Kinetic and Photoredox Behaviour of Iron(III) Complexes with Kojic Acid

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Bidentate kojic acid anions L^- form Fe(III) chelates $[FeL(H_2O)_4]^{2+}$, $[FeL_2(H_2O)_2]^+$, and $[FeL_3]$. The rate of the chelates formation is proportional both to the concentration of hydrated Fe^{3+} and kojic acid HL. Using stopped-flow technique the pH dependence of the rate of $[FeL(H_2O)_4]^{2+}$ formation was followed. Being in dark, the chelates are redox-stable, the absorption of ultraviolet or visible radiation results in the photoreduction of Fe(III) to Fe(II). The overall quantum yields of Fe(II) formation for all individual chelates at the wavelengths of incident radiation $\lambda_{irr} = 366$ nm and 436 nm were determined. Using spin-trapping EPR, the radicals $OH^\bullet$ were identified in irradiated aqueous solutions of FeL^{2+}

Anion of kojic acid (kojic acid, HL = 5-hydroxy-2-hydroxymethyl-4*H*-pyran-4-one) behaves as a bidentate ligand coordinated to a central atom *via* the carbonyl and hydroxyl oxygen atoms [1]. The anion can participate in ion-pair formation as observed in systems containing cytochrome c and kojic acid [2]. In the visible region of electronic absorption spectra of the complexes containing kojic acid anion(s) bound to a reducible transition metal both the bands of ligand-to-metal charge-transfer transitions and those of ligand field nature can be observed. The bands of intraligand transitions dominate in the ultraviolet part of the spectra. No luminescence has been detected in solutions of kojic acid at room temperature [3].

Kojic acid has attracted attention thanks to its practical importance. It inhibits various microbial processes, suppresses microorganism multiplication in oil-water emulsions used at working-up of metals [4—7], acts as an efficient substance in sun-tan oils and other photoprotective mixtures and cosmetics [8, 9], is applied in food preservation [10], plays the role of a chelator for some transition metals in human medicine [11], *etc.* In connection with its application, electrochemical properties [6], mutagenicity [4], cytotoxic IC_{50} values and antimicrobial MIC values [5], preischemic values [11], and the ability of kojic acid to undergo oxidation [12] have been investigated.

In the framework of its utilization, kojic acid itself and its complexes can be exposed to artificial radiation or sunlight. It has been shown in our previous papers [3, 13] that contrary to the photoredox stability of free kojic acid, its anions, coordinated to a reducible central atom or being present in ion pairs, are photoredox reactive and harmful radicals might be formed within their photooxidation. The efficiency of such processes, expressed in photochemistry as overall quantum yield, depends on the wavelength of the incident radiation, the distribution of the complexes in irradiated systems, the rate of back coordination, and on other factors. A key importance of the rate of L^- coordination to the Fe(III) central atom for the photoredox behaviour and electrochemical reversibility of the formed complexes has led us to use stopped-flow method to treat the rate. In the present paper the results obtained within the study of kinetic properties and photoredox behaviour of the chelates $[FeL(H_2O)_4]^{2+}$, $[FeL_2(H_2O)_2]^+$, and $[FeL_3]$, denoted herein for the sake of simplicity as FeL^{2+}, FeL_2^+, and FeL_3, respectively, are reported.

EXPERIMENTAL

Kojic acid was prepared according to [5]. Potassium tris(oxalato)ferrate(III) (Oxford Organic Chemicals), 1,10-phenanthroline (Aldrich), 5,5-dimethyl-1-pyrroline *N*-oxide (Sigma) were used without further

purification. The other chemicals were purchased from Lachema and used as received. All commercial chemicals were of anal. grade.

