

Photochemistry of the iron(III) complex with pyruvic acid in aqueous solutions

X. Zhang,^a Y. Gong,^a F. Wu,^a N. Deng,^a I. P. Pozdnyakov,^{b,c} E. M. Glebov,^{b,c*} V. P. Grivin,^{b,c}
V. F. Plyusnin,^{b,c} and N. M. Bazhin^{b,c}

^aDepartment of Environmental Science, Wuhan University,
430072 Wuhan, Hubei, P. R. China.

Fax: +86 (27) 687 78893. E-mail: fengwu@whu.edu.cn

^bInstitute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences,
3 ul. Institutskaya, 630090 Novosibirsk, Russian Federation.

Fax: +7 (383) 330 7350. E-mail: glebov@kinetics.nsc.ru

^cNovosibirsk State University,

2 ul. Pirogova, 630090 Novosibirsk, Russian Federation

Photochemistry of the 1 : 1 Fe^{III} complex with pyruvic acid (PyrH) in aqueous solutions was studied by stationary photolysis and nanosecond laser flash photolysis with the excitation by the 3rd harmonics of an Nd:YAG laser. The quantum yield of [Fe^{III}Pyr]²⁺ under the excitation at 355 nm is 1.0±0.1 and 0.46±0.05 in the absence and in the presence of dissolved oxygen, respectively. In experiments on laser flash photolysis, a weak intermediate absorption in the region 580–720 nm was found. The absorption was ascribed to the [Fe^{II}...MeC(O)COO[•]]²⁺ radical complex. Laser flash photolysis of [FePyr]²⁺ in the presence of methyl viologen dications (MV²⁺) resulted in the formation of the MV^{•+} radical cations. The proposed reaction mechanism includes the inner-sphere electron transfer in the light-excited complex accompanied by the formation of the [Fe^{II}...MeC(O)COO[•]]²⁺ radical complex followed by its transformation into the reaction products.

Key words: photochemistry, Fe^{III} complexes, carboxylic acids, methyl viologen, aqueous solutions, UV spectra, laser flash photolysis, radical complexes.

Photochemistry of the iron(III) complexes with organic acids is one of important factors determining the balance of organic compounds in natural aqueous systems.^{1–7} Photolysis of the Fe^{III} complexes with carboxylic acids is an object of intensive studies.^{1–4,8–16} The photolysis mechanisms proposed in literature are based, as a rule, on an analysis of the final reaction products.^{1–4,9–14} Data on direct experiments on observation of intermediate photolysis products are rather scarce.

It is assumed that the primary photochemical process of the iron(III) complexes with carboxylic acids is the inner-sphere electron transfer accompanied by the reduction of Fe^{III} to Fe^{II} and the escape of the free radical to the solvent bulk¹² followed by the fast decarboxylation of the latter. The secondary radical formed due to the decarboxylation reacts with various species in solution, for instance, with the Fe^{III} complexes and dissolved oxygen.^{12,17}

Mechanisms of photochemical reactions based on the analysis of the final products require experimental confirmation by direct methods of detection of assumed intermediates, ions, or radicals. However, in the case of

transition metal complexes with carboxylic acids, certain difficulties appear when direct methods, for example, laser flash photolysis, are used. This is due to the fact that intermediates, as a rule, have no noticeable absorption in the accessible (visible and near-UV) spectral region. Possibly, the only exception is Fe^{III} trioxalate. The laser flash photolysis of this complex produces intermediate products absorbing at 400 nm, being presumably Fe^{II} complexes with organic radicals.^{14–16}

Radical acceptors are needed to detect weakly absorbing radical photolysis products. Such an acceptor should react with the detected radical to form another intermediate with an intense characteristic absorption. The direct proof^{18–23} for the formation of the hydroxyl radical upon the photolysis of the Fe(OH)_{aq}²⁺ complex can be presented as an example of using acceptors in photochemical experiments.

A promising acceptor for the detection of weakly absorbing reducing radicals is the methyl viologen dication (MV²⁺). The standard reduction potential of the redox pair MV²⁺/MV^{•+} relative to the hydrogen electrode is –0.45 V.²⁴ The absorption spectrum of the MV^{•+} radical

cation contains very intense bands in the visible and near-UV regions.²⁵ The MV²⁺ cation was used^{16,17} in experiments on laser flash photolysis of the Fe^{III} complex with tartaric and oxalic acids.

In the present work, the primary intermediates in the Fe^{III} complex—pyruvic acid system were studied by laser flash photolysis. This system has earlier been studied by stationary photolysis.²⁶

Experimental

Reagents. Sodium pyruvate (purity 99% and higher, Sigma—Aldrich) and Fe^{III} perchlorate hydrate (Aldrich) were used for the preparation of solutions of the iron(III) complexes. Methyl viologen hydrochloride (purity 98%, Aldrich) served as a source of MV²⁺ dications. Recrystallized K₃Fe(C₂O₄)₃ (reagent grade) was used for the preparation of the ferrioxalate actinometer. Necessary pH values were established by the addition of perchloric acid or sodium hydroxide. Deionized water was used to prepare the samples. All samples were prepared prior to experiment.

Stationary photolysis. Experiments on stationary photolysis were carried out in standard quartz cells (optical path length 1 cm). Aqueous solutions of Fe^{III} pyruvate and oxalate were irradiated with the light with $\lambda = 355$ nm (Nd:YAG laser). If necessary, the solutions were purged with argon or oxygen (high-purity) during experiments. UV spectra were recorded at 298 K on an Agilent 8453 spectrophotometer. A standard ferrioxalate actinometer was used when measuring quantum yield for the determination of the light intensity.²⁷ The quantum yields were obtained by averaging of the results of three independent experiments.

Laser flash photolysis. A setup with the excitation of an Nd:YAG laser ($\lambda = 355$ nm, pulse duration 5 ns, average energy in a pulse 1–2 mJ) analogous to the installation described previously²⁸ was used in experiments on laser flash photolysis. All experiments were carried out in standard quartz cells (optical path length 1 cm) at 298 K in deoxygenated solutions. Samples for laser flash photolysis were used to the 10% decrease in the absorption at the excitation wavelength.

Results and Discussion

UV spectrum and composition of the Fe^{III} complex with pyruvic acid. The UV spectrum of the Fe^{III} complex with pyruvic acid is shown in Fig. 1 (curve 1). The spectrum coincides with the known²⁶ one and is characterized by the charge-transfer band with a maximum at $\lambda = 327$ nm and a more intense band in a short-wave region.

