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Mechanism of Initiation of the Radical Chain Oxidation by Molecular Oxygen of Hydroxymethylferrocene and Its Ethyl Ether in Organic Solvents

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Abstract—Autooxidation of ethoxymethylferrocene at 30–50ºC promoted by the participation of strong and weak carboxylic acids HX is studied. The radical chain mechanism of the process is established, its kinetics characteristics are determined as well as the composition of the products among which other derivatives of ferrocene have been found. Based on the results of the present study and the earlier obtained data on oxidation of hydroxymethylferrocene a mechanism of initiation of the chains general for both metallocomplexes is suggested. It includes the formation of the intermediate CH_2OR (R = H, C_2H_5) and its subsequent oxidative transformations leading to the formation of the peroxide radical $C_5H_4Fe^{+\cdot}C_5H_4–CH_2O_2^{\cdot}$ and ROH. The role of the approaching and orientation effect in transformations of this intermediate is discussed as well as the mechanism of the investigated reaction in general.

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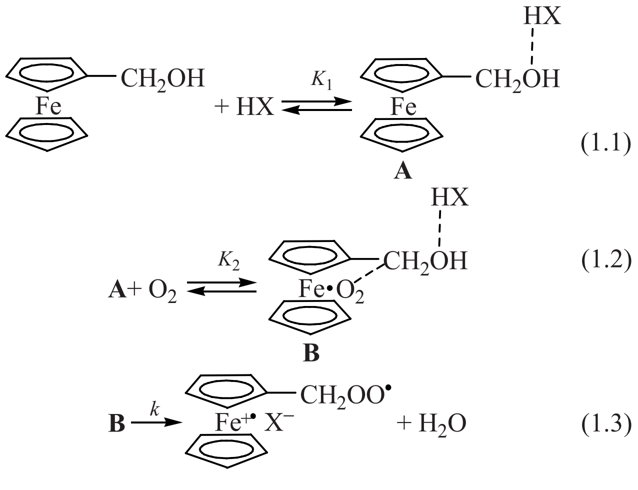
Earlier we showed [1] that oxidation of hydroxymethylferrocene (compound **I**) with molecular oxygen in organic solvents in the presence of trifluoroacetic **II** or benzoic **III** acid (HX) proceeded as a sequence of two macrosteps, the first of which is the molecular oxidation of the metallocomplex leading to generation of radicals, and the second step was the radical chain oxidation initiated by these radicals. Based on the results of the kinetic studies, the data on the composition of the products of oxidation and some other specific features of oxidation of compound **I**, tentative mechanisms of the two macrosteps of the investigated process were suggested [2]. The mechanism of molecular oxidation of compound **I** leading to the formation of oxygen-centered radicals is shown in Scheme 1.

As distinct from the earlier suggested mechanisms of oxidation of hydroxyferrocene [2] and ferrocenylacetic acid [2, 3] also including the stage of formation of adducts metallocomplex–O_2, it is assumed that coordination of the molecule of oxidant with **I** occurs by means of its interaction with the electrophilic carbon atom of the methylene group of the latter rather than due to a hydrogen bond formation with the hydroxyl hydrogen atom of the substituent. The electrophilicity of the methylene carbon atom is confirmed, for example, by the results of calculation of the charge distribution in the molecule of ethanol, which give the following values of the positive charge on the methylene carbon atom: 0.372 (method ESP [4, 5]), 0.572 (method AIM [6]). According to [7], the ferrocenyl fragment by its electron-donor properties is

Scheme 1.

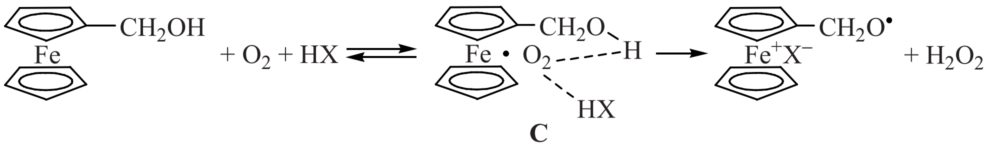


comparable to the methylene group. Bonding of the carbon atom with the molecule O_2 favors the transfer of electron from the iron atom to the molecule of oxygen and as a result increases the polarity of the C–OH bond. This makes possible the proton transfer to the hydroxy group from the coordinated molecule HX and transformation of the triple complex as shown in Scheme 1.

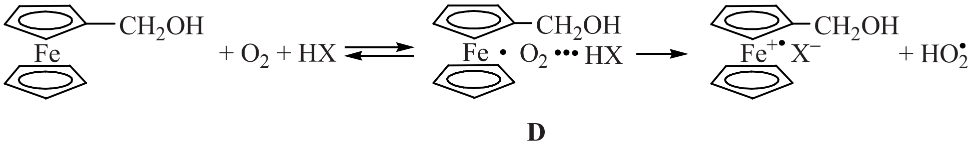
The presented mechanism of oxidation of **I** is of principal importance, since until now no such mechanisms of generation of oxygen-centered radicals upon oxidation of oxygen-containing organic or organometallic compounds were known [8, 9].

In principle, the molecule of oxygen coordinated with metal atom by means of donor-acceptor interaction can either form a hydrogen bond with the hydroxy group of the substituent or do not interact with it at all. In this case, the participation of an acid in the process of oxidation of the metallocomplex can be represented by alternative Schemes 2 and 3, respectively.

Scheme 2.



Scheme 3.



Formation of intermediates **C** and **D** occurs as a result of successive addition of O_2 and HX to **I**.

To conclude which of the mechanisms 1–3 is preferable it is necessary to analyze the thermodynamic and kinetic aspects of these processes.

It is known that the thermodynamic criterion for any reactions to occur including those described by Schemes 1–3 is the value of their Gibbs free energy $\Delta_r G^0$. Unfortunately, direct calculation of these values or even the values of standard enthalpies $\Delta_r H^0$ of the reactions under consideration is impossible due to the absence of the data on standard enthalpies of formation and absolute entropies of metallocomplex reagents taking part in these reactions. It is possible, however, to estimate the differences in the free energies $\Delta_r G^0(1) - \Delta_r G^0(2)$ and $\Delta_r G^0(1) - \Delta_r G^0(3)$ or at least the differences in the enthalpies $\Delta_r H^0(1) - \Delta_r H^0(2)$ and $\Delta_r H^0(1) - \Delta_r H^0(3)$ if to make use of model reactions for which the standard enthalpies of formation of the reagents and their absolute entropies are known. It will allow to reveal which of the processes 1–3 is thermodynamically more favorable. Such model reactions for processes 1, 2, 3 are reactions (1), (2) and (3), respectively:

$$CH_3CH_2OH + O_2^{\bar{\cdot}} + HX \rightarrow CH_3CH_2O_2^{\cdot} + H_2O + X^-,\ \Delta_r H_1^0 \quad (1)$$

$$CH_3CH_2OH + O_2^{\bar{\cdot}} + HX \rightarrow CH_3CH_2O^{\cdot} + H_2O_2 + X^-,\ \Delta_r H_2^0 \quad (2)$$

$$CH_3CH_2OH + O_2^{\bar{\cdot}} + HX \rightarrow CH_3CH_2OH + HO_2^{\cdot} + X^-,\ \Delta_r H_3^0 \quad (3)$$

