

Photochemistry of iron(III)—lactic acid complex in aqueous solutions*

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Photochemistry of a 1 : 1 Fe^{III}—lactic acid complex, [Fe(Lact)]⁺, in aqueous solutions was studied by stationary photolysis, nanosecond laser flash photolysis (355 nm, 6 ns), and femto-second pump—probe spectroscopy (400 nm, 200 fs). The quantum yield of photolysis of [Fe(Lact)]⁺ upon excitation at 355 nm is 0.4 and 0.22 in the deoxygenated and air-saturated solutions, respectively. Weak transient absorption in the range 500–750 nm was observed in the nanosecond experiments. It was assigned to a [Fe^{II}...O—CH(Me)—COO·]⁺ radical complex. The spectral properties of the ligand-to-metal charge transfer excited state and the characteristic time of formation of the radical complex (1.5 ps) were determined in the femtosecond spectroscopy experiments. A reaction mechanism was proposed, which involves inner-sphere electron transfer in the excited complex with the formation of a radical complex [Fe^{II}...O—CH(Me)—COO·]⁺ and its subsequent transformation to the end product of the photochemical reaction.

Key words: photochemistry, Fe(III) complexes, carboxylic acids, methyl viologen, laser flash photolysis, radical complexes.

Photochemistry of Fe^{III} carboxylate complexes with natural carboxylic acids (tartaric, pyruvic, lactic, succinic, as well as humic and fulvic acids) is of considerable interest from the standpoint of environmental photochemistry and photocatalysis because photolysis of these compounds is accompanied by the formation of reactive oxygen species ([•]OH, HO₂[•], and H₂O₂)^{1–5} which leads to mineralization of organic matter and to CO and CO₂ generation in natural water.^{6–8}

A traditional mechanism of photolysis of Fe^{III} carboxylate complexes implies that the primary photochemical event involves inner-sphere electron transfer accompanied by reduction of Fe^{III} to Fe^{II} and escape of a free radical into the solvent bulk^{9,10} followed by fast decarboxylation of the radical.^{11,12} A secondary radical generated as a result of decarboxylation reacts with Fe^{III} complexes and dissolved oxygen to give reactive oxygen species (Scheme 1).^{1,2,5}

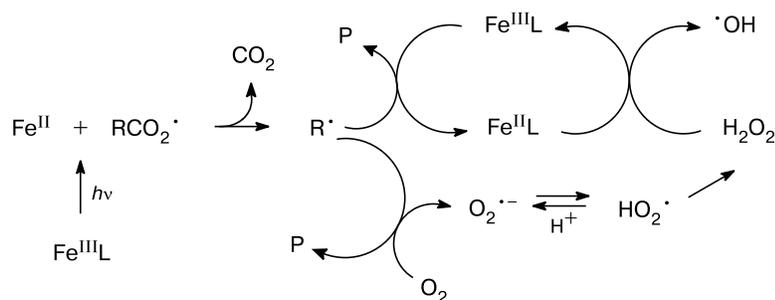
This mechanism is based on the results of analysis of the end products of photochemical reactions^{1–5} and the generation of organic radicals in the primary photochemical process was often not confirmed experimentally. At the same time, studies on the photochemistry of iron(III) complexes with oxalic acid¹³ and ethylenediaminetetraacetic acid^{12,14} by pulsed methods made it possible to formulate an alternative mechanism of photolysis, based on production of a long-lived radical complex [Fe^{II}s[•]OOC—R]²⁺ in the primary photochemical event.

Previously,^{15–20} we studied peculiar features of the mechanism of photolysis of iron(III) carboxylate complexes by laser flash photolysis with nano- and femtosecond temporal resolution. It was found that, contrary to earlier assumptions, excitation of some complexes with natural organic acids (tartaric, citric, pyruvic, glycolic, and oxalic acids) is followed by the formation of corresponding long-lived radical complexes rather than short-lived organic radicals as primary intermediates.

