

# Intermediates in photochemistry of Fe(III) complexes with carboxylic acids in aqueous solutions†

Evgeni M. Glebov,<sup>\*a,b</sup> Ivan P. Pozdnyakov,<sup>a,b</sup> Vjacheslav P. Grivin,<sup>a,b</sup> Victor F. Plyusnin,<sup>a,b</sup> Xu Zhang,<sup>c</sup> Feng Wu<sup>c</sup> and Nansheng Deng<sup>c</sup>

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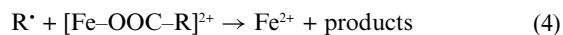
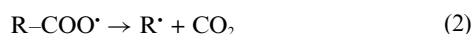
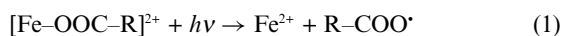
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The primary processes in the photochemistry of Fe(III) complexes with carboxylic acids (glyoxalic, tartaric, pyruvic and lactic) were studied by means of laser flash photolysis. The inner-sphere electron transfer with the formation of Fe(II) complex and an escape of an organic radical to the solution bulk was shown to be a minor channel of the photolysis. The main channel was proposed to be the formation of a long-lived radical complex  $[\text{Fe}^{\text{II}} \cdots \cdot\text{OOC-R}]^{2+}$ . Spectral and kinetic parameters of the radical complexes are determined.

## 1. Introduction

Photochemistry of Fe(III) complexes with organic ligands has been the subject of extensive studies for the past two decades<sup>1–15</sup> because it is an important factor determining the balance of organic compounds in natural aqueous systems. In particular, the photochemistry of Fe(III) complexes with carboxylic acids was studied.<sup>1–7,11–15</sup> To construct reasonable models of the photochemical processes in natural waters, one needs information on the primary photochemical processes. For Fe(III) carboxylates, the mechanisms of photolysis put forward in the literature are usually based on the results of the analysis of final reaction products.<sup>1–10</sup> Direct observations of the intermediates are scarce<sup>11–15</sup> in spite of great possibilities given by modern experimental techniques.

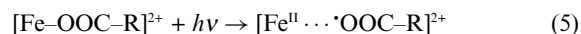
It is typically believed that the primary process in the photochemistry of Fe(III) carboxylate complexes is an inner-sphere electron transfer with the formation of Fe(II) and an escape of an organic radical to the solution bulk<sup>16</sup> followed by its fast decarboxylation:<sup>17,18</sup>



The secondary aliphatic radicals formed in the reaction (2), in addition to their recombination (3), can interact with the different substances in the solution (e.g., with initial Fe(III) complexes, which increases the quantum yield of photolysis (reaction (4))

and dissolved oxygen. As a result, active oxygen species (AOS), namely  $\cdot\text{OH}$ ,  $\text{HO}_2^{\cdot}$  and  $\text{H}_2\text{O}_2$ , are formed, which are reported to provide the mineralization of organic compounds in natural water systems.<sup>1–5</sup>

It should be noted that the reaction mechanism ((1)–(3)) was put forward based on the results of the stationary experiments. Direct experimental support for reaction (1) is lacking. On the other hand, in works on the photochemistry of Fe(III) complexes with oxalic<sup>11</sup> and ethylenediaminetetraacetic<sup>19,20</sup> acids, an alternative photolysis mechanism was proposed. This mechanism is based on the formation of a long-lived complex between Fe(II) and organic radical:



The lifetime of the radical complex could reach several milliseconds.<sup>19</sup> The reactions of this intermediate determine the content of the final photolysis products.

Recently, the results on the photochemistry of ferrioxalate  $\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3^{3-}$  were re-examined by two research groups.<sup>20,13</sup> The interpretation of the results was contradictory. In both works, the successive formation of two intermediates was observed in flash photolysis experiments. In ref. 20 these intermediates were interpreted as tetrahedral-like four-coordinate  $\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_2^-$  complex and  $\text{Fe}^{\text{II}}(\text{C}_2\text{O}_4)_3^{4-}$  complex. In ref. 13 the intermediates were interpreted as a primary radical complex  $[(\text{C}_2\text{O}_4)_2\text{Fe}^{\text{II}}(\text{C}_2\text{O}_4^{\cdot})]^{3-}$  and a secondary radical complex  $[(\text{C}_2\text{O}_4)\text{Fe}^{\text{II}}(\text{C}_2\text{O}_4^{\cdot})]^-$ . Therefore, the mechanism of  $\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3^{3-}$  photolysis (especially primary stage of this mechanism) is still open for discussion.

Recently we have applied laser flash photolysis to study the photochemistry of Fe(III) complexes with glyoxalic<sup>14</sup> and tartaric<sup>15</sup> acids. As distinct from the case of ferrioxalate, only one intermediate was observed. The results were explained based on reaction (5), but not on reactions (1) and (2). It seems that the formation of a radical complex is a characteristic feature of the photolysis of Fe(III) complexes with carboxylic acids.

