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Original Scientific Paper

Mechanism of Photoredox Reactions of Iron(III) Complexes Containing Salen-type Ligands*

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A mechanism of photoredox processes occurring in irradiated methanolic solutions of *trans*-[Fe(R-salen)(CH_3OH)F], where $(\text{R-salen})^{2-}$ are tetradentate open-chain Schiff base *N,N′*-ethylenebis(5-R-salicylideneiminato) N_2O_2-ligands (R = F, I, CH_3, CF_3, OCH_3, NO_2), has been investigated and proposed. The complexes are redox stable in the dark. The photoreduction of Fe^{III} to Fe^{II} induced by ultraviolet irradiation of the complexes is associated with the radical $^{\bullet}CH_2OH$ formation, which is subsequently transformed to formaldehyde CH_2O, the mole ratio of Fe^{II} and CH_2O approaching 2:1. The efficiency of the photoredox process is strongly wavelength dependent and influenced by the peripheral R groups of the tetradentate ligands. Electrode potentials $E_{1/2}(Fe^{III/II})$ correlate with Hammett constants of the R substituents. When compared with analogous halogeno *trans*-[Fe(R-salen)(CH_3OH)X] complexes, significant stabilization of Fe^{III} by F^- ligands in the photochemical reduction is observed.

Key words: iron(III) complexes, fluoro complexes, Schiff base ligands, photoredox processes, electrode potentials, mechanism of photoprocesses.

INTRODUCTION

The importance of electron-donor and electron-acceptor properties of ligands or their functional groups for the structure and reactivity of coordination compounds has been underlined in numerous papers.[1–3] Electrochemical[4–6]

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[*] Dedicated to Professor Smiljko Ašperger on the occasion of his 80th birthday.

and structural[7,8] studies have revealed that, along with the electronic nature of ligands, their position in the coordination sphere related to the redox orbital symmetry may be the key factor determining the redox stability/reactivity of transition metal complexes of the redox active central atoms.

Stabilization of the ground state iron(III) complexes by fluoride anions is a well-known empirical fact, exploited mainly in analytical chemistry. On the other hand, the excited state properties and electrochemical behaviour of iron(III) fluoro complexes belong to the blank areas of chemistry.[9,10] Searching for the possibilities and limitations in optimizing the course and efficiency of redox properties of iron(III) complexes has led us to systematic investigation of different families of such complexes, those containing tetradentate Schiff bases and monodentate acidoligands being among them.[11]

In this contribution, the results on photochemical and electrochemical properties of the *trans*-[Fe(R-salen)(CH_3OH)F] complexes are presented and compared with their chloro, bromo or iodo analogues. The structure of the R-salen ligands is shown in Figure 1.

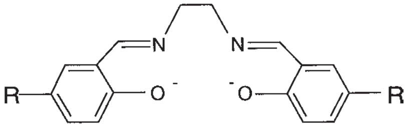

Figure 1. Structure of (R-salen)$^{2-}$ ligands.

EXPERIMENTAL

The Schiff bases H_2(5-F-salen), H_2(5-I-salen), H_2(5-NO_2-salen), H_2(5-CF_3-salen), H_2(5-CH_3-salen) and H_2(5-OCH_3-salen) were synthesized by condensation of the corresponding R-salicylaldehyde with 1,2-ethanediamine in a 2:1 mole ratio in methanol.[12] The ligands were characterized by elemental analysis, melting point, ^{1}H NMR and electronic absorption spectra.

Methanol (Lachema, reagent grade) was distilled before use from $Mg(OCH_3)_2$. 1,2-Ethanediamine (Lachema) was distilled at reduced pressure prior to use. Potassium tris(oxalato)ferrate(III) (Oxford Organic Chemicals), nitrosodurene (nd) and 5,5-dimethyl-1-pyrrolidine-*N*-oxide (dmpo) (Sigma), $[N(C_2H_5)_4]F$ and 1,10-phenanthroline (phen) (Aldrich) were used without further purification. Other chemicals were purchased from Lachema and used as received. All commercial chemicals were of analytical grade.

