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Features of the Oxidation of Certain Hydroxy Derivatives of Ferrocene with Molecular Oxygen in Organic Solvents

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Abstract—Features of the oxidation of hydroxymethylferrocene with molecular oxygen in organic solvent in the presence of weak and strong Broensted acids were studied. The resulting data were compared with published data on ferrocene and hydroxyferrocene oxidation, which made it possible to assess the trend in the oxidation mechanism in going from ferrocene π complexes to their hydroxyferrocene and hydroxymethylferrocene analogs. A conclusion was drawn that each of the ferrocenes reacts with oxygen in quite a specific way.

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The ability of π complexes of transition metals to react with molecular oxygen can be considered as one of the fundamental properties of these compound [1, 2]. However, even though the chemistry of ferrocene is extensively developed, almost no information on oxidation of ferrocene derivatives is available.

The aim of the present work was to study features of the reaction of hydroxymethylferrocene (**I**) with molecular oxygen in organic solvents and to compare our results with published data on the oxidation of hydroxyferrocene (**II**) and ferrocene (**III**). Thus we expected to obtain evidence to show how the oxidation mechanism changes in going from ferrocene π-complexes to their hydroxyferrocene and hydroxymethylferrocene analogs.

As known, ferrocene (**III**) is highly resistant to oxygen and can be oxidized exclusively in the presence of strong Brønsted acids (HX) according to Eq. (1) [4, 5].

$$4Cp_2Fe + O_2 + 4H^+ \rightarrow 4Cp_2Fe^{\dot{+}} + 2H_2O. \qquad (1)$$

The reason for such an inertness of ferrocene (**III**) lies in the fact that its standard redox potential $\{E^0(Cp_2Fe^+|Cp_2Fe)$ 0.59 V [6]$\}$ is much higher than that of oxygen $\{E^0(O_2^-|O_2)$ –0.56 V [7]$\}$. In a strongly acidic media, the redox potential of oxygen increases to 1.23 V, which makes reaction (1) thermodynamically favorable. The mechanism of reaction (1) has been suggested in [8] as a result of a detailed analysis of published data on ferrocene oxidation (Scheme 1).

Scheme 1.

$$Cp_2Fe + H^+ \underset{}{\overset{K_1}{\rightleftarrows}} Cp_2Fe{-}^{+}H, \qquad (1.1)$$

$$Cp_2Fe{-}^{+}H + O_2 \overset{K_2}{\rightleftarrows} Cp_2Fe{-}^{+}H{\cdots}O_2\,, \qquad (1.2)$$

$$Cp_2Fe{-}^{+}H{\cdots}O_2 + Cp_2Fe{-}^{+}H \xrightarrow{K_3} 2Cp_2Fe^+ + H_2O_2, \qquad (1.3)$$

$$Cp_2Fe{-}^{+}H + H_2O_2 \rightarrow Cp_2Fe^+ + H_2O + HO^{\cdot}, \qquad (1.4)$$

$$Cp_2Fe{-}^{+}H + HO^{\cdot} \rightarrow Cp_2Fe^+ + H_2O. \qquad (1.5)$$

The mechanism was based on the following evidence related, directly or indirectly, to properties of ferrocene (**III**):

(1) ability to fast equilibrium protonation with strong acids [3, 9, 10];

(2) ability of protonated ferrocene ($Cp_2Fe{-}^{+}H$) to reaction with oxygen to form the ferricinium ion $Cp_2Fe^{\dot{+}}$ and H_2O [4];

(3) low energy of the Fe–H bond in $Cp_2Fe{-}^{+}H$, equal to 209.2 kJ mol^{-1} [10], which allows the latter molecule to be considered as an efficient donor of atomic oxygen to oxidant;

(4) results of kinetic research [11], according to which the ferrocene oxidation rate is described by Eq. (2).

$$\nu = k_{\mathrm{app}}[\mathrm{Cp_2Fe}]^2[\mathrm{O_2}][\mathrm{H^+}]^2. \qquad (2)$$

The kinetic analysis of the suggested analysis under the assumption that the limiting stage is reaction (1.3), gives rate Eq. (3).

$$\nu = \frac{k_3 K_1^2 K_2 [\mathrm{Cp_2Fe}]_0^2 [\mathrm{O_2}]_0 [\mathrm{H^+}]_0^2}{(1 + K_1[\mathrm{H^+}]_0)^2}. \qquad (3)$$

At $K_1[\mathrm{H^+}]_0 << 1$ this equation transforms in Eq. (2), where $k_{\mathrm{app}} = k_3K_1^2K_2$. The thermodynamic characteristics of reactions (1.2), (1.3) and (1.4), (1.5) show that the latter two reactions have higher negative standard enthalpies and Gibbs energies (see table), which, in terms of the thermodynamic criteria, confirms the suggested mechanism, even though these characteristics relate to the gas phase [8].

A different picture is observed in the oxidation of hydroxy derivatives of ferrocene, which are highly reactive toward oxygen. Monohydroxyferrocene $C_5H_5FeC_5H_4OH$ (**II**) and 1,1'-dihydroxyferrocene (**IV**) are readily oxidized with air oxygen both in an ether solution and in the crystalline state at room temperature in the absence of any protic acids [12]. The example of compound **IV** was used to show that the reaction destroys the sandwich structure of the complexes and results in preferential formation of cyclopentadienone dimer and an inorganic Fe^{3+} derivative.

Such an essential effect of the OH substituent on the reactivity of metal complexes and their oxidation products points to the fact that ferrocene and hydroxyferrocene (**II**) react with oxygen by a radically different mechanism. This difference is associated with direct involvement of the substituent in the oxidation process.

