water (1:1)–$HClO_4$ solution ($c$ = 0.2 M) the $N$(CO) and $N(CO_2)$ values are 0.025 and 0.045, respectively, in mixed solvent dioxane–trifluoroacetic acid at the same concentration of $HClO_4$ ($c$ = 0.2 M), 0.06 and 0.1, respectively.

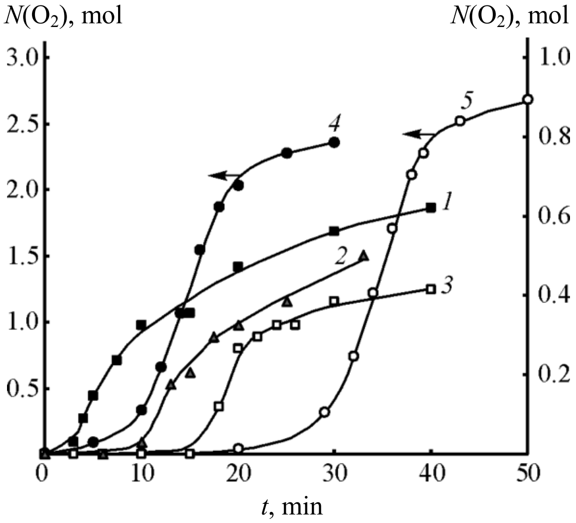


**Fig. 3.** The effect of inhibitor on the oxidation of compound **I** in dioxane (*1–3*) and dioxane–water mixture (*4*, *5*): (*1*, *4*) without the inhibitor, (*3*, *5*) with the addition of *o*-phenylenediamine, (*2*) with the addition of ionol. $c^0_{\rm I}$ = 0.01 M, $c_{\rm HX}$ = 0.2 M, $c^0_{\rm In}$ = $4\times10^{-4}$ M, $T$ = 50°C, $p(O_2)$ = $0.67\times10^5$ Pa.

The results of the study of kinetics of compounds **I** and **II** oxidation by an example of the former (Fig. 3) indicate that the initial reaction rate $W_0$ in DMF is proportional to the initial concentration of the metallocomplex and the oxygen pressure, indicating a first order process on the concentrations of each of these reagents.

The dependence of the reaction rate $W$ = $f[c^0(HClO_4)]$ in DMF is more complex, as illustrates Fig. 4: at low acid concentrations the concentration growth leads to a linear increase in reaction rate, which then slows down considerably with further increase in concentration of $HClO_4$, leading ultimately to the extreme nature of this dependence. In dioxane such a character of this dependence is even more pronounced, despite the much lower rate of the process in comparison with DMF (Fig. 4). The kinetic equation of oxidation of compound **I** in DMF at low concentrations of $HClO_4$ is as follows:

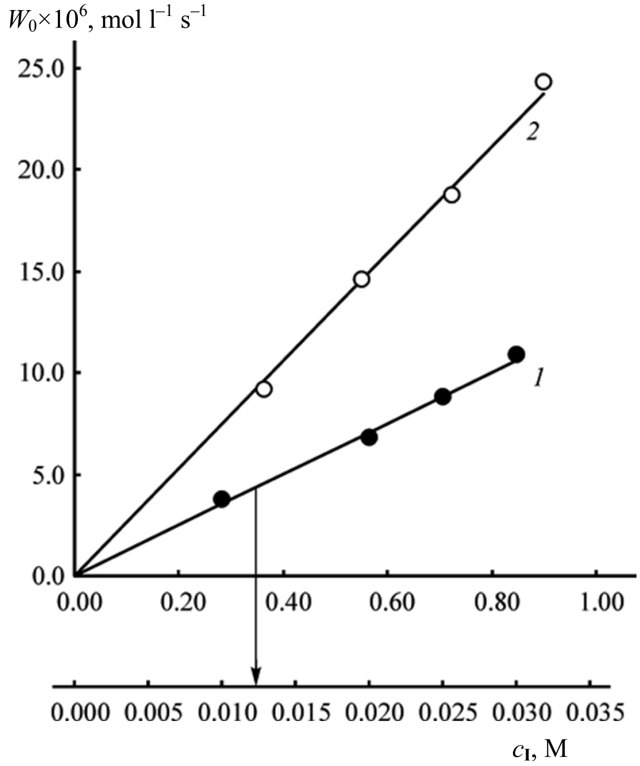


**Fig. 4.** The dependence of the rate of oxidation of compound **I** in DMF on the concentration of metal complex (*1*) and oxygen pressure (*2*). $c^0_{III}$ = 0.217 M, $p(O_2)$ = 0.66× $10^5$ Pa, $c^0_I$ = 0.05 M, $T$ = 50°C.