Subtracting Eq. (2) from Eq. (1) gives the equation of the resulting reaction (4), whose enthalpy $\Delta_r H_4^0 = \Delta_r H_1^0 - \Delta_r H_2^0$ can be taken as the desired difference of enthalpies $\Delta_r H^0(1) - \Delta_r H^0(2)$.

$$CH_3CH_2O^{\cdot} + H_2O_2 \rightarrow CH_3CH_2O_2^{\cdot} + H_2O,\ \Delta_r H_4^0. \quad (4)$$

Similarly, by subtracting Eq. (3) from Eq. (1) the equation of another resulting reaction (5) is obtained whose enthalpy $\Delta_r H_5^0 = \Delta_r H_1^0 - \Delta_r H_3^0$ can be taken as the difference of enthalpies $\Delta_r H^0(1) - \Delta_r H^0(3)$.

$$CH_3CH_2OH + HO_2^{\bullet} \rightarrow CH_3CH_2O_2^{\bullet} + H_2O,\ \Delta_r H_5^0. \quad (5)$$

Using the known thermochemical equation for calculation of the reaction enthalpies:

$$\Delta_r H_i^0 = \Sigma \nu_j \Delta_f H_j^0 - \Sigma \nu_i \Delta_f H_i^0, \quad (6)$$

where $\Delta_f H_{i,j}{}^0$ are standard enthalpies of formation of the reagents (*i*) and reaction products (*j*) in the gas phase, $\nu_{i,j}$ are stoichiometric coefficients, we have calculated the values of enthalpies $\Delta_r H_4^0$ and $\Delta_r H_5^0$ equal to –85.2 and –17.4 kJ mol^{-1}, respectively. The values of $\Delta_f H_{i,j}^0$ for the compounds participating in reactions (4) and (5) were taken for calculations from [10, 11].

The calculation of the standard entropies of reactions $\Delta_r S_4^0$ and $\Delta_r S_5^0$ and, correspondingly, the values of $\Delta_r G_4^0$ and $\Delta_r G_5^0$ is complicated by the absence of the data on the absolute entropies of radicals $CH_3CH_2O^{\bullet}$ and $CH_3CH_2O_2^{\bullet}$; however, there is an indirect way for calculation of these values. In the radicals $RO^{\bullet}$ and $RO_2^{\bullet}$ the entropy contribution of fragment R is the same, so that the difference $S^0(RO_2^{\bullet}) - S^0(RO^{\bullet})$ must be practically constant irrespective of the nature of radical R. Using the data for radicals $HO^{\bullet}$ and $HO_2^{\bullet}$ from [11], the entropy difference for them will be equal to $S^0(HO_2^{\bullet}) - S^0(HO^{\bullet}) = 229.1 - 183.7 = 45.4$ J mol^{-1} K^{-1}. The equation for calculation of the entropy of reaction (4) $\Delta_r S_4^0$ is of the form:

$$\Delta_r S_4^0 = [S^0(CH_3CH_2O_2^{\bullet}) - S^0(CH_3CH_2O^{\bullet})] - [S^0(H_2O_2) - S^0(H_2O)], \quad (7)$$

Substituting in this expression the value of 45.4 J mol^{-1} K^{-1} instead of the difference of the absolute entropies of the radicals and the known values of entropy $S^0(H_2O_2) = 232.9$ J mol^{-1} K^{-1} and $S^0(H_2O) = 188.8$ J mol^{-1} K^{-1} [11] we obtain that $\Delta_r S_4^0 = 1.3$ J mol^{-1} K^{-1}. The close to zero value of $\Delta_r S_4^0$ suggests that the following equation is fulfilled:

$$S^0(ROOH) - S^0(ROH) = S^0(RO_2^{\bullet}) - S^0(RO^{\bullet}). \quad (8)$$

which may be used for calculation of the entropy of reactions proceeding with participation of peroxide compounds and radicals.

For reaction (5) the expression for calculation of the entropy $\Delta_r S_5^0$ is of the form:

$$\Delta_r S_5^0 = [S^0(CH_3CH_2O_2^{\bullet}) - S^0(CH_3CH_2OH)] - [S^0(HO_2^{\bullet}) - S^0(HOH)]. \quad (9)$$

Using the same reasonings as those used for calculation of the entropy $\Delta_r S_4^0$ it becomes evident that in Eq. (9) the difference of the entropies of the reagents in the first brackets must be equal to the difference of the entropies of the reagents in the second brackets, that means that $\Delta_r S_5^0$, as well as $\Delta_r S_4^0$, must be equal to zero within the error of calculations.

Close to zero values of $\Delta_r S_4^0$ and $\Delta_r S_5^0$ indicate that within the error of the calculations the equalities $\Delta_r H_4^0 = \Delta_r G_4^0$ and $\Delta_r H_5^0 = \Delta_r G_5{}^0$ are fulfilled and the found values of $\Delta_r H_4^0$ and $\Delta_r H_5^0$ can be considered as thermodynamic criteria of reactions (4) and (5) to occur.

According to the aforesaid, the value of $\Delta_r G_4^0$ can be taken to be equal to the difference of the Gibbs standard energies $\Delta_r G^0(1) - \Delta_r G^0(2)$, and the value of $\Delta_r G_5^0$, equal to the difference $\Delta_r G^0(1) - \Delta_r G^0(3)$. Negative values of these differences suggest that molecular oxidation of **I** by the mechanism described by Scheme 1 is thermodynamically preferable than by mechanisms 2 and 3 and, hence, coordination of molecule O_2 with the electrophilic carbon atom of the substituent in complex **B**, as shown in Scheme 1, is the most effective energetically as far as generation of radicals is concerned. Although the above calculations refer to the oxidation of **I** in the gas phase, in principle, there are no serious reasons to assume that on carrying out the reaction in the liquid phase the differences of the values $\Delta_r G^0(1) - \Delta_r G^0(2)$ and $\Delta_r G^0(1) - \Delta_r G^0(3)$ will become substantially more positive. It should be noted that although the absolute value of $\Delta_r G^0(1)$ is not known, it can be assumed a priori to be slightly negative or positive value taking into account the fact that the main contribution into the total process of oxidation of **I** is from the radical chain mechanism rather than the molecular one.

Alternatives, when $\Delta_r G^0(1)$ is much larger or smaller than zero do not correspond to reality since in this case compound **I** either would not be oxidized at all since its molecular oxidation would be energetically unfavorable or it must be oxidized mainly by molecular mechanism, which inevitably must lead to a substantial decrease of the value of $N(O_2)$ [where $N(O_2)$ is the number of moles of oxygen absorbed by the reaction mixture calculated to the mole of the starting complex].

From the kinetic point of view, the most plausible is the mechanism with the lowest energy of activation provided that it is not prohibited thermodynamically.

