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# Common Relationships of Ferrocene Oxidation with Oxygen and Sulfur Dioxide in Acid Solutions and of Its Direct Oxidation with Carboxylic Acids

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Received October 20, 2006

**Abstract**—Mechanisms of ferrocene oxidation with molecular oxygen and sulfur dioxide in acid solutions and of its direct oxidation with carboxylic acids were suggested on the basis of kinetic and thermodynamic analysis of the published data. All the mechanisms are based on a common proposition: The species reacting with an oxidant is the protonated ferrocene molecule acting as a donor of atomic hydrogen, which is favored by the low energy of the Fe–H bond.

**DOI:** 10.1134/S1070363207050246

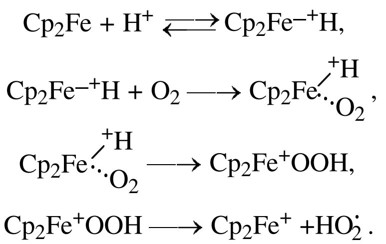
Among numerous reactions of ferrocene oxidation with various oxidants [1], we can distinguish a separate group including the reactions that occur in the presence of strong Brønsted acids, such as autooxidation of ferrocene [1–4], its reaction with $SO_2$ [4], and also direct oxidation of ferrocene with strong carboxylic acids (e.g., trifluoroacetic acid) [5]. The mechanisms of these reactions adequately describing their specific features have not been described. At the same time, apparently, all these mechanisms should have much in common and should involve the same key steps. Here I attempt to summarize and correlate the available data with the aim to reveal common relationships of these reactions.

It is known that in the absence of strong acids ferrocene is very stable to oxygen, because its redox potential ($E^0_{\mathrm{Cp_2Fe^+/Cp_2Fe}}$ 0.59 V [5]) is significantly higher than that of oxygen ($E^0_{\mathrm{O_2^{-\cdot}/O_2}}$ −0.56 V). In acid solutions, the oxidative power of oxygen increases considerably; therefore, from the thermodynamic viewpoint, the oxidation of ferrocene in accordance with Eq. (1) [6] becomes favorable, as the standard redox potential of the system $O_2 + 4H^+$ is as high as 1.23 V [7]:

$$4Cp_2Fe + O_2 + 4H^+ \longrightarrow 4Cp_2Fe^+ + 2H_2O. \quad (1)$$

The possibility of occurrence of reaction (1) was proved by Bitterwolf and Ling [4] who studied oxidation of ferrocene in trifluoroacetic acid and suggested the mechanism of primary steps of this reaction (Scheme 1), which is the only mechanism known by now.

**Scheme 1.**



$$Cp_2Fe + H^+ \rightleftarrows Cp_2Fe{-}^{+}H,$$

$$Cp_2Fe{-}^{+}H + O_2 \longrightarrow Cp_2Fe\begin{array}{l}{}^{+}H\\ \cdot O_2\end{array},$$

$$Cp_2Fe\begin{array}{l}{}^{+}H\\ \cdot O_2\end{array} \longrightarrow Cp_2Fe^+OOH,$$

$$Cp_2Fe^+OOH \longrightarrow Cp_2Fe^+ + HO_2^{\cdot}.$$

The overall equation is

$$Cp_2Fe + O_2 + H^+ \longrightarrow Cp_2Fe^{+\cdot} + HO_2^{\cdot} \quad (2)$$

Bitterwolf and Ling [4] believe that, in coordination with $Cp_2Fe–H^+$, the $O_2$ molecule behaves as a Lewis acid, interacting with the filled *d* orbitals of iron; the protonation of ferrocene, yielding a structure with inclined Cp ligands, facilitates the attack of the Fe atom with oxygen owing to a decrease in the steric hindrance. The scheme given above, however, seems doubtful because of the following facts.

(1) Altough oxygen forms highly labile adducts with $Cp_2Fe$, recorded at a liquid nitrogen temperature [8], protonation of the metal complex and appearance of a positive charge, as noted in [9], make it too weak base for the coordination with another Lewis acid; therefore, e.g., the dication $Cp_2FeH_2^{2+}$ is not formed. The coordination of such a weak Lewis acid as the $O_2$ molecule to $Cp_2Fe–H^+$ seems still less probable.

(2) The insertion of triplet oxygen into the Fe–H bond by the molecular mechanism is spin-forbidden.

