PHOTOREDOX REACTIONS OF IODO IRON(III) COMPLEXES CONTAINING TETRADENTATE LIGANDS

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The paper is dedicated to the memory of Professor Antonín A. Vlček.

Photoredox reactions occurring in irradiated methanolic solutions of *trans*-[Fe^{III}(R,R′-salen)(CH_3OH)I], where R,R′-$salen^{2-}$ are *N,N′*-ethylenebis(R,R′-salicylideneiminato), tetradentate open-chain N_2O_2-Schiff bases with R,R′ = H, 5-Cl, 5-Br, 3,5-di-Br, 3,5-di-(CH_3), 3-OCH_3, 5-OCH_3, have been investigated and their mechanism proposed. The complexes are redox-stable in the dark. Ultraviolet and/or visible irradiation of methanolic solution of the complexes induces photoreduction of Fe(III) to Fe(II). Depending on the composition of the irradiated solutions, $^{\bullet}CH_2OH$ radicals or solvated electrons were identified by the EPR spin trapping technique. The final product of the photooxidation coupled with the photoreduction of Fe(III) is formaldehyde and the molar ratio of Fe(II) and CH_2O is close to 2 : 1. The efficiency of the photoredox process is strongly wavelength-dependent and influenced by the peripheral groups R,R′ of the tetradentate ligands.

Keywords: Photoreduction; Iron(III) complexes; Iodo ligand; Schiff bases; Salen complexes; Chelates; Mechanism; EPR spin trapping.

Iron(III) iodide and iodo iron(III) complexes are still “unusual” compounds. Their existence has not been mentioned even in fundamental inorganic compendia[1,2] or only few data are given[3]. In one of the principal monographs devoted to inorganic photochemistry[4], it is stated that “the complexes between Fe^{3+} and strongly reducing ligands (*e.g.* I^-) are so black that they cannot exist”. The existence and redox stability of iodo iron(III) complexes are conditioned predominantly by the solvent used (influencing the redox potentials of the Fe(III)/Fe(II) and I_2/I^- pairs) and/or by the application of ligands stabilizing the Fe(III) oxidation state. As an example of such

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ligands, tetradentate open-chain salen-type Schiff base ligands may be given.

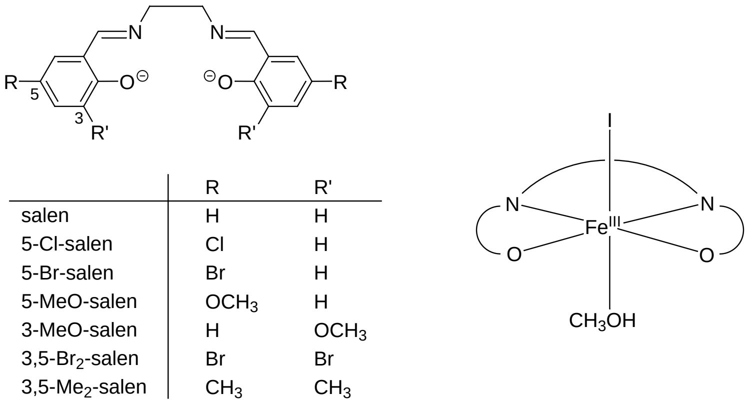
Comparing the photoredox chemistry of other structurally related halo iron(III) complexes, two specific and counter-acting factors characterize the iodo complexes. The first, thermodynamic factor, lies in the facile oxidation of the I^- ligand, giving a chance to reach the highest photoredox quantum yield. The second is the "heavy-atom effect" causing in some cases significantly lower net photoredox reactivity of iodo complexes[5].

In this contribution, the results are presented on photochemical properties of the complexes *trans*-[Fe^{III}(R,R′-salen)(CH_3OH)I], obtained within the attempts to examine the significance of the above mentioned factors. The schematic structures of the R,R′-$salen^{2-}$ ligands and *trans*-[Fe^{III}(R,R′-salen)-(CH_3OH)I] are shown in Fig. 1.

EXPERIMENTAL

The Schiff bases H_2(salen), H_2(5-Cl-salen), H_2(5-Br-salen), H_2(3,5-Br_2-salen), H_2(3,5-Me_2-salen), H_2(3-MeO-salen), and H_2(5-MeO-salen) were synthesized by condensation of corresponding R-salicylaldehyde with ethane-1,2-diamine in 2 : 1 molar ratio in methanol, using a general procedure[6]. The purity of the ligands was checked by elemental analysis, melting point, ^{1}H NMR and electronic absorption spectra.