Coordination of fluoride anions to the Fe^{III} central atom was monitored by potentiometric titration of 2.0×10^{-3} mol dm^{-3} [Fe(5-CH_3-salen)($CH_3OH)_2]^+$ with 2.0×10^{-3} mol dm^{-3} $[N(C_2H_5)_4]F$ at the ionic strength $I(NaClO_4) = 0.1$ mol dm^{-3} using a fluoride-ion selective electrode.

The irradiated oxygen-free solutions of the [Fe(R-salen)(CH_3OH)F] complexes were prepared *in situ* from stock methanolic solutions of $Fe(NO_3)_3$, the corresponding

H_2(R-salen) and $[N(C_2H_5)_4]F$ so as to obtain solutions with the initial concentrations of $c(Fe^{III}) = 2.0 \times 10^{-4}$ mol dm^{-3}, $c(H_2(\text{R-salen})) = 2.0 \times 10^{-4}$ mol dm^{-3}, and $c(F^-) = 4.0 \times 10^{-4}$ mol dm^{-3}. The solutions were deoxygenated by purging with a solvent-saturated stream of argon 30 minutes before and during irradiation. The complexes containing other halogenoligands were prepared in an analogous way using the corresponding $[N(CH_3)_4]X$. Fe^{II} was determined as $[Fe(phen)_3]^{2+}$, CH_2O as 3,5-diacetyl-1,4-dihydrolutidine, $^{\bullet}CH_2OH$ was identified by EPR spectroscopy in the form of its spin adduct with nd or dmpo; details on the used photochemical procedures, electrochemical measurements, analytical methods and treatment of experimental data are described elsewhere.[13]

Electrode potentials were scanned on a RA3 polarographic analyzer (Laboratorní Prístroje, Praha) equipped with a standard three-electrode configuration. Electronic absorption spectra were recorded on a Specord M-40 spectrophotometer. In potentiometric titrations, a Radelkis (type 211/1) pH meter in combination with a fluoride-ion selective electrode (Radelkis, model OP-F-O711P) was used. EPR spectra were recorded on a Brucker 200D spectrometer coupled with an Aspect 2000 computer.

RESULTS AND DISCUSSION

Treatment of the data obtained by standard potentiometric titration[14] of $[Fe(CH_3\text{-salen})(CH_3OH)_2]^+$ with fluoride ions ($c_{total}(Fe^{III}) = 2.0 \times 10^{-4}$ mol dm^{-3}, $c_{total}(F^-)$ increased from 5.0×10^{-5} mol dm^{-3} to 1.0×10^{-3} mol dm^{-3} in solutions) documented (Figure 2) that in the range of $c_{total}(F^-) : c_{total}(Fe^{III}) = 1.2 : 1$ to $2.3 : 1$, one F^- ligand is coordinated to the Fe^{III} central atom. Given the known tendency of the high-spin Fe^{III} to form hexacoordinated complexes[3,15] and that of tetradentate salen-type ligands to form their equatorial plane,[16–18]

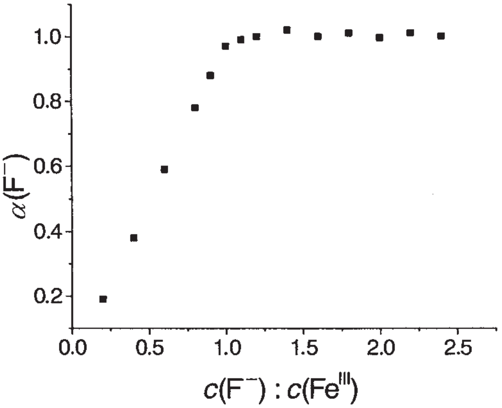

Figure 2. Dependence of the average number, $\alpha(F^-)$, of F^- anions coordinated to the Fe^{III} central atom on $c_{total}(F^-) : c(Fe^{III})$ obtained by potentiometric titration of 2.0×10^{-3} mol dm^{-3} $[Fe(CH_3\text{-salen})(CH_3OH)_2]^+$ with 2.0×10^{-3} mol dm^{-3} $[N(C_2H_5)_4]F$ at the ionic strength $I(NaClO_4) = 0.1$ mol dm^{-3} in methanol.

the composition of the complexes present in methanol in such conditions can be expressed as *trans*-[Fe(R-salen)(CH_3OH)F].