In this work, we studied primary photochemical processes taking a Fe^{III} complex with lactic acid as an example. The emphasis is placed on the detection of corre-

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Scheme 1

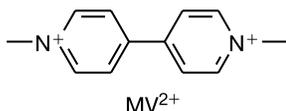


P are products.

sponding radical complex and its precursor, *i.e.*, excited state, and on the determination of their spectral and kinetic properties.

Experimental

Iron(III) complexes were prepared using 90% lactic acid (Aldrich) and Fe^{III} perchlorate hydrate (Aldrich). Methyl viologen dichloride hydrate (Aldrich, 98%) was used as the source of methyl viologen dications MV²⁺. The necessary pH value (pH ~3) was adjusted using perchloric acid ("chemically pure" grade) and sodium hydroxide. All samples were prepared immediately before the photochemical experiments. Deionized water was used for sample preparation. The concentrations of iron(III) and lactic acid were (i) $5 \cdot 10^{-4}$ and $2 \cdot 10^{-3}$ mol L⁻¹, respectively, for the nanosecond photolysis and stationary photolysis experiments and (ii) $5 \cdot 10^{-3}$ and $2 \cdot 10^{-2}$ mol L⁻¹, respectively, for the femtosecond experiments.



Stationary photolysis. Aqueous solutions of the complex [Fe(Lact)]⁺ were irradiated using a pulsed Nd:YAG laser at 355 nm. The concentration of Fe^{II} in the course of photolysis was determined spectrophotometrically from the formation of a stable complex with *o*-phenanthroline.²¹ The UV spectra were recorded using an Agilent 8453 spectrophotometer (Agilent Technologies) at room temperature. In determining the quantum yields the light intensity was measured with a Gentec PH100-SiUV photo detector. The quantum yield values reported here were obtained by averaging the results of two independent experiments. The measuring error was $\pm 15\%$.

Laser flash photolysis. Nanosecond laser flash photolysis experiments (excitation with a Nd:YAG laser at 355 nm, pulse duration 5 ns, average energy 3–5 mJ per pulse) were carried out on a setup analogous to that described earlier.²² Samples for laser flash photolysis were used until a 10% decrease in absorption at the excitation wavelength. All experiments were performed in conventional quartz cells (optical path length 1 cm) at 298 K. When necessary, the solutions were purged with high-purity argon in the course of experiments.

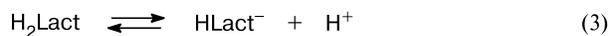
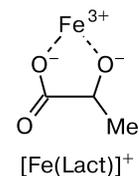
Ultrafast kinetic spectroscopy experiments were carried out on a setup that was thoroughly described earlier.²³ Samples were

exposed to second-harmonic radiation of a generator–amplifier system based on a Ti–sapphire laser (pulse duration about 60 fs at nearly 400 nm, energy 5 μ J per pulse, repetition frequency 1 kHz, laser beam diameter nearly 0.5 mm). Part of the excitation beam was focused on a cell filled with water to generate the probe radiation (continuum). A single time-resolved spectrum was obtained by averaging a total of 200 excitation pulses; the time delay increment was 100 fs. Spectra were recorded using a flow quartz cell (optical thickness 1 mm); the total volume of the system was 15 mL. The flow system made it possible to ensure uniform illumination of samples and to preclude undesired thermal effects due to heating of the sample by the excitation pulse. The degree of photodegradation of the sample during the experiment was at most 10%. Experimental data (kinetic curves) were treated using a global fit procedure upon applying correction for dispersion of the group velocity. The temporal resolution of the system was about 200 fs.

Results and Discussion

Chemical composition of the Fe^{III} complex with lactic acid and its UV spectrum. A study²⁴ of complexation of Fe^{III} with lactic acid (from this point on, H₂Lact) by the stopped flow method revealed the formation of a 1 : 1 complex [Fe^{III}Lact]⁺.

The concentration of [Fe^{III}Lact]⁺ was calculated using the equilibrium constant values for reactions (1)–(3) ($K_1 = 0.026$, $K_2 = 6.5 \cdot 10^{-3}$, $K_3 = 1.38 \cdot 10^{-4}$).^{24,25} Typically, the concentration of the complex [Fe^{III}Lact]⁺ was >85%, the complex being the main photoactive form of Fe^{III} at the excitation wavelength.



