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Conditions for Manifestation of Approachment and Orientation Effect at the Oxidation of Ferrocenylacetic Acid and Its Methyl Ester by Molecular Oxygen in Organic Solvents

V. M. Fomin and A. E. Shirokov

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

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Abstract—By comparison of reactivity of the ferrocene derivatives differing in the nature of the substituents the conditions were revealed of their participation as Brønstedt and Lewis acidic centers in the process of the metallocomplex molecular oxidation with oxygen in terms of manifestations of the effects of rapproachment and orientation. From this standpoint were analyzed the experimental data obtained in the oxidation of methyl ferrocenylacetate. A probable mechanism of the process is proposed that includes the molecular and radical-chain macro steps.

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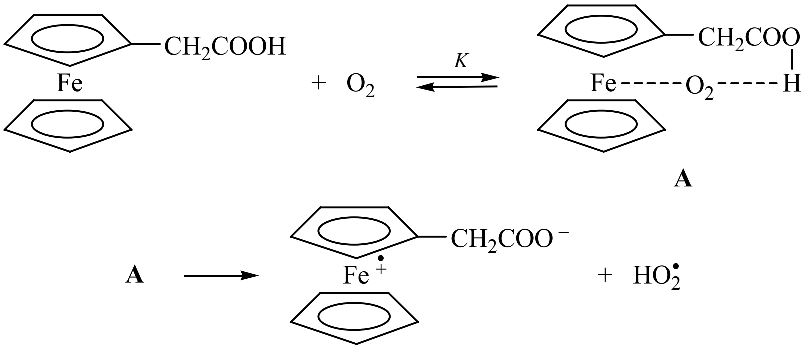
It is known that ferrocene can be oxidized in a solution by molecular oxygen, but only in the presence of a strong Brønsted acid [1, 2]. The known characteristic of ferrocenylacetic acid (**I**) is abnormally high reactivity toward O_2 as compared not only with ferrocene, but also with a model system Cp_2Fe + RCOOH, where RCOOH is a carboxylic acid of the strength comparable with that of **I** ($pK_a \approx 5$) [3, 4]. This is manifested in the ability of ferrocenylacetic acid to be readily oxidized by oxygen at 20–50ºC in low-polar solvents such as dioxane, in the absence of any additional acid. Under the same conditions a model system remains unchanged for a long time. The analysis of the causes of this phenomenon has led us [5] to the conclusion that it is based on the ability of compound **I** to act as a bifunctional reagent in the reaction with O_2, as shown in Scheme 1.

This scheme is a revised version [5] of the previously suggested scheme of oxidation of molecular compound **I** [4] and takes into account only one route of complex **A** transformation leading to the formation of internal ferricenyl salt and the radical $HO_2^{\bullet}$, which initiates the radical-chain oxidation of the complex. The oxidation of compound **I** in accordance with Scheme 1 leads to a substantial gain in entropy of

Scheme 1.



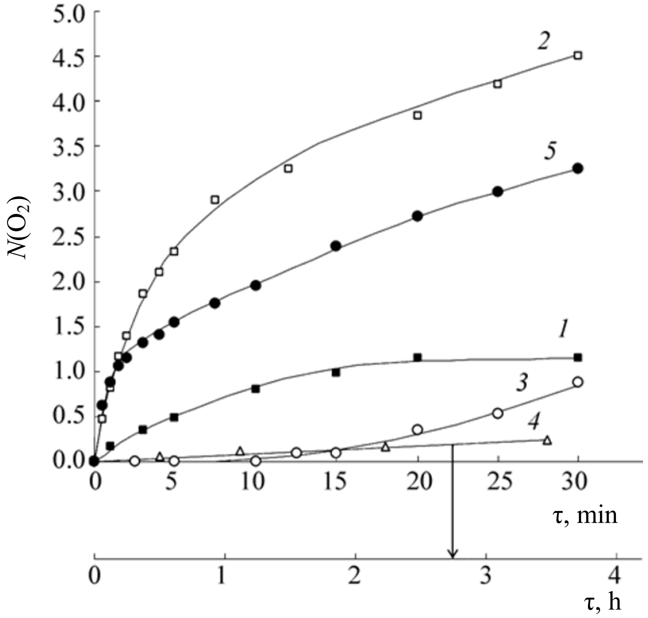


Fig. 1. Comparative kinetic curves of oxidation of compounds (*1*, *2*) **I** and (*3–5*) **II** in dioxane at $T = 50°C$ and $p(O_2) = 4\times10^4$ Pa: (*1–3*) no acid, (*2*, *5*) in the presence of acid **III**, (*4*) in the presence of acid **IV**, $C^0_{\mathrm{I,II}} = 0.005$, $C^0_{\mathrm{III,IV}} = 0.05$ M.

activation and thus to a decrease in the free activation energy compared with the activation parameters at the ferrocene oxidation in the model system, in which the same reaction centers belong to different molecules, as is shown in the following equation:

$$\mathrm{Cp_2Fe + O_2 + RCOOH \rightarrow Cp_2Fe^+ + HO_2^{\bullet} + RCOO^-}$$

In the reactions involving multifunctional enzyme systems such gain in free activation energy, which can reach 10–11 kcal $\mathrm{mol^{-1}}$ [6], is known as a manifestation of the rapproachment and orientation effect.