In this work, we summarize the results on the photochemistry of Fe(III) complexes with glyoxalic, tartaric, pyruvic and lactic acids. In all the cases, the experimental results are well described using the hypothesis of the radical complex.

<sup>a</sup>Institute of Chemical Kinetics and Combustion, 3 Institut'skaya St., 630090, Novosibirsk, Russian Federation. E-mail: glebov@kinetics.nsc.ru; Fax: +7 383 3307350; Tel: +7 383 3332385

<sup>b</sup>Novosibirsk State University, 2 Pirogova St., 630090, Novosibirsk, Russian Federation

<sup>c</sup>Department of Environmental Science, Wuhan University, 430072, Wuhan, Hubei, P. R. China. E-mail: fengwu@whu.edu.cn

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## 2. Materials and methods

Iron(III) perchlorate (Aldrich) was used as a source of Fe(III) cations. Analytical grade glyoxalic acid, sodium pyruvate (Sigma–Aldrich, 99+%), tartaric acid (Aldrich, 98%), and lactic acid (Aldrich, 98%) were used for preparation of Fe(III) glyoxalate, pyruvate, tartrate and lactate. Methyl viologen dichloride hydrate (Aldrich, 98%) was used as a source of MV<sup>2+</sup> cations. The samples were prepared with deionized water. If necessary, the samples were deaerated by bubbling with argon.

Fe(III) glyoxalate, tartrate and lactate were prepared by mixing the solutions of Fe(III) perchlorate with the solutions of the corresponding organic acids. [Fe<sup>III</sup>Pyr]<sup>2+</sup> complex was prepared by mixing Fe(III) perchlorate with sodium pyruvate. Final pH value for all solutions was about 3.

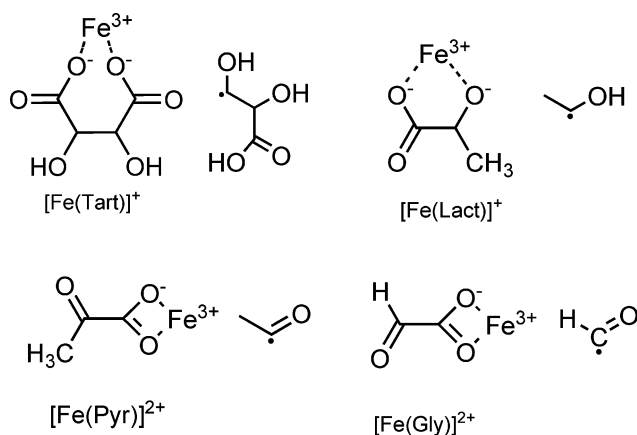
Laser flash photolysis experiments were performed using a setup with a YAG laser (355 nm, pulse duration 5 ns, mean energy 5 mJ per pulse) similar to that described elsewhere.<sup>21</sup> For calculation of quantum yields in both laser flash photolysis experiments and photolysis by a set of laser pulses, laser intensity was measured by means of SOLO 2 laser power and energy meter (Gentec EO).

UV absorption spectra were recorded on an Agilent 8453 spectrophotometer (Agilent Technologies). Quantum yields of Fe(II) formation were determined in experiments with excitation of solutions by pulses of a YAG laser (355 nm). Fe(II) quantum yields were calculated by approach similar to described in ref. 22 using 1,10-phenanthroline as complexant. Stationary photolysis was performed by irradiation of a high-pressure mercury lamp with a set of glass filters for selecting necessary wavelengths.

## 3. Results and discussion

### 3.1. Composition and UV spectra of the complexes

The complexes studied in this work are shown in Fig. 1. All the experiments were performed under conditions which provided the existence of 1 : 1 complexes.



**Fig. 1** Fe(III) complexes with carboxylic acids and corresponding free radicals.

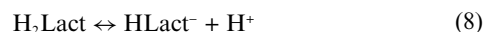
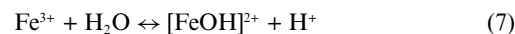
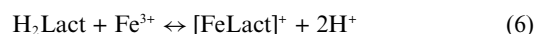
For the complexes between Fe(III) and tartaric acid the equilibrium constants are known from literature ( $\log K_1 = 7.49$  and  $\log K_2 = 11.86$ <sup>23</sup>). The typical concentrations of the both reagents

were  $5 \times 10^{-4}$  M at pH 3.0. In these conditions, *ca.* 76% of Fe(III) formed the [Fe<sup>III</sup>Tart]<sup>+</sup> complex.

For [Fe<sup>III</sup>Pyr]<sup>2+</sup> complex the 1 : 1 composition was proved in ref. 15 using Job's plot method,<sup>24</sup> which is in agreement with the results of Ghandour *et al.*<sup>25</sup> The value of equilibrium constant for 1 : 1 complex is  $\log K_1 = 4.83$ .<sup>25</sup> At typical experimental conditions (Fe(ClO<sub>4</sub>)<sub>3</sub>:  $5 \times 10^{-4}$  M, NaPyr:  $1.5 \times 10^{-3}$  M, pH 3.0), *ca.* 86% of Fe(III) formed [Fe<sup>III</sup>Pyr]<sup>2+</sup> complex.