The absorption spectrum of this complex (Fig. 1) is characterized by a charge transfer band with a maximum in the region 348 nm ($\epsilon = 1700$ L mol⁻¹ cm⁻¹) and by

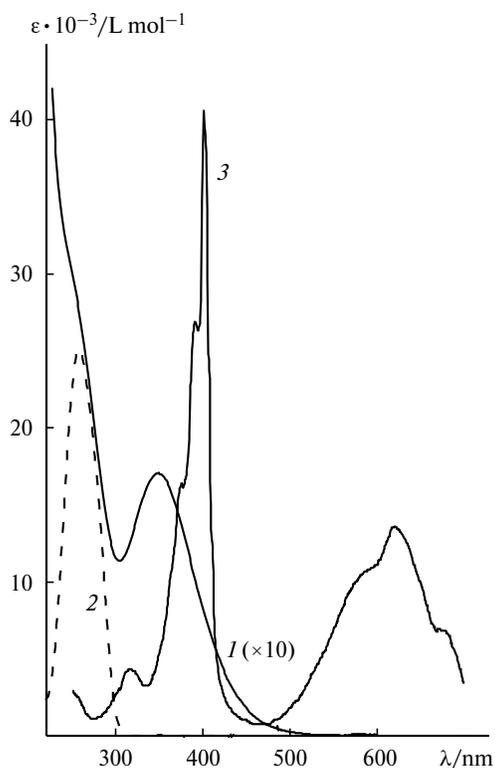


Fig. 1. UV spectra of Fe^{III} complex with lactic acid (1; $[\text{Fe}(\text{ClO}_4)_3] = 5 \cdot 10^{-4} \text{ mol L}^{-1}$, $[\text{H}_2\text{Lact}] = 2 \cdot 10^{-3} \text{ mol L}^{-1}$; pH 3.1), MV^{2+} dication (2), and radical cation $\text{MV}^{\cdot+}$ (3; data taken from Ref. 31).

a number of more intense bands in the short-wavelength spectral region.

Stationary photolysis and laser flash photolysis of $[\text{Fe}^{\text{III}}\text{Lact}]^+$. Stationary photolysis in both deoxygenated and air-saturated solutions of $[\text{Fe}^{\text{III}}\text{Lact}]^+$ is accompanied by gradual disappearance of the absorption of the initial complex. No new absorption bands appear due to small extinction coefficient of the end product of photolysis, *viz.*, the aquated complex of Fe^{2+} ($\lambda_{\text{max}} = 239 \text{ nm}$, $\epsilon^{239} = 20 \text{ L mol}^{-1} \text{ cm}^{-1}$).²⁶ Photolysis of deoxygenated solutions of $[\text{Fe}^{\text{III}}\text{Lact}]^+$ proceeds faster.

The quantum yields of photolysis of $[\text{Fe}^{\text{III}}\text{Lact}]^+$ in deoxygenated and air-saturated solutions are 0.4 and 0.22, respectively. It should be noted that high quantum yields of photolysis are characteristic of many Fe^{III} carboxylate complexes.^{1,19,27} The mechanism of the effect of oxygen on photolysis of the complex $[\text{Fe}^{\text{III}}\text{Lact}]^+$ will be considered below.

Figure 2, *a* presents the transient absorption spectrum recorded 50 ns after excitation of air-saturated solutions of the complex $[\text{Fe}^{\text{III}}\text{Lact}]^+$. The UV region of the spectrum exhibits a bleaching signal due to disappearance of the absorption of complex $[\text{Fe}^{\text{III}}\text{Lact}]^+$ as a result of flash excitation (inverted absorption spectrum of the complex is shown by the solid line in Fig. 2, *a*). In the time range