Typically, the electronic absorption spectra of the [Fe(R-salen)(CH_3OH)F] complexes consist of several broad, poorly resolved bands and shoulders. Based on previously published results on the spectra of transition metal complexes with salen-type ligands,[11,19–21] the absorption of a photon in the visible region can be attributed to ligand-to-metal charge transfer (LMCT) transitions O(2p) → Fe(3d) (Eq. 2), the ultraviolet bands centered at 225–280 nm and 300–350 nm to the intraligand transitions IL($\pi \rightarrow \pi^*$) predominantly located on the phenyl rings and on the azomethine C=N fragment of the R-salen ligands, respectively (Eq. 1). Owing to their spin-forbidden nature, bands of ligand-field (LF) states were not observed in solution spectra.

Neither the [Fe(R-salen)(CH_3OH)F] complexes nor their chloro, bromo or iodo analogues undergo spontaneous redox changes in methanolic solutions in the dark.

Irradiation of methanolic solutions of the investigated complexes by ultraviolet radiation leads to photoreduction of Fe^{III} to Fe^{II}. The overall quantum yield values of Fe^{II} formation depend on the wavelength of incident radiation and on the peripheral R groups of the R-salen ligands (Table I). The quantum yields of Fe^{III} photoreduction at irradiation with 436 nm were very low ($\Phi(Fe^{II}) < 10^{-5}$) and are not included in Table I.

TABLE I

Quantum yields of Fe^{II} formation, $\Phi(Fe^{II})$, for [Fe(R-salen)(CH_3OH)X] irradiated in methanol; half-wave potentials, $E_{1/2}(Fe^{III/II})$, for the complexes (expressed *vs.* NHE) and Hammett constants, σ(R), of the R groups[24]

5-R-salen	X^-	$\Phi(Fe^{II}) \times 10^4$			$E_{1/2}(Fe^{III/II})$/V	σ(R)
		λ_{irr}/nm: 254	313	366		
NO_2-salen	F^-	6.5	1.8	<0.1	0.100	0.78
CF_3-salen	F^-	12.0	3.5	<0.1	0.075	0.54
I-salen	F^-	2.0	<0.1	<0.1	–0.005	0.18
F-salen	F^-	25.5	7.0	0.55	–0.030	0.06
CH_3-salen	F^-	5.0	1.5	<0.1	–0.065	–0.17
OCH_3-salen	F^-	4.5	2.0	0.30	–0.085	–0.27
OCH_3-salen	Cl^-	160	90	55	–0.100	–0.27
OCH_3-salen	Br^-	80	25	1,85	–0.105	–0.27
OCH_3-salen	I^-	550	385	300	–0.115	–0.27

Using the spin trapping EPR technique, $^{\bullet}CH_2OH$ was the only radical found in the irradiated system of the $[Fe(CH_3\text{-salen})(CH_3OH)F]$ complex. The adduct of the $^{\bullet}CH_2OH$ radical with the nd spin trap gave an EPR spectrum characterized by the splitting constants $a_N^{NO} = 1.398$ mT and $a_H^{CH_2} = 0.775$ mT; for the adduct with dmpo, the constants $a_N = 1.521$ mT and $a_H = 2.135$ mT were calculated from its spectrum. Experimental and simulated EPR spectra matched very well.

Formaldehyde and Fe^{II} were formed as the final products of photoredox processes. Within the first minutes of irradiation, the rise in the products concentration is linear with time and the mole ratio of $c(Fe^{II}) : c(CH_2O)$ was generally close to 2 : 1 (*e.g.*, for $[Fe(CH_3\text{-salen})(CH_3OH)F]$, the rates of product formation were $dn(Fe^{II})/dt_{irr} : dn(CH_2O)/dt_{irr} = 1.96 : 1$ at $\lambda_{irr} = 254$ nm). Introducing oxygen into the systems after switching off irradiation led to reappearance of the original parent iron(III) complex spectra, Eq. (9), within a few minutes.

The proposed mechanism of the processes occurring in irradiated systems of fluoro complexes may be described by the following groups of steps (in equations, GS, IL and LMCT mean the corresponding ground state, intraligand and ligand-to-metal excited states of Fe^{III} complexes, respectively, left superscripts denote the multiplicity of a given state; the composition of Fe^{II} complexes is suggested to satisfy the stoichiometry requirements; for simplicity, non-redox reactions are not presented).

