ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 6, pp. 1080–1089. © Pleiades Publishing, Ltd., 2012.
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Kinetics and Mechanism of Formyl- and Acetylferrocene Oxidation with Molecular Oxygen in Organic Solvents

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Received April 18, 2011

Abstract—Kinetic laws and the products of autoxidation of formyl- and acetylferrocene in organic solvents in the presence of strong and weak Brønsted acids were investigated. The special feature of the studied reactions is the extreme dependence of the metal complex oxidation rate on the strong acid concentration. This is explained by protonation of the metal complex at high concentrations of the acids leading to the formation of stable to oxidation α-ferrocenylcarbenium complexes $C_5H_5FeC_5H_4C^+(OH)R$.

DOI: 10.1134/S1070363212060072

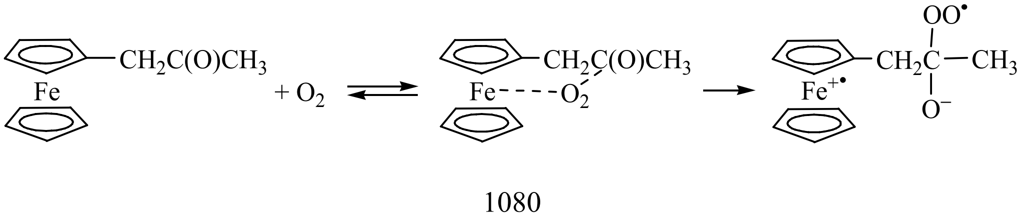
Continuing the study of the ferrocene derivatives oxidation with molecular oxygen in organic solvents [1–4], we examined the features of the oxidation of formyl- and acetylferrocene (**I** and **II**, respectively). These compounds were selected as the objects of study primarily due to the expected difference in the oxidation mechanisms from the previously studied hydroxymethylferrocene and ferrocenylacetic acid and related esters [3, 4] as a consequence of different nature of the functional groups of the substituent in these metal complexes. It has been shown that substituents are directly involved in the oxidation. As is known [5], ferrocenylacetone **III,** an analog of compound **II**, is highly reactive toward oxygen, and in contrast to ferrocene can be oxidized in organic solvents to the diketone $C_5H_5FeC_5H_4$–C(O)C(O)CH_3 under mild temperature conditions in the absence of a strong Brønsted acid. The electron-donating ability of the substituent $CH_2C(O)CH_3$ is unlikely to exceed substantially that of a hydrogen atom [6], therefore the high reactivity of compound **III** indicates direct participation of the substituent functional group in the oxidation. There is no data on the mechanism of oxidation of compound **III**, but it was suggested [4] that the formation of the diketone, taking into account the electrophilic properties of carbonyl group, is a result of the radical-chain oxidation of the substituent in the metal complex initiated by the interaction with oxygen in accordance with Scheme 1.

The interaction of the peroxide radical formed with a neutral metal complex molecule leads to the formation of the radical $C_5H_5FeC_5H_4$–$C^{\bullet}HC(O)CH_3$ initiating the start of the oxidation chain.

In compounds **I** and **II**, in contrast to compound **III**, there is no methylene fragment between the Cp-ligand and the carbonyl group. This makes the CHO and $COCH_3$ substituents strong electron acceptors by both inductive and conjugation mechanisms [6], so the standard redox potentials of these complexes should be significantly higher compared with compound **III**. This should certainly affect both the reactivity of compounds **I** and **II** and the mechanism of oxidation.

We found that compounds **I** and **II** are resistant to oxygen in organic solvents (dioxane, ethanol, DMF) at *T* = 298–333 K and are oxidized only in the presence

Scheme 1.



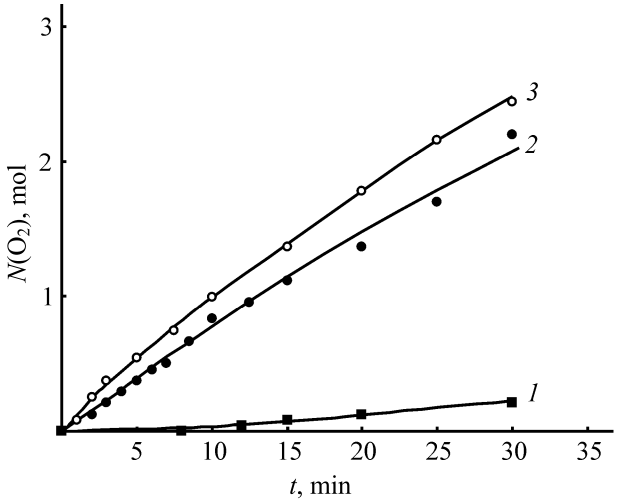


Fig. 1. Effect of the acid nature (HX) on the oxidation of compound **I** in dioxane: (*1*) **IV**, (*2*) **V**, (*3*) **VI**. c_{HX} = 0.2 M, c_I = 0.01 M, $p(O_2) = 0.46 \times 10^5$ Pa, T = 50°C.