In this connection it is interesting to perform a comparative analysis of the oxidation features of compound **I** and its methyl ester **II** under the same conditions. Replacing the hydroxy groups by methoxy one affects slightly the electron-acceptor properties of substituent in the metal complexes ($\mathrm{–CH_2COOH}$ and $\mathrm{–CH_2COOCH_3}$ both are weak electron-acceptors [7]), but compound **II** loses the ability to coordinate a molecule of O_2 by the way characteristic of compound **I**. It certainly should affect the compound **II** reactivity and the mechanism of its interaction with oxygen as well.

Figure 1 shows the comparative kinetic curves of oxidation of compounds **I** and **II**. Hereinafter, $N(O_2)$ is the amount of the oxygen absorbed in the reaction mixture per 1 mol of the taken metallocomplex. It is evident from Fig. 1 that the replacement in the compound **I** of the hydroxy substituent by the methoxy group reduces significantly the reactivity of the metallocomplex with respect to oxygen under these conditions. The rate of oxidation of compound **II** significantly increased in the presence of a Brønsted acid, therewith the positive kinetic effect of the latter depends on the acid strength: the effect of trifluoroacetic acid (**III**, $\mathrm{p}K_\mathrm{a} = 0$) is significantly higher than that of benzoic acid (**IV**, $\mathrm{p}K_\mathrm{a} = 4.2$). It should be noted that the addition of acid **III** leads also to strong acceleration of the oxidation of compound **I**, whereas acid **IV** taken in the same ratio to compound **I** has no influence on this process, like in the oxidation of compound **II** [8].

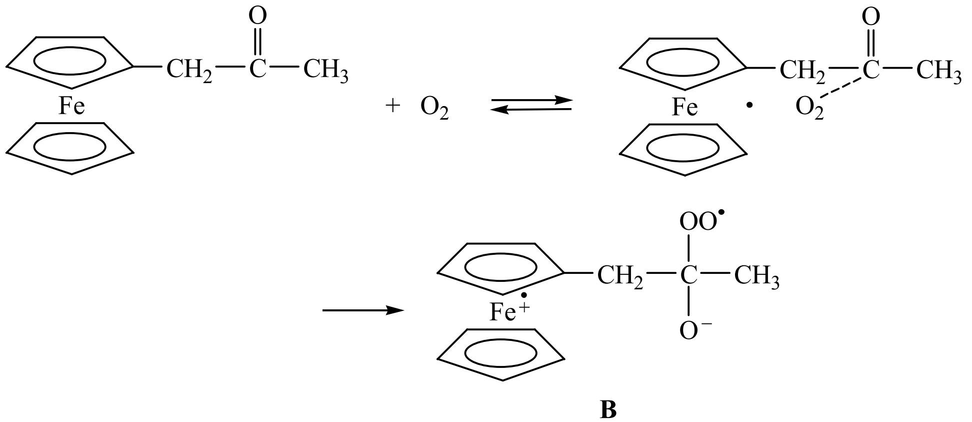
Such a large difference in the rates of oxidation of compound **II** and **I** in the absence of acids confirms the mechanism of oxidation of the latter described by the Scheme 1 and strongly suggests that it is the effect of rapproachment and orientation which determines the high reactivity of this compound with respect to oxygen.

As is known, also another complex, the ferrocenylacetone (**V**), shows an abnormally high reactivity toward O_2 in comparison with ferrocene: It is readily oxidized at room temperature to diketone $\mathrm{C_5H_5Fe{\cdot}C_5H_4C(O)C(O)CH_3}$ in the absence of acids [9]. Like the case of the oxidation of compound **I**, the reason for this, in our opinion, is the participation of the substituent in the oxidation of complex **V** due to the presence of electrophilic carbon atom of carbonyl group, as shows Scheme 2.

The electron transfer from the metal atom to the O_2 molecule driven by bonding of the latter with the electrophilic carbon atom converts O_2 into a nucleophile (in the limit, this is $O_2^{\bullet-}$) which is strong enough for adding to the carbonyl group.

The formed peroxide radicals can initiate radical-chain oxidation of compounds **V** to the above α-diketone. We found that in a model system $\mathrm{Cp_2Fe–O_2–CH_3CH_2C(O)CH_3}$ [$C^0(\mathrm{Cp_2Fe}):C^0(\mathrm{C{=}O}) = 1:10$] the oxidation of the complex with an appreciable rate does not occur for a long time. Compound **V**, like compound **I**, behaves as a bifunctional reagent that makes possible the manifestation of rapproachment and orientation effect in the process of molecular oxidation.

Scheme 2.



B

Based on the above it would be expected that compound **II** could in principle be oxidized in accordance with the Scheme 2, as its substituent also contains electrophilic carbon atom of carbonyl group which is not in conjugation with the Cp ligand being separated from it by the methylene fragment, like the carbonyl group in compound **V**.