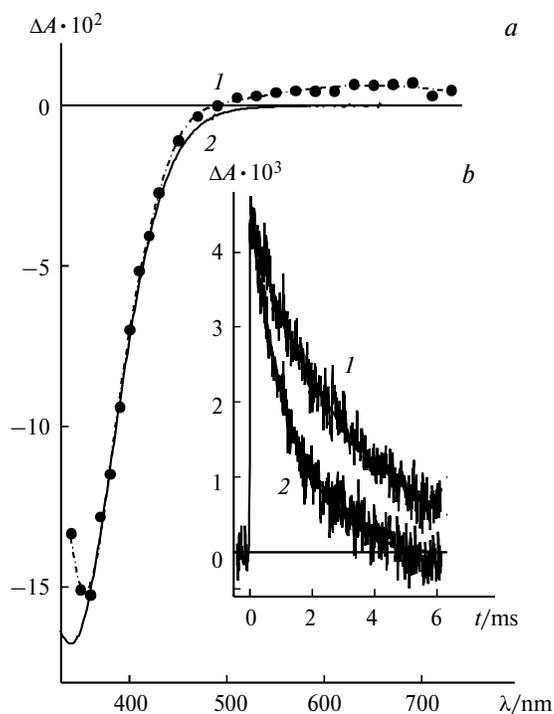


Fig. 2. Laser flash photolysis (355 nm) of complex $[\text{Fe}^{\text{III}}\text{Lact}]^+$ ($[\text{Fe}(\text{ClO}_4)_3] = 5 \cdot 10^{-4} \text{ mol L}^{-1}$, $[\text{H}_2\text{Lact}] = 2 \cdot 10^{-3} \text{ mol L}^{-1}$; pH 3.0) in air-saturated solution: *a* – transient absorption spectrum recorded 0.05 μs after excitation (1, solid circles denote experimental data) and inverted absorption spectrum of $[\text{Fe}^{\text{III}}\text{Lact}]^+$ (2); *b* – kinetic curves at $\lambda = 630 \text{ nm}$ in deoxygenated (1) and in air-saturated (2) solutions.

from 0.1 to 200 μs after the laser pulse, the amplitude of bleaching in the absorption band of the complex remains almost unchanged (Fig. 3, curve 1). This indicates the lack of fast reactions of the reactive intermediates generated under the action of laser pulse (*e.g.*, free radicals) with Fe^{III} or Fe^{II} complexes.

Figure 2, *a* also demonstrates the formation of weak long-lived absorption in the region 500–750 nm in the course of photolysis. Disappearance of this transient absorption is shown in Fig. 2, *b*. The kinetic curve is well fitted by a single exponent with a characteristic time of 3.1 and 1.5 ms for deoxygenated and air-saturated solutions, respectively. The band in the visible region can most probably be assigned to the radical complex $[\text{Fe}^{\text{II}} \dots \text{O}-\text{CH}(\text{Me})-\text{COO}^{\cdot+}]$, a possible primary product of photolysis of $[\text{Fe}^{\text{III}}\text{Lact}]^+$. Photochemistry of the Fe^{III} complexes with pyruvic, tartaric, glycolic, and succinic acids was explained analogously.^{16–19}

It is believed^{9–13} that the primary photochemical process for the Fe^{III} complexes with carboxylic acids is inner-sphere electron transfer. The formation of a Fe^{II} complex upon electron transfer can be followed by different processes (reactions (4)–(8)). First, a free radical can escape into the solvent bulk (see reaction (4)). Next, stabilization