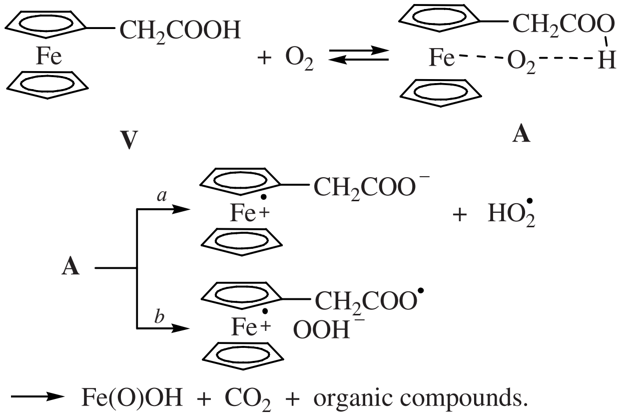
Such involvement can be considered quite possible in view of the known ability of the OH group to donate electrons to the CP ligand by the conjugation mechanism [13] and thus reduce the redox potential of the metal complex. Moreover, the OH group can act as a Broensted acid (pK_a 10.16 [12]) and take part in binding of oxygen with the metal complex due to H-bond formation with the oxygen molecule. This increases the redox potential of the oxidant. Evidence for these suggestions about reasons for the effect of the OH substituent on the reactivity of compounds is provided by the three obrservables: (1) methyl and ethyl ether of hydroxyferrocene (**II**) fail to react with oxygen in the absence of acids [12]; (2) the ferrocene (**III**)–O_2-weak carboxylic acid system (pK_a ~4–5; $c^0_{\mathrm{HX}}/c_{\mathrm{III}}$ 1–10) undergoes no changes in organic solvents for several weeks [14]; (3) ferrocenylacetic acid which is a bifunctional reagent containing an electron-donor (metal) and an electron acceptor (COOH group) reaction centers that take part in the initial binding of oxygen and further transformations of the resulting oxygen complex is readily oxidized according to Scheme 2 [14].

Thermodynamic characteristics of ferrocene oxidation [reactions (1.2), (1.3), (1.4), and (1.5)]

Reaction	Δ_rH^0 (298.15), kJ mol^{-1}	Δ_rS^0 (298.15), kJ mol^{-1}	Δ_rG^0 (298.15), kJ mol^{-1}
$2Cp_2Fe{-}^{+}H + O_2 \rightarrow P_1$[a]	–168.1	–29.5	–159.3
$Cp_2Fe{-}^{+}H + H_2O_2 \rightarrow P_2$	–82.4	112.3	–115.7
$Cp_2Fe{-}^{+}H + HO^{\cdot} \rightarrow P_3$	–297.2	–23.0	–290.3

[a] (P_i) Reaction products shown in Scheme 1.

Scheme 2.