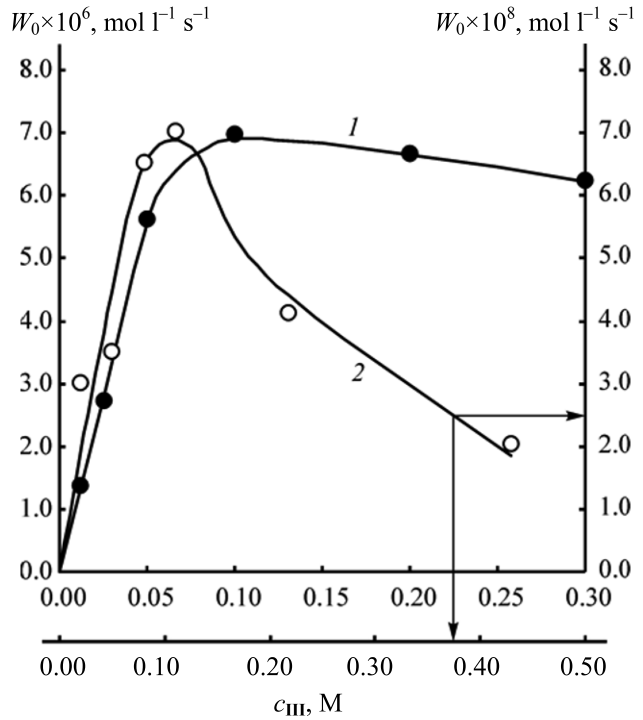


**Fig. 5.** Effect of concentration of acid **III** on the rate of oxidation of **I** in DMF (*1*) and dioxane (*2*). $c^0_I$ = 0.02 M, $p(O_2)$ = 0.66×$10^5$ Pa, (*1*) $T$ = 50°C, (*2*) $T$ = 60°C.

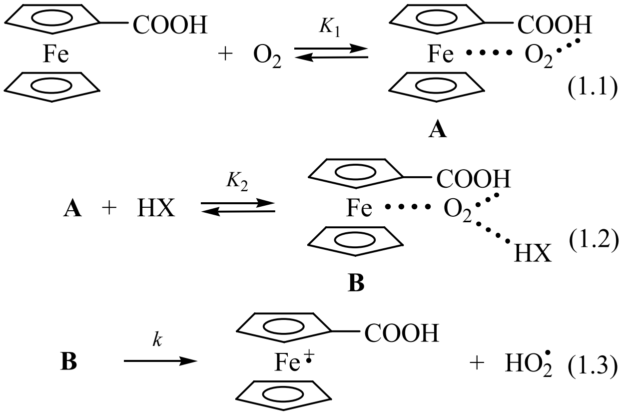
$$W = k_{\text{eff}}\,[\mathbf{I}]\,[\text{HX}]\,[\text{O}_2]. \tag{3}$$

We also found that the oxidation of compound **I** in dioxane in the presence of trifluoroacetic acid is described by a similar kinetic equation.

The results of these studies suggest that the kinetic Eq. (3) characterized mainly the radical-chain oxidation of compound **I**, since it was making a decisive contribution to the overall oxidation of the metal complex. In this regard, the molecular mechanism of oxidation of the latter is of interest, which should be considered as the chain initiation stage. Given the data obtained, the properties of reactants and certain analogy with the previously studied system of ferrocenylacetic acid–strong acid–$O_2$ we suggests two more or less probable mechanism of the ferrocenylcarboxylic acid oxidation, differing by the mode of coordination of the acid with the metallocomplex (Schemes 1 and 2)

As can be seen from Scheme 1, the carboxy group of ferrocenylcarboxylic acid does not undergo any transformations during the oxidation of the complex, although certainly it affects the process rate.

**Scheme 1.**



Hydrogen bonding between a molecule of $O_2$ and the carboxy group in the complex **A** helps to keep the oxidant in the coordination sphere of the iron atom and increases the equilibrium concentration of the oxygen adduct, but in the absence of a strong acid the latter is not reactive. At the oxidation of ferrocenylacetic acid, the formation of a similar complex with oxygen is already sufficient for the subsequent transformation to form the corresponding ferrocenium cation and HO$_2^{\bullet}$ radical [1]. The peroxide radical formed in the reaction (1.3) capable, in principle, of interacting with ferrocenylcarboxylic acid with the generation of the FcCOO$^{\bullet}$ radical (Fc = $C_5H_5FeC_5H_4$) and further, the Fc$^{\bullet}$ radical that initiates the chain of oxidation of the metallocomplex. Thus, the overall reaction of molecular oxidation of compound **I** can be represented by Eq. (4) and overall reaction of the chain initiation by the Eq. (5):