The rate of FeL^{2+} formation was followed by stopped-flow spectrophotometry [14] at ionic strength $I(NaNO_3) = 0.2$ mol dm^{-3} at 25 °C and variable pH (0.75, 1.00, 1.25 or 1.50) under pseudo-first-order conditions in the systems with $c(Fe^{III}) = 1.0 \times 10^{-4}$ mol dm^{-3} or 2.0×10^{-4} mol dm^{-3} and the ratio $c(HL):c(Fe^{III}) = 10, 20, 50$ or 100, as well as in the systems with $c(HL) = 1.0 \times 10^{-4}$ mol dm^{-3} and the ratio $c(Fe^{III}):c(HL) = 10, 20, 50$ or 100. The absorbance vs. time data, resulting from the increase in absorbance at $\lambda = 320—620$ nm were computer-fitted to a suitable equation.

Steady-state photolysis was performed in a three-chambered temperature-controlled $((20 \pm 2)\,°C)$ quartz photoreactor. As a radiation source, a medium-pressure Hg-lamp (Tesla RVK, 125 W, radiation monochromatized by solution filters [3, 15]) was used. The irradiated solutions were deoxygenated by bubbling with argon for 30 min prior to and during irradiation. Amount of photons of the incident radiation passing through solution filters, determined by a ferrioxalate actinometer [15], was of the order 10^{-5} mol dm^{-3} s^{-1}

The course of photoredox changes was monitored by electronic absorption spectroscopy as time evolution of $c(Fe^{II})$ in the systems with the initial $c(Fe^{III}) = 4.0 \times 10^{-4}$ mol dm^{-3} The total content of kojic acid in solution before and after irradiation was determined as FeL^{2+} Details on the used photochemical procedure, analytical methods, and evaluation of experimental data are described elsewhere [13].

Radical formation was followed using a spin trap added to a deoxygenated aqueous solution of the complex FeL^{2+} irradiated with polychromatic radiation emitted by a 250 W medium-pressure Hg-lamp (Applied Photophysics) directly in the rectangular cavity of an EPR equipment. EPR spectra simulation was performed using a standard Bruker program.
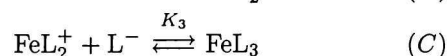
Electronic absorption spectra were scanned on a Specord M-40 spectrophotometer. Kinetic measurements were performed on a Durrum (type D 110) stopped-flow spectrophotometer. EPR spectra were recorded on a Bruker 200D spectrometer coupled with an Aspect 2000 computer. Solution pH values were measured using a Metrohm (type 654) or a Radelkis (type 211/1) pH-meter in combination with a glass electrode.

RESULTS AND DISCUSSION

Kinetics of the FeL^{2+} Chelate Formation

In the systems containing hydrated Fe^{3+} cations and kojic acid HL, three kojato chelates, namely FeL^{2+}, FeL_2^+, and FeL_3 are formed in dependence on

the composition of solution [16, 17]. The formation of the complexes can be simply described by the relations

$$Fe^{3+} + L^- \overset{K_1}{\rightleftharpoons} FeL^{2+} \qquad (A)$$

$$FeL^{2+} + L^- \overset{K_2}{\rightleftharpoons} FeL_2^+ \qquad (B)$$

$$FeL_2^+ + L^- \overset{K_3}{\rightleftharpoons} FeL_3 \qquad (C)$$

Along with reactions $(A—C)$, deprotonization of HL and protonization of L^- occur in solutions

$$L^- + H_2O \overset{K_b}{\rightleftharpoons} HL + OH^- \qquad (D)$$
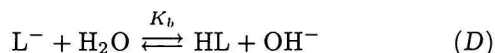
and, predominantly at higher pH, hydroxoiron(III) species can appear.

Combining eqns (A) and (D), the formation of the complex FeL^{2+} can be expressed as

$$Fe^{3+} + HL + OH^- \rightleftharpoons FeL^{2+} + H_2O \qquad (E)$$
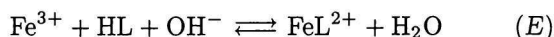
Kojic acid is a weak acid ($pK_a(HL) = 7.18$ [18]) and in systems with an excess of HL its concentration is nearly constant, i.e. the equilibrium constant for reaction (E) may be written as

$$K_h = [FeL^{2+}]/([Fe^{3+}][OH^-]) \qquad (1)$$

In the spectral region where Fe^{3+} and FeL^{2+} are the only absorbing species, absorbance A is for any wavelength at equilibrium conditions given by