Methanol (Lachema, reagent grade) was distilled before use from $Mg(OCH_3)_2$. Ethane-1,2-diamine (Lachema) was distilled at a reduced pressure prior to use. 5,5-Dimethyl-3,4-dihydropyrrole-*N*-oxide, DMPO (Aldrich) was freshly distilled before use and stored under argon in a freezer. Potassium tris(oxalato)ferrate(III) (Oxford Organic Chemicals),



	R	R'
salen	H	H
5-Cl-salen	Cl	H
5-Br-salen	Br	H
5-MeO-salen	OCH_3	H
3-MeO-salen	H	OCH_3
3,5-Br_2-salen	Br	Br
3,5-Me_2-salen	CH_3	CH_3

FIG. 1

Schematic representation of the R,R′-$salen^{2-}$ ligands and the coordination sphere of [Fe^{III}(R,R′-salen)(CH_3OH)I] nitrosodurene (ND; Sigma), $[N(CH_3)_4]I$ and 1,10-phenanthroline (Aldrich) were used without further purification. The other chemicals were purchased from Lachema and used as received. All commercial chemicals were of analytical grade.

Solid complexes [Fe(R,R′-salen)I] were synthesized as described in ref.[7] and characterized by elemental analysis and electronic absorption spectra.

Solutions of $[Fe^{III}(R,R'\text{-salen})(CH_3OH)I]$ were prepared either from solid $[Fe^{III}(R,R'\text{-salen})I]$, NMe_4I and methanol or *in situ* from stock methanolic solutions of $Fe(NO_3)_3$, corresponding $H_2(R,R'\text{-salen})$ and NMe_4I, so as to obtain solutions with the initial concentrations of $c(Fe^{III}) = 2.0 \cdot 10^{-4}$ mol l^{-1} and $c(I^-) = 2.0 \cdot 10^{-3}$ mol l^{-1}.

Steady-state photolysis was performed in a three-chambered temperature-controlled (T = 20 ± 1 °C) quartz photoreactor. As a radiation source, a medium-pressure Hg lamp (Tesla RVK, 125 W, radiation monochromatized with solution filters) or a low-pressure Hg lamp (germicidal lamp G8T5) were used. The irradiated solutions were deoxygenated by purging with argon 30 min before and during irradiation. The intensity of the incident monochromatized radiation was determined with a ferrioxalate actinometer[8].

The course of photoredox changes was monitored by electronic absorption spectroscopy as a time change of $c(Fe^{II})$. In certain intervals of irradiation, a 2-ml aliquot of irradiated solution was transferred from a photoreactor to a cell containing 0.02 ml of 30% H_3PO_4 and a few crystals of solid 1,10-phenanthroline. After incorporating Fe(III) into phosphate complexes and Fe(II) into $[Fe(phen)_3]^{2+}$, the concentration of Fe(II) in the irradiated sample was calculated from the absorbance measured at 512 nm, using a value[8] of $1.11 \cdot 10^4$ mol^{-1} l cm^{-1} for the molar absorption coefficient of $[Fe(phen)_3]^{2+}$. The absorption of Fe(III) phosphates in the region $\lambda \geq 500$ nm can be neglected.

Formaldehyde was determined as 3,5-diacetyl-2,6-dimethyl-1,4-dihydropyridine. Details on the experiments performed and experimental data treatment are described in our previous papers[9,10].

The EPR spectra were measured at a temperature of 290 K using a Bruker 200D spectrometer (Germany) interfaced to an Aspect 2000 computer (Germany). The standard spectrometer settings were as follows: center field, 349 mT; sweep width, 10 mT; scan time, 50 or 100 s; microwave frequency, 9.72 GHz; microwave power, 3 or 10 mW; modulation amplitude, 0.005–0.05 mT; spectrometer gain, $1 \cdot 10^5$–$5 \cdot 10^5$. The freshly prepared solutions containing spin traps (c(DMPO) = $1 \cdot 10^{-2}$ mol l^{-1}; saturation concentrations of ND under the given experimental conditions) were carefully purged with argon, then placed in a quartz cell optimized for the Bruker TM cavity. The samples were irradiated directly in the cavity with a 250-W medium-pressure Hg-lamp (Applied Photophysics, England) and the EPR spectra were monitored *in situ*. A Pyrex filter was used to cut off the radiation below 300 nm. The *g*-value was determined with an uncertainty of ±0.0001 using a marker containing 1,1-diphenyl-2-picrylhydrazyl built into the spectrometer. Simulations of the EPR spectra were obtained using the program *SimFonia* (Bruker, Germany). Complex experimental EPR spectra were fitted as linear combinations of individual simulations by a least-squares procedure using the Scientist program (MicroMath).

Electronic absorption spectra were recorded on a Specord 200 spectrophotometer.

RESULTS AND DISCUSSION

Given the known tendency of the high-spin Fe(III) to form hexacoordinated complexes both in the solid state and solutions[11,12], as well as that of salen-type ligands to reside in the equatorial plane[13–15], the composition of the complexes present in methanol can be expressed as *trans*-[Fe^{III}(R,R′-salen)(CH_3OH)I].

Typically, electronic absorption spectra of the complexes [Fe^{III}(R,R′-salen)-(CH_3OH)I] consist of several broad, poorly resolved bands and shoulders (Fig. 2).

