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Photoredox Properties of Kojic Acid and Its Derivatives Complexed to Iron(III).

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Summary. Iron(III) complexes of the form *cis*-[Fe(SB)($X-K$)] in which SB^{2-} are open-chain tetradentate *Schiff* base N_2O_2-ligands of *acacen, benacen* or *salen* type, and $X-K^-$ are bidentate anions of kojic acid (5-hydroxy-2-hydroxymethyl-4*H*-pyran-4-one) or other γ-pyranones undergo photoredox transformations when being irradiated in methanol into intraligand or *LMCT* bands. The quantum yields of the photoredox reactions depend on the peripheral constitution of the N_2O_2 ligands, the substituents A and B of the ligands $X-K^-$, and the wavelength of irradiation λ_{irr}. The proposed mechanism involves the population of photoredox reactive *LMCT* states by photophysical deactivation steps, primary photoredox formation of $X-K^{\cdot}$radicals and Fe(II), and subsequent "dark" redox processes giving back the anions $X-K^-$ and the final products Fe(II) and formaldehyde formed in the molar ratio 2:1.

Keywords. Photoredox processes; Iron(III) complexes; γ-Pyranones; Tetradentate *Schiff* base ligands.

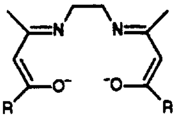
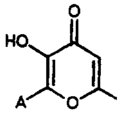
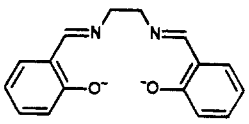
Photoredoxeigenschaften von Fe(III)-Komplexen von Kojic Acid und ihren Derivaten

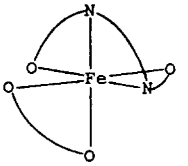
Zusammenfassung. Eisen(III)-Komplexe der Form *cis*-[Fe(SB)($X-K$)] mit SB^{2-} = offenkettige tetradentate *Schiff*-Basen-N_2O_2-Liganden und $X-K^-$ = bidentate Anionen von 5-Hydroxy 2-hydroxymethyl-4*H*-pyran-4-on oder andere β-Pyranone unterliegen bei Bestrahlung in Methanol Photoredoxumwandlungen, was durch Intraligand- oder *LMCT*-Banden belegt wird. Die Quantenausbeuten der Reaktionen hängen von der Konstitution der N_2O_2-Liganden, den Substituenten A und B und dem Liganden $X-K^-$ sowie der Anregungswellenlänge λ_{irr} ab. Der vorgeschlagene Mechanismus beinhaltet die Population photoredoxreaktiver *LMCT*-Zustände durch photophysikalische Deaktivierungsschritte, die Bildung von $X-K^{*}$-Radikalen und Fe(II) und–über Dunkelprozesse – die Rückbildung der Anionen $X-K^-$ sowie die Reaktion zu den Endprodukten Fe(II) und Formaldehyd im molaren Verhältnis 2:1.

Introduction

Kojic acid (5-hydroxy-2-hydroxymethyl-4*H*-pyran-4-one) and its derivatives (see Scheme 1) inhibit various microbial processes, suppress microorganism multiplication in oil-water emulsions, act as an efficient substance in sun-tan oils and other photoprotective mixtures, play the role of a chelator for some metal ions in medicine, *etc.* [1–8]. γ-Pyranones can form transition metal complexes and be, as free compounds or complexes, exposed to sunlight. The knowledge of photochemical properties of such complexes seems therefore to be of importance.

The first results on the photochemical behaviour of iron(III) complexes [Fe(*X*–*K*)$_3$] with homogeneous coordination sphere have been published in a previous paper [9]. In this investigation, the results obtained studying complexes *cis*-[Fe(*SB*)(*X*–*K*)], containing in addition to *X*–*K*$^-$ ligands also redox stable N_2O_2 ligands of the *acacen*, *benacen*, and *salen* type [10], are presented. Structures and abbreviations of the ligands used and the chromophore structure are shown in Scheme 1.

R	N_2O_2 ligand	*A*	*B*	H(*X*–*K*)
				
CH_3	*acacen*	H	CH_2OH	H(H–*K*)
C_6H_5	*benacen*	H	CH_2Cl	H(Cl–*K*)
		H	CH_2Br	H(Br–*K*)
		H	CH_2N_3	H(N_3–*K*)
		CH_3	H	H(CH_3–*K*)
	salen			



Scheme 1. Structures and abbreviations of ligands; chromophore structure

Results and Discussion

Due to their open-chain structure, the used *Schiff* bases behave as flexible ligands. In the presence of a bidentate ligand they form low-spin cobalt(III) and high-spin iron(III) complexes with *cis*-configuration of the coordination polyhedra [14, 16] (Scheme 1).

