

photochemistry of Fe(III) complexes with salicylic acid derivatives in aqueous solutions



Ivan P. Pozdnyakov^{a,b,*}, Victor F. Plyusnin^{a,b}, Vjacheslav P. Grivin^{a,b}, Esther Oliveros^c

^a Institute of Chemical Kinetics and Combustion, Institutskaya 3, 630090 Novosibirsk, Russia

^b Novosibirsk State University, Pirogova str. 2, 630090 Novosibirsk, Russia

^c Laboratoire des IMRCP, UMR CNRS 5623, Université Toulouse III (Paul Sabatier, UPS), 118 route de Narbonne, F-31062 Toulouse Cedex 9, France

ARTICLE INFO

Article history:

Received 14 November 2014

Received in revised form 17 March 2015

Accepted 21 March 2015

Available online 23 March 2015

Keywords:

Salicylic acid derivatives

Iron complexes

Laser flash photolysis

Phenoxy radicals

Photoreduction

Hydroxyl radical

ABSTRACT

The photochemistry of a series of 1:1 Fe(III) complexes with salicylic acid derivatives (SADs) in aqueous solution has been investigated, using the following model compounds: salicylic acid (SA), 5-sulfoSA (5SSA), 4-hydroxySA (2HSA), 6-hydroxySA (6HSA), 4-nitroSA (4NSA) and 5-nitroSA (5NSA). The results of optical spectroscopy, steady-state and nanosecond laser flash photolysis experiments show that all Fe(III)–SAD complexes exhibit good photochemical stability upon 355 nm excitation (quantum yields of photolysis do not exceed 0.01). No evidence of hydroxyl radical formation was observed in laser flash experiments. Therefore, the primary photoprocess was assumed to be an electron transfer from coordinated SAD to the Fe (III) ion in the excited complex, leading to the formation of Fe(II) and the corresponding SAD[•] phenoxy radical. SADs containing electron-withdrawing groups (4NSA, 5NSA, 5SSA) exhibit the smallest quantum yields of photolysis of the series, whereas the highest values were observed for SA and SADs containing electron-donating groups (4HSA, 6HSA). Therefore, in contrast to Fe(III)–complexes with aliphatic carboxylates, sunlight photolysis of Fe(III)–SAD complexes cannot be an effective way for the degradation of SADs in natural water systems.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Organic acids (R-CO₂H) represent a class of compounds abundant in natural waters [1] and are able to form complexes with a variety of transition metals (including Fe(III)). These complexes absorb radiation in the UV and visible spectral regions and their photochemistry can contribute substantially to the balance of dissolved organic matter in water [2–4]. Among organic acids, salicylic acid (SA) and its derivatives (SADs) are common compounds, widely present in natural waters and many industrial waste streams [5,6]. They are also highly relevant pollutants because of their toxicity and relatively low biodegradability [7]. Moreover, advanced oxidation techniques for water treatment based on the use of ferrous/ferric salts and hydrogen peroxide (Fenton-like and photo-Fenton processes, see e.g., [8]) could be adversely affected by the presence of SADs. Indeed, their ability to form stable complexes with Fe(III) could lead to increased treatment times and hydrogen peroxide consumption [6,9].

This behavior is strikingly different from that reported for aliphatic carboxylates (oxalate, citrate, etc.) and catecholates. In these cases, complex formation with Fe(III) was found to improve both accessible pH range and efficiency of photo-Fenton treatment due to a better solubilization of the Fe(III) ions, the enhancement of the UV–vis absorption and the generation of active oxygen species by excitation of the ligand-to-metal charge transfer (LMCT) bands [10–12].

SADs are considered representative of the functional groups able to complex metal ions in humic substances contained in natural waters [13] and can serve as model compounds for investigating the photochemical properties of natural organic matter (NOM). Therefore, the study of the photochemistry of SADs and Fe(III)–SAD complexes is also of environmental interest.

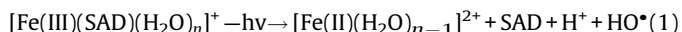
In our previously published work [14–16], we have studied the photochemistry of 5-sulfosalicylic acid (5SSA) and its complexes with Fe(III) (Fe(5SSA)_n, *n* = 1–3) in aqueous solutions. The excitation of the Fe(5SSA)_n complexes in the absorption region of the LMCT bands (λ_{ex} = 400 and 530 nm) is followed by an ultrafast relaxation to the ground electronic state which is the reason for the observed photochemical stability of the complexes under near UV and visible irradiation [16]. When the solution contains both Fe(III)–5SSA and the free HSSA²⁻ ligand, UV irradiation (308 nm) results in the reduction of Fe(III) to Fe(II), due to the electron transfer from the free

* Corresponding author at: Institute of Chemical Kinetics and Combustion, Institutskaya 3, 630090 Novosibirsk, Russia. Tel.: +7 383 3332385; fax: +7 383 3307350.

E-mail address: pozdneyak@kinetics.nsc.ru (I.P. Pozdnyakov).

ligand in its triplet state ($^1\text{HSSA}^{2-}$, $\phi_T=0.34$) to the Fe(III)(5SSA) complex [15]. The energy transfer between $^1\text{HSSA}^{2-}$ and Fe(III)(5SSA) competes with the electron transfer, but does not cause any chemical change. The photoreduction of transition metal complexes by electron transfer from the long-lived triplet states of aromatic carboxylates could be one of the possible mechanisms of photodegradation of organic compounds in natural waters under anaerobic conditions.

Very recently a new mechanism was postulated for the photochemical reaction of selected Fe(III)–SAD complexes upon polychromatic irradiation in the 300–400 nm wavelength range: electron transfer from coordinated water molecules to the metal center was proposed to yield Fe(II) and the hydroxyl radical ($\text{HO}^\bullet$) that escapes to the bulk [17]:



Evidence in favor of Reaction (1) was obtained from steady-state photolysis experiments, by trapping $\text{HO}^\bullet$ with benzene in large excess and monitoring Fe(II) by optical spectroscopy using *o*-phenanthroline as complexing agent. Although quantum yields of Reaction (1) were not determined, it was shown that the efficiencies were significantly lower than those observed for the Fe(III) aqua complex.

