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Ultrafast photophysical processes for Fe(III)-carboxylates

Ivan P. Pozdnyakov,^{*a,b} Alexey A. Melnikov,^c Nikolai Tkachenko,^d Sergey V. Chekalin,^c Helge Lemmetyinen^d and Victor F. Plyusnin^{a,b}

Photochemical reactions with the participation of iron(III) carboxylates are important for environmental photochemistry and have a great potential of application in water purification (advanced oxidation processes, photo-Fenton and Fenton-like processes). In spite of this, information about excited states and primary intermediates in the photochemistry of Fe(III) complexes with carboxylic acids is scarce. This mini-review presents and discusses the results of several recent publications in the field of ultrafast spectroscopy of natural Fe(III) carboxylates.

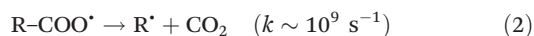
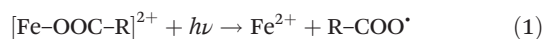
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Introduction

Photochemical reactions of Fe(III)-(poly)carboxylate complexes influence many iron-dependent biogeochemical processes and are responsible for the photochemical production of CO and CO₂, as well as for oxygen consumption in natural waters.^{1–4} It is assumed that photolysis of Fe(III)-(poly)carboxylate complexes is one of the main sources of reactive oxygen species (ROS·OH, HO₂[·], H₂O₂). The formation of these species is catalyzed by Fe(II) and Fe(III) ions in Fenton-like reactions.^{4–7} ROS influence the chemical composition and the redox capacity of natural water systems, in particular causing the oxidation of sulfur- and nitrogen-containing compounds in the atmosphere.^{8,9}

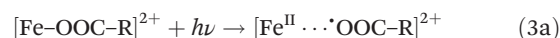
Historically, it was typically believed that the primary process in the photochemistry of Fe(III) complexes with aliphatic (poly)carboxylic acids (further Fe(III)-ALCA) is an inner-sphere electron transfer with the formation of Fe(II) and an escape of an organic radical to the solution bulk (reaction (1))^{6,7,10} followed by its fast decarboxylation (reaction (2)):^{11,12}



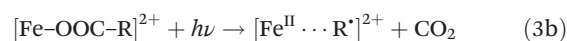
The secondary radical formed because of the decarboxylation could react with the different components of the reaction

system (e.g., Fe(III) complexes or molecular oxygen). ROS are consequently formed that cause the mineralization of organic compounds in natural waters.^{6,7,10}

The reaction mechanism (1–2) was put forward based on the results of stationary experiments. Recently, nanosecond laser flash photolysis (LFP) technique was used to clarify the mechanism of photolysis of Fe(III)-ALCA complexes.^{13–16} The main intermediate in the photochemistry of Fe(III) complexes with several natural organic acids (lactic, [Fe(Lact)]⁺, tartaric, ([Fe(Tart)]⁺; pyruvic, [Fe(Pyr)]²⁺; oxalic, [Fe(Ox)₃]³⁻ and glyoxalic, [Fe(AG)]²⁺) was found to be a corresponding long-lived radical complex rather than a short-lived organic radical (the yield of the organic radicals in the primary process does not exceed 7% for all the studied complexes).¹⁵



Fe(II)-radical complexes exhibit weak absorption bands in the visible region (maximum at 620–670 nm) and monoexponential decays in millisecond time scale (1–5 ms) due to dissociation and reaction with dissolved oxygen ($k = (1-3) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$).^{13–16} The formation of long-lived radical complexes is a common case in the photochemistry of transition metals, which has been shown for numerous coordination compounds (including carboxylate complexes of Fe(III) and Co(III)).^{17–19} The long lifetime of the Fe(II) radical complex could be explained by the essential elongation of Fe–O bonds (difference between Fe(II)–O and Fe(III)–O bonds is about $\sim 0.2 \text{ \AA}$)^{20,21} leading to the large structural changes in the Fe(II)-radical complex. This structural difference may result in a potential barrier preventing back electron transfer. Another reason for the stability of the radical complexes could be fast CO₂ detachment after the inner-sphere electron transfer with the formation of [Fe(II)⋯R[·]] radical complex:



