



## Photochemistry of Fe(III) and sulfosalicylic acid aqueous solutions

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### Abstract

Femtosecond and nanosecond laser flash photolysis was used to determine the photophysical and photochemical processes in aqueous solutions of Fe(III) ion and 5-sulfosalicylic acid (SSA) containing the FeSSA complex and the free ligand. Excitation of the FeSSA complex in the charge transfer band ( $\lambda_{\text{max}} = 505 \text{ nm}$ ) is followed by an ultrafast relaxation to the ground electronic state with two characteristic times of 0.26 and 1.8 ps. The shorter time constant is ascribed to internal conversion to the vibrationally hot electronic ground state of FeSSA and the 1.8 ps time constant is assigned to the vibrational cooling of the ground state. The UV irradiation of the solution (308 nm) leads to the excitation of both the free ligand and the FeSSA complex. The latter relaxes rapidly and the free ligand undergoes intersystem crossing to the triplet state. This system undergoes an irreversible photochemical reaction originating from an electron transfer ( $k = (9 \pm 2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) from the free ligand in the triplet state to the FeSSA complex. This electron transfer is accompanied by an energy transfer between these species ( $k = (1.3 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ).

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### 1. Introduction

Processes involving complexes of transition metal ions with organic acids are prominent among the photoreactions in natural water [1]. The photochemistry of these complexes with Fe(III) ions can contribute substantially to the balance of organic compounds in aqueous systems [2–9]. In recent works [10,11], we have studied the photochemistry of aqueous solutions of 5-sulfosalicylic acid (SSA), which refers to aromatic oxyacids and can serve as model compounds for investigating the photochemical properties of natural acids. The main photoactive form of SSA over a wide pH range (1–10) is the dianion ( $\text{HSSA}^{2-}$ ). Excitation of  $\text{HSSA}^{2-}$  (308 nm) leads to the population of the triplet state of the dianion ( $^1\text{HSSA}^{2-}$ ) and to the formation of the hydrated electron and of the  $\text{SSA}^{2\bullet-}$  radical anion. The latter two species are formed as results of two-photon process via the excited singlet state of  $\text{HSSA}^{2-}$ . In an acid medium, the

$\text{SSA}^{2\bullet-}$  radical anion and  $^1\text{HSSA}^{2-}$  are protonated to form the  $\text{HSSA}^{\bullet-}$  radical anion and  $^1\text{H}_2\text{SSA}^-$ , respectively.

In the present work, the photochemical and photophysical properties of aqueous solutions of Fe(III) ion and 5-sulfosalicylic acid (SSA) containing the FeSSA complex and the free ligand were studied. The origin and the spectral and kinetic parameters of the primary intermediates have been determined. A study of such model systems can be highly important for determining photochemical processes in natural water which contains complexes of transition metals with organic acids.

### 2. Experimental

For measurements on a microsecond time scale, we employed a set-up for laser flash photolysis using excimer XeCl laser excitation (308 nm) with a pulse duration of 15 ns and a mean pulse energy of 20 mJ [11]. Ultrafast processes were investigated by femtosecond laser flash photolysis on a set-up developed in the Department of Physical Chemistry of the University of Geneva [12]. Briefly, excitation was performed by a standard 1-kHz amplified Ti:Sapphire system (Spitfire, Spectra-Physics)

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connected to an optical parametrical amplifier in noncollinear configuration which generates ultrashort (70 fs) pulses tunable between 480 and 700 nm. For the experiments reported here, both the pump and probe wavelengths were centered at 530 nm.

The absorption spectra were recorded using an HP 8453 (Hewlett Packard) spectrophotometer. The laser pulse power was estimated using solutions of anthracene in benzene as a relative actinometer. The extinction coefficient of anthracene T–T absorption (TTA) in this solvent at 431 nm amounts to  $\varepsilon = 4.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  and the triplet yield is  $\phi_T = 0.53$  [13].

5-Sulfosalicylic acid (99+%, Aldrich) and Fe(III) perchlorate hydrate (Aldrich) were employed without further purification. The solutions were prepared using bidistilled water. FeSSA complex were prepared by mixing of stock solutions of Fe(III) perchlorate and SSA. Concentration of the complex was calculated from absorbance at 505 nm using known literature absorption coefficient of FeSSA  $\varepsilon(505 \text{ nm}) = 1.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  [14,15]. Working concentrations of Fe(III) ions and SSA were usually about  $10^{-4}$  and  $3 \times 10^{-4}$  M, accordingly. Unless otherwise specified, all experiments were carried out with oxygen-free samples at pH 3 and 298 K in a 1 cm optical cell. Oxygen was removed by bubbling solutions with gaseous argon.