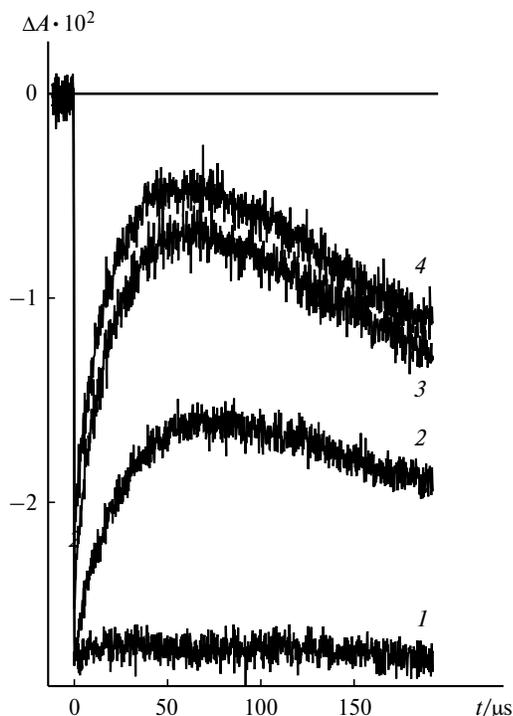
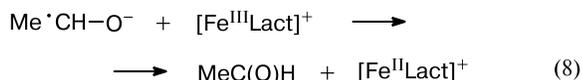
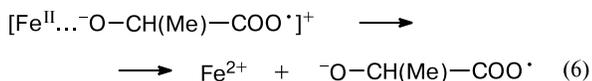
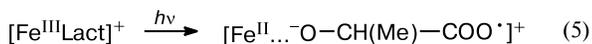
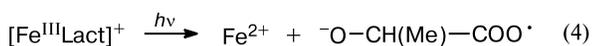


Fig. 3. Kinetic curves for laser flash photolysis (355 nm) of deoxygenated solutions of complex $[\text{Fe}^{\text{III}}\text{Lact}]^+$ in the presence of MV^{2+} : $[\text{MV}^{2+}] = 10^{-5}$ (1), 10^{-4} (2), and 10^{-3} mol L^{-1} (3); $[\text{Fe}(\text{ClO}_4)_3] = 5 \cdot 10^{-4}$ mol L^{-1} , $[\text{H}_2\text{Lact}] = 2 \cdot 10^{-3}$ mol L^{-1} ; pH 3.0).

of the radical complex is possible (see reaction (5)), as is the case for iron(III) oxalate.^{13,16} To discriminate between the two processes, we carried out laser flash photolysis of $[\text{Fe}^{\text{III}}\text{Lact}]^+$ in the presence of methyl viologen, an acceptor of organic radicals.



An acyloxy radical anion $\text{}^-\text{O}-\text{CH}(\text{Me})-\text{COO}^\cdot$ generated in the course of the primary process (4) should undergo fast decarboxylation (see reaction (7)) with a characteristic time lying between 10 and 1000 ps. These times were measured in direct experiments for aryl acyloxy radicals^{11,28,29} and estimated indirectly for alkyl acyloxy radi-

icals.^{28,30} Based on the results obtained,^{11,28–30} one can assume that the characteristic time of reaction (7) is *a priori* much shorter than the temporal resolution of the laser flash photolysis setup (50 ns).

Radical $\text{Me}^\cdot\text{CH}-\text{O}^-$ generated in the reaction (7) should react with the initial complex $[\text{Fe}^{\text{III}}\text{Lact}]^+$ to give the end product of photolysis, *viz.*, acetaldehyde $\text{MeC}(\text{O})\text{H}$.

Laser flash photolysis of $[\text{Fe}^{\text{III}}\text{Lact}]^+$ in the presence of methyl viologen. Since aliphatic radicals weakly absorb in the visible and near-UV regions, their absorption spectra can be recorded only using an acceptor of radicals. The latter should react with the radical being detected to produce a certain intermediate characterized by intense characteristic absorption in a spectral region convenient for measurements. In this work, the role of acceptor was played by MV^{2+} dication, a compound that proved itself in studies on laser flash photolysis of Fe^{III} complexes with a number of aliphatic carboxylic acids.^{15–18} The advantages of the MV^{2+} dication are as follows:

1) no intrinsic photochemical activity upon excitation at $\lambda = 355$ nm because of negligibly weak absorption at this wavelength (see Fig. 1, curve 2);

2) high rate constants for reactions with organic radical reducing agents, namely, $(3–16) \cdot 10^9$ L mol $^{-1}$ cm $^{-1}$;^{16–18} and