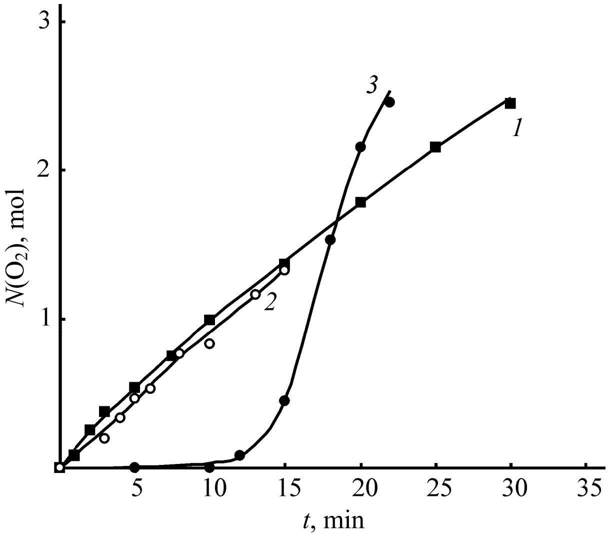


Fig. 2. Effect of the solvent nature on the oxidation of compound **I** in the presence of acid **V**: (*1*) dioxane, (*2*) DMF, (*3*) ethanol. c_V = 0.2 M, c_I = 0.025 M, $p(O_2) = 0.45 \times 10^5$ Pa, T = 50°C.

of Brønsted acids. At low concentrations of acids HX (< 0.1 M) the dependence of the oxidation rate of the metal complex on the acid nature is characterized by a sequence PhCOOH (**IV**) < $HClO_4$ (**V**) ≤ CF_3COOH (**VI**), that Fig. 1 illustrates by the example of compound **I**. Kinetic curves of the oxygen consumption during the oxidation of metal complex depend also on the nature of the solvent: in ethanol and in the mixed solvent dioxane–water (9:1) the process includes a pronounced induction period, in dioxane and DMF such delay is absent (Fig. 2). Note that small amount of water leads to an increase in the rate of oxidation of compound **I**. Raising the concentration of water in the mixed solvent increases the induction period, up to complete termination of the reaction.

Primary products of oxidation of compounds **I** and **II** are the corresponding ferricinium cations. Their formation in dioxane and DMF was registered immediately after the start of bubbling oxygen through the reaction mixture in the spectrophotometric cell as appearance of absorption bands at λ_{max} 628 and 629 nm, respectively [c^0(**I,II**) = 0.01 M, $c^0(HClO_4)$ = 0.5 M, T = 323 K]. In ethanol and mixed dioxane–water solvent where, as noted above, the kinetic curves of oxidation of compounds in the presence of $HClO_4$ are characterized by a noticeable induction period, the formation of the cations in the induction period was not observed.

The introduction of *o*-phenylenediamine, which is known as an effective inhibitor of radical–chain oxidation of organic and organometallic compounds, into the reaction mixture containing compound **I** or **II** before the reaction was found to result in a significant deceleration of the oxidation of the metal complex regardless of the nature of the used acid and solvent (Fig. 3). It was found also that the replacement of dioxane by the mixed dioxane–water (1:9) solvent leads to almost complete inhibition of the process of **I** or **II** oxidation even in the absence of an inhibitor additives, which is typical of the radical–chain oxidation of organic compounds [7]. These results indicate that the oxidation of compounds **I** and **II**, like the oxidation of previously studied ferrocene derivatives [1–4], proceeds as a sequence of two macro steps. First, the molecular oxidation occurs of the metal complex leading to the generation of free radicals, including in their composition a ferricinium cation. Second, the radical chain oxidation of the metal complex initiated by the formed radical, therewith the second macro step makes a decisive contribution to the overall oxidation process.

The results of kinetic studies indicate that the oxidation of compounds **I** and **II** in dioxane is described by the kinetic equation of a first-order reaction with respect to the initial concentrations of the metal complex and oxygen, regardless of the nature of acid. This follows from the fact of a linear increase in the initial reaction rate with increasing concentrations of these reagents (Fig. 4). The dependence of the rate of studied reactions on the acid concentration is more complex. In the presence of acid **VI** the rate of

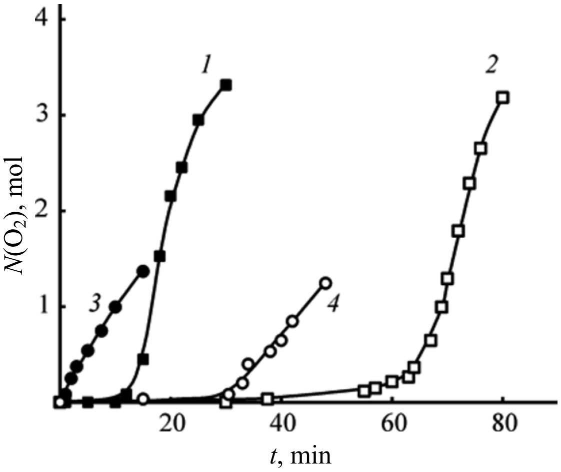


Fig. 3. Effect of *o*-phenylenediamine on the oxidation of **I** in the presence of acid **V** in ethanol (*1*, *2*) and in dioxane (*3*, *4*): *1*, *3* - without inhibitor, *2*, *4* - with the inhibitor. c_I = 0.025 M, c_V = 0.2 M, $c_{In} = 2.5\times10^{-4}$ M, $p(O_2) = 0.46\times10^5$ Pa, *T* = 50°C.