### 3. Results and discussion

#### 3.1. Ultrafast processes in the FeSSA complex

Depending on the pH, the concentrations of Fe(III) ions and sulfosalicylic acid, complexes with one, two, and three SSA molecules in the coordination sphere of Fe(III) ion can exist in aqueous solutions [16]. In the present work, we have chosen conditions that correspond to reagent concentrations in natural water and at which the FeSSA monocomplex is the main form of Fe(III) ion. The FeSSA solutions are violet due to a charge transfer (CT) band with a maximum at 505 nm (Fig. 1). In the UV region, FeSSA complex displays a stronger

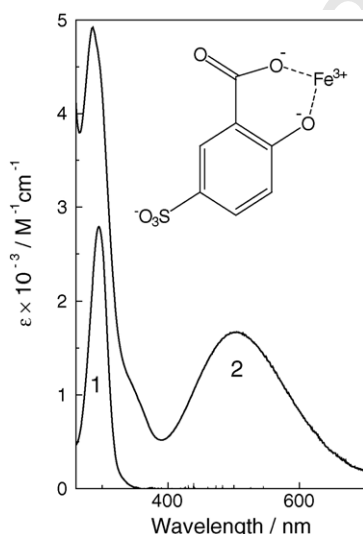


Fig. 1. Optical absorption spectra of HSSA<sup>2-</sup> dianion (1) and FeSSA complex (2) in aqueous solution.

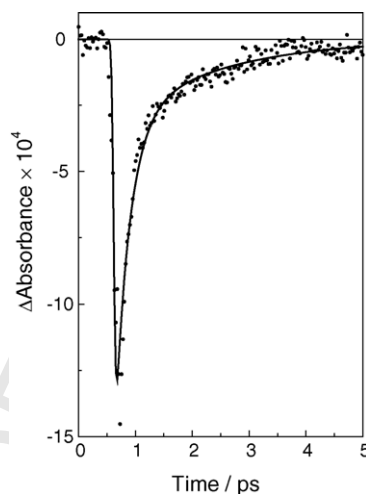


Fig. 2. Time profile of the bleach at 530 nm after excitation of the FeSSA complex by a femtosecond pulse (530 nm). Solid line: best two-exponential fit after reconvolution with the instrument response function. Cell thickness: 1 mm, [FeSSA] =  $3.7 \times 10^{-3}$  M, [SSA] =  $4.7 \times 10^{-3}$  M, pH 2.1.

band ( $\lambda_{\text{max}} = 286 \text{ nm}$ ). The absorption band with a maximum at 297 nm (Fig. 1) is typical of the free noncoordinated ligand.

Under stationary irradiation in the UV (308 nm) and visible region (530 nm), the FeSSA complex does not exhibit any photochemical activity. A long irradiation with light in these regions fails to cause any changes in the optical absorption spectrum of the solution.

Let us consider the processes that occur under the flash excitation of FeSSA complex in the long wavelength absorption band. Just after excitation of the complex with a femtosecond pulse ( $\lambda_{\text{ex}} = 530 \text{ nm}$ ), a bleach of the absorption at 530 nm was observed (Fig. 2). The absorption of the complex is almost completely recovered after about 5 ps, which is in fair agreement with a photochemical stability of the complex under irradiation in the visible region. The analysis of this time profile by iterative reconvolution of a biexponential function with the instrument response function gives the time constants  $\tau_1 = 260 \text{ fs}$  and  $\tau_2 = 1.8 \text{ ps}$ .

Such biphasic dynamics is rather typical for ultrafast ground state recovery upon CT excitation [17,18]. Excitation in the CT band is followed by an ultrafast internal conversion to the vibrationally hot electronic ground state, which is then thermalized by vibrational cooling. Therefore the 260 fs component is ascribed to the internal conversion while the 1.8 ps is assigned to the vibrational cooling.