For the complexes between Fe(III) and glyoxalic acid the equilibrium constants were taken from literature ( $\log K_1 = 13.9$  and  $\log K_2 = 12.2$ ).<sup>26</sup> At typical experimental conditions (Fe(ClO<sub>4</sub>)<sub>3</sub>:  $5 \times 10^{-4}$  M, glyoxalic acid:  $1.5 \times 10^{-3}$  M, pH 3.0) iron(III) almost completely forms [Fe<sup>III</sup>Gly]<sup>2+</sup> complex. The existence of only 1 : 1 complex is supported by the fact that the characteristic absorption of the complex was linear with Fe(III) concentration.

The complexes between Fe(III) and lactic acid (H<sub>2</sub>Lact) were studied in ref. 27. The formation of an only 1 : 1 [Fe<sup>III</sup>Lact]<sup>+</sup> complex with the structure shown in Fig. 1 was proved. The concentration of [Fe<sup>III</sup>Lact]<sup>+</sup> was calculated using the values of equilibrium constants for reactions (6) and (8) determined in ref. 27 and for reaction (7) determined in ref. 28 ( $K_6 = 0.026$ ;  $K_7 = 1.66 \times 10^{-3}$ ;  $K_8 = 1.38 \times 10^{-4}$ ).



According to the calculations, at the typical experimental conditions (Fe(ClO<sub>4</sub>)<sub>3</sub>:  $5 \times 10^{-4}$  M, lactic acid:  $1 \times 10^{-3}$  M, pH 3.0) *ca.* 90% of Fe(III) forms the [Fe<sup>III</sup>Lact]<sup>+</sup> complex. Again, the existence of only 1 : 1 complex was supported by the fact that the characteristic absorption of the complex was linear with Fe(III) concentration.

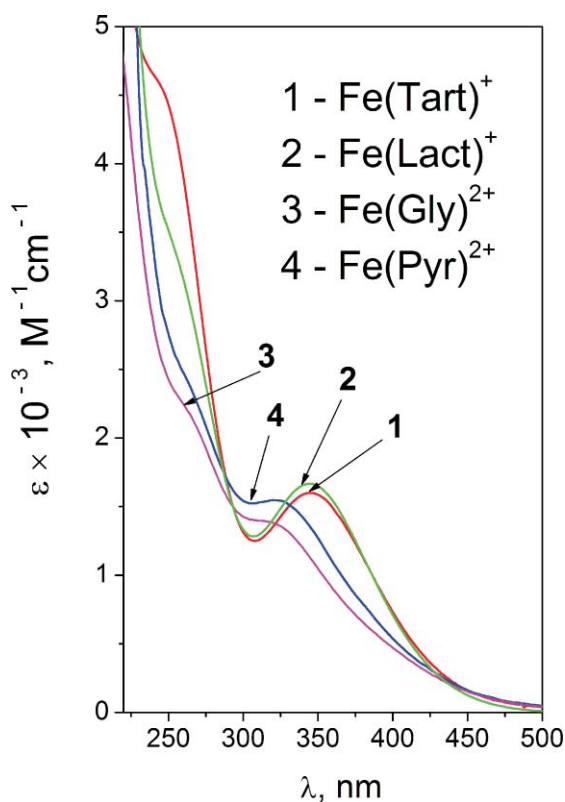
Fig. 1 presents the structures of free radicals resulted by decarboxylation of the primary R-COO<sup>•</sup> radicals in the case if reaction mechanism (1)–(2) is realized.

UV spectra of the studied complexes are shown in Fig. 2. All the spectra demonstrate the LMCT absorption bands in the near UV spectral region with the maximal extinction coefficients *ca.* 1500 M<sup>-1</sup> cm<sup>-1</sup>.

### 3.2. Quantum yields

The photolysis of all the complexes results in the formation of Fe(II). The experiments were performed at pH *ca.* 3.0. The quantum yields were measured both in oxygen-free and in aerated solutions. Primary quantum yields of Fe(III) disappearance were measured in laser flash photolysis experiments (355 nm) by an instant decrease in the absorbance of the initial complexes immediately after the laser pulse. Quantum yields of Fe(II) formation were measured in experiments with excitation of a set of laser pulses (355 nm). The changes in the UV spectra in a course of laser photolysis were the same as in the stationary photolysis by the irradiation of a high-pressure mercury lamp. Fe(II) was quantified by addition of 1,10-phenanthroline and measuring the absorption of Fe(II)-phenanthroline complex at 510 nm.<sup>22</sup>

The results are listed in Table 1. The obtained values of quantum yields agreed satisfactorily with those measured previously