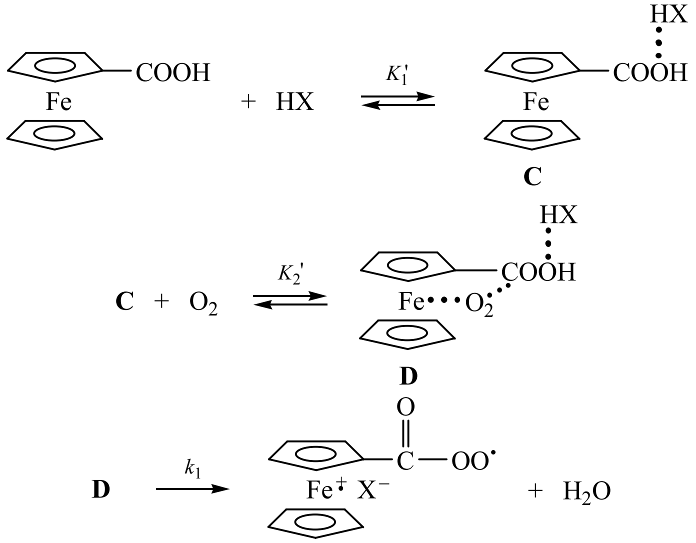
$$\mathrm{FcCOOH + O_2 + H^+ \rightarrow Fc^{+\cdot}COOH + HO_2^{\cdot}}, \quad (4)$$

$$\mathrm{2FcCOOH + O_2 + H^+ \rightarrow FcCOO^{\cdot} + H_2O_2 + Fc^{+\cdot}COOH}. \quad (5)$$

The possibility of reaction (4) is limited energetically: It is known that the analogous reaction with ferrocene is thermodynamically unfavorable because of the low standard redox potential of the system {$O_2 + H^+$}, equal to –0.13 V [7], while the value of the standard redox potential of ferrocene is 0.59 V [8]. Reaction (4) is energetically much less favorable, as the redox potential of FcCOOH must be substantially larger than 0.59 V.

Scheme 2 takes into account a possibility of coordination of the acid with reagents otherwise than in Fig. 1, which should lead to a different composition of the primary products of ferrocenylcarboxylic acid oxidation and thus to different values of the activation energy, as well as $\Delta_rH^0$ and $\Delta_rG^0$ for this process.

**Scheme 2.**



Scheme (2.1) accounts for the ability of carboxylic acids to easily undergo protonation at the action of strong acids. This protonation is a first stage of the whole process [9]. The protonation of the ferrocene derivatives with strong electron-withdrawing substituents at the metal atom usually does not occur, and only superacids can protonate it [10, 11]. In the complexes **C** the carbon atom of the carboxy group should be more electrophilic than in the free compound **I** due to the polarizing effect of the proton, and its affinity to oxygen should be higher in both neutral and reduced states. This provides a possibility of coordination of the $O_2$ molecule with this center [Eq. (2.2)], which will stimulate the transfer of electrons from the metal atom on the oxidant molecule. This stage is a part of a common synchronous process of transformation of the complex **D** in the reaction products, which is possible due to the presence of the conjugation chain between the elements of transformation in this complex.

Also the fact is noteworthy that the equilibrium in step (2.1) is reached instantly, and complex **C** reacts with $O_2$ as a bifunctional reagent having electron-donor (iron atoms) and electron-acceptor (COOH) reaction centers, whose conjugation through a molecule $O_2$ causes the described transformation of the complex **D**. This suggests a certain role of the effect of rapprochement in the orientation at the ferrocenylcarboxylic acid oxidation along the mechanism shown in Scheme 2, which leads, as is well known [12], to a gain in the activation entropy.

The overall reaction of molecular oxidation of ferrocenylcarboxylic acid in accordance with the Scheme 2 is described by Eq. (6) and the overall reaction of the chain initiation by Eq. (7):

$$\mathrm{FcCOOH + O_2 + H^+ \rightarrow Fc^{+\cdot}C(O)OO^{\cdot} + H_2O}, \qquad (6)$$

$$\mathrm{2FcCOOH + O_2 + H^+}$$

$$\mathrm{\rightarrow Fc^{+\cdot}C(O)OOH + H_2O + FcCOO^{\cdot}}. \qquad (7)$$

Comparing the energy of the reactions (5) and (7) to make a choice in favor of one of them is not possible due to the lack of the data on standard enthalpies of formation and absolute entropies of reagents that would allow the calculation of the values of $\Delta_r G_5^0$ and $\Delta_r G_7^0$. However, it is possible to compare estimated values of the Gibbs free energy for reaction (5) and (7), if subtract the equation for the first from that of the second to get the equation of the resulting reaction (8):