#### 3.2. The photochemistry of FeSSA in the presence of free ligand

Although FeSSA complex itself does not exhibit any photochemical activity, stationary irradiation (excimer XeCl laser,  $\lambda_{\text{ex}} = 308 \text{ nm}$ ) of solutions containing both complex and free ligand initiates a rather effective disappearance of the FeSSA complex absorption (Fig. 3). The flash excitation (excimer XeCl laser,  $\lambda_{\text{ex}} = 308 \text{ nm}$ ) is followed by the buildup of the absorption band with a maximum at 440 nm (Fig. 4). A study of

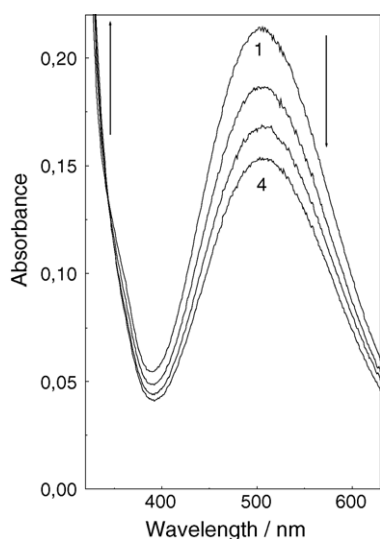


Fig. 3. Stationary photolysis (XeCl laser, 308 nm) of an aqueous solutions of FeSSA ( $1.3 \times 10^{-4}$  M) and SSA ( $3.0 \times 10^{-4}$  M). (1–4) Absorption spectra of the solution after 0, 50, 100, and 150 pulses, respectively.

the spectroscopy and photochemistry of SSA aqueous solutions indicates that this band is due to the absorption of  ${}^1\text{H}_2\text{SSA}^-$  [11], which results from the absorption of light by the free, non-coordinated  $\text{HSSA}^{2-}$ . When  $\text{HSSA}^{2-}$  is excited into the singlet  $\text{S}_1$  state (308 nm), the triplet state of  ${}^1\text{HSSA}^{2-}$ , which has a T–T absorption band with a maximum at 470 nm, is populated with a quantum yield of  $\varphi_T = 0.34$  [11]. In acid solution (pH 3), the  ${}^1\text{HSSA}^{2-}$  is rapidly protonated to form the  ${}^1\text{H}_2\text{SSA}^-$ , whose band shifts to 440 nm and has an absorption coefficient of  $6.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  [11].

The absorption of  ${}^1\text{H}_2\text{SSA}^-$  decays within about 20  $\mu\text{s}$  with a simultaneous buildup of a broad bleaching band (negative optical density) at 505 nm (Fig. 4) caused by the decreased FeSSA

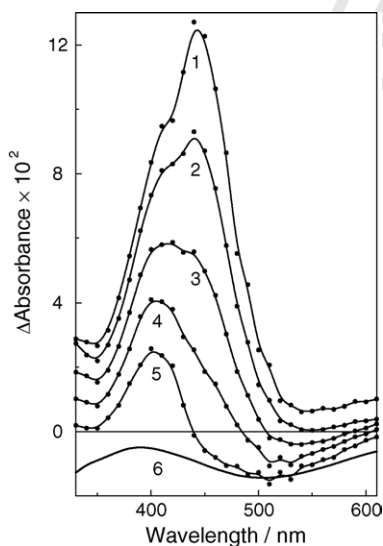


Fig. 4. Transient absorption spectra after excitation at 308 nm of an aqueous solution of FeSSA complex ( $6.8 \times 10^{-5}$  M) and SSA ( $2.9 \times 10^{-4}$  M). (1–5) The spectra after 0, 1.6, 4, 8, and 48  $\mu\text{s}$  after the pulse; (6) inverted absorption spectrum of FeSSA complex.

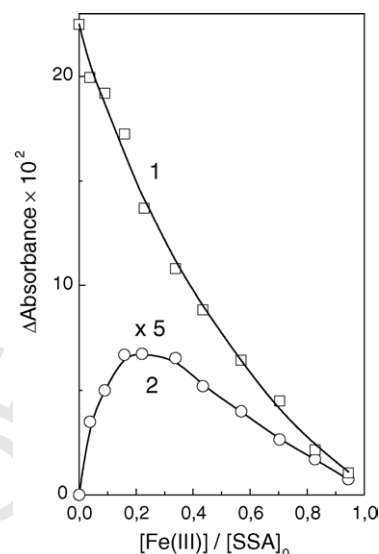


Fig. 5. Dependence of  ${}^1\text{H}_2\text{SSA}^-$  absorption at 440 nm after the excitation pulse (1) and values of the bleaching at 505 nm after 50  $\mu\text{s}$  (2) on the  $[\text{Fe(III)}]/[\text{SSA}]_0$  ratio. The concentration of SSA in all cases was  $2.9 \times 10^{-4}$  M; only the concentration of Fe(III) was varied.