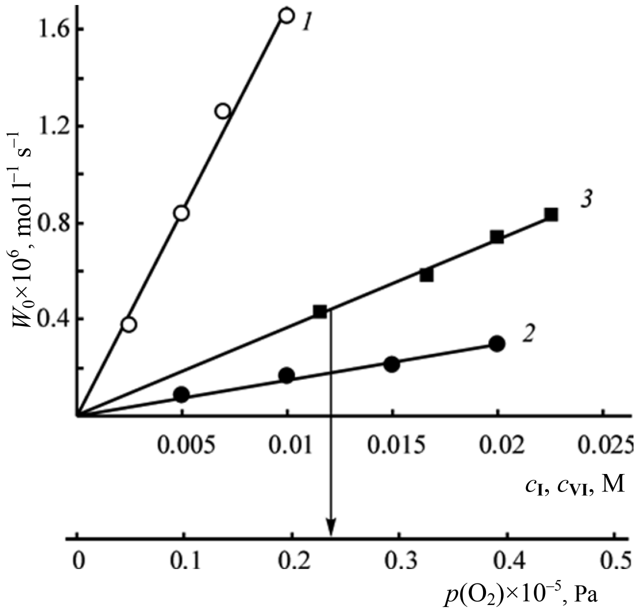


Fig. 4. Dependence of the initial rate of oxidation of compound **I** on the concentration of the (*1*) metal complex, (*2*) acid **VI,** and (*3*) oxygen pressure at *T* = 50°C. (*1*) c_{VI} = 0.2 M, $p(O_2) = 0.45\times10^5$ Pa, (*2*) c_I = 0.02 M, $p(O_2) = 0.47\times10^5$ Pa; (*3*) c_I = 0.005 M, c_{VI} = 0.2 M.

oxidation of the metal complex increases linearly with its concentration only when the latter is low. At relatively high concentrations of acid the linear dependence $W = f(c_{HX})$ is violated, and the order with respect to the acid becomes less than unity. In the presence of perchloric acid the dependence of the oxidation rate of the metal complex on the acid concentration varied from zero to 2 M is of extreme character (Fig. 5). The reaction in this case was performed in a mixed solvent dioxane–water (9:1) containing water in the amount which is introduced in dioxane by commercial acid at its concentration in the reaction mixture 2 M. Since the increase in the initial concentration of perchloric acid also led to an increase in the induction period of the process (Fig. 5), we measured not the initial rate, as in anhydrous dioxane, but the maximum reaction rate. It should also be noted that at the acid concentration 2 M the $N(O_2)$ value (a number of moles of oxygen per one mole of the initial metal complex) is reduced to less than a half as compared, for example, with the experiments where the acid concentration is equal to 0.05 or 0.1 M.

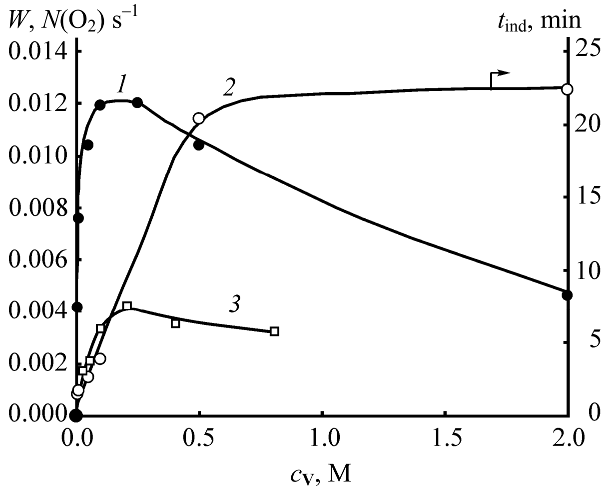
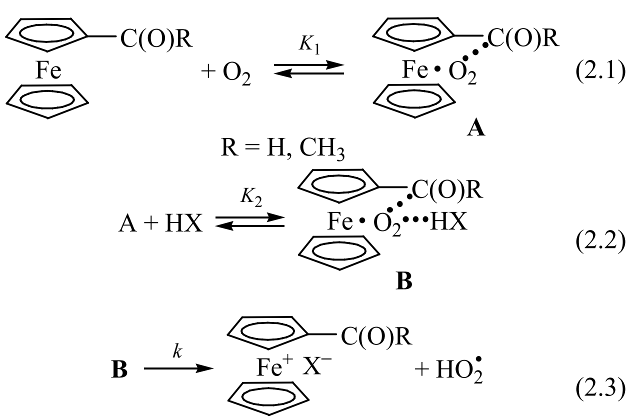


Fig. 5. Dependence of the maximum rate of reaction (*1*) and the induction period (*2*) on the concentration of acid **V** at the oxidation of **I** with oxygen in dioxane. c_I = 0.01 M, $p(O_2) = 0.52\times10^5$ Pa, $c(H_2O)$ = 0.55 M, *T* = 50°C. Curve (*3*) corresponds to the oxidation of ferrocene under similar conditions.

While examining the products of the oxidation of compounds **I** and **II** in dioxane in the presence of acid **VI**, we found among them, in addition to the corresponding ferricinium cations, the products of their degradation: the gaseous compounds CO and CO_2 and the ferrocene derivatives differing from the original metal complex. We revealed that the latter include the compounds containing Fe^{3+}, cyclopentadiene and cyclopentadienone dimer. The new ferrocene derivatives result from the radical–chain oxidation of compounds **I** and **II** involving the substituent at the Cp-ligand. The oxidation of compound **I** leads to the formation of ferrocenecarboxylic acid **VII**. Compound **II** affords the same acid and ferrocenylglyoxal $C_5H_5FeC_5H_4C(O)\cdot CHO$ **VIII**. Noteworthy is the low yield of these products. For example, the yield of product **VII** at the oxidation of **I** does not exceed 2–3% of the theoretically possible for different values of $N(O_2)$. The yield of gaseous products $N(CO)$ and $N(CO_2)$ at the oxidation of compound **I** is 0.1 and 0.15, respectively, and in the oxidation of compound **II** it is somewhat less: 0.07 and 0.11, respectively.

It is known that a key stage in the radical–chain oxidation of organic compounds with oxygen in the absence of an initiator is the stage of the chain initiation [7]. Therefore, the analysis of the mechanism of oxidation of compounds **I** and **II** should be started with an analysis of the mechanism of this particular stage, which, as noted above, is just the reaction of the molecular oxidation of the investigated metal complexes with oxygen, which leads to the generation of radicals. Based on the results obtained and considering the similarities in the properties of the carbonyl group as an electrophile in aldehydes and ketones [8], it is possible to give the generalized scheme of the mechanism of this reaction. For the oxidation of the studied molecular complexes two alternative mechanisms may be suggested distinguished by the mode of coordination of acid with the oxidized compounds, as show Schemes 2 and 3.

