Photosensitized oxidation of iron(II) to iron(III) in systems of iron chloro complexes in nonaqueous medium

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Results of the study of the oxidation of Fe(II) to Fe(III) photosensitized by the Fe(III) complexes or tetracene in electronic-excited states are presented in this paper. The course of this oxidation was investigated with the systems of Fe(II) and Fe(III) chloro complexes in acetone—methanol mixtures.

The values of constants of the Stern—Volmer equation are given and the mechanism of photoprocesses in these systems is discussed.

В работе приводятся результаты изучения окисления Fe(II) в Fe(III), фотосенсибилизованного комплексами Fe(III) или тетраценом в электронно-возбужденном состоянии. Ход окисления был изучен в системах хлоридных комплексов Fe(II) и Fe(III) в смесях ацетона с метанолом.

Приводятся значения констант уравнения Штерна—Вольмера и обсуждается механизм фотопроцессов в исследованных системах.

The spontaneous[a] oxidation of Fe(II) to Fe(III) accompanied by reduction of acetone [1, 2] and the photoreduction of Fe(III) to Fe(II) accompanied by oxidation of methanol and/or chloro ligand [3] depending on composition of the system may take place in the irradiated systems of Fe(II) and Fe(III) chloro complexes in acetone—methanol mixtures. In abstract [4] we have stated that the oxidation of Fe(II) to Fe(III) sensitized by the photoexcited Fe(III)* complexes also proceeds in such systems.

In this study, the progress of the oxidation of Fe(II) to Fe(III) sensitized by electronic-excited Fe(III) complexes or tetracene was quantitatively and kinetically investigated in the systems of iron chloro complexes in acetone—methanol mixtures at varying composition of these systems. Thus it could also be examined whether Fe(II) was oxidized by acetone in triplet state and whether the oxidation of

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[a] In literature the terms "dark reaction" or "thermal reaction" are also used instead of the term "spontaneous reaction". The term "spontaneous reaction" is preferred in this paper because of its use for description of the reactions due to mutual influence of the ligands [5].

Fe(II) might be sensitized by other photoexcited particles different from the Fe(III)* complexes. For this purpose, tetracene was used as a sensitizer.

Experimental

The preparation of anhydrous Fe(II) chloride and anhydrous Fe(III) chloride, purification of solvents, preparation of solutions and the procedure of spectrophotometric measurements are described in [1, 3]. Before use, the solvents were deaerated by boiling and bubbling through with argon. The solutions were handled in argon atmosphere at red light.

The solutions were irradiated in vapourtight quarz cells of 1 cm³ volume, the width of the layer of solution being 0.5 cm. The source of radiation was a medium-pressure mercury lamp Tesla RKV, 125 W. The radiation was monochromatic, which was achieved by interference filters (Schott u. Gen., Jena, GDR). The positions of the maximum transmittance of these filters were at 365, 404, and 465 nm. After passing the filters, the flux of radiation was estimated with a ferric oxalate actinometer [6]. At certain time intervals of irradiation, Fe(II) in the presence of Fe(III) was determined with 2,2'-bipyridine [3]. The data obtained were treated by the least squares method.

Results and discussion

The composition of the systems in which the course of the photosensitized redox processes was investigated is given in Table 1. The initial concentration of the sensitizers, *i.e.* Fe(III) and tetracene was 2.0×10^{-4} M and 1.6×10^{-4} M, respectively. The initial concentrations of Fe(II) were 1.0×10^{-4} M, 1.5×10^{-4} M, 2.0×10^{-4} M, 4.0×10^{-4} M, 7.0×10^{-4} M, and 1.0×10^{-3} M for each system investigated. The progress of oxidation of Fe(II) to Fe(III) was investigated by determining

Table 1

Composition of the systems containing iron chloro complexes in acetone—methanol mixtures (content of acetone is given in volume %) and the values of $\Phi_{\text{Fe(III)lim}}$, a, K_{SV}, and ϱ for the photosensitized oxidation of Fe(II) to Fe(III)