absorption. After the disappearance of  ${}^1\text{H}_2\text{SSA}^-$  (50  $\mu\text{s}$ ), the spectrum still contains an absorption band at 400 nm (Fig. 4), which belongs to the  $\text{HSSA}^{2\bullet-}$  radical [11]. For this radical, we get  $\text{p}K_a = 3.1$  [11]. Therefore, at pH 3, it is partially (45%) in the deprotonated form ( $\text{SSA}^{2\bullet-}$ ).

The relation between the  ${}^1\text{H}_2\text{SSA}^-$  T–T absorption band (440 nm) and the excitation of the free ligand is confirmed by a decrease of the band intensity with increasing concentration of the Fe(III) ion. Fig. 5 shows the dependence of amplitude of the optical density at 440 nm ( $\Delta D^{440}$ ) after the excitation pulse on the  $[\text{Fe(III)}]/[\text{SSA}]_0$  ratio. When this ratio is close to unity, and the concentration of the noncoordinated ligand is minimal, the T–T absorption band of  ${}^1\text{H}_2\text{SSA}^-$  actually vanishes. The amount of the FeSSA complex disappearing 50  $\mu\text{s}$  after excitation, determined from the amplitude of the bleaching at 505 nm ( $\Delta D^{505}$ ), passes through a maximum with the ratio of concentrations  $[\text{Fe(III)}]/[\text{SSA}]_0 \approx 1:4$  and tends to zero in the absence of a free ligand in the solution (Fig. 5). These data clearly indicate that under irradiation in the UV region, the FeSSA complex disappears because of reactions with the intermediates formed upon photolysis of the noncoordinated ligand.

### 3.3. The mechanism of FeSSA photoreduction

As mentioned above, excitation (308 nm) of the free ligand (the  $\text{HSSA}^{2-}$ ) at pH 3 leads to the formation of  ${}^1\text{H}_2\text{SSA}^-$ . At high laser pulse intensity, a second photon absorption by the excited singlet state of  $\text{HSSA}^{2-}$  results in the photoionization of this ion with the appearance of the hydrated electron and of  $\text{HSSA}^{\bullet-}$  radical anion [10,11]. In acid medium, the hydrated electron converts into a hydrogen atom ( $k(e_{\text{aq}}^- + \text{H}^+) = 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  [19]).

Thus, the species that can react with the FeSSA complex in oxygen-free solutions at pH 3, are  ${}^1\text{H}_2\text{SSA}^-$  and the hydro-

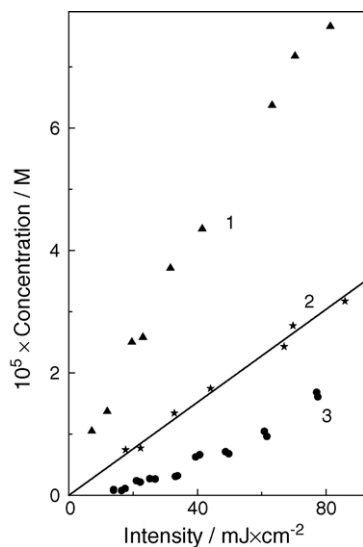


Fig. 6. Dependence on the laser pulse intensity: (1) amount of FeSSA disappeared at 50  $\mu\text{s}$  after laser pulse, (2) initial concentration of  $^1\text{H}_2\text{SSA}^-$ , (3) initial concentration of hydrated electron (flash photolysis of  $\text{HSSA}^{2-}$  at pH 10), respectively. (1–2)  $[\text{FeSSA}] = 1.2 \times 10^{-4} \text{ M}$ ,  $[\text{SSA}] = 3.1 \times 10^{-4} \text{ M}$ . (3)  $[\text{SSA}] = 1.3 \times 10^{-4} \text{ M}$ , pH 10. All data normalized to 100% absorption of non-coordinated  $\text{HSSA}^{2-}$  dianion. Solid line: best linear fit of (2).