Scheme 2.



The overall reaction corresponding to Scheme 2 is described by Eq. (1):

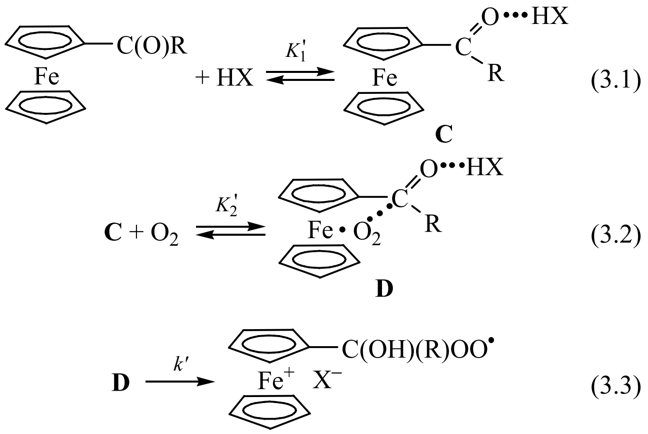
$$\mathrm{FcC(O)R + O_2 + HX \rightarrow Fc^+C(O)RX^- + HO_2^{\bullet}}, \qquad (1)$$

Fc = **I** or **II**.

In Scheme 2 the C(O)R substituent at the Cp-ligand of the metal complex is involved in the oxidation only indirectly, contributing to the coordination of oxygen, and therefore is not transformed.

The mechanism described by Scheme 3 takes into account a possibility of another way of coordinating the acid to the metal complex, resulting in a direct participation of the carbonyl group of the substituent in the process of oxidation leading to another composition of the reaction product.

Scheme 3.



$\mathrm{Fc^+C(OH)(R)OO^{\bullet}X^-}$

The overall reaction in this case is described by Eq. (2):

$$\mathrm{FcC(O)R + O_2 + HX \rightarrow Fc^{+\bullet}C(OH)(R)OO^{\bullet}X^-}. \qquad (2)$$

Scheme 3 takes into account that the interaction of acid with the carbonyl group of ketone or aldehyde includes the formation of hydrogen bond with the latter that increases its reactivity towards nucleophilic reagents, in particular, to oxygen in its neutral and reduced ($O_2^{\bullet-}$ in the limit) forms, by increasing the electrophilicity of the carbon atom [8]. According to [9], compounds **I** and **II** are easily protonated at the carbonyl group by excess of a strong acids.

Using the principle of quasi-equilibrium, one can show that both mechanisms are described by the similar kinetic equations differing in the expressions for the effective reaction rate constant

$$V = k_{\mathrm{eff}}[\mathbf{I}][O_2][HX]. \qquad (3)$$

$$k_{\mathrm{eff2}} = kK_1K_2;\ k_{\mathrm{eff3}} = kK'_1K'_2.$$

The comparison of the expressions for $k_{\mathrm{eff2}} = kK_1K_2$; $k_{\mathrm{eff3}} = kK'_1K'_2$ and Eqs. (1) and (2) suggests that the processes described by Schemes 2 and 3 differ not only by the activation parameters, but also by the thermodynamic characteristics, which are determined by the composition of the end products.

The formed radicals $HO_2^{\bullet-}$ and $\mathrm{Fc^+C(OH)(R)OO^{\bullet}}$ further initiate radical chain oxidation of compounds **I** and **II** by generating radicals $\mathrm{FcC^{\bullet}O}$ and $\mathrm{FcC(O)C^{\bullet}H_2}$ respectively, propagating the oxidation chain.

$$\mathbf{I}\,(\mathbf{II}) + HO_2^{\bullet} \rightarrow FcC^{\bullet}O\,[FcC(O)C^{\bullet}H_2] + H_2O_2, \qquad (4)$$

$$\mathbf{I}\,(\mathbf{II}) + Fc^{+}C(OH)(R)OO^{\bullet} \rightarrow FcC^{\bullet}O\,[FcC(O)C^{\bullet}H_2] + Fc^{+}C(OH)(R)OOH. \qquad (5)$$

Thus, it follows from Eqs. (1), (4) and (2), (5) that the generation of each of radicals $FcC^{\bullet}O$ and $FcC(O)C^{\bullet}H_2$ requires participation in the process of two molecules of complex **I** or **II**. We consider this process in more detail by an example of compound **I**. The generalized equations of the reactions leadining to radicals $FcC^{\bullet}O$ in accordance with Schemes 2 and 3 are as follows:

$$2\,FcCHO + O_2 + H^{+} \rightarrow Fc^{+\bullet}CHO + H_2O_2 + FcC^{\bullet}O,\ \Delta_rG_6^0, \qquad (6)$$

$$2\,FcCHO + O_2 + H^{+} \rightarrow Fc^{+}C(OH)(H)OOH + FcC^{\bullet}O,\ \Delta_rG_7^0. \qquad (7)$$