^aInstitute of Chemical Kinetics and Combustion, Siberian Branch of Russian Academy of Sciences, Institutskaya 3, 630090 Novosibirsk, Russian Federation. E-mail: pozdnyak@kinetics.nsc.ru

^bNovosibirsk State University, Pirogova 2, 630090 Novosibirsk, Russian Federation

^cInstitute of Spectroscopy, Russian Academy of Sciences, Physicheskaya 5, 142190 Troitsk, Moscow, Russian Federation

^dDepartment of Chemistry and Bioengineering, Tampere University of Technology, 33101, Korkeakoulunkatu 8, Tampere, Finland

Current LFP data does not allow to distinguish between mechanisms (3a) and (3b) and additional experiments with the involvement of ESR technique and quantum-chemistry calculations are needed to clarify the situation.

It is known that the quantum yield of Fe(II) formed by the photolysis of Fe(III)-ALCA complexes depends rather weakly on excitation wavelength (λ_{ex}) and is equal to 1.25 for Fe(III)-oxalate ($\lambda_{\text{ex}} = 260\text{--}365\text{ nm}$),²² ~ 0.28 for Fe(III)-citrate ($\lambda_{\text{ex}} = 366$ and 436 nm)^{7,23} ~ 0.5 for Fe(III)-tartrate ($\lambda_{\text{ex}} = 313\text{--}366\text{ nm}$)^{15,23-25} and ~ 0.4 for Fe(III)-lactate ($313\text{--}366\text{ nm}$)^{15,25} complexes. This fact indicates that the formation of the Fe(II) radical complex is caused due to a certain thermalized excited state of corresponding Fe(III)-ALCA complex.

Ultrafast processes for Fe(III)-ALCA complexes

Unfortunately, information about excited states of Fe(III) complexes with aliphatic acids is scarce. Few publications concerning the ultrafast spectroscopy of Fe(III)-ALCA complexes could be found in literature.^{16,21,26} It is worth noting that the investigation of femtochemistry of these complexes is a challenge for the experimentalists due to considerably low absorption coefficients of the initial compounds and transient species.

In some studies,^{16,26} pump-probe spectroscopy ($\lambda_{\text{ex}} = 320$ and 400 nm) was used to study ultrafast processes for [Fe(Lact)]⁺, [Fe(Tart)]⁺ and [Fe(Cit)] in the femto-to-picosecond time domain. Both excitation wavelengths (400 or 320 nm) fall to the same broad LMCT band of the complexes²⁷ from the right and left sides of the maximum of the absorption band, respectively (Fig. 1).

The excitation of the Fe(III)-ALCA complexes with a femto-second pulse ($\lambda_{\text{ex}} = 400\text{ nm}$) leads to the formation of transient absorption, which gets almost completely decayed in 30 ps. Kinetic curves at several selected wavelengths for [Fe(Tart)]⁺ and [Fe(Cit)] complexes are presented in Fig. 2a and b. The global analysis of the time profile in the wavelength range

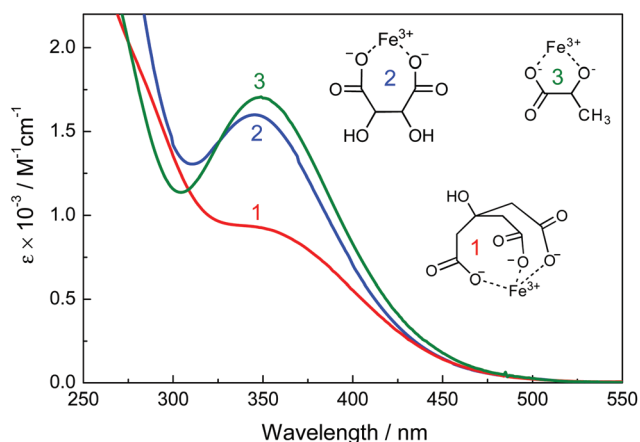


Fig. 1 Absorption spectra and chemical structures of Fe(III) complexes with citric (1), tartaric (2), and lactic (3) acids.