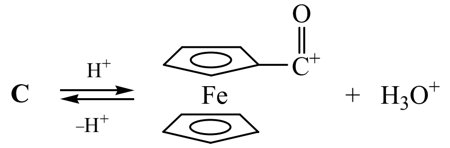
$$\mathrm{Fc^{+\cdot}COOH + H_2O_2 \rightarrow Fc^{+\cdot}C(O)OOH + H_2O}. \qquad (8)$$

The sign and value of $\Delta_r G_8^0$ allows us revealing which of the overall reactions and, therefore, which of the mechanisms (1) or (2) are thermodynamically more favorable: at $\Delta_r G_8^0 < 0$ they are the reaction (7) and mechanism (2) and vice versa. It is noteworthy that reaction (8) is analogous to the reaction of carboxylic acids with hydrogen peroxide catalyzed by strong acids [Eq. (9)], which is sufficiently well studied and is used to obtain the peracid formed with a yield of 90% [13].

$$\mathrm{RCOOH + H_2O_2 \overset{K_9}{\rightleftarrows} RC(O)OOH + H_2O}. \qquad (9)$$

The fact that in the reaction (9) the equilibrium is shifted toward the formation of peracids even in aqueous solutions containing $H_2O$ up to 70 wt % [13] shows that $K_{(9)} > 1$ and $\Delta_r G_9^0 < 0$. This conclusion can be quite reasonably extended to reaction (8). Then, if $\Delta_r G_8^0 < 0$, we can assume that mechanism (2) is more preferable than mechanism (1). This does not mean that $\Delta_r G_7^0$ is negative. Most likely, this is a positive quantity, as it is common for the $\Delta_r G^0$ of the chain initiation at the autoxidation of organic compounds in the absence of initiators [4].

The mechanism (2) can explain the observed dependence of the oxidation rate of ferrocenylcarboxylic acid on the concentration of perchloric acid (Fig. 4). At low concentrations of the latter only its coordination with ferrocenylcarboxylic acid occurs, leading to the formation of complex **A'**, resulting in a linear increase in the rate of oxidation of metal complex with increasing acid concentration. At sufficiently high concentrations of the acid the protonation of the carboxyl group of ferrocenylcarboxylic acid occurs leading to the formation acylium ion [9, 14]:



(10)

The carbocation in α-position to the Cp-ligand is a strong electron-acceptor, therefore the standard redox potential of the ferrocene with such a substituent is much higher than that of ferrocenylcarboxylic acid, and thus the protonated form is more resistant to oxidation. The stability of α-ferrocenylcarbonium ions with respect to $O_2$ has previously been shown in [10]. With increasing concentration of the acid the equilibrium in the reaction (5) is shifted to the right, that is, to increasing the equilibrium content of the carbocation, and thus to reducing the free ferrocenylcarboxylic acid concentration and its oxidation rate. The result of superimposing process (10) on the process of the ferrocenylcarboxylic acid oxidation, moreover, on both macrostages of the latter, is the observed dependence $W = f(c_{\mathrm{HX}}^0)$. Another reason for the deviation of $W = f(c_{\mathrm{HX}}^0)$ function from linear with increasing concentration of acids is the binding by the acid and also by the proton-donor solvents of peroxy radicals leading the oxidation chain into strong H-bond associates of the type $\mathrm{RO_2^{\cdot}\cdots HX}$, which are inactive in the chain propagation [4].

The $\mathrm{FcCOO^{\cdot}}$ radical formed at the oxidation of ferrocenylcarboxylic acid in the reaction (5) or (7) initiate further radical-chain oxidation of the metallocomplex. The absence among the oxidation products of new neutral ferrocene derivatives and sufficiently high yield of $CO_2$ indicate a certain specificity of this reaction among the radical-chain process (Scheme 3).

To verify the validity of the proposed mechanism, let us analyze the individual stages of this process, which, unfortunately, is only possible with model reactions. As a model of the substituted Cp-ligand $C_5H_4COOH$ we can take benzoic acid.