The mechanism of oxidation of compounds **I** and **II** in accordance with Scheme 3 seems more probable, because previously [10], while analyzing the mechanism of oxidation of ferrocene in acidic medium, it has been shown that the process in accordance with Eq. (1) is energetically unfavorable (Δ_rG^0 = 69.5 kJ mol^{-1}). This process is even less favorable in the case of compounds **I** and **II** which contain strong electron-withdrawing substituents at the Cp-ligand and therefore their standard redox potentials, which determine the Δ_rG^0 values of the reaction, are higher than that of ferrocene. Another mechanism of the acid participation in the oxidation of these metal complexes resulting in another composition of the reaction product can make the process more advantageous by energy. To prove this possibility it is necessary to calculate the values of changes in the standard Gibbs function $\Delta_rG_6^0$ and $\Delta_rG_7^0$ for the reactions (6) and (7), respectively, but the calculation requires the data on the standard enthalpy of formation and absolute entropy of the reactants, which, unfortunately, are absent from the literature. Nevertheless, the values of $\Delta_rG_6^0$ and $\Delta_rG_7^0$ can be estimated using a system of model reactions (8), (9) with benzaldehyde as an analog of the substituted Cp ligand in compound **I,** instead of the reactions (6), (7).

$$2\,PhCHO + O_2^{\bullet-} + H^{+} \quad PhCHO + H_2O_2 + PhC^{\bullet}O,\ \Delta_rG_8^0, \qquad (8)$$

$$2\,PhCHO + O_2^{\bullet-} + H^{+} \rightarrow PhC(OH)(H)OOH + PhC^{\bullet}O,\ \Delta_rG_9^0. \qquad (9)$$

It is obvious that the changes in $\Delta_rG_8^0$ and $\Delta_rG_9^0$ are proportional to the changes in $\Delta_rG_6^0$ and $\Delta_rG_7^0$, respectively. To simplify the calculations of thermodynamic functions of the analyzed reactions, we subtract Eq. (8) from Eq. (9) to obtain Eq. (10) of the resulting reaction.

$$PhCHO + H_2O_2 \rightarrow PhCH(OH)(OOH),\ \Delta_rG_{10}^0, \qquad (10)$$
$$\Delta_rG_{10}^0 = \Delta_rG_9^0 - \Delta_rG_8^0.$$

The sign and value of $\Delta_rG^0_{10}$ suggest, which of the reactions, (8) or (9), and accordingly, which of the mechanisms, (2) or (3), are preferable. In this regard, we note that the reaction of hydrogen peroxide with carbonyl compounds is a way of producing organic hydroperoxides, the yield of which can be quite high [8]. The calculation of $\Delta_rG_{10}^0$ requires the knowledge of $\Delta_rH_{10}^0$ and $\Delta_rS_{10}^0$, because these quantities are related as

$$\Delta_rG_{10}^0 = \Delta_rH_{10}^0 - 298\Delta_rS_{10}^0.$$

The reaction enthalpy can be estimated from the known energy values of cleaved and formed bonds. Reaction (10) proceeds with the cleavage of a π-bond in the carbonyl group ($D_{C–O}\pi \approx$ 290 kJ mol^{-1} [11]) and a H–O bond in the hydroperoxide ($D_{H–O} \approx$ 369 kJ mol^{-1} [12]), and the formation of one H–O bond ($D_{O–H} \approx$ 427 kJ mol^{-1} [13]) and the C–OOH bond ($D_{C–O} \approx$ 310 kJ mol^{-1} [13]) in the hydroxy product. These data lead to a value of $\Delta_rH^0_{10}$ equal to –78 kJ mol^{-1}. Reaction (10) proceeds with the entropy loss. It is known that for many associative bimolecular reactions the entropy loss in gas phase may be of the order –120 to –140 J mol^{-1} K^{-1} [14]. If we assume for reaction (10) the value $\Delta_rS_{10}^0 \approx$ –130 J mol^{-1} K^{-1}, the $\Delta_rG_{10}^0$ value for it will be equal ~ –39 kJ mol^{-1}. Extrapolating this value to the system of reactions (6), (7), we can conclude that mechanism (3) is thermodynamically more favorable than mechanism (2) for the oxidation of compound **I**. This result suggests that the formal equilibrium constant of reaction (7) is higher by more than 6 orders of magnitude than the formal equilibrium constant of reaction (6), despite the fact that K_7 actually may be less than unity, and respectively, $\Delta_rG_7^0$ may be greater than zero. Otherwise, at $\Delta_rG_7^0 < 0$, the reaction could end at the stage of molecular oxidation of the metal complex.

The energy parameters of similar reactions involving compound **II** are unlikely to be materially different from that of compound **I**. Returning to the analysis of Scheme 3, we emphasize that the stage (3.1) instantaneously reaches equilibrium, and the resulting complex **B** reacts with oxygen as a bifunctional reagent. This should lead to a gain in the activation entropy due to the effect of rapprochement and orientation in the stage (3.3) that limits the rate of the whole process, as follows from the comparison of the activation parameters of this reaction with similar parameters of the reaction (2.3) in Scheme 2 describing the oxidation of compound **I** [15]. If the standard oxidation potential of the oxidation system $\{Ox + H^+\}$ is significantly higher than that of the system $\{O_2 + H^+\}$ ($\varphi° = –0.13$ V [16]), then the mechanism of oxidation of compounds **I** and **II** similar to mechanism (2) may be kinetically more favorable, due to the simplicity of the structure of the transition complex.

The mechanism of the radical–chain oxidation of compound **I** involving radicals $FcC^{\bullet}O$ formed in the reactions (6) and (7) can be represented by Scheme 4 that includes only the principal stages. This scheme resembles the well-known scheme of oxidation of benzaldehyde [7], but differs from it by some features characteristic of compound **I**.