In the present work, we have investigated the photochemical properties of a series of Fe(III)–SAD complexes. The following model compounds bearing different substituents on the aromatic ring have been selected: salicylic acid (SA), 5-sulfoSA (5SSA), 4-hydroxySA (4HSA), 6-hydroxySA (6HSA), 4-nitroSA (4NSA) and 5-nitroSA (5NSA). Using optical spectroscopy, steady-state and nanosecond laser flash photolysis (further LFP), the origin of the primary intermediates and their spectral and kinetic characteristics has been determined. Formation of hydroxyl radicals upon excitation of the aforesaid complexes in the near UV region (355 nm) has been carefully investigated on a short time scale. Based on these results, the efficiency of the photolysis of Fe(III)–SAD complexes under sunlight UV irradiation could be evaluated.

2. Experimental

Sodium salicylate (99.5+%, Fluka), 5-sulfosalicylic acid (99+%, Aldrich), 2-hydroxysalicylic acid (98+%, Fluka), 6-hydroxysalicylic acid (98%, Aldrich), 4-nitrosalicylic acid (98%, Fluka), 5-nitrosalicylic acid (99%, Aldrich) and Fe(III) perchlorate hydrate (Aldrich) were employed without further purification. Typical concentrations of SADs and Fe(III) for optical measurements, determination of complex formation (stability) constants and photochemical experiments were $[1-6] \times 10^{-4}$ M and $[0-6] \times 10^{-4}$ M, respectively. Stock solutions of Fe(III) (5×10^{-3} M) at pH 2 and SADs ($(1-2) \times 10^{-3}$ M) were used for the preparation of the working solutions. HClO_4 (chemically pure) and NaHCO_3 (chemically pure) were used for pH adjustment. Unless otherwise specified, all photochemical experiments were performed in a 1 cm quartz cell in air-equilibrated or argon-saturated solutions at initial pH 2.8–3.3, temperature 298 K and atmospheric pressure. Double distilled water was used in all experiments.

The absorption spectra were recorded using an Agilent HP8453 spectrophotometer. Molar absorption coefficients of SADs and Fe(III)–SAD complexes were determined from three independent runs with a precision better than 10%.

The LFP experiments were carried out using the third harmonic (355 nm) of a Nd:YAG laser (LS-2137U, Solar, Belarus) as an excitation source (pulse duration 6 ns, pulse energy 0.5–10 mJ/pulse) [14]. The time resolution of the set up was 50 ns. For steady-state photolysis, a high pressure mercury lamp DRSH-500 combined with a set of glass

filters (UFS8 and BS7) for selecting the 365 nm wavelength was used. Stability studies were also performed under prolonged pulsed irradiation using the Nd:YAG laser (third harmonic, 355 nm).

Quantum yields of Fe(III)–SAD disappearance were determined in air-equilibrated solutions under different conditions. LFP experiments at times shorter than 50 μs were performed for evaluating the initial quantum yields (Φ_{ILFP355}): they were calculated from the amplitude of instant bleaching at the absorption maximum of the LMCT band of the Fe(III)–SAD complex in the visible spectral region. Quantum yields of Fe(III)–SAD disappearance were also determined from the bleaching of the LMCT band under continuous irradiation with the DRSH-500 lamp (Φ_{Cl365}) and under prolonged irradiation with repeated laser pulses (Φ_{RLP355}). Fe(II) concentration during photolysis was measured spectrophotometrically by formation of the colored *o*-phenanthroline complex [18]. For calculation of quantum yields (mean errors ± 20 –30%), laser and lamp intensities were measured by means of a SOLO 2 power meter (Gentec EO).

3. Results and discussion

3.1. Absorption spectra of SADs and Fe(III)–SAD complexes [1:1]

The main spectral parameters of the various forms of the SADs and the equilibrium constants of the acid-base dissociation of the –COOH and –OH groups are listed in Tables 1 and 2. All forms of SADs exhibit a long-wave absorption band with a maximum at 300–350 nm (π – π^* transition [32]) and a moderately high molar absorption coefficient ($(2.6$ – $9.3) \times 10^3$ $\text{M}^{-1} \text{cm}^{-1}$). These results are in good agreement with literature data [17].

Addition of Fe(III) ions at acidic pH (<4) leads to the formation of 1:1 complexes exhibiting ligand-to-metal charge transfer (LMCT) bands with an absorption maximum in the 495–560 nm wavelength range depending on the organic ligand type (Figs. 1 and 2 and Fig. 1S in ESI, Tables 1 and 2). Absorption coefficients of the complexes ($(1.4$ – $2.0) \times 10^3$ $\text{M}^{-1} \text{cm}^{-1}$) were determined from both the linear dependence of the complex absorbance as a function of the organic ligand (L = SAD) concentration at low Fe(III)/L ratio and from the constant value of the absorbance at high Fe(III)/L ratio (Insets in Figs. 1 and 2). Both methods give the same values of the molar absorption coefficients within experimental error ($\pm 10\%$). The stability constants (K_{st}) of 1:1 complex formation were determined from the variation of the complex absorbance as a function of the pH (see ESI for details). Obtained values are in agreement with literature data within experimental error (Table 2). It is worth noting that the absorption spectra of the Fe–SAD species are rather complex and contain intra-ligand transitions in the UV and different LMCT transitions in the UV and visible spectral regions. Fig. 2 shows the absorption spectrum of the Fe–4HSA complex, in comparison with the spectra of 4HSA and the ferrous aqua complex ($\text{FeOH}_{\text{aq}}^{2+}$). The decomposition of the Fe–4HSA

Table 1
Spectroscopic data on SADs and Fe(III)–SAD complexes: wavelengths of maximum absorption and corresponding molar absorption coefficients.^a

SADs	$\lambda_{\text{abs}}^{\text{L}}$ nm	ϵ^{L} $\text{M}^{-1} \text{cm}^{-1}$	$\lambda_{\text{abs}}^{\text{FeL}}$ nm	ϵ^{FeL} $\text{M}^{-1} \text{cm}^{-1}$
SA	296	3500	525	1600, 1500 [19]
5SSA	298	2800	505	1700, 1800 [19,20]
4HSA	292	4600	520	1400
6HSA	307	3000	560	1500
4NSA	347	2600	495	1450
5NSA	315	9300	495	2000

^a Superscripts FeL and L stand for the 1:1 complex and the monoanionic form of SADs, respectively.