**Fig. 2** UV spectra of Fe<sup>III</sup> complexes with carboxylic acids in aqueous solutions (pH 3.0).

**Table 1** Quantum yields<sup>a</sup> of photolysis (355 nm) of [Fe–OOC–R]<sup>2+</sup> complexes in aqueous solutions (pH 3.0) and spectral parameters of [Fe<sup>II</sup>...·OOC–R]<sup>2+</sup> radical complexes (quantum yields of Fe(III) disappearance  $\phi(\text{Fe}^{\text{III}})$ , Fe(II) formation in deaerated  $\phi(\text{Fe}^{\text{II}})_{\text{Ar}}$  and aerated  $\phi(\text{Fe}^{\text{II}})_{\text{Air}}$  solutions, and free radical formation  $\phi_{\text{R}}$ ) and spectral parameters of [Fe<sup>II</sup>...·OOC–R]<sup>2+</sup> radical complexes (position of maxima in the UV spectra  $\lambda_{\text{max}}$  and absorption coefficient  $\epsilon_{\text{max}}$ )

Complex	$\phi(\text{Fe}^{\text{III}})$	$\phi(\text{Fe}^{\text{II}})_{\text{Ar}}$	$\phi(\text{Fe}^{\text{II}})_{\text{Air}}$	$\phi_{\text{R}}$	$\lambda_{\text{max}}/\text{nm}$	$\epsilon_{\text{max}}/\text{M}^{-1}\text{cm}^{-1}$
[Fe <sup>III</sup> Gly] <sup>2+</sup>	0.70	1.05	0.80	$\leq 0.01$	650	80
<sup>a</sup> [Fe <sup>III</sup> Pyr] <sup>2+</sup>	0.53	1.0 <sup>b</sup>	0.46 <sup>b</sup>	$\leq 0.01$	650	70
[Fe <sup>III</sup> Tart] <sup>+</sup>	0.47	0.44	0.40	0.07	620	18
[Fe <sup>III</sup> Lact] <sup>+</sup>	0.22	0.40	0.22	$< 0.002$	670	60

<sup>a</sup> Experimental error does not exceed 20%. <sup>b</sup> Measured in ref. 15.

for [Fe<sup>III</sup>Gly]<sup>2+</sup> <sup>29</sup> and [Fe<sup>III</sup>Tart]<sup>+</sup> <sup>5,29</sup> complexes in the stationary photolysis experiments. Typically, the quantum yield of Fe(II) formation is larger than the primary quantum yield of Fe(III) photolysis due to the secondary reactions (e.g., reaction (4)). The increase could be in a factor of two or less, except for the case of [Fe<sup>III</sup>Tart]<sup>+</sup> complex. In the last case the quantum yields of Fe(III) and Fe(II) coincide within the limits of experimental error. It could be explained by the low value of the rate constant of reaction (4), which could not effectively compete with the recombination of radicals (reaction (3)).

If the photolysis is performed in the presence of oxygen, the quantum yield of Fe(II) formation drops (Table 1) due to the formation of peroxy radicals and their reactions with Fe(II) complexes (for example, see ref. 15). In the case of the complex

with tartaric acid the effect of oxygen is not pronounced because of low impact of reaction (4) on the quantum yield of Fe(II).

### 3.3. Methods of detecting organic radicals

Direct observation of simple organic radicals (like those shown in Fig. 1) in pulsed experiments presents a real challenge because the radicals have no intensive absorption bands in the near UV and visible spectral regions. In this case, scavengers of the radicals are used. The scavenger should (i) not obey its own photochemical activity and (ii) react with the radicals of interest resulting in the formation of other intermediates, which are easily detectable. In this work, methyl viologen dication (MV<sup>2+</sup>) was used as a scavenger. Advantages of MV<sup>2+</sup> are:<sup>30</sup> (i) negligibly small absorption at the wavelength of laser irradiation ( $\epsilon_{355} \leq 5 \text{ M}^{-1} \text{ cm}^{-1}$  <sup>30</sup>), which makes impossible the direct photolysis of dianion, (ii) high rate constants of the reactions with organic radicals,<sup>30</sup> and (iii) MV<sup>•+</sup> radical cation, which is a product of one-electron reduction of MV<sup>2+</sup>, features intensive absorption bands in the near UV and visible spectral regions ( $\epsilon_{396 \text{ nm}} = 41\,500 \text{ M}^{-1} \text{ cm}^{-1}$ ). MV<sup>2+</sup> was successfully used as a scavenger both for reducing radicals and for  $\cdot\text{OH}$  radical in pulse radiolysis and flash photolysis experiments.<sup>30</sup>

### 3.4. Laser flash photolysis in the absence of scavengers

Fig. 3a shows an intermediate absorption spectrum appeared immediately after the laser pulse excitation of [Fe<sup>III</sup>Tart]<sup>2+</sup> complex. In the UV part of the spectrum only instant bleaching is observed, and the spectrum of this bleaching coincides with the absorption spectrum of the initial complex. An intermediate is observed in the region of 550–700 nm (Fig. 3b). Its absorption is weak, it decays with a characteristic time of 1.3 ms (Fig. 3c). The features of the spectral changes are typical of all the studied complexes (Table 1).

