ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 11, pp. 2304–2316. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © V.M. Fomin, A.E. Shirokov, 2009, published in Zhurnal Obshchei Khimii, 2009, Vol. 79, No. 11, pp. 1782–1795.

Specific Features of Oxidation of Ferrocenylacetic Acid with Molecular Oxygen in the Absence and in the Presence of Brønsted Acids

V. M. Fomin and A. E. Shirokov

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

Received February 9, 2009

Abstract—Comparative analysis of the specific features of autooxidation of ferrocenylacetic acid ($FcCH_2COOH$) in organic solvents at 30–50°C in the absence and in the presence of trifluoroacetic acid (processes 1 and 2 respectively) was carried out. It was shown that both reactions proceed as a sequence of two macrostages, the molecular and the chain radical oxidation of the metal complex. Introduction of acid (HX) in the reaction mixture leads to a significant increase in the rate of the process, in the amount of oxygen per one mole of metal complex absorbed by the reaction mixture, and to the change in the yields of main reaction products like hydroxymethylferrocene, formylferrocene, ferrocenylpyruvic acid, and CO_2. On the basis of results of the investigation performed, the kinetic and thermodynamic analysis of primary reactions of the process probable mechanisms of both macrostages in both processes were suggested. The significant effect of approach and orientation on the rate of the molecular oxidation of complex as the bifunctional reagent was noted. An assumption was made that the acid takes place in the molecular oxidation of $FcCH_2COOH$ according to two alternative mechanisms differing by the way of its coordination with O_2 and the metal complex in the prereactional intermediates. The oxidative transformation of these intermediates leads to the generation of radicals of different nature, $Fc^{+\cdot}CH_2C(O)OO^{\cdot}$ and $HO_2^{\cdot}$ which initiate the chain radical oxidation of the metal complex.

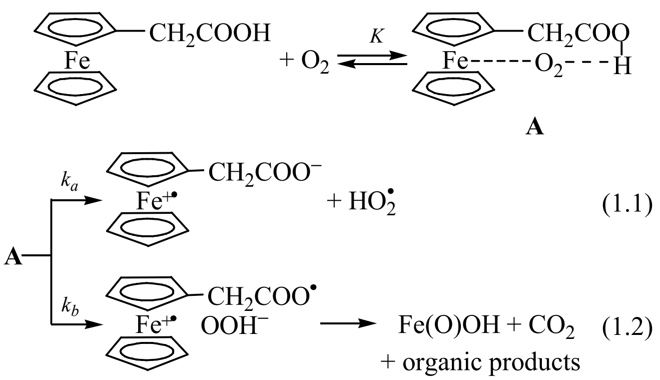
DOI: 10.1134/S107036320911005X

The interest to investigation of autooxidation processes of ferrocene derivatives with various functional groups is caused by the fact that many of them are bifunctional reagents having the electron-donor reaction site localized on the metal atom and the electron-acceptor one, the Lewis or Brønsted center, localized on the substituent. These sites may take part in conjugation with one another through a molecule of oxygen (or some other oxidant), and that should initiate the oxidation of substrate at the metal atom. From this point of view the ferrocene derivatives may be regarded as models of enzymatic systems in the processes of oxidation. Effects of approach and orientation are characteristic of such reactions. These effects lead to significant decrease in the activation free energy of the process (up to 50 kJ mol^{-1}) due to the gain in activation entropy as compared to the reacting systems where the analogous participating reaction sites are present in different molecules [1, 2].

In this connection the ferrocenylacetic acid (**I**) is one of the most interesting objects for investigation because it exhibits the abnormally high reactivity in relation to oxygen as compared to the model ferrocene–carboxylic acid system ($pK_a \approx 5$). Compound **I** is easily oxidized at 20–50°C in the absence of any acids [3–5]. On the basis of the results of kinetic studies and the data on the composition of the reaction products a probable mechanism of oxidation of compound **I** was suggested [5] including two pathways (Scheme 1).

The formation of the internal ferricinium salt testifies in favor of the pathway *a* significantly contribution in the total oxidation process of compound **I**. The existence of the pathway *b* was deduced from the formation of CO_2 (yield about 0.2–0.25 mol/mol of the consumed compound **I**) and the products of the oxidative degradation of the ferricinium ion. The internal ferricinium salt is stable against heating up to

Scheme 1.



250°C [3] and cannot be the source of $CO_2^{\bullet}$ $RCOO^-$ anions are usually decarboxylated under the anodic oxidation [6]. Therefore the suggestion that the carbon dioxide is the product of oxidative decarboxylation of compound **I** seems quite logical. According to the Scheme (1) it is suggested that this reaction proceeds under the action of superoxide oxygen $O_2^{\bullet-}$ formed by electron transfer on the O_2 molecule. Being the radical anion this particle is capable of abstracting not only proton, but also the hydrogen atom from the carboxy group of the substituent. The first process (pathway *a*) is doubtless, but the oxidative decarboxylation of compound **I** under the action of $O_2^{\bullet-}$ is not so evident without the evaluation of the energy of the process. Besides, the oxidation of compound **I** according to the pathway *a* leads to formation alongside the internal ferricinium salt of $HO_2^{\bullet}$ peroxide radical which not only can take part in the reaction of oxidative decarboxylation of the starting compound [7], but also can initiate this process, for example, according to the Scheme (2).

Scheme 2.

$$\mathbf{I} + O_2 \to HO_2^{\bullet} \xrightarrow{\mathbf{I}} \underset{\overline{R}^{\bullet}}{C_5H_5FeC_5H_4C^{\bullet}HCOOH}, \qquad (2.1)$$

$$\overline{R}^{\bullet} + O_2 \to \overline{R}O_2^{\bullet}, \qquad (2.2)$$

$$\overline{R}O_2^{\bullet} + \mathbf{I} \to ROOH + C_5H_5FeC_5H_4CH_2COO^{\bullet} \qquad (2.3)$$

$$C_5H_5FeC_5H_4CH_2COO^{\bullet} \to \underset{\overline{R}_1^{\bullet}}{C_5H_5FeC_5H_4C^{\bullet}H_2} + CO_2. \qquad (2.4)$$

In general, reaction (2.3) may be written as Eq. (1). Its validity was shown on a series of examples in the course of studies of the radical chain oxidation of organic compounds [7].

$$RCOOH + RO_2^{\bullet} \to ROOH + RCOO^{\bullet}. \qquad (1)$$

If the pathway *a* is energetically more favorable than the pathway *b*, and reaction (1) is more favorable than reaction (2) of acid decarboxylation under the action of $O_2^{\bullet-}$, the mechanism of molecular oxidation of compound **I** must include only the pathway *a* described by Eq. (1.1).

$$RCOOH + O_2^{\bullet-} \to RC(O)O^{\bullet} + HO_2^{-}. \qquad (2)$$

The decarboxylation of the complex in this case must be considered as the secondary process. It follows from Scheme (2) that this process must be undoubtedly the radical chain one. This conclusion produces logically at least two questions concerning the mechanism of oxidation of compound **I** which were not considered in [4, 5]. Firstly, what is the mechanism of the radical chain oxidation of compound **I**, and what kind of products are formed? Secondly, if the presence of a substituent containing the carboxy group ($pK_a \approx 5$ [8]) plays the determining role in the reaction of the metal complex with oxygen, what kind of influence will be exerted by strong Brønsted acids (HX) such as $HClO_4$ **II** or CF_3COOH **III** upon the reactivity of this complex and the mechanism of its oxidation?

This study deals with solving of these problems.

To make a conclusion on the possibility of compound **I** decarboxylation under the action of $O_2^{-\bullet}$ it is necessary to compare the energies of the reactions (1) and (2) taking that complex **I** = RCOOH. For the calculation of standard enthalpies $\Delta_rH_1^0$ and $\Delta_rH_2^0$ of these reactions relationships (3) and (4) can be used.

$$\Delta_rH_1^0 = D(\text{RCOO–H}) - D(\text{HOO–H}), \qquad (3)$$

$$\Delta_rH_2^0 = D(\text{RCOO–H}) - D(\text{H–O}),^{-} \qquad (4)$$

where D_i is the energy of the corresponding O–H bonds.

As known, D(RCOO–H) bond energy in the carboxylic acids containing no strong electron-acceptor substituents in the radical R varies within the range 435–448 kJ mol^{-1} [9]. For compound **I** it may be accepted as equal to the O–H bond energy in phenylacetic acid, 448 kJ mol^{-1} which we shall regard as the model analog of ligand π-$C_5H_4CH_2COOH$ in the metal complex. D(ROO–H) bond energy equals 365 kJ mol^{-1} [10]. $D(H\text{–}O_2^-)$ bond energy can be calculated from Eq. (5) because $D(H\text{–}O_2^-) = -\Delta_rH_5^0$.

$$O_2^{-\bullet} + H^{\bullet} \to HO_2^{-}. \qquad (5)$$

Reaction enthalpy $\Delta_r H_5^0$ can be found from the well-known thermochemical relationship (6).

$$\Delta_r H_i^0 = \Sigma v_j \Delta_f H_j^0 - \Sigma v_i \Delta_f H_i^0. \qquad (6)$$

Here $\Delta_f H_{i,j}^0$ are standard enthalpies of formation of the reaction products (*j*) and the starting substances (*i*). Values of standard enthalpies of formation of $O_2^{\bullet -}$, of HO_2^-, and of $H^{\bullet}$ are –43.23 kJ mol^{-1} [11], –102.03 kJ mol^{-1} [12, 13], and 218 kJ mol^{-1} [13] respectively.