The composition of the complex has been studied earlier²⁹ using the polarographic method. The interpretation of the data of the present work depends on the properties of the Fe^{II} complex with pyruvic acid. According to the literature data,²⁹ if the [Fe^{II}Pyr] complex exists, the [Fe^{III}Pyr] complex should be of 1 : 1 composition, in the opposite case it should be 1 : 2. No information on Fe^{II} complexes with pyruvic acid is known.

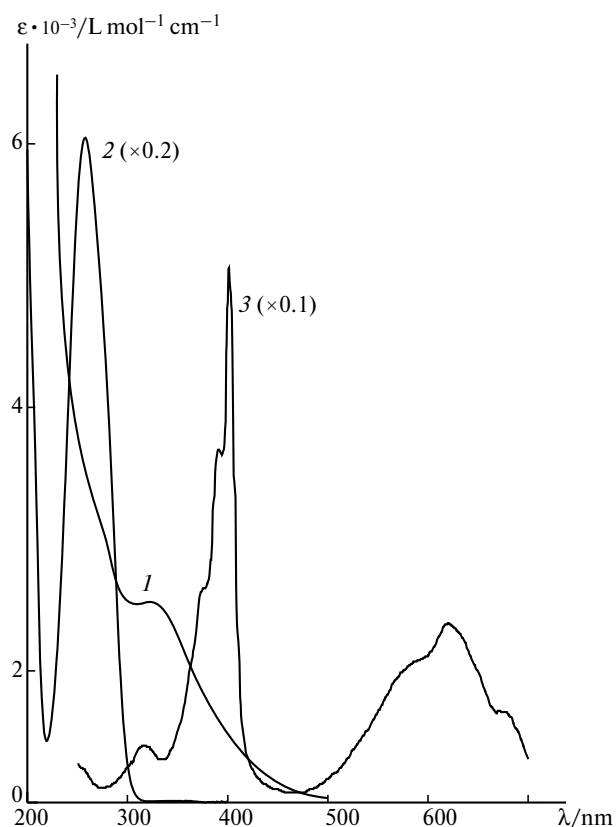
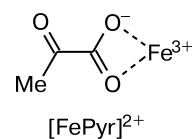


Fig. 1. UV spectra of the Fe^{III} complex with pyruvic acid (1) ($[\text{Fe}(\text{ClO}_4)_3] = 5 \cdot 10^{-4}$ mol L⁻¹, $[\text{NaPyr}] = 1.5 \cdot 10^{-3}$ mol L⁻¹, pH 3.0), MV²⁺ dication (2), and MV^{•+} radical cation (3, lit. data⁴⁸).

Since published data are contradictory, we studied the composition of the [Fe^{III}Pyr] complex by spectroscopy. Figure 2 presents Job's plot³⁰ for the Fe^{III}—pyruvic acid system. The wavelength 400 nm was chosen for the construction of this curve in order to exclude a possible influence of the absorption band of the Fe(OH)_{aq}²⁺ complex with a maximum at $\lambda = 300$ nm.³¹ As can be seen from Fig. 2, Job's plot unambiguously indicates that the Fe^{III} complex with pyruvic acid has the composition 1 : 1. An increase in the acid concentration (up to large excess) at a constant concentration of Fe^{III} produces no new absorption bands. Thus, Fe^{III} with pyruvic acid gives the [FePyr]²⁺ complex. No spectral manifestations of the 1 : 2 complexes or other were revealed.



Assuming that the Fe^{III} complex with the pyruvate anion has the composition [Fe^{III}Pyr]²⁺, one can use the earlier²⁹ obtained equilibrium constants for the formation

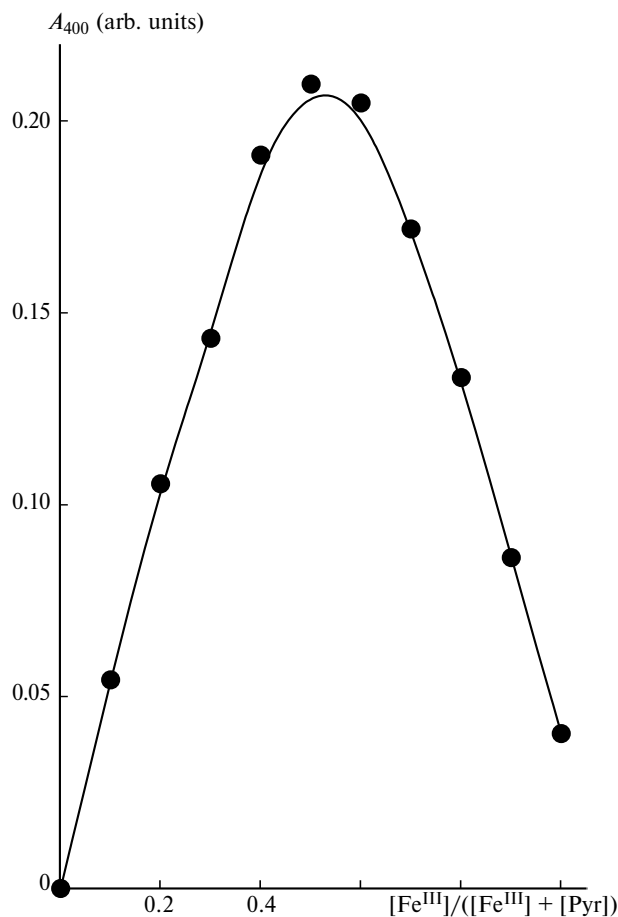


Fig. 2. Determination of the composition of the $\text{Fe}^{\text{III}}\text{Pyr}$ complex obtained by mixing of $\text{Fe}(\text{ClO}_4)_3$ and NaPyr in a 1-cm cell by Job's plot at $\lambda = 400$ nm ($[\text{Fe}(\text{ClO}_4)_3] + [\text{NaPyr}] = 1 \cdot 10^{-3}$ mol L^{-1} , pH 3.0).

of the 1 : 1 complex ($\text{p}K = 4.83$). Taking into account the dissociation constants of pyruvic acid ($\text{p}K_{\text{a}} = 2.5$)³² and the stability constants of the Fe^{III} hydroxo complexes ($\text{p}K_1 = 11.87$; $\text{p}K_2 = 9.3$; $\text{p}K_3 = 9.5$),³³ one can calculate the content of various complexes for the Fe^{III} –pyruvate ion system at different pH values. The results for concentrations of iron(III) ions and pyruvate ions of $5 \cdot 10^{-4}$ and $1.5 \cdot 10^{-3}$ mol L^{-1} , respectively, are shown in Fig. 3 (at pH > 4 the precipitation of hydroxide $\text{Fe}(\text{OH})_3$ becomes the determining factor). Thus, under the typical conditions of our experiments (pH 3), the content of the $[\text{Fe}^{\text{III}}\text{Pyr}]^{2+}$ complex was about 86%.