(3) If we assume that in Scheme 1 the limiting step is $O_2$ insertion into the Fe–H bond, then it can be readily shown that the reaction rate is described by Eq. (3):

$$V = k_{app}[Cp_2Fe][O_2][H^+]. \qquad (3)$$

The experimental rate equation has form (4) [3], which suggests its different mechanism.

$$V_{exp} = k_{app}[Cp_2Fe]_2[O_2][H^+]^2. \qquad (4)$$

(4) The standard Gibbs energy of reaction (2), calculated by the well-known relationship $\Delta G_2^0 = -zFE_0$ (where $z$ is the number of electrons participating in the process, $E^0$ is the difference between the standard potentials of the oxidant and substance being oxidized, and $F$ is the Faraday number), is large and positive, 69.5 kJ $mol^{-1}$, and the corresponding formal equilibrium constant at 298 K is $6.3 \times 10^{-13}$, i.e., the reaction is improbable. Reaction equation (1) bears no information about its mechanism, and the corresponding value of $\Delta_r G^0$, equal to –247.0 kJ $mol^{-1}$, cannot be considered as a thermodynamic criterion of the oxidation of ferrocene in acid solutions, because it characterizes the energies of all the steps of the process, including those following the limiting step and leading to the cleavage of the $O_2$ molecule and formation of $H_2O$. Taking into account the rate equation (4) of ferrocene oxidation and the fact that the maximal number of electrons that the oxygen molecule can accept as oxidant without rupture of the O–O bond is two, it is appropriate to estimate the Gibbs energy for the oxidation reaction involving two ferrocene molecules, i.e., reaction (5):

$$2Cp_2Fe + O_2 + 2H^+ \longrightarrow 2Cp_2Fe^+ + H_2O_2. \qquad (5)$$

Lubach and Drenth [3], who studied the kinetics of ferrocene oxidation in the presence of perchloric acid in the mixed ethanol–water solvent, were the first who considered this reaction, which led them to Eq. (4). However, hydrogen peroxide was not detected in the reaction products, which was attributed to its possible consumption for oxidation of ethanol under the action of $Fe^{2+}$ ions released in the course of oxidative degradation of ferrocene. Indeed, the ethanol oxidation products (acetaldehyde, acetic acid, ethyl acetate) were detected in the reaction mixture.

The standard redox potential of the oxidizing system $O_2 + 2H^+$ is 0.682 V [7], whence follows that the Gibbs energy of reaction (5) is –17.8 kJ $mol^{-1}$, i.e., it is considerably lower than that of reaction (2).

Thus, specifically for reaction (5) it is necessary to find a mechanism consistent with rate equation (4).

It should be noted that Scheme 1 supplemented with the reactions

$$Cp_2Fe + HO\cdot \longrightarrow Cp_2Fe^+OOH^-,$$

$$Cp_2Fe^+OOH^- + H^+ \longrightarrow Cp_2Fe^+ + H_2O_2$$

leads to Eq. (5). However, in this case the reaction will be described by rate equation (3) rather than (4), because both steps are fast [10, 11] and cannot be considered as limiting. The mechanism of reaction (5) can be based on the following data directly or indirectly characterizing the properties of ferrocene.

(1) Capability of ferrocene for fast equilibrium protonation with strong acids, proved in numerous papers [1, 9, 12–16].

(2) Capability of protonated ferrocene to react with oxygen, proved, e.g., by ready oxidation of an ionic complex $[Cp_2FeH]^+AlCl_4^-$ containing protonated ferrocene to the radical ion salt $Cp_2Fe^+AlCl_4^- \cdot H_2O$ containing ferricenium ion [4].

(3) Low energy of the Fe–H bond in protonated ferrocene, equal to 209.2 kJ $mol^{-1}$ [15], which allows it to be considered as an efficient donor of atomic hydrogen for the oxidant molecule. All these data and the results of kinetic studies can be summarized in the form of the probable mechanism of ferrocene oxidation, shown in Scheme 2.