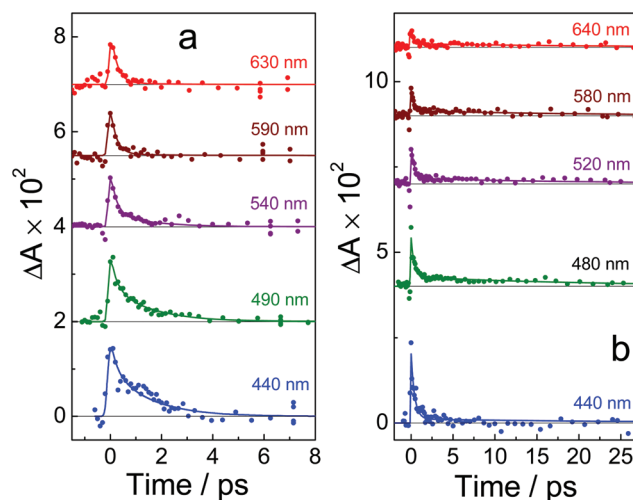


Fig. 2 Femtosecond ($\lambda_{\text{ex}} = 400\text{ nm}$) photolysis of $1.5 \times 10^{-2}\text{ M}$ [Fe(Cit)] (a) and $1.5 \times 10^{-2}\text{ M}$ [Fe(Tart)]⁺ (b) complexes. Kinetic curves of transient absorption change at different wavelengths. Solid lines: best two-exponential fit after reconvolution with the instrument response function.

440–760 nm by iterative reconvolution shows that the use of a two-exponential function (4) with the instrument response function gives a good fitting with the time constants, collected in Table 1.

$$\Delta A(\lambda, t) = A_1(\lambda)e^{-t/\tau_1} + A_2(\lambda)e^{-t/\tau_2} + A_3(\lambda) \quad (4)$$

Similar biphasic dynamics was also observed for the Fe(III)-ALCA complexes upon LMCT band excitation at 320 nm (Fig. 3a and b).

The first process with observed time constant τ_1 was assigned to the combination of an ultrafast vibrational cooling and solvent relaxation of Franck–Condon excited state to the thermalized one. This situation is typical for the relaxation of the Franck–Condon excited states of transition metal complexes in polar solvents, exhibiting inertial solvation time of about 100 fs.²⁸ One can expect that the relaxation of the Franck–Condon excited state leads to certain narrowing of the absorption band due to vibrational relaxation;²⁹ this was practically confirmed by experimental observations (Fig. 3a and 4a, b).

The thermalized excited state undergoes decay with time constant τ_2 at a longer timescale leading to the formation of a constant bleaching in the UV part of the spectrum and practically zero signal in the visible (Fig. 3b; Fig. 2b). This coincides

Table 1 Observed absorption maxima and the lifetimes of the excited states of Fe(III)-carboxylate complexes^{16,21,26}

Complex	$\lambda_{\text{ex}}/\text{nm}$	τ_1/ps	$\lambda_{\text{max}}(\tau_1)/\text{nm}$	τ_2/ps	$\lambda_{\text{max}}(\tau_2)/\text{nm}$
[Fe(Cit)]	400	0.2	<440	1.4	≈ 450
	320	N/D ^a	N/D	≈ 2	≈ 440
[Fe(Tart)] ⁺	400	0.4	<440	≈ 40	≈ 470
	320	≈ 1	<440	40	≈ 500
[Fe(Lact)] ⁺	400	0.4	≈ 465	1.5	≈ 455
[Fe(Ox) ₃] ³⁻	400	≈ 1	<420	N/D	≈ 430

^a Not determined.