$$A = l\varepsilon(Fe^{3+})[Fe^{III}] + l\{\varepsilon(FeL^{2+}) - \varepsilon(Fe^{3+})\}\cdot$$
$$\{K_h[Fe^{III}][OH^-]/(1 + K_h[OH^-])\} \qquad (2)$$

where l is the path length of the cell, $\varepsilon(Fe^{3+})$ and $\varepsilon(FeL^{2+})$ are the molar absorption coefficients for Fe^{3+} and FeL^{2+} at a given wavelength, respectively, $[Fe^{III}]$ is the total concentration of Fe(III), $[OH^-]$ is the equilibrium concentration of OH^- ions. In relationships $(A—F)$ and $(1—4)$ all concentrations, molar absorption coefficients, and cell path length are expressed as dimensionless quantities related to the reference concentration 1 mol dm^{-3}, molar absorption coefficient 1 mol^{-1} dm^3 cm^{-1} and path length 1 cm, respectively.

Time evolution of absorbance A in a system containing hydrated Fe^{3+} as a reactant and FeL^{2+} as a product is for any wavelengths in which only these two species absorb radiation expressed [14, 19] by the equation

$$A = [A(FeL^{2+}) - A(Fe^{3+})] \exp(-k_{obs}t) + A(FeL^{2+}) \qquad (3)$$

where A is the absorbance at the time t, $A(FeL^{2+})$ and $A(Fe^{3+})$ are absorbances of systems in which the whole Fe(III) content is present as FeL^{2+} and Fe^{3+},

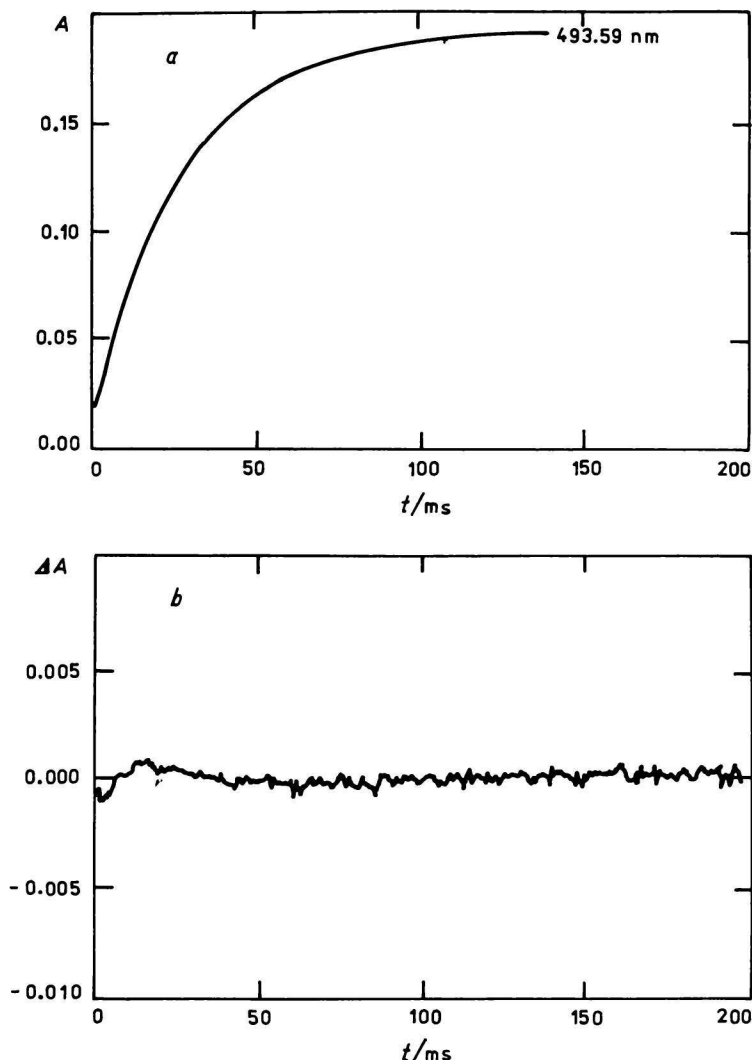**Fig. 1.** *a*) Time evolution of absorbance at $\lambda = 493.6$ nm in the system with $c(Fe^{III}) = 2.0 \times 10^{-4}$ mol dm^{-3} and $c(HL) = 1.0 \times 10^{-2}$ mol dm^{-3}, pH 1.25, ionic strength $I(NaNO_3) = 0.20$ mol dm^{-3}, temperature 25 °C, 1 cm cell. *b*) Deviation of experimental absorbance at $\lambda = 493.6$ nm from that calculated according to eqn (*3*).