The electronic absorption spectra of all complexes are very similar. As an example, the spectral characteristics of *cis*-[Fe(*benacen*)(H–*K*)] are given in Table 1. Based on the interpretation of the electronic absorption spectra of complexes containing N_2O_2 ligands and/or *X*–*K*$^-$ ligands [17–20], the excited states populated by photo-excitations using our incident radiation wavelengths can be described as follows. The absorption of a photon at 254 nm is connected with a change in the π-system of the phenyl groups of the N_2O_2-ligands; photons of 313 nm induce transitions (n $\rightarrow \pi^*$ or $\pi \rightarrow \pi^*$) localized at coordinated *X*–*K*$^-$ ligands; by a photon of 365 nm, predominantly the $\pi \rightarrow \pi^*$ transition localized at the C=N double bond of the N_2O_2 ligands is induced. Visible light absorption is associated with an electron transfer from a donor oxygen atom (of both $X{-}K^-$ and N_2O_2 ligands) to the central atom. The molar absorption coefficients of the spin-forbidden ligand-field transitions are very low for Fe(III) complexes (usually $\varepsilon < 1\,M^{-1}\cdot\mathrm{cm}^{-1}$), and the bands of the LF transitions are not observable in solution spectra.

In the absence of radiation the complexes are redox stable in methanol. They do not provide any luminescence at our experimental conditions. Irradiation of methanolic solutions of the complexes gives rise to the photoreduction of Fe(III) to Fe(II). The quantum yield values of the formation of Fe(II), $\phi_{\mathrm{Fe(II)}}$, are gathered in Table 2. As a final product of oxidation, formaldehyde was determined in the molar ratio of approximatively 1:2 with respect to formed Fe(II).

Using the spin trap *TBN* it has been shown previously [9] that in an aqueous solution (water was used as a solvent in order to avoid complications arising from the possible presence of the radicals $^{\cdot}CH_2OH$ or $CH_3O^{\cdot}$ derived from methanol) irradiation of complexes $[\mathrm{Fe}(X{-}K)_3]$ leads to the formation of radicals $X{-}K^{\cdot}$ in the primary photoredox step. The first photochemical deactivation redox step (which can be realized after some photophysical deactivations occur) can be, therefore, postulated as follows:

$$cis\text{-}[\mathrm{Fe^{III}}(SB)(X{-}K)] \xrightarrow{h\nu} [\mathrm{Fe^{II}}(SB)] + X{-}K^{\cdot}$$

Table 1. Values of band maxima (λ_{max}), shoulders (sh), and corresponding molar absorption coefficients ε_λ in the electronic absorption spectrum of *cis*-[Fe(*benacen*)(H–*K*)]

λ_{max} (sh) (nm)	238	(252)	(290)	331	(355)	(439)	521
ε_λ, $M^{-1}\mathrm{cm}^{-1}$	54000	34200	26700	39500	34000	2200	2450

Table 2. Quantum yield values of Fe(II) formation ($\phi_{\mathrm{Fe(II)}}$) for *cis*-[Fe(*SB*)(*X*–*K*)] irradiated in methanol (standard deviation ≤ ± 8%)

λ_{irr} (nm)	N_2O_2 ligand	$\phi_{\mathrm{Fe(II)}} \times 10^2$				
		H–*K*	Cl–*K*	Br–*K*	N_3–*K*	CH_3–*K*
254	*benacen*	4.72	5.86	5.87	2.55	1.07
313		2.89	3.22	3.75	1.00	0.75
365		1.79	1.02	1.27	0.17	0.12
436		0.035	0.062	0.045	0.090	0.040
254	*acacen*	4.51	13.73	6.07	1.84	1.91
313		2.50	7.80	4.00	1.15	0.078
365		0.41	2.75	1.78	0.23	0.025
436		0.049	0.15	0.035	0.042	0.026
254	*salen*	1.58	2.45	1.96	1.08	0.72
313		1.12	2.15	1.38	0.71	0.59
365		0.085	2.00	0.95	0.12	0.080
436		0.037	0.070	0.048	0.042	0.030