Reaction (3.1) is similar to the reaction of phenyl radicals with oxygen, which, according to [15], proceeds with a high rate (the rate constant of these reactions is close to the diffusion, 2–5×$10^9$ l $\mathrm{mol^{-1}}$ $\mathrm{s^{-1}}$

**Scheme 3.**

$$\left.\begin{aligned} &\mathrm{FcCOOH + O_2 + H^+} \\ &\xrightarrow{\mathrm{FcCOOH}} \mathrm{Fc^{+\cdot}C(O)OOH + H_2O + FcCOO^{\cdot}}, \\ &\mathrm{FcCOO^{\cdot}} \xrightarrow{\text{fast}} \mathrm{Fc^{\cdot} + CO_2}, \end{aligned}\right\} \quad (3.0)$$

$$\mathrm{Fc^{\cdot} + O_2} \xrightarrow{k_1} \mathrm{FcOO^{\cdot}}, \quad (3.1)$$

$$\mathrm{FcOO^{\cdot} + FcCOOH} \xrightarrow{k_2} \mathrm{FcOOH + FcCOO^{\cdot}}, \quad (3.2)$$

$$\mathrm{FcCOO^{\cdot}} \xrightarrow{k_3} \mathrm{Fc^{\cdot} + CO_2}, \quad (3.3)$$

$$\mathrm{FcOO^{\cdot} + FcCOOH} \xrightarrow{k_4} \mathrm{Fc^{+}COOH + FcOO^{-}}, \quad (3.4)$$

$$\mathrm{FcCOO^{\cdot} + FcCOOH} \xrightarrow{k_5} \mathrm{Fc^{+}COOH + FcCOO^{-}}. \quad (3.5)$$

[16]), and the arylperoxide radicals $PhOO^{\bullet}$ formed in the reaction are highly reactive towards various reagents. Reaction (3.2) is a key stage of the chain propagation, because just this step limits the rate of oxidation of ferrocenylcarboxylic acid by the radical-chain mechanism. The occurrence of such reactions is considered as a necessary condition for the decarboxylation of carboxylic acids under the influence of peroxide radicals, which takes place in the later stages of the radical-chain oxidation of organic compounds [4, 5]. As noted above, the reaction of this type is endothermic: $D_{\mathrm{PhC(O)O–H}} = 439$ kJ mol$^{-1}$, $D_{\mathrm{ROO–H}} \approx 365$ kJ mol$^{-1}$ [5], $\Delta_r H_1^0 \approx 74$ kJ mol$^{-1}$ for the reaction of PhCOOH with peroxide radical, and its activation energy, by definition, is greater than or equal to this value. Nevertheless, reaction (1) and the analogous reaction (3.2) occur, and their driving force should be the fast decarboxylation of the $PhCOO^{\bullet}$ ($FcCOO^{\bullet}$) radicals, which shifts the equilibrium in these reactions to the right. The reaction of the $PhCOO^{\bullet}$ radical decomposition has the following parameters: $k = 4.2\times10^6$ s$^{-1}$, $E = 39.3$ kJ mol$^{-1}$, $\Delta_r H_2^0 = 18.1$ kJ mol$^{-1}$ [17]. The free activation energy $\Delta G^{\#}$ must be less than the activation energy, since the $\Delta H^{\#} = E - RT$, and $\Delta S^{\#} > 0$, given the reaction nature. The Gibbs energy change in the reactions of $PhCOO^{\bullet}$ decomposition can be estimated by considering its entropy component $298\times\Delta_r S_2^0$. For similar reactions the value of $\Delta_r S_2^0$ can be taken as ~130 kJ mol$^{-1}$ K [18], which leads to $\Delta_r G_2^0(298) = -25.6$ kJ mol$^{-1}$. Extrapolation of these data on the reaction (3.3) of Scheme 3 suggests a high rate of its occurrence, the released energy can contribute to the compensation of the energy of bond cleavage $D_{\mathrm{FcC(O)O–H}}$ in the reaction (3.2).

Reactions (3.4) and (3.5) are regarded as the chain termination, since, firstly, the two peroxy radicals involved in the reaction of the chain propagation are strong one-electron oxidants, and they oxidize ferrocene and its derivatives with a high rate to the ferrocenium cation (in the case of peroxide radicals $RO_2^{\bullet}$, $k \approx 10^5$ l mol$^{-1}$ s$^{-1}$ [19], in the case of the radicals $RCOO^{\bullet}$ a priori $k$ must be greater than $10^5$ l mol$^{-1}$ s$^{-1}$) and; secondly, [FcCOOH] >> [$FcOO^{\bullet}$]. This allows to exclude from consideration the quadratic chain termination by the peroxide radicals.

The hydroperoxide FcOOH formed in the presence of acids **III** and **IV** is a strong oxidant. For example, for the oxidative system $\{H_2O_2 + H^+\}$ the standard redox potential is 0.72 V [7] and in the absence of $O_2$ it easily oxidizes ferrocenylcarboxylic acid to the ferrocenium cation that we has found by direct experiments. Reaction of FcOOH with ferrocenylcarboxylic acid reduces concentration of the peroxide in the reaction with $O_2$, which explains the relatively low yield of $CO_2$ in the process under the study.

$$\mathrm{FcOOH + FcCOOH + H^+ \rightarrow Fc^{+\bullet}COOH + FcO^{\bullet} + H_2O \rightarrow P},$$

where P denotes the products of oxidative degradation of ferrocenylcarboxylic acid.