Content of AC %	[Fe]:[Cl⁻]	λ_{irr}, nm	$\Phi_{\text{Fe(III)lim}}$	$a \cdot 10^3$	$K_{\text{SV}} \cdot 10^{-3}$	ϱ
60	1:3	365	0.213 ·	2.77	1.69	0.991
60	1:3	404	0.201	2.81	1.77	0.988
60	1:20	365	0.775	1.21	1.01	0.989
60	1:2 (T)	465	0.535	0.94	1.97	0.985
30	1:3	365	0.177	0.43	13.14	0.972

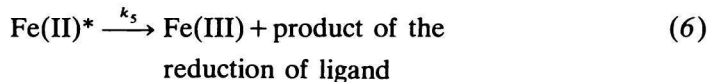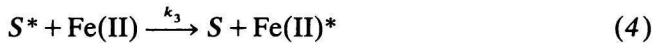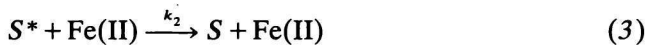T designates a system with tetracene.

[Fe(II)] in the systems at certain time intervals of irradiation (between 2 and 10 min).

Since the temporal change of [Fe(II)] or [Fe(III)] in irradiated systems could be also a consequence of a spontaneous oxidation of Fe(II) or photoreduction of Fe(III), these processes were studied as well.

The solution of 1.0×10^{-3} M-FeCl$_2$ in a mixture of 60% acetone and 40% methanol did not show any change in [Fe(II)] even after 100 min since the preparation of solution.

If the solution of 2.0×10^{-4} M-FeCl$_3$ in mixtures of 60% acetone and 40% methanol or 30% acetone and 70% methanol was irradiated through the filters used, no reduction of Fe(III) to Fe(II) was observed during 15 min irradiation.

The change of [Fe(II)] and [Fe(III)] by the irradiation of the investigated systems (Table 1) is therefore related only to the photosensitized oxidation of Fe(II) to Fe(III). The particular photoreactions proceeding during irradiation of these systems may be expressed by eqns (1—6)

$$S \xrightarrow{h\nu} S^* \tag{1}$$

$$S^* \xrightarrow{k_1} S \tag{2}$$

$$S^* + Fe(II) \xrightarrow{k_2} S + Fe(II) \tag{3}$$

$$S^* + Fe(II) \xrightarrow{k_3} S + Fe(II)^* \tag{4}$$

$$Fe(II)^* \xrightarrow{k_4} Fe(II) \tag{5}$$

$$Fe(II)^* \xrightarrow{k_5} Fe(III) + \text{product of the} \tag{6}$$
$$\text{reduction of ligand}$$

in which S (sensitizer) is the Fe(III) complex or tetracene.

For the dependence of the quantum yield of Fe(III) arisen by the photosensitized oxidation of Fe(II) on concentration of Fe(II) functioning as a quencher, the Stern—Volmer equation was derived [7] in the form

$$\frac{1}{\Phi_{Fe(III)}} = \frac{k_2 + k_3}{k_3} \frac{k_4 + k_5}{k_5} + \frac{k_1}{k_3} \frac{k_4 + k_5}{k_5} \frac{1}{[Fe(II)]} \tag{7}$$

or on simplification

$$\frac{1}{\Phi_{Fe(III)}} = \frac{1}{\Phi_{Fe(III)lim}} + \frac{a}{[Fe(II)]} \tag{8}$$

where $\Phi_{Fe(III)lim}$ is the so-called limiting quantum yield and a is a constant. The value of the Stern—Volmer constant of sensitization K_{SV} may be calculated according to the following equation

$$K_{SV} = (\Phi_{Fe(III)lim}\, a)^{-1} = \frac{k_2 + k_3}{k_1} \qquad (9)$$

In the study of the oxidation of Fe(II) to Fe(III) sensitized by the Fe(III)* complexes the systems were irradiated with the light of the wavelength $\lambda = 365$ nm and $\lambda = 404$ nm (light is absorbed only by the Fe(III) complexes). The systems containing tetracene as a sensitizer were irradiated with the light of $\lambda = 465$ nm (light is absorbed only by tetracene).