Stationary photolysis of $[\text{Fe}^{\text{III}}\text{Pyr}]^{2+}$. The changes in the absorption spectrum of the $[\text{Fe}^{\text{III}}\text{Pyr}]^{2+}$ irradiated with the light at $\lambda = 355$ nm are shown in Fig. 4. No absorption bands appear upon the photolysis of both deoxygenated (see Fig. 4, *a*) and oxygen-saturated solutions (see Fig. 4, *b*). The photolysis of deoxygenated solutions of $[\text{Fe}^{\text{III}}\text{Pyr}]^{2+}$ occurs with a higher rate.

The quantum yield of photolysis of $[\text{Fe}^{\text{III}}\text{Pyr}]^{2+}$ in deoxygenated and oxygen-saturated solutions measured

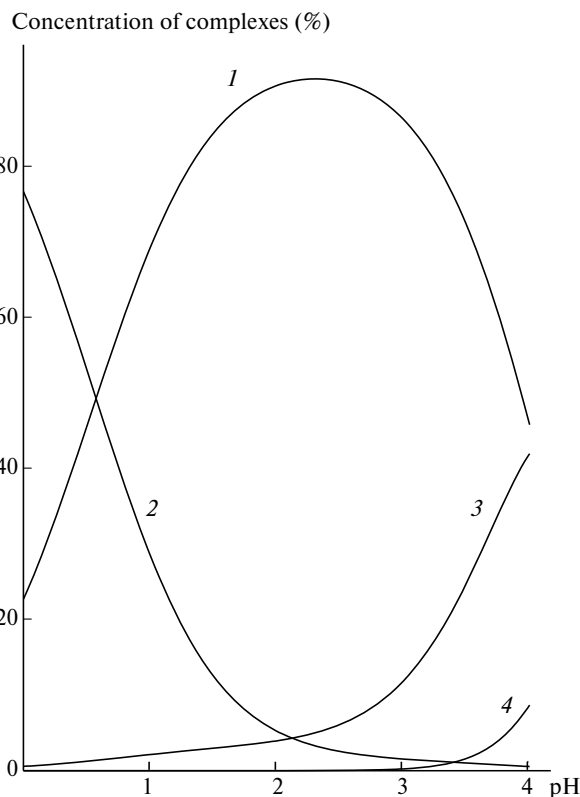


Fig. 3. Dependences of the composition of an Fe^{III} –pyruvate aqueous system on the pH of the medium: 1, $[\text{Fe}^{\text{III}}\text{Pyr}]^{2+}$; 2, $\text{Fe}^{3+}_{\text{aq}}$; 3, $[\text{Fe}(\text{OH})_2]^{2+}$; 4, $[\text{Fe}(\text{OH})_2]^{+}$ ($[\text{Fe}^{\text{III}}]_0 = 5 \cdot 10^{-4}$ mol L^{-1} , $[\text{Pyr}^-]_0 = 1.5 \cdot 10^{-3}$ mol L^{-1}).

with a ferrioxalate actinometer is 1.0 ± 0.1 and 0.46 ± 0.05 , respectively. It should be mentioned that high quantum yields of photolysis are characteristic of many Fe^{III} carboxylate complexes.^{1,3,34} The mechanism of the effect of oxygen on the photolysis of the $[\text{Fe}^{\text{III}}\text{Pyr}]^{2+}$ complex will be discussed below.

Laser flash photolysis of deoxygenated solutions of $[\text{Fe}^{\text{III}}\text{Pyr}]^{2+}$. In the absence of methyl viologen, the pulse irradiation of the $[\text{Fe}^{\text{III}}\text{Pyr}]^{2+}$ complex with the light at $\lambda = 355$ nm results in the immediate change in the character of its absorption. The corresponding kinetic curves and the transient absorption spectrum are shown in Fig. 5. Points in Fig. 5 correspond to the change in the absorption of the sample immediately after the laser pulse. Solid line represents the inverted absorption spectrum of the $[\text{Fe}^{\text{III}}\text{Pyr}]^{2+}$ complex. The absorption of the sample remains unchanged within the time interval 0.1–50 μs after the laser pulse (see inset in Fig. 5). The unchanged absorption in the band of $[\text{Fe}^{\text{III}}\text{Pyr}]^{2+}$ after the laser pulse indicates that active intermediate species that formed, for example, free radicals, do not react rapidly with the Fe^{III} or Fe^{II} complexes. The transient absorption spectra in the time interval from 0.1 to 1000 μs are independent of the dissolved oxygen concentration.