**Scheme 2.**

$$Cp_2Fe + H^+ \overset{K_1}{\rightleftarrows} Cp_2Fe\text{–}{}^+H \,|\times 2, \qquad (2.1)$$

$$Cp_2Fe^{-+}H + O_2 + H^+\text{–}Cp_2Fe \xrightarrow{k_2} 2Cp_2Fe^+ + H_2O_2, \qquad (2.2)$$

$$V = k_2[Cp_2Fe\text{–}{}^+H]^2[O_2].$$

Close analogs of reaction (2) are the well-known steps of chain initiation in liquid-phase autooxidation of hydrocarbons [17, 18]:

$$R\text{–}H + O_2 \longrightarrow R^{\cdot} + HO_2^{\cdot}, \qquad (6)$$

$$R\text{–}H + O_2 + H\text{–}R \longrightarrow 2R^{\cdot} + H_2O_2. \qquad (7)$$

The calculations and experimental studies [17, 18] show that, in oxidation of hydrocarbons with relatively weak C–H bonds whose energy does not exceed 330 kJ $mol^{-1}$, reaction (7) is considerably more favorable kinetically and thermodynamically than reaction (6). The energies of the Fe–H and $Cp_2Fe\text{–}{}^+H$ bonds are substantially lower than this threshold value. Reaction (7) is not necessarily trimolecular and may involve intermediate formation of a hydrogen-bonded complex of oxygen with one of RH molecules [17, 18]. This fact was reflected in Scheme 3 of ferrocene oxidation. The capability of protonated ferrocene to form hydrogen-bonded complexes with *n*-electron donors such as $O_2$ molecule was proved in [15].

**Scheme 3.**

$$Cp_2Fe + H^+ \xrightleftharpoons{K_1} Cp_2Fe{-}^+H \,\Big|\, \times 2, \qquad (3.1)$$

$$Cp_2Fe{-}^+H + O_2 \xrightleftharpoons{K_2} Cp_2Fe{-}^+H\cdots O_2, \qquad (3.2)$$

$$Cp_2Fe{-}^+H\cdots O_2 + H^+{-}FeCp_2 \xrightarrow{k_3} 2Cp_2Fe^+ + H_2O_2, \qquad (3.3)$$

$$V_3 = k_3[Cp_2Fe{-}^+H\cdots O_2][Cp_2Fe{-}^+H].$$

Schemes 2 and 3 suggest the same structure of the transition state in the limiting step: $[Cp_2Fe^+\cdots H\cdots|\overline{\underline{O}}\cdots\overline{\underline{O}}|\cdots H\cdots{}^+FeCp_2]^{\#}$.

This structure, optimal from the viewpoints of the steric hindrance to the reaction and of the product composition, favors concerted breakdown of old and formation of new bonds in reagent molecules, which should lead to a decrease in the activation energy of the limiting step.

The validity of the suggested mechanisms from the thermodynamic standpoint is proved by the results of the calculation of $\Delta_rH^0(298.15)$ and $\Delta_rG^0(298.15)$ of reaction (22) in the gas phase (see below). We also give for comparison the related parameters for reaction (8):

$$Cp_2Fe{-}^+H + O_2 \longrightarrow Cp_2Fe^+ + HO_2^{\bullet}. \qquad (8)$$

| Reaction | $\Delta_rH^0$, kJ mol$^{-1}$ | $\Delta_rS^0$, J mol$^{-1}$ K$^{-1}$ | $\Delta_rG^0$, kJ mol$^{-1}$ |
|---|---|---|---|
| $2Cp_2Fe{-}^+H + O_2 \rightarrow$ P* | –168.1 | –29.5 | –159.3 |
| $Cp_2Fe{-}^+H + O_2 \longrightarrow$ P* | –13.9 | –4.2 | –12.6 |

* P denotes products indicated in the reaction equations.

To calculate $\Delta_rH^0$ of reactions, we used the well-known thermochemical relationship $\Delta_rH^0(298.15) = \Sigma\nu_j\delta_fH^0(298.15,\ j) - \Sigma\nu_i\Delta_rH^0(298.15,\ i)$, where $\Delta_fH^0(298.15,\ j)$ and $\Delta_fH^0(298.15,\ i)$ are the standard enthalpies of formation of the reaction products and starting substances, respectively.

The standard enthalpy of formation of protonated ferrocene $Cp_2Fe{-}H^+$ used in the calculations and equal to 897.9 kJ mol$^{-1}$ was found from the relationship $\Delta_fH^0(298.15,\ Cp_2Fe{-}H^+) = \Delta_fH^0(298.15,\ Cp_2Fe) + \Delta_fH^0(298.15,\ H^+) - \bar{PA}$, because this quantity is not available from the literature; here $\bar{PA}$ is the mean proton affinity of ferrocene (863.6 kJ mol$^{-1}$) [19].