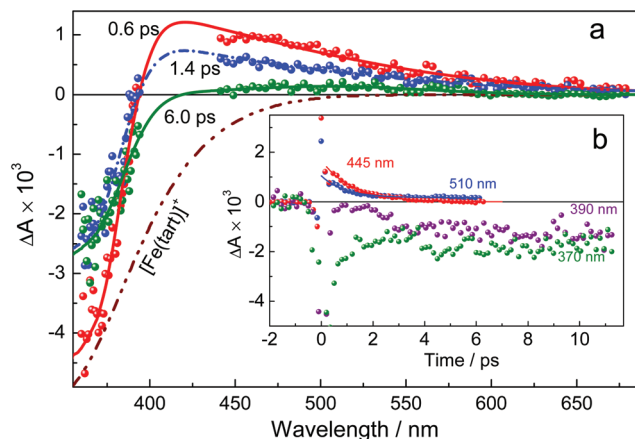


Fig. 3 Femtosecond ($\lambda_{\text{ex}} = 320$ nm) photolysis of 5×10^{-3} M $[\text{Fe}(\text{Tart})]^+$ complex. (a) Transient spectra at different time delay between the probe and pump pulses together with the inverted absorption spectrum of $[\text{Fe}(\text{Tart})]^+$. (b) Kinetic curves of transient absorption change at selected wavelengths. Solid lines: best two-exponential fit.

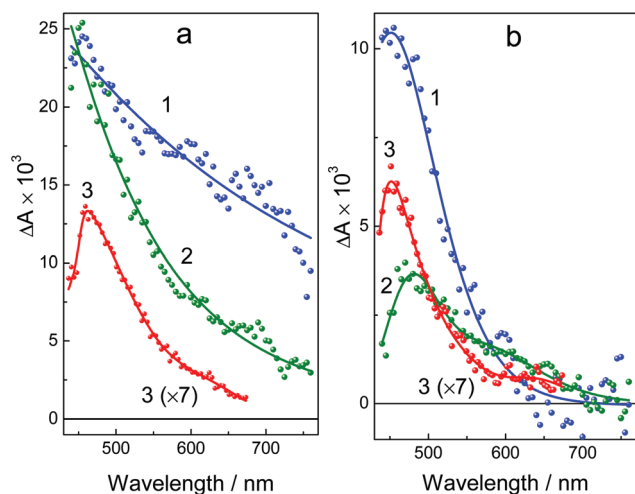
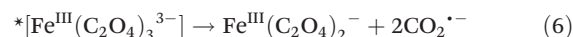
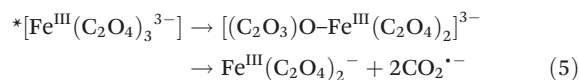


Fig. 4 Femtosecond ($\lambda_{\text{ex}} = 400$ nm) photolysis of Fe(III) carboxylates. (a) Spectrum at zero time for $[\text{Fe}(\text{Cit})]$ (1), $[\text{Fe}(\text{Tart})]^+$ (2) and $[\text{Fe}(\text{Lact})]^+$ (3), respectively; (b) spectrum after the end of ultrafast process for $[\text{Fe}(\text{Cit})]$ (1), $[\text{Fe}(\text{Tart})]^+$ (2) and $[\text{Fe}(\text{Lact})]^+$ (3), respectively. For better comparison, data for $[\text{Fe}(\text{Lact})]^+$ complex is multiplied by a factor of 7.

well with the data obtained by nanosecond laser flash photolysis technique.¹⁵ It is worth noting that the characteristic absorption bands of $[\text{Fe}^{\text{II}}\dots\text{OOC-R}]^{2+}$ complexes ($\lambda_{\text{max}} = 620\text{--}650$ nm), recorded by nanosecond laser flash photolysis^{13–15} were not observed in femtosecond experiments with $[\text{Fe}(\text{Tart})]^+$ and $[\text{Fe}(\text{Cit})]$ complexes. This is because of the extremely low absorption coefficients of the radical complexes ($\epsilon^{620} = 18 \text{ M}^{-1} \text{ cm}^{-1}$ for $[\text{Fe}(\text{tart})]^+$).¹⁵ For $[\text{Fe}(\text{Lact})]^+$ complex, a very weak long-lived component ($A_3(\lambda)$) was observed, whose spectrum is in good agreement with the spectrum of $[\text{Fe}^{\text{II}}\dots\text{O-CH}(\text{Me})\text{-COO}^{\cdot-}]^+$ radical complex ($\epsilon^{670} = 60 \text{ M}^{-1} \text{ cm}^{-1}$).¹⁶ Therefore, the authors^{16,26} concluded that the thermalized excited state decays with time constant τ_2 by two processes:

internal conversion to the ground state and the formation of the long-lived Fe(II) radical complex in reaction (3a) or (3b). The competition among these processes determines the quantum yield of the photolysis of Fe(III)-ALCA complexes.