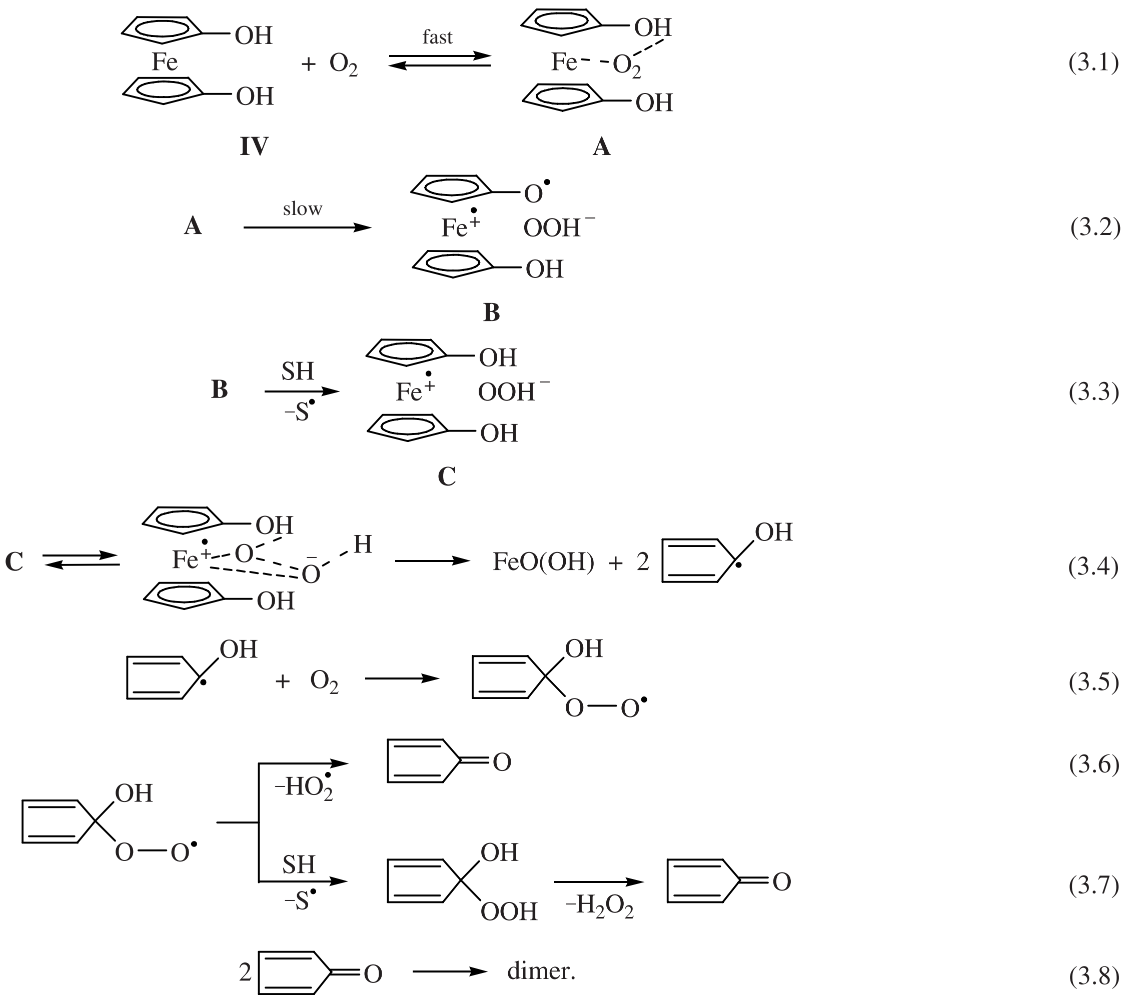


The CH_2COOH substituent is not an electron donor, like OH, but it has a much higher acidity than hydroxyl (pK_a ~5 [3], which probably explains the fact that acid **V** is quite reactive toward oxygen.

There is no information in the literature, concerning oxidation kinetics of compound **IV**, but Scheme 2 and data on the oxidation products of dihydroxyferrocene **IV** can be used as the basis for the probable mechanism of its oxidation (Scheme 3). This scheme can also be extended to hydroxyferrocene (**II**).

Path *a* in Scheme 2 involves proton abstraction of the oxygen molecule being reduced from the acidic substituent, is most likely not realized in the case of

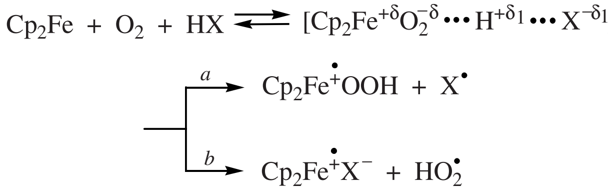
Scheme 3.



compound **IV**, since the O–H group in its hydroxy group is much less polar. The Fe–O_2 bond in complex A should be considered as donor–acceptor with a small contribution, like in charge-transfer complexes, charge transfer. This bond is formed by the higher occupied molecular orbitals of compound **IV** (d_{xy} and $d_{x^2-y^2}$), localized on the metal atom [3], and low-lying $1\pi_g^*$ orbital of O_2.

As O_2 coordinates with metal complexes, its interaction with an electron-donor reaction center enhances interaction eith electron-acceptor (and vice versa), which stabilizes adduct **A** and its structurally related transition state, and results in a considerable gain of energy required for overcoming the energy barrier during motion along the reaction coordinate. This picture is characteristic of bifunctional reacting systems that are common under enzymatic catalysis conditions [15, 16].

The anomalously high reactivity of compounds **II**, **IV**, and **V** toward oxygen compared to the system ferrocene (**III**)–weak HX is a typical manifestation of the effect of mutual approach and orientation, associated with thermodynamically unfavorable entropy losses characteristic of intermolecular interactions of a high kinetic order [15, 16], including the suggested model reaction (4) [14].



$$\mathrm{Cp_2Fe} + \mathrm{O_2} + \mathrm{HX} \rightleftarrows [\mathrm{Cp_2Fe^{+\delta}O_2^{-\delta}\cdots H^{+\delta_1}\cdots X^{-\delta_1}}]^{\#} \begin{cases} \xrightarrow{a} \mathrm{Cp_2\dot{F}e^{+}OOH} + \mathrm{X^{\bullet}} \\ \xrightarrow{b} \mathrm{Cp_2\dot{F}e^{+}X^{-}} + \mathrm{HO_2^{\bullet}} \end{cases} \qquad (4)$$

The effect of mutual approach and orientation intrinsic in enzymatic polyfunctional catalysis is measured thermodynamically ($\Delta G^{\#}_{\mathrm{appr,\ orient}}$ 10–12 kcal mol^{-1})

and kinetically as the ratio of the rate constants of the enzymatic and homogeneous catalytic reactions (10^7 M, where M is the molarity of excess reagent) [15, 16].

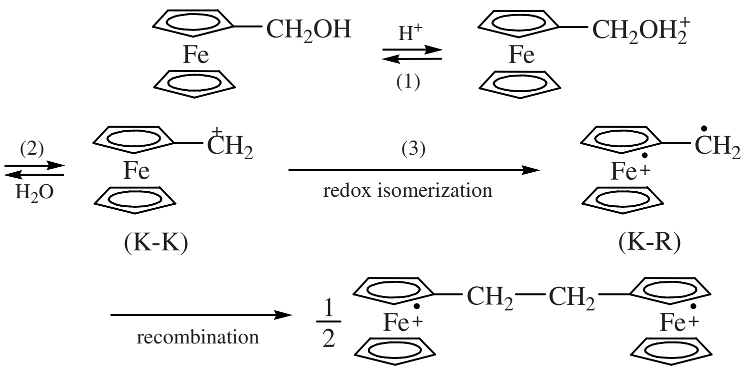
The conjugation chain developed in complex **A** and including the metal atom, O_2 molecule, and acid group provides, by analogy with enzymatic processes referred to as "conjugate catalysis" [16, 17], synchronous electron transfer from the metal atom and hydrogen abstraction from the OH group by the reduced O_2 molecule, which decreases the activation energy of the process. The transformation of hydroperoxide complex **C**, leading to final reaction products, is explained by the lability of the hydroperoxide anion bound with the metal atom [18]. If for compounds **II** and **V** to be oxidized several chemical bonds between O_2 and reaction centers in the metal complex should form, then here we can speak about quite a stringent complementarity of the reacting molecules both at the stage of formation of adduct **A** and during its motion along the reaction coordinate, which provides a substantial rate gain [19].

