

Spontaneous and photochemical redox reactions of iron(II) and iron(III) bromo complexes in nonaqueous media

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The results of the study of spontaneous and photosensitized oxidation of Fe(II) to Fe(III), as well as the photoreduction of Fe(III) to Fe(II) in the systems of Fe(II) and Fe(III) bromo complexes in the acetone—methanol mixtures are presented. Some kinetic data on the investigated reactions are given and their mechanism is discussed.

В работе даны результаты изучения самопроизвольного и фотосенсибилизированного окисления Fe(II) до Fe(III) и фотовосстановления Fe(III) до Fe(II) в системах бромидных комплексов Fe(II) и Fe(III) в смесях ацетона и метилового спирта. Приводятся некоторые кинетические данные изученных реакций и обсуждаются их механизмы.

In the irradiated systems of Fe(II) and Fe(III) chloro complexes in acetone, methanol, and their mixtures depending on their composition a spontaneous^a oxidation of Fe(II) to Fe(III) due to the mutual influence of ligands through the central atom [1], an oxidation of Fe(II) to Fe(III) sensitized with the excited Fe(III)* complexes [2], a photoreduction of Fe(III) to Fe(II) [3], eventually all cited processes [4] can occur simultaneously. The observed changes in the Fe(II) and Fe(III) concentrations in such systems in dependence on time are the results of all redox processes. The kinetic study of the redox reactions in the systems with simultaneous occurrence of the above-mentioned processes has been generally described in paper [5].

In connection with the study of the effect of ligands of different σ - and π -bonding properties on the course of spontaneous and photochemical redox reactions of the copper and iron complexes following the results of the investigation of the Fe(II) and Fe(III) chloro complex properties we have started with the study of the above-mentioned redox reactions of Fe(II) and Fe(III) bromo complexes in

^a In the literature the terms "thermal" or "dark" reaction are also used in place of the term "spontaneous" reaction. For the redox reactions occurring due to the mutual influence of ligands [6] the term "spontaneous" reaction has been preferred and therefore we use it in this paper as well.

the acetone—methanol mixtures. In this paper the relationship between the composition of the systems under investigation, bonding properties of the central atoms and individual ligands in the complexes as well as the course of the cited redox reactions is discussed.

Experimental

Anhydrous ferrous bromide, anhydrous ferric bromide (Cerac Pure, Inc.), tetramethylammonium bromide, and 2,2'-bipyridine (Lachema, Brno) were used without further purification. Acetone and methanol (Lachema, Brno) were deoxygenated by boiling and bubbling through with argon. Purification of solvents, preparation and handling of solutions, and the spectrophotometric measurements are given elsewhere [3].

The photochemical experiments and determination of the Fe(II) concentration in the presence of Fe(III) are described in paper [3]. The intensity of incident light passing through the used filters was measured by means of the chemical actinometry [7]. The kinetic data were processed by the least-square method, the regression quality is expressed by the values of correlation coefficients ρ .

Results

The course of spontaneous and photochemical redox reactions was investigated in the systems of the following composition

System	[Fe]:[Br ⁻]	AC/volume %	MeOH/volume %
1	1:10	80	20
2	1:3	80	20
3	1:10	20	80
4	1:3	20	80

When following the Fe(II) spontaneous oxidation the initial concentration was $[\text{Fe}] = [\text{Fe(II)}] = 2.8 \times 10^{-4} \text{ mol dm}^{-3}$; when studying the Fe(III) photoreduction the initial concentration was $[\text{Fe}] = [\text{Fe(III)}] = 3.0 \times 10^{-4} \text{ mol dm}^{-3}$; when investigating the Fe(II) oxidation sensitized by the Fe(III)* photoexcited complexes, $[\text{Fe}] = ([\text{Fe(II)}] + [\text{Fe(III)}])$, the initial $[\text{Fe(III)}]/\text{mol dm}^{-3} = 3.0 \times 10^{-4}$ and initial $[\text{Fe(II)}]/\text{mol dm}^{-3}$ for each system were as follows: 2.0×10^{-4} , 3.0×10^{-4} , 4.0×10^{-4} , 6.0×10^{-4} , and 1.0×10^{-3} .