In addition, due to this position of carbonyl group the *–I* (inductive) effect of the substituents in the compared compounds is reduced to almost zero [10], which acts in favor of reducing their standard redox potentials. In fact, oxidation of compound **II** proceeds very slowly. This suggests that for a substantial increase in reactivity of the ferrocene derivatives with respect to oxygen due to the effect of rapproachment and orientation it is necessary that several conditions were fulfilled:

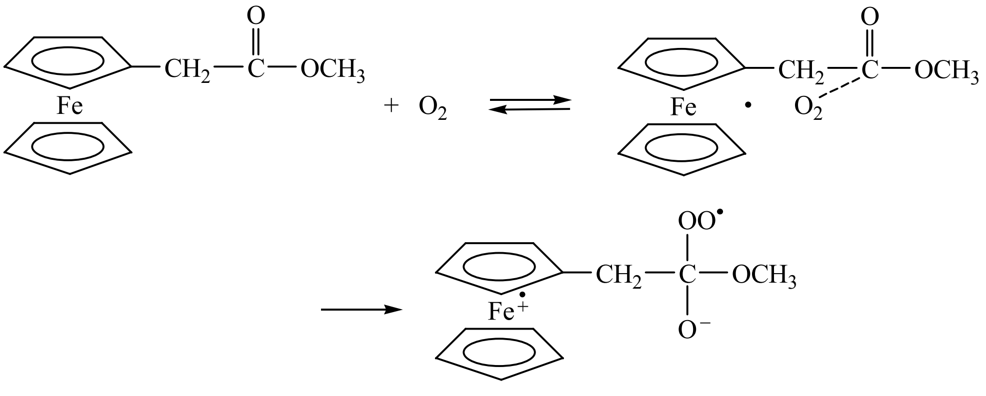
(1) The molecular reaction of the metal complexes with oxygen should not be forbidden thermodynamically. Such forbidding would make impossible the reaction course that includes generation of radicals. To confirm this statement, we compare reactivity of the compounds in the following pairs: (a) complex **I,** ferrocenylcarboxylic acid **VI**, (b) complex **V,** acetylferrocene **VII**. The substituents in compounds **I** and **V** are characterized by nearly zero *–M* (mesomeric) and *–I* effects [10]. In contrast, the substituents in compounds **VI** and **VII** show strong *–M* and *–I* effects. This is a significant, if not the main, reason for the oxidative stability of the latter two compounds, which can be oxidized only in the presence of strong Brønsted acids [11]. Note that the values of standard Gibbs free energy $\Delta_r G^0$ for the reactions of molecular oxidation of compounds **I** and **V** certainly are larger than zero (being evaluated from the standard redox potentials of reagents), but they apparently are not large enough to prevent these reactions completely.

(2) The ability of electron-acceptor center of substituent to coordinate the oxygen molecule, locate it in the bridge position between this center and the metal atom. Such coordination should provide a high stationary concentration of the adduct with oxygen and facilitate the electron transfer from the metal atom to the oxygen. Either Brønsted, or Lewis acid center can act as the coordination center.

(3) The high reactivity of the electron-acceptor center of substituent toward the reduced form of the oxygen. The fact of conjugation of the electron-donor (metal atom) and electron-acceptor centers of the metallocomplex through the O_2 molecule allows an assumption that the stage of electron transfer to O_2 and subsequent interaction of the reduced form of the latter with Brønsted or Lewis acidic center occur as a single synchronous process. In this case the maximum compensation of energy consumed in the step of electron transfer can be achieved, and the formation of relatively stable reaction intermediates. This will work in favor of reducing the activation energy of the reaction making the reaction energetically more favorable. The above Schemes 1 and 2 of oxidation of compounds **I** and **V** are based on the conditions (1)–(3).

It should be noted that the products of molecular oxidation of both metallocomplexes are internal ferricenyl salts with the cation and anion stabilizing each other, which leads to an additional energy gain. In nonpolar solvents the stabilization energy of the ion pair by electrostatic interactions can reach 90–100 kJ mol^{-1} [12]. The reason for the low reactivity of compound **II** compared with **I** is obvious: the methoxy group does not possess the properties of a Brønsted center in the reaction with O_2. Therefore, in terms of condition 3 it is important to understand the reasons for the large difference in the reactivity of compounds **II** and **V**, while both include substituents posessing electrophilic carbon atom of the carbonyl group located in the β-position to the Cp-ligand, and their inductive and mesomeric effects differ little [7, 10]. From the thermodynamic and kinetic points of view, the preference in molecular oxidation of compound **V** over **II** is likely based on the difference in the reactivity of the carbonyl group in these compounds with respect to the reduced form of the oxidizer, and the stability of the intermediates formed, which, naturally, differ by nature. It is known [13] that carbonyl group in esters is stabilized due to the mesomerism, and its reactivity is considerably lower compared with ketones. For this reason, electrophilicity of carbonyl carbon atom and its affinity for the neutral and reduced form of O_2 molecules are lower in compound **II** than in **V**. In the tetrahedral intermediates formed at the addition of nucleophilic species to esters such stabilization is not the case. Therefore, their formation is energetically unfavorable and they are so labile that cannot be isolated, in contrast to related products derived from ketones. Suggesting that the reaction of oxidation of compound **II,** like the oxidation of compound **V,** proceeds by Scheme 3, we have to conclude that despite the formal similarity in the structure of intermediates **B** (Scheme 2) and **C** (Scheme 3), the latter intermediate certainly must be much less stable, which leads to a certain kinetic and thermodynamic ban on the oxidation of compound **II**.

Scheme 3.