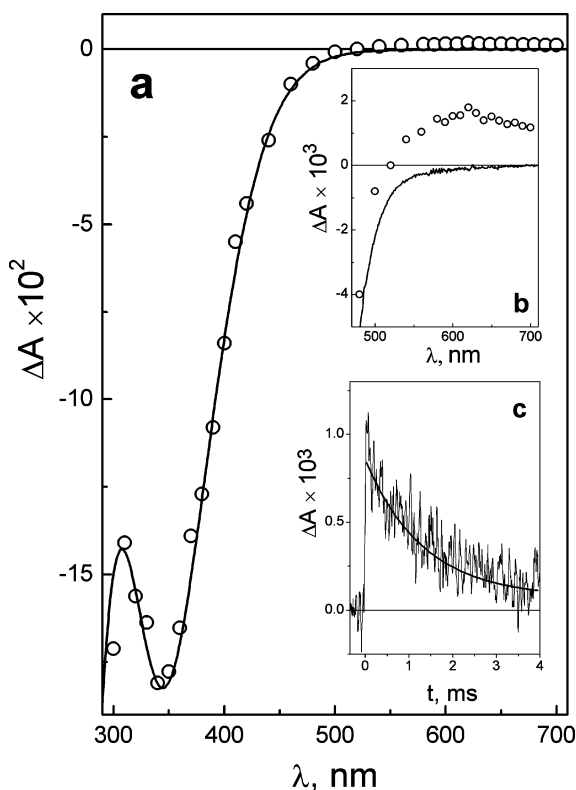
The intermediate absorption in the region of 550–700 nm was attributed to the radical complexes (RC) formed in the reaction (5). The arguments in favour of this assumption were obtained from the experiments on the laser flash photolysis in the presence of MV<sup>2+</sup>.

### 3.5. Laser flash photolysis in the presence of MV<sup>2+</sup>

Laser flash photolysis of Fe(III) complexes with carboxylic acids in the presence of MV<sup>2+</sup> gives evidence of MV<sup>•+</sup> radical cations formation. Fig. 4 shows the results of this experiment for the case of [Fe<sup>III</sup>Gly]<sup>2+</sup> complex. The intermediate absorption spectrum (Fig. 4a) contains the bands in the regions of 396 and 600 nm superimposed with the bleaching due to disappearance of the initial complex. The new bands belong to the MV<sup>•+</sup> radical cation.<sup>30</sup> Kinetic curves of its formation and decay are shown in Fig. 4b. The formation of radical cation occurs in the reaction between MV<sup>2+</sup> and the secondary organic radicals R<sup>•</sup> (its formula is shown in Fig. 1) resulted by decarboxylation of primary organic radicals (reactions (1) and (2))



The occurrence of MV<sup>•+</sup> in reaction (9) is supported by the linear dependence of the effective rate constant of its formation vs. MV<sup>2+</sup> concentration (Fig. 4c). MV<sup>•+</sup> radical cations decay in the reaction



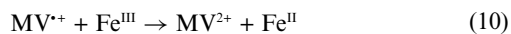
**Fig. 3** Laser flash photolysis (355 nm) of  $[\text{Fe}^{\text{III}}\text{Tart}]^{2+}$  complex ( $5 \times 10^{-4}$  M in a 1 cm cell) in deaerated aqueous solution (pH 2.8). (a) Intermediate absorption spectrum; dots – intermediate absorption immediately after the laser pulse, full line – inverted  $[\text{Fe}^{\text{III}}\text{Tart}]^{2+}$  spectrum; (b) red part of the spectrum on an increased scale; (c) kinetic curve at 620 nm (experimental curve and 1-exponential fit).

**Table 2** Rate constants of reactions (9)–(12)

Complex	$k_9/\text{M}^{-1}\text{s}^{-1}$	$k_{10}/\text{M}^{-1}\text{s}^{-1}$	$k_{11}/\text{s}^{-1}$	$k_{12}/\text{M}^{-1}\text{s}^{-1}$
$[\text{Fe}^{\text{III}}\text{Gly}]^{2+}$	$1.6 \times 10^{10}$ <sup>a</sup>	$5 \times 10^7$	$2.4 \times 10^2$	$1.0 \times 10^6$
$[\text{Fe}^{\text{III}}\text{Pyr}]^{2+}$	$3.0 \times 10^9$ <sup>b</sup>	$1.0 \times 10^8$ <sup>b</sup>	$1.3 \times 10^3$	$3.0 \times 10^6$
$[\text{Fe}^{\text{III}}\text{Tart}]^{2+}$	$8.9 \times 10^7$	$1.8 \times 10^8$ <sup>c</sup>	$7.7 \times 10^2$	
$[\text{Fe}^{\text{III}}\text{Lact}]^{2+}$	— <sup>d</sup>	$\sim 10^7$	$3.2 \times 10^2$	$1.6 \times 10^6$

<sup>a</sup> Measured in ref. 14. <sup>b</sup> Measured in ref. 15. <sup>c</sup> Measured in ref. 12. <sup>d</sup> Process is not observable.