From the experimental dependences of $[\text{Fe(III)}]$ on time at the spontaneous oxidation of Fe(II) to Fe(III) the following values of k , n , and ρ were calculated using the kinetic equation

$$\frac{d[\text{Fe(III)}]/\text{mol dm}^{-3}}{dt} = k \left\{ \frac{[\text{Fe(II)}]}{\text{mol dm}^{-3}} \right\}^n$$

These values are as follows: $k = 12.75$ and/or 2.59 min^{-1} , $n = 2.06$ and/or 1.97 , and $\rho = 0.996$ and/or 0.992 for the system 1 and/or 2. In the systems 3 and 4

Fe(II) is oxidized at a relatively slow rate. During 5 h 3% of the present Fe(II) was oxidized in the system 3 and in the system 4 it was about 4.5% of Fe(II).

The course of the Fe(III) to Fe(II) photoreduction was followed irradiating the systems with light at $\lambda_{\text{irr}} = 365, 396,$ and 427 nm. In the case of irradiation at the wavelength $\lambda_{\text{irr}} = 427$ nm neither spectral changes nor Fe(II) formation were observed in the systems. The overall quantum yield values of $\Phi_{\text{Fe(II)}}$ extrapolated to the time of irradiation $t = 0$ are given in Table 1 for $\lambda_{\text{irr}} = 365$ and 396 nm.

Table 1

Values of $\Phi_{\text{Fe(II)}}$ for the photoreduction of Fe(III) to Fe(II)
 $\Phi_{\text{im}}, K_{\text{sv}},$ and ϱ for the photosensitized oxidation of Fe(II) to Fe(III)

System	$\lambda_{\text{irr}}/\text{nm}$	$\Phi_{\text{Fe(II)}}$	Φ_{im}	K_{sv}	ϱ
1	365	0.001	0.295	1163	0.997
	396	0.001	0.843	428	0.992
2	365	0.008	0.872	247	0.995
	396	0.013		nonreproducible	
3	365	0.051	0.174	1131	0.997
	396	0.091	0.126	945	0.995
4	365	0.036	0.113	3600	0.998
	396	0.065	0.181	2021	0.997

The rate of the Fe(II) to Fe(III) oxidation in the irradiated systems containing Fe(II) and Fe(III) complexes with light absorbed by only Fe(III) complexes was higher than the rate of the Fe(II) spontaneous oxidation in such systems. The dependence of the [Fe(III)] increase on time for the system 1 irradiated with light at $\lambda_{\text{irr}} = 365$ nm and that of a nonirradiated one is given in Fig. 1. Analogous

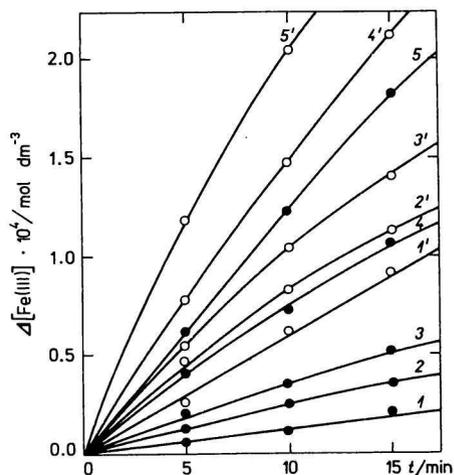


Fig. 1. Dependence of [Fe(III)] on time in the system 1 for the initial concentration [Fe(III)] = 3.0×10^{-4} mol dm $^{-3}$; [Fe(II)] = 2.0×10^{-4} , 3.0×10^{-4} , 4.0×10^{-4} , 6.0×10^{-4} , and 1.0×10^{-3} mol dm $^{-3}$ in irradiated (curves 1'—5') and in nonirradiated systems (curves 1—5).

$\lambda_{\text{irr}} = 365$ nm, 0.5 cm cells, I^0 (365 nm) = 9.8×10^{-8} Nh ν min $^{-1}$, temperature 20°C.

relationship was found also for other systems irradiated at $\lambda_{\text{irr}} = 365$ and 396 nm. When irradiating the systems with light at $\lambda_{\text{irr}} = 427$ nm the dependences of $[\text{Fe(III)}]$ on time were practically identical with those in systems in dark.