From this standpoint, mechanism 1 is also more preferable than mechanisms 2 or 3. Indeed, the formation of a strong hydrogen bond of HX with the oxygen atom of the substituent in **I** results in an increase of polarity of the C–O bond and, hence, the electrophilic properties of the carbon atom. The addition of oxygen to complex **I** · HX gives rise to the formation of the triple complex O_2 · **I** · HX in which the molecule of O_2 is simultaneously bound with the iron atom and the electrophilic carbon atom, that promotes strengthening of each of these donor-acceptor bonds and facilitates the electron transfer from atom Fe to molecule O_2. On the whole, this favors stabilization of the oxygen adduct, the structurally close to it transition state, and provides considerable gain in energy required to overcome the energy barrier on moving the reacting system along the reaction coordinate. Since the equilibrium upon the formation of hydrogen bond is established instantly and it is the bifunctional reagent **I** · HX that enters the reaction with O_2, it corresponds to a total decrease in the reaction order and, correspondingly, to the gain in the entropy of activation. The presence of the chain of conjugation $\mathrm{Fe}\cdots\mathrm{O_2}\cdots\overset{\diagdown\diagup}{\underset{|}{\mathrm{C}}}\text{–}\overset{|}{\mathrm{O}}\cdots\mathrm{H}\text{–}\mathrm{X}$ provides synchronicity of transformation of complex **B** into the reaction products, which, in turn, leads to a decrease in the energy of activation of the process and, taking into account a gain in the entropy of activation, the free energy of activation $\Delta G^{\#}(1)$. Jointly, this can be considered as a manifestation of the effect of approaching and orientation, similar to what happens in the reactions with participation of polyfunctional enzyme systems. According to [12, 13], the gain in $\Delta G^{\#}_{\text{appr.+orient.}}$ can reach 42–50 kJ mol^{-1}.

Thermodynamically less favorable mechanisms 1 and 3 will be kinetically also less likely than mechanism 1. Mechanism 3 is disadvantageous compared to mechanism 1 first of all due to the fact that for such a structure of the intermediate **C** and the corresponding transition state there is no possibility for the approaching and orientation effect on moving the reacting system along the reaction coordinate because the metal complex in this case acts as a monofunctional reagent and, therefore, the free energy of activation $\Delta G^{\#}(3)$ may be much larger than $\Delta G^{\#}(1)$ due to large losses in entropy. Besides, by all evidence, complex **C** must be less stable than complex **B** and, hence, the steady concentration of the former complex will be less than that of the latter. Mechanism 2 does not differ principally from mechanism 3, since the reduction of molecule O_2 upon the electron transfer to it from the iron atom must first cause fast proton transfer to it from the molecule of the strong acid (rate constants for such processes are of the order 10^9–10^{10} l mol^{-1} s^{-1} [14]), and only then, as a secondary rather than synchronous act, the energetically unfavorable and therefore much more slow abstraction of hydrogen atom from the hydroxy group of the substituent, leading to formation of H_2O_2 showed occur. In mechanism 3 this endothermic step {$D(\mathrm{RCH_2O–H})$ ~425 kJ mol^{-1} [10], $D(\mathrm{H–OOH})$ ~369 kJ mol^{-1} [15]} is lacking and this is the reason why it is energetically more favorable than mechanism 2.

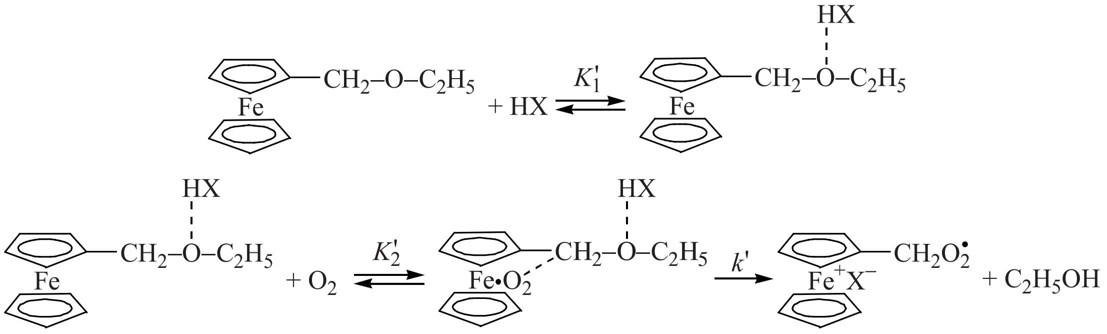
To make sure that the above reasonings is valid we have studied oxidation of hydroxymethylferrocene ethyl ether **IV**. This compound does not contain hydroxy hydrogen atom but has the same electrophilic carbon atom and the oxygen atom capable of forming a strong hydrogen bond with the molecule of acid. In this case it should be anticipated, first, a negligible difference in the rates of oxidation of **I** and **IV**, second, the appearance of ethanol in the products of oxidation of **IV** as a result of transformation of complex HX · **IV** · O_2 according to Scheme 4, similar to Scheme 1, and, third, full analogy in the main trends of oxidation of **I** and **IV** and some correspondence in the composition of the products of the radical chain oxidation of these compounds.

Compound **IV**, similar to **I**, is stable to the action of oxygen both in individual state (viscous liquid) and in solution and is oxidized only in the presence of carboxylic acids.

Comparative kinetic curves for oxidation of compounds **I** and **IV** in dioxane in the presence of acids **II** and **III** at $T = 50$ºC are shown in Fig. 1. It is clearly seen that at low concentrations of acid **II** oxidation of **I** proceeds at a faster rate than the oxidation of **IV**, whereas with increasing concentration of the acid the pattern changes to the opposite. Less strong acid **III** affects the oxidation of **I** and **IV** also in a different manner.

Compound **IV** does not undergo oxidation in the presence of perchloric acid, and neither does compound **I** [2]. The reason for this lies in the instant protonation of the metal complex with the formation of the same ferrocenylmethyl cation $C_5H_5FeC_5H_4C^+H_2$, detected by the absorption bands with $\lambda_{\max}$ 626, 453 nm [16]. The cation is rather stable to oxygen but upon long exposure to air it undergoes oxidative destruction, apparently due to the transformation into the dimeric

Scheme 4.



(4.1)

(4.2)

ferricinium complex $C_5H_5Fe^+C_5H_4CH_2CH_2C_5H_4Fe^+\cdot C_5H_5$ owing to the process of the redox isomerism [17]. The latter complex can apparently react though slowly [2] with oxygen or disproportionate with destruction of the sandwich structure [18].

It is established that the main contribution to the total process of oxidation of **IV**, as in the case of oxidation of **I**, is from the radical chain pathway; that is proved by the retarding action of *o*-phenylenediamine (known to be an effective inhibitor of radical chain reactions) on the rate of the process (Fig. 2) and the polymerization of methyl methacrylate (MMA) when it is used as a solvent. Noteworthy, that at the oxidation of compounds **I** and **IV** in MMA the value of $N(O_2)$ is substantially higher than for their oxidation in dioxane (Fig. 3). This may be due to the ability of peroxide radicals to add to the monomer molecule and molecule O_2 to the molecule of the growing oligomer or polymer [19]. The polymer isolated from the reaction mixture initiates polymerization of fresh portions of MMA at T = 50°C, that suggests the presence in it of labile peroxide groups.