In other works,^{21,30} the photochemistry of $\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3^{3-}$ was investigated by the combination of time-resolved EXAFS spectroscopy, flash photolysis with different time resolution (from femto- to milliseconds), radical scavenging technique and theoretical calculations. Ultrafast formation ($<2\text{--}3$ ps) of an absorption band with a maximum near 430 nm (Table 1) was observed upon excitation at 400 nm, which was assigned to the excited state of $\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3^{3-}$. At 4 and 9 ps after excitation, the length of Fe–O bond was found to decrease from 2.02 (the ground state of $\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3^{3-}$) to 1.93 and 1.87 Å, respectively. Taking into consideration that the experimental values of Fe(II)–O bonds are always higher than Fe(III)–O,^{20,21} the primary photoprocess was proposed to be the cleavage of Fe–O bond in the excited state with the formation of five-coordinated $[(\text{C}_2\text{O}_3)\text{O-Fe}^{\text{III}}(\text{C}_2\text{O}_4)_2]^{3-}$ intermediate. This process is accompanied by the C–C bond cleavage of the ligand leading to the formation of a tetrahedral-like four-coordinated $\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_2^-$ complex and $\text{CO}_2^{\cdot-}$ radical:



The authors^{21,30} could not distinguish between reactions (5) and (6) due to the insufficient time resolution of the EXAFS method. For both $[(\text{C}_2\text{O}_3)\text{O-Fe}^{\text{III}}(\text{C}_2\text{O}_4)_2]^{3-}$ and $\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_2^-$, theoretical calculations predict Fe–O bond length of about 1.9 Å. The existence of reactions (5) and (6) was also supported by more than 50% decrease of Fe(II) quantum yield due to the addition of radical scavenger (thymine) in ferrioxalate solution.

The interpretation^{21,30} was contradictory to the mechanism, based on the formation of the radical complex $[(\text{C}_2\text{O}_4)_2\text{Fe}^{\text{II}}(\text{C}_2\text{O}_4^{\cdot-})]^{3-}$ as a primary photoproduct, and to the very low quantum yield of organic radicals observed in nanosecond flash photolysis of $\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3^{3-}$.¹³ Alternative interpretation of EXAFS data^{21,30} was done in a work,³¹ which showed that the variation of Fe–O bond length during the first 10 ps after the excitation was linked to the population and thermal relaxation of the long-lived thermally equilibrated secondary excited state (THEXI state)²⁸ of $\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3^{3-}$. Decay of the THEXI state leads to the formation of $[(\text{C}_2\text{O}_4)_2\text{Fe}^{\text{II}}(\text{C}_2\text{O}_4^{\cdot-})]^{3-}$ radical complex observed by nanosecond flash photolysis.¹³ The following discussion³¹ regarding the results of two groups^{13,21} leads to the conclusion that both interpretations need to be supported by additional femtochemistry experiments and quantum-chemistry calculation. Therefore, the primary stage of the mechanism of photolysis of Fe(III)-ALCA complexes is still open for discussion.

Ultrafast processes for Fe(III) complexes with aromatic carboxylates

In contrast to the Fe(III)-ALCA complexes that demonstrate good quantum yields of Fe(II) production upon LMCT band excitation,^{7,15,22–25} Fe(III) complexes with derivatives of salicylic acid (aromatic carboxylates, SADs) demonstrate excellent photochemical stability.^{32,33} SADs refer to aromatic carboxylic acids and can serve as model compounds for investigating the photochemical properties of natural humic and fulvic acids and their complexes with Fe(III) ions.