Table 2

Equilibrium constants of the acid–base dissociation of SADs and stability constants of the Fe(III)–SAD complexes (1:1 stoichiometry).

SADs	pK _{a1} (–COOH)	pK _{a2} (–OH)	pK _{st}
SA	3.0 [21–23]	13.4 [23,24]	16.4 [24]
5SSA	2.6 [24]	11.7 [24]	14.6 [24]
4HSA	3.3 [21,22]	8.8 [25,26]	12.5 ^a , 13.2 [24]
6HSA	1.2 [27]	12.9 [23]	16.1 ^a , 16.2 [28]
4NSA	2.3 [29]	10.2 [30]	13.8 ^a
5NSA	2.0 [23,26]	10 [23,26]	13.4 ^a , 12.8 [23], 13.9 [31]

^a This work.

spectrum into six Gaussian functions is presented in the inset of Fig. 2. Although this decomposition is purely descriptive, it may be used to underline the complexity of the Fe–SAD absorption spectra. In the 200–350 nm spectral region, the absorption of the complex results from both SAD intra-ligand transitions and transitions due to charge transfer from coordinated hydroxide (HO[–]) and H₂O ligands to the Fe(III) ion (denoted as “water-to-iron” CT bands below). In the 300–800 nm spectral region, the very broad and moderately intense absorption is traditionally assigned to electronic transitions from the coordinated SAD ligand to Fe(III) (denoted as “SAD-to-iron” CT bands below). It is clearly seen (Fig. 2, Inset) that this absorption cannot be described by a single transition and at least three Gaussian functions are needed to provide an adequate fit. Two Gaussians in the visible region surely belong to the “SAD-to-iron” CT bands. But absorption in the 300–400 nm region could be assigned to different types of transitions including both “SAD-to-iron” and “water-to-iron” CT bands [17]. Additional spectroscopic studies supported by quantum-chemical calculations would be needed for more precise assignments but such investigations were out of scope of this work.

3.2. Thermal and photochemical stability of SADs and Fe(III)–SAD complexes

In the absence of Fe(III) ions, SADs in acidic aqueous solutions demonstrate an excellent stability both in the dark at room temperature and under irradiation at 355 nm. In the latter case, the photolysis quantum yields were determined to be lower than 10^{–4}.

Fe(III) complexes with SA and 5-SSA also showed a good thermal stability, but all of the other complexes were slowly

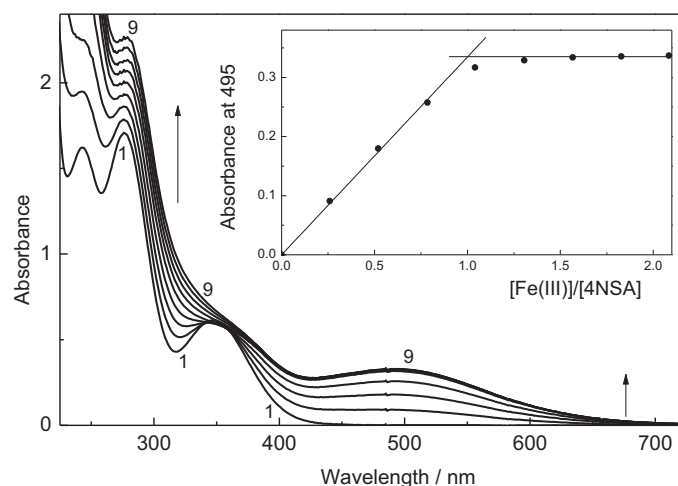


Fig. 1. Absorption spectra of 4NSA (2.1×10^{-4} M) in the presence of Fe(III) ions in aqueous solution. Spectra 1–9: 0, 0.6, 1.2, 1.8, 2.3, 2.9, 3.4, 3.9 and 4.4×10^{-4} M Fe(III), respectively. During Fe(III) addition, the pH of the solution gradually decreased from 3.9 to 2.9. Inset: dependence of the absorbance at 495 nm on the metal to ligand molar ratio.

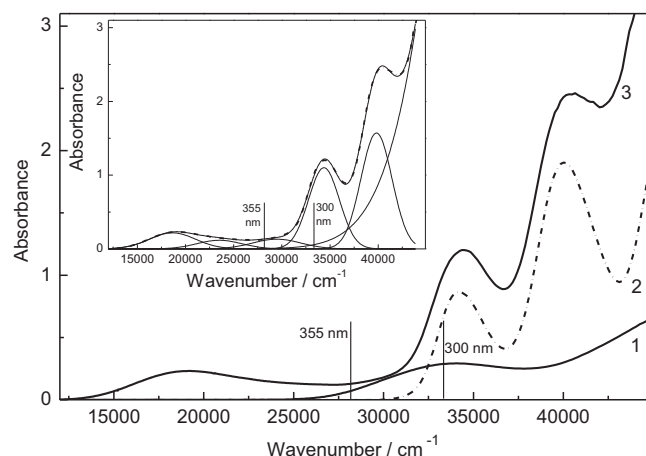


Fig. 2. Absorption spectra of Fe(III) perchlorate (1), 4HSA (2) and the Fe(III)–4HSA complex (3) in aqueous solution. Concentration of all species was 1.8×10^{-4} M, pH 3. Inset: absorption spectrum of the Fe(III)–4HSA complex (bold dotted line) and its decomposition into 6 Gaussian functions (solid lines).

decomposed in the dark (conversion rates of 9–33% after 190 h, Table 3). Irradiation of the Fe(III)–SAD complexes using a laser (accumulation of pulses at 355 nm) or a mercury lamp combined with filters (365 nm) resulted in the progressive disappearance of the visible LMCT band of the Fe(III)–SAD complexes (Figs 3 and 4). Whatever the irradiation means (laser or lamp), the same quantum yields of Fe(III)–SAD complex photolysis in air-equilibrated solutions were obtained within experimental error (Φ_{RLP355} , Φ_{Cl365} , Table 3). This result indicates that monophotonic photoreduction is the main photochemical process under both excitation conditions.