Oxidation of **IV**, as well as of **I**, is practically completely suppressed when ethanol or water–dioxane mixture (1:1) are used as solvents (Fig. 3). The inhibiting effect of alcohols and water on the reactions of radical chain oxidation of hydrocarbons is usually attributed to their ability to form strong hydrogen bonds with the chain propagating peroxide radicals $RO_2^•$, that leads to a decrease in their activity [9]. In ethylbenzene, oxidation of **IV** also does not occur (Fig. 3), although the reason of it lies most probably in its extremely low solvating ability as compared to dioxane. Indifference of this solvent to the process of

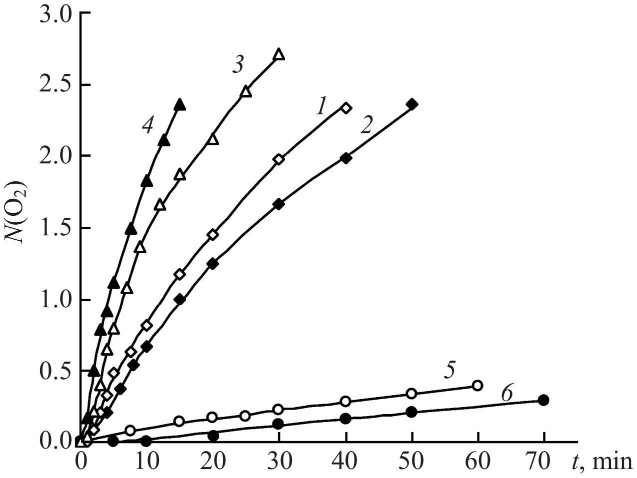


Fig. 1. Curves of comparative kinetics of oxidation of (*1, 3, 5*) **I** and (*2, 4, 6*) **IV** in the presence of (*1–4*) acids **II** and (*5, 6*) **III** in dioxane M: (*1, 2*) C^0_{II} = 0.05, (*3, 4*) C^0_{II} = 0.2, (*5, 6*) C^0_{III} = 0.55, $C^0_{I,IV}$ = 0.01. T = 50°C, $p(O_2)$ = 0.47×10^5 Pa.

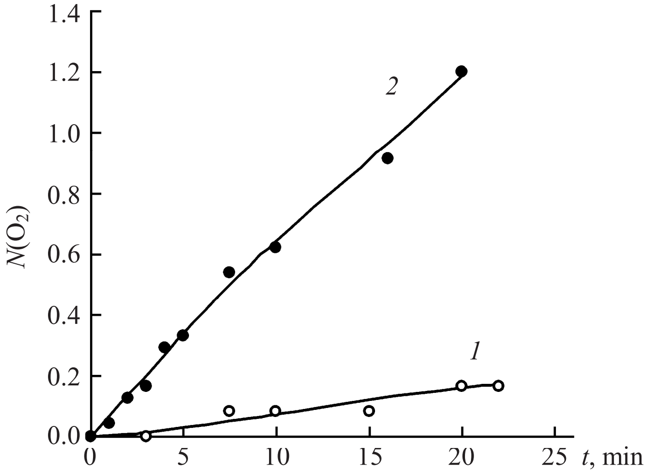


Fig. 2. Effect of *o*-phenylenediamine (In) on the rate of oxidation of (*1*) **IV** in the presence of (*2*) **II** in dioxane, M: C^0_{IV} = 0.01 M, $C^0_{In}(2)$ = 5×10^{-4}, C^0_{II} = 0.02 M. T = 50°C, $p(O_2)$ = 0.47×10^5 Pa.

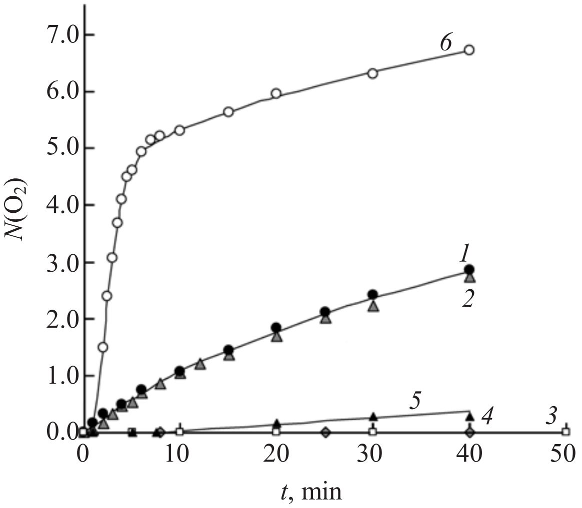


Fig. 3. Effect of the solvent nature on the rate of oxidation of **IV** in the presence of **II**. (*1*) dioxane, (*2*) dioxane–ethylbenzene (1:1), (*3*) dioxane–water (1:1), (*4*) ethylbenzene, (*5*) ethanol, and (*6*) MMA. C^0_{IV} = 0.01 M, C_{II} = 0.1 M, T = 50°C, $p(O_2) = 0.47\times10^5$ Pa.

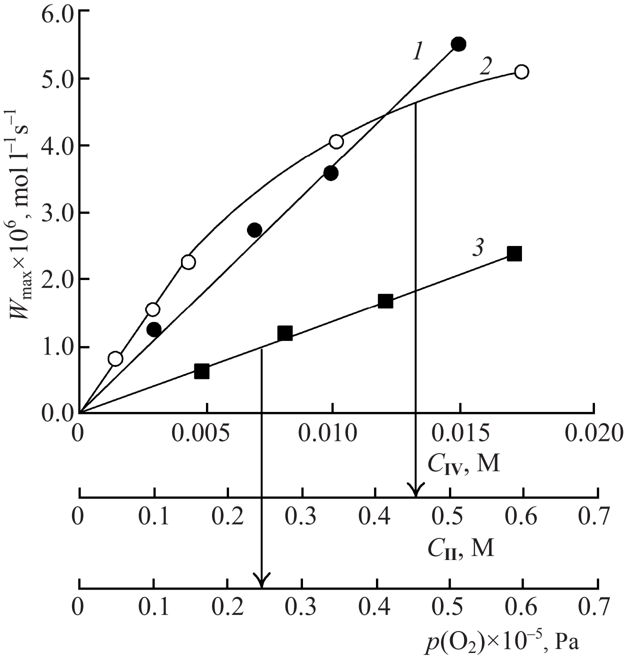


Fig. 4. Dependence of the rate of oxidation of **IV** on (*1*) its concentration, (*2*) oxygen pressure, and (*3*) concentration of acid in dioxane at T = 50°C. (*2, 3*) C^0_{IV} = 0.01 M, (*1, 3*) $p(O_2) = 0.42\times10^5$ Pa, C^0_{II} = 0.2 M.

oxidation of **IV** is manifested also in the fact that its presence has no effect on the rate of the process, if to use the dioxane–ethyl benzene mixture 1:1v/v instead of pure dioxane (Fig. 3). A similar effect on the oxidation of **I** has toluene when used as a solvent [2].

The results of investigation of kinetic trends in the oxidation of **IV** in the presence of acid **II** show that the process is described by the kinetic equation of the first order in the initial concentrations of the metal complex, oxygen and acid. This follows from the linear increase of the maximum rate of the reaction (W_{max}) with concentrations of these reagents (Fig. 4).