respectively (all the absorbance and molar absorption coefficient values relate to a specific wavelength). In the spectral region $\lambda = 320$—650 nm the portion of absorbance due to Fe^{3+} cations can be omitted as $\varepsilon(FeL^{2+}) \gg \varepsilon(Fe^{3+}) \approx 0$. In such an instance the meaning of k_{obs} followed at pseudo-first-order conditions from the relation

$$dA/dt = l\varepsilon(FeL^{2+})k_2 c(Fe^{3+})c(HL)$$
$$= l\varepsilon(FeL^{2+})k_{obs}c(Fe^{3+}) \qquad (4)$$

For each of the investigated systems some tens of the spectra were scanned in the region of $\lambda = 320$—650 nm within 150 ms after mixing the stock solution of Fe^{3+} cations and HL. Computer fitting of the obtained absorbance *vs.* time data provided the values of k_{obs}.

A typical time dependence of absorbance is exhibited in Fig. 1*a* for the system with $c(Fe^{III}) = 2.0 \times 10^{-4}$ mol dm^{-3} and $c(HL) = 1.0 \times 10^{-2}$ mol dm^{-3}

at pH = 1.25. The final spectrum with an absorption maximum at 493.6 nm corresponds to the spectrum of the complex FeL^{2+}. Justification to apply eqn (*4*) for calculating the rate constant k_{obs} from the absorbance *vs.* time dependence was checked by two independent modes. The first one lies in an evaluation of deviation of the experimental *vs.* calculated absorbance values at 493.6 nm (Fig. 1*b*) within the used time interval. It is obvious that an excellent agreement of both values was achieved for the whole time interval. The second mode stems from checking the validity of the Lambert—Beer law in the entire investigated spectral region. If the observed spectral changes correspond only to the formation of one light absorbing FeL^{2+} complex from hydrated Fe^{3+} cations, the observed spectral changes should obey the Lambert—Beer law in the entire spectral region and, therefore, the rate constant k_{obs} should be independent of the wavelength. Evaluation of the data documented that

Table 1. Experimental Rate Constants k_{obs} for Systems with Different Concentration Ratio $c(Fe^{III}):c(HL)$ and pH. In the Systems with an Excess of HL, at pH 0.75 or 1.00, $c(Fe^{III}) = 1.0 \times 10^{-4}$ mol dm^{-3}, and at pH 1.25 or 1.50, $c(Fe^{III}) = 2.0 \times 10^{-4}$ mol dm^{-3} In the Systems with an Excess of Fe(III), $c(HL) = 1.0 \times 10^{-4}$ mol dm^{-3}

$c(Fe^{III}):c(HL)$	k_{obs}/s^{-1}			
	pH = 0.75	pH = 1.0	pH = 1.25	pH = 1.50
1:10	0.15	0.16	0.28	0.25
1:20	0.19	0.26	0.35	0.41
1:50	0.38	0.54	0.77	1.12
1:100	0.70	1.04	1.54	2.31
10:1		0.17	–	–
20:1		0.28		–
50:1		0.65		
100:1		1.14		

this was the case. The experimental rate constants k_{obs} for all investigated systems were obtained as average values of five parallel measurements. Uncertainty in the determined k_{obs} values does not exceed 1 %. The results are summarized in Table 1. To be sure that in the above experiments the complex FeL^{2+} is the only Fe(III) chelate formed, spectral properties and kinetics of complex formation in systems with pH = 1.0, $c(HL) = 2.0 \times 10^{-4}$ mol dm^{-3}, and an excess of Fe^{3+} cations were followed. As proved by their spectral features, in such acidic systems FeL^{2+} is the only Fe(III) kojato complex present.