Scheme 4.

$$\mathbf{I} + O_2 + HX \xrightarrow{\mathbf{I}} FcC^{\bullet}O, \qquad (4.0)$$

$$FcC^{\bullet}O + O_2 \rightarrow FcC(O)OO^{\bullet}, \qquad (4.1)$$

$$FcC(O)OO^{\bullet} + \mathbf{I} \rightarrow FcC(O)OOH + FcC^{\bullet}O, \qquad (4.2)$$

$$FcC(O)OOH + \mathbf{I} \rightarrow 2\,FcCOOH, \qquad (4.3)$$

$$FcC(O)OO^{\bullet} + \mathbf{I} \rightarrow FcC(O)OO^{-} + Fc^{+\bullet}CHO. \qquad (4.4)$$

The reaction analogous to (4.3) of benzaldehyde with a peracid is catalyzed by acids [7]. This phenomenon is characteristic also of compound **I**.

Reaction (4.4) is regarded as a reaction of chain termination, since it is known that peroxide radicals $RC(O)OO^{\bullet}$ are highly reactive in the reactions of one-electron transfer, significantly higher by the reactivity than the peroxide radicals $R'O_2^{\bullet}$ [14]. The involvement of the ferrocenyl-containing radicals $R'O_2^{\bullet}$ in the chain termination similar to the reaction (4.4) has been shown in the study of radical–chain oxidation of other ferrocene derivatives [1–4], so the quadratic chain termination by the $FcC(O)OO^{\bullet}$ radicals is omitted in Scheme (4). At the autoxidation of benzaldehyde the chain termination by the radicals $PhC(O)OO^{\bullet}$ is considered as a the major process [7]. Naturally, the stage of the chain initiation in this process differs from that of compound **I**.

$$PhCHO + O_2 + PhCHO \rightarrow 2PhC^{\bullet}O + H_2O_2.$$

The peracid FcC(O)OOH, being a strong oxidant, can oxidize both compound **I** and the product FcCOOH to form the corresponding ferricinium cation, but process (12) dominates.

$$\begin{gathered} FcC(O)R + FcC(O)OOH \\ \rightarrow Fc^{+}C(O)R + FcC(O)O^{-} + HO^{\bullet}, \end{gathered} \qquad (11)$$

$$\begin{gathered} FcC(O)R + FcC(O)OOH + HX \\ \rightarrow Fc^{+}C(O)R + X^{-} + FcCOOH + HO^{\bullet}. \end{gathered} \qquad (12)$$

Compound **I** can also react with the peracid in the Bayer–Villiger reaction [8].

The formation of CO and CO_2 at the oxidation of compounds **I** may correspond to the possibility of the following reactions:

$$FcC^{\bullet}O \rightarrow Fc^{\bullet} + CO, \qquad (13)$$

$$FcCOOH + FcC(O)OO^{\bullet} \rightarrow FcCOO^{\bullet} + FcC(O)OOH, \qquad (14)$$

$$FcCOO^{\bullet} \rightarrow Fc^{\bullet} + CO_2. \qquad (15)$$

Reaction (14) can proceed in parallel with the reaction (16)

$$FcCOOH + FcC(O)OO^{\bullet} \rightarrow FcC(O)OO^{-}{\cdot}Fc^{+\bullet}COOH. \qquad (16)$$

It follows from the above that reactions (12), (14), (16) occurring in the later stages of oxidation of compounds **I** and leading to the consumption both of compound **I** and the resulting acid FcCOOH are the main reason of the low yield of the latter.

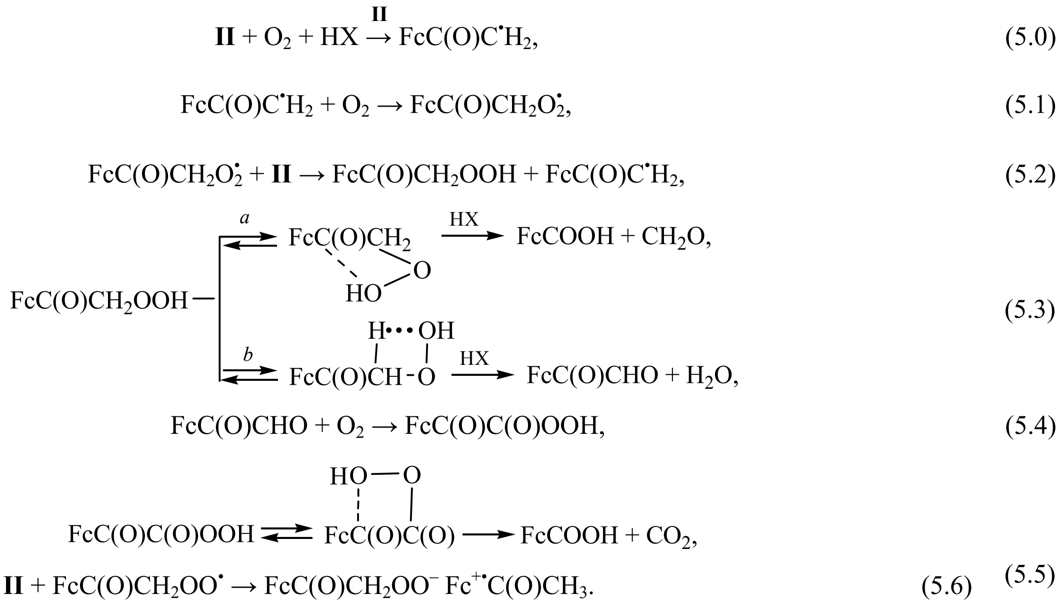
The products of the oxidative destruction of compound **I** are formed by the same route as in the oxidation of the other ferrocene derivatives, that is, through a stage of the formation of the corresponding ferricinium cation and its destruction by disproportionation and oxidation [1–4]. A role in the degradation of the metal complex can also play the reaction of the $Fc^{\bullet}$ radical with oxygen.

The features of the radical–chain oxidation of compound **II** can be illustrated by Scheme 5.