Kinetic correspondence of the mechanisms (2) and (3) can be seen from the following reasoning. The rate of generation of radicals $Fc^{\bullet}$($w_0$) is limited by the rate of oxidation of molecular ferrocenylcarboxylic acid, which by all indications is significantly lower than the reaction rate of the metallocomplexes with the $Fc^{+}C(O)OO^{\bullet}$ radical. Applying the principle of quasi-equilibrium to the Scheme 2, we can show that

$$W_0 = k_1K_1'K_2'[\mathrm{I}][\mathrm{O_2}][\mathrm{HX}] = k_0[\mathrm{I}][\mathrm{O_2}][\mathrm{HX}], \quad (11)$$

where $k_0 = k_1K_1'K_2'$. If so, then by the kinetic analysis of Scheme 3 an equation can be derived for the rate of radical-chain oxidation of ferrocenylcarboxylic acid ($w_r$), which should be similar to the experimentally established kinetic equation (3). In accordance with the classical scheme of radical chain oxidation of organic compounds with oxygen [4] the investigated reaction rate $w_r$ will be equal to

$$w_r = k_2\,[\mathrm{I}]\,[\mathrm{FcOO^{\bullet}}]. \quad (12)$$

In the steady state

$$w_0 = w_t = k_4\,[\mathbf{I}]\,[\mathrm{FcOO^{\bullet}}] + k_5\,[\mathbf{I}]\,[\mathrm{FcCOO^{\bullet}}], \quad (13)$$

where $w_t$ is the rate of chain termination.

Applying the principle of stationarity to the radicals $FcOO^{\bullet}$ it can be shown that the concentration of the radical $FcCOO^{\bullet}$ is defined by Eq. (14).

$$[\mathrm{FcCOO}^{\cdot}] = \frac{k_2[\mathbf{I}][\mathrm{FcOO}^{\cdot}]}{k_3 + k_5[\mathbf{I}]}. \qquad (14)$$

At the concentration of the oxidized compounds $\mathbf{I} \leq 0.02$ M and $k_3 \geq k_5$ it can be assumed that $k_3 >> k_5[\mathbf{I}]$. Then

$$[\mathrm{FcCOO}^{\cdot}] = \frac{k_2}{k_3}[\mathrm{I}][\mathrm{FcOO}^{\cdot}] \qquad (15)$$

and the expression for the steady-state concentration of radicals $\mathrm{FcOO}^{\bullet}$ in accordance with Eq. (13) becomes:

$$[\mathrm{FcOO}^{\cdot}] = \frac{W_0}{k_4[\mathbf{I}] + k_5\dfrac{k_2}{k_3}[\mathbf{I}]^2} = \frac{k_0[\mathrm{O}_2][\mathrm{HX}]}{k_4 + k_5\dfrac{k_2}{k_3}[\mathbf{I}]}. \qquad (16)$$

Since $k_3 >> k_2$ and $k_4 >> k_2$, then $k_4 >> \mathrm{k}_5(k_2/k_3)[\mathbf{I}]$ and expression (16) is transformed into Eq. (17):

$$[\mathrm{FcOO}^{\cdot}] = \frac{k_0}{k_4}[\mathrm{O}_2][\mathrm{HX}]. \qquad (17)$$

From this follows that the rate of radical-chain oxidation of ferrocenylcarboxylic acid is described by Eq. (18):

$$W_\mathrm{p} = \frac{k_2 k_0}{k_4}[\mathbf{I}][\mathrm{O}_2][\mathrm{HX}], \qquad (18)$$

which fully corresponds to Eq.(3). Comparing these equations, we get that $k_\mathrm{eff} = k_2k_0/k_4 = k_2k'_1K'_1K'_2/k_4$.

Thus, kinetic compliance of the Schemes 2 and 3 confirmed by the results of this study suggests that these schemes together describe a single mechanism of oxidation of the ferrocenylcarboxylic acid.

The kinetics of the oxidation of compound **II** have not been studied, but a priori it can be argued that the mechanisms of molecular oxidation of the ferrocenylcarboxylic acid and its methyl ester are similar and lead to the formation of peroxide radicals $\mathrm{Fc}^+\mathrm{C(O)OO}^{\bullet}$. At the same time, the overall reaction of generating the radical leading the metallocomplex oxidation chain [Eq. (19)] differs from the reaction (7), since the radical-chain oxidation of compound **II** is associated only with the presence of a methyl group in the substituent

$$2\mathrm{FcC(O)OOCH_3} + \mathrm{O_2} + \mathrm{H^+} \rightarrow \mathrm{Fc^+C(O)OOH} + \mathrm{CH_3OH} + \mathrm{FeC(O)OCH_2^{\cdot}}. \qquad (19)$$

The probable mechanism of the radical-chain oxidation of compounds **II**, which explains the formation of the main reaction product can be represented by the Scheme 4.