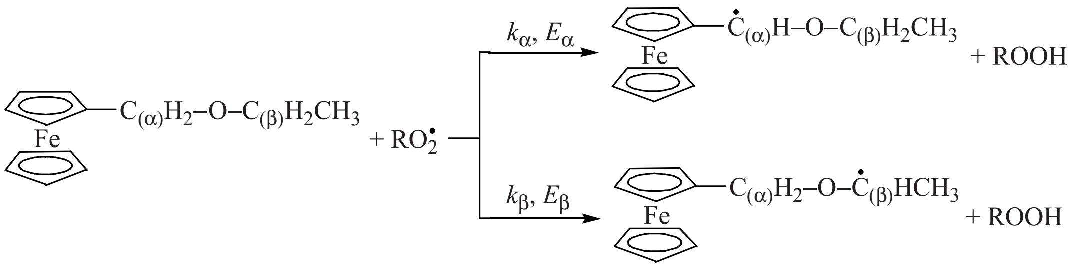
For acid **II**, the value of W_{max} linearly depends on its concentration only when the latter is relatively low. With increase in the concentration of **II**, the order of the process on the acid becomes lower than unity Fig. 4). A similar dependence of W_{max} on concentration of **II** is observed for oxidation of **I**; note that this dependence is valid in the range of lower concentrations than for oxidation of **IV**. These data, as well as those illustrated in Fig. 1, are indicative of the fact that the acid has different effect on the rate of generation of the radicals due to molecular oxidation of metal complexes and of their radical chain oxidation. In the latter case, this effect, most probably, is similar to the inhibiting effect of water and alcohol. Since the peroxide radical formed upon oxidation of compound **I** has more centers of specific interaction with OH-acids than the corresponding radical generated by oxidation of **IV**, the inhibiting effect of acid **II** with increase of its concentration on the radical chain oxidation of **I** is revealed at lower concentrations than in oxidation of **IV**.

The lower rate of oxidation of **IV** in the presence of **III** can be ascribed to the steric effects upon its coordination to the oxygen atom of the substituent in **IV**, as shown in Scheme 4.

With the aim of more detailed study of the reaction under consideration we have performed the analysis of the products composition at $N(O_2)$ = 0.7 [T = 30 and 50ºC, $p(O_2) = 0.5\times10^5$ Pa, C^0_I = 0.07 M], 1.4 [T = 50ºC, $p(O_2) = 0.5\times10^5$ Pa, C^0_I = 0.07 M] and 5 [T = 50ºC, $p(O_2) = 0.5\times10^5$ Pa, C^0_I = 0.01 M].

It was established that at $N(O_2)$ = 0.7 oxidation of **IV** occurs mainly on the methylene group of the substituent connected with the cyclopentadienyl ligand, that leads to formation of the ethyl ester of ferrocenecarboxylic acid $C_5H_5FeC_5H_4–C(O)–O–C_2H_5$ (**V**) as the main product, as well as formylferrocene $C_5H_5FeC_5H_4–CHO$ (**VI**), ethanol, acetic acid, and water. The results of analysis of the amount of the oxidized compound **IV** at $N(O_2)$ = 0.7 suggest that for oxidation of 1 mol of metal complex to the above products ~2.5 mol of oxygen is consumed. With increase in the initial concentration of **IV** and **II** in the solution to be oxidized and increase in $N(O_2)$ to 1.4, among the products of the reaction, along with the aforementioned, the formation of anhydrides of the composition $C_5H_5FeC_5H_4–C(O)–O–CHO$ **VII**, $C_5H_5FeC_5H_4–C(O)–O–COOH$ **VIII** and of ferrocenecarboxylic acid **IX** was detected, that pointed to the successive oxidation of the second methylene group of the substituent in compound **IV**. At $N(O_2) = 5$ or more, the main product of the reaction is still compound **V**, and in the gas phase CO and CO_2 appear. Compounds **VI**, **VII**, and **IX** practically disappear. Under all conditions of oxidation of **IV** the products of its oxidative degradation were also found, among which were derivatives of Fe^{3+}, dimer of cyclopentadienone $[N(O_2) = 1.4]$ and cyclopentenedione $[N(O_2) \geq 5]$. The latter two compounds are known to be formed upon oxidation of ferricinium ion [20, 21]. Noteworthy is rather high yield of ethanol, which at $N(O_2) = 5$ consists of ~0.29 mol per mol of the oxidized metal complex. Since, as was shown above, the main contribution to the total process of oxidation of **IV** is from the radical chain pathway, such a high yield of ethanol cannot be attributed only to the reaction of molecular oxidation of metal complex.

Therefore, the data obtained suggest that the radical chain oxidation of **IV** affects both methylene groups of the substituent, the one connected with the Cp-ligand being oxidized first. This fact is due to a substantial difference in the energies of the C–H bonds in these methylene groups and, hence, in the activation energies of the reactions of hydrogen atom abstraction with peroxide radicals, as shown in Eqs. (10) and (11).



(10)

(11)

Reactions (10) and (11) are limiting steps for the radical chain oxidation of **IV** along each pathway. It is known that in alkenes and alkylaromatic hydrocarbons the energy of the C–H bond ($D_{C–H}$) in the methylene group directly attached to the alkene or aromatic fragment is 46–58 kJ mol^{-1} (from [15]) or 50–70 kJ mol^{-1} (from [10]) less than in the methylene groups of saturated organic compounds. These data can be used to assess the ratio k_α/k_β and, hence, the contribution of pathways (10) and (11) to the process of oxidation of **IV**, based on the known equation of Polanyi-Semenov relation for reactions of this type $\Delta E = \alpha\Delta D_{C-H}$, where $\Delta E = E_\beta - E_\alpha$, $\Delta D_{C–H} = D_{C(\beta)–H} - D_{C(\alpha)–H}$, $\alpha = 0.4$ [9, 22]. Assuming that $\Delta D_{C–H} \approx 52$ kJ mol^{-1}, the value of ΔE will be equal to ~21 kJ mol^{-1}. In this case, the ratio k_α/k_β at 323 K will be equal to:

$$k_\alpha/k_\beta = (k_{0,\alpha}/k_{0,\beta})e^{\Delta E/RT} \approx (k_{0,\alpha}/k_{0,\beta})\times 10^{3.4}. \tag{12}$$