It gives the value of $D(H–O_2^-)$ bond energy 276.8 kJ mol^{-1}. From the relationships (3) and (4) it follows that $\Delta_r H_1^0 = 83$ kJ mol^{-1}, $\Delta_r H_2^0$ is 171.2 kJ mol^{-1}.

Note that while calculating $D(H–O_2^-)$ the value $\Delta_f H^0(HO_2^-)$ was found from the relationship (7)

$$\Delta_f H^0(HO_2^-) = \Delta_f H^0(HO_2^{\bullet}) + EA(HO_2^{\bullet}), \qquad (7)$$

where $EA(HO_2^{\bullet})$ is the affinity of $HO_2^{\bullet}$ radical to an electron.

Reported data on this value vary in a wide range (3.04 eV [14], 1.88 eV [15], 1.078 eV [12]. It may bring significant difference in the results of the energy effect calculation of the reactions and in the conclusions following from them. The above-given $\Delta_f H^0(HO_2^-)$ value –102.03 kJ mol^{-1} relates to the EA $(HO_2^{\bullet})$ value 1.078 eV reported recently. If $EA(HO_2^{\bullet})$ value 3.04 eV[1] is considered, $D(H–O_2^-)$ value occurs to be higher than D(RCOO–H) which certainly is not the case. The contribution of the entropic increment in the standard Gibbs energy of the reactions (1) and (2) is most probably small. It is much lower than $\Delta_r H_1^0$ and $\Delta_r H_2^0$ values. Therefore these characteristics of reactions can be considered as thermodynamic criteria of their occurrence.

Comparison of $\Delta_r H_1^0$ and $\Delta_r H_2^0$ shows that though the reaction (1) is by 87.2 kJ mol^{-1} more favorable than the reaction (2), its proceeding is hampered by thermodynamic reasons. Nevertheless, decarboxylation of carboxylic acids takes place under the action of peroxy radicals. It is caused firstly by the high decomposition rate of the $RC(O)O^{\bullet}$ radicals (rate constant of decomposition of $PhCH_2C(O)O^{\bullet}$ at 298 K is 7.84×10^9 s^{-1}, reaction enthalpy –98.3 kJ mol^{-1} [9]) what shifts the equilibrium of the reaction (1) to the right and makes it more thermodynamically favorable. Secondly, the reaction mechanism includes the stage of formation of a strong hydrogen bond between RCOOH and $RO_2^{\bullet}$ [7]. It leads to the decrease in the energy of O–H bond in the acid, and to the possibility of synchronic transfer of hydrogen atom in the $RCOOH\cdots{}^{\bullet}OOR$ hydrogen complex from the acid to $RO_2^{\bullet}$ radical, resulting in the decrease in the activation energy of the process. Considering the above reaction (1) for phenylacetic acid may be represented as follows:

$$PhCH_2COOH + RO_2^{\bullet} \rightarrow PhCH_2^{\bullet} + CO_2 + ROOH. \qquad (1')$$

The standard enthalpy value for this reaction obtained from relationship (6) or taking into account the data [9] is –15.3 kJ mol^{-1} ($\Delta_f H^0$ values for the acid and $PhCH_2^{\bullet}$ are taken from [9]). The value of Gibbs free energy $\Delta_r G_{1'}^0$ of the reaction considering a positive $\Delta_t S_{1'}^0$ value will be still lower than $\Delta_f H_{1'}^0$ explaining the possibility of the reaction.

The variation of entropy in the decomposition of $RCOO^{\bullet}$ will most probably be practically independent of the nature of the R radical. It permitted to use the entropy value for the reaction of decomposition of $CH_3COO^{\bullet}$ $\Delta_f S_p^0$ 106.1 J mol^{-1} K^{-1} [$S^0(CO_2)$ 213.6 kJ mol^{-1} K^{-1}, $S^0(CH_3^{\bullet})$ 194.3 kJ mol^{-1} K^{-1} [13], $S^0(CH_3COO^{\bullet})$ 301.8 kJ mol^{-1} K^{-1}; the last value was calculated using the G03W[2] software] for calculation of $\Delta_r G_{1'}^0$ which proved to be equal –46.9 kJ mol^{-1}. Results of these calculations may be extended also to the process of decarboxylation of compound **I**.

Enthalpy of reaction (2) for $PhCH_2COOH$ even considering the decomposition of $PhCH_2C(O)O^{\bullet}$ radical is a large positive value equal 72.9 kJ mol^{-1} which is not compensated by the increase in the reaction entropy ($298\Delta_r G_p^0$ 31.6 kJ mol^{-1}). Hence, the extrapolation to compound **I** of the above results of thermochemical calculations fot the decarboxylation of the phenylacetic acid under the action of $O_2^{\bullet -}$ and $RO_2^{\bullet}$ radicals makes it clear that the oxidative decarboxylation of this complex is based on the molecular oxidation according to the pathway *a* leading to generation of $HO_2^{\bullet}$ peroxide radicals. The conclusion that the pathway *a* is the only route of molecular oxidation of compound **I** may be substantiated also by another procedure, namely, by comparison of the energies of the pathways *a* and *b*. In this case model reactions look like the following.

$$PhCH_2COOH + O_2^{\bullet -} \rightarrow PhCH_2COO^- + HO_2^{\bullet}, \Delta_r H_8^0, \qquad (8)$$

$$PhCH_2COOH + O_2^{\bullet -} \rightarrow PhCH_2COO^{\bullet} + HO_2^-, \Delta_r H_9^0. \qquad (9)$$

---

[1] The value of [14] as a whole is not diminished by this note.

[2] Authors express their gratitude to Doctor of Chemical Sciences S.K. Ignatov for the performed calculations, and to the administration of Lobachevskii Nizhnii Novgorod State University for the offered software.

Equation (10) of the resulting reaction is obtained by subtraction of Eq. (9) from (8).

$$PhCH_2COO^{\bullet} + HO_2^{-} \rightarrow PhCH_2COO^{-} + HO_2^{\bullet}, \Delta_r H^0_{10}. \quad (10)$$

Reaction enthalpy $\Delta_r H^0_{10}$ is equal to the difference in enthalpies $\Delta_r H^0_8 – \Delta_r H^0_9$. This difference may be taken as equal to the difference in enthalpies $\Delta_r H^0_a – \Delta_r H^0_b$. Using relationship (6) it can be shown that $\Delta_r H^0{}_{10}$ = $\Delta_r H^0_a$ – $\Delta_r H^0_b$ –228 kJ mol^{-1} {$\Delta_f H^0(PhCH_2COO^{-})$ = –88 kJ mol^{-1} [9], $\Delta_f H^0(PhCH_2COO^{-})$ = –420 kJ mol^{-1} [16]}. As the reaction (10) results in the electron transfer between the reagents it must be accepted according to [17] that the the variation in entropy of this reaction $\Delta_r S^0_{10} \sim 0$. From that it follows that $\Delta_r H^0_{10}$ = $\Delta_r G^0_{10}$ = $\Delta_r G^0_a – \Delta_r G^0_b$. Therefore it is possible to regard $\Delta_r H^0_{10}$ value as the thermodynamic criterion of the proceeding of reaction (10). This large negative value shows that among the pathways *a, b* presented in the Scheme 1 the first one is significantly more favorable thermodynamically as compared to the second route. But final conclusion can be made after consideration of the high rate of decomposition of $PhCH_2COO^{\bullet}$ radical, of the high exothermic effect, and of the positive $\Delta_r S^0_p$ value for this process. In this case Eqs. (9) and (10) are transformed into Eqs. (9') and (10').

$$PhCH_2COOH + O_2^{-\bullet} \rightarrow PhCH_2^{\bullet} + CO_2 + HO_2^{-}, \Delta_r H^0_{9'}, \quad (9')$$

$$PhCH_2^{\bullet} + CO_2 + HO_2^{-} \rightarrow PhCH_2COO^{-} + HO_2^{\bullet}, \Delta_r H^0_{10'}. \quad (10')$$

The pathway *b* transforms to the pathway *b*' analogously to the reaction (9). Then $\Delta_r H^0_{10'} = \Delta_r H^0_a – \Delta_r H^0_{b'} = \Delta_r H^0_{10}$ + 98.3 kJ mol^{-1} = –129.7 kJ mol^{-1}.

As compared to the reaction (9) the entropy of the reaction (9') increases by the value $\Delta_r S^0_p$ = 106.1 J mol^{-1} K^{-1}. The entropy of reaction (10') decreases by the same value as compared to the entropy of reaction (10) where $\Delta_r S^0_{10}$ = 0. It provides the opportunity to calculate the free Gibbs energy of reaction (10') according to the equation: $\Delta_r G^0_{10'} = \Delta_r G^0_a – \Delta_r G^0_{b'}$ = –129300 – 298(–106.1) = –98.1 kJ mol^{-1}.