Excited states population:

$$_{GS}{}^{6}[Fe^{III}(R\text{-salen})(CH_3OH)F] \xrightarrow{h\nu(UV)} {}_{IL}{}^{6}[Fe^{III}(R\text{-salen})(CH_3OH)F] \quad (1)$$

$$_{GS}{}^{6}[Fe^{III}(R\text{-salen})(CH_3OH)F] \xrightarrow{h\nu(Vis)} {}_{LMCT}{}^{6}[Fe^{III}(R\text{-salen})(CH_3OH)F] \quad (2)$$

Physical deactivation by intersystem crossing (isc) or internal conversion (ic):

$$_{IL}{}^{6}[Fe^{III}(R\text{-salen})(CH_3OH)F] \xrightarrow{ic/isc} {}_{LMCT}{}^{6\text{ or }4}[Fe^{III}(R\text{-salen})(CH_3OH)F] \quad (3)$$

$$_{LMCT}{}^{6}[Fe^{III}(R\text{-salen})(CH_3OH)F] \xrightarrow{isc} {}_{LMCT}{}^{4}[Fe^{III}(R\text{-salen})(CH_3OH)F] \quad (4)$$

$$_{LMCT}{}^{6\text{ or }4}[Fe^{III}(R\text{-salen})(CH_3OH)F] \xrightarrow{ic/isc} {}_{LF\text{ or }GS}[Fe^{III}(R\text{-salen})(CH_3OH)F] \quad (5)$$

Primary photoredox step:

$$_{LMCT}{}^{6\text{ or }4}[Fe^{III}(R\text{-salen})(CH_3OH)F] \rightarrow [Fe^{II}(R\text{-salen})F]^- + H^+ + {}^{\bullet}CH_2OH \quad (6)$$

Secondary thermal redox steps:

$$[\mathrm{Fe^{II}(R\text{-}salen)F}]^- + \mathrm{H}^+ + {}^\bullet\mathrm{CH_2OH} \rightarrow [\mathrm{Fe^{III}(R\text{-}salen)(CH_3OH)F}] \quad (7)$$

$$[\mathrm{Fe^{III}(R\text{-}salen)(CH_3OH)F}] + {}^\bullet\mathrm{CH_2OH} \rightarrow [\mathrm{Fe^{II}(R\text{-}salen)F}]^- + \mathrm{H}^+ + \mathrm{CH_2O} \quad (8)$$

Dark reoxidation of Fe(II):

$$4\,[\mathrm{Fe^{II}(R\text{-}salen)F}]^- + \mathrm{O_2} + 2\,\mathrm{H}^+ + 4\,\mathrm{CH_3OH} \rightarrow 4\,[\mathrm{Fe^{III}(R\text{-}salen)(CH_3OH)F}] + 2\,\mathrm{OH}^- \quad (9)$$

Of all accessible excited states, only the spin allowed sextet and spin forbidden quartet LMCT states have the electron distribution suitable for an inner-sphere electron transfer leading to the observed photoreduction of $\mathrm{Fe^{III}}$ to $\mathrm{Fe^{II}}$.[9,10] One of the LMCT states deactivations is a complex redox decomposition leading to the formation of $\mathrm{Fe^{II}}$ and ${}^\bullet\mathrm{CH_2OH}$, Eq. (6). As documented by the value $E°({}^\bullet\mathrm{CH_2OH/CH_2O}) = -1.180$ V,[22] the radical ${}^\bullet\mathrm{CH_2OH}$ is a strong reducing agent able to further reduce $\mathrm{Fe^{III}}$, Eq. (8).

The ratio of $c(\mathrm{Fe^{II}}) : c(\mathrm{CH_2O}) = 2 : 1$ determined in the systems investigated in this work shows that, along with the back reaction (7), the reduction of Fe(III) by ${}^\bullet\mathrm{CH_2OH}$ is the main (if not the only) reactivity mode of ${}^\bullet\mathrm{CH_2OH}$. Its transformation to $\mathrm{HOCH_2{-}CH_2OH}$ or other products would increase the mentioned ratio. Moreover, no such product has been found so far in irradiated methanolic solutions of $\mathrm{Fe^{III}}$ complexes.[9,10]

The observed wavelength dependence of the quantum yield $\Phi(\mathrm{Fe^{II}})$ may be explained, on the basis of generally valid conclusions,[23] understood and summarized in four points:

– Communication between the populated IL and photoredox reactive LMCT states, Eq. (3), is very effective.