The curves expressing the dependence of [Fe(III)] on irradiation time for the system containing 60% of acetone with the ratio ([Fe(II)] + [Fe(III)]):[Cl$^-$] = 1:3 are represented in Fig. 1. Further [Fe(II)] + [Fe(III)] = [Fe].
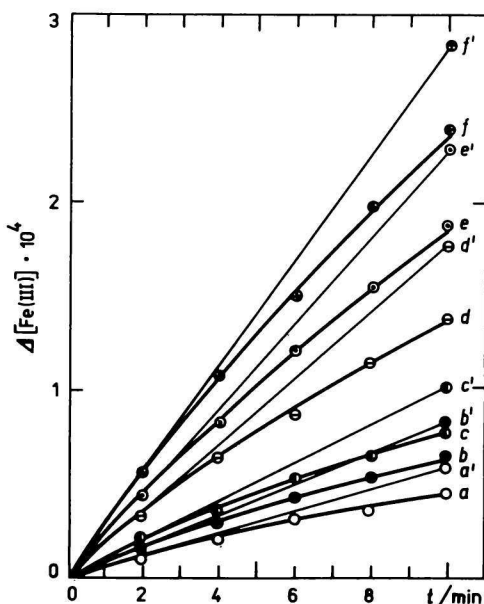

Fig. 1. The increase Δ[Fe(III)] as a function of time in the irradiated systems of the chloro complexes of Fe(II) and Fe(III) containing 60% of acetone and 40% of methanol.
[Fe]:[Cl$^-$] = 1:3; initial concentration of Fe(III) 2.0×10^{-4} M; initial concentrations of Fe(II): a) 1.0×10^{-4} M; b) 1.5×10^{-4} M; c) 2.0×10^{-4} M; d) 4.0×10^{-4} M; e) 7.0×10^{-4} M; f) 1.0×10^{-3} M.
The dashed symbols (a', b', ...) denote the tangents of individual curves at $t = 0$.
I_{abs} (365 nm) = 1.95×10^{-7} einstein min^{-1}, 20°C.

The values of the rate of oxidation of Fe(II) to Fe(III) at the time $t = 0$ expressed in mol min^{-1} (tangents of particular curves at $t = 0$) and the values of flux of the radiation absorbed in this time by the sensitizer (for the investigated system I_{abs} (365 nm) $= 1.95 \times 10^{-7}$ einstein min^{-1}) have been used for calculating the values of $\Phi_{Fe(III)}$ according to the following equation

$$\Phi_{Fe(III)} = \frac{\dfrac{dn_{Fe(III)}}{dt}}{I_{abs}} \qquad (10)$$

The symbol n in eqn (10) stands for the substance amount.

The values of $\Phi_{Fe(III)lim}$, a, and K_{SV} were calculated from the relationship between $(\Phi_{Fe(III)})^{-1}$ and $[Fe(II)]^{-1}$ (Fig. 2). These values as well as the coefficient of correlation ϱ (calculated according to the least squares method) are given in Table 1.