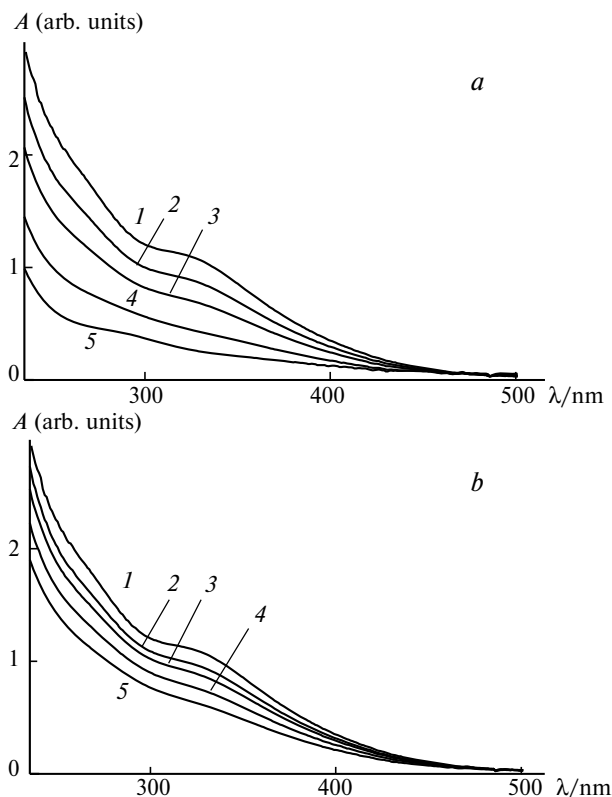


Fig. 4. Changes in the absorbance in the UV spectrum of an aqueous solution of the $[\text{FePyr}]^{2+}$ complex under the radiation with $\lambda = 355 \text{ nm}$ (3rd harmonics of an Nd:YAG laser) ($[\text{Fe}(\text{ClO}_4)_3]_0 = 7.4 \cdot 10^{-4} \text{ mol L}^{-1}$, $[\text{NaPyr}]_0 = 1.5 \cdot 10^{-3} \text{ mol L}^{-1}$, pH 3.0, 1-cm cell). Curves for deoxygenated solutions (a) and oxygen-saturated solutions (b) obtained at 0 (1), 100 (2), 200 (3), 400 (4), and 700 (5) laser pulses.

The change in the absorption of the initial complex during photolysis (see Fig. 5) makes it possible to estimate the amount of the $[\text{Fe}^{\text{III}}\text{Pyr}]^{2+}$ complex disappeared within one laser pulse. The molar absorption coefficient of the complex at $\lambda = 400 \text{ nm}$ is $540 \text{ L mol}^{-1} \text{ cm}^{-1}$ (see Fig. 1). Correspondingly, for the case shown in Fig. 5 (inset), $5.6 \cdot 10^{-5} \text{ mol L}^{-1}$ of the $[\text{Fe}^{\text{III}}\text{Pyr}]^{2+}$ complex is photolyzed within one laser pulse.

It is seen from the data in Fig. 5 that a small absorption appears at 580–720 nm upon photolysis. The process of disappearance of this intermediate absorption is illustrated in Fig. 6 (to increase the initial amplitude of the signal, the experiment presented in Fig. 6 was carried out at a laser pulse with an energy higher than that shown in Fig. 5). The kinetic curve is well approximated by the monoexponential function with the characteristic decay time 0.8 ms (see Fig. 6). The band in the visible region can belong to the radical complex $[\text{Fe}^{\text{II}}\cdots\text{MeC}(\text{O})\text{COO}^\cdot]^{2+}$, which is one of probable primary photolysis product $[\text{Fe}^{\text{III}}\text{Pyr}]^{2+}$.

It is commonly accepted^{12,14,17} that the inner-sphere electron transfer is the primary photochemical process for

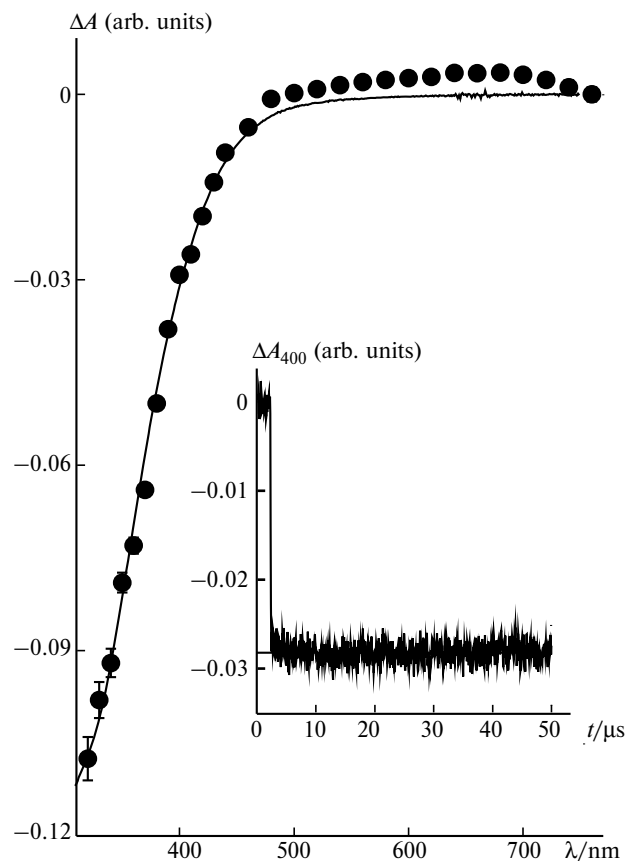
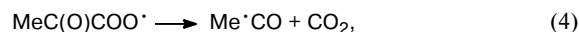
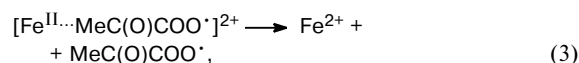
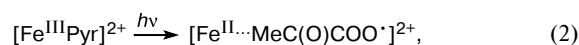
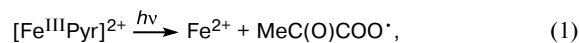


Fig. 5. Intermediate absorption spectrum upon laser flash photolysis ($\lambda = 355 \text{ nm}$) of the $[\text{Fe}^{\text{III}}\text{Pyr}]^{2+}$ complex ($[\text{Fe}(\text{ClO}_4)_3] = 5 \cdot 10^{-4} \text{ mol L}^{-1}$, $[\text{NaPyr}] = 1.5 \cdot 10^{-3} \text{ mol L}^{-1}$, deoxygenated solutions, pH 3.0, 1-cm cell): points are experiment, and solid line is the inverted absorption spectrum of $[\text{Fe}^{\text{III}}\text{Pyr}]^{2+}$. Inset: an example of the kinetic curve.

the Fe^{III} complexes with carboxylic acids. After the Fe^{II} complex was formed due to this electron transfer, various processes presented by Eqs (1)–(9) can occur. First, the free radical can escape into the solvent bulk (Eq. (1)). Second, the radical complex can be stabilized (Eq. (2)) as in the case of iron(III) oxalate.^{14,16} To distinguish these two processes, we carried out experiments on the laser flash photolysis of $[\text{Fe}^{\text{III}}\text{Pyr}]^{2+}$ in the presence of methyl viologen.