Methanol behaves as a good radical scavenger and reacts with the radicals $X\text{–}K^{\bullet}$ producing the radicals $^{\bullet}CH_2OH$:

$$X\text{–}K^{\bullet} + CH_3OH \rightarrow H(X\text{–}K) + {}^{\bullet}CH_2OH$$

The adduct of the radical $^{\bullet}CH_2OH$ with the spin trap *ND* gave an EPR spectrum characterized by the splitting constants $a_N^{NO} = 1.37\,mT$, and $a_H^{CH_2} = 0.70\,mT$. The radical $^{\bullet}CH_2OH$ is a strong reducing agent ($E^0(^{\bullet}CH_2OH/CH_2O) = -0.92\,V$ [21]) and it is converted to CH_2O through the redox reaction

$$^{\bullet}CH_2OH + cis\text{-}[Fe^{III}(SB)(X\text{–}K)] \rightarrow [Fe^{II}(SB)] + CH_2O + H(X\text{–}K)$$

The efficiency of the above reaction is very high as evidenced by the molar ratio of $c(Fe^{II})\!:\!c(CH_2O) = 2\!:\!1$ which suggests that the rate constant of the reaction is higher than that of the possible disproportionation of the radicals $^{\bullet}CH_2OH$ into CH_3OH and CH_2O and by the finding that at a higher complex concentration (solutions with initial $c(Fe^{III}) > 0.05\,M$) no EPR signal of a spin-adduct was observed. It should be mentioned that, due to their kinetic lability, the composition of the formed Fe(II) complexes is only tentatively suggested.

The overall quantum yields of Fe(II) formation (Table 2) depend both on the remote parts of the ligands and the wavelength of incident light. The influence of the periphery of the ligands is in agreement with a general observation according to which the peripheral ligand's parts influence the efficiency of photochemical deactivation processes [22], but no correlation exists between the quantum yield of the photoprocesses (excited state parameters) and ground-state parameters of these parts.

Of all the populated excited states, the ligand-to-metal charge transfer (*LMCT*) states are responsible for an inner sphere electron transfer leading to the observed photoreduction of Fe(III) to Fe(II). Such states can be populated directly with visible light or by partial deactivations (both spin allowed internal conversion and spin forbidden intersystem crossing can proceed) from the primary populated higher energy intraligand excited states.

Taking into consideration the photoredox reactivity (expressed by means of $\phi_{Fe(II)}$ values) of our complexes and the localization of the incident radiation absorption, two ostensible paradoxes emerge. The first one is that the complexes in the photoredox reactive *LMCT* states being directly populated exhibit a lower photoreactivity than those excited primarily into the intraligand states. The second apparent paradox on is that the primary absorption of a photon at the peripheral phenyl groups of the N_2O_2 ligand induces the photooxidation of the other ligand ($X\text{–}K^-$) with the highest of all quantum yield values.

The wavelength dependence of $\phi_{Fe(II)}$ for our non-luminescent complexes may be interpreted as a consequence of two factors. The first one is the different ratio of the short-lived spin-allowed to the longer-lived spin-forbidden *LMCT* states depending on a path of partial deactivations. The second factor is the different content of vibrational energy (the higher excitation energy, the higher the vibrational energy of the photoredox reactive *LMCT* states) which influences the efficiency of separation of the primary photoproducts and/or the efficiency of their recombination.

In the fields of application of chemical substances there is frequently a necessity to prevent undesirable reactions to occur or to minimize their extent in order to avoid the formation of harmful products (*e.g.* radical and toxic species in photoredox processes). Of all the studied derivatives, maltol $H(CH_3-K)$ fits the above requirement in the best way, as both its complexes $[Fe(CH_3-K)_3]$ [9] and *cis*-$[Fe(SB)(CH_3-K)]$ undergo the photoredox reactions with the lowest efficiency at all wavelengths of incident radiation used. Moreover, the ligands $X-K^-$ take part in the radical redox reactions; however, their net concentration does not change, which is an advantage for their role in application processes.

Experimental

The *Schiff* bases H_2(*acacen*), H_2(*benacen*), H_2(*salen*), chlorokojic acid $H(Cl-K)$, bromokojic acid $H(Br-K)$, azidokojic acid $H(N_3-K)$, and maltol $H(CH_3-K)$ were available from our previous work [9, 10]. Kojic acid $H(H-K)$ was purchased from Fluka, potassium *tris*-(oxalato)-ferrate(III), from Oxford Organic Chemicals. The spin trap nitrosodurene (*ND*) was kindly supplied by Prof. *D. Rehorek* (Leipzig University, FRG). The other chemicals were from Lachema, all of them being of analytical grade and used as received. Methanol (Lachema) was distilled from $Mg(OCH_3)_2$ prior to use.

The complexes were prepared *in situ* by subsequent dissolution of $Fe(NO_3)_3 \cdot 9H_2O$, $H_2(SB)$, and $H(X-K)$ in the molar ratio 1:1:10 in methanol so that $c(Fe^{III}) = 2.0 \times 10^{-4}\,M$.