The quantity $\Delta_fH^0(298.15,\ Cp_2Fe^+)$ was found as the sum of $\Delta_fH^0(298.15,\ Cp_2Fe)$ [20] and the ionization potential of ferrocene *IE* [21].

In the calculation of $\Delta_rS^0(298.15)$, $S^0(298.15,\ Cp_2Fe{-}H^+)$ was taken equal to 393.5 J mol$^{-1}$ K$^{-1}$ [15], and the absolute entropy of the ferricenium ion was taken equal to the absolute entropy of ferrocene, 365.3 J mol$^{-1}$ K$^{-1}$, assuming that they differ insignificantly [20]. The validity of this approach is proved by the results of calculation of the absolute entropy of ferrocene and ferricenium ion by the DFT B3LYP method in the 6-311G* basis set. The calculations showed that, within the calculation error, the quantities $S^0(298.15,\ Cp_2Fe)$ and $S^0(298.15,\ Cp_2Fe^+)$ are virtually equal: 373 ± 10 and 378 ± 10 J mol$^{-1}$ K$^{-1}$, respectively. Nevertheless, the $\Delta_rS^0$ and $\Delta_rG^0$ values for reactions (22) and (8) should be considered as estimates. The thermodynamic functions of the other reagents were taken from [21, 22].

The above data show that reaction (22) is considerably more favorable thermodynamically than reaction (8), which ultimately determines the mechanism and kinetic features of ferrocene oxidation. It should be noted that the energy characteristics of these reactions in solution will undoubtedly be somewhat different, but there are no grounds to expect different trends in their variation.

Kinetic analysis of Schemes 2 and 3 leads to the rate equation identical to the experimental equation. Let us illustrate this by the example of Scheme 2. Let us write the expression for the reaction rate:

$$V = k_2[Cp_2Fe{-}^+H]^2[O_2].$$

The quantity $[Cp_2Fe^+{-}H]$ can be found from the equilibrium condition for step (21) assuming that $[H^+] >> [Cp_2Fe]_0$ and $[Cp_2Fe]_0 = [Cp_2Fe] + [Cp_2Fe{-}^+H]$. Then we obtain

$$[Cp_2Fe{-}^+H] = \frac{K_1[Cp_2Fe]_0[H^+]_0}{1 + K_1[H^+]_0},$$

$$V = \frac{k_2K_1^2[Cp_2Fe]_0^2[O_2][H^+]^2}{(1 + K_1[H^+]_0)^2}. \qquad (9)$$

At $K_1[H^+]_0 << 1$, Eq. (9) transforms into Eq. (4), where $k_{app} = k_2K_1^2$. At high acid concentrations ($K_1[H^+]_0 >> 1$), the reaction rate will tend to the maximal value, $V_{max}$:

$$V_{max} = k_2[Cp_2Fe]_0^2[O_2]_0. \qquad (10)$$

Scheme 3 differs from Scheme 2 in that it includes one more rapidly attained equilibrium: formation of the hydrogen-bonded complex $Cp_2Fe–{}^+H\cdots O_2$. It can be shown that, at a steady-state concentration of the complex $Cp_2Fe–{}^+H\cdots O_2$, with $[O_2]_0 >> [Cp_2Fe–{}^+H\cdots O_2]$ and $[Cp_2Fe–{}^+H] >> Cp_2Fe–{}^+H\cdots O_2$, the reaction rate will be described by an equation similar to Eq. (9):

$$V = \frac{k_3K_1^2K_2[Cp_2Fe]_0^2[O_2][H^+]_0^2}{(1 + K_1[H^+]_0)^2}. \qquad (11)$$

The possibility of $H_2O_2$ formation in the course of $Cp_2Fe$ autooxidation, following from the above schemes, accounts also for the final stoichiometry of the process, described by Eq. (1). It is known that, in acid solutions, hydrogen peroxide is a strong oxidant [7] and readily oxidizes ferrocene to ferricenium ion [3]. The possible oxidation equations are as follows:

$$Cp_2Fe–{}^+H + H_2O_2 \longrightarrow Cp_2Fe^+ + H_2O + HO^{\cdot}, \qquad (12)$$