**Scheme 4.**

$$\underset{(\mathrm{R}^{\cdot})}{\mathrm{FcC(O)OC^{\cdot}H_2}} + \mathrm{O_2} \rightarrow \underset{(\mathrm{RO_2^{\cdot}})}{\mathrm{FcC(O)OCH_2O_2^{\cdot}}}, \qquad (4.1)$$

$$\mathrm{RO_2^{\cdot}} + \mathrm{FcC(O)OCH_3} \rightarrow \mathrm{ROOH} + \mathrm{R^{\cdot}}, \qquad (4.2)$$

$$\mathrm{ROOH} \xrightarrow{\mathrm{H^+}} \mathrm{FcC(O)OC(O)H} + \mathrm{H_2O}, \qquad (4.3)$$

$$\begin{aligned}\mathrm{FcC(O)OCH_3} + \mathrm{RO_2^{\cdot}} &\rightarrow \mathrm{Fc^+C(O)OCH_3 \cdots OOR^-} \\ &\rightarrow \mathrm{Fc^+C(O)OCH_3 \cdots OH^-} + \mathrm{FcC(O)OC(O)H}, \qquad (4.4)\end{aligned}$$

$$\mathrm{RO_2^{\cdot}} + \mathrm{FcC(O)OC(O)H} \rightarrow \mathrm{ROOH} + \mathrm{FcC(O)OC^{\cdot}{=}O}, \qquad (4.5)$$

$$\mathrm{FcC(O)OC^{\cdot}{=}O} \xrightarrow[-\mathrm{CO}]{} \mathrm{FcC(O)O^{\cdot}} \xrightarrow[-\mathrm{CO_2}]{} \mathrm{Fc^{\cdot}}. \qquad (4.6)$$

Reactions (19) and (4.1–4.4) should be considered as the main stages of the radical-chain oxidation of methyl ferrocenylcarboxylate, reaction (4.5), (4.6), as the secondary stages. The radicals $\mathrm{FcC(O)OC^{\bullet}{=}O}$ and $\mathrm{Fc}^{\bullet}$ formed will react readily with $\mathrm{O_2}$ to give the corresponding peroxy radicals and then peroxyacid and hydroperoxide. Together with the hydroperoxide $\mathrm{R^1OOH}$ and $\mathrm{FcC(O)O^{\bullet}}$ radical they form a set of intermediates, which are strong one-electron oxidants, capable of readily oxidize under acidic conditions both the original metallocomplex and the newly formed ferrocene derivative FcC(O)OC(O)H to the corresponding cations subjected then to oxidative degradation to the known products. These reactions explain the low yield of the complex FcC(O)OC(O)H at the oxidation of methyl ferrocenylcarboxylate. The possibility of oxidation of the product to the mixed anhydride ferrocenylcarboxylic acid and carbonic acid, FcC(O)OC(O)OH, and the high probability of conversion of the latter with elimination of $\mathrm{CO_2}$ by reaction (20) explains the higher yield of $\mathrm{CO_2}$ compared with CO at the oxidation of methyl ferrocenylcarboxylate regardless of the nature of the acid.

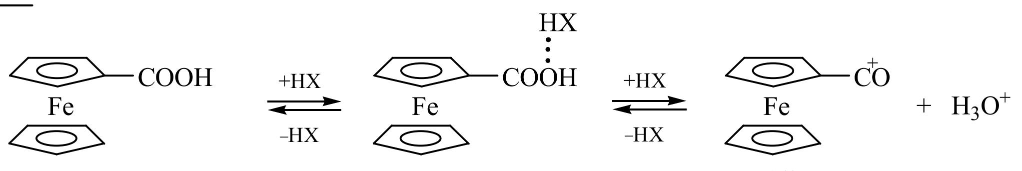
$$\mathrm{FcC(O)OC(O)OH} \rightleftarrows \mathrm{FcCOOH} + \mathrm{CO_2}. \qquad (20)$$

Thermoneutrality of this reaction, which can be seen by comparing the energy of cleaved and formed bonds during this reaction, stresses its equilibrium character.