C

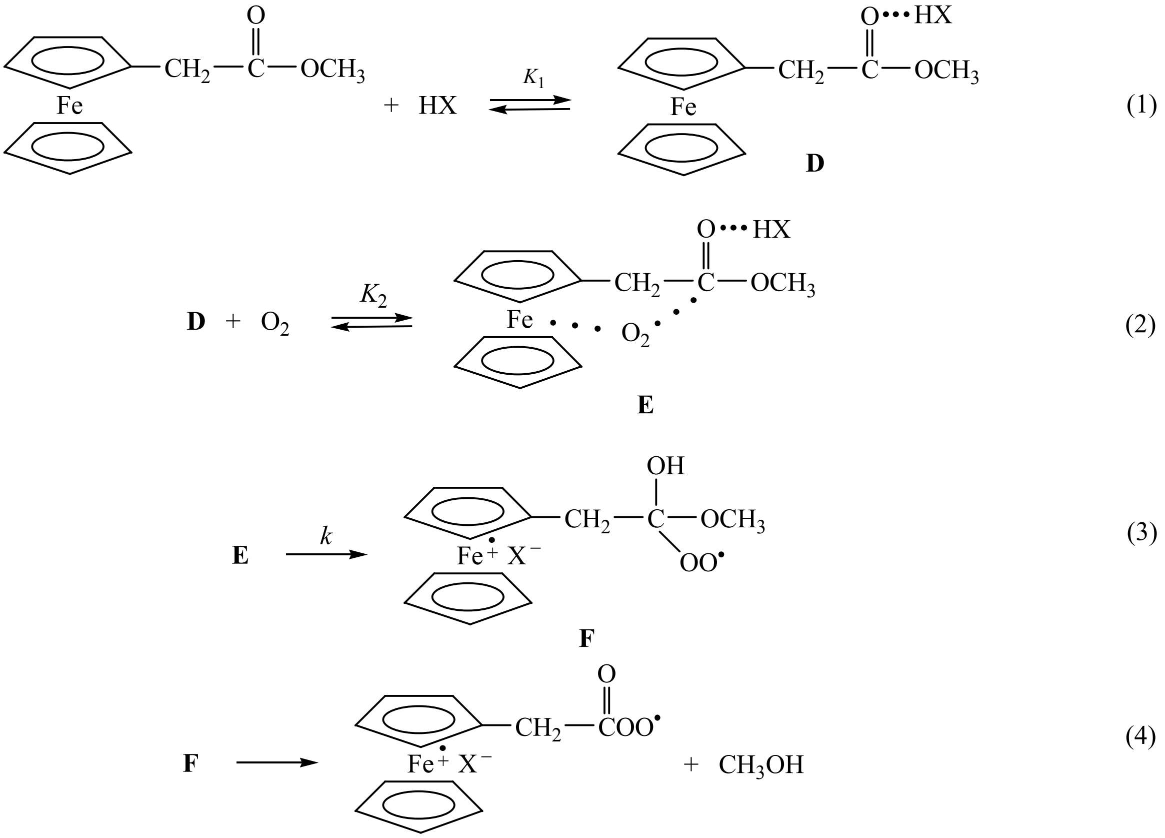
(4) Favorable steric factors that depend both on the size and configuration of the oxidant and its reduced form, as well as its accessibility to the metal atom and the coordination center of the substituent. Naturally, the more pronounced steric hindrance in the transition state, the less favorable the latter is energetically and is realized more difficultly. For the compounds containing a carbonyl group as a reaction center, this is particularly relevant [13].

From this viewpoint, it becomes clear why acid **III** shows strong accelerating effect on the oxidation of compounds **I** and **II**. An acid may be involved in the oxidation of metal not only as the agent, but also as a catalyst accelerating addition of nucleophilic species to the carbonyl group of organic compound [13]. The reaction takes place either through the stage of protonation of the carbonyl group, or through a stage of formation of hydrogen bond between it and the acid. In both cases the positive charge on the carbonyl carbon atom, and hence its electrophilicity, increase, favoring addition of the nucleophilic species. The mechanism of oxidation of compound **II** in this case can be represented by Scheme 4.

Although the participation of HX can contribute to oxidation of compound **II**, as shown in Scheme 4, nevertheless, the reaction course through the formation of a highly labile complex **F**, which must be considered as limiting step, makes this route very problematic from the energetic viewpoint.

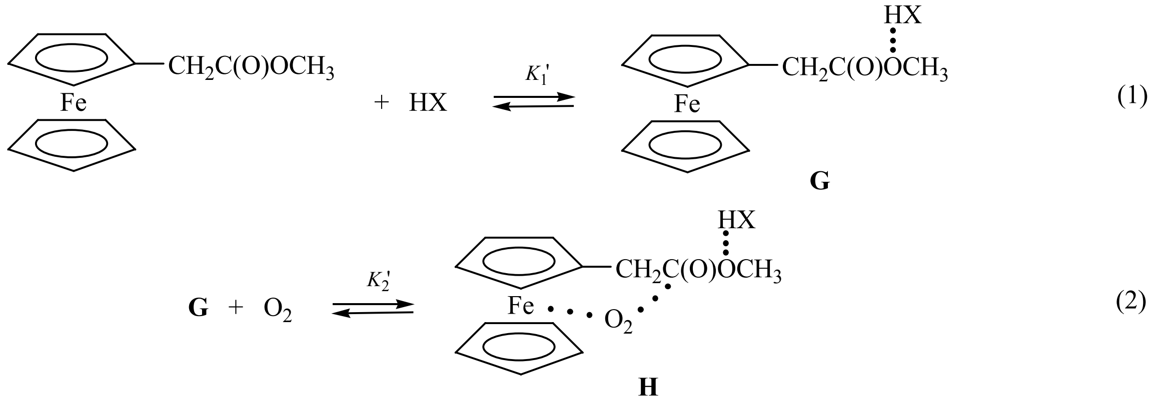
It should be emphasized that, anyway, the participation of acid in the oxidation of metal complex makes the route more favorable thermodynamically,

Scheme 4.