$$Cp_2Fe + H_3O_2^+ \longrightarrow Cp_2Fe^+ + H_2O + HO^{\cdot}. \qquad (13)$$

Just these reactions are primarily responsible for the absence of $H_2O_2$ in the final products of ferrocene oxidation. The protonation of $H_2O_2$ and formation of $H_3O_2^+$ are characterized by the equilibrium constant of $\sim 10^{-3}$ [23]. The $HO^{\cdot}$ radical is simultaneously a strong one-electron oxidant ($\varphi^0$ 2.0 V in alkaline solutions and 2.8 V in acid solutions [7]) and an active radical; thus, it can oxidize nonprotonated ferrocene and abstract the hydrogen atom from protonated ferrocene:

$$Cp_2Fe–{}^+H + HO^{\cdot} \longrightarrow Cp_2Fe^+ + H_2O, \qquad (14)$$

$$Cp_2Fe + HO^{\cdot} \longrightarrow Cp_2Fe^+OH^-, \qquad (15)$$

$$Cp_2Fe^+OH^- + H^+ \longrightarrow Cp_2Fe^+ + H_2O. \qquad (16)$$

These assumptions are confirmed by the thermodynamic characteristics of reactions (12) and (14) in the gas phase:

| Reaction | $\Delta_rH^0$, kJ mol$^{-1}$ | $\Delta_rS^0$, J mol$^{-1}$ K$^{-1}$ | $\Delta_rG^0$, kJ mol$^{-1}$ |
|---|---|---|---|
| $Cp_2Fe–{}^+H + H_2O_2 \to P$* | –82.4 | 112.3 | –115.7 |
| $Cp_2Fe–{}^+H + HO^{\cdot} \to P$* | –297.2 | –23.0 | –290.3 |

* P denotes products indicated in the reaction equations.

The set of reactions (2.1), (2.2) or (3.1)–(3.3) and Eqs. (12)–(16) leads to overall stoichiometric equation (1) of ferrocene oxidation.

Thus, it can be concluded that the suggested mechanism of ferrocene oxidation including Scheme 2 or 3 and Eqs. (12)–(16) describes most adequately (from the thermodynamic and kinetic viewpoints) the features of this reaction in acid solutions.

In conclusion, we should note that autooxidation of ferrocene in ethanol can be complicated by oxidation of ethanol to acetaldehyde and acetic acid [3]. It is known that these compounds are products of radical chain oxidation of ethanol [18]. Under the conditions of ferrocene oxidation, this process can be initiated, most likely, by $HO^{\cdot}$ radicals generated by reactions (12) and (13), and also by the redox system $H_2O_2$–$Fe^{2+}$–$Fe^{3+}$ suggested in [3]. The consumption of $H_2O_2$ for ethanol oxidation accounts for the fact that in this solvent the maximal yield of the ferricenium ion is ~2.9 mol per mole of $O_2$ taken up [3], whereas in oxidation of $Cp_2Fe$ in trifluoroacetic acid it is 4 mol per mole of $O_2$ [4].

An analog of molecular oxygen as ferrocene oxidant is sulfur dioxide. This analogy is manifested in that, first, it reacts with ferrocene only in the presence of strong acids (oxidizing systems $CF_3SO_3H$–liquid $SO_2$, $CH_3COOH$–gaseous $SO_2$); second, the stoichiometry of $Cp_2Fe$ oxidation with sulfur dioxide is described by Eq. (17), similar to Eq. (1) of the oxidation of this metal complex with oxygen [4]:

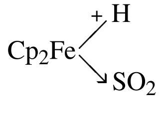
$$4Cp_2Fe + SO_2 + 4H^+ \longrightarrow 4\,Cp_2Fe^+ + 2H2O + S. \qquad (17)$$

Apparently, for this reason Bitterwolf and Ling [4] assume for the initial steps of ferrocene oxidation with $SO_2$ the same reaction sequence as in its oxidation with oxygen, namely: coordination of $SO_2$ as a Lewis acid with the iron atom of the protonated ferrocene molecule, insertion of the coordinated oxidant into the Fe–H bond with the formation of the intermediate $Cp_2Fe^+–SO_2H$, and its subsequent transformation with the elimination of the $HS^{\cdot}O_2$ radical and formation of the $Cp_2Fe^{+\cdot}$ cation. The overall equation for these steps is as follows:

$$Cp_2Fe–{}^+H + SO_2 \longrightarrow Cp_2Fe^+ + HS^{\cdot}O_2 \qquad (18)$$

Further transformations of the $HS^{\cdot}O_2$ radical were not discussed.