The quantum yields of photoreduction of the Fe(III)–SAD complexes investigated are rather low ($(1\text{--}11) \times 10^{-3}$) in comparison with those of complexes of Fe(III) with aliphatic carboxylates (0.2–1.2 [33]). The reason for this result is discussed in Section 3.3. It is worth noting that SADs containing electron-withdrawing groups (4-NSA, 5-NSA, 5-SSA) exhibit smaller photolysis quantum yields than those of the SA and SADs containing electron-donating groups (4-HSA, 6-HSA). A similar trend was reported in [17], based on measurements of relative efficiencies of Fe(II) production upon photolysis of selected Fe–SAD complexes.

3.3. Mechanism of the photolysis of Fe(III)–SAD complexes

As discussed in Section 1, the excitation of Fe(III)–SAD complexes in the near UV (300–400 nm) region could be followed by inner-sphere electron transfer either from the coordinated water molecules or from the SAD ligand, depending on the excited LMCT bond. In the former case, the formation of the hydroxyl radical (HO[•], Reaction (1)) would result, whereas, in the latter case, the SAD ligand would be oxidized to a SAD phenoxyl type radical (SAD[•], Reaction (2)).



To discriminate between the two possible pathways (Reaction (1) or (2)), we have investigated the reaction of HO[•] with the Fe(III)–SA complex by LPE. Solutions containing 6×10^{-4} M Fe(III) perchlorate and $(0.3\text{--}3.0) \times 10^{-4}$ M SA at pH 3 were excited at 355 nm. Due to the excess of Fe(III) ions practically all the SA ligand was bound to the iron center in the complex. Under these conditions, the main photochemically active form of Fe(III) in solution is the aqua complex $\text{FeOH}_{\text{aq}}^{2+}$ which generates HO[•] (Reaction (3)) with a quantum yield of 0.096 (value determined in this work and close to the literature value of 0.085 [34]).

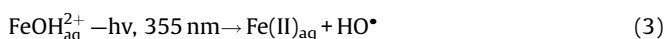
Table 3

Thermal and photochemical stability of Fe(III)–SAD complexes in air-equilibrated aqueous solutions: percent of the Fe(III)–SAD complex decomposed in the dark ($\Delta[\text{Fe(III)–SAD}]$) and quantum yields of photolysis (Φ) under different irradiation conditions.

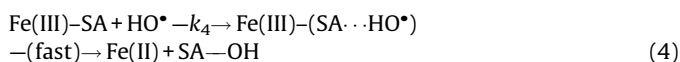
SAD	$\Delta[\text{Fe(III)–SAD}]$ % ^a after 18, 90, 190 h in the dark	Φ_{ILFP355}	Φ_{RLP355}	Φ_{Cl365nm}
SA	Stable	0.008	0.008	0.011
5SSA	Stable	0.0033	0.0039	0.0036
4HSA	2, 5, 9	0.003	0.0082	0.01
6HSA	8, 21, 33	0.0036	0.006	0.0042
4NSA	4, 7, 10	<0.001 ^b	0.0021	0.0023
5NSA	2, 5, 10	<0.001 ^b	0.0009	0.0009

^a The change in complex concentration was calculated from the relative decrease of the absorbance at the absorption maximum of the LMCT band in the visible range after 18, 90 and 190 h in the dark.

^b Transient signal was too weak to measure the exact value of the quantum yield.



Excitation of $\text{FeOH}_{\text{aq}}^{2+}$ leads to the disappearance of the Fe(III)–SA complex, a direct evidence of its reaction with $\text{HO}^{\bullet}$ (Fig. 5, Reaction (4)).



It may be assumed that adduct of $\text{HO}^{\bullet}$ to SA is oxidized rapidly in the coordination sphere of Fe(III). Therefore, the limiting step of the process (4) is the reaction of $\text{HO}^{\bullet}$ with the Fe(III)–SA complex. The value of k_4 ($3.5 \pm 0.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) was calculated from the linear dependence of the observed rate constant of Fe(III)–SA disappearance at 530 nm ($k_{\text{obs}}^{530 \text{ nm}}$) on its concentration. This value is three times lower than the rate constant of the $\text{HO}^{\bullet}$ reaction with

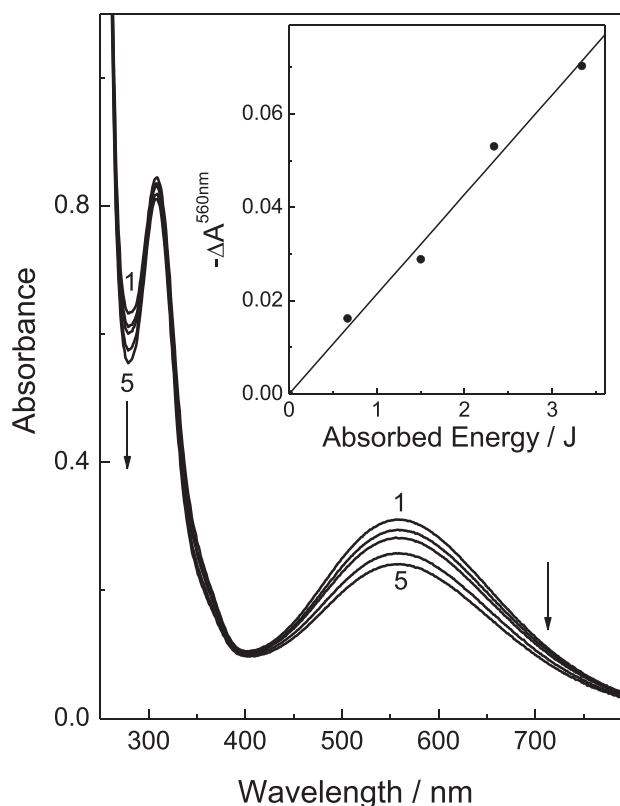


Fig. 3. Steady-state photolysis of the Fe(III)–6HSA complex ($2 \times 10^{-4} \text{ M}$) at 365 nm. Absorption spectra 1–5: 0, 4, 9, 14 and 20 min of irradiation with an incident energy of 0.45 J/min. Sample volume: 1 ml, air-equilibrated solution. Inset: dependence of the absorbance changes at 560 nm on the energy absorbed.

