Photophysics of Fe(III)–sulfosalicylic acid complexes in aqueous solutions

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Abstract

Femtosecond pump-probe spectroscopy ($\lambda_{pump} = 420$ nm) was used to determine the photophysical processes of Fe(III) complexes with 5-sulfosalicylic acid ($Fe(SSA)_n$, $n = 2, 3$) in aqueous solutions. The excitation of the $Fe(SSA)_n$ complexes in the charge transfer bands is followed by an ultrafast relaxation to the ground electronic state with two characteristic times. The shorter time constant is ascribed to internal conversion to the vibrationally hot electronic ground state of $Fe(SSA)_n$ and the second time constant is assigned to the vibrational cooling of the ground state.
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1. Introduction

During the last two decades, growing interest to the investigation of fast light-induced processes in natural waters was observed. This is connected with increased anthropogenic activity, importance of understanding of photoprocesses in environment and search for new high-efficient photocatalysts for water treatment. Natural water systems as well as model systems are investigated widely [1–9]. Accumulated data supports an importance of transient metal (TM) photochemistry (especially Fe(III)) in transformation of organic compounds dissolved in natural waters.

However, overwhelming majority of works devoted to environmental photochemistry were carried out using steady-state techniques. Suggestions about primary photoprocesses and the nature of transient species were done by the analysis of final products of photochemical reactions and integral kinetic characteristics. Few works in this field could be found in which time-resolved techniques (with nanosecond time resolution only) were applied [6,7,10, 11]. However, times from femtosecond to nanosecond are very important for the investigation of photoreactions of coordination compounds, as the processes of electron and energy transfer in the excited states of the metal complexes and geminate recombination of primary transient species take place in this timescale. That is why the nature of ultrafast photophysical and photochemical processes of TM complexes in aqueous solutions are still open to discussion.

In [12–14], we have studied the photochemistry of aqueous solutions of 5-sulfosalicylic acid (SSA) in non-coordinate state and in monocomplex with Fe(III) ion (FeSSA). Sulfosalicylic acid refers to aromatic oxyacids and can serve as model compounds for investigating the photochemical properties of natural acids and their complexes with Fe(III) ions. It was found that the excitation of the FeSSA complex in the ligand-to-metal charge transfer (LMCT) band ($\lambda_{max} = 505$ nm) by femtosecond laser pulse ($\lambda_{pump} = 530$ nm, $\lambda_{probe} = 530$ nm) leads to ultrafast relaxation processes with two characteristic times 260 fs and 1.8 ps [14]. The shorter time constant was assigned to the

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internal conversion to the vibrationally hot electronic ground state of FeSSA and the 1.8 ps time constant was assigned to the vibrational cooling of the ground state.

When the solution contains both FeSSA and noncoordinated $HSSA^{2-}$ ligand, UV irradiation causes a photoreduction of the complex [14]. This process is due to the electron transfer from the noncoordinated ligand in the triplet state to the FeSSA complex. The energy transfer between these species, which fails to cause any photochemical reaction, competes with the electron transfer. As applied to photoprocesses in natural water, the data obtained allow us to define one of the important mechanisms of active photodegradation of organic compounds in anaerobic conditions, i.e. the photoreduction of transition metal complexes due to the electron transfer from the long-lived triplet states of organic aromatic acids.

In the present work, we investigate the photophysical properties of aqueous solutions of Fe(III) complexes with 2 and 3 ions of 5-sulfosalicylic acid in the coordination sphere. The origin and the spectral and kinetic parameters of the excited states of the complexes have been determined. A study of such model systems can be highly important for determining primary photophysical and photochemical processes in natural water, which contains complexes of transition metals with organic acids.

2. Experimental

A pump-probe spectroscopy was used to study transient absorption of the samples in femto- picosecond time domain. The instrument used was described in details elsewhere [15]. The samples were excited by ~60 fs pulses at ~420 nm (second harmonic of a Ti:sapphire generator-amplifier system, CDP Ltd., Moscow, Russia). The excitation pulse repetition rate was 10 Hz and 200 pulses there used to recorded single time-resolved spectrum. The samples were placed in 1 mm rotating cuvette to provide the uniform irradiation of the sample and to avoid unwanted thermal effects from the heating of the sample by the pump pulse. Typically time-resolved spectra were collected with delay displacement of 100 fs in first 3 ps after excitation and with exponentially increasing delay times at longer delays. Usually 60–70 spectra were collected for each sample with longest delay of ~20 ps. The fitting program also did the corrections of the group velocity dispersion and calculated the response time of the instrument. The overall time resolution was 150–200 fs. All pump-probe measurements were carried out at room temperature.