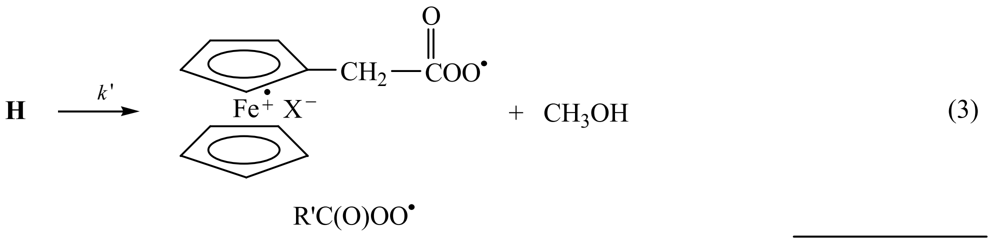


due to the increase of the standard redox potential of oxygen [14]. We must however take into account the kinetic aspect of the influence of acid on the course of the process, which is associated with the mechanism of its participation, influencing activation parameters of the process. The coordination of acid with compound **II** through the carbonyl group (Scheme 4) is typical for aldehydes and ketones. With carboxylic acid or ester, the HX coordination can occur through the oxygen atom of the hydroxy or alkoxy group, which takes place at the protonation of these compounds by a strong acid [15] or at the hydrolysis of esters [16]. This mode of coordination of acid **III** with compound **II** can occur also at the oxidation of the latter (Scheme 5).

Scheme 5.



Scheme 5. (Contd.)

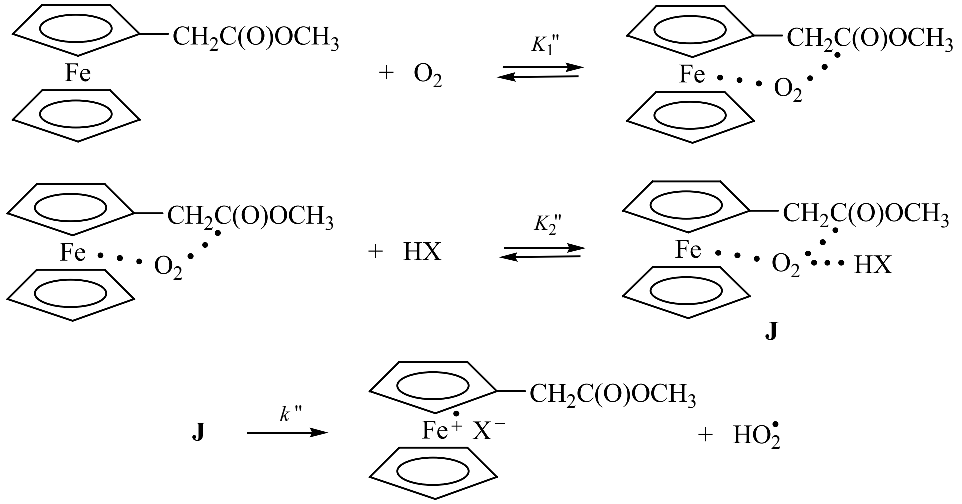


From the viewpoint of thermodynamics and kinetics, the mechanisms shown in Schemes 4 and 5 are indistinguishable, since in both cases the process rate is described by the equation $W_0=k_0[\mathbf{II}][O_2][HX]$, where k_0 is equal to $k_1K_1K_2$ or $k'_1K'_1K'_2$, which can be shown using a principle of quasi-equilibrium [17]. Nevertheless, the mechanism in Scheme 5 seems preferable, since the oxidation of compound **II** to the same products as in the Scheme 4 proceeds bypassing the stage of formation of the labile intermediate **F.** This route is shorter and kinetically more favorable if we compare the activation energy in the limiting steps [Scheme 4, Eq. (3)] and [Scheme 5, Eq. (3)]. Note also that hydrogen complexes **D** and **G**, reaching equilibrium concentrations instantaneously, react with O_2 as bifunctional reagents. This suggests a possibility of manifestation in these cases of the effect of rapproachment and orientation, since the preliminary coordination of compound **II** with the acid formally leads to a decrease in reaction order and hence to a gain in the activation entropy. For comparison, if the oxidation of compound **II** proceeds in accordance with Scheme 6 which does not include coordination of the acid with the metallocomplex, the manifestation of the effect of rapproachment and orientation is excluded.

Clearly, this mechanism differs from that in Scheme 5 both by the value of Δ_rG^0 for the overall reaction and the activation parameters of the limiting step of the process. Unfortunately, it is impossible to compare the energy of these two processes due to the lack of necessary data. Note that complex **H** is more preferable than complex **J** from the viewpoint of the hydrogen bond energy.

In accordance with Schemes 4 and 5, the oxidation of molecular compound **II** in the presence of acids HX should lead to the formation of peroxide radicals $C_5H_5\overset{\bullet}{Fe}{}^{+}C_5H_4CH_2C(O)OO^{\bullet}$, which can initiate radical-chain oxidation of the metallocomplex. This is demonstrated indirectly by the high rate of oxidation of compound **II** in the presence of acid **III**, which is comparable with the rate of oxidation of compounds **I** under similar conditions, and by high consumption of oxygen per 1 mol of oxidized compound **II** [$N(O_2)$] (Fig. 1). Earlier we showed that the radical-chain path contributes predominantly to the whole process of

Scheme 6.