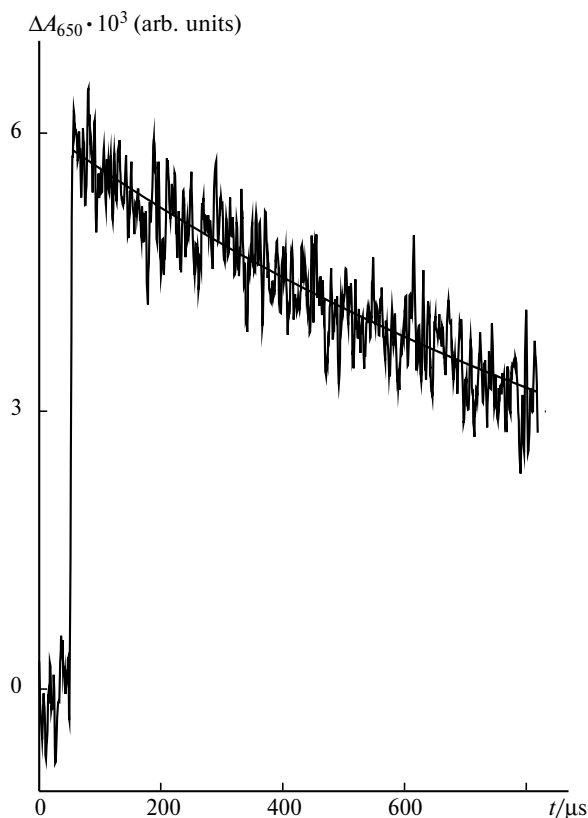
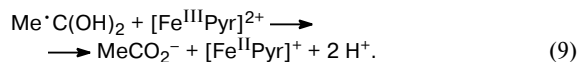
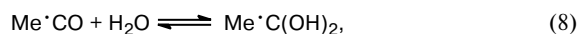
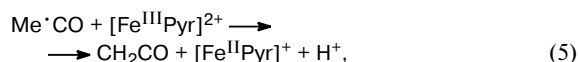


Fig. 6. Kinetic curve upon laser flash photolysis ($\lambda = 355$ nm) of the $[\text{Fe}^{\text{III}}\text{Pyr}]^{2+}$ complex obtained at $\lambda = 650$ nm (for concentrations of the reactants and photolysis conditions, see Fig. 5).



The acyloxy radical $\text{MeC}(\text{O})\text{COO}^{\cdot}$ formed in the primary process (1) should rapidly be decarboxylated (reaction (4)). The characteristic times of decarboxylation of the acyloxy radicals are 10–1000 ps. These times were measured in direct experiments for the aryl acyloxy radicals^{35,36} and estimated by indirect methods for the alkyl acyloxy radicals.^{35,37} The assumption about the fast decarboxylation of the $\text{MeC}(\text{O})\text{COO}^{\cdot}$ radicals was used to explain the results of photochemical studies of pyruvic acid in solutions³⁸ and aqueous-acidic glasses.³⁹ Based on the results of these works,^{35–39} we assumed that the characteristic time of reaction (4) is definitely shorter than the time resolution of a laser flash photolysis technique (50 ns).

The UV spectrum of the acetyl radical $\text{Me}^{\cdot}\text{CO}$ formed due to the decarboxylation of the primary free radical in an aqueous solution contains the band with a maximum at $\lambda = 260$ nm and the molar absorption coefficient $\epsilon = 940 \text{ L mol}^{-1} \text{ cm}^{-1}$ (see Refs 40 and 41). In our experiments, no absorption bands were observed in the visible spectral range, which could be ascribed to the acyl radical. The presence of such bands could be predicted from the fact that in the gas phase the broad band with a maximum at 530 nm corresponds to the $\text{Me}^{\cdot}\text{CO}$ radical.⁴² The absorption of the $\text{Me}^{\cdot}\text{CO}$ radical in organic glasses at 550 nm was reported.⁴³ However, the authors of this work carried out no quantitative measurements. It seems probable that the molar absorption coefficients of the bands of the $\text{Me}^{\cdot}\text{CO}$ radical in aqueous solutions in the visible region are too low to be detected in laser flash photolysis experiments.

The $\text{Me}^{\cdot}\text{CO}$ radical can decay in decarbonylation, recombination, and hydration reactions (Eqs (6)–(8)). The reaction of radical recombination (Eq. (7)) is usually diffusion controlled with the random spin factor 1/4. The recombination rate constants for a large amount of radicals under normal conditions are close to the value $2k_7 = 2 \cdot 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ (see Ref. 44). Assuming that all $[\text{Fe}^{\text{III}}\text{Pyr}]^{2+}$ complexes, which disappeared during photolysis, yielded the $\text{Me}^{\cdot}\text{CO}$ radicals, one can estimate the initial concentration of the radicals under typical experimental conditions: $5 \cdot 10^{-5} \text{ mol L}^{-1}$. In this case, the characteristic time of the diffusionally controlled radical recombination (reaction (7)) is approximately 10 μs .

Acetyl radicals are stable toward decarbonylation (reaction (6)). The rate constants for reaction (6) measured in the gas phase range from 0.01 to 1.00 s^{-1} (see Ref. 44 and references cited therein). A possibility of the hydration of the acetyl radical and the backward dehydration reaction of the hydrated acetyl radical (Eq. (8)) should also be taken into account. The rate constants for these reactions measured previously⁴⁵ are as follows: $k_8 = 2 \cdot 10^4 \text{ s}^{-1}$, $k_{-8} = 3 \cdot 10^4 \text{ s}^{-1}$. Thus, under our experimental conditions, the decay of acetyl radicals in reactions (6) and (8) is insignificant compared to the recombination (Eq. (7)).

The reaction of the $\text{Me}^{\cdot}\text{CO}$ radical with the initial complex (Eq. (5)) was not experimentally observed. This makes it possible to estimate the upper limit of its rate constant from the inequality $k_5 \cdot [\text{Fe}^{\text{III}}\text{Pyr}]^{2+} \ll 2k_7 \cdot [\text{Me}^{\cdot}\text{CO}]_0$. Assuming that $2k_7 = 2 \cdot 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$, $[\text{Fe}^{\text{III}}\text{Pyr}]^{2+} = 5 \cdot 10^{-4} \text{ mol L}^{-1}$, and $[\text{Me}^{\cdot}\text{CO}]_0 \approx 5 \cdot 10^{-5} \text{ mol L}^{-1}$, we obtain $k_5 \ll 2 \cdot 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$.