The above results lead to two important conclusions: *1.* single-exponential equation (*5*) describes correctly the kinetic behaviour of investigated systems; *2.* the rate of complex formation reaction (*A*) is linearly proportional to the concentrations of Fe(III) and HL.

The pH dependence of k_{obs} is a well-known feature for systems where many protonated and deprotonated forms of the reactants are in equilibrium. In our systems HL, L$^-$, Fe^{3+}, and Fe(OH)$^{2+}$ belong to such species. On one hand the concentration $c(Fe(OH)^{2+})$ is relatively small at low pH. A simple calculation based on the equilibrium constant K_i [20]

$$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H_3O^+$$
$$K_i = 1.84 \times 10^{-3} \tag{F}$$
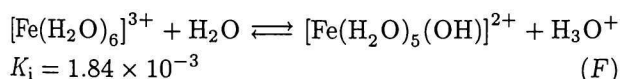
shows that it does not exceed 4.3 % of the total amount of Fe(III) at pH = 1.5 and it decreases with lowering pH. On the other hand, the substitutional reactivity of hydroxoiron(III) species is much higher compared to that of the hydrated Fe^{3+} cation. The difference in the kinetic lability can be exemplified by the rate contants k_{exch} for water-exchange reactions, which are [21] 1.5×10^5 s^{-1} for Fe(OH)$^{2+}$ and 1.6×10^2 s^{-1} for hydrated Fe^{3+}

Obviously, only deprotonated form of kojic acid can participate in the complex formation reactions (in an opposite case, the value of k_{obs} would not depend on pH). There is, however, a linear double-logarithmic
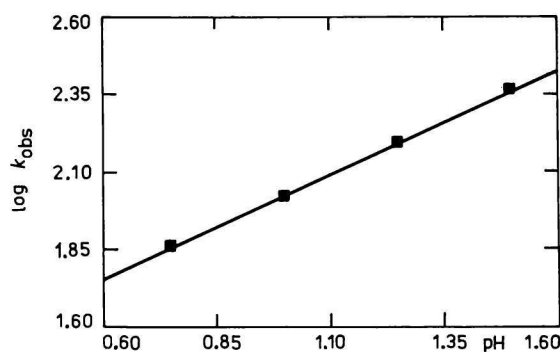
Fig. 2. The pH dependence of $\log k_{obs}$ for systems with $c(HL):c(Fe^{III}) = 10, 20, 50$ or 100.

dependence of $\log k_2$ *vs.* pH (Fig. 2). A correction of k_{obs} either for equilibrium concentration of [L$^-$] or [Fe(OH)$^{2+}$], however, does not solve the problem of species involved in the rate-determining step of the formation of the complex FeL^{2+} To offer a definite and acceptable answer to this question, further experiments, which are beyond the aims of the present work, must be performed.

Photochemical Properties of Kojato Iron(III) Complexes

The complexes FeL_n^{3-n} do not undergo spontaneous redox changes in aqueous solutions in the absence of light.

Irradiation of aqueous solutions of the complex FeL_3 (the solutions having pH 6.45 and $c(Fe^{III}):c(HL) = 1:10$) with ultraviolet or visible radiation leads to the photoreduction of Fe(III) to Fe(II). The overall quantum yield value of Fe(II) formation depends on the wavelength of incident radiation (Table 2). For the complex FeL_3 the quantum yield was determined also at $\lambda = 313$ nm being $\phi(FeL_3, 313$ nm$) = 2.2 \times 10^{-2}$ Increasing the concentration of HL in the irradiated solutions does not influence the efficiency of Fe(II) formation, *i.e.* neither free HL nor anions L$^-$ quench the excited FeL_3.