Except for the stages of the chain initiation (5.0) and termination (5.6), the oxidation of compound **II** proceeds by the mechanism similar to that of oxidation of acetophenone and acetone [7]. The transformation of hydroperoxide $FcC(O)CH_2OOH$ in reaction (5.3) and the peroxyacid FcC(O)C(O)OOH in reaction (5.5) can be catalyzed by the acids present in the reaction mixture [7, 17]. Reasons of the low yield of final reaction products **VII** and **VIII** are the same as for product **VII** in the oxidation of compound **I**: the consumption of these compounds, as well as complex **II,** in the secondary reactions with the intermediates of peroxide nature.

The absence of the induction period in the kinetic curves of the oxygen consumption in the course of oxidation of compounds **I** and **II** in dioxane and DMF

Scheme 5.



$$\mathbf{II} + O_2 + HX \xrightarrow{\mathbf{II}} FcC(O)C^{\bullet}H_2, \quad (5.0)$$

$$FcC(O)C^{\bullet}H_2 + O_2 \rightarrow FcC(O)CH_2O_2^{\bullet}, \quad (5.1)$$

$$FcC(O)CH_2O_2^{\bullet} + \mathbf{II} \rightarrow FcC(O)CH_2OOH + FcC(O)C^{\bullet}H_2, \quad (5.2)$$

$$FcC(O)CH_2OOH \xrightarrow{HX} FcCOOH + CH_2O, \quad FcC(O)CH_2OOH \xrightarrow{HX} FcC(O)CHO + H_2O, \quad (5.3)$$

$$FcC(O)CHO + O_2 \rightarrow FcC(O)C(O)OOH, \quad (5.4)$$

$$FcC(O)C(O)OOH \rightleftarrows FcC(O)C(O) \longrightarrow FcCOOH + CO_2, \quad (5.5)$$

$$\mathbf{II} + FcC(O)CH_2OO^{\bullet} \rightarrow FcC(O)CH_2OO^{-}\ Fc^{+\bullet}C(O)CH_3. \quad (5.6)$$

suggests that the degenerate branching of chains due to the involvement of the formed peroxide intermediates either does not occur, or is insignificant, because their steady-state concentration is low: they can enter in the unimolecular transformations and react with the initial and final metal complexes. On the other hand, the peroxyacid FcC(O)OOH in some cases is not thermally decomposed: it may be considered as an analog of perbenzoic acid, which is decomposed at $T >$ 80°C [18]. The presence of an induction period in the oxidation of **I** in ethanol and in the mixed solvent dioxane–water is due, most likely, to the associative process involving the solvent, e.g., the formation of the hydrogen-bonded complexes $C_5H_5FeC_5H_4CHO\cdots HOR$ and the complexes of $R'O_2^{-}\cdot HOR$ ($R = H, C_2H_5$) that are inactive in the chain propagation [17].

By the example of compound **I** it is possible to estimate the correspondence between kinetic Eq. (3) derived from the analysis of the molecular mechanism of oxidation of the complexes, and kinetic Eq. (17) found experimentally, which characterizes the radical chain route of the process involving the substituent.

$$V_{\exp} = k_{\exp}[\mathbf{I}][O_2][HX]. \quad (17)$$

According to [7] and Scheme 4, the rate of radical–chain oxidation of compound **I** is:

$$V_r = k_{4.2}[\mathbf{I}][Fc(O)OO^{\bullet}]. \quad (18)$$

Then the rate of chain termination V_t according to Eq. (4.4) is expressed by Eq. (19)

$$V_t = k_{4.4}[I][Fc(O)OO^{\bullet}]. \quad (19)$$

Equating the reaction rates in Eqs. (17) and (18), we obtain an expression for the concentration of radicals $FcC(O)OO^{\bullet}$ as a dependence on the concentration of initial reagents.

$$[Fc(O)OO^{\bullet}] = (k_{\exp}/k_{4.2})[O_2][HX]. \quad (20)$$

Substituting (20) into the equation for the rate of chain termination, we obtain an expression for the chain initiation rate V_0, which in the steady state is equal to V_t.

$$V_0 = V_t = [(k_{4.4}k_{\exp})/k_{4.2}]\ [I][O_2][HX] = k_0[I][O_2][HX]. \quad (21)$$

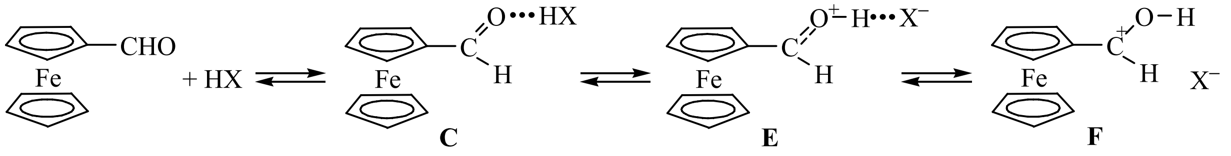
Equation (21) is fully consistent with Eq. (3) derived from the analysis of the Schemes 2 and 3, if we assume that k_0 is equal to kK_1K_2 or $kK'_1K'_2$.

Thus, the kinetic correspondence of the molecular and radical chain mechanisms of oxidation of compound **I** allows us to regard them together as unique mechanism of the oxidation of the metal complex.

In conclusion, we consider the causes of the observed dependence of the rate of oxidation of compound **I** on the concentration of perchloric acid in the mixed solvent dioxane–water passing through extremum. Mechanism (2) cannot explain this phenomenon due to the lack of direct link between them. Mechanism (3) in this regard can be considered as a basis for understanding the causes. This mechanism takes into account the properties of the carbonyl group with respect to strong acids and its participation in the process of oxidation of compound **I**. With this in mind, we suggest that there are several reasons for the appearance of extrema in the $W = f(c_{HX})$ plot at the oxidation of compound **I**.