The aforesaid points a great similarity of the oxidation mechanisms of the mentioned bifunctional ferrocene derivatives and the mechanisms of a series of known processes involving polyfunctional enzymatic systems [15, 16], which predetermines, in the final count, the high reactivity of hydroxyferrocene (**II**) and ferrocenylacetic acid (**V**) toward oxygen.

Hydroxymethylferrocene (**I**) differs from hydroxyferrocene (**II**) by that the former contains a methylene group between OH and CP. This, first of all, reverses the properties of the substituent, since the CH_2OH group is already electron acceptor rather than electron donor, and, moreover, it is a stronger electron-acceptor than the CH_2COOH substituent in compound **V** [20]. The second consequence is that the energy of the O–H bond in the CH_2OH group to ~102 kcal mol^{-1} [21] against 84 kcal mol^{-1} in the OH substituent in hydroxyferrocene (**II**) [20, 21]. Third, the CH_2OH group has a lower acidity ($pK_a \approx 16–18$), which is characteristic of alcohols RCH_2OH [22]. As a result, compound **I** is much more resistant to O_2. Hydroxymethylferrocene (**I**) is oxidized for a long time neither in the solid state nor in organic solvents. For this reason, the oxidation of this complex in organic solvents was studied in the presence of strong and weak Brønsted acids.

Various-strength acids quite specifically affect the reaction of compound **I** with oxygen. As the metal complex ($c^0_{\mathbf{I}}$ 0.01 M) is mixed with perchloric acid (c^0_{HX} 0.2 M, pK_a –10) in dioxane, ethanol, toluene, and DMF in a vacuum or in an oxygen atmosphere, the light yellow solution immediately gets green and remains unchanged for a long time in the presence of oxygen. No oxygen is therewith absorbed (20–50°C). The electronic absorption spectrum of the resulting compound in dioxane is similar to that of the ferricinium ion (λ_{max} 626, 453, 346, and 258 nm) [23]. The long-wave absorption band (λ_{max} 626 nm) is asymmetric and has a shoulder at ~580 nm, which may imply overlapping bands of two different ferrocene derivatives. The changes of compound **I** under the action of $HClO_4$ are due to the formation of the ferrocenylmethyl cation which is prone to further conversion to the ferricinium ion according to Scheme 4 [3, 24].

Scheme 4.



In dilute solutions of strong acids, all the stages of Scheme 4 are reversible, except for dimerization of the radical cation [25]. Therefore, the presented spectrum of the reaction product of compound **I** with $HClO_4$ is better treated as a combination of the spectra of the ferrocenylmethyl and ferricinium ions.

It is known that α-ferrocenylcarbenium ions are resistant to molecular oxygen in strongly acidic solutions [3]. Therefore, according to the reaction mixture containing reaction products of compound **I** with $HClO_4$ may absorb oxygen due to oxidation of the radical cation (RC) and its dimer 1,2-diferricinioethane. Monomeric unsubstituted ferricinium ion is readily oxidized with decomposition of its sandwich structure [26]. Since solutions of compounds **I** in the presence of $HClO_4$ absorbed no oxygen, we can conclude that the steady-state concentration of RC is low, and 1,2-diferricinioethane is much less reactive toward oxygen than monomeric ferricinium ion. This can be explained both by steric reasons and by that the highly rigid structure of the dimer prevents the ferricinium ion, on its reaction with O_2, from adopting a configuration with tilted Cp ligands, thus hindering their subsequent π–σ rearrangement in the course of further transformations of the resulting oxygen adduct [27].

No similar transformations are observed with compound **I** in the presence of benzoic acid (**VI**) (p*K*$_a$ 4.2) in the above solvents and in the presence of trifluoroacetic acid (**VII**) (p*K*$_a$ 0.3) in dioxane, but the metal complex can be oxidized with oxygen in this case.

Figure 1 shows the kinetic curves of oxidation of compound **I** in various solvents in the presence of acids **VI** and **VII**. As seen from the figure, the oxidation rate increases with increasing strength of the carboxylic acid, and the solvent effect varies in the series dioxane > toluene > dioxane–H_2O >> ethanol, which shows that solvation palys a considerable role in the reaction in hand (dioxane > toluene) and on the other, solvents are capable of inhibiting oxidation by binding one of the starting reagent and/or intermediate reaction products into inactive hydrogen complexes (toluene > dioxane–H_2O >> ethanol). When the concentration of water in dioxane is 4 M, compound **I** is scarcely oxidized, like in ethanol.

Addition of pyridine which can form strong complexes with acids in a quantity equimolar to the concentration of acids **VI** and **VII** retards oxidation of compound **I** completely.