Table 2. Relative Fractional Concentrations α_i of Individual Kojatoiron(III) Complexes, Molar Absorption Coefficients ε_i of the Complexes at 436 nm, Quantum Yields ϕ_i of Fe(II) Formation, and Amount of Incident Radiation I_i Absorbed by Each of the Complexes, Calculated from Eqn (5). The Data Relate to the System with $c(Fe^{III}) = 4.0 \times 10^{-4}$ mol dm^{-3}, $c(HL) = 4.0 \times 10^{-3}$ mol dm^{-3}, pH 2.98, Irradiated at 436 nm, $I_o(436\ nm) = 2.85 \times 10^{-5}$ mol dm^{-3} s^{-1} or 366 nm, $I_o(366\ nm) = 3.00 \times 10^{-5}$ mol dm^{-3} s^{-1}

Complex	α_i	$\lambda_{irr} = 366$ nm			$\lambda_{irr} = 436$ nm		
		$\varepsilon_i/(\text{mol}^{-1}\ \text{dm}^3\ \text{cm}^{-1})$	$I_i/(\text{mol dm}^{-3}\ \text{s}^{-1})$	ϕ_i	$\varepsilon_i/(\text{mol}^{-1}\ \text{dm}^3\ \text{cm}^{-1})$	$I_i/(\text{mol dm}^{-3}\ \text{s}^{-1})$	ϕ_i
FeL^{2+}	0.245	1100	4.3×10^{-6}	9.9×10^{-4}	1200	3.3×10^{-6}	8.9×10^{-4}
FeL$_2^+$	0.570	1900	1.74×10^{-5}	1.4×10^{-3}	2800	1.79×10^{-5}	1.1×10^{-3}
FeL$_3$	0.185	2800	8.3×10^{-6}	8.7×10^{-4}	3550	7.3×10^{-6}	7.3×10^{-4}

Solutions with $c(Fe^{III}) = 4.0 \times 10^{-4}$ mol dm^{-3}, $c(HL) = 1.0 \times 10^{-3}$ mol dm^{-3}, and pH = 1.81 contain three species (L^-, FeL^{2+}, and Fe^{3+}) [18] absorbing radiation at $\lambda = 313$ nm. Consequently, such systems were irradiated at $\lambda = 436$ nm or 366 nm, where the only light-absorbing species was the complex FeL^{2+} The corresponding values of overall quantum yield are collected in Table 2.

As follows from the complex distribution curves [17, 22] for the radiation-absorbing kojato complexes, Fe(III) can never be exclusively in the form of FeL$_2^+$ The maximum portion of the complex FeL$_2^+$ (57.0 % of all Fe(III) species) is in solution with pH 2.98, containing in equilibrium along with the complex FeL$_2^+$ also complexes FeL^{2+} (24.5 %) and FeL$_3$ (18.5 %). It means that photoredox properties of FeL$_2^+$ cannot be determined directly; they can be, however, evaluated from spectral and photochemical data obtained for the systems, containing the complex FeL$_2^+$

The amount of incident radiation I_i absorbed at a given wavelength by i-th Fe(III) complex in systems, containing two or more absorbing Fe(III) species is

$$I_i = I_o \alpha_i \varepsilon_i \Big/ \sum (\alpha_i \varepsilon_i) \qquad (5)$$

where I_o is the total amount of incident radiation absorbed by the system, α_i is the fractional concentration of the i-th complex, defined as

$$\alpha_i = c(i\text{-th complex})/c_o(Fe^{III}) \qquad (6)$$

ε_i is the molar absorption coefficient of the i-th complex at the wavelength of incident radiation λ_{irr}, $\sum$ means summation for all complexes present in the system, $c_o(Fe^{III})$ is the total concentration of Fe(III). The values of α_i are obtainable from the distribution curves, ε_i are available from the spectra of individual species, I_o is determined by actinometry. The observed overall rate v_{obs} of photochemical Fe(II) formation is given [23] as

$$v_{obs} = -dc(Fe^{III})/dt = \phi_{obs}\ I_o = \sum (\phi_i\ I_i) \quad (7)$$

where ϕ_i are quantum yields for individual complexes and ϕ_{obs} is the experimental overall value of the quan-