The knowledge of $\Delta_r G^0_a – \Delta_r G^0_b$ value permits the calculation of the ratio of the formal equilibrium constants of the pathways *a* and *b*' $K_a/K_{b'}$ for the molecular oxidation of compound **I** which proved to be equal 1.67×10^{17}. This result unambiguously shows that only one pathway of molecular oxidation of compound **I** leading to the formation of the internal ferricinium salt and $HO_2^{\bullet}$ radical takes place.

Though the calculations presented correspond to the gas phase, the conclusions made will be most probably true for the same reactions in solutions. In the aprotic solvents with low polarity and permittivity significant difference in the values of energy effects of the reactions under consideration from that obtained for the gas phase can hardly be expected. The increase in the polarity and permittivity of solvents favorable for proceeding of the electron and proton transfer reactions will lead to still more contrast in the energy characteristics of the pathways *a* and *b* of the compound **I** oxidation.

Radical $HO_2^{\bullet}$ can initiate the radical chain oxidation of the metal complex. With the purpose to confirm this statement we carried out more detailed analysis of the products of oxidation of compound **I** than it had been performed in [5]. The aim of these studies was the establishing of the presence of the compounds which together with CO_2 unambiguously show that oxidation of this metal complex may proceed not only by the molecular, but also by the radical chain mechanism.

It was found that together with the previously found oxidation products of compound **I** also neutral ferrocene derivatives formed, the main products being hydroxymethylferrocene **IV** and formylferrocene **V**. Yields of compounds **IV**, **V** are 0.28 and 0.11 mol per mol of consumed metal complex respectively. Among the minor products ferrocenylpyruvic acid **VI**, ferrocenecarboxylic acid **VII**, and CO were found. The products of oxidative degradation of ferricinium ion contained also cyclopentadiene and cyclopentadienone dimer.

Radical chain oxidation of compound **I** was confirmed by deceleration of the process on the addition of *o*-phenylenediamine known as the inhibitor of the radical chain reactions (Fig. 1) and at the use of ethanol instead of dioxane as a solvent. But contrary to the example of compound **IV** whose oxidation is almost completely suppressed by the action of the above-mentioned substances [18], the total cessation of compound **I** oxidation does not occur because of the noticeable role of the molecular pathway of oxidation of the metal complex. Rate of the CO_2 accumulation in alcohols is also lower than in dioxane (Fig. 2).

Formation of oxoacid **VI** and hydroxymethylferrocene **IV** in the oxidation of compound **I** shows that its radical chain oxidation proceeds with the simultaneous participation of two reaction centers, the methylene and the carboxy groups of the substituent. Oxidation of the methylene group initiated by peroxy radicals is a process quite natural from the thermodynamic and the kinetic point of view because

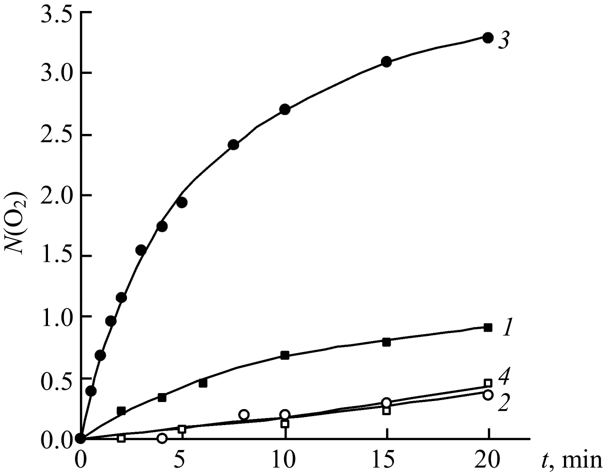


Fig. 1. Effect of *o*-phenylenediamine (In) on the oxidation of compound **I** (*1, 2*) in the absence of acid **III** and (*3, 4*) in the presence of it. C^0_{I} 0.005 M, C^0_{III} 0.05 M, $C^0_{\mathrm{In}}(2)$ 1×10^{-4} M, $C^0_{\mathrm{In}}(4)$ 2.5×10^{-4} M, $P(O_2)$ 0.42×10^5 Pa, *T* 50°C.

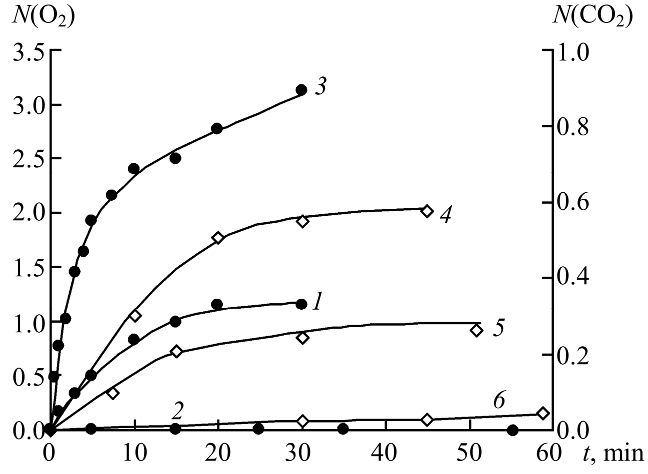


Fig. 2. Kinetic curves of oxidation of (*1–3*) compound **I** and (*4–6*) accumulation of CO_2 in (*1–5*) dioxane and (*6*) in methanol in (*1, 5, 6*) the absence of acids and (*2*) in the presence of acid **II** and (*3, 4*) acid **III** (3,4). C^0_{I} 0.01 M, C^0_{III} 0.03 M, C^0_{II} 0.1 M, $P(O_2)$ 0.42×10^5 Pa, *T* 50°C.

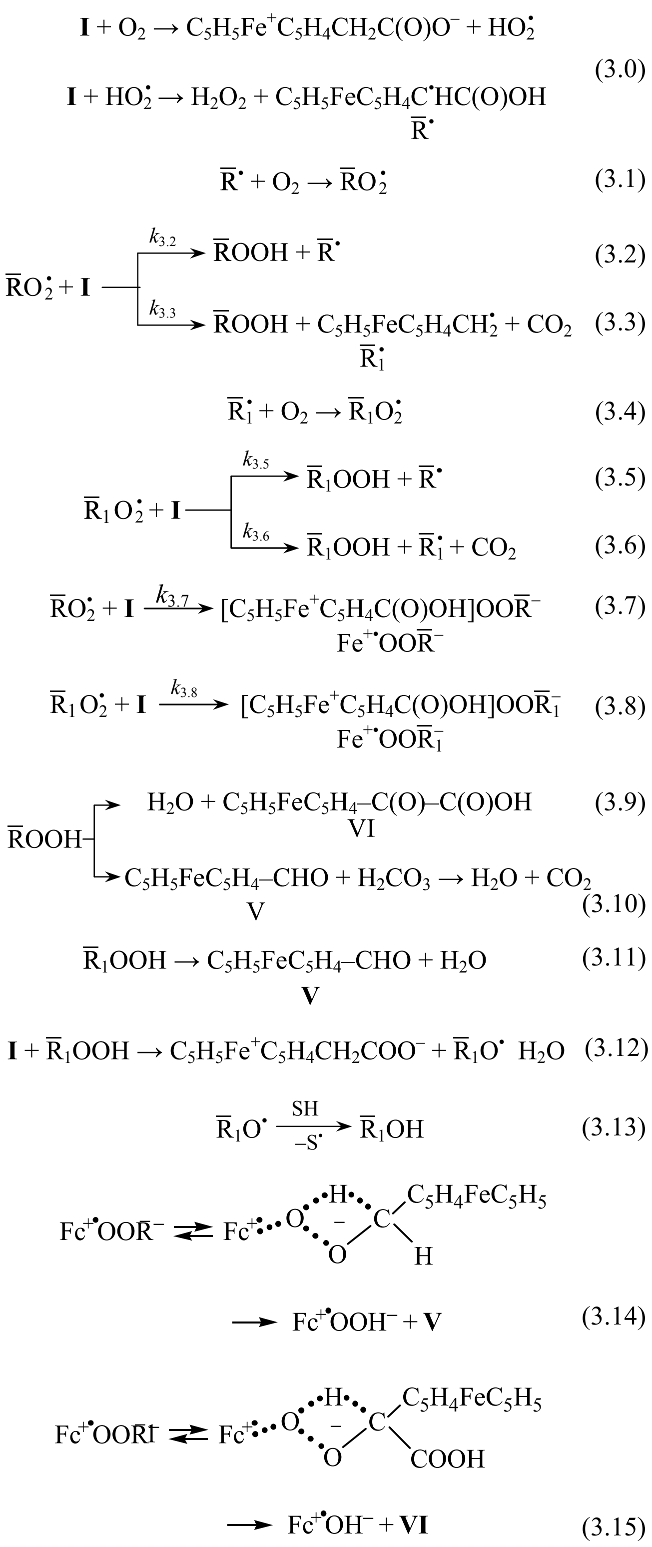
it is known that the C–H bond energy in alkylaromatic hydrocarbons is 50–60 kJ mol^{-1} lower than in the saturated ones [10, 14]. Because of that the C–H bond energy in the methylene group of compound **I** can be without a large error to be taken at ~330 kJ mol^{-1}. In this case the enthalpy of hydrogen atom abstracting from it with $RO_2^{\cdot}$ radical must be equal to –35 kJ mol^{-1} because the activation energy of this process does not exceed 42 kJ mol^{-1} [10]. The paricipation of COOH group in the radical chain oxidation of compound **I** besides the above-presented reasons is confirmed by some others. First of all it is the presence of compound **IV** in the reaction products because its formation cannot be explained without the oxidative decarboxylation of compound **I**. From the kinetic point of view the hydrogen transfer in the $\mathrm{COOH}\cdots{}^{\cdot}\mathrm{OOR}$ hydrogen complex whose equilibrium concentration is established immediately can be considered as the monomolecular reaction proceeding with the sufficient gain in the activation entropy as compared to bimolecular reaction of hydrogen abstraction from methylene group with $RO_2^{\cdot}$ radicals. It must lead to considerable equalization of the activation free energy of the abstraction of hydrogen atom from CH_2 and COOH groups. The activation energy in the first case will be undoubtedly lower than in the second one. Besides, the lifetime of $\overline{R}_1C(O)O^{\cdot}$ radical is about 1.27×10^{-10} s. Since it can exist only in the cage of solvent in the moment of its formation, the radical leaving the cage is $\overline{R}_1^{\cdot}$. It quickly reacts with oxygen [k ~ $(2–5)\times10^9$ l mol^{-1} s^{-1}] to give $\overline{R}_1O_2^{\cdot}$ radical [19] which produces compound **IV**.