The main factor preventing the realization of this mechanism is the low probability of formation of the coordination complex



for the reason noted above in the discussion of Scheme 1. Unfortunately, data required for discussing the kinetic and thermodynamic aspects of reaction (18) are lacking.

Considerably less contradictory and more logical is the mechanism of $Cp_2Fe$ oxidation with sulfur dioxide, based on the capability of protonated ferrocene to act as a donor of atomic hydrogen for an oxidant molecule, as it was shown in Schemes 2 and 3 of ferrocene oxidation with oxygen.

$$\mathrm{Cp_2Fe + H^+ \rightleftarrows Cp_2Fe{-}^+H} \;|\times 2 \text{ (or 4)}, \tag{19}$$

$$\mathrm{Cp_2Fe{-}^+H + SO_2 \rightleftarrows \underset{(A)}{Cp_2Fe{-}^+H\cdots|\underline{\bar{O}}{-}\bar{S}{=}\underline{\bar{O}}}}, \tag{20}$$

$$\begin{gathered}\mathrm{Cp_2Fe{-}^+H\cdots|\underline{\bar{O}}{-}\bar{S}{=}\underline{\bar{O}} + H^+{-}FeCp_2} \\ \longrightarrow \mathrm{2Cp_2Fe^+ + H_2O + SO}.\end{gathered} \tag{21}$$

The standard Gibbs energy of reduction of $SO_2$ to SO in the gas phase in accordance with Eqs. (20) and (21) is a small negative quantity, –1.46 kJ $mol^{-1}$.

The SO biradical $\{\Delta_f H^0$(298.15) 5.01 kJ $mol^{-1}$ [21]$\}$ is extremely reactive [24] and can readily transform either by disproportionation [25] [reaction (22)] or by successive or simultaneous abstraction of two hydrogen atoms from two $Cp_2FeH^+$ molecules [reaction (23)]:

$$\mathrm{2SO \longrightarrow S + SO_2}, \tag{22}$$

$$\mathrm{Cp_2Fe{-}^+H + SO + H^+{-}FeCp_2 \rightarrow 2\,Cp_2Fe^+ + H_2O + S}. \tag{23}$$

The calculations show that in the gas phase reactions (22) and (23) are characterized by negative standard Gibbs energies, –21.6 and –25.2 kJ $mol^{-1}$, respectively. Since reaction (17) occurs in the liquid phase and the released sulfur is in the crystalline state, the quantities $\Delta_r G^0_{22}$ and $\Delta_r G^0_{23}$, taking into account the crystalline state of the formed sulfur and the enthalpy (–277 kJ $mol^{-1}$) and entropy ($S^0_{\mathrm{rhomb}} - S^0_{\mathrm{gas}}$ = 31.88 – 167.83 J $mol^{-1}$ $K^{-1}$ [21]) of its crystallization, become equal to –258.1 and –261.7 kJ $mol^{-1}$, respectively. This fact indicates that these reactions, if they occur in the liquid phase, are very favorable from the thermodynamic viewpoint, although the solvation effects can somewhat alter $\Delta_r G^0_{22}$ and $\Delta_r G^0_{23}$.

The set of reactions (19)–(21) and (22), or reactions (19)–(21) and (23), taking into account the corresponding stoichiometric coefficients for the step of ferrocene protonation, leads to the final stoichiometric equation of ferrocene oxidation with sulfur dioxide in the presence of strong Brønsted acids (17).

Oxidation of ferrocene with some carboxylic acids, e.g., trifluoroacetic and trichloroacetic, in benzene solution at 25°C occurs in accordance with Eq. (24) [5]:

$$\begin{gathered}\mathrm{2Cp_2Fe + 3RCOOH} \\ \mathrm{2Cp_2Fe^+OCOR^- + RCHO + H_2O}.\end{gathered} \tag{24}$$

The reaction rate grows as the acid concentration, its strength, and basicity of the metal complex are increased. In particular, whereas ferrocene does not react with acetic acid, decamethylferrocene is oxidized with both strong and weak carboxylic acids RCOOH, with the reaction rate increasing in the following order of substituents R: $CH_3 < CH_2Cl < CHCl_2 < CCl_3 < CF_3$.