Laser flash photolysis of the $[\text{FePyr}]^{2+}$ complex in the presence of methyl viologen. Experiments on laser flash photolysis of the $[\text{Fe}^{\text{III}}\text{Pyr}]^{2+}$ complex in the presence of methyl viologen demonstrate the change in the kinetic curves of intermediate absorption. The typical kinetic curves are shown in Fig. 7: the appearance and disappearance of new absorption bands at 400 and 600 nm are

observed. The transient absorption spectrum is shown in Fig. 8. New narrow bands in a region of 370–400 nm and a less intense band at 600 nm appear along with instant change in the absorbance of a solution due to the disappearance of the [Fe^{III}Pyr]²⁺ complex (see Fig. 8). These bands belong to the radical cation MV^{•+} (see Ref. 25). In the absence of dissolved oxygen and other potential oxidants, the concentration [MV^{•+}] remains almost unchanged within several minutes.²⁵ In our case, the disappearance of the MV^{•+} radical cation (see Fig. 7) is determined, most probably, by its reaction with the Fe^{III} ([Fe^{III}Pyr]²⁺ and Fe(OH)²⁺_{aq}) complexes.

For the MV^{•+} radical cation, the molar absorption coefficient is 41 500 L mol⁻¹ cm⁻¹ at λ = 396 nm.⁴⁶ Taking into account the decrease in the absorption due to the disappearance of the [Fe^{III}Pyr]²⁺ cations, one can calculate the maximum concentration of the MV^{•+} radical cations from the data in Fig. 8. The latter turned out to be 1.2 · 10⁻⁶ mol L⁻¹, *i.e.*, being only about 2% of the total amount of the [Fe^{III}Pyr]²⁺ complex disappeared under the action of a laser pulse.

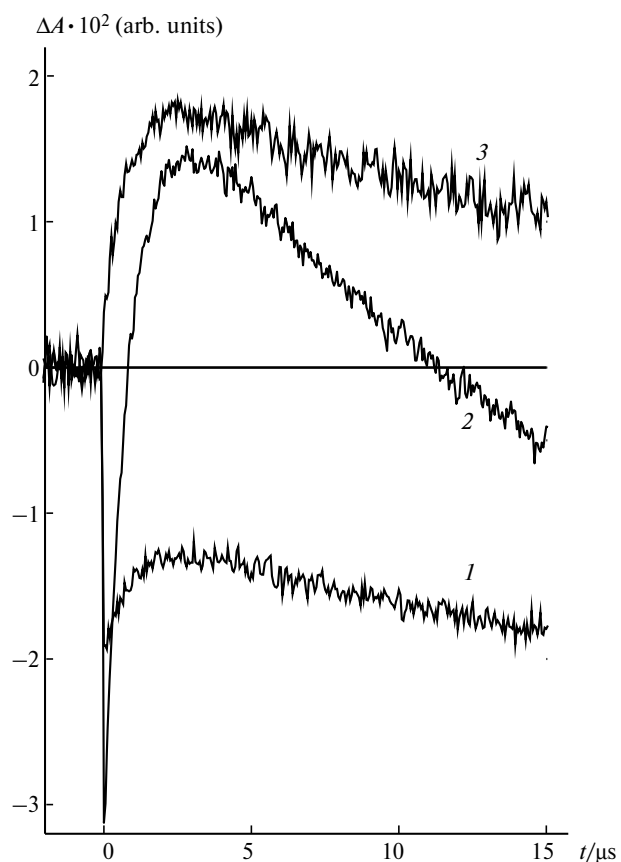
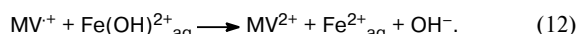
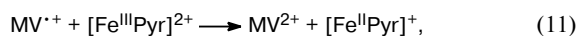
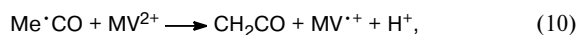


Fig. 7. Kinetic curves upon laser flash photolysis (λ = 355 nm) of the [Fe^{III}Pyr]²⁺ complex in the presence of MV²⁺ (for concentrations of the reactants and photolysis conditions, see Fig. 5, [MV²⁺] = 1 · 10⁻⁴ mol L⁻¹) obtained at λ = 405 (1), 395 (2) and 600 nm (3).

In the presence of methyl viologen, at least three reactions should be added to Eqs (1)–(9). They describe the formation of the MV^{•+} radical cation and its disappearance due to the interaction with the initial Fe^{III} complexes (Eqs (10)–(12)). In spite of the small amount of the MV^{•+} radical cations, the kinetic curves of their formation and decay are experimentally observed due to high molar absorption coefficient.



The full kinetic scheme of photolysis can include the reactions of the radical complex with the MV²⁺ radical and (or) MV^{•+} radical cation in addition to reactions (1)–(12).

The kinetic curves of formation and decay of the MV^{•+} radical cations at λ = 620 nm were detected in order to

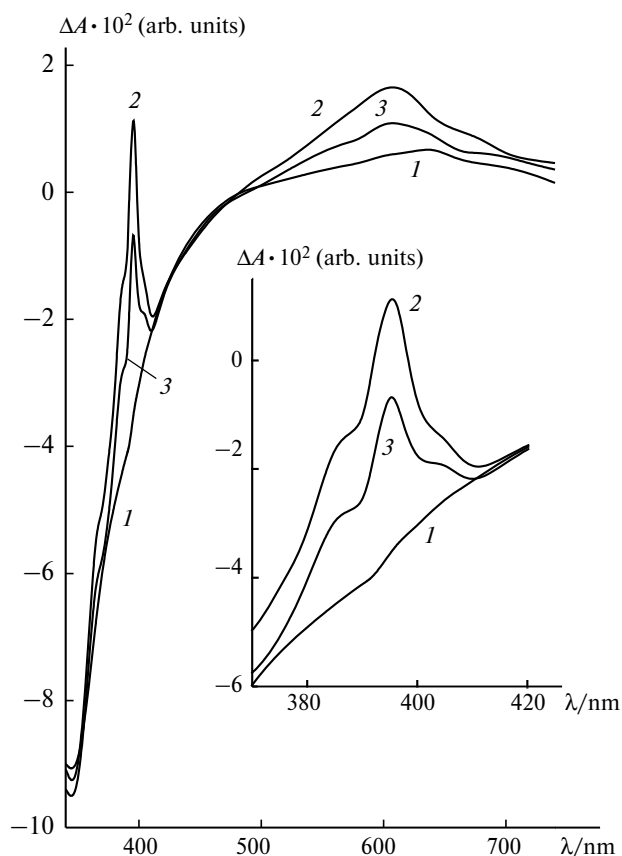


Fig. 8. Transient absorption spectra upon laser flash photolysis (λ = 355 nm) of the [Fe^{III}Pyr]²⁺ complex in the presence of MV²⁺ (for concentrations of the reactants and MV²⁺ and photolysis conditions, see Fig. 7) 0.05 (1), 3.2 (2), and 14 μs (3) after the laser pulse. Inset: initial regions of curves 1–3.