On the basis of the above data the probable mechanism of the radical chain oxidation of compound **I** uncomplicated by the degenerate branching of chains and including only its main stages can be described by Scheme 3.

Despite certain specific differences between the classic scheme of the radical chain oxidation of hydrocarbons RH [7] and this scheme of compound **I** oxidation they are in general analogous. Reactions (3.0) are the stages of generation of the $\overline{R}^{\cdot}$ radical starting the chain. Reactions (3.1)–(3.6) describe the propagation of the chain, and the reactions (3.7), (3.8), its termination. The termination of the chain by the reaction of the metal complex with peroxy radical is confirmed in [19] by an example of oxidation of compound **IV**. Reactions (3.9)–(3.15) describe the main pathways of transformation of hydroperoxides ROOH and R_1OOH and the radical-ion salts $\mathrm{Fc}^{+\cdot}\mathrm{OO}\overline{R}^{-}$ and $\mathrm{Fc}^{+\cdot}\mathrm{OO}\overline{R}_1^{-}$ leading to formation of the established metal complex products of the radical chain oxidation of compound **I**.

It is seen from the presented scheme that CO_2 formation may proceed not only by the oxidative decarboxylation of the starting metal complex, but also in the course of oxidation of the methylene group. Transformation of ROOH hydroperoxide according to the reaction (3.10) leading to formation of compound **V** and carbonic acid is similar to the transformation of

Scheme 3.



$$\mathbf{I} + O_2 \rightarrow C_5H_5Fe^+C_5H_4CH_2C(O)O^- + HO_2^\bullet \tag{3.0}$$

$$\mathbf{I} + HO_2^\bullet \rightarrow H_2O_2 + \underset{\bar{R}^\bullet}{C_5H_5FeC_5H_4C^\bullet HC(O)OH}$$

$$\bar{R}^\bullet + O_2 \rightarrow \bar{R}O_2^\bullet \tag{3.1}$$

$$\bar{R}O_2^\bullet + \mathbf{I} \xrightarrow{k_{3.2}} \bar{R}OOH + \bar{R}^\bullet \tag{3.2}$$

$$\bar{R}O_2^\bullet + \mathbf{I} \xrightarrow{k_{3.3}} \bar{R}OOH + \underset{\bar{R}_1^\bullet}{C_5H_5FeC_5H_4CH_2^\bullet} + CO_2 \tag{3.3}$$

$$\bar{R}_1^\bullet + O_2 \rightarrow \bar{R}_1O_2^\bullet \tag{3.4}$$

$$\bar{R}_1O_2^\bullet + \mathbf{I} \xrightarrow{k_{3.5}} \bar{R}_1OOH + \bar{R}^\bullet \tag{3.5}$$

$$\bar{R}_1O_2^\bullet + \mathbf{I} \xrightarrow{k_{3.6}} \bar{R}_1OOH + \bar{R}_1^\bullet + CO_2 \tag{3.6}$$

$$\bar{R}O_2^\bullet + \mathbf{I} \xrightarrow{k_{3.7}} \underset{Fe^{+\bullet}OO\bar{R}^-}{[C_5H_5Fe^+C_5H_4C(O)OH]OO\bar{R}^-} \tag{3.7}$$

$$\bar{R}_1O_2^\bullet + \mathbf{I} \xrightarrow{k_{3.8}} \underset{Fe^{+\bullet}OO\bar{R}_1^-}{[C_5H_5Fe^+C_5H_4C(O)OH]OO\bar{R}_1^-} \tag{3.8}$$

$$\bar{R}OOH \rightarrow H_2O + \underset{\mathrm{VI}}{C_5H_5FeC_5H_4\text{–}C(O)\text{–}C(O)OH} \tag{3.9}$$

$$\bar{R}OOH \rightarrow \underset{\mathrm{V}}{C_5H_5FeC_5H_4\text{–}CHO} + H_2CO_3 \rightarrow H_2O + CO_2 \tag{3.10}$$

$$\bar{R}_1OOH \rightarrow \underset{\mathbf{V}}{C_5H_5FeC_5H_4\text{–}CHO} + H_2O \tag{3.11}$$

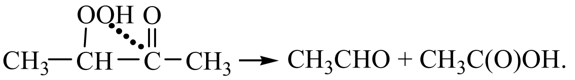
$$\mathbf{I} + \bar{R}_1OOH \rightarrow C_5H_5Fe^+C_5H_4CH_2COO^- + \bar{R}_1O^\bullet\ H_2O \tag{3.12}$$

$$\bar{R}_1O^\bullet \xrightarrow[-S^\bullet]{SH} \bar{R}_1OH \tag{3.13}$$

$$Fc^{+\bullet}OO\bar{R}^- \rightleftarrows \ldots \rightarrow Fc^{+\bullet}OOH^- + \mathbf{V} \tag{3.14}$$

$$Fc^{+\bullet}OO\bar{R}_1^- \rightleftarrows \ldots \rightarrow Fc^{+\bullet}OH^- + \mathbf{VI} \tag{3.15}$$

hydroperoxide $CH_3\text{–}CH(OOH)\text{–}C(O)\text{–}CH_3$ formed in the course of the oxidation of methyl ethyl ketone [7].

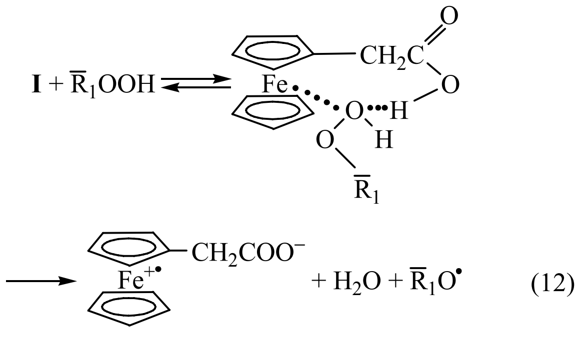


$$CH_3\text{—}\overset{OOH}{CH}\text{—}\overset{O}{\overset{\|}{C}}\text{—}CH_3 \rightarrow CH_3CHO + CH_3C(O)OH. \tag{11}$$

Compound **V** is formed in three reactions, (3.10), (3.11), and (3.14). Under mild conditions at low temperature reaction (3.11) is considerably more favorable thermodynamically than the hemolytic decomposition of hydroperoxide $\bar{R}_1OOH$ requiring about 165 kJ mol^{-1} [19]. In the course of transformation of R_1OOH according to the reaction (3.11) the cleavage of one O–O bond [D(O–O) 165 kJ mol^{-1}] and of one C–H bond [D(C–H) ~330 kJ mol^{-1}) takes place. Then one H–O bond in water {D(H–O) 498 kJ mol^{-1} [14]} and one π-bond in C=O group {$D(C^{\pi}\text{–}O)$ ~290 kJ mol^{-1} [20]} are formed. Total gain in energy is ~–273 kJ mol^{-1}. Besides, this reaction most probably proceeds according to synchronic mechanism and should have low activation energy. It is not by chance that in the course of the radical chain oxidation of ethylbenzene the yield of acetophenone is 6.5 times higher than that of methylphenylcarbinol [21]. Note that these speculations can be completely applied also to reaction (11). Evaluation of the enthalpy variation on the basis of energies of the ruptured and forming bonds leads to the value about –240 kJ mol^{-1}. Standard enthalpy of the reaction (3.10) is undoubtedly less negative because of low stability of H_2CO_3. But considering that the reaction proceeds with the significant increase in entropy which for such processes may reach 120–189 J mol^{-1} K^{-1} [1], the Gibbs free energy in this case will have the large negative value. Synchronic reaction mechanism should also provide low activation energy. Together with thermodynamic factor it will favor the high rate of the process.