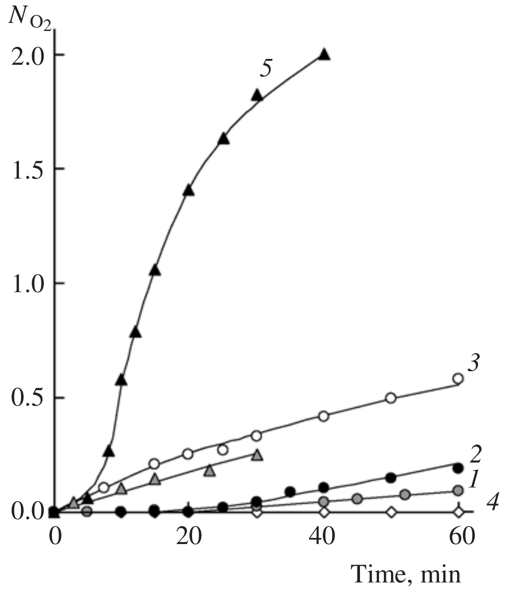


Fig. 1. Kinetic curves of oxidation of hydroxymethylferrocene (**I**) in the presence of (*1–4*) benzoic (**VI**) and (*5, 6*) trifluoroacetic (**VII**) acid in (*3, 5*) dioxane, (*2*) toluene, (*1, 6*) dioxane–water, and (*4*) ethanol. c_{I}^0 0.02, c_{VI}^0 0.55, c_{VII}^0 0.2, $c(H_2O)$ 2 M, $P(O_2)$ 0.47×10^5 Pa, T 50°C.

Oxidation of hydroxymethylferrocene (**I**) in the presence of acids **VI** and **VII** involves the CH_2OH substituent and gives rise to ferrocenecarbaldehyde (**VIII**) and ferrocenecarboxylic acid (**IX**). The highest detected yields of aldehyde **VIII** in the oxidation of **I** at oxygen consumptions of up to $N_{O_2} \approx 1$ (N_{O_2} is the number of oxygen moles absorbed by the reaction mixture per 1 mol of metal complex) in the presence of acids **VI** and **VII** are ~0.5 and ~0.3 mol per 1 mol of the starting complex, respectively. The yield of acid **IX** is lower by an order of magnitude. Compounds formed by oxidative destruction of compound **I** were also found in the reaction mixture: cyclopentadiene, cyclopentadiene dimer, and a Fe^{3+} derivative. A more profound oxidation of compound **I** ($N_{O_2} > 2$) gave CO, CO_2, and unidentified organic compounds. As one of the intermediate reaction product we detected the corresponding ferricinium ion whose electronic absorption spectrum contains in the long-wave region a band with λ_{max} 616 nm, which distinguished this spectrum of the spectrum of a compound obtained by treatment of **I** with perchloric acid. Noteworthy is the fact that the oxygen consumption in the oxidation of **I** is much greater than in the oxidation of ferrocene (~0.3).

The kinetic results show that the oxidation of hydroxymethylferrocene (**I**) in the presence of acids **VI** and **VII** is a first-order reaction in metal complex, oxygen, and benzoic acid (Fig. 2). With trifluoroacetic acid (**VII**), the maximum reaction rate W_{max} linearly varies with acid concentration only at low concentrations of **VII**. As higher acid concentrations,

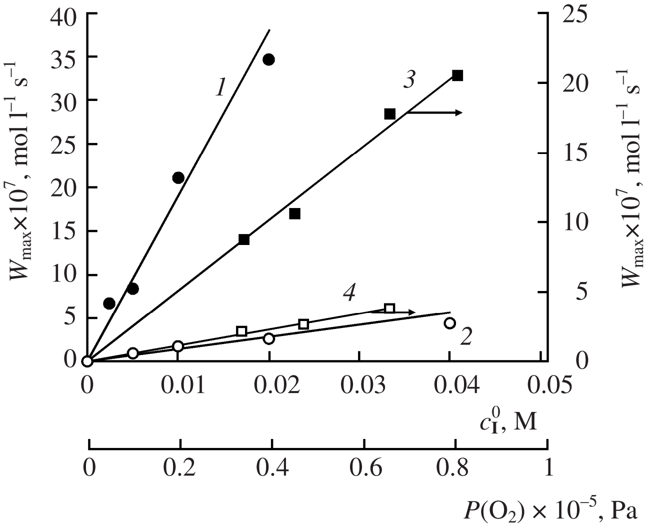


Fig. 2. Dependences of the oxidation rates of compound **I** on (*1, 2*) its concentration and (*3, 4*) oxygen pressure in the presence of (*1, 3*) benzoic (**VI**) and (*2, 4*) trifluoroacetic (**VII**) acid. c^0_{VI} 0.55, c^0_{VII} 0.06 M; $P(O_2)$ (*1, 2*) 0.47×10^5 Pa; c^0_{I} 0.02 M, *T* 50°C.