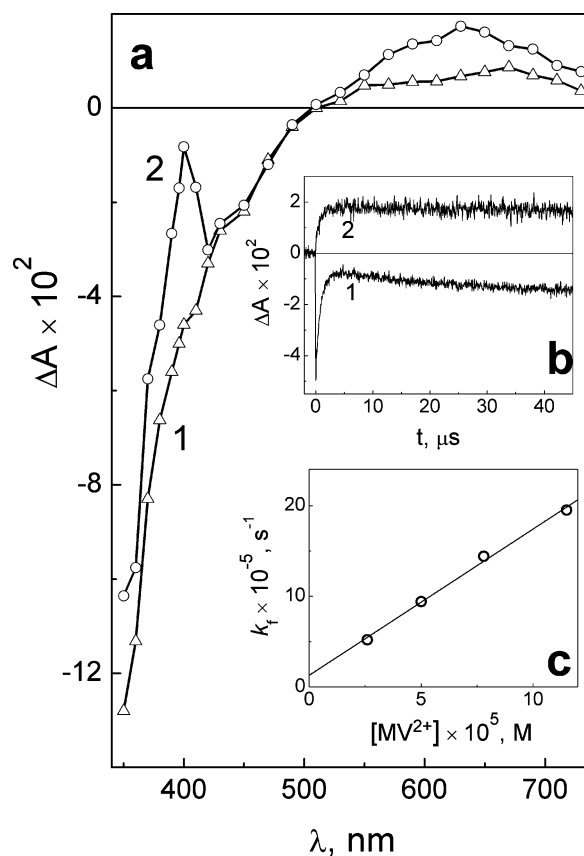
with the initial complex, because the rate of their disappearance grows up with an increase in  $\text{Fe}^{\text{III}}$  concentration.



The rate constants of reactions (9) and (10) are listed in Table 2.

The intermediate absorption spectrum in Fig. 4a allows one to rule out the formation of a hydroxyl radical in a course of photochemical reactions in studied systems. In the case of  $\cdot\text{OH}$  radical formation it should react with  $\text{MV}^{2+}$  yielding  $\text{MV}(\cdot\text{OH})^{2+}$  radical cation, which has an intense absorption band with the maximum at 470 nm (see, for example, Solar *et al.*<sup>30</sup>). Recently we used  $\text{MV}^{2+}$  as a scavenger for  $\cdot\text{OH}$  radicals formed by the photolysis of  $[\text{Fe}(\text{OH})]^{2+}$  complex.<sup>31</sup>

The estimations of the  $\text{MV}^{++}$  yield show that the amount of organic radicals formed in reactions (1) and (2) is typically about several percent of the disappeared initial complexes. For example,



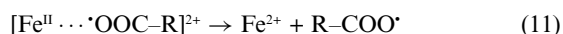
**Fig. 4** Laser flash photolysis (355 nm) of  $[\text{Fe}^{\text{III}}\text{Gly}]^{2+}$  complex ( $5 \times 10^{-4}$  M in a 1 cm cell) in deaerated aqueous solution (pH 3.0) in the presence of  $5 \times 10^{-5}$  M  $\text{MV}^{2+}$ . (a) Intermediate absorption spectra 0.05 (1) and 4  $\mu\text{s}$  (2) after the laser pulse; (b) kinetic curves of  $\text{MV}^{++}$  radical cations formation and decay at 396 (1) and 610 (2) nm; (c) dependence of the observed rate constant of  $\text{MV}^{++}$  formation ( $k_t$ ) on the initial  $\text{MV}^{2+}$  concentration.

in the case of  $[\text{Fe}^{\text{III}}\text{Gly}]^{2+}$  complex (Fig. 4a) this value is about 2%. In the case of lactic acid, the formation of  $\text{MV}^{++}$  radical cation by the  $\alpha$ -hydroxyethyl radical occurred in reactions (1) and (2) is not observable at all. The values of the quantum yields of free radicals listed in Table 1 show that the escape of  $\text{R}\text{-COO}\cdot$  radicals to the solution bulk (reaction (1)) is a minor channel of the photolysis. The main channel is proposed to be the formation of radical complex  $[\text{Fe}^{\text{II}} \cdots \text{R}\text{-COO}\cdot]^{2+}$  in the reaction (5). The absorption bands formed in the region of 550–700 nm seems to be the spectral manifestations of the radical complexes. Therefore, the photolysis pathway (reactions (1) and (2)), often considered as the general mechanism,<sup>1,2,5,8,16</sup> is in fact a minor channel.