Rearrangements of the radical ion salts $Fc^{+\bullet}OO\bar{R}^-$ and $Fc^{+\bullet}OO\bar{R}_1^-$ leading to formation of compounds **V**, **VI** are characteristic of the peroxide metal complexes $L_nM^+(OOCHR_1R_2)^-$ (L_nM is the transition metal complex) when the carbon atom bound to the peroxy group bears a hydrogen atom [22]. Compound **VI** can be formed also by transformation of peroxide $\bar{R}OOH$ according to the equation (3.9). Low yield of this product can be explained by the higher rate of transformation of the above-mentioned peroxide by the reaction (3.10) and also by the extremely high reactivity of carbonyl group in it in relation to the reactions characteristic of ketones, for example, with hydroperoxides [23] and water [6].

As it follows from the above-presented scheme, the formation of compound **IV** is caused by the oxidative decarboxylation of compound **I**. It is connected not with the homolysis of peroxide bond in $\bar{R}_1OOH$, but with the reaction of this hydroperoxide with metal complex according to Eq. (3.12). Characteristic feature of this reaction is the possibility of participation of the substituent carboxy group in oxidation as it is shown below:



The coordination of compound **I** with $\bar{R}OOH$ by the iron atom may take place by means of interaction of the metal complex HOMO localized on the metal atom (d_{xy} or $d_{x^2-y^2}$ [24]) with the vacant σ*-orbital of the peroxide bond.

In such mechanism of oxidation of metal complex with hydroperoxide as well as in its reaction with oxygen it plays the role of bifunctional reagent. It is the necessary condition for exhibiting the effect of approach and orientation that significantly accelerates the oxidation. As is known, homolytic decay of $\bar{R}_1OOH$ must lead to the degenerate branching of chains. It should cause autoacceleration of oxidation of com-pound **I** with time. The character of the kinetic curves of oxygen consumption with the reaction mixture (Fig. 2) disagrees with that.

In addition to the mechanism of the reaction (12) it should be noted that under the analogous conditions the oxidation of ferrocene with hydroperoxides [H_2O_2 or $(CH_3)_3COOH$] proceeds extremely slow.

Analogous reaction of compound **I** with $\bar{R}OOH$ is hindered evidently by steric reasons. For the reaction of this complex with $\bar{R}O_2^{\bullet}$ described by Eq. (3.7) the steric factor is significantly less important because of the another orientation of peroxide radical in the attack of metal atom. Formation of the internal ferricinium salt, on the one side, and of compounds **IV**, **V** and CO_2, on the other, in comparable amounts, and also a weak consumption of oxygen for the oxidation of 1 mol of compound **I** [$N(O_2)$ ~ 1.3] show that the contributions of rates of molecular (v_0) and the radical chain (v_r) pathways of oxidation of metal complex in the total rate of the process (v) are comparable. Due to that the overall rate can be presented as sum of oxidation rates of compound **I** along each pathway.

$$v = v_0 + v_r. \quad (13)$$

It was shown previously that the experimental rate of the process is described by Eq. (14).

$$v = k_{\text{eff}}[\text{I}][O_2]. \quad (14)$$

Then

$$v = v_0 + v_r = k_{\text{eff}}[\text{I}][O_2]. \quad (15)$$

For v_0 such dependence on the concentration of reagents is evident

$$v_0 = k_aK[\text{I}][O_2] = k_0[\text{I}][O_2], \quad (16)$$

where $k_0 = k_aK$.

For the fulfillment of relationship (15) it is necessary that the analogous dependence of the reaction rate on the starting concentrations of reagents must be fulfilled also for v_r. According to [7] the rate of the radical chain oxidation of hydrocarbons RH is determined by the rate of the reaction of chain propagation.

$$RO_2^{\bullet} + RH \xrightarrow{k_r} ROOH + R^{\bullet}.$$

According to Scheme 3 each of the peroxide radical formed $\bar{R}O_2^{\bullet}$ and $\bar{R}_1O_2^{\bullet}$ can enter the analogous reaction with the molecule of compound **I** by two pathways described by the reactions (3.2), (3.3), and (3.5), (3.6) respectively. For the equation of the rate of compound **I** oxidation by the radical chain mechanism considering all the reactions of chain propagation and termination with the participation of $\bar{R}O_2^{\bullet}$ and $\bar{R}_1O_2^{\bullet}$ the following admissions should be accepted.

(1) Quasistationary concentration of both peroxide radicals is achieved quickly due to the high rate of radical generation (v_0) [19].

(2) In the quasistationary regime the rates of chain propagation involving $\bar{R}O_2^{\bullet}$ and $\bar{R}_1O_2^{\bullet}$ are equal.

$$v(\bar{R}O_2^{\bullet}) = v(\bar{R}_1O_2^{\bullet}), \quad (17)$$

$$v(\bar{R}O_2^{\bullet}) = (k_{3.2} + k_{3.3})[\bar{R}O_2^{\bullet}][\mathbf{I}], \quad (18)$$

$$v(\bar{R}_1O_2^{\bullet}) = (k_{3.5} + k_{3.6})[\bar{R}_1O_2^{\bullet}][\mathbf{I}]. \quad (19)$$

From that follows:

$$\nu_r = 2\nu(\overline{R}O_2^{\bullet}) = \nu(\overline{R}_1O_2^{\bullet}). \quad (20)$$

(3) Rates of the chain termination involving $\overline{R}O_2^{\bullet}$ and $\overline{R}_1O_2^{\bullet}$ slightly differ. Though the reaction of $\overline{R}_1O_2^{\bullet}$ radical with compound **I** is more favorable by steric reasons, the presence of carboxy group exhibiting strong electron-acceptor properties in $\overline{R}_1O_2^{\bullet}$ radical increases its activity in the one-electron transfer reactions.

$$v_{3.7} = v_{3.8}, \quad (21)$$

$$v_{3.7} = k_{3.7}[\overline{R}O_2^{\bullet}][I], \quad (22)$$

$$v_{3.8} = k_{3.8}[\overline{R}_1O_2^{\bullet}][I]. \quad (23)$$

It follows that the total rate of chain termination (ν_t) is equal to:

$$v_t = 2v_{3.7} = 2v_{3.8}. \quad (24)$$

(4) Rate of radical generation is equal to the total rate of chain termination.

$$v_0 = v_t. \quad (25)$$

(5) From the relationships (22)–(25) the expression for the concentration of $\overline{R}O_2^{\bullet}$ and $\overline{R}_1O_2^{\bullet}$ radicals can be found. Then using the relationships (18)–(20) the equation for the rate of oxidation of compound **I** (ν_r) can be written as follows:

$$\nu_r = 2v(\overline{R}O_2^{\bullet}) = [(k_{3.5} + k_{3.6})k_0/k_{3.7}][\mathbf{I}][O_2]. \quad (26)$$

The obtained expression for ν_r completely corresponds to the relationship (15) which in this case acquires the following shape:

$$\begin{aligned} v = v_0 + v_r &= [k_0 + (k_{3.2} + k_{3.3})k_0/k_{3.7}][\mathbf{I}][O_2] \\ &= [1 + (k_{3.2} + k_{3.3})/k_{3.7}]k_0[\mathbf{I}][O_2] = k_{\mathrm{eff}}[\mathbf{I}][O_2], \quad (27) \end{aligned}$$

$$k_{\mathrm{eff}} = k_0[1 + (k_{3.2} + k_{3.3})/k_{3.7}] = k_aK[1 + (k_{3.2} + k_{3.3})/k_{3.7}]. \quad (28)$$

Hence, the assumed mechanism of oxidation of compound **I** including the molecular and the radical chain pathways corresponds to the experimentally established kinetic rule describing the course of this reaction. The authors realize that the admissions accepted are quite approximate, but such approach to the analysis of mechanism of the radical chain oxidation of organic compounds (in our case of compound **I**) never used before leads to the results completely corresponding to the experimental data.

As it was mentioned already, the generation of radicals in the molecular oxidation of compound **I** proceeds with the direct participation of the carboxy group of substituent in this process. In this connection the establishment of the effect of acid additives of different strength on the rate of oxidation of metal complex, its kinetic rules and the mechanism of the process presented the doubtless interest.

It was shown previously [4] that the addition of benzoic acid ($C^0_{\mathrm{HX}}/C^0_{\mathrm{I}} = 8$) with p$K_a$ close to that of compound **I** does not affect the rate of its oxidation because of the stronger influence of carboxy group of substituent on the reactivity of metal complex due to effects of the approach and orientation. Additives of strong acids like $HClO_4$ (**II**) and CF_3COOH (**III**) exhibit different effects. It turned out that in presence of compound **II** complex **I** lost its ability to get oxidized with the noticeable rate for a long time.