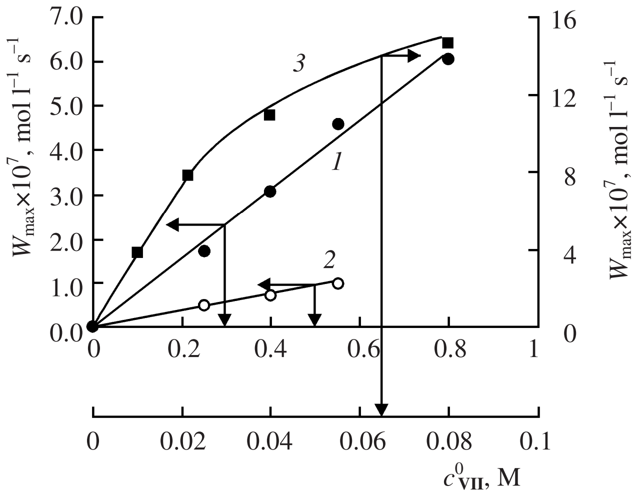


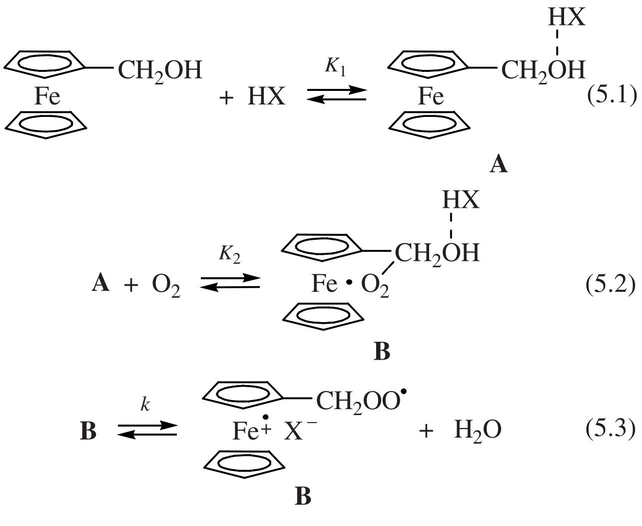
Fig. 3. Dependences of the oxidation rates of compound **I** on the concentration of (*1, 2*) benzoic (**VI**) and (*3*) trifluoroacetic (**VII**) acid in (*1, 3*) dioxane and (*2*) toluene. c^0_{I} 0.02 M, *T* 50°C, $P(O_2)$ 0.47×10^5 Pa.

the reaction order in the acid becomes lower than 1 (Fig. 3). The reaction time in the kinetic experiments was taken to be no longer than 10–15 min to exclude variation in the concentration of compound **I** due to its possible reaction with the acid and intramolecular dehydration with ether formation.

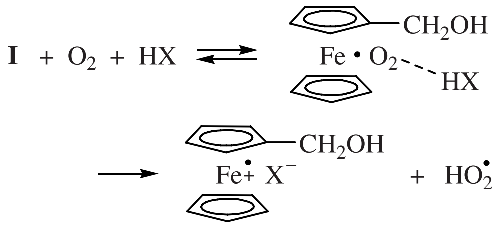
To gain insight into the reaction mechanism, we studied the effect of additives known as free-radical inhibitors (Ionol, *o*-phenylenediamine) on the oxidation rate of compound **I**. The results of this study, illustrated in Fig. 4, show that the above additives strongly decelerate oxidation. This finding implies that the overall oxidation process is mostly contributed by the radical chain path, and the revealed formal kinetic regularities relate just to this path. Evidence for this conclusion comes from the fact that the oxidation of compound **I** in the presence of acid **VII** in methyl methacrylate or in the dioxane–methyl methacrylate system is accompanied by polymerization of the monomer. The radical chain mechanism explains the formation of aldehyde **VIII** and acid **IX** in the oxidation of alcohol **I**, since aldehydes and carboxylic acids are known to be the major products of the radical chain oxidation of alcohols with oxygen [28].

The above-presented data raise two principal questions: (1) How radicals are generated at the initial stages of the process and (2) how the chain process itself develops? Since compound **I** is oxidized in miles temperature conditions (30–50°C) and only in the presence of acids, we can suggest that radicals are generated by molecular oxidation of the metal complex (Scheme 5).

Scheme 5.



The key stage in this scheme is the formation of ternary complex HX·**I**·O$_2$ in which the O$_2$ molecule is simultaneously bound with the metal atom and the electrophilic carbon atom, which strengthens each of these donor–acceptor bonds. The C–O$_2$ bond formation stimulates electron transfer from O_2 to iron and, as a result, polarizes the C–OH bond. This makes possible proton transfer to the hydroxyl group from the coordinated HX molecule and transformation of the ternary complex according to Eq. (5.3). The formation of water in this reaction makes it thermodynamically favorable. Complex **A** can be considered as a bifunctional reagent, and, therefore, it is safe to state that the effect of mutual approach and orientation contributes something to make reaction of this complex with molecular oxygen possible in principle. Scheme 5 can explain in part the retarding effect of water and ethanol on the reaction in hand, since they both can prevent the OH group from coordination with HX, thus slowing down radical generation. At a different mode of coordination of O_2 with HX and **I** [Eq. (5)], the oxidation of the latter becomes even less thermodynamically favorable compared to ferrocene [8], since alcohol **I** contains an electron-acceptor substituent.



(5)

As seen, Eq. (5) is identical to model Eq. (4).

The principal stages of the radical chain process are shown in Scheme 6.

Reaction (6.10) generates chain-propagating radicals $C_5H_5FeC_5H_4C^{\cdot}HOH$ but does not affect their generation rate.

Reactions (6.2)–(6.4) are analogous to reactions involved in the radical chain oxidation of ethanol, leading to acetaldehyde and acetic acid [28]. Reaction (6.5) can be considered as a chain-terminating reaction, since it is known that ferrocene and its derivatives easily react with peroxide radicals ($k \sim 10^5$ l mol^{-1} s^{-1}) according to Eq. (6) [29].

$$C_5H_5FeC_5H_4X + RO_2^{\cdot} \rightarrow (C_5H_5)Fe^{\dot{+}}(C_5H_4X)OOR^-, \quad (6)$$

X = H, alkyl, CHO, COOH, CN, COR.