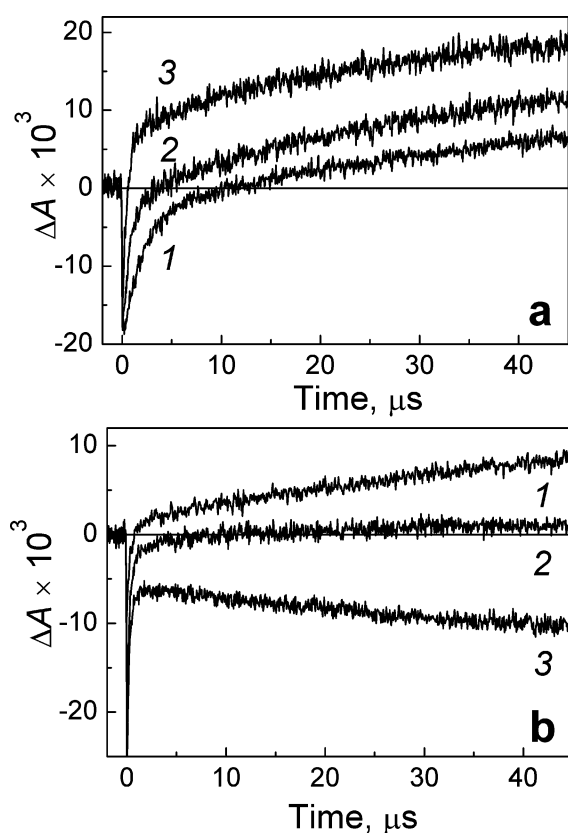
The absorption bands of the radical complexes are weak. The values of their extinction coefficients estimated from the laser flash photolysis data fall within the interval 18–80  $\text{M}^{-1}\text{cm}^{-1}$  (Table 1). The smallest value (18  $\text{M}^{-1}\text{cm}^{-1}$ ) was measured for the  $[\text{Fe}^{\text{III}}\text{Tart}]^{2+}$  complex. This is the reason why we have not found the absorption of the radical complex in the previous work on  $[\text{Fe}^{\text{III}}\text{Tart}]^{2+}$  photolysis.<sup>12</sup> As a result, the value of the rate constant  $k_6$  for the case of  $\cdot\text{C}(\text{OH})\text{C}(\text{OH})\text{COOH}$  radical reported in ref. 12 was underestimated. Now we report its corrected value ( $8.9 \times 10^7$   $\text{M}^{-1}\text{s}^{-1}$ , Table 2).



The lifetime of the radical complex is probably determined by its dissociation to the organic radical R-COO<sup>•</sup> (which is then decarboxylated) and Fe<sup>II</sup> aquacomplex.



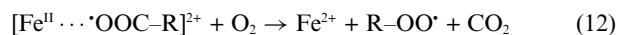
The R-COO<sup>•</sup> radical formed in reaction (11) converts *via* reaction (2) to the “secondary” R<sup>•</sup> radical, which reacts with methyl viologen *via* reaction (9) opening a “slow” channel of MV<sup>•+</sup> formation. These processes were observed for the cases of Fe(III) complexes with glyoxalic and lactic acids. Fig. 5 shows the “delayed” formation of MV<sup>•+</sup> radical cation in the sequential reactions (5, 11, 2, 10). Fig. 5a demonstrates the kinetic curves at 396 nm recorded at different concentrations of the acceptor. It is evident that the MV<sup>•+</sup> radical cation is formed in two processes. The rate of the fast process depends on the concentration of MV<sup>2+</sup> (similar to that shown in Fig. 4c), and the rate of the slow process does not depend on the concentration of methyl viologen.



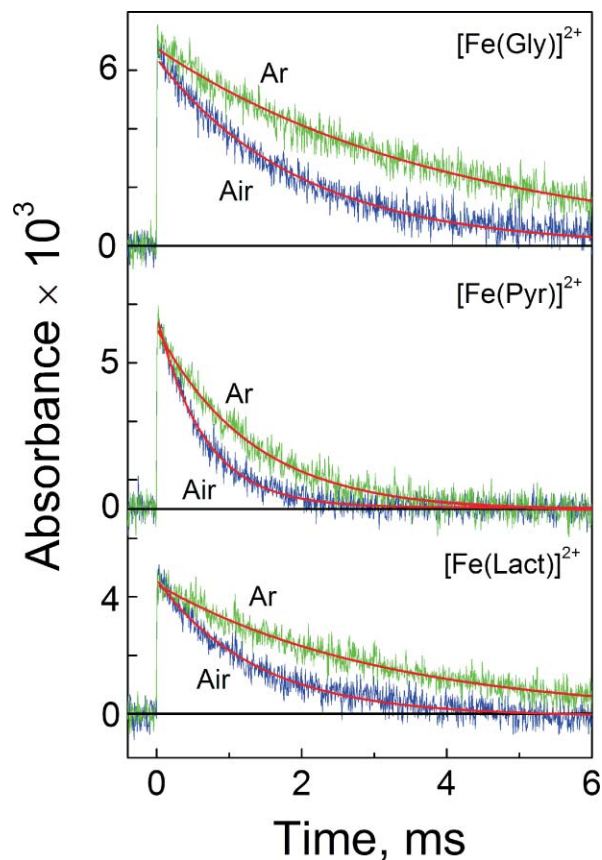
**Fig. 5** Laser flash photolysis (355 nm) of  $[\text{Fe}^{\text{III}}\text{Gly}]^{2+}$  complex in deaerated aqueous solution (pH 3.0) in the presence of MV<sup>2+</sup>. Kinetic curves at 396 nm. (a) Initial concentration of  $[\text{Fe}^{\text{III}}\text{Gly}]^{2+}$  is  $2.9 \times 10^{-4}$  M; curves 1–3 correspond to MV<sup>2+</sup> concentrations  $1.8 \times 10^{-5}$ ,  $5.5 \times 10^{-5}$  and  $1.1 \times 10^{-4}$  M. (b) Initial concentration of MV<sup>2+</sup> is  $2.0 \times 10^{-4}$  M; curves 1–3 correspond to  $[\text{Fe}^{\text{III}}\text{Gly}]^{2+}$  concentrations  $1.7 \times 10^{-4}$ ,  $3.8 \times 10^{-4}$  and  $6.4 \times 10^{-4}$  M.