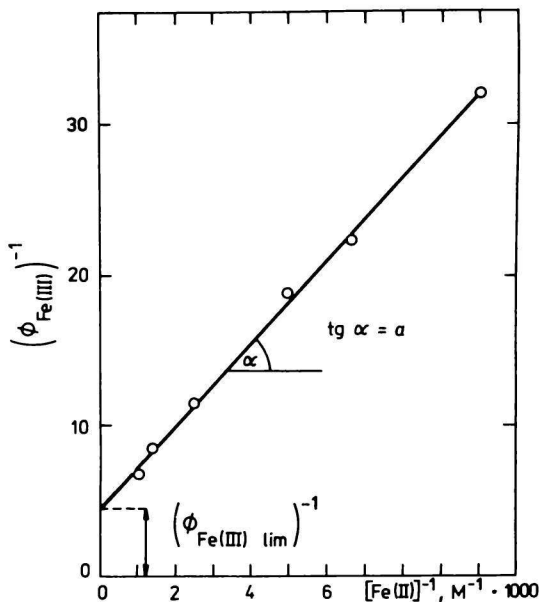The values of $\Phi_{Fe(III)lim}$, a, K_{SV}, and ϱ were analogously calculated for the other systems and are listed in Table 1.

Fig. 2. Variation of $(\Phi_{Fe(III)})^{-1}$ with initial $[Fe(II)]^{-1}$ for the systems of the chloro complexes of Fe(II) and Fe(III) containing 60% of acetone and 40% of methanol. $[Fe]:[Cl^-] = 1:3$; irradiation with the light of $\lambda = 365$ nm.

The high values of K_{SV} suggest that the excited Fe(III)* complexes or tetracene are deactivated especially by collisions with the Fe(II) complexes while their deactivation by substitutions and photophysical processes is characterized by low quantum yields.

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On the basis of the values of $\Phi_{Fe(III)lim}$ it may be assumed that the energy transfer between Fe(III)* and the Fe(II) complexes and the subsequent deactivation of the Fe(II)* complex by a redox process takes place with relatively high efficiency not only in the systems where the anionic complexes $[FeCl_4]^-$ and $[FeCl_4]^{2-}$ prevail (systems with the ratio $[Fe]:[Cl^-] = 1:20$) but also in the other systems.

In spite of different values of the constants of the Stern—Volmer equation found for individual systems, no real conclusions about the relationships between the composition of the systems and their photochemical properties are to be drawn from the results obtained. These constants are given by the ratios of the rate constants of particular processes (2—6) and do not enable us to assess the absolute values of these rate constants.

The redox potential of the couple Fe(III) + e $\rightleftharpoons$ Fe(II)*, calculated according to [8] on the assumption that the energetic difference between the excited and ground state of the Fe(II) complex expressed in the wavelength units is 465 nm (radiation of the lowest energy used in this study), should have the approximate value

$$E^0_{Fe(III)/Fe(II)^*} \doteq -1.9 \text{ V} \qquad (11)$$

The calculation analogously performed [8] for the redox potential of the couple $^3AC^* + e \rightleftharpoons AC^-$ where $^3AC^*$ denotes acetone in the excited triplet state gives

$$E^0_{^3AC^*/AC^-} \doteq +1.5 \text{ V} \qquad (12)$$

as the energy of the triplet level of acetone in the wavelength units is 355 ± 6 nm [6].

Thus from the thermodynamic view-point, Fe(II)* may be a reducing agent with respect to acetone and $^3AC^*$ may be an oxidizing agent with respect to Fe(II) (the values of E^0 for the couples Fe(III) + e $\rightleftharpoons$ Fe(II) and AC + e $\rightleftharpoons$ AC$^-$ are approximately + 0.8 and − 1.8 V, respectively).

The progress of the photosensitized oxidation of Fe(II) to Fe(III) during irradiation of the systems with the light of $\lambda = 404$ nm and the very close values of constants of the Stern—Volmer equation (Table 1) found for this system irradiated with the light of $\lambda = 365$ nm and $\lambda = 404$ nm indicate that the reactions in these systems are not set run by acetone in the triplet state (acetone cannot be excited by irradiation with the light of $\lambda = 404$ nm). This conclusion has been also confirmed by the results of the study of processes in the systems containing tetracene as a sensitizer.

It results from these facts that the Fe(II) complexes are able to quench the excited states not only of the Fe(III)* complexes but also of other particles (in our case those of tetracene).

References

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