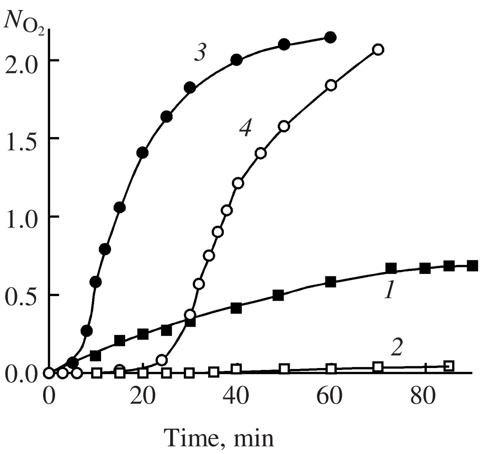


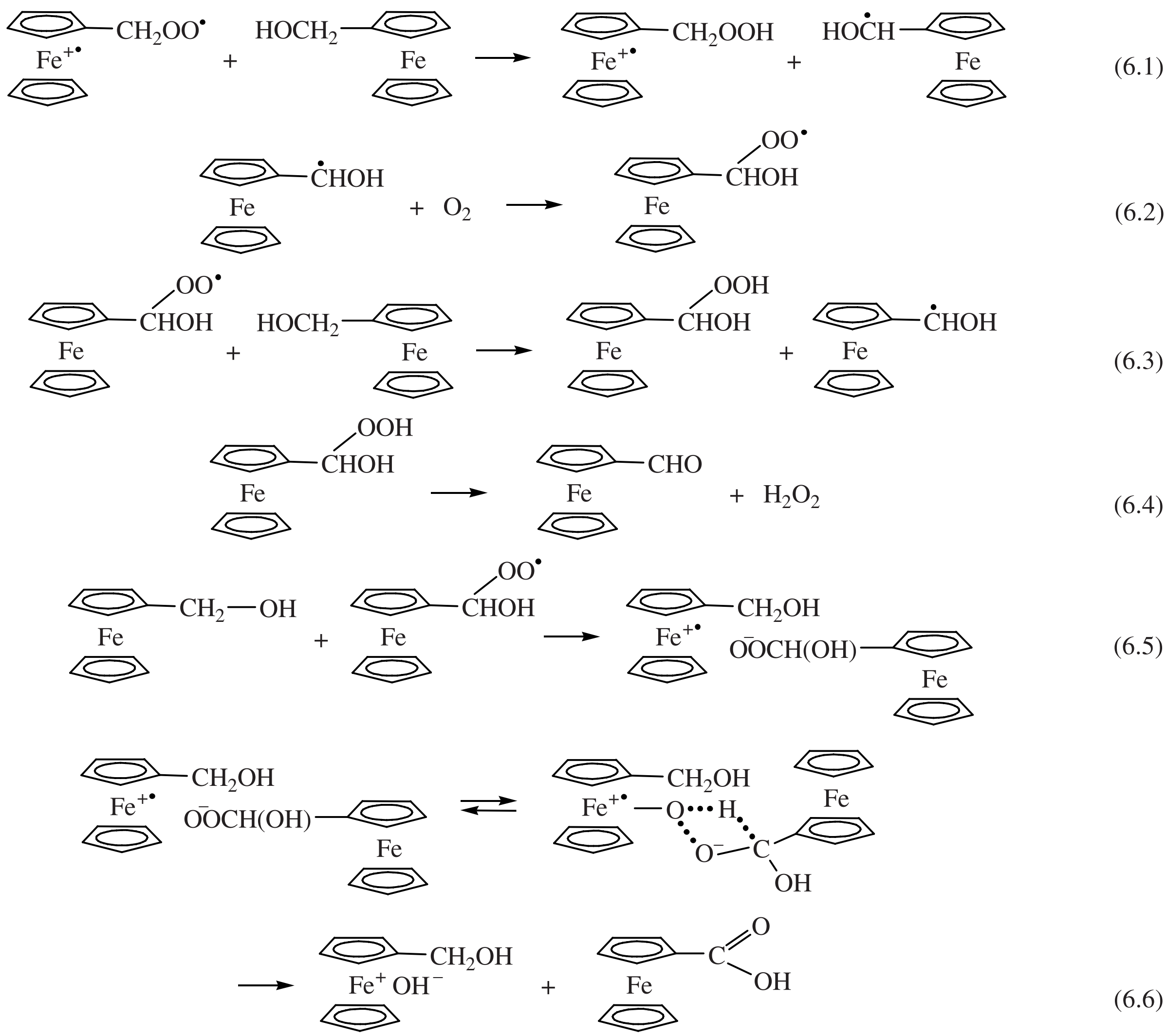
Fig. 4. Effect of *o*-phenylenediamine (In) on the oxidation rate of compound **I** in the presence of (*1, 2*) benzoic (**VI**) and (*3, 4*) trifluoroacetic (**VII**) acid. c^0_{I} 0.02; c^0_{In} 4×10^{-4}, c^0_{VI} 0.55, c^0_{VII} 0.2 M; $P(O_2)$ 0.47×10^5 Pa; T 50°C.

Quadratic chain termination on peroxide radicals is not included in Scheme 6 by the following reasons. The rate constant of reaction (6) compares with the recombination rate constant of the peroxide radicals formed by oxidation of alkylaromatic hydrocarbons [30]. At the same time, the concentration of the $C_5H_5FeC_5H_4CH(OH)OO^{\cdot}$ radicals is much lower than the concentration of compound **I**. For example, the steady-state concentration of $C_6H_5CH(CH_3)OO^{\cdot}$ in the oxidation of ethylbenzene is $\sim10^{-6}$ M at the reaction initiation rate $\sim10^{-5}$ mol l^{-1} s^{-1}. In our case, the rate of inhibited oxidation of compound **I**, which can be taken as the rate of initiation by Scheme 5 is $\sim 10^{-9}$ mol l^{-1} s^{-1}. Consequently, the steady-state concentration of peroxide radicals in the oxidation of alcohol **I** will be much lower than 10^{-6} M, from which it follows that $v_6 >> v_t = 2k_t[RO_2^{\cdot}]^2$. Rearrangement (6.6) is characteristic of ionic peroxide complexes like $L_nM^+OOCH_2R^-$ (L_nM is a transition metal complex), when the carbon atom attached to the peroxide group bears hydrogen [18]. Thus, Scheme 6 is analogous a classical scheme of hydrocarbon oxidation not complicated by degenerate chain branching [28].