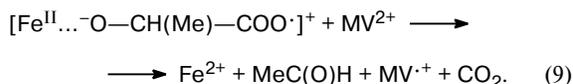
3) generation of $\text{MV}^{\cdot+}$ radical cation characterized by strong absorption in the visible and near-UV regions (see Fig. 1, curve 3).³¹

Production of radical cation $\text{MV}^{\cdot+}$ in the course of flash photolysis of complex $[\text{Fe}^{\text{III}}\text{Lact}]^+$ in the presence of methyl viologen is detected from the appearance of transient absorption signal at the absorption maximum of the radical cation at $\lambda = 396$ nm (see Fig. 3). However, the radical cation $\text{MV}^{\cdot+}$ is mainly generated during a process whose rate is almost independent of the initial concentration of MV^{2+} . Therefore, there are no kinetic indicators of the reaction between the organic radical anion $\text{Me}^\cdot\text{CH}-\text{O}^-$ produced in the successive processes (4) and (7) and the dication MV^{2+} . This suggests a very low quantum yield of reaction (4) with participation of the $[\text{Fe}^{\text{III}}\text{Lact}]^+$ complex.

Estimates of the yield of $\text{MV}^{\cdot+}$ using the known extinction coefficient (41500 L mol $^{-1}$ cm $^{-1}$ at $\lambda = 396$ nm, see Ref. 31) show that the total percentage of organic radicals produced in the primary photochemical event (see reaction (4)) is at most 0.4% of the overall number of photolyzed initial complexes (see Fig. 3). The last-mentioned value was determined using the known extinction coefficient of the complex at $\lambda = 396$ nm (900 L mol $^{-1}$ cm $^{-1}$) and the bleaching amplitude at $\lambda = 396$ nm (no MV^{2+}). The low yield of organic radicals immediately after excitation is also indicated by the lack of changes in the absorption band of the complex at $t < 200$ μs (see Fig. 3, curve 1). Therefore, process (4) that is usually treated as the major photolysis channel^{1–5,9,10} appears to be a side one for the

complex under study and some other complexes with structurally similar ligands.^{15–19} The formation of a long-lived radical complex in reaction (5) followed by its slow decomposition into the Fe^{II} complex and free radical (see reaction (6)) seems to be the most plausible major channel of photolysis. The estimate of the extinction coefficient of the [Fe^{II}...-O-CH(Me)-COO·]⁺ band is very small, namely, about 60 L mol⁻¹ cm⁻¹ at λ = 670 nm.

Slow production of the radical cation MV^{·+} depends only slightly on the acceptor concentration. This is probably due to the interaction between the dication MV²⁺ and an organic radical produced upon monomolecular decomposition of the radical complex (see reaction (6)) or to reaction (9) with the radical complex.



The lifetime of the radical cation MV^{·+} in deoxygenated media containing no other potential oxidants is of the order of a few minutes.³¹ In our case, MV^{·+} disappears at *t* > 100 μs (see Fig. 3, *b*); this time is most likely determined by the reaction with the Fe^{III} complexes [Fe^{III}Lact]⁺ and [Fe(OH)]²⁺ (see reaction (2)).^{16–18}

Femtosecond spectroscopy of complex [Fe^{III}Lact]⁺. To determine the characteristic time of formation of the radical complex and the spectroscopic properties of its precursor (*i.e.*, excited state), we carried out experiments on excitation of the complex [Fe^{III}Lact]⁺ by femtosecond pulses and detection of transient absorption at the picosecond time scale. Excitation is immediately followed by the appearance of a broad absorption band with a maximum at about 465 nm (Fig. 4, *a*). Within 2 ps after excitation, this band narrows and the observed maximum is shifted by 455 nm. After 7–8 ps, the optical density reaches a constant value throughout the spectral region under study and a bleaching signal in the absorption region of the initial complex [Fe^{III}Lact]⁺ is observed. Weak absorption in the visible region is also recorded; its spectrum is similar to that of the radical complex [Fe^{II}...-O-CH(Me)-COO·]⁺ (see Fig. 2, *a* and Fig. 4, *a*). The kinetic curves are correctly fitted by expression (10) with two characteristic times, τ₁ = 0.4 and τ₂ = 1.5 ps, in the whole range of wavelengths.