The absorption spectra were recorded using an Shimadzu UV 2501 PC and HP-8453 spectrophotometers. 5-sulfosalicylic acid (99+%, Aldrich) and Fe(III) perchlorate hydrate (Aldrich) were employed without further purification. The solutions were prepared using bidistilled water. pH was adjusted by addition of necessary quantities of concentrated solutions of NaOH and $HClO_4$ (analytical grade).

3. Results and discussion

3.1. Ultrafast processes for Fe(SSA)$_n$ complexes

The structure of Fe(SSA)$_n$ complexes depend on the concentrations of Fe(III) ions and sulfosalicylic acid, the pH of medium. The complexes with one, two and three SSA molecules in the coordination sphere can exist in aqueous solutions [16]. All Fe(SSA)$_n$ complexes exhibit LMCT bands [17,18] in visible region (Fig. 1) which maximum shifts to UV with increasing of ligand number in coordination sphere of Fe(III) (Table 1). Steady-state irradiation in region of CT bands does not cause any photodegradation of aqueous solutions of Fe(SSA)$_n$ complexes [14].

Excitation of the Fe(SSA)$_3$ complex with a femtosecond pulse ($\lambda_{pump} = 420$ nm) leads to formation of transient absorption which is almost completely decayed in 5 ps. Kinetic curves at several selected wavelengths are presented at Fig. 2. The global analysis of the time profile in the wavelength range 440–780 nm by iterative reconvolution shows that the use of a two-exponential function.

$$\Delta A(\lambda, t) = A_1(\lambda)e^{-\frac{t}{\tau_1}} + A_2(\lambda)e^{-\frac{t}{\tau_2}} \qquad (1)$$

with the instrument response function gives a good fitting with the time constants $\tau_1 = 170$ fs and $\tau_2 = 1.5$ ps (solid
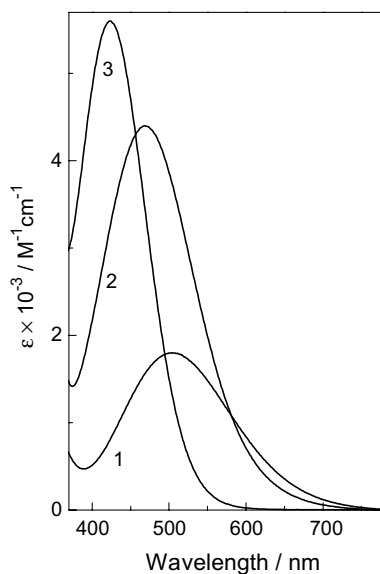

Fig. 1. Absorption spectra of Fe(III) complexes with 5-sulfosalicylic acid. (1–3) – FeSSA, Fe(SSA)$_2$, Fe(SSA)$_3$ complexes, correspondingly.

Table 1
Spectral properties of Fe(III) complexes with 5-sulfosalicylic acid

Complex	pH range	λ_{max}/nm	ε/M^{-1} × cm^{-1}
FeSSA	1.8–3.5	505	1800[15]
Fe(SSA)$_2^{3-}$	3.5–8	470	4400[16]
Fe(SSA)$_3^{6-}$	>8	420	5600[16]
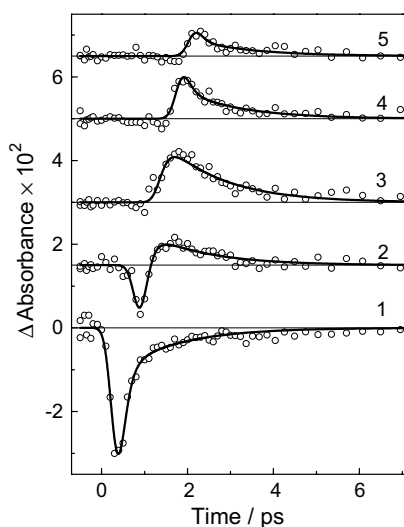
Fig. 2. Femtosecond ($\lambda_{pump} = 420$ nm) photolysis of Fe(SSA)$_3$ complex (3.3×10^{-3} M, pH = 10.3). The kinetic curves of transient absorption change at 440 (1), 480 (2), 520 (3), 580 (4) and 640 (5) nm, correspondingly. Solid lines: best two-exponential fit after reconvolution with the instrument 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.

lines in kinetic curves). Spectra of $A_1(\lambda)$ and $A_2(\lambda)$ amplitudes corresponding to calculated lifetimes are shown in Fig. 3a.