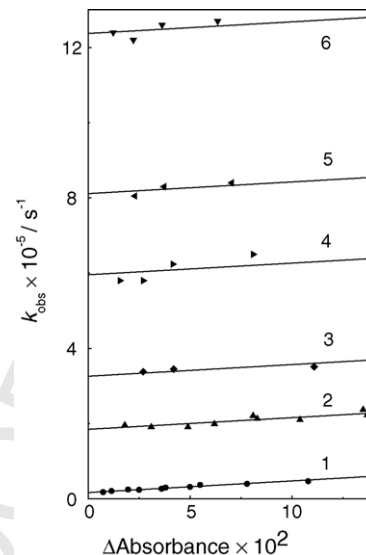


Fig. 7. Dependence of the  $k_{\text{obs}}$  of  $^1\text{H}_2\text{SSA}^-$  disappearance on the initial absorption amplitude at 440 nm (variation of laser pulse intensity) at different concentrations of FeSSA complex. (1–6) 0, 0.7, 1.4, 2.7, 3.8, and  $5.5 \times 10^{-4} \text{ M}$  of FeSSA, the initial concentration of SSA in all cases was  $1.3 \times 10^{-3} \text{ M}$ ; cell thickness: 2 mm. The solid lines are the best linear fits of Eq. (1) with  $2k_3 = 1.8 \pm 0.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and  $\epsilon^{440} = 6.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ .

gen atom. The yield of  $^1\text{H}_2\text{SSA}^-$ , i.e., the product of one-photon process, depends linearly on the laser pulse intensity. The appearance of electron (and hydrogen atom, accordingly) from a two-photon process leads to a quadratic dependence of the yield of these species on the laser pulse intensity [10]. Fig. 6 presents the dependence of concentrations of  $^1\text{H}_2\text{SSA}^-$  just after the pulse and the amount of disappearing FeSSA after 50  $\mu\text{s}$  on the laser pulse intensity. At the same figure dependence of initial concentration of hydrated electron on the laser pulse intensity obtained by flash photolysis of  $\text{HSSA}^{2-}$  solutions at pH 10 is also presented. For comparison all data was normalized to 100% absorption of noncoordinated  $\text{HSSA}^{2-}$  dianion.

The hydrated electron appears in the process of two-photon ionization of  $\text{HSSA}^{2-}$  at pH 3 as well as at pH 10. This process does not depend on pH of aqueous solution so the primary yield of the electron at pH 3 should be the same as at pH 10. It is clearly seen, that yield of hydrated electron (hydrogen atom) is not sufficient to provide observed changes of FeSSA concentration and one can neglect reaction of the complex with this species at pulse energy less than 40  $\text{mJ}/\text{cm}^2$ . In case of  $^1\text{H}_2\text{SSA}^-$  and the amount of disappearing FeSSA, we observe the practically linear dependence on pulse intensity, which indicates  $^1\text{H}_2\text{SSA}^-$  (the product of one-photon process) as a partner in the reaction with the complex. Indeed, quenching of  $^1\text{H}_2\text{SSA}^-$  by the FeSSA is clearly demonstrated by increase of the observed rate constant ( $k_{\text{obs}}$ ) of T–T absorption disappearance at 440 nm with increasing the concentration of the complex in the solution (Fig. 7).

In this case of quenching the observed rate constant of T–T absorption disappearance at 440 nm can be written as

$$k_{\text{obs}} = (k_2 + k_q[\text{FeSSA}]) + \frac{2k_3\Delta D^{440}}{\epsilon^{440}} \quad (1)$$

where  $k_2 = (1.7 \pm 0.2) \times 10^4 \text{ s}^{-1}$  and  $2k_3 = (1.8 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  are the rate constants of  $^1\text{H}_2\text{SSA}^-$  disappearance upon the first and second order reactions (2) and (3), respectively [11],  $k_q$  = rate constant of  $^1\text{H}_2\text{SSA}^-$  quenching by the complex FeSSA,  $\Delta D^{440}$  = optical density of  $^1\text{H}_2\text{SSA}^-$  absorption at 440 nm just after the pulse and  $\epsilon^{440}$  = absorption coefficient of the triplet state at 440 nm:



The first order reaction (2) is probably due to the presence of either residual oxygen with a concentration of  $\sim 10^{-6} \text{ M}$  or other impurities that quench the triplet state, as it has lifetime about 0.6 s in the absence of the quenchers [10]. Reaction (3) is the T–T annihilation, which leads to the appearance of “delayed” fluorescence for many systems [20].