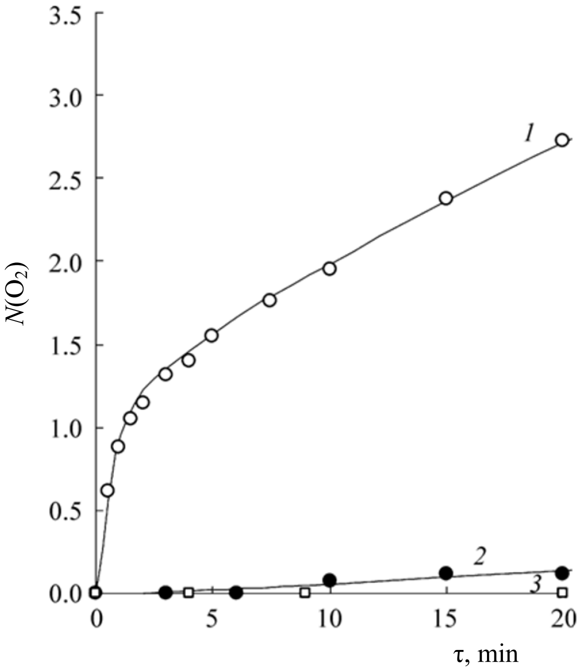


Fig. 2. Oxidation of compound **II** in (*1, 2*) dioxane and (*3*) ethanol in the presence of acid **III** at T = 50°C and $p(O_2) = 4.1\times10^4$ Pa: (*1*) no inhibitor, (*2*) in the presence of o-phenylenediamine (In); $C^0_{\rm II}$ = 0.005, $C^0_{\rm III}$ = 0.05, $C^0_{\rm In}$ = 2.5×10^{-4} M.

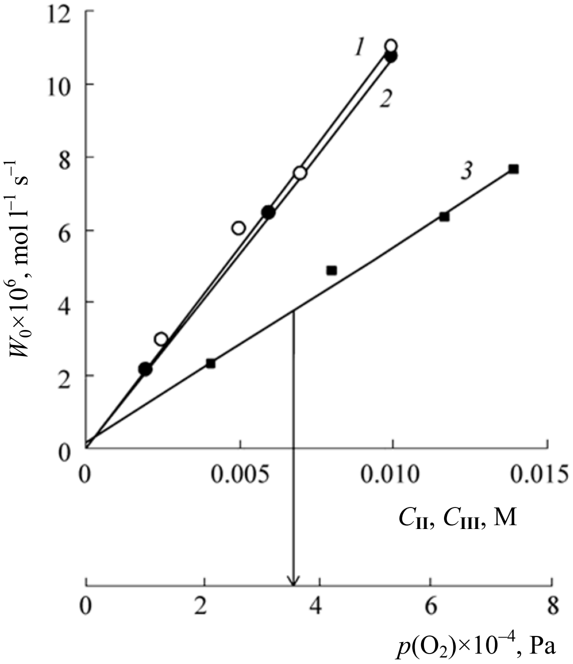


Fig. 3. Dependence of the initial rate of oxidation of compound **II** on the concentration of (*1*) complex and (*2*) acid, and on the oxygen pressure, at T = 50°C: (*1*) $C^0_{\rm III}$ = 0.01 M, $p(O_2) = 4.1\times10^4$ Pa; (*2*) $C^0_{\rm II}$ = 0.01 M, $p(O_2) = 4.1\times10^4$ Pa; (*3*) $C^0_{\rm II}$ = 0.005 M, $C^0_{\rm III}$ = 0.01 M.

interaction of O_2 with metal at the oxidation of compound **I** in the presence of acid **III** [5].

To verify the validity of the assumptions made above and to show that the rate of oxidation of the molecular compound **II** in the presence of acid **III** is described by the equation $W_0 = k_0[\mathbf{II}][O_2][HX]$, we have studied the kinetic regularities of the reaction and the composition of the products. Besides, it was interesting to compare the compositions of the main products of the compound **II** oxidation in the presence and absence of acid **III**. The comparison of the kinetic regularities of these processes presents some difficulties due to the low reaction rate in the latter case.

We found that as in the case of oxidation of compounds **I**, the radical chain route contributes mainly to the overall oxidation of compound **II**. This is confirmed by several observations. Firstly, the inhibition of the oxidation at adding *o*-phenylenediamine, known as an effective inhibitor of radical chain reactions (Fig. 2). Secondly, the inhibitory effect of ethanol on the rate of oxidation of compound **II**, up to virtually complete suppression of the process when ethanol is used as the solvent instead of dioxane (Fig. 2), explainable by the ability of alcohol to deactivate peroxide radicals binding them to low reactive hydrogen complexes and thus suppresing the chain propagation [18]. Thirdly, if the oxidation is carried out in methyl methacrylate, the latter is polymerized. Previously, similar effects of *o*-phenylenediamine, ethanol and methyl methacrylate were observed at the oxidation of compounds **I** [5], ferrocenylmetanol, and ethyl ether of the latter [19].

The results of the study of the kinetic regularities of the compound **II** oxidation in dioxane in the presence of acid **III** indicate that the process is described by the kinetic equation of first order with respect to the initial concentrations of the metallocomplex, oxygen and acid. This follows from the linear increase in the initial rate W_0 of the compound **II** oxidation with increasing concentration of any of these reagents (Fig. 3).