At zero time a bleaching in range 440–510 nm was observed due to depopulation of the ground state of the complex upon excitation. The optical density of bleaching
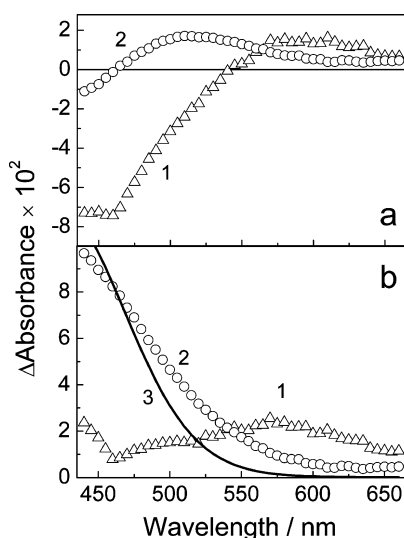

Fig. 3. Femtosecond ($\lambda_{pump} = 420$ nm) photolysis of Fe(SSA)$_3$ complex (3.3×10^{-3} M, pH = 10.3). (a) – spectra of $A_1(\lambda)$ (1) and $A_2(\lambda)$ (2) components (Eq. (1)), corresponding to 0.17 and 1.5 ps lifetimes. (b) – spectra at different times. 1 – spectrum at zero time (sum of amplitudes $A_1(\lambda) + A_2(\lambda)$ corrected to depopulation of ground state); 2 – spectrum after the end of ultrafast process (amplitude $A_2(\lambda)$ corrected to depopulation of ground state). Both spectra corrected to depopulation of ground state of Fe(SSA)$_3$ (ca. 3×10^{-4} M). Solid curve – the absorption spectrum of ground state of Fe(SSA)$_3$ (3×10^{-4} M).

at 440–510 nm indicates that about 3×10^{-4} M of Fe(SSA)$_3$ is excited per pulse (total concentration of Fe(SSA)$_3$ is 3.3×10^{-3} M). The absorption of the ground state of Fe(SSA)$_3$ complex is almost completely recovered after about 5 ps, which is in fair agreement with observed photochemical stability of the complex upon steady-state irradiation in the visible region.

Spectra of $A_1(\lambda)$ and $A_2(\lambda)$ amplitudes allow one to construct the spectra at different times (Fig. 3b). The total sum of amplitudes corrected to the depopulation of ground state is the spectrum at zero time, the $A_2(\lambda)$ spectrum corrected to the depopulation of ground state is the spectrum at the end of first fast process ($\tau_1 = 170$ fs). Immediately after excitation (zero time) the transient absorption is the very wide band with ~570 nm maximum. After finishing of the first fast process (τ_1), the absorption band is blue-shifted and has maximum at $\lambda < 440$ nm.

The similar results were obtained in pump-probe experiments with aqueous solutions of Fe(SSA)$_2$ complex (Table 2). For FeSSA, no reliable data was obtained due to rather low absorption coefficients of the complex in CT band. However, in our previous work [14] the biexponential kinetics of ground state recovery of FeSSA at 530 nm after excitation in LMCT band ($\lambda_{pump} = 530$ nm) was also observed. Lifetimes obtained from single-wavelength measurements for FeSSA complex are very similar to ones found for Fe(SSA)$_2$ and Fe(SSA)$_3$ complexes (Table 2).

3.2. Mechanism of relaxation of Fe(SSA)$_n$ complex excited states

The biphasic dynamics observed for Fe(SSA)$_n$ is rather typical for ultrafast ground state recovery of TM complexes upon charge transfer (CT) band excitation [19–24]. The excitation is followed by population of the Frank–Condon excited state, which is then undergone an ultrafast (100–700 fs) back electron transfer (ET) to the vibrationally hot electronic ground state. The later is thermalized in picosecond time domain (1–10 ps) by vibrational cooling [21–24]. Another way of Frank–Condon excited state disappearance is a ultrafast internal conversion to the vibrationally hot lower-lying exited state, which is then undergone vibrational cooling. Thermalized lower-lying exited state is rather long-lived and converts to the ground one in nanosecond time scale. Such situation observed at excitation of CT bands of some Ru(II), Cr(III) and Fe(II) complexes [20, 22–24]. However, the fast (<10 ps) recovery of the ground state absorption of Fe(SSA)$_n$ complexes allows to exclude the later process.