From a comparison of the data on the oxidation of methyl ferrocenylcarboxylate and methyl ferrocenylacetate [2] it follows that the oxidation rate of the second complex is more than by two orders of magnitude higher than tha of the first under the same reaction conditions. This difference in the rates of oxidation almost completely corresponds to the difference in energies of the C–H bonds in the methylene and methoxy groups that determine the rate constant for the limiting stage of the process (21) during the oxidation of RH (RH is a conventional reagent) [20]

$$RO_2^{\bullet} + RH \rightarrow ROOH + R^{\bullet}. \qquad (21)$$

Finally we consider the reasons for the unusually low rate of oxidation of the ferrocenylcarboxylic acid and methyl ferrocenylcarboxylate in dioxane in the presence of $HClO_4$. As pointed out above, there is an equilibrium of reactive (**A'**) and inert (**IA**) toward $O_2$ forms of intermediates arising during the interaction of ferrocenylcarboxylic acid (or methyl ferrocenylcarboxylate) with an acid HX in relation to:



**A' = C** **A''** (22)

Coordination of intermediate **A'** with a molecule of $O_2$, when the latter occupies a bridging position between the iron atom and the electrophilic carbon atom of the carboxy group, leads to further oxidation of the metal complex, as shown in Scheme (2). Dioxane, being a stronger electron donor compared with a molecule of $O_2$, would form a more stable complex with the intermediate of **A'** through the same carbon atom and thereby block the access of oxygen to it, inhibiting the oxidation process as a whole and promoting the formation of carbocation, stabilizing it. It is no coincidence that for the generation of α-ferrocenylcarbenium ions the most commonly either concentrated acids, or their solutions in dioxane are used [10]. For example, ferrocenylmetanol is easily protonated with perchloric acid to α-ferrocenylcarbenium ion in dioxane. In DMF this complex is not actually protonated. It is not excluded that the degree of protonation of **I** in dioxane is significantly higher than in DMF that explains in principle the large difference in the rates of oxidation of the metal complex in these solvents (Fig. 4). It should be noted that in general dioxane tends to give stable adducts with various substances [21].

The formation of such a complex between the intermediate **A'** and ethanol is difficult, since the latter is prone to self-association with the formation of linear multimers [21]. Therefore, the overall rate of oxidation of ferrocenylcarboxylic acid and methyl ferrocenylcarboxylate in ethanol is higher than in dioxane irrespective of the nature of the acid primarily due to the higher rate of initiation of radicals in the molecular oxidation of the metallocomplexes, although alcohol is known to be able to inhibit the radical-chain oxidation of organic compounds [4]. In dioxane this rate seems so low that the radical-chain oxidation of metal actually does not develop. Dilution of dioxane with water (1:1) binds it to the H-bond complex and increases the medium dielectric constant. Both these factor contribute to the reaction of molecular oxidation of ferrocenylcarboxylic acid and methyl ferrocenylcarboxylate and the development of radical-chain route of oxidation. The formation of H-bond complexes between ferrocenylcarboxylic acid (methyl ferrocenylcarboxylate) and ethanol or water in the mixed solvents dioxane–water or DMF–water impeding the formation of intermediate **A'** may be the cause of the induction period on kinetic curves of oxidation of the metallocomplexes in these solvents. A more valid explanation of the nature of the solvent effect on the oxidation of metal complexes under study can be done after a more detailed study of these processes.

## EXPERIMENTAL

The oxidation of compounds **I** and **II** was performed on a static vacuum apparatus at vigorous stirring the reaction mixture. The reaction was monitored by registering the oxygen absorption with a pressure gauge.

Compound **I** was synthesized according to [22] and purified by double recrystallization from a mixture of toluene and ligroin (1:1). The metallocomplex is provided by Sinor Ltd. Compound **II** was obtained by the reaction of compound **I** with diazomethane [23] immediately before the oxidation.

Analysis of the metal complexes during oxidation and the oxidation products was performed by gas chromatography–mass spectrometry. For analysis a Crystall 5000.1 chromatograph (Chromatec) was used coupled with a mass spectrometer TRACE DSQ (Termo Finnigan): column RTX-5MS, $T_{\text{init}}$ = 110ºC, keeping 1 min, heating at a rate 15ºC min$^{-1}$ to 250ºC, the total analysis duration 30 min, $T_{\text{vap}}$ = 250ºC, the split ratio 1:30, the sample volume 1 µl, scan time 30 min, scan range 50 to 500 atomic mass units multiplication factor 3, scaning frequency 5 scans per sec, the electrons energy 70 eV.

The gaseous products, CO and $CO_2$, were analyzed by GLC on a Tsvet-100 chromatograph with the DIP detector; column: $l$ = 0.5 m, $d$ = 4 mm, sorbent charcoal (SKT), carrier gas argon, $T$ = 90°C, reactor temperature $T_{\text{cat.reactor}}$ = 450°C.

Electronic spectra of the reaction mixtures were taken on a spectrophotometer UV-1700 (Shimadzu) in the range of 250–750 nm.

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