Analysis of the composition of the reaction products indicates that the radical-chain oxidation of compound **II** in the presence of acid **III** leads to the formation of other ferrocene derivatives, namely methyl ferrocenylpiruvate $C_5H_5FeC_5H_4C(O)C(O)OCH_3$ **VIII**, which, judging from the results of the analysis, is the main product, and formylferrocene **IX**, formed in

2–3% yield. In addition to compounds **VIII** and **IX** methanol, H_2O, CO, and CO_2 were found as well as products of oxidative degradation of compound **II:** cyclopentadiene, cyclopentadienone dimer, and a resinous residue containing Fe^{3+}. Yield of methanol could not be determined accurately. The maximum yields of CO and CO_2 [$N(O_2) \approx 4$] are 0.07 and 0.35 mol, respectively, per 1 mol of the oxidized metallocomplex.

The oxidation of compound **II** in the absence of an acid leads wholly to the products of the same composition as in the presence of acid **III**. The main products are also complexes **VIII** and **IX**. But also methyl ferrocenylhydroxyacetate $C_5H_5FeC_5H_4CH(OH)C(O)OCH_3$ **X** was found**,** albeit in a small quantity. The formation of **X**, as well as the formation of the complex **VIII**, suggests that the radical-chain oxidation of the initial metallocomplex affects only methylene group. This is quite natural, since the energy of the C–H bond in a group associated with aromatic ring, such as the Cp ligand, is known [20] to be by over 70 kJ mol^{-1} less than in the methyl ester group $RC(O)OCH_3$. In accordance with the results obtained and the generally accepted scheme of radical-chain oxidation of hydrocarbons [18], the probable mechanism of radical-chain oxidation of compound **II** reflecting its main stage and explaining the composition of the reaction products can be represented by scheme (7). As a radical R leading the chain in the initial stage of the process the radical $C_5H_5FeC_5H_5C^{\bullet}HC(O)OCH_3$ is considered formed in the reaction of peroxide radicals $C_5H_5\overset{\bullet}{Fe}{}^{+}C_5H_5CH_2C\cdot(O)OO^{\cdot}[R'C(O)OO^{\cdot}]$ generated in accordance with the Scheme 5 with the compound **II** to be oxidized.

Scheme 7.

$$R'C(O)OO^{\bullet} + \mathbf{II} \longrightarrow R'C(O)OOH + R^{\bullet} \quad (1)$$

$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet} \quad (2)$$

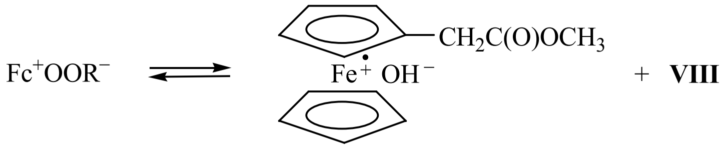
$$RO_2^{\bullet} + \mathbf{II} \longrightarrow ROOH + R^{\bullet} \quad (3)$$

$$ROOH \xrightarrow{HX} \underset{\mathbf{VIII}}{C_5H_5FeC_5H_4C(O)C(O)OCH_3} + H_2O \quad (4)$$

$$ROOH \xrightarrow{HX} \underset{\mathbf{IX}}{C_5H_5FeC_5H_4CHO} + HOC(O)OCH_3 \quad (5)$$

$$HOC(O)OCH_3 \longrightarrow CH_3OH + CO_2 \quad (6)$$

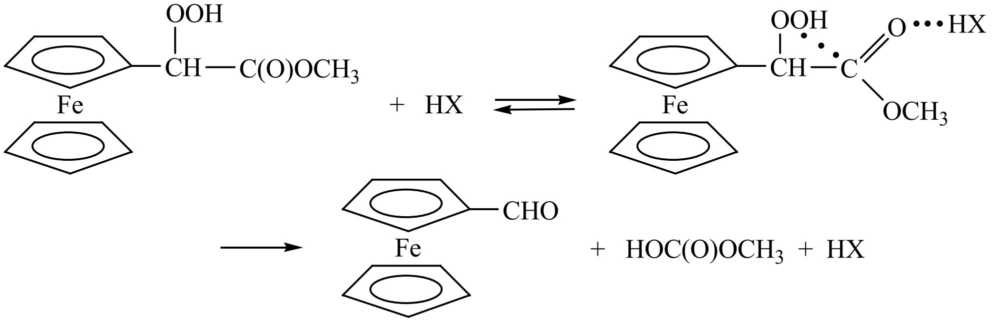
$$\mathbf{II} + RO_2^{\bullet} \longrightarrow \underset{Fc^{+}OOR^{-}}{[C_5H_5\overset{\bullet}{Fe}{}^{+}C_5H_4CH_2C(O)OCH_3]OOR^{-}} \quad (7)$$



(8)

The reactions (1) and (2) are the typical reaction of the chain propagation, the reaction (7) corresponds to the chain termination. Evidences that the chain termination occurs predominantly by the reaction of the radical $RO_2^{\bullet}$ with the initial metallocomplexes at the radical-chain oxidation of some ferrocene derivatives are given in [21]. Reactions (4), (5), and (8) describe the main routes of the transformation of hydroperoxide ROOH and ion-radical salt $\overset{\bullet}{Fc}{}^{+}OOR$, respectively, leading to the formation of the found metallocomplexes and several other reaction products.

Acids are known [13] to catalyze the decomposition of secondary hydroperoxides as shows Eq. (4) in Scheme 7. Obviously, acid **III** also catalyzes decomposition of ROOH in accordance with Eq. (5) in Scheme 7. The difference in the catalysis mechanism for these two reactions is that in order to accelerate the first of them the acid must protonate the hydroperoxide fragment, while to accelerate the second reaction the acid should protonate the carbonyl or methoxy group, or at least form a hydrogen bond. This will increase the electrophilicity of the carbonyl carbon atom and thereby facilitate its interaction with the peroxide fragment.