Fig. 7 represents good linear fits of experimental data by Eq. (1) for all concentration of FeSSA used. The dependence of the intercepts of the linear plots in Fig. 7 on the FeSSA concentration allows the determination of a rate constant for  $^1\text{H}_2\text{SSA}^-$  quenching by the complex ( $k_q = (2.2 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ).

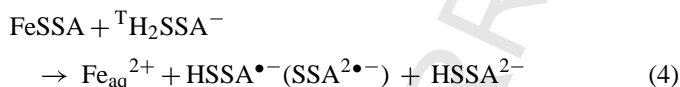
The quenching of the triplet states of organic molecules by coordinated compounds was first revealed in 1958 [21]. It is assumed that the quenching can follow two mechanisms related to either energy or electron transfer [22]. For example, the rate constant of energy transfer to acetylacetonate complexes, Cr(III) and Ni(II), increases until reaching a plateau (below  $k_{\text{diff}}$ ), if the energy of the donor triplet state ( $E_T$ ) exceeds the energy of the lower excited electronic state of the complex ( $^2E_g$  for Cr(III)) [23,24]. A new jump of the rate constant is observed when the triplet energy coincides with higher excited states of the complex.

The quenching of triplet states of organic molecules by lanthanide complexes is accompanied by metal ion luminescence [25]. Such sensitized luminescence is considered a direct evidence of energy transfer. For lanthanide complexes, the energy transfer rate constants were also observed to sharply vary with changes in the triplet energy of the donor [25]. The theory of energy transfer between the triplet state of organic donor and coordination compounds is given in [26].

More recently, systems where both energy and electron transfer occurs in competition have been found. For example, it was shown by Wilkinson and Tsiamis [27] that when the triplet states are quenched by the Cr(hfac)<sub>3</sub> complex, the rate constant is large ( $\sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) even though the donor triplet energy is substantially lower than the energy of the lower excited  $^2E_g$  state of the quencher. The analysis shows that for almost all the donors used [27],  $\Delta G_{el} \leq 0$  and electron transfer is operative. In the study of Chow et al. [28], the authors have studied the quenching of the triplet states of aromatic ketones by the Ni(acac)<sub>2</sub> complex. The appearance of ESR bands of the Ni(I) ion during the photolysis of solutions containing Ni(acac)<sub>2</sub> and benzophenone confirms the occurrence of electron transfer from the triplet state of the donor to the complex. The quenching rate constants are close to the diffusion limit and for various donors are in the range of  $(0.2\text{--}6) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

The complex of bivalent copper, Cu(acac)<sub>2</sub>, exhibits a d–d transition in the range of  $10,000 \text{ cm}^{-1}$  and effectively quenches the triplet states of donors with higher energy [29,30]. For the lower  $E_T$  values, the constant decreases by two to three orders of magnitude. In this case, the quenching is caused by energy transfer. However, the Cu(hfac)<sub>2</sub> complex with the same d–d state energy effectively quenches by electron transfer donors with a very low triplet energy such as pentacene ( $E_T = 8000 \text{ cm}^{-1}$ ,  $k = 0.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) or  $\beta$ -carotene ( $E_T = 6300 \text{ cm}^{-1}$ ,  $k = 0.41 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ).

Thus, the quenching of  $^1\text{H}_2\text{SSA}^-$  can occur by both electron transfer (4) leading to FeSSA reduction and energy transfer (5). In the latter case, the physical quenching causes no changes in the oxidation state of the Fe(III) ion:



In reaction (4), the Fe(II) ion is given in the hydrated form because it fails to form complexes with sulfosalicylic acid in an acid medium [31]. In conditions when  $^1\text{H}_2\text{SSA}^-$  disappears predominantly in reactions (4) and (5) (i.e.,  $(k_4 + k_5)[\text{FeSSA}] \gg (k_2 + 2k_3[^1\text{H}_2\text{SSA}^-])$ ) one should observe linear dependence of  $\Delta D^{505}$  (decrease in optical density at 505 nm after 50  $\mu\text{s}$  due to the disappearance of FeSSA) on  $\Delta D^{440}$  (optical density of  $^1\text{H}_2\text{SSA}^-$  absorption just after the pulse):

$$\Delta D^{505} = \frac{\varepsilon^{505}}{\varepsilon^{440}} \left( \frac{k_4}{k_4 + k_5} \right) \Delta D^{440} \quad (6)$$