It is sufficient to state that keeping the compound **I** solution in dioxane in the presence of acid **II** ($C^0_{\mathrm{HX}}/C^0_{\mathrm{I}} = 10$) in the atmosphere of oxygen for 10 h at 50°C yields only 0.02 mol of CO_2 per 1 mol of the starting complex. The addition of acid to the solution of compound **I** in dioxane causes an immediate change in its color from yellow to green. Electron absorption spectrum of the solution contains the bands at $\lambda_{\max}$ 450 and 620 nm (Fig. 2) corresponding to α-ferrocenylcarbenium ion [25]. The formation of the latter may be due to the protonation of compound **I** proceeding with the formation of ferrocenylacetylium cation. It quickly converts into more stable α-ferrocenylcarbenium ion by the elimination of CO [26]. The oxidation of the latter carbocation is very specific and slow.

$$\begin{aligned} &C_5H_5FeC_5H_4CH_2COOH + 2HX \\ &\rightarrow C_5H_5FeC_5H_4CH_2C^+O + H_3O^+ + 2X^-. \quad (29) \end{aligned}$$

In the presence of acid **III** the formation of ferrocenylacetylium cation does not take place (Fig. 3) but a strong acceleration of the compound **I** oxidation and the simultaneous increase in $N(O_2)$ to 4–5 are observed. These effects are demonstrated by Fig. 1. The results obtained show that significant increase occurs in the role of the radical chain pathway in the total process of compound **I** oxidation. Some other facts also support this statement. Firstly, oxidation of compound **I** is decelerated by additive of *o*-phenylenediamine (Fig. 1) known as the inhibitor of the radical chain reactions. The effect of deceleration of oxidation of compound **I** by the additives of this inhibitor in the absence of acid is significantly less. Secondly, the oxidation of compound **I** is decelerated by using ethanol instead of dioxane as a solvent (Fig. 4) which can inhibit oxidation by binding the starting metal complex and the intermediates, first of

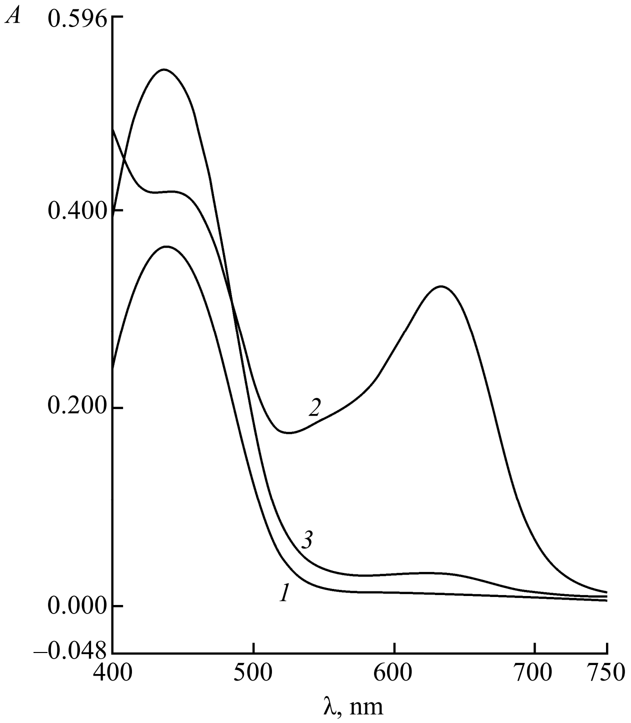


Fig. 3. Electron absorption spectrum of the solution of compound **I** in dioxane under argon: (*1*) in the absence of acids, (*2*) in the presence of the acid **II**, (*3*) in the presence of the acid **III**. C_{I}^{0} 0.005 M, C_{II}^{0} 0.5 M, C_{III}^{0} 0.5 M.

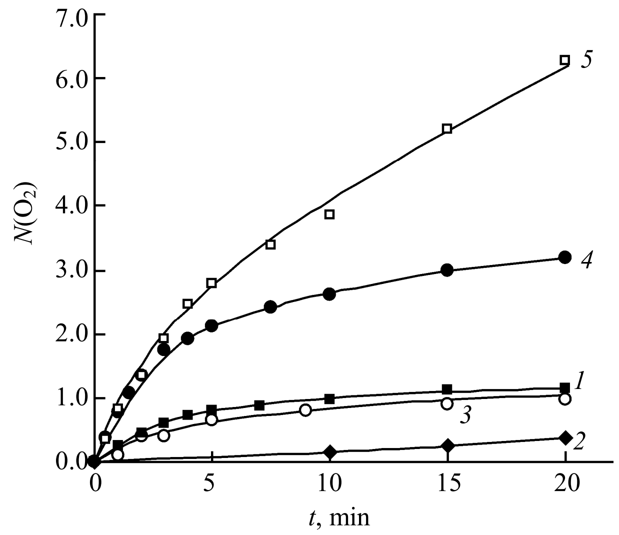


Fig. 4. Effect of the nature of solvent on the oxidation of compound **I** (*1, 2*) in the absence of the acid **III** and (*3–5*) in the presence of it: (*1, 4*) dioxane, (*2, 3*) ethanol, (*5*) methyl metacrylate. C_{I}^{0} 0.01 M, C_{III}^{0} 0.05 M; $P(O_2)$ 0.42×10^5 Pa, T 50°C.

all $\overline{\mathrm{R}}\mathrm{O}_2^{\cdot}$ and $\overline{\mathrm{R}}_1\mathrm{O}_2^{\cdot}$ in the stable hydrogen complexes [7]. Finally, the oxidation of compound **I** in methyl metacrylate solution causes the polymerization of the latter. Analogous effect we established in the course of the radical chain oxidation of compound **IV** in methyl metacrylate [18]. It is characteristic that $N(O_2)$ value in the oxidation of compounds **I**, **IV** in methyl metacrylate is significantly higher than in the oxidation in dioxane. That means that oxygen is included in the form of labile peroxide group in the composition of the polymer formed. Considering the significant effect of acid **III** on the rate of oxidation of compound **I** and $N(O_2)$ value it presented the doubtless interest to compare kinetic rules and the composition of the products of oxidation of metal complex in the absence and in the presence of this acid.

Results of investigation of the kinetic rules of compound **I** oxidation in the presence of acid **III** are shown in Fig. 5 from which it follows that for the initial rate of the process the reaction order is equal to one with respect to the initial concentration of compound **I** and oxygen [$P(O_2)$]. At the same time the kinetic equation includes the concentration of acid in the first power. It follows from the fact of the linear increase in the initial rate W_0[3] with the increase in concentration of each of the above-mentioned reagents. It is characteristic that the dependence W_0–$f(C_{\mathrm{HX}})$ does not pass through the origin indicating that even in this case compound **I** participates in the bimolecular oxidation, but its contribution in the total oxidative process is much smaller than the contribution of the radical chain pathway. As it was shown above, in the absence of HX these contributions are practically comparable.

The comparison of composition of the oxidation products of compound **I** in the absence of the acid **III** (process 1) and in its presence (process 2) showed that on the whole they were analogous, but a significant difference in the yields existed. In this respect the most demonstrative are the variations in the yields of compounds **IV**, **V**, and CO_2 as illustrated by the data from the table.

Besides, in going from the process 1 to the process 2 [$N(O_2) = 1.5$] a significant decrease in the yield of compound **VII** and the increase in the yield of compound **VI** are observed. At $N(O_2) \geq 4$ compounds **IV–II** are absent.

---

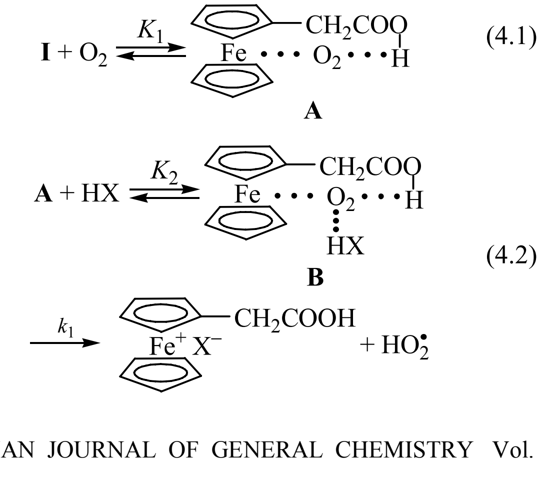
[3] Symbol W is used for the definition of experimental data.

Experimental data presented in the table can be explained proceeding from the assumed scheme of the radical chain oxidation of compound **I**.

The main reason of the increase in CO_2 yield in the oxidation of compound **I** in the presence of the acid **III**, as well as the yield of the compound **VI,** is the preferred oxidation of the metal complex under these conditions along the radical chain mechanism. Effect of additives of acid **III** on the ratio of the yields of compounds **IV**, **V** in the processes (1) and (2) is caused by its effect on the direction of transformations of the formed peroxides $\overline{R}OOH$ and $\overline{R}_1OOH$ [7]. In the absence of HX the hydroperoxide $\overline{R}_1OOH$ evidently very quickly transforms by Eq. (3.11), and only its insignificant part enters reaction (3.12) with compound **I** leading to the formation of $\overline{R}_1O^{\cdot}$ radical and further of compound **IV**. It is known that the acids catalyze such direction of decomposition of secondary hydroperoxides [7]. Acid **III** must also catalyze the transformation of $\overline{R}OOH$ to α-ketoacid **VI** according to Eq. (3.9), but it cannot be excluded that the acid also catalyzes another pathway of the hydroperoxide decay leading to the formation of compound **V** and the labile carbonic acid [Eq. (3.10)]. As is known, strong acids favor the decomposition of carbonic acid. Compound **VII** is the product of oxidation of compound **V**. In the absence of strong acids it is stable to oxygen, but in the presence of acid it is capable of oxidation. The absence of products **IV**–**VII** in the process (2) when $N(O_2) \geq 4$ arises from their acid-stimulated oxidation.

The strong acceleration of compound **I** oxidation under the action of the acid **III** and its preferred course by the radical chain mechanism under these conditions suggests the appearance of new, more abundant source of radicals generated only under the direct participation of the acid. In the simplest form this participation can be described by Scheme 4.