$$\Delta A(\lambda, t) = A_1(\lambda)\exp(-t/\tau_1) + A_2(\lambda)\exp(-t/\tau_2) + A_3(\lambda) \quad (10)$$

Most probably, the first process with τ₁ = 0.4 ps involves vibrational relaxation and solvation of a Franck–Condon excited state. This situation is typical of transition-metal complexes in polar solvents, where the solvation time can be as long as hundreds of femtoseconds.³² Narrowing of the absorption band corresponds to vibrational relaxation of the excited state,³³ while the observed hypsochromic shift of the absorption maximum is due to the so-called dynamic Stokes shift.³⁴ The second process with τ₂ = 1.5 ps results in the appearance of long-lived absorption and can

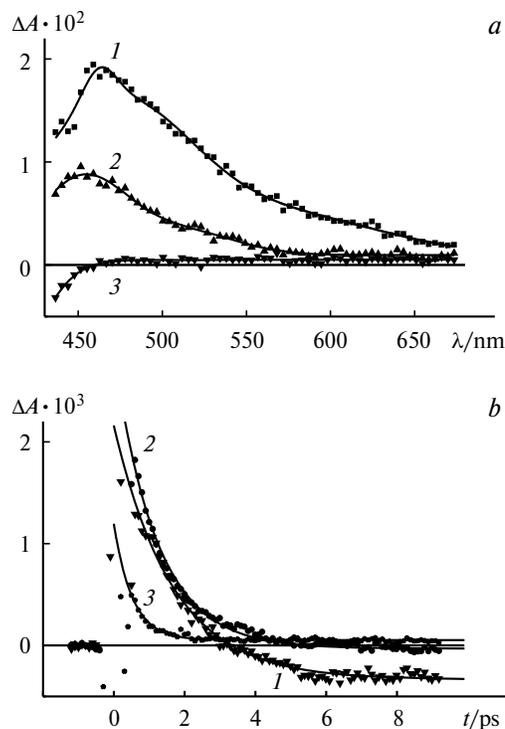
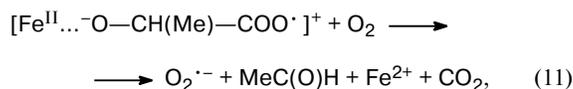


Fig. 4. Femtosecond spectroscopy (400 nm) data for complex [Fe^{III}Lact]⁺ ([Fe(ClO₄)₃] = 5 · 10⁻³ mol L⁻¹, [H₂Lact] = 2 · 10⁻² mol L⁻¹; pH 3.0) in air-saturated solution: *a* – transient optical absorption spectra recorded 0.6 (1), 1.5 (2), and 9 ps after excitation (3); *b* – kinetic curves for changes in the optical density at λ = 436 (1), 465 (2), and 600 nm (3) and corresponding best-fit plots (solid lines) obtained using expression (10) with two characteristic times, τ₁ = 0.4 and τ₂ = 1.5 ps.

logically be assigned to superposition of inner-sphere electron transfer with the formation of a radical complex and internal conversion to the ground state. The quantum yield of photolysis of [Fe^{III}Lact]⁺ is determined by competition between these two processes. Ultrafast relaxation of the Franck–Condon state and fast relaxation of the thermalized excited state to the radical complex agree with the fact that the quantum yield of photolysis of many Fe^{III} carboxylate complexes is independent of the excitation wavelength.^{20,27,35,36} It should also be noted that the photophysical parameters of the picosecond dynamics of [Fe^{III}Lact]⁺ are very close to those of the complexes with tartaric and citric acids studied earlier.²⁰

Photolysis of [Fe^{III}Lact]⁺ in the presence of oxygen. In air-saturated systems, the quantum yield of photolysis of the complex [Fe^{III}Lact]⁺ becomes nearly halved (see above). This is most probably due to the reactions of the radical complex [Fe^{II}...-O-CH(Me)-COO·]⁺ and radical Me·CH-O⁻ with oxygen:



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