The kinetic curves of oxygen consumption in the reaction (Figs. 1, 2) in the chain-radical oxidation of compound **II** evidence the absence of degenerate chain branching due to homolytic decomposition of peroxide ROOH. This can be attributed to a significantly higher rate of conversion of hydroperoxide by the routes (4) and (5) in Scheme 7 not only due to catalysis, but also because of the much more favorable energetics of these reactions.

The difference in the yield of CO_2 at the oxidation of compounds **I** and **II** in the presence of acid **III** [for compound **I** the maximum yield of CO_2 is $N(O_2) = 0.62$] is due to the fact that the oxidative decarboxylation of the first complex can be procced by two routes, one similar to the reaction (5) in Scheme 7, and the other described by the following equation [5]:

$$C_5H_5FeC_5H_4CH_2COOH + R''O_2^{\bullet}$$
$$\rightarrow R''OOH + C_5H_5FeC_5H_4CH_2COO^{\bullet}$$
$$\rightarrow C_5H_5FeC_5H_4C^{\bullet}H_2 + CO_2.$$

Here $R''O_2^{\bullet}$ is the peroxide radical corresponding to compound **I.**

The ferrocenylcarboxylic acid formed at the radical-chain oxidation of compound **IX** in the later stages of oxidation of compounds **I** and **II** can enter the similar reaction, although in the latter case it was not detected. To the formation of CO_2 (most likely as at the oxidation of compounds **I** and **II**) the oxidative decarboxylation of acid **III** may possibly contribute. The oxidation of compound **IX** explains the presence of CO in the reaction products. The absence of methyl ferrocenylhydroxyacetate **X** in the reaction product obtained at the oxidation of compound **II** in the presence of acid **III**, which could be formed in the same reactions, can be explained by a significantly higher rate of conversion of hydroperoxide ROOH along the reactions (4) and (5) in Scheme 7.

The formation of products of oxidative degradation of compound **II** may result from the oxidation of the formed ferrocinium ion [22], its disproportionation [23] and decay, if it contains a peroxide anion [24].

$$\mathbf{II} + ROOH + HX \rightarrow Fe^{\dot{+}}X^{-} + H_2O + RO^{\bullet}$$

SH
$RO^{\bullet}$ ROH
–S

In accordance with the suggested Scheme 7 and data of [18], the rate of radical-chain oxidation of compound **II** is described by Eq. (1). [k_3 and k_7 below correspond to the rate constants of reactions (3) and (7) in the Scheme 7].

$$W_0 = k_3[\mathrm{II}][RO_2^{\bullet}]. \quad (1)$$

Experimentally determined kinetic equation of this process has the form (2).

$$W = k_{\mathrm{eff}}[\mathrm{II}][O_2][HX]. \quad (2)$$

The chain termination rate (W_t), which in the steady state is equal to the rate of its initiation (W_0), corresponds to Eq. (3).

$$W_\tau = W_0 = k_7[\mathrm{II}][RO_2^{\bullet}]. \quad (3)$$

A comparison of Eqs. (1)–(3) gives an expression for the rate of chain generation (4).

$$W_0 = [(k_7k_{\mathrm{eff}})/k_3][\mathrm{II}][O_2][HX] = k_0'[\mathrm{II}][O_2][HX]. \quad (4)$$

Comparing this expression with the above expression for the rate of the molecular oxidation of compound **II** in accordance with the Scheme 5 shows their complete analogy, which implies Eq. (5):

$$k_0' = k_0 = k_1'K_1'K_2'. \quad (5)$$

Thus, the Schemes 5 and 7 complement each other and collectively describe the complete picture of the oxidation of compound **II**.

EXPERIMENTAL

To measure the kinetics of oxidation of compound **II** we used a static vacuum setup with intensive stirring the reaction mixture. The reaction course was monitored by measuring the oxygen absorption manometrically.

The analysis of reaction products of compound **II**, organometallic or organic (cyclopentadienone dimer, cyclopentadiene) was carried out by gas chromatography/mass spectrometry. For the analysis we used a Crystal 5000.1 (SKB Khromatek) gas chromatograph coupled with a Termo Finnigan mass spectrometer TRACE DSQ: column RTX-5MS, T_{init} = 110ºC, dwell time 1 min, heating 15º/min to 250ºC, the total analysis time 30 min, T_{evap} = 250ºC, discharge 1:30, the sample volume 1 ml; scan time 30 min, scanning range 50 to 500 atomic mass units, amplifying 3, scanning frequency five scans per second, ionizing electrons energy 70 eV.

Content of methanol was determined by GLC on a Crystal 5000.1 (SKB Khromatek) chromatograph, column: ZB-FFAP, length 50 m, diameter 0.32 mm, with a flame ionization detector.

Water content was determined by GLC on a Separone-CHN (detector katharometer), column length 2 m, diameter 4 mm, temperature 120°C, the evaporator temperature 150°C.

The gaseous products CO and CO_2 were determined by GLC on a Tsvet-100 chromatograph, with flame ionization detector and rod tap dispenser; the column length 0.5 m, diameter 4 mm, sorbent activated carbon (CKT), carrier gas argon, the column temperature 90°C, the reactor catalyst temperature 450°C.

Compound **II** was synthesized from compound **I** with diazomethane as described in [25].

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