Scheme 4.



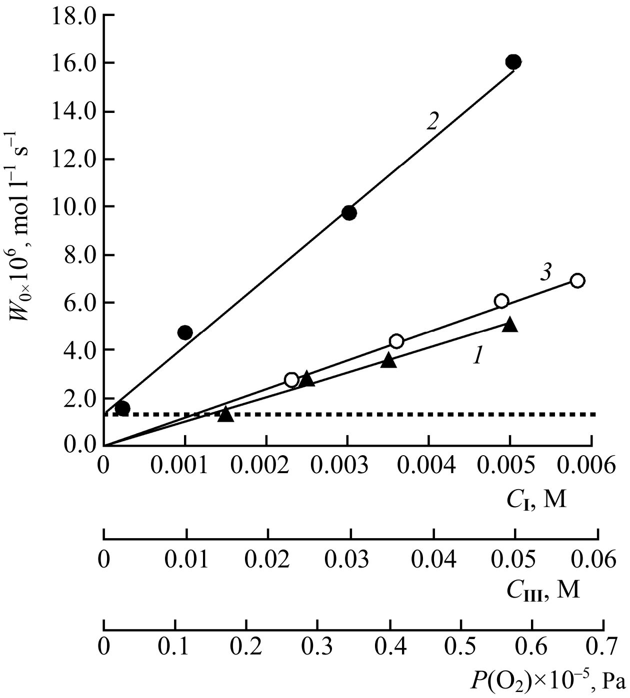


Fig. 5. Dependences of the initial oxidation rate of compound **I** (*1*) on its concentration, (*2*) concentration of acid **III** and (*3*) on oxygen pressure on dioxane at *T* 50°C. (*1*) C^0_{III} 0.01 mol l^{-1}, P_0 0.41×10^5 Pa, (*2*) C^0_I 0.01 mol l^{-1}, P_0 0.41×10^5 Pa, and (*3*) C^0_I 0.01 mol l^{-1}, C^0_{III} 0.01 mol l^{-1}.

The role of the substituent in this process is limited only to the keeping of oxygen in the coordination sphere of metal because the protonation of superoxide oxygen $O_2^{\cdot-}$, formed by the electron transfer from the iron atom to the molecule of oxygen, by means of acid **III** ($pK_a = 0$) will proceed much faster than by the acid group of compound **I** ($pK_a > 5$). This process is significantly more favorable energetically than the oxidation of compound **I** in the absence of acid as follows from the comparison of standard enthalpies of reactions (30) and (31).

Yield of the reaction products of compound **I** oxidation (mol/mol of starting complex), *T* 50°C

Yield of the product	Compound **IV**	Compound **V**	CO_2
Process 1[a]	0.28	0.11	0.24
Process 2[b]	traces	0.30	0.15
Process 2[c]	traces	traces	0.62

[a] Complete oxidation of compound **I** [$N(O_2)$ ~1.3]. [b] $N(O_2) = 1.5$.
[c] Complete oxidation of compound **I** [$N(O_2)$ ~ 4].

$$CF_3COOH + O_2^{\cdot -} \rightarrow CF_3COO^- + HO_2^{\cdot}, \Delta_rH^0_{30}, \quad (30)$$

$$PhCH_2COOH + O_2^{\cdot -} \rightarrow PhCH_2COO^- + HO_2^{\cdot}, \Delta_rH^0_{31}. \quad (31)$$

The subtraction of Eq. (31) from Eq. (30) gives the equation of the resulting reaction (32).

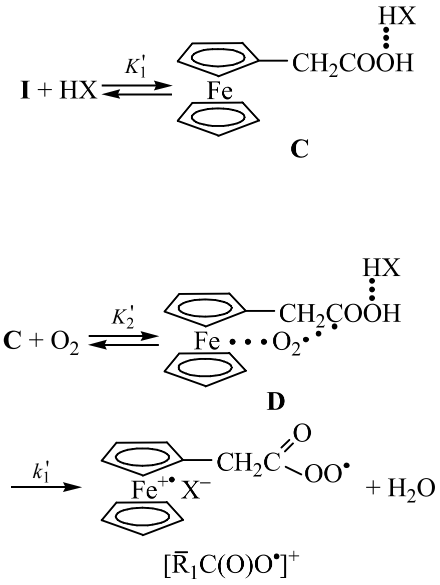
$$CF_3COOH + PhCH_2COO^- \rightarrow CF_3COO^- + PhCH_2COOH, \Delta_rH^0_{32}. \quad (32)$$

The standard enthalpy of this reaction $\Delta_rH^0_{32} = \Delta_rH^0_{30} - \Delta_rH^0_{31}$ will characterize the ability of compared acids to lend the proton to the molecule of superoxide oxygen. The calculation of the reaction enthalpy $\Delta_rH^0_{32}$ using relationship (6) leads to the value –74 kJ mol^{-1}. Values of standard enthalpies of formation of reagents are taken from [27] (CF_3COOH) and [16] (CF_3COO^- and $PhCH_2COO^-$). Since the variation in entropy value for the reaction (32) may be accepted equal to zero, as follows from the Eq. (33), the obtained $\Delta_rH^0_{32}$ value will be equal to $\Delta_rG^0_{32}$ Therefore it may be used as a thermodynamic criterion for the occurrence of the reaction (32). $\Delta_rH^0{}_{32}$ value –74 kJ mol^{-1} seems sufficient for considering that Scheme 4 is a really existing process.

$$\Delta_rS^0_{33} = [S^0(PhCH_2COOH) - S^0(PhCH_2COO^-)] - [S^0(CF_3COOH) - S^0(CF_3COO^-)] = 0. \quad (33)$$

Fundamentally different mechanism of participation of HX in the process of compound **I** oxidation is presented in Scheme 5 considering the possibility of coordination of O_2 molecule to another electrophilic site of substituent if its carboxy group is bound with the acid by a strong hydrogen bond.

Scheme 5.



(5.1)

(5.2)

As known, the equilibrium (5.1) should be established immediately, and complex **C** may be regarded as the starting compound in the reaction with oxygen. Formally it may be regarded as the decrease in the order of the reaction under investigation leading to the gain in activation entropy. The electrophilicity of the carbon atom of the carboxy group is confirmed by the estimation of the electronic density distribution in the molecule of formic acid. It shows that positive charge on the carbon atom (+0.401 [28]) is higher than that on the hydrogen atom of hydroxy group.

Regretfully, the comparison of energies of total reactions described by Schemes 4 and 5 is impossible because of the absence of the necessary data on the enthalpies of formation $\Delta_fH^0_i$ not only of the real reagents, but also of the phenylacetic acid derivatives used in model calculations.

Nevertheless, from the kinetic point of view the oxidation of compound **I** described by Scheme 5 seems more attractive than the mechanism shown in Scheme 4. Just in such way of HX coordination with the molecule of compound **I** the metal complex can enter the reactions with oxygen as the bifunctional reagent. This is the necessary condition for exhibiting the effects of approach and orientation in the oxidation of compound **I**. It may result in the significant gain in the free activation energy as compared to the process described by Scheme 4. The bonding of the oxygen molecule with the electrophilic carbon atom of the substituent stimulates the electron transfer from the metal atom to oxygen. In its turn it leads to the increase in polarity of C–OH bond and in nucleophilicity of the hydroxy group. The latter in its turn is capable of protonation by the acid HX coordinated with it. These synchronic transformations of the triple complex **D** while moving along the reaction coordinate result in the formation of the metal complex peroxide radical $[\bar{R}_1C(O)O^{\cdot}]^+$ and water. For compound **I** oxidation according to Scheme 4 the effect of approach and orientation is excluded. The reaction scheme offering the location of O_2 molecule in the bridge position between the metal atom and the hydrogen atom of the carboxy group of substituent as in the complex **A** of the Scheme 4 does not explain the influence of HX in the Scheme 5 on the rate of the process, because the energy of the reaction will be the same as in the bimolecular interaction of compound **I** with O_2 (Scheme 1). It is not excluded that in the oxidation of compound **I** in presence of the acid **III** mechanism (4) contributes something to the radicals generation, but the authors given preference to mechanism (5). More detailed analysis of the role of the approach and orientation effect in oxidation of ferrocene derivatives is presented in [18]. Note also that in the reaction of hydrogen abstraction from the molecule of compound **I** leading to formation of the radicals $R^{\cdot}$ and $R_1^{\cdot}$ the peracyl radical must be more active than $HO_2^{\cdot}$ because the energy of O–H bond in RC(O)OOH (~406 kJ mol^{-1}) is significantly higher than the energy of this bond in H_2O_2 (~369 kJ mol^{-1} [10]). At the same time the reaction of $HO_2^{\cdot}$ with the molecule of compound **I** is sterically more favorable. This kinetic factor may lead to equalization of activity of the radicals compared.