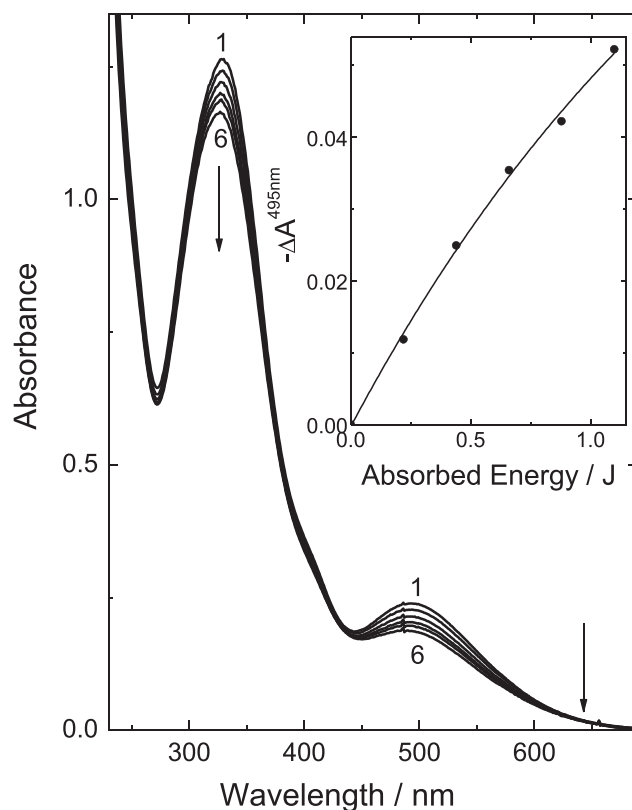


Fig. 4. Steady-state photolysis of the Fe(III)–5NSA complex ($1.25 \times 10^{-4} \text{ M}$) at 355 nm. Absorption spectra 1–6: 0, 50, 100, 150, 200 and 250 laser pulses with an incident energy of 2.3 mJ/pulse. Sample volume: 1 ml, air-equilibrated solution. Inset: dependence of the absorbance changes at 495 nm on the energy absorbed.

SA ($k = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ [35]). This result could be explained by both steric factors and a decrease of the diffusion mobility of SA upon complexation. Nevertheless, the value of k_4 remains close to the values typical for diffusion controlled reactions.

Consequently, if Reaction (1) would be responsible for the photolysis of the Fe(III)–SAD complexes, instant bleaching in the spectral region of the Fe(III)–SAD LMCT band should be observed in LPF experiments due to the primary process (1), followed by additional bleaching due to Reaction (4). Indeed, the excitation of

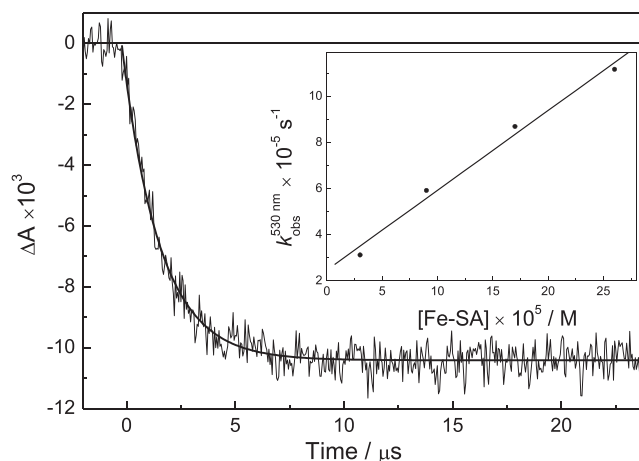


Fig. 5. LPF of Fe(III) perchlorate ($6 \times 10^{-4} \text{ M}$) at 355 nm (excitation energy 5 mJ/pulse) in the presence of SA at different concentrations. Kinetic decay curve observed at 530 nm with the best monoexponential fit (solid line); concentration of Fe(III)–SA: $9 \times 10^{-5} \text{ M}$. Inset: dependence of the observed rate constant of Fe(III)–SA disappearance at 530 nm ($k_{\text{obs}}^{530 \text{ nm}}$) on its concentration.

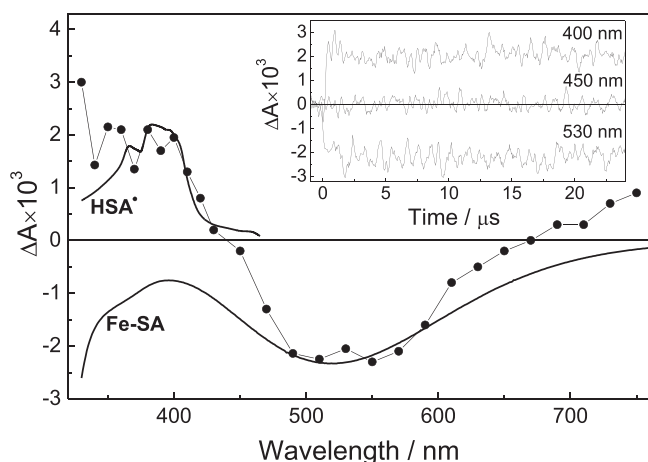


Fig. 6. Flash photolysis of the Fe(III)–SA complex (6×10^{-4} M) at 355 nm (excitation energy 5.5 mJ/pulse). Dots: differential spectrum of transient absorption recorded 50 ns after excitation. Solid bold curves: absorption spectrum of the HSA phenoxyl radical taken from [36] and inverted absorption spectrum of the Fe(III)–SA complex, respectively. Inset: kinetic curves of transient absorption decay at characteristic wavelengths.