On the basis of experimental results the values of quantum yields of the Fe(III) to Fe(II) photoreduction, $\Phi_{\text{Fe(III)}}$, limiting quantum yields of Fe(III) arisen by the photosensitized oxidation of Fe(II), Φ_{lim} , and the values of the Stern—Volmer constant of sensitization, K_{SV} were determined. These are connected with the observed rate of oxidation of Fe(II) according to the following equation

$$\frac{d[\text{Fe(III)}]/\text{mol dm}^{-3}}{dt} = k \left\{ \frac{[\text{Fe(II)}]}{\text{mol dm}^{-3}} \right\}^2 + I_0(1 - 10^{-A}) \left(\frac{\Phi_{\text{lim}} K_{\text{SV}} [\text{Fe(II)}]}{1 + K_{\text{SV}} [\text{Fe(II)}]} - \Phi_{\text{Fe(III)}} \right)$$

where k is the rate constant of the spontaneous Fe(II) oxidation, I_0 is the incident light intensity, A is the absorbance of the system. The values of $\Phi_{\text{Fe(III)}}$, Φ_{lim} , and K_{SV} are given in Table 1 together with the values of the correlation coefficient ρ .

Discussion

From the aspects of the phenomenon of the mutual influence of ligands [6] the conditions for the intramolecular spontaneous redox process of the complexes under investigation may be explained as the consequence of the interaction of σ - and π -donor bromo ligands with a σ -donor and π -acceptor acetone ligand through the Fe(II) central atom electronic system. This interaction results in the transfer of the electron density into the π^* orbital of acetone. In case of the redox decomposition of such a complex Fe(II) is oxidized to Fe(III) and acetone is reduced to pinacol [8]. As in the systems which do not contain a bromo ligand (solutions of ferrous nitrate in acetone) or which do not contain acetone (solutions of ferrous bromide in methanol) the spontaneous oxidation of Fe(II) to Fe(III) does not occur [9] it proves that the π -system formation



is one of the essential conditions for the spontaneous Fe(II) oxidation.

Higher values of $\Phi_{\text{Fe(III)}}$ in the systems 3 and 4 when compared with those in the systems 1 and 2 prove the validity of the assumption that the Fe(III) photoreduction is accompanied by oxidation of methanol in both the systems of Fe(III) chloro and bromo complexes. The dependence of $\Phi_{\text{Fe(III)}}$ on λ_{irr} for individual systems has not been satisfactorily explained yet. In contrast to the Fe(III) chloro complexes with the photoredox processes even in case of the excitation into the energetically lowest CT state, Fe(III) in bromo complex systems is reduced only at the photoexcitation into energetically higher CT states. This fact can be associated with both the energy required for the methanol oxidation and/or different rate of photophysical deactivation processes of Fe(III) chloro and bromo complexes from

individual CT states. The effect of delocalization of some molecular orbitals in the $[\text{FeBr}_4]^-$ ions which is the dominating complex of Fe(III) in the system 1, and the effect of the electron π -system of acetone on the probability of the Fe(III) complex deactivation in the CT excited states by redox reaction can be discussed analogically as in the case of the Fe(III) chloro complexes [3].

The only process which can cause the experimentally found fact, *i.e.* higher rate of Fe(II) oxidation in irradiated than in nonirradiated systems containing Fe(II) and Fe(III) bromo complexes, is the Fe(II) excitation by the energy transfer from Fe(III)* complex and successive deactivation of Fe(II)* by redox process [2]. The calculation of the redox potentials of couples ${}^3\text{AC}^* + e \rightleftharpoons \text{AC}^-$ ($E^0 = 1.5 \text{ V}$) and $\text{Fe(III)} + e \rightleftharpoons \text{Fe(II)}^*$ ($E^0 = -1.9 \text{ V}$) [2] has shown that Fe(II)* can be a reducing agent with respect to acetone and ${}^3\text{AC}^*$ can act as an oxidant of Fe(II) (${}^3\text{AC}^*$ denotes acetone in the triplet excited state). However, the Fe(II) oxidation during irradiation of the systems of Fe(II) and Fe(III) bromo complexes at $\lambda_{\text{irr}} = 396 \text{ nm}$ documents that the energy transfer between Fe(III)* and Fe(II), or oxidation of Fe(II) are not mediated through the acetone triplet level.

Higher values of Φ_{lim} in the systems 1 and 2 in comparison with those of the systems 3 and 4 are probably the consequence of a higher probability of the Fe(II)* complex interaction with acetone as the component able to be reduced. Relatively high values of K_{sv} and Φ_{lim} in all systems show that the Fe(III)* complexes are deactivated mostly by interaction with Fe(II) complexes and that Fe(II)* complexes are deactivated efficiently by the redox decomposition.

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