Oxidation of MV<sup>•+</sup> radical cation by Fe(III) (reaction (10)) leads to the dependence of its decay rate on the concentration of the initial complex (Fig. 5b). Therefore, varying the concentrations of the initial complex and substrate one can dramatically change the lifetimes of intermediates.

In the presence of dissolved oxygen, another channel of the radical complex decay becomes possible.



The evidence of reaction (12) is demonstrated in Fig. 6. The rate of the radical complex decay in the presence of dissolved oxygen is always higher than in argon saturated solutions. Taking into account the concentration of dissolved oxygen in aerated aqueous solutions ( $2.5 \times 10^{-4}$  M<sup>32</sup>), one can calculate that the rate constants of reaction (12) fall within the interval  $(1-4) \times 10^6$  M<sup>-1</sup> s<sup>-1</sup>. The measured rate constants of reactions (11) and (12) are listed in Table 2.



**Fig. 6** Laser flash photolysis of  $[\text{Fe-OOC-R}]^{2+}$  complexes (pH 3.0). Kinetic curves of the radical complexes decay (630 nm) in deaerated and aerated solutions.

### 3.6. Radical complexes as intermediates of photochemical reactions

Weakly-bound charge transfer complexes between metal cations and free radicals could occur as intermediates in the photolysis of transition metal complexes. When experiments are performed in frozen matrices, these intermediates could be stabilized and characterized by means of UV and ESR spectroscopy. Several examples could be found in the literature. The formation of the intermediate radical complex  $[\text{Mo}(\text{v}) \cdots \text{R}^{\bullet}]$  has been recorded in the photolysis of Mo(v) oxocomplexes in alcohol matrices.<sup>33</sup> The photolysis of  $\text{CuCl}_4^{2-}$  complex in frozen organic matrices gives rise to optical absorption bands and the ESR spectrum of  $[\text{CuCl}_4^{3-} \cdots \text{R}^{\bullet}]$  radical complex.<sup>34</sup> Its structure was supported by quantum chemical calculations. Formation of  $[\text{IrCl}_6^{3-} \cdots \text{CH}_2\text{OH}]$  and  $[\text{IrCl}_6^{3-} \cdots \text{CH}_3\text{CHOH}]$  radical complexes upon the

photolysis of  $\text{IrCl}_6^{2-}$  complex in frozen alcohol matrices was proved in ref. 35.

When the experiments are performed in liquid solutions, it is usually not possible to use ESR for the direct approval of the structure of intermediates. In this case, the hypothesis of a radical complex is supported only by means of indirect kinetic data. For example,  $[\text{PtCl}_6^{3-} \cdots \text{R}]$  and  $[\text{PtCl}_6^{3-} \cdots \text{RO}_2]$  radical complexes were attributed to the intermediate absorption recorded by the laser flash photolysis of  $\text{PtCl}_6^{2-}$  alcohol solutions in the temperature range 160–220 K.<sup>36</sup> Such is the case of Fe(III) complexes with organic acids described in ref. 11, 19 and 20 and in this work.

## Conclusions

The results of this work show that the traditional mechanism of the photolysis of  $[\text{Fe}-\text{OOC}-\text{R}]^{2+}$  complexes based on reactions (1)–(4) is not completely satisfied. The number of free radicals escaped to the solution bulk is estimated by the value of several percents of the disappeared initial complexes. The kinetic data could be explained by introducing a long-lived intermediate, which was proposed<sup>13–15</sup> to be the  $[\text{Fe}^{\text{II}} \cdots \text{OOC}-\text{R}]^{2+}$  radical complex (reaction (5)). Spectral and kinetic parameters of the radical complexes for several carboxylic acids are determined. These data allow one to put forward a new insight into the primary photochemical processes for Fe(III) carboxylate complexes. When photolysis is performed in the presence of different substrates (like in natural aquatic systems), the formation of the “secondary” radicals via the decay of radical complexes (reaction (11)) and the oxidation of radical complexes by oxygen (reaction (12)) could affect the content of the final reaction products.

It should be noted that the existence of long-lived intermediates is unaltered. However, the nature of these intermediates is a question open for discussion. To examine the radical character of these intermediates, the experiments in low-temperature matrices with the ESR registration seems to be prospective. Another possible way of solving the problem is to perform the quantum chemical calculations of the radical complexes.

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