tum yield of Fe(II) formation in irradiated system containing all Fe(III) kojato complexes, determined to be $\phi_{obs} = 9.9 \times 10^{-4}$ at $\lambda_{irr} = 436$ nm, and $\phi_{obs} = 1.2 \times 10^{-3}$ at $\lambda_{irr} = 366$ nm. Based on relations (5) and (7), equation allowing the calculation of quantum yield ϕ_2 of photoreduction of Fe(III) to Fe(II) in FeL$_2^+$ complex can be derived

$$\phi_2 = \left(\phi_{obs} \sum (\alpha_i \varepsilon_i) - \phi_1 \alpha_1 \varepsilon_1 - \phi_3 \alpha_3 \varepsilon_3\right)/(\alpha_2 \varepsilon_2) \quad (8)$$

The values needed to obtain the quantum yield value ϕ_2 at 436 nm and 366 nm are gathered in Table 2. Using eqn (8), the quantum yield value for Fe(III) photoreduction in the complex FeL$_2^+$ is $\phi_2(436\ nm) = 1.1 \times 10^{-3}$ and $\phi_2(366\ nm) = 1.4 \times 10^{-3}$

It is a generally accepted fact that the lifetime of LMCT or LF excited high-spin Fe(III) complexes does not exceed nanosecond time domain, *i.e.* the photoreduction of Fe(III) in its complexes is associated rather with innersphere photooxidation of a ligand present in the primary coordination sphere than with an outer sphere bimolecular electron transfer. Nonluminescent LMCT excited states are postulated to be responsible for such reactions [24].

In our systems, three different ligands, namely molecules of H_2O and anions of L^- and OH^-, can be coordinated to the Fe(III) central atom and be, therefore, photooxidized. Oxidation of kojic acid in acidic solutions by Ce(IV) species gave rise to phenoxyl-like radicals directly observed in flow systems by EPR spectroscopy [12]. In our previous work [25], using the spin trap *tert*-butylnitroxide (TBN), kojic acid radical L$^{\cdot}$ was identified in irradiated aqueous solution of FeL$_3$. In a methanolic solution of FeL$_3$ the formation of $^{\cdot}CH_2OH$ radicals was observed [26] by spin-trapping EPR using nitrosodurene as a spin trap. In this work a solution containing FeL^{2+} as the only kojato complex was irradiated in the presence of 5,5-dimethyl-1-pyrroline N-oxide as a spin trap. The irradiation caused the formation of a radical adduct characterized by the coupling constants $a_H = 1.50$ mT, $a_N = 1.50$ mT and the value of $g = 2.0057$. Experimental and calculated spectrum is shown in Fig. 3. A tentative interpretation of the results of EPR investigations is as follows. Photoreduction of the central atom
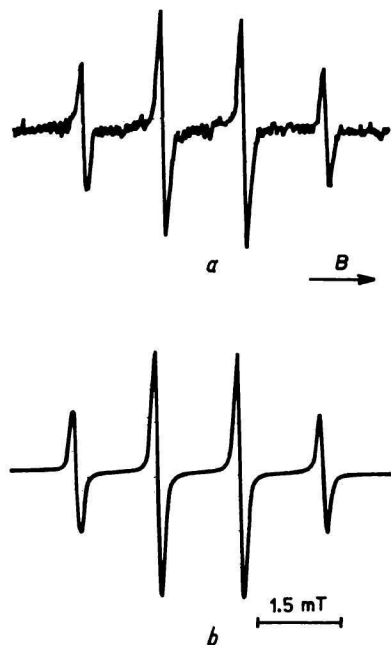
Fig. 3. Experimental (*a*) and calculated (*b*) EPR spectrum of the adduct of OH· radical with spin trap 5,5-dimethyl-1-pyrroline *N*-oxide, formed in irradiated aqueous FeL^{2+} solution.