Hence, the comparison of the specific features of oxidation of compound **I** in the absence and in the presence of the acid **III**, i.e., the composition of products, kinetic rules, and the effect of different factors on the reaction rate, it may be concluded on certain closeness of mechanisms of the radical chain oxidation of compound **I** in the processes (1) and (2) excluding the stage of chain generation. Just the participation of HX in this stage of the process gives rise to appearance of the dependence of its rate on the concentration of acid and minimization of the contribution of the bimolecular reaction of compound **I** with O_2 in the total process of oxidation of metal complex. At the neglect of this contribution the experimentally established rule for the rate of oxidation of compound **I** may be regarded analogously to the process (1) as the sum of rates of oxidation of complex according to the molecular (v'_0) and the radical chain (v'_p) mechanisms.

$$v' = k_{eff}[\mathbf{I}][O_2][HX], \tag{34}$$

$$v' = v'_0 + v'_p \tag{35}$$

Considering the assumptions similar to those accepted in the kinetic analysis of the process (1) and using the same numbering of the reactions as in the Scheme 3 we obtain:

$$v'_0 = k'_1K'_1K'_2[\mathbf{I}][O_2][HX] = k'_0[\mathbf{I}][O_2][HX]. \tag{36}$$

Here $k'_0 = k'_1K'_1K'_2$.

$$v'_p = 2\,(k_{3.2} + k_{3.3})[\overline{R}O_2^{\cdot}][\mathbf{I}], \tag{37}$$

$$v'_0 = 2\,k_{3.7}[\overline{R}O_2^{\cdot}][\mathbf{I}]. \tag{38}$$

Expressing the radical concentration $[RO_2^{\cdot}]$ from the relationships (36) and (38) we obtain the equation for the rate of oxidation of compound **I** according to the chain-radical mechanism and in the summary process.

$$v'_p = [(k_{3.2} + k_{3.3})k'_0/k_{3.7}][\mathbf{I}][O_2][HX], \tag{39}$$

$$v' = [1 + (k_{3.2} + k_{3.3})/k_{3.7}]k'_0\,[\mathbf{I}][O_2][HX]. \tag{40}$$

Equation (40) completely corresponds to the Eq. (34). From that it follows:

$$k_{eff} = k'_1K'_1K'_2[1 + (k_{3.2} + k_{3.3})/k_{3.7}]. \tag{41}$$

EXPERIMENTAL

Oxidation of compound **I** was carried out in a vacuum static installation with the intense stirring of reaction mixture. Reaction progress was monitored by the absorption of oxygen which was controlled manometrically. Synthesis of compound **I** was carried out according to the procedure [3]. The samples were two times crystallized from diethyl ether.[4]

Solvents of the "pure for analysis" grade were additionally purified according to the routine procedures [29]. Analysis of compound **I** and the products of its oxidation was carried out on a SKB "Khromatek" Kristall 5000.1 chromatograph coupled with the Termo Finnigan TRACE DSQ mass spectrometer, RTX-5MS column, T_i 110°C, 1 minute keeping, heating rate 15°C/min up to 250°C. Total analysis time 30 min, vaporizer temperature 250°C, reset 1:30, sample volume 1 μl, scanning time 30 min, scanning rate 50–500 atomic units, amplification factor 3, scanning rate 5 scans per second, ionizing electrons energy 70 eV.

Electron absorption spectra of solutions were measured on a Shimadzu UV-1700 spectrophotometer in the range 250–750 nm using the 1 cm quartz cells. The cells with the corresponding pure solvents were used for comparison.

Analysis of water was carried out by means of GLC on a Separone CHN chromatograph equipped with katharometer, 2000×4 mm column, oven temperature 120°C, vaporizer temperature 150°C.

Analysis of CO and CO_2 was carried out by GLC on a Tsvet-100 chromatograph equipped with a flame ionization detector and a plunger dosing valve, 500×4 mm column filled with the SKT activated carbon, carrier gas argon, column temperature 90°C, reactor temperature $T_{cat.}$ 450°C.

---

[4] Authors express their gratitude to Candidate of Chemical Sciences A.S. Smirnov for supplying samples of compound **I**.

The work was carried out on an equipment provided within the framework of the Federal Innovational Educating Program "Innovational-telecommunicational Systems: Physical Basis and Mathematical Software. "

REFERENCES

1. Berezin, I.V. and Martinek, K., *Osnovy fizicheskoi khimii fermentativnogo kataliza* (Essential Physical Chemistry of Fermentative Catalysis), Moscow: Vysshaya Shkola, 1977.
2. Duga, G. and Penny, K., *Bioorganicheskaya khimiya* (Bioorganic Chemistry), Moscow: Mir, 1983, p. 512.
3. Perevalova, E.G., Ustynyuk, Yu.A., and Nesmeyanov, A.N., *Izv. Akad. Nauk SSSR, Ser. Khim*., 1963, no. 11, p. 1967.
4. Fomin, V.M., Pukhova, I.V., and Smirnov, A.S., *Zh. Obshch. Khim*., 2003, vol. 73, no. 10, p. 1756.
5. Fomin, V.M., Klimova, M.N., and Smirnov, A.S., *Koord. Khim*., 2004, vol. 30, no. 5, p. 355.
6. *Comprehensive Organic Chemistry*, Barton D. and Ollis W.D., Eds., Moscow: Khimiya, 1983, vol. 4.
7. Emmanuel, N.M., Zaikov, G.E., and Maizus, Z.K., *Rol' sredy v radikal'no-tsepnykh reaktsiyakh okisleniya organicheskikh soedinenii* (Role of the Medium in the Radical chain Reactions of Oxidation of Organic Compounds), Moscow: Nauka, 1973.
8. Perevalova, E.G., Grandberg, K.I., Zharikova, N.A., Gubin, S.P., and Nesmeyanov, A.N., *Izv. Akad. Nauk SSSR, Ser. Khim*., 1966, no. 5, p. 832.
9. Pokidova, T.S., Denisov, E.T., and Shestakov, A.F., *Neftekhimiya*, 2008, vol. 48, no. 3, p. 174.
10. Denisov, E.T. and Denisova, T.G., *Kinetika i Kataliz*, 1993, vol. 34, no. 2, p. 199.
11. Ervin, K.M., Anusiewicz, W., Skurski, P., Simons, J., and Lineberger, W.C., *J. Phys. Chem., A,* 2003, vol. 107, no. 41, p. 8521.
12. Ramond, T.H., Blanksby,S.J., Kato, S., Bierbaum, V.M., Davico, G.E., Schwartz, R.L., and Lineberger, W.C., *J. Phys. Chem., A,* vol. 106, no. 42, p. 9641.
13. Chase, M.W., Jr., *NIST-JANAF Thermodynamical Tables*, 4th edition, J. Phys. Chem. Ref. Data, Monograph 9, 1998, 1-1951.
14. *Energii razryva khimicheskikh svyazei. Potentsialy ionizatsii i srodstvo k elektronu* (Energies of Cleavage of Chemical Bonds. Ionization Potentials and Electron Affinities), Kondrat'ev, V.N., Ed., Moscow: Nauka, 1974, p. 325.
15. Benson, S.W. and Nangia, P.S., *J. Am. Chem. Soc*., 1980, vol. 102, no. 8, p. 2843.
16. Caldwell, G., Renneboog, R., and Kebarle, P., *Can. J. Chem*., 1989, vol. 67, no. 4, p. 661.
17. Egorochkin, A.N., Kuznetsova, O.V., and Novikova, O.V., *Zh. Obshch. Khim*., 2007, vol. 77, no. 1, p. 68.
18. Fomin, V.M., Shirokov, A.E., and Polyakova, N.G., *Zh. Obshch. Khim*., 2008, vol. 78, no. 7, p. 1125.
19. Denisov, E.T. and Azatyan, V.V., *Ingibirovanie tsephykhreaktsii* (Inhibiting of Chain Reactions), Chernogolovka, 1997.
20. Kotton, F. and Wilkinson, J., *Sovremennaya neorganicheskaya khimiya* (Modern Inorganic Chemistry), Moscow: Mir, 1969, vol. 1, p. 121.
21. Rudler, H. and Denise, B., *J. Mol. Catal., A: Chem*., 2000, vol. 54, p. 277.
22. Fomin, V.M., *Koord. Khim*., 1996, vol. 22, no. 2, p. 125.
23. Chichibabin, A.E., *Osnovnye nachala organicheskoi khimii* (Essential Organic Chemistry), Moscow: GNTI Khimicheskoi Literatury, 1963, vol. 1, p. 605.
24. *Metody elementoorganicheskoi khimii. Zhelezoorganicheskie soedineniya* (Methods of Organoelement Chemistry. Organoiron Compounds), Nesmeyanov, A.N. and Kochetkov, K.A., Eds., Moscow: Nauka, 1983, p. 135.
25. Nesmeyanov, A.N., Reshetova, M.D., and Perevalova, E.G., *Izv. Akad. Nauk SSSR, Ser. Khim*., 1967, no. 23, p. 2746.
26. Betel, D. and Gold, V., *Carbonievye iony Carbonium Ions*, Moscow: Mir, 1970, p. 334.
27. Guthrie, J.P., *Can. J. Chem*., 1976, vol. 54, no. 2, p. 202.
28. Hehre, J. and Pople, J.A., *J. Am. Chem. Soc*., 1970, vol. 92, no. 8, p. 2191.
29. Weisberger, A., Proskauer, E., Riddik, J., and Tups, E., *Organicheskie rastvoriteli. Fisicheskie svoistva i metody ochistki* (Organic Solvents. Physical Properties and Methods of Purification), Moscow: Inostrannaya Literatura, 1958.