Castagnola et al. [5] suggested that oxidation of $Cp_2Fe$ with acids is a radical process, with the primary event not involving the metal atom. They rule out the protonation of ferrocene, which seems quite logical at first glance, taking into account that acids, even strong, occur in the nondissociated form in nonpolar aprotic solvents like benzene [11, 26]. At the same time, all the above factors characterizing reaction (24) favor protonation of ferrocene [12–16]. Furthermore, even in inert nonpolar solvents such as heptane, the proton transfer from an acid to a base is possible [11, 26], and the resulting product is a stable ion pair.

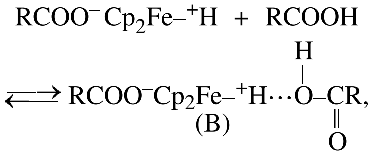
$$\mathrm{B + HX \xrightleftharpoons{K_{BHX}} BH^+X^-}. \tag{25}$$

For reaction (25), close correlation is often observed between the equilibrium constants $K_{\mathrm{BHX}}$ and $pK_a$ values for acids in water, which is consistent with the fact that the rate of reaction (24) grows with an increase in the acid strength [5]. Comparison of Eq. (24) with the well-known equation (26) of the reduction of carboxylic acids in acid solutions [7] also supports the assumption that protonation of $Cp_2Fe$ plays an important role in its oxidation with acids.

$$\mathrm{RCOOH + 2H^+ + 2e \longrightarrow RCHO + H_2O}. \tag{26}$$

This comparison shows that the roles of three acid molecules in the oxidation of $Cp_2Fe$ are different: Two of them act as proton donors, and the third is an acceptor of two hydrogen atoms which can originate only from two molecules of protonated ferrocene. Therefore, the following mechanism, actually analogous to the mechanisms of $Cp_2Fe$ oxidation with oxygen and sulfur dioxide, can be suggested for reaction (24):

$$\mathrm{Cp_2Fe + RCOOH \rightleftarrows RCOO^-Cp_2Fe{-}^+H}, \tag{27}$$



$$\begin{gathered}\mathrm{RCOO^-Cp_2Fe{-}^+H + RCOOH} \\ \rightleftarrows \mathrm{\underset{(B)}{RCOO^-Cp_2Fe{-}^+H}\cdots\overset{\displaystyle H}{\overset{|}{O}}{-}\underset{\underset{\displaystyle O}{\|}}{C}R},\end{gathered} \tag{28}$$

$$\mathrm{B \longrightarrow Cp_2Fe^+RCOO^- + H_2O + RC^{\bullet}O}, \tag{29}$$

$$\begin{gathered}\mathrm{RC^{\bullet}O + H^+{-}FeCp_2RCOO^-} \\ \longrightarrow \mathrm{RCHO + Cp_2Fe^+RCOO^-}.\end{gathered} \tag{30}$$

The structure of hydrogen-bonded complex B suggests that it can transform into the reaction products by a concerted mechanism. For the $RC^{\cdot}O$ radical arising in the process, protonated ferrocene is the most probable donor of hydrogen atom; the dissociation energy of the Fe–H bond in protonated ferrocene (209.2 kJ mol$^{-1}$) is considerably lower than the energy of the forming C–H bond in the aldehyde (~370 kJ mol$^{-1}$ [22]). The set of reactions (27)–(30) leads to the stoichiometric equation of ferrocene oxidation with carboxylic acids (24).

As a limiting step of the process, taking into account the reaction conditions, we can consider both the step of ferrocene protonation and the step of the reaction of $Cp_2Fe{-}^{+}H$ with oxygen. In the gas phase, this reaction is unambiguously endothermic, as it involves cleavage of two bonds, Fe–H (209.2 kJ mol$^{-1}$) and C–OH (~452 kJ mol$^{-1}$), in the reagent molecules, with only one H–O bond in the water molecule forming instead (499 kJ mol$^{-1}$ [22]). Naturally, the activation energy of the reaction cannot be lower than the difference $D_{\text{Fe–H}} + D_{\text{RCO–OH}} - D_{\text{R–OH}}$.

The above facts provide convincing evidence to show that the mechanisms of ferrocene oxidation with different oxidants (molecular oxygen, sulfur dioxide, carboxylic acids) are essentially similar, as they involve the same key sequence of primary reactions: protonation of ferrocene and reaction of the protonated complex with an oxidant, in which this complex acts as a donor of atomic hydrogen.

## ACKNOWLEDGMENTS

The authors are grateful to Dr. Sci. (Chem.) Yu.A. Borisov for submitting the results of quantum-chemical calculations.

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