Fe(III) is associated with oxidation of a ligand (L^-, H_2O) being coordinated in the primary coordination sphere or with a solvent molecule (H_2O, CH_3OH) located in the vicinity of excited Fe(III) complex. EPR measurements do not allow to distinguish between a radical formation in the primary photochemical deactivation step and that in a secondary dark reaction. Electrochemical [27] and photochemical [3] investigation of kojato complexes, performed in methanolic media, manifested a strong tendency of the radical L· to revert to L^- which should rationalize the identification of solvent radicals in the systems containing FeL_3 as the only Fe(III) species. It seems to be worth mentioning that in methanolic solutions the reversion of L· to L^- is a fast and quantitative process and no net destruction of L^- or HL occurred [3].

REFERENCES

1. Koch, S. and Ackermann, G., *Z. Chem. 30*, 33 (1990).
2. Šima, J., Bradiaková, A., and Antalík, M., *J. Photochem. Photobiol. A94*, 163 (1996).
3. Šima, J., Chochulová, B., Veverka, M., Makáňová, J., Hajšelová, M., and Bradiaková, A., *Pol. J. Chem. 67*, 1369 (1993).
4. Wei, C. I., Huang, T. S., Fernando, S. Y., and Chung, K. T., *Toxicol. Lett. 59*, 213 (1991).
5. Hudecová, D., Jantová, S., Melník, M., and Uher, M., *Folia Microbiol. 41*, 473 (1996).
6. Kovacic, P., Kassel, M. A., Ames, J. R., Feinberg, B. A., and Sliwa, W., *J. Biopharm. Sci. 1*, 331 (1990).
7. Nippon Steel Corp., *Jpn. Kokai Tokyo Koho, JP 112,482* (1981).
8. Bissett, D. L., Bush, R. D., and Chatterjee, R. (Procter & Gamble Co.), *Eur. Pat. Appl., EP 313,305* (1989).
9. Seiwa Oil and Chemetics Co. Ltd., *Jpn. Kokai Tokyo Koho, JP 231,661* (1990).
10. Kallio, H., *J. Agric. Food Chem. 37*, 1367 (1989).
11. Katoh, S., Toyama, J., Kodama, I., Kamiya, K., Akita, T., and Abe, T., *Eur. Surg. Res. 24*, 349 (1992).
12. Dixon, W. T., Moghimi, M., and Murphy, D., *J. Chem. Soc., Perkin Trans. II 1975*, 101.
13. Šima, J., Makáňová, J., and Štibrányi, L., *J. Photochem. Photobiol. A84*, 173 (1994).
14. Hirsch, J., Paulus, H., and Elias, H., *Inorg. Chem. 35*, 2343 (1996).
15. Murov, S. L., *Handbook of Photochemistry*. Dekker, New York, 1973.
16. Okáč, A. and Kolařik, Z., *Collect. Czech. Chem. Commun. 24*, 266 (1959).
17. McBryde, W. A. E. and Atkinson, G. F., *Can. J. Chem. 39*, 510 (1961).
18. Petrola, P., *Finn. Chem. Lett. 1985*, 207.
19. Ewert, A., Wannowius, K., and Elias, H., *Inorg. Chem. 17*, 1691 (1978).
20. Cotton, F. A. and Wilkinson, G., *Inorganic Chemistry*, 4th Edition, p. 718. Wiley, New York, 1987.
21. Wilkins, R., *Kinetics and Mechanism of Reactions of Transition Metal Complexes*, 2nd Edition. Verlag Chemie, Weinheim, 1991.
22. Makáňová, J., Šima, J., Brezová, V., and Elias, H., in *Progress in Coordination and Organometallic Chemistry*. (Ondrejovič, G. and Sirota, A., Editors.) P. 201. STU Press, Bratislava, 1997.
23. Sýkora, J. and Šima, J. *Coord. Chem. Rev. 107*, 1 (1990).
24. Šima, J. and Makáňová, J. *Coord. Chem. Rev.*, in press.
25. Šima, J., Havašová, K., and Ducárová, T., *Z. Chem. 30*, 446 (1990).
26. Šima, J., Makáňová, J. and Veverka, M., *Monatsh. Chem. 126*, 149 (1995).
27. Šima, J., Makáňová, J., Kotočová, A., and Bradiaková, A., *J. Photochem. Photobiol.*, in press.

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