estimate the rate constants for reactions (10)–(12). The methyl viologen concentration was varied in the interval 10^{-5} – 10^{-3} mol L⁻¹. These curves are satisfactorily described by the simple biexponential model (Eq. (13)) with close values of coefficients A_1 and A_2 . This model corresponds to the consecutive reactions of formation and decay of MV^{•+} radical cations.

$$D(t) = D_0 + A_1 e^{-k_f t} + A_2 e^{-k_d t} \quad (13)$$

An example of the kinetic curve with extrapolation by Eq. (13) is shown in Fig. 9, *a*. The rate constant for the formation of radical cations (k_f) depends linearly on the methyl viologen concentration (see Fig. 9, *b*). Assuming that the k_f value in Eq. (13) is equal to the rate constant k_{10} from Fig. 9, *b*, we have $k_{10} = (3.0 \pm 0.3) \cdot 10^9$ L mol⁻¹ s⁻¹. Obviously, reaction (7) for the recombination of the acetyl radicals in the range of high ($>10^{-4}$ mol L⁻¹) concentrations of the MV²⁺ cations makes a negligible contribution to the decay rate of the Me[•]CO radicals compared to reaction (10).

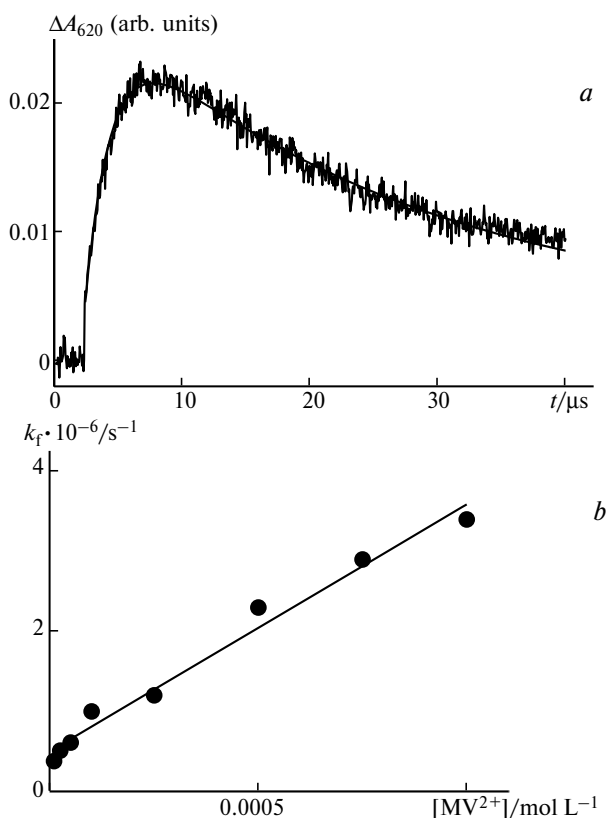


Fig. 9. Example of the kinetic curve (*a*) upon laser flash photolysis ($\lambda = 355$ nm) of the $[\text{Fe}^{\text{III}}\text{Pyr}]^{2+}$ complex in the presence of MV^{2+} (for concentrations of the reactants and photolysis conditions, see Fig. 5, $[\text{MV}^{2+}] = 2.5 \cdot 10^{-4}$ mol L⁻¹) obtained at $\lambda = 620$ nm (solid line is the approximation of the curve by Eq. (13)) and the dependence of the best k_f values (points) on the MV^{2+} concentration (*b*) (straight line is the result of linear regression).

The rate constant for MV^{•+} radical cation decay (k_d) in Eq. (13) is $(5 \pm 1) \cdot 10^4$ s⁻¹ regardless of the concentration $[\text{MV}^{2+}]$. The decay of the MV^{•+} radical cations is determined by reactions (11) and (12). Assuming that the rate constants for these reactions (k_{11} and k_{12}) are close and taking into account the value of the total concentration of Fe^{III} ions in solution ($5 \cdot 10^{-4}$ mol L⁻¹), we can estimate k_{11} and k_{12} : $1 \cdot 10^8$ L mol⁻¹ s⁻¹. However, we were not aimed at detailed studying the decay of the MV^{•+} radical cations.

Experiments with the MV²⁺ cations show that the formation of free radicals Me[•]CO is a secondary channel of photolysis of the $[\text{Fe}^{\text{III}}\text{Pyr}]^{2+}$ complex. The most probable channel of the process is the formation of a long-lived complex *via* reaction (2) followed by the slow decomposition to the Fe^{II} complex and free radical (reaction (3)). The absorption in the region 580–720 nm (see Figs 5, *b* and 6) belongs, most likely, to the radical complex $[\text{Fe}^{\text{II}}\text{---MeC(O)COO}^{\bullet}]^{2+}$. The estimation of the molar absorption coefficient of the band give a very low value (~ 70 L mol⁻¹ cm⁻¹ at $\lambda = 650$ nm).