In some works,^{32,33} pump-probe spectroscopy ($\lambda_{\text{ex}} = 420$ and 530 nm) was used to study the reasons of the photostability of Fe(III) complexes with 5-sulfosalicylic acid (SSA) with 1, 2 and 3 SSA molecules in the coordination sphere. All Fe(SSA)_n ($n = 1-3$) complexes exhibit LMCT bands³⁴ in the visible region (Fig. 5a), the maximum of which shifts to UV with increase in ligand number in the coordination sphere of Fe(III). It is known that steady-state irradiation in the region of LMCT bands does not cause any photodegradation of aqueous solutions of Fe(SSA)_n complexes.³²

It was observed that the excitation of the Fe(SSA)_n complexes with a femtosecond pulse leads to biphasic dynamics of evolution of transient absorption, which is almost completely decayed in 5 ps (Fig. 5b). The initial intermediate, with the absorption spectrum (Fig. 6a, curve 1) exhibiting a significant red shift (~ 150 nm) compared with the ground state absorption spectrum (Fig. 6a, curve 3), was assigned to Franck-Condon electronic excited state. This state undergoes an ultrafast (100–300 fs, Table 2) back electron transfer (ET) to get transformed into a vibrationally hot electronic ground state.

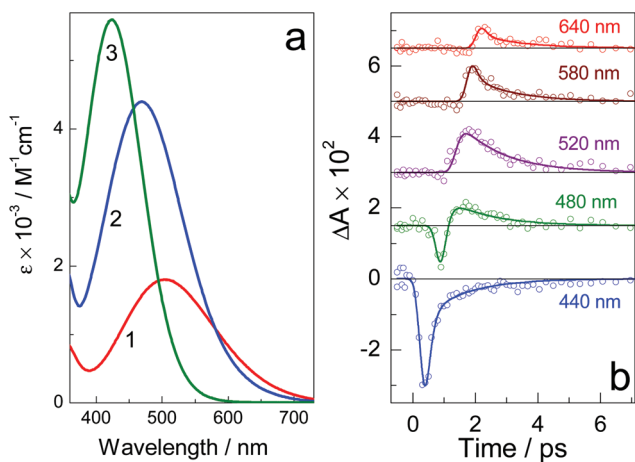


Fig. 5 (a) Absorption spectra of Fe(III) complexes with 5-sulfosalicylic acid. (1–3) FeSSA, Fe(SSA)₂, Fe(SSA)₃ complexes, respectively. (b) Femtosecond ($\lambda_{\text{ex}} = 420$ nm) photolysis of Fe(SSA)₃ complex (3.3×10^{-3} M, pH = 10.3). Kinetic curves of transient absorption change at selected wavelengths. Solid lines: best two-exponential fit after deconvolution with the instrument response function. The apparent shift of “zero” position to the longer times with wavelength increase is due to temporal chirp in the continuum probe pulse.

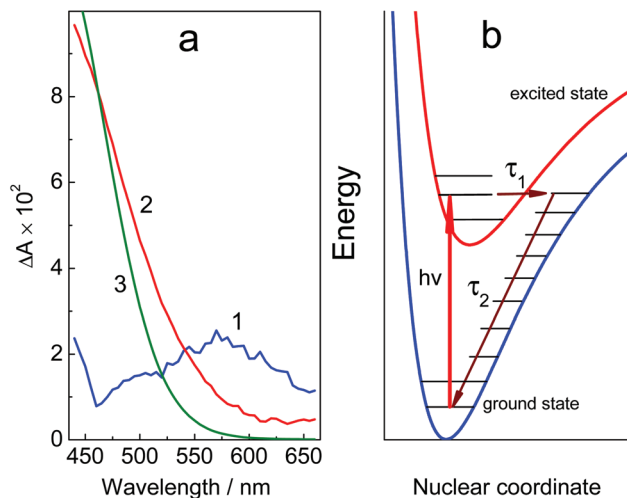


Fig. 6 (a) Femtosecond ($\lambda_{\text{ex}} = 420$ nm) photolysis of Fe(SSA)₃ complex (3.3×10^{-3} M, pH = 10.3). 1 – spectrum at zero time; 2 – spectrum after the end of the ultrafast process. Both spectra are corrected for the depopulation of the ground state of Fe(SSA)₃ (ca. 3×10^{-4} M). Solid curve 3 – the absorption spectrum of the ground state of Fe(SSA)₃ (3×10^{-4} M). (b) Generalized potential energy surface diagram for the excited-state evolution of Fe(SSA)_n complexes. τ_1 and τ_2 are the time constants of back ET and vibrational cooling, correspondingly.