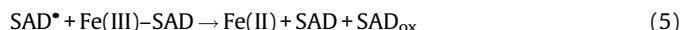
the Fe(III)–SA complex was followed by the instant (time scale < 50 ns) formation of an absorption band with a maximum at ≈ 390 nm and bleaching at ≈ 530 nm (LMCT band involving Fe(III) and SA) (Fig. 6). But no evidence of additional bleaching kinetics due to Reaction (4) was observed (under the experimental conditions used, the characteristic time of the reaction of $\text{HO}^\bullet$ with the Fe(III)–SA complex is estimated to be $0.5 \mu\text{s}$). No characteristic absorption of the SA triplet excited state ($\lambda_{\text{max}} = 450$ nm [36]) was observed either (Fig. 6). It should be noted that, assuming the predominance of Reaction (1), no instant (< 50 ns) formation of absorption at 390 nm would be expected. On the contrary, the bleaching due to the disappearance of the $[\text{Fe(II)}(\text{SAD})(\text{H}_2\text{O})_n]^+$ complex should be observed at this wavelength and this is not the case.

The absorption spectrum of the intermediate with a maximum at 390 nm is very close to that of the salicylic acid phenoxyl radical ($\text{HSA}^\bullet$) [36]. The quantum yields of $\text{HSA}^\bullet$ formation (if this species is assumed to be formed in the primary photochemical process) and of Fe(III)–SA disappearance have the same value of 0.008, within experimental error (Table 3). Therefore, all findings presented above are in favor of Reaction (2) rather than Reaction (1).

To obtain additional evidence of the absence of $\text{HO}^\bullet$ formation upon excitation of the Fe(III)–SA complex under our experimental conditions, LPF experiments at 355 nm were performed in the presence of 1.2×10^{-2} M phenol. It is known that phenol reacts rapidly with $\text{HO}^\bullet$ (value of rate constant of $1.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) with formation of the long-lived phenoxyl radical ($\text{C}_6\text{H}_5\text{O}^\bullet$) which is rather stable in the presence of Fe(III) ions [37]. It was found (Fig. 3S) that addition of phenol influences the transient signal amplitude, neither at 530 nm (disappearance of the Fe(III)–SA complex), nor at 400 nm (characteristic absorption of $\text{C}_6\text{H}_5\text{O}^\bullet$). Therefore, direct LPF experiments give strong evidence that radiation at 355 nm is primarily absorbed by the “SAD-to-iron” CT band (or the corresponding excited state is effectively populated during processes of excitation energy relaxation). Subsequently, electron transfer from the coordinated ligand to the central ion (Reaction (2)) takes place with the formation of Fe(II) and of the corresponding $\text{SAD}^\bullet$ phenoxyl radical. Lower quantum yields of photoreduction of the investigated Fe(III)–SAD complexes in comparison with complexes of Fe(III) with aliphatic carboxylates could be explained by fast internal conversion of the corresponding “SAD-to-iron” excited state to the ground state [16,38]. This

process prevents formation of the long lived radical pair as observed for aliphatic carboxylates [33].

Finally, It is worth noting that quantum yields of disappearance of Fe(III)–SAD complexes (Φ_{RLP355} , Φ_{CI365} , Table 3) measured at longer irradiation times (i.e., after all fast processes came to an end) are higher than the primary ones measured by LPF experiments (Φ_{LFP355} , Table 3). This fact indicates the existence of a reaction between $\text{SAD}^\bullet$ and the initial complex occurring at time scales $> 50 \mu\text{s}$ and leading to additional formation of Fe(II) and oxidized ligand (SAD_{ox}):



It is also probable that SAD_{ox} can in turn react with Fe(III) ions leading to additional Fe(II) production. Several Fe(III) reducing intermediates of SAD oxidation have been identified by HPLC and LC–MS analyses [17]. Indeed, taking into account concentrations of $\text{SAD}^\bullet$ ($\approx 10^{-6}$ M) and Fe(III)–SAD ($\approx 5 \times 10^{-4}$ M) in flash experiments and typical rate constants of radical self-reaction ($\approx 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [36,37]) and reaction with Fe(III) ions ($\approx 10^7 \text{ M}^{-1} \text{ s}^{-1}$ [37]), it can be estimated that more than 80% of $\text{SAD}^\bullet$ could decay in Reaction (5) with a characteristic lifetime of about $200 \mu\text{s}$.

Our findings in favor of the predominance of Reaction (2) appear to be in contradiction with the results recently published [17] indicating that $\text{HO}^\bullet$ formation occurred upon excitation of the “water-to-iron” CT band of Fe(III)–SAD complexes under polychromatic irradiation at $\lambda > 300$ nm (Reaction (1)). The different conclusions reached in the two studies could result from the different irradiation conditions, polychromatic irradiation at $\lambda > 300$ nm in [17] and monochromatic excitation at 355 nm in this work. It is indeed highly probable that the “water-to-iron” CT band overlaps with the “SAD-to-iron” CT band in the spectral region 300–400 nm (note that both $\text{FeOH}_{\text{aq}}^{2+}$ and $\text{Fe}_{\text{aq}}^{3+}$ complexes exhibit a tail of LMCT absorption band at $\lambda > 300$ nm [34]). Therefore, the contribution of shorter irradiation wavelengths when using a polychromatic light source [17] could be favorable to the excitation of the “water-to-iron” CT band and to $\text{HO}^\bullet$ formation.

3.4. Environmental meaning of direct excitation of Fe(III)–SADs complexes

Our results demonstrate that irradiation of 1:1 Fe(III)–SAD complexes in the UV–A spectral region in aqueous solution at pH 3 leads to rather ineffective photolysis with the generation of Fe(II) and corresponding SAD radicals. This is in good agreement with published results [6,9], demonstrating mostly negative effects of SAD complexation on photo-Fenton processes due to a lower efficiency of Fe(III) photoreduction in comparison with ferric aqua complexes. Under environmentally relevant conditions (pH 6–8, low Fe(III) content), pH would affect complex formation and, depending on the relative concentrations of Fe(III) and SADs, complexes of higher stoichiometries (1:2 or 1:3) might be formed. The photochemistry of these complexes could differ from that observed for ferric complexes with 1:1 stoichiometry. Another important factor affecting the efficiency of the photolysis of Fe(III)–SAD complexes is the excitation wavelength. The decrease of the quantum yield of Fe(III) photoreduction with increasing irradiation wavelength is a rather typical feature of Fe(III)–complexes photochemistry [39]. It was shown in particular that Fe(III)–SAD complexes are inert upon excitation of the LMCT bands involving the organic ligand, i.e., upon irradiation in the visible spectral region that represents most of the solar spectrum [17]. Moreover, different CT bands of the complexes (“water-to-iron” or/and “SAD-to-iron”) may be excited depending on the irradiation wavelength in the UV spectral region. Albeit by

different mechanisms, both excitation processes would lead to Fe(II) production and SAD oxidation products in the presence of molecular oxygen. However, excitation into the “water-to-iron” CT band produces HO[•], a highly efficient oxidizing species that initiates the degradation of most organic compounds.