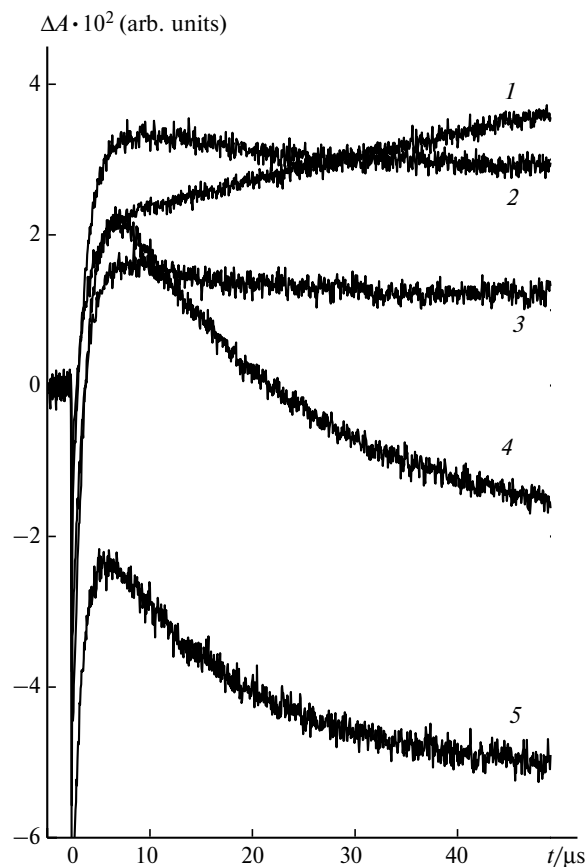


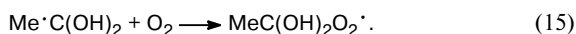
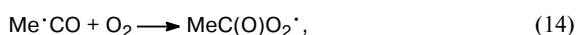
Fig. 10. Kinetic curves obtained at $\lambda = 396$ nm and initial concentrations $[\text{Fe}^{\text{III}}\text{Pyr}]^{2+} = 8.0 \cdot 10^{-5}$ (1), $1.6 \cdot 10^{-4}$ (2), $2.7 \cdot 10^{-4}$ (3), $4.8 \cdot 10^{-4}$ (4), and $7.5 \cdot 10^{-4}$ mol L⁻¹ (5) ($[\text{NaPyr}] = 1.5 \cdot 10^{-3}$ mol L⁻¹, $[\text{MV}^{2+}] = 4.7 \cdot 10^{-5}$ mol L⁻¹, deoxygenated solutions, pH 3.0).

An indirect argument in favor of the formation of the radical complex is the dependence of the time of achievement of the maximum concentration of the MV^{•+} radical cations on the concentration of the initial complex (Fig. 10). The experiment was carried out at the low ($4.7 \cdot 10^{-5}$ mol L⁻¹) initial concentration of methyl viologen. Since the MV^{•+} radical cation is oxidized by the initial complex (reaction (11)), the time of achievement of the maximum concentration of the radical cations depends on the initial concentration [Fe^{III}Pyr]²⁺. The time-delayed increase in the MV^{•+} radical cations concentration is observed at the low concentration [Fe^{III}Pyr]²⁺ (see Fig. 10, curve 1). The time of achievement of the maximum MV^{•+} concentration decreases with an increase in the [Fe^{III}Pyr]²⁺ concentration (see Fig. 10, curves 2–5).

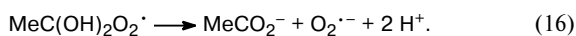
The observed effect is explained by the fact that the MV^{•+} radical cations are formed during two processes: the fast process, whose rate depends on the initial concentration of the MV²⁺ cations, and the slow process, whose rate is independent of the acceptor concentration. Reaction (10) of the Me[•]CO radical, formed in the primary process (1) and subsequent decarboxylation (Eq. (4)), with methyl viologen is responsible for the fast process. The additional formation of the MV^{•+} radical cations at times longer than 10 μs is due to the interaction of the MV²⁺ cations with the Me[•]CO radical appeared due to the monomolecular decomposition of the radical complex (reaction (3)).

Photolysis of [FePyr]²⁺ in the presence of oxygen. As indicated above, if the system contains dissolved oxygen, the quantum yield of photolysis of the [FePyr]²⁺ complex decreases twofold (see Fig. 4). The qualitative explanation of this fact is based on the formation of peroxy radicals and their subsequent reactions.

Peroxy radicals can be formed from both acetyl radicals Me[•]CO and products of their hydration (Eq. (8)), viz., radicals Me[•]C(OH)₂ (see Refs 45, 47)

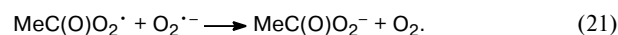
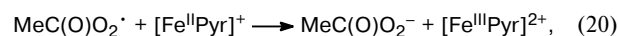
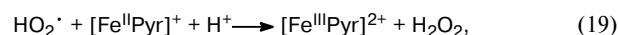


The hydrated acetylperoxy radical rapidly decomposes to give two anions and two protons⁴⁵



The superoxide radical anion, being equilibrated with the HO₂[•] radical (Eq. (17)), can react with iron complexes of any oxidation state (Eqs (18), (19)). In addition, Fe^{II} in complexes can be oxidized to Fe^{III} with the acetylperoxy radical (Eq. (20)). Probably, reactions (19) and (20) result in the twofold decrease in the quantum yield of photolysis of [FePyr]²⁺ in oxygen-containing solutions. In the quantitative study of the photolysis mechanism one should take into account the reaction

between the acetylperoxy radical and superoxide radical anion (Eq. (21)), whose rate constant is estimated as 10⁹ L mol⁻¹ s⁻¹ (see Ref. 45).



In our opinion, the competition of reactions (18)–(21) is a reason for the decrease in the quantum yield of the [Fe^{III}Pyr]²⁺ photolysis in the presence of dissolved oxygen. The characteristic time of re-oxidation of Fe^{II} substantially exceeds 1 ms, due to which no changes in the concentration of the Fe^{III} complexes are observed in laser flash photolysis experiments.

Thus, it was shown that the primary process in photolysis of the [Fe^{III}Pyr]²⁺ complex is the inner-sphere electron transfer. This result corresponds to the known concepts on the photochemistry of the Fe^{III} complexes with carboxylic acids. However, the detailed study of the process by the laser flash photolysis technique showed that the escape of the free radicals MeC(O)COO[•] into the solvent bulk is a secondary (not more than 2%) photolysis channel. It is most likely that the main channel is the formation of the radical complex [Fe^{III}...MeC(O)COO[•]]²⁺, whose decomposition results in the final photolysis products. The formation of the radical complex is indicated by the experimentally detected weak absorption band at 650 nm.

The formation of the Fe^{II} complexes with free radicals has earlier been found during the photolysis of iron(III) oxalate.^{14–16} In the case of photolysis of the Fe^{III} complex with tartaric acid [Fe^{III}Tart]⁺, the escape of the free radical into the solvent bulk is also a secondary reaction channel.¹⁷ It is quite probable that the photoexcitation of the [Fe^{III}Tart]⁺ complex similarly results in the formation of a radical complex, although its spectral manifestations were not observed.¹⁷ Based on all data listed above, we may conclude that the formation of radical complexes is a characteristic feature of photochemistry of the Fe^{III} complexes with carboxylic acids.

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