(1) Protonation of compound **I**. At low concentrations of acid, only the hydrogen-bonded complex **C** is formed, which leads to activation of the carbonyl group toward oxygen in the neutral and reduced forms of the latter (the limit is O_2^{-}). This contributes to the electron transfer from the metal atom to the oxygen. The consequence is a linear increase in the rate of oxidation with increasing acid concentration. At high concentrations of acid the protonation of substituent becomes possible leading to the formation of carbenium cation in the α-position with respect of Cp-ligand. The mechanism of this process can be represented by Scheme 6 [8].

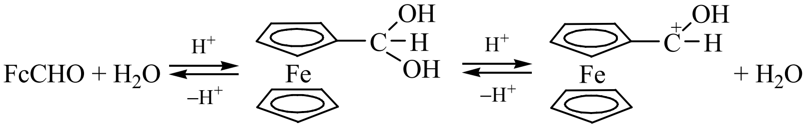
Scheme 6.



The carbenium cation is the strongest electron acceptor, therefore the standard redox potential of the ferrocene with such substituent is significantly higher than that of compound **I**. This results in the resistance of the carbocationic complex **F** to oxidation. Stability of α-ferrocenylcarbenium ions to O_2 was noted in [9]. With increasing concentration of the acid the equilibrium in the process described by Scheme 6 is shifted to the right, that is, to the increase in the equilibrium yield of the complex **F**. This consequently leads to a simultaneous decrease in the concentration of **I** and its rate of oxidation.

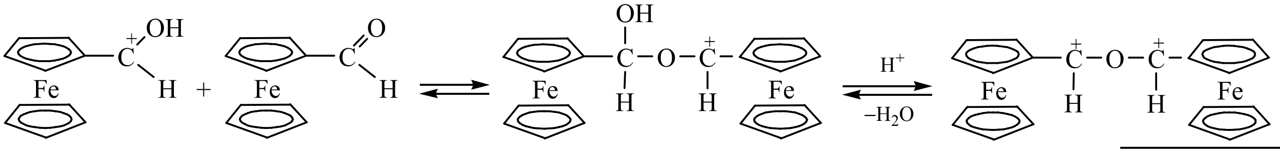
(2) The hydration of **I** and subsequent protonation of the resulting product at a high concentration of acid, leading to the formation of the same carbocationic complex **F** [8] as illustrates Scheme 7.

Scheme 7.



The resulting α-ferrocenylcarbenium ion can react with the carbonyl group of the initial metal complex in accordance with Scheme 8 [9] decreasing its involvement in the target reaction. It is not excluded that this process may involve more than two molecules of the metal complex.

Scheme 8.



From the above said it follows that, at a certain high enough concentrations of acid the process of converting compound **I** in an α-ferrocenylcarbenium ion can prevail over the process of oxidation. This would lead to the extremum in the dependence of the oxidation rate of the initial metal complex on the concentration of acid. This is confirmed by the relatively low $N(O_2)$ value at high concentrations of acid (Fig. 3). It should be noted that the kinetic Eq. (3) describing the molecular oxidation of compound **I** is valid at any concentration of acid involved in this process.

Finally, when the acid is taken in a considerable quantity, it can contribute significantly to the deactivation of peroxy radicals $Fc(O)OO^{\bullet}$ leading the chain in the radical–chain oxidation of compounds **I**, due to the formation of stable hydrogen-bonded complexes Fc(O)OO$^{\bullet}\cdots$HX, which should decrease the reaction rate. This would contribute to the appearance of an extremum in the $W = f(c_{HX})$ curve. This cause has been considered as the main one in the discussion of the dependence of oxidation rate of hydroxymethylferrocene on the concentration of acid **VI**, which is linear only at low concentrations of the acid [2]. Unfortunately, the possibility of protonation of the metal complex with the formation of α-ferrocenylcarbenium ion $FcC^{+}H_2$ has been ignored, although there are the relevant data on its formation and resistance to oxygen [9].

Study of the dependence $W = f(c_{HX})$ for compound **II** in a wide range of concentrations of acid has not been performed. However, the ability of this compound to be protonated by strong acids [9] suggests that the extreme dependence $W = f(c_{HX})$ found for compound **I** would be also typical for **II**. The general nature of this relationship is confirmed by the data obtained in the study of oxidation of 1,1'-diacetylferrocene (Fig. 5). We emphasize that just for this complex the possibility of the process described by Scheme 8 has been established [9].

EXPERIMENTAL

The oxidation of compounds **I** and **II** was performed in a static vacuum apparatus at vigorous stirring the reaction mixture. The reaction was monitored by measuring the oxygen consumption manometrically.

Synthesis of compounds **I** and **II** was performed by procedures [19] and [20], respectively.

Analysis of the metal complexes to be oxidized and the volatile products of their oxidation was carried out by gas chromatography–mass spectrometry. For the analysis a Kristall 5000.1 gas chromatograph of Khromatek design bureau was used, coupled with a mass spectrometer TRACE DSQ from Termo Finnigan, column RTX-5MS, T_{beg} = 110ºC, exposure 1 min., heating 15º/min to 250ºC, the total analysis time 30 min, $T_{evaporation}$ = 250ºC, split ratio 1:30, the sample volume 1 μl; scan time 30 min, scan range 50 to 500 wt. units, gain 3, scan rate 5 scans per second, the electron energy 70 eV.

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

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

ACKNOWLEDGMENTS

The authors are grateful to Dr. A.S. Smirnov for providing the samples of metal complexes.

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