Table 2
Lifetimes and observed absorption maxima of excited states of Fe(III) complexes with 5-sulfosalicylic acid

Complex	τ_1/ps	λ_{max} (τ_1)/nm	τ_2/ps	λ_{max} (τ_2)/nm
FeSSA	0.26[14]	–	1.8[14]	–
Fe(SSA)$_2^{3-}$	0.1	600	1.4	<490
Fe(SSA)$_3^{6-}$	0.17	570	1.5	<440

So one can assign the time constants τ_1 to back ET to the vibrationally hot electronic ground state of Fe(SSA)$_n$ and the second time constant τ_2 to the vibrational cooling of the ground state (Fig. 4). It is worth noting, that characteristic times of vibrational cooling of the ground state are the same in the range of experimental errors (mean value ≈ 1.6 ps) for all of Fe(SSA)$_n$ complexes and coincide well with the corresponding times obtained in aqueous solutions by other scientific groups [19,21,25].

The absorption spectrum of Frank–Condon electronic excited state (Fig. 3b) exhibits red shift (~ 150 nm) comparing with ground state absorption spectrum (Fig. 1). This indicates to the existence of higher-lying exited state of Fe(SSA)$_n$ complexes. The population of vibrationally hot electronic ground state of Fe(SSA)$_n$ leads to blue shift of transient absorption spectra (Fig. 3b) on 60–80 nm comparing with absorption spectrum of Frank–Condon electronic excited state. It is worth to note that the absorption maximum of the hot ground state of Fe(SSA)$_3$ is close to the maximum of thermilized ground state, but the width of the former is much higher due to redistribution of vibrational energy on several vibrational modes.

Ultrafast back ET in Frank–Condon excited state of Fe(SSA)$_n$ is the reason of observed photochemical stability of the complexes under irradiation in the LMCT band. For example, excitation of FeOH$_{aq}^{2+}$ complex in LMCT band leads to formation of excited state with lifetime about 55 ps [26]. Such rather long lifetime allows the relaxation of the excited state to [Fe(II)...$^{\cdot}$OH] radical pair with escape $^{\cdot}$OH radical to in the bulk volume with high quantum yield ≈ 0.2 [5,6]. In the case of Fe(SSA)$_n$ complexes, the ultrafast back ET to the ground state prevents formation of [Fe(II)(SSA)$_{n-1}$...SSA$^{2-\cdot}$] radical pair and escape of SSA$^{2-\cdot}$ radical from coordination sphere of the complexes.

4. Conclusion

Femtosecond pump-probe technique was applied to investigate the photophysical properties of aqueous solutions of Fe(III) complexes with 5-sulfosalicylic acid. Biphasic dynamics of ground state recovery upon LMCT excitation of Fe(SSA)$_n$ was observed. The shorter time constant ($\tau_1 = 0.1$ and 0.17 ps for $n = 2$ and 3, correspondingly) is ascribed to back ET to the vibrationally hot electronic ground state of Fe(SSA)$_n$ and the second time constant ($\tau_2 = 1.4$ and 1.5 ps for $n = 2$ and 3, correspondingly) is assigned to the vibrational cooling of the ground state. Ultrafast back ET in Frank–Condon excited state of Fe(SSA)$_n$ is the reason of observed photochemical stability of the complexes under irradiation in the LMCT band.

Acknowledgements

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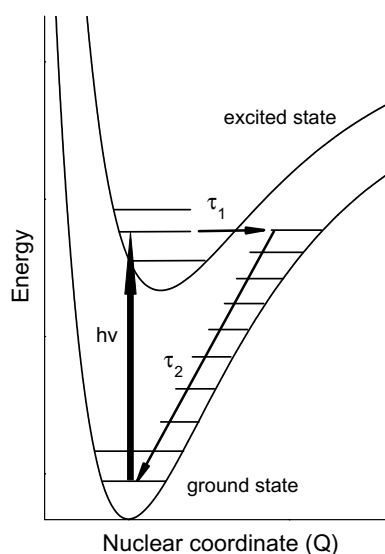[20] A. Vlcek Jr., Coord. Chem. Rev. 200–202 (2000) 933.

Fig. 4. Generalized potential energy surface diagram for excited state evolution of Fe(SSA)$_n$ complexes. τ_1 and τ_2 are the time constants of back ET and vibrational cooling, correspondingly.

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