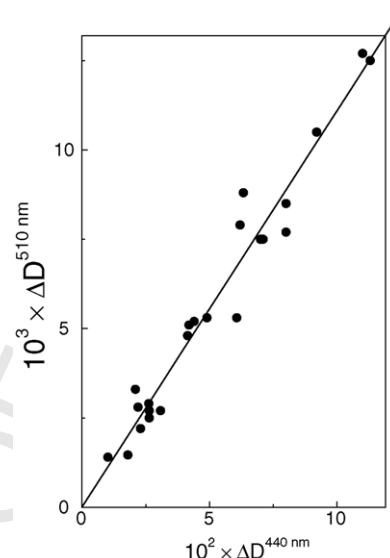


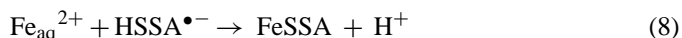
Fig. 8. Dependence of  $\Delta D^{505}$  (the amount of disappearing FeSSA complex at 50  $\mu\text{s}$ ) on  $\Delta D^{440}$  (the initial amplitude of  $^1\text{H}_2\text{SSA}^-$  absorption at 440 nm). The solid line: the best fit of Eq. (6) with  $k_4 = 9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ .

where  $\varepsilon^{440} = 6.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  [11] and  $\varepsilon^{505} = 1.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  [14,15] are the absorption coefficients of  $^1\text{H}_2\text{SSA}^-$  at 440 nm and of the FeSSA complex at 505 nm, respectively. The sum of constants  $(k_4 + k_5) = (2.2 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  has been determined above from the change in the rate of disappearance of  $^1\text{H}_2\text{SSA}^-$  absorption in the presence of FeSSA. Thus, in Eq. (6), the  $k_4$  value is the only unknown. The best linear fit of Eq. (6) to the experimental dependence of  $\Delta D^{505}$  on  $\Delta D^{440}$  (Fig. 8) was obtained with  $k_4 = (9 \pm 2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . In this case,  $k_5 = (1.3 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , that means practically equal probability of electron and energy transfer from the  $^1\text{H}_2\text{SSA}^-$  to the complex. The quantum yield of FeSSA disappearance  $\varphi(-\text{FeSSA}) = \varphi_T(k_4/(k_4 + k_5)) = 0.14 \pm 0.04$  is in fair agreement with that calculated from the initial part of the dependence of  $\Delta D^{505}$  on the laser pulse intensity  $\varphi(-\text{FeSSA}) = 0.15 \pm 0.03$  (Fig. 6) using Eq. (7):

$$\varphi(-\text{FeSSA}) = \frac{\Delta D^{505} V_{\text{irr}} N_A}{\varepsilon^{505} l N} \quad (7)$$

where  $l$  is the length of optical cell,  $V_{\text{irr}}$  the irradiated volume,  $N_A$  the Avogadro constant and  $N$  is the number of quanta absorbed by noncoordinated dianion of SSA. This agreement gives an additional evidence that FeSSA complex disappears mainly in reaction with  $^1\text{H}_2\text{SSA}^-$ .

It worth noting, that stationary measurements (excimer XeCl laser,  $\lambda_{\text{ex}} = 308 \text{ nm}$ ) of the quantum yield of FeSSA disappearance give  $\varphi_{\text{st}} \approx 0.03$ . A substantial decrease in  $\varphi_{\text{st}}$  as compared with the quantum yield of the complex disappearance in flash experiments is determined by reactions between the Fe(II) ion and the  $\text{HSSA}^{\bullet-}$  and  $\text{SSA}^{2\bullet-}$  radical anions:



291 These reactions cause a reverse reduction of a certain amount  
292 of the FeSSA complex thus decreasing the final quantum yield.  
293 On the other hand, the disappearance of the FeSSA complex  
294 absorption upon stationary photolysis (Fig. 3) indicates that  
295 some  $\text{SSA}^{2\bullet-}$  and  $\text{HSSA}^{\bullet-}$  radical anions disappear in other  
296 reactions, e.g., recombination processes [11]:



299 Despite a small Onsager radius for water ( $r = e^2/\epsilon kT \approx 6.7 \text{ \AA}$ ),  
300 the existence of charges in reacting species can give large rate  
301 constants for reactions of the species with the different charges,  
302 (8) and (9), as compared with reactions of the partners with the  
303 same charges, (10) and (11). This difference in constants can  
304 decrease the quantum yield in stationary measurements.