Table 2 Observed absorption maxima and the lifetimes of excited states of Fe(III) complexes with 5-sulfosalicylic acid^{32,33}

Complex	τ_1/ps	$\lambda_{\text{max}}(\tau_1)/\text{nm}$	τ_2/ps	$\lambda_{\text{max}}(\tau_2)/\text{nm}$
FeSSA	0.26	N/D ^a	1.8	N/D
Fe(SSA) ₂ ³⁻	0.1	600	1.4	<490
Fe(SSA) ₃ ⁶⁻	0.17	570	1.5	<440

^a Not determined.

The population of vibrationally hot electronic ground state of Fe(SSA)_n leads to a blue shift of the transient absorption spectra (Fig. 6a, curve 2) of 60–80 nm compared with the absorption spectrum of Franck-Condon electronic excited state. It is worth noting that the absorption maximum of the hot ground state of Fe(SSA)_n is close to the maximum of thermalized ground state, but the width of the former is much higher due to the redistribution of vibrational energy on several vibrational modes. The hot ground state of Fe(SSA)_n is thermalized in picosecond time domain (1–5 ps, Table 2) by vibrational cooling.^{35,36} Generalized potential energy surface diagram for the excited-state evolution of Fe(SSA)_n complexes is shown in Fig. 6b.

Conclusions

In the case of Fe(SSA)_n complexes, the ultrafast back ET to the ground state prevents the formation of [Fe(II)(SSA)_{n-1}...SSA²⁻·] radical pair and the escape of SSA²⁻ radical from the coordi-

nation sphere of the complexes. This is caused by the observed photochemical stability of the complexes under irradiation in the LMCT band. It is most probable that the different photochemical behavior of aliphatic and aromatic carboxylates is related to the different nature of the organic radical formed by the electron transfer from ligand to Fe(III) ion.

In the case of aliphatic acids, the formation of $[\text{Fe}^{\text{II}} \cdots \text{OOC-R}]^{2+}$ radical complex with COO^{\cdot} -centered radical (mechanism (3a)) or carbon-centered R^{\cdot} radical (mechanism (3b)) takes place in the coordination sphere of the iron ion. From thermodynamic reasons, the realization of mechanism (3b) is more probable because R-COO^{\cdot} radicals are oxidant (redox potential $\geq 2 \text{ V}$)^{37,38} and reoxidize Fe(II) ion with the restoration of initial complex. Thus, it can be tentatively proposed that the long lifetime and the absence of the effective back electron transfer in the radical complexes is due to fast CO_2 detachment and the formation of reductive radical R^{\cdot} in the coordination sphere of Fe(II) ion by mechanism 3b.

In the case of SSA, the intermolecular electron transfer leads to the formation of Fe(II)-phenoxyl radical pair. Phenoxyl radicals with electron-withdrawing groups are considerably good oxidants; thus, ultrafast back electron transfer from Fe(II) to coordinated phenoxyl radical with the restoration of initial complex is very efficient. Another possible reason for the observed photostability of Fe(III) complexes with aromatic ligands is that the delocalization of the "hole" formed upon the excitation stabilizes the oxidized ligand with respect to bond splitting and CO_2 loss, thus enabling an effective back electron transfer. Further studies of the femtochemistry of aliphatic and aromatic Fe(III) carboxylates combined with the quantum-chemistry calculation of the properties of possible excited states and radical complexes are needed to clarify the photochemistry of these environmentally important species.

Acknowledgements

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