Further systematic studies of the influence of the excitation wavelength, ligand to metal molar ratio and oxygen content on the quantum yields of Fe(II) and HO[•] formation and on the nature of the SAD oxidation products, combined with quantum-chemistry calculations of the properties of possible Fe(III)–SAD excited states, are needed to clarify the photochemistry of these environmentally important compounds. However, from the results obtained in this work and previously published data, it may be concluded that sunlight photolysis of Fe(III)–SAD complexes cannot be an effective way for degradation of SADs in natural water systems.

4. Conclusions

Fe(III) complexes with salicylic acid (SA) derivatives of 1:1 stoichiometry (Fe(III)–SAD) exhibit good photochemical stability upon 355 nm excitation. No evidence of hydroxyl radical (HO[•]) formation was observed in LPF experiments so that the primary photoprocess in the excited complex was assumed to be an electron transfer from coordinated SAD to the Fe(III) ion leading to formation of Fe(II) and the corresponding SAD[•] radical. Quantum yields of photolysis for all complexes are rather low and do not exceed 0.01, in agreement with the low quantum yields of phenoxy radicals formation observed in LPF studies. SADs containing electron-withdrawing groups (4-NSA, 5-NSA, 5-SSA) exhibited the smallest photolysis quantum yields, whereas the highest values were observed for SA and SADs containing electron-donating groups (4-HSA, 6-HSA). These findings are in agreement with ultrafast back electron transfer observed in femtosecond experiments with Fe(III)–SADs complexes [16,38]. Hence, sunlight photolysis of Fe(III)–SAD complexes can only represent a very minor pathway of oxidative degradation of SADs in natural water systems. Probably, enhancement of SADs degradation could be obtained: (i) by direct excitation of SADs in the presence of Fe(III) ions, resulting in a redox process due to electron transfer from the triplet excited states of SADs to the Fe(III)–SAD complexes [14] or (ii) by HO[•] formation resulting from excitation of the “water-to-iron” CT band at short enough wavelength in the UV [17].

Acknowledgement

The work was financially supported by the Russian Foundation for Fundamental Research (grants 12-03-00482_a, 14-03-00692_a, 14-03-31003_mol_a).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jphotochem.2015.03.018>.