305 The formation of the absorbing recombination products of  
306 the  $\text{HSSA}^{\bullet-}$  and  $\text{SSA}^{2\bullet-}$  radicals in the nearest UV region  
307 provides the existence of isosbestic points at 311 and 344 nm  
308 upon the stationary photolysis of FeSSA (Fig. 3). In the pho-  
309 tolysis of the noncoordinated  $\text{HSSA}^{2-}$  anion, 3-(2-carboxy-  
310 4-sulfo-phenoxy)-sulfosalicylic acid is the main photoreaction  
311 product [11]. Irradiating the FeSSA and  $\text{HSSA}^{2-}$  solutions  
312 is likely to give the same final product (the same origin of  
313 intermediates).

### 314 3.4. Energy and electron transfer processes in the 315 ${}^1\text{H}_2\text{SSA}^-$ –FeSSA pair

316 The energy of the  ${}^1\text{H}_2\text{SSA}^-$ , determined from the phos-  
317 phorescence spectrum in aqueous solutions, amounts to  
318  $26,100 \text{ cm}^{-1}$  (383 nm) [32]. Thus, energy transfer to the excited  
319 state of the complex, which are related to absorption bands with a  
320 maximum with  $\lambda > 383 \text{ nm}$ , can be realized. For the FeSSA com-  
321 plex, the charge transfer (CT) band with a maximum at 505 nm,  
322 i.e., with an energy much lower than  $E({}^1\text{H}_2\text{SSA}^-)$ , can provide  
323 a high energy transfer constant. The energy transfer from the  
324  ${}^1\text{H}_2\text{SSA}^-$  fails, however, to cause a photoreduction of the com-  
325 plex due to its ultrafast relaxation from the excited to the ground  
326 electronic state.

327 The photoreduction of the complex is due to the electron  
328 transfer in the  ${}^1\text{H}_2\text{SSA}^-$ –FeSSA pair with the rate constant  
329  $k_4 = 9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , which is six times as small as the diffusion  
330 limit ( $k_{\text{diff}} = 5.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in water). The redox potentials  
331 of both the FeSSA complex and the SSA dianion are unavail-  
332 able. Therefore, the  $k_4$  value cannot be used to determine the  
333 electron transfer parameters (the change in free energy upon  
334 electron transfer ( $\Delta G_{\text{el}}$ ), the energy of the medium reorganiza-  
335 tion). It is worth noting, however, that usually, with  $\Delta G_{\text{el}} \approx 0$ ,  
336 the electron transfer rate constant is smaller by an order of mag-  
337 nitude than the diffusion limit and only with  $\Delta G_{\text{el}} \approx -0.5 \text{ eV}$ , it  
338 approaches  $k_{\text{diff}}$  [20]. This holds for both the Marcus theory and  
339 the Rehm–Weller model [33,34]. These theories are different at  
340 largely negative values of  $\Delta G_{\text{el}}$  (the inverted Marcus region).  
341 Thus, for the  ${}^1\text{H}_2\text{SSA}^-$ –FeSSA pair, the case which is close to  
 $\Delta G_{\text{el}} \leq 0$  is realized.

## 4. Conclusions

342  
343 Femtosecond laser flash photolysis shows that excitation  
344 of the FeSSA complex in the CT band ( $\lambda_{\text{max}} = 505 \text{ nm}$ ,  
345  $\lambda_{\text{ex}} = 530 \text{ nm}$ ) leads to an ultrafast relaxation processes with two  
346 characteristic times 260 fs and 1.8 ps. The shorter time constant  
347 is likely to correspond to the internal conversion to the vibra-  
348 tionally hot electronic ground state of FeSSA and the 1.8 ps time  
349 constant corresponds the vibrational cooling of the ground state.

350 When the solution contains both FeSSA and noncoordinated  
351  $\text{HSSA}^{2-}$  ligand, UV irradiation causes a photoreduction of the  
352 complex. This process is due to the electron transfer from the  
353 noncoordinated ligand in the triplet state to the FeSSA com-  
354 plex. The energy transfer between these species, which fails to  
355 cause any photochemical reaction, competes with the electron  
356 transfer. As applied to photoprocesses in natural water, the data  
357 obtained allow us to define one of the important mechanisms of  
358 active photodegradation of organic compounds in anaerobic con-  
359 ditions, i.e., the photoreduction of transition metal complexes  
360 due to the electron transfer from the long-lived triplet states of  
361 organic aromatic acids.

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