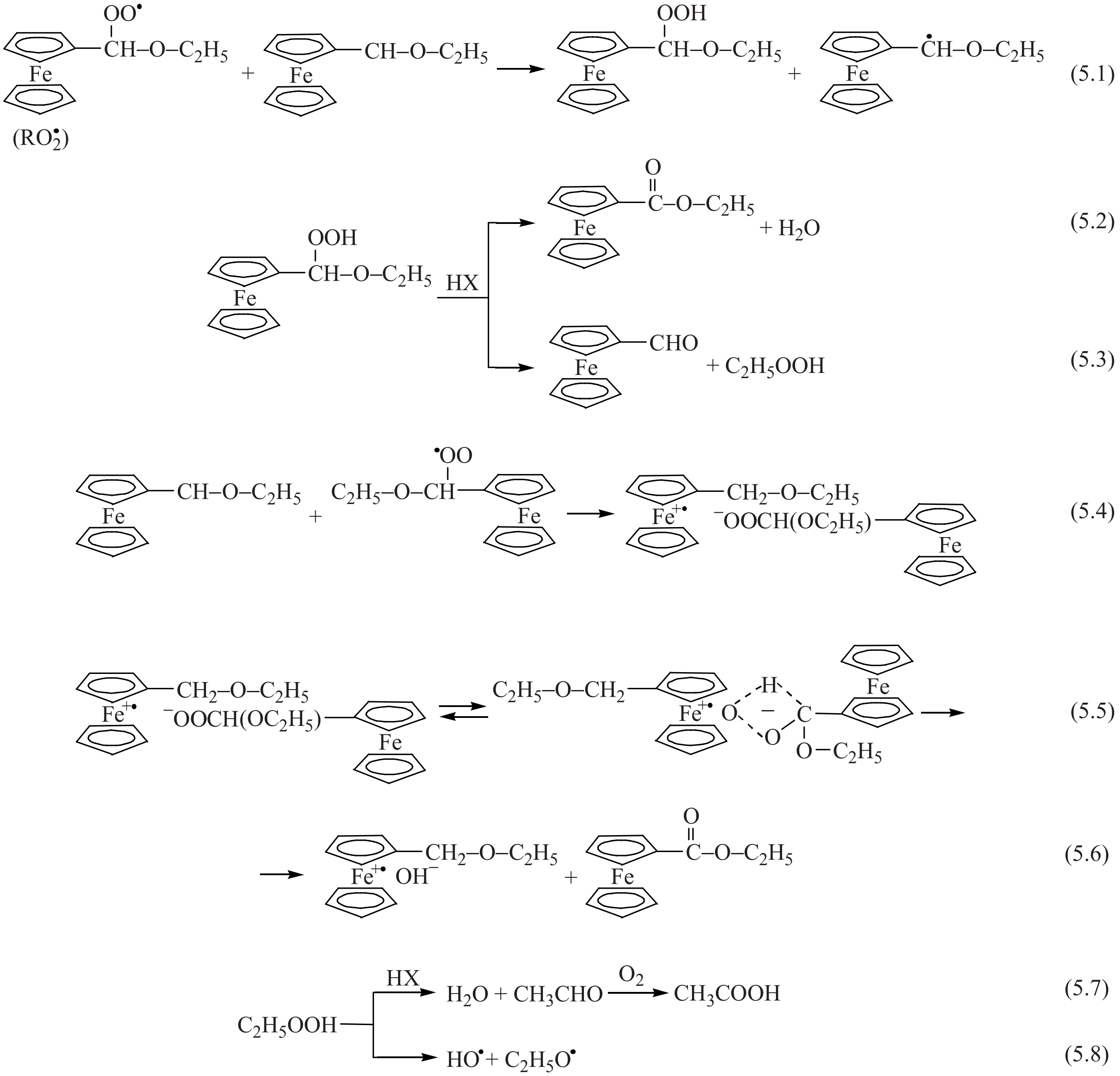
From the data of [15] containing a detailed analysis of kinetic parameters of reactions $RO_2^{\bullet} + R_1H \rightarrow ROOH + R_1^{\bullet}$, the value of the preexponential factor characterizing oxidation of methylene group in alkylaromatic hydrocarbons (in our case it is identical to oxidation of **IV** at the $C_{(\alpha)}H_2$-methylene group) equals ~10^7 l mol^{-1} s^{-1}, and the one characterizing oxidation of saturated hydrocarbons (corresponding to oxidation of **IV** at the $C_{(\beta)}H_2$-methylene group) is ~10^8 l mol^{-1} s^{-1}. With these data taken into account, the ratio k_α/k_β will be ~$10^{2.4}$. Such a large difference in constants k_α and k_β is a confirmation of the obtained experimental data suggesting that at the zero time of the reaction it is the $C_{(\alpha)}H_2$-methylene group of the substituent which is predominantly subjected to oxidation and the above kinetic characteristics of **IV** refer to this very process. This conclusion, which is in full accordance with the experimental data on successive oxidation of the methylene groups $C_{(\alpha)}H_2$ and $C_{(\beta)}H_2$ in the substituent, will be, in general, true also in the case when the ratio $k_{0,\alpha}/k_{0,\beta}$ will be less than 10^{-1}, but no less than 10^{-2}, and k_α/k_β will be no less than $10^{1.4}$. With this value of k_α/k_β the contribution of reaction (11) into the total process [(10)+(11)] is ~3.8%. With decrease in the reaction temperature the ratio k_α/k_β will increase.

In connection with the aforesaid, it was of interest to determine the values of activation energies for the radical chain oxidation of compounds **I** and **IV**. The results of the performed study suggest that within the errors of measurements these values determined from the reaction rates are virtually identical and equal to (29.7±2.1) kJ mol^{-1} and (31.4±1.7) kJ mol^{-1} respectively.

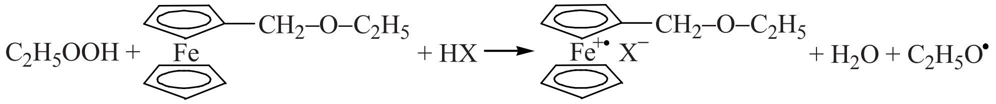
This result is another confirmation that the aforesaid kinetic regularities of oxidation of **IV** characterize oxidation of the α-methylene group of the substituent.

In accordance with the adopted scheme on the radical chain oxidation of hydrocarbons [9] and oxidation of **I** [2], the plausible mechanism of the radical chain oxidation of **IV** reflecting its principal stages and plausible for understanding the composition of the determined reaction products is presented in Scheme 5. As the chain-growing radical $\mathrm{RO}_2^{\bullet}$ in the initial stage of the process the radical $\mathrm{C_5H_5FeC_5H_4CH(OO^{\bullet})\text{–}O\text{–}C_2H_5}$ is considered, which is formed by the reaction of the peroxide radical $\mathrm{C_5H_5Fe^{+}C_5H_4\text{–}CH_2O_2^{\bullet}}$ (Scheme 4) with the oxidized complex **IV** in the presence of oxygen.

Scheme 5.



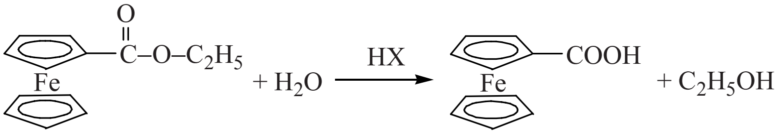
Scheme 5. (Contd.)



(5.9)

$$C_2H_5O^{\bullet} \xrightarrow[-S^{\bullet}]{SH} C_2H_5OH \qquad (5.10)$$

$$HO^{\bullet} \xrightarrow[-S^{\bullet}]{SH} H_2O \qquad (5.11)$$



(5.12)