It is known that radical chain hydrocarbon oxidation reactions are solvent-sensitive. This explains why ethanol, water, and even carboxylic acids in considerable quantities adversely affect reaction rate, since solvents and compounds capable of forming strong hydrogen bonds with radicals $RO_2^{\cdot}$ deactivate the latter and thus inhibit radical chain reactions [28]. By the same reason, acids differently affect the rates of molecular and radical chain oxidation of compound **I**.

The oxidative destruction of hydroxymethylferrocene (**I**) can involve oxidation of the ferricinium ion formed [26, 27] and its disproportionation [31] and decomposition, provided it contains a perioxide anion

Scheme 6.



[18]. As known, CO and CO_2 result from oxidative decarbonylation and decarboxylation of aldehydes and carboxylic acids, respectively.

Let us find out whether Scheme 5 corresponds to the kinetics of radical chain oxidation of compound **I**. Kinetic equation (7) relates to the radical chain reaction path involving the substituent.

$$\nu = k_{app}[\mathbf{I}][O_2][HX]. \qquad (7)$$

According [28], the rate of radical chain oxidation of hydrocarbons is limited by the chain propagation stage involving peroxide radicals.

$$\nu = k_p[RO_2^{\cdot}][RH]. \qquad (8)$$

Let $RO_2^{\cdot} = C_5H_5FeC_5H_4CH(OH)OO^{\cdot}$ and $RH = \mathbf{I}$. Let us assume that the chain is terminated by peroxide radicals by reaction (6), and, therewith, the steady-state chain termination rate ν_t is equal to the rate of $R^{\cdot}$ generation ν_0. According to Eq. (6.5), the rate of chain termination will be given by Eq. (9).

$$\nu_t = k_t[I][C_5H_5FeC_5H_4CH(OH)\text{–}O\text{–}O^{\cdot}]$$
$$k_t[RH][RO_2^{\cdot}]. \qquad (9)$$

Equating the reaction rates given by Eqs. (7) and (8), we obtain Eq. (10) that relates the $RO_2^{\cdot}$ concentrations to the concentrations of the starting compounds. Substituting this expression in the chain termination rate equation we obtain Eq. (11) for the rate of chain initiation.

$$[RO_2^{\cdot}] = \frac{k_{app}}{k_p}[O_2][HX], \qquad (10)$$

$$\nu_0 = \nu_t = \frac{k_t k_{app}}{k_p}[RH][O_2][HX] = k_0[RH][O_2][HX]. \quad (11)$$

Analyzing Scheme 5 for the suggested molecular oxidation of compound **I** under the assumption that the process is quasi-equilibrium, and the concentrations of complexes **A** and **C** are much lower than the concentrations of the starting reagents, we can show [32] that the rate of the radical generation process has Eq. (12).

$$\nu = k_1K_1K_2[I][O_2][HX]. \quad (12)$$

This equation can be shown to be equivalent to Eq. (11) for the rate of chain initiation, obtained by an analysis of the radical chain oxidation of compound **I**, under the assumption $k_0 = k_1K_1K_2$.

This result points to a complete kinetic equivalence of Schemes 5 and 6, which allows one to combine these two schemes a single scheme of oxidation of compound **I** with oxygen.

Summarizing the aforesaid, we can say that the results obtained provide convincing evidence to show that OH- or CH_2OH-substituted ferrocenes have a radically different mechanism of oxidation with oxygen and radically differ from unsubstituted ferrocene in reactivity toward oxygen. With compound **II** as a bifunctional reagent, these changes are associated with a well-pronounced effect of mutual approach and orientation, and with compounds **I**, with a new, radical chain oxidation path. The appearance of this new path, too, is due to the effect of mutual approach and orientation, that reveals itself at the chain initiation stage.

EXPERIMENTAL

The electronic absorption spectra were measured on a Varian Cary 50 spectrophotometer. Analysis of the reaction products was performed by two methods: TLC and GC–MS. In the first case, Sorbfil (eluent chloroform–methyl acetate, 1:1) and Silufol (eluent chloroform). In the second case, a Kristall 5000.1 (Khromatek Construction and Design Office) coupled with a TRACE DSQ (Termo Finnigan): column RTX-5MS, T_{init} 110°C, hold 1 min, ramp 15 deg min^{-1}, T_{fin} 250°C, total time of analysis 30 min, T_{inj} 250°C, split ratio 1:30, injection volume 1 μl; scan time 30 min, scan range 50–500 amu, gain factor 3, scan rate 5 scans sec^{-1}, ionizing electron energy 70 eV.

The oxidation of ferrocenylmethanol (**I**) was performed in a vacuum static device under vigorous stirring. The reaction progress was followed by oxygen absorption measured by manometry.

Compound **I** was synthesized by the procedure in [33] and purified by column chromatography on Al_2O_3 using the Trappe solvent series [22]. Ferrocenecarbaldehyde (**VIII**) was synthesized by the procedure in [34] and crystallized from ether. Ferrocenecarboxylic acid (**IX**) was synthesized according [35] and crystallized from ligroin and ethanol.

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