Solutions of the complexes were irradiated at 254 nm, 313 nm, 365 nm or 436 nm in a three-chambered quartz photoreactor at 21 ± 2 °C by a medium-pressure Hg-lamp (Tesla RVK, 125 W) or a low-pressure Hg-lamp (Germicidal Lamp G8T5). Solutions were deoxygenated by bubbling with pure argon 30 minutes before and during irradiation. The intensity of incident monochromatized light [9] was determined by a ferrioxalate [11] or *Reinecke's* salt actinometer [12] and was of the order 10^{18} quanta$\cdot s^{-1} \cdot cm^{-3}$.

The photoreduction of Fe(III) to Fe(II) was followed by ploting Fe(II) concentration *vs.* irradiation time. The content of the photochemically formed Fe(II) in the irradiated systems was determined on the basis of known spectral properties of the complex $[Fe(phen)_3]^{2+}$ [11]. Details on the evaluation of photochemical data are given elsewhere [9, 10]. Formaldehyde was determined spectrophotometrically by the method described in Ref. [13]. The total concentration of kojic acid or its derivatives before and after irradiation was determined on the basis of spectral properties of the complexes $[Fe(X-K)(CH_3OH)_4]^{2+}$ which were formed after addition of a 2 ml sample to 8 ml of $5.0 \times 10^{-3}\,M$ $Fe(NO_3)_3$ in acidified methanol (1.0 ml of concentrated H_2SO_4 in 100 ml of solution). The radical $^{\bullet}CH_2OH$ was identified by EPR spectroscopy in the form of its spin adducts with the spin trap nitrosodurene.

Electronic absorption spectra were recorded on a Specord M-40 spectrophotometer (Zeiss, Jena, FRG); EPR spectra were scanned on a Brucker ER 200E-SRC spectrometer by irradiating the solutions directly in a cavity of the spectrometer, luminescence was measured on a Perkin Elmer LS 50 spectrofluorimeter. All experiments were repeated at least three times and the data were evaluated by the standard least square method.

References

[1] Bissett D. L., Bush R. D., Chatterjee R. (Procter and Gamble Comp.) (1989) Eur. Pat. Appl. EP 313, 305

[2] Seiwa Oil and Chemetics Comp. Ltd. (1990) Jpn. Kokkai Tokyo Koho, JP 231, 661

[3] Kallio H. (1989) J. Agric. Food Chem. **37**: 1367

[4] Nippon Steel Corp. (1981) Jpn Kokkai Tokyo Koho JP 81, 112, 482

[5] Dowd P. F. (1988) U.S. Pat. Appl. US 207, 589

[6] Silver J. (1986) GB Pat. Appl. GB 86/15, 041

[7] Weeks P. D., Allingnham R. P. (1983) U.S. Pat. Appl., US 371, 932

[8] Van der Kraaij A. M. M., Van Eijk H. G., Koster J. F. (1989) Circulation **80**: 158

[9] Šima J., Chochulová B., Veverka M., Makáňová J., Hajšelová M., Bradiaková A. (1993) Polish J. Chem. **67**: 1369

[10] Šima J., Mašlejová M., Ducárová T., Kotočová A. (1990) Z. Anorg. Allg. Chem. **589**: 207

[11] Murov S. L. (1973) Handbook of photochemistry. Dekker, New York

[12] Wegner E. E., Adamson A. W. (1966) J. Am. Chem. Soc. **88**: 394

[13] Nash T. (1953) Biochem. J. **55**: 417

[14] Takahashi S., Fujii Y. (1977) Ibaraki Kogyo Koto Semmon Gakko Kenkyu Iho **12**: 265

[15] Lloret F., Julve M., Mollar M., Castro I., Lattore J., Faus J., Solans X., Morgenstern-Badarau I. (1983) J. Chem. Soc., Dalton Trans. 729

[16] Lauffer R. B., Heinstand R. H., Que L. (1983) Inorg. Chem. **22**: 50

[17] Bosnich B. (1968) J. Am. Chem. Soc. **90**: 627

[18] Petrola R. (1985) Finn. Chem. Lett. 207

[19] Šramko T., Šima J., Fodran P. (1992) Acta Chim. Hung. **129**: 215

[20] Lever A. B. P. (1984) Inorganic electronic spectroscopy. Elsevier, Amsterdam

[21] Endicott J. F. (1975) Charge-Transfer Photochemistry. In: Adamson A. W., Fleischauer P. D. (eds.) Concepts of inorganic photochemistry. Wiley, New York, p 81

[22] Šima J. (1992) Comments Inorg. Chem. **13**: 277

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