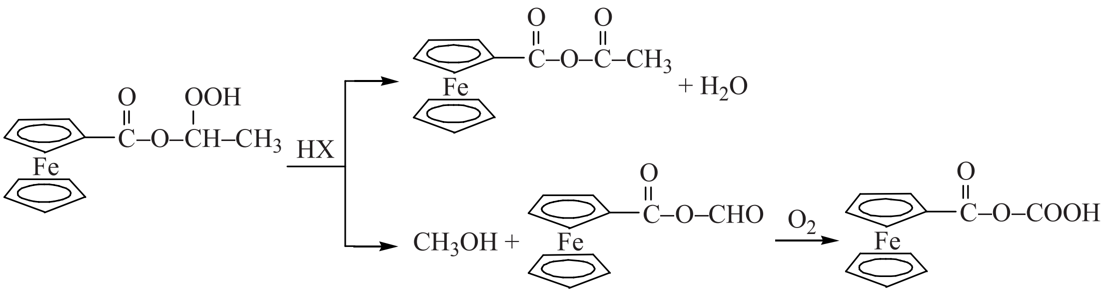
Reactions (5.2) and (5.3) represent the main routes of transformation of the hydroperoxide $C_5H_5FeC_5H_4\cdot CH(OOH)–O–C_2H_5$ in the presence of acid, since the ethyl ester of ferrocenylcarboxylic acid and formylferrocene are formed under any conditions of oxidation of **IV** at *T* = 30–50ºC. Among the products of oxidation of **IV**, ethoxyhydroxymethylferrocene $C_5H_5Fe\cdot C_5H_4CH(OH)OC_2H_5$, which could be formed by homolytic cleavage of the above peroxide, was not detected. Apparently, this is an indication of a negligible role of this route of transformation of the peroxide in the presence of HX, if it takes place at all. The possibility of fast conversion of $C_5H_5FeC_5H_4CH(OH)OC_2H_5$ by Eq. (13) or its oxidation to $C_5H_5FeC_5H_4C(O)–O–C_2H_5$ also cannot be ruled out. Possible formation of ethanol by the radical chain oxidation of **IV** explains rather high yield of this product.

$$C_5H_5FeC_5H_4CH(OH)–O–C_2H_5 \rightarrow C_5H_5FeC_5H_4CHO + C_2H_5OH. \qquad (13)$$

As in oxidation of **I** [2], the chain termination occurs by the reaction of the chain-growing radical $RO_2^{\bullet}$ with complex **IV** by Eq. (5.4). Rearrangement (5.5) is typical for ionic peroxide complexes of the type $L_nM^+OOCH_2R^-$ (L_nM is a transition metal complex), when the carbon atom connected with the peroxide group has a hydrogen atom [23].

The formation of the products of oxidative degradation of **IV** is connected with oxidation of the formed ferricinium ion [20, 21], its disproportionation [18] and degradation, if it contains a peroxide anion [23]. CO and CO_2 (yield ~5% of each calculated per one mol of the oxidized **IV**) are, as is well known, the products of oxidative decarbonylation and decarboxylation of aldehydes and carboxylic acids, respectively [9].

The oxidation of the formed products, in particular, $C_5H_5FeC_5H_4C(O)–O–C_2H_5$, affecting the second methylene group $C_{(\beta)}H_2$, results in successive formation of the aldehyde and acid of composition $C_5H_5FeC_5H_4C(O)–O–CHO$ and $C_5H_5FeC_5H_4C(O)–O–COOH$. Evidently, the primary product of this oxidation is hydroperoxide $C_5H_5FeC_5H_4C(O)–O–CH(OOH)–CH_3$, which can undergo virtually the same transformations as hydroperoxide $C_5H_5FeC_5H_4CH(OOH)–O–C_2H_5$.

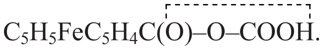


(14)

(15)

The absence in the products of oxidation of **IV** of anhydride $C_5H_5FeC_5H_4C(O)–O–C(O)CH_3$ in amounts sufficient for its detection is, probably, due to the high rate of its hydrolysis with the formation of ferrocenylcarboxylic and acetic acid.

Somewhat unexpected is the detection of a mixed anhydride of ferrocenylacetic and carbonic acids $C_5H_5FeC_5H_4C(O)–O–COOH$, which, by all reasons should be unstable and either decompose with the formation of CO_2 and ferrocenylcarboxylic acid or undergo hydrolysis. Perhaps, the reason of the relative stability of this complex is the formation of a strong intramolecular hydrogen bond:



$$C_5H_5FeC_5H_4C(O)–O–COOH.$$

Earlier we have shown [2] that the expression for the rate of the radical chain oxidation of compound **I**, taking into account the mechanism of initiation and termination of chains, is of the form

$$\nu_p = k_p(k_0/k_t)[I][O_2][HX],$$

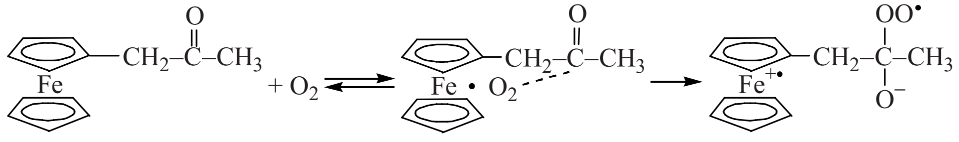
where k_p is the rate constant for the chain propagation, k_t is the rate constant for the chain termination on metal complex, $k_0 = kK_1K_2$ is the rate constant for the chain initiation (Scheme 1).

Similar expression could be obtained for the rate of oxidation of **IV** at the early stage of the process. In this case, $k_0 = k'K_1'K_2'$ (Scheme 4).

Therefore, the obtained results unambiguously point to virtually complete similarity of specific features of oxidation of compounds **I** and **IV**, that may serve as a strong confirmation of the general character of the mechanisms of radicals generation described by Schemes 1 and 4.

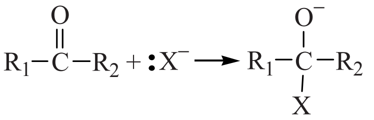
In conclusion, it deserves to be mentioned that the participation of electrophilic carbon atom of the substituent in the process of molecular oxidation of ferrocene derivatives is, apparently, a rather frequent but so far unnoticed phenomenon, and can be manifested more definitely than in oxidation of **I** and **IV**. In our opinion, the example of this is the oxidation of ferrocenylacetone **X** in benzene or CCl_4 to diketone $C_5H_5FeC_5H_4–C(O)C(O)CH_3$ and the products of its oxidative destruction readily proceeding at room temperature [24]. Even in the absence of other data on this process, the composition of the main product of oxidation of **X** allows a definite conclusion that the process has a radical chain character. To the formation of diketone leads, for example, the radical chain oxidation of methyl ethyl ketone [9].

The only reason of the reactivity of compound **X** with respect to oxygen is the participation of electrophilic oxygen atom of the carbonyl group in the process of molecular oxidation of metal complex [Eq. (16)] and clearly expressed manifestation of the approaching and orientation effect responsible for the low value of the free energy of activation of the process $\Delta G^{\#}$. It should be noted, that according to calculations of the charge distribution in acetone, the carbon atom of the carbonyl group bears substantial positive charge equal to +0.260 [25], that endows it with electrophilic properties.



(16)

In a similar way occurs the addition of nucleophilic agents with lone electron pair to the carbonyl group of ketones according to Eq. (17) [26].



$$R_1-\overset{\overset{\displaystyle O}{\|}}{C}-R_2 + :X^- \longrightarrow R_1-\underset{\underset{\displaystyle X}{|}}{\overset{\overset{\displaystyle O^-}{|}}{C}}-R_2 \qquad (17)$$

The peroxide radical formed by reaction (16) can easily abstract a weakly bound hydrogen atom from the methylene group of the substituent in X, thus initiating the radical chain oxidation of the latter to α-ketohydroperoxide $C_5H_5FeC_5H_4CH(OOH)–C(O)CH_3$. Conversion of the latter with elimination of H_2O results in the formation of the corresponding diketone.