References

- [1] E.M. Thurman, *Organic Geochemistry of Natural Waters*, Martinus Nijhoff/Dr W. Junk Publisher (Kluwer Academic Publishers Group), Dordrecht, Boston, Lancaster, 1985, pp. 610.
- [2] B. Voelker, F.M.M. Morel, B. Sulzberger, Iron redox cycling in surface waters: effects of humic substances and light, *Environ. Sci. Technol.* 31 (1997) 1004–1011.
- [3] H. Gao, R.G. Zepp, Factors Influencing photoreactions of dissolved organic matter in a coastal river of the southeastern United States, *Environ. Sci. Technol.* 32 (1998) 2940–2946.
- [4] C.J. Miles, P.L. Brezonik, Oxygen consumption in humic-colored waters by a photochemical ferrous-ferric catalytic cycle, *Environ. Sci. Technol.* 15 (1981) 1089–1095.
- [5] L.H. Keith, Identification of organic compounds in unbleached treated kraft paper mill waste waters, *Environ. Sci. Technol.* 10 (1976) 555–564.
- [6] D. Nichela, M. Haddou, F. Benoit-Marquie, M.-T. Maurette, E. Oliveros, F.S. Garcia Einschlag, Degradation kinetics of hydroxy and hydroxynitro derivatives of benzoic acid by Fenton-like and photo-Fenton techniques: a comparative study, *Appl. Catal. B Environ.* 98 (2010) 171–179.
- [7] Y. Kamaya, Y. Fukaya, K. Suzuki, Acute toxicity of benzoic acids to the crustacean *Daphnia magna*, *Chemosphere* 59 (2005) 255–261.
- [8] J.J. Pignatello, E. Oliveros, A. Mackay, Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, *Crit. Rev. Environ. Sci. Technol.* 36 (2006) 1–84.
- [9] A. Goi, Y. Veressina, M. Trapido, Degradation of salicylic acid by Fenton and modified Fenton treatment, *Chem. Eng. J.* 143 (2008) 1–9.
- [10] L. Wang, C. Zhang, H. Mestankova, F. Wu, N. Deng, G. Pan, M. Bolte, G. Mailhot, Photoinduced degradation of 2,4-dichlorophenol in water: influence of various Fe(III) carboxylates, *Photochem. Photobiol. Sci.* 8 (2009) 1059–1065.
- [11] A.P.S. Batista, B.A. Cottrell, R.F.P. Nogueira, Photochemical transformation of antibiotics by excitation of Fe(III)-complexes in aqueous medium, *J. Photochem. Photobiol. A Chem.* 274 (2014) 50–56.
- [12] Z. Wang, Y. Guo, Z. Liu, X. Feng, Y. Chen, T. Tao, Catechin as a new improving agent for a photo-Fenton-like system at near-neutral pH for the removal of inderal, *Photochem. Photobiol. Sci.* 14 (2015) 473–480.
- [13] F.J. Stevenson, *Humus Chemistry: Genesis, Composition, Reactions*, 2nd ed., J. Wiley & Sons, New York, 1994, pp. 512.
- [14] I.P. Pozdnyakov, V.F. Plyusnin, V.P. Grivin, D.Yu. Vorobyev, N.M. Bazhin, E. Vauthey, Photolysis of sulfosalicylic acid in aqueous solutions over a wide pH range, *J. Photochem. Photobiol. A Chem.* 181 (2006) 37–43.
- [15] I.P. Pozdnyakov, V.F. Plyusnin, V.P. Grivin, D.Yu. Vorobyev, N.M. Bazhin, S. Pagés, E. Vauthey, Photochemistry of Fe(III) and sulfosalicylic acid aqueous solutions, *J. Photochem. Photobiol. A Chem.* 182 (2006) 75–81.
- [16] I.P. Pozdnyakov, V.F. Plyusnin, N. Tkachenko, H. Lemmetyinen, Photophysics of Fe(III)–sulfosalicylic acid complexes in aqueous solutions, *Chem. Phys. Lett.* 445 (2007) 203–207.
- [17] D.A. Nichela, A. Donadelli, B. Caram, M. Haddou, F. Rodriguez Nieto, E. Oliveros, F.S. Garcia Einschlag, Iron cycling during the autocatalytic decomposition of benzoic acid derivatives by Fenton-like and photo-Fenton techniques, *Appl. Catal. B Environ.* 170 (2015) 312–321.
- [18] J.G. Calvert Jr., J.N. Pitts, *Photochemistry*, Wiley, New York, 1966, pp. 782.
- [19] J.C. Collette, *Ann. Chim. (France)* 5 (1960) 415.
- [20] K. Ogawa, N. Tobe, A spectrophotometric study of the complex formation between iron(III) and sulfosalicylic acid, *Bull. Chem. Soc. Jpn.* 39 (1966) 223–227.
- [21] N. Papadopoulos, A. Avranas, Dissociation of salicylic acid, 2,4-, 2,5- and 2,6-dihydroxybenzoic acids in 1-propanol–water mixtures at 25 °C, *J. Solution Chem.* 20 (1991) 293–300.
- [22] J.F.J. Dippy, S.R.C. Hughes, L.G. Bray, Chemical constitution and the dissociation constants of monocarboxylic acids. Part XIX. Dihydroxy- and dichloro-benzoic acids, *J. Chem. Soc. (1959)* 1717–1719.
- [23] L.H.J. Lajunen, R. Portanova, J. Piispanen, M. Tolazzi, Critical evaluation of stability constants for alpha-hydroxycarboxylic acid complexes with protons and metal ions and the accompanying enthalpy changes (V.6), *Pure Appl. Chem.* 69 (1997) 329–381.
- [24] L.G. Sillen, A.E. Martell, *Stability Constants of Metal-Ion Complexes*, The Chemical Society, Burlington House, 1964, pp. 549.
- [25] M.M. de Souza Sierra, K. Arend, A.N. Fernandes, M. Giovanela, B. Szpoganicz, Application of potentiometry to characterize acid and basic sites in humic substances: testing the BEST7 program with a weak-acid mixture, *Anal. Chim. Acta* 445 (2001) 89–98.
- [26] R. Aydin, U. Özer, N. Türkel, Potentiometric and spectroscopic determination of acid dissociation constants of some phenols and salicylic acids, *Turk. J. Chem.* 21 (1997) 428–436.
- [27] B.M. Lowe, D.G. Smith, Dissociation constant of 2,6-dihydroxybenzoic acid in water and in deuterium oxide at 25 °C, *J. Chem. Soc. Faraday Trans. 1* 169 (1973) 1934–1944.
- [28] M.S. Hosseini, S. Madarshahian, Investigation of charge transfer complex formation between Fe(III) and 2,6-dihydroxy benzoic acid and its applications for spectrophotometric determination of iron in aqueous media, *E-J. Chem.* 6 (2009) 985–992.
- [29] K.S. Lee, D.W. Lee, Anion exchange chromatography of salicylic acid and its derivatives, *Anal. Chem.* 46 (1974) 1903–1908.
- [30] A. Vyas, R.P. Mathur, pH-metric and thermodynamic studies of rare earth metal chelates, *J. Rare Earths* 27 (2009) 457–460.
- [31] V.M. Nurchi, T. Pivetta, J.I. Lachowicz, G. Crisponi, Effect of substituents on complex stability aimed at designing new iron(III) and aluminum(III) chelators, *J. Inorg. Biochem.* 103 (2009) 227–236.
- [32] A.L. Sobolewski, W. Domcke, Ab initio study of excited-state intramolecular proton dislocation in salicylic acid, *Chem. Phys.* 232 (1998) 257–265.
- [33] E.M. Glebov, I.P. Pozdnyakov, V.P. Grivin, V.F. Plyusnin, X. Zhang, F. Wu, N. Deng, Intermediates in photochemistry of Fe(III) complexes with carboxylic acids in aqueous solutions, *Photochem. Photobiol. Sci.* 10 (2011) 425–430.
- [34] H.-J. Benkelberg, P. Warneck, Photodecomposition of iron(III) hydroxo and sulfato complexes in aqueous solution: wavelength dependence of OH and SO₄^{•−} quantum yields, *J. Phys. Chem.* 99 (1995) 5214–5221.

- [35] C.B. Amphlett, G.E. Adams, B.D. Michael, Pulse radiolysis studies of deaerated aqueous salicylate solutions, *Radiation Chemistry*, in: E. Hart (Ed.), *Advances in Chemistry*, American Chemical Society, Washington, DC, 1968, pp. 231–250.
- [36] I.P. Pozdnyakov, Yu.A. Sosedova, V.F. Plyusnin, V.P. Grivin, N.M. Bazhin, Photochemistry of salicylate anion in aqueous solution, *Russ. Chem. Bull. Int. Ed.* 56 (2007) 1318–1324.
- [37] I.P. Pozdnyakov, Yu.A. Sosedova, V.F. Plyusnin, V.P. Grivin, D.Yu. Vorobyev, N.M. Bazhin, Optical spectra and kinetic characteristics of radicals formed upon the photolysis of aqueous solutions of a $\text{Fe}(\text{OH})_{\text{aq}}^{2+}$ complex and phenol, *Russ. Chem. Bull. Int. Ed.* 53 (2004) 2715–2722.
- [38] I.P. Pozdnyakov, A.A. Melnikov, N. Tkachenko, S.V. Chekalin, H. Lemmetyinen, V.F. Plyusnin, Ultrafast photophysical processes for $\text{Fe}(\text{III})$ -carboxylates, *Dalton Trans.* 43 (2014) 17590–17595.
- [39] J. Sima, J. Mankanova, Photochemistry of iron(III) complexes, *Coord. Chem. Rev.* 161 (1997) 161–189.