– Photoreduction (6) of $\mathrm{Fe^{III}}$ to $\mathrm{Fe^{II}}$ is the most significant (if not the only) mode of photoredox deactivation.

– The content of rovibrational energy of the photoreactive LMCT states is proportional to the energy of an absorbed photon. The higher the difference between the rovibrational energy of a given LMCT state and the threshold energy of the primary photoproducts formation (6), the higher is the probability of their separation, *i.e.* the lower is the probability of their recombination (7) and, consequently, the higher is $\Phi(\mathrm{Fe^{II}})$.

– Since the investigated complexes do not show any luminescence, continuous photolysis does not allow distinguishing between the photoredox reactivity of the quartet and sextet LMCT states.

A fair correlation of the Hammett constants $\sigma(\mathrm{R})$ of the ligand peripheral R groups and the electrode potential values $E_{1/2}(\mathrm{Fe}^{\mathrm{III/II}})$ of the complexes (Table I) was found. The reaction constant ρ defined as[25]

$$\rho = \frac{\mathrm{d}E_{1/2}(\mathrm{Fe}^{\mathrm{III/II}})}{\mathrm{d}\sigma(\mathrm{R})} \tag{10}$$

is $\rho = 0.183 \pm 0.008$ V, *i.e.* the redox orbital of the $\mathrm{Fe}^{\mathrm{III}}$ central atom is influenced by the R substituents. In accordance with the data published for other iron complexes,[26] axial halogenoligand X^- has only slight influence on the electrode potential.

Contrary to the $E_{1/2}(\mathrm{Fe}^{\mathrm{III/II}})/\sigma(\mathrm{R})$ correlation found in electrochemistry, no $\Phi(\mathrm{Fe}^{\mathrm{II}})/\sigma(\mathrm{R})$ correlation was observed in photochemistry of the studied complexes. The reasons for this phenomenon are well understood and explained in detail elsewhere.[11]

A comparison of the quantum yields $\Phi(\mathrm{Fe}^{\mathrm{II}})$ for $[\mathrm{Fe(R\text{-}salen)(CH_3OH)F}]$ and those for their structural analogues with axial Cl^-, Br^-, I^- ligands for which the quantum yields are substantially higher, indicates that the stabilization effect of fluoride anions towards $\mathrm{Fe}^{\mathrm{III}}$ can be extended also to the realm of excited state chemistry. Since the photoredox reactions occur from an excited state and the quantum yield values reflect the kinetics of all deactivation modes, there is no reason for the reactivity to follow expectations stemming from thermodynamics (electrode potentials $E^\circ(\mathrm{X_2/X^-})$ of halogens X). Thus, also the presented results indicate a higher kinetic stability of bromo complexes compared to analogous chloro derivatives (a phenomenon observed also for other halogeno complexes).[11]

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SAŽETAK

Mehanizam fotoredoks reakcija kompleksa željeza(III) koji sadržavaju ligande salenskog tipa

Jozef Šima

Predložen je mehanizam za istraživane fotoredoks-procese u ozračenim metanolnim otopinama *trans*-[Fe(R-salen)(CH_3OH)F], gdje su (R-salen)$^{2-}$ tetradentatni, Shiffove baze otvorenog lanca, *N,N'*-etilenbis(5-R-salicilideniminato) N_2O_2 ligandi (R = F, I, CH_3, CF_3, OCH_3, NO_2). Kompleksi su u mraku stabilni. Fotoredukcija Fe^{III} u Fe^{II} inducirana ultraljubičastim ozračivanjem kompleksa vezana je uz stvaranje radikala $^{\bullet}CH_2OH$ koji zatim prelazi u formaldehid CH_2O pri čemu se množinski odnos Fe^{II} i CH_2O približava 2:1. Efikasnost fotoredoks-procesa jako zavisi o valnoj duljini, i na nju utječu periferne grupe R tetradentatnih liganada. U usporedbi s analognim halogeno-kompleksima, *trans*-[Fe(R-salen)(CH_3OH)X], opažena je znatna stabilizacija Fe^{III} ligandom F$^-$ tijekom fotokemijske redukcije.