Participation of the electrophilic carbon atom of the substituent should be also anticipated in oxidation of formylferrocene, acetylferrocene, ferrocenecarboxylic acid and its esters, and a number of other ferrocene derivatives. In oxidation of the four former compounds the participation of an acid in the process is obligatory [1], since the formyl, acetyl and carboxylic groups are much stronger electron acceptors than acetylmethyl group [4].

EXPERIMENTAL

Oxidation of **IV**, as well as of **I**, was performed on a vacuum static unit with a vigorous stirring of the reaction mixture. The reaction was followed manometrically by oxygen consumption.

Compound **IV** was synthesized from **I** and ethanol by the procedure [27], purified by a double vacuum distillation: bp = 112.3–113.2ºC/2.665×10^2 Pa, n_D^{20} = 1.5852. It contained compound **I** as an impurity.

Electron spectra of solutions were taken on a SHIMADZU UV-1700 spectrophotometer in the range 250–750 nm. Analysis of organometallic and some organic (cyclopentadienone and its dimer) products was performed using the method of chromatomass spectrometry on a "Kristall 5000.1" chromatograph (SKB "Chromatek"), equipped with mass spectrometer TRACE DSQ ("Termo Finnigan"): column RTX-5MS, temperature from 110ºC, conditioning for 1 min, heating 15º/min to 250ºC, full time of analysis 30 min, T_{inject} = 250ºC, sample volume 1 μl; scanning time 30 min, range of scanning from 50 to 500 *m/z*, amplification factor 3, 5 scans s^{-1}, energy of ionizing electrons 70 eV.

Volatile organic products (ethanol, methanol, acetaldehyde and acetic acid) were analyzed by GC method on a "Kristall 5000.1" chromatograph (SKB "Chromatek"), column ZB-FFAP, length 50 m, diameter 0.32 mm, temperature from 75ºC, conditioning for 7 min, heating 15º/min to 220ºC, T_{det} = 250°C, carrier gas is nitrogen, detector is FID.

Analysis of water was performed on a "Separone–CHN" analyzer, detector – catharometer, l_{col} = 2 m, d_{col} = 4 mm, T_{col} = 120°C, T_{inject} = 150°C.

Analysis of gaseous reaction products was performed by GC method on a "Tsvet 100" chromatograph with detector FID and rod metering valve; column: l_{col} = 0.5 m, d_{col} = 4 mm, sorbent is activated charcoal (SKT); carrier gas is argon; T_{col} = 90°C; T_{cath} = 450°C.

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REFERENCES

1. Fomin, V.M., Shirokov, A.E., Polyakova, N.G., and Smirnov, P.A*., Russ. J. Gen. Chem*., 2007, vol. 77, no. 4, p. 652.
2. Fomin, V.M., Shirokov, A.E., and Polyakova, N.G., *Russ. J. Gen. Chem*., 2008, vol. 78, no. 7, p. 1361.
3. Fomin, V.M., Klimova, M.N., and Smirnov, A.S., *Russ. J. Coord. Chem*., 2004, vol. 30, no. 5, p. 332.
4. Besler, B.H., Merz K.M., Jr., and Kollman, P.A., *J. Comp. Chem*., 1990, no. 11, p. 431.
5. Singh, U.C. and Kollman, P.A., *J. Comp. Chem*., 1984, no. 5, p. 129.
6. Bader, R.F.W., *Atoms in Molecules: A Quantum Theory*, Oxford Univ. Press: Oxford, 1990.
7. Nesmeyanov, A.N., *Khimiya ferrotsena* (Ferrocene Chemistry), Moscow: Nauka, 1969.
8. Denisov, E.T., Mitskevich, N.I., and Agabekov, V.E., *Mekhanizm okislenija kislorodsoderzhashchikh soedinenii* (Oxidation Mechanism of Oxygen-Containing Compounds) Minsk: Nauka i tekhnika, 1975.
9. Emmanuel, N.M., Zaikov, G.E., and Maizus, Z.K., *Rol' sredy v radikal'no-tsepnykh reaktsiyakh okisleniya organicheskikh soedinenii* (Medium Role in the Chain Radical Reactions of Oxidation of Organic Compounds), Moscow: Nauka, 1973.
10. *Energii razryva khimicheskikh svyazei. Potentsialy ionizatsii i srodstvo k elektronu* (Energy of the Rupture of Chemical Bonds. Ionization Potentials and Electron Affinity), Kondrat'ev, V.N., Moscow: Nauka, 1974.
11. Chase, M.W., Jr., *NIST-JANAF Themochemical Tables, Fourth Edition, J. Phys. Chem. Ref. Data*, Monograph 9, 1998, 1-1951.
12. Berezin, I.V. and Martinek, K., *Osnovy fizicheskoi khimii fermentativnogo kataliza* (Fundamentals of Physical Chemistry of Enzyme Catalysis), Moscow: Vysshaya Shkola, 1977.
13. Dugas, H. and Penni, K., *Bioorganicheskaya khimiya* (Bioorganic Chemistry), Moscow: Mir, 1983.
14. Bell, R., *Proton v khimii* (Proton in Chemistry), Moscow: Mir, 1977.
15. Denisov, E.T. and Denisova, T.G., *Kinetika i Kataliz*, 1993, vol. 34, no. 2, p. 199.
16. Nesmeyanov, A.N., Reshetova, M.D., and Perevalova, E.G., *Izv. Akad. Nauk SSSR, Ser. Khim*., 1967, no. 23, p. 2746.
17. Riuchart, K.L., Michejda, C.J., and Kittle, P.A., *J. Am. Chem. Soc*., 1959, vol. 81, no. 12, p. 3162.
18. Domrachev, Yu.A., Sorokin, Yu.A., Razuvaev, G.A., and Suvorova, O.N., *Dokl. Akad. Nauk SSSR*, 1968, vol. 183, no. 5, p. 1085.
19. Denisov, E.T. and Azatyan, V.V., *Ingibirovanie tsepnykh reaktsii* (Inhibition of Chain Reactions), Chernogolovka, 1997.
20. Abakumova, L.G., Abakumov, G.A., and Razuvaev, G.A., *Dokl. Akad. Nauk SSSR*, 1975, vol. 220, no. 6, p. 1317.

21. Pendin, A.A., Leont'evskaya, P.K. Suverneva, O.L., Rozenkova, I.V., and Nikol'skii, B.P., *Dokl. Akad. Nauk SSSR*, 1987, vol. 293, no. 6, p. 1411.
22. Semenov, N.N., *O nekotorykh problemakh kinetiki i reaktsionnoi sposobnosti* (Some Problems of Kinetics and Reactivity), Moscow: Akad. Nauk SSSR, 1958.
23. Fomin, V.M., *Russ. J. Coord. Chem.*, 1996, vol. 22, no. 2, p. 116.
24. Toma, S. and Salisova, M., *J. Organometal. Chem.*, vol. 55, no. 2, p. 371.
25. Hehre, W.J. and Pople, J.A., *J. Am. Soc.*, 1970, vol. 92, no. 8, p. 2191.
26. Mathieu, G. and Panikot, R., *Cours de Chimie Organique*, Moscow: Mir, 1975.
27. Nesmeyanov, A.N., Perevalova, E.G., and Ustynyuk, Yu.A., *Dokl. Akad. Nauk SSSR*, 1960, vol. 133, no. 5, p. 1105.