On the basis of previously published results[7,16,17], the absorption of a photon in the visible region can be attributed mainly to ligand-to-metal charge transfer (LMCT) transitions O2p or I5p→Fe3d (Eq. (*2*)), and the ultraviolet bands centred at 230–260 and 270–380 nm to the intraligand transitions IL(π→π*) localized predominantly on the benzene rings and on the azomethine C=N fragment of the R,R′-salen ligands, respectively (Eq. (*1*)). Photons with $\lambda \le 255$ nm are absorbed predominantly by I^- anions (Eq. (*8*)) and the optically populated charge transfer-to-solvent (CTTS) state is deactivated by solvated electron formation with a high quantum yield. Owing to their spin-forbidden nature, bands of ligand field (LF) states were not observed in solution spectra.

Blank experiments confirmed that the complexes [Fe(R,R′-salen)(CH_3OH)I] do not undergo spontaneous redox changes in methanolic solutions in the dark.

Irradiation of methanolic solutions of the investigated complexes with ultraviolet radiation or visible light leads to the photoreduction of Fe(III) to Fe(II). The integral quantum yield values of the Fe(II) formation, Φ, depend

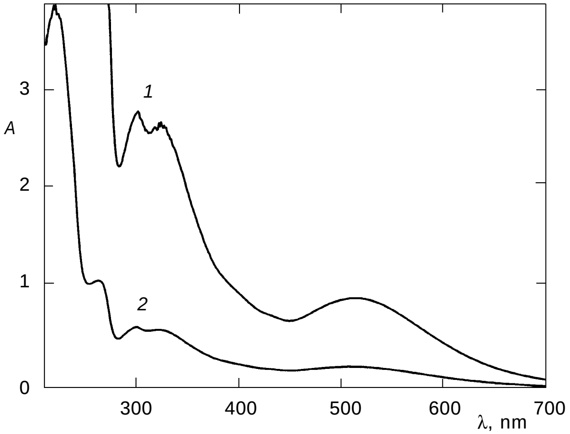


FIG. 2
Electronic absorption spectra of $2.0 \cdot 10^{-4}$ M [Fe^{III}(salen)(CH_3OH)I] in methanolic $2.0 \cdot 10^{-3}$ M NMe_4I recorded in 1.0 cm (*1*) and 0.2 cm (*2*) cells

on the wavelength of incident radiation and on the peripheral groups R and R′ of the R,R′-salen ligand (Table I).

In accordance with our previous experience regarding the photoredox reactions of Fe(III) complexes in methanolic solutions[18], we proposed that using DMPO and ND spin traps we could obtain evidence for the formation of radicals in the irradiated systems. Surprisingly, using ND in saturated ($c \approx 10^{-2}$ mol l^{-1}) solutions of the [Fe^{III}(salen)(CH$_3$OH)I] complex, only poor-quality low-intensity EPR spectra of $^{\bullet}$CH$_2$OH adduct were obtained.

Irradiation of [Fe^{III}(salen)(CH$_3$OH)I] solutions with lower concentrations ($c = 10^{-4}$–10^{-3} mol l^{-1}) in the presence of the ND spin trap resulted in the formation of a three-line EPR spectrum as is shown in Fig. 3a. The absence of β-hydrogen splitting in the experimental spectrum eliminated the trapping of $^{\bullet}$CH$_2$OH radicals.

In agreement with the analysis of photoredox mechanism (as will be shown below), we propose that the EPR signal monitored upon irradiation corresponds to the anion radical of the nitrosodurene spin trap (ND$^{-\bullet}$), formed by the reduction of ND with photoproduced solvated electrons[19]. The Hamiltonian parameters, *viz.* $g = 2.0055$, $a_N = 1.376$ mT, and $6a_H = 0.054$ mT (the hydrogen splittings are invisible due to the peak-to-peak EPR line-width of 0.15 mT), derived from the simulations of experimental spectra (Fig. 3a), are in good agreement with the EPR spectra of ND$^{-\bullet}$ recorded[19] upon photochemical oxidation of [Fe(CN)$_6$]$^{4-}$. Further evidence for the formation of solvated electrons was obtained on addition of benzyl chloride

TABLE I

Quantum yields, $\Phi \cdot 10^3$, of Fe(II) formation in $2.0 \cdot 10^{-4}$ M methanolic solutions of [Fe^{III}(R,R′-salen)(CH$_3$OH)I] on irradiation with various wavelengths

R-salen dianion	254 nm	313 nm	366 nm	546 nm
Salen	2.35	0.90	0.60	0.51
5-Cl-salen	1.85	0.80	0.52	0.41
5-Br-salen	2.07	1.55	0.37	0.36
3,5-Br$_2$-salen	3.38	2.00	0.78	0.41
3,5-Me$_2$-salen	2.73	1.85	0.90	0.37
3-MeO-salen	3.11	2.25	1.20	0.22
5-MeO-salen	1.65	1.10	0.64	0.42

into the experimental systems. The reaction of benzyl chloride with electrons leads to the formation of $^{\bullet}CH_2C_6H_5$ radicals which are trapped by ND (ref.[19]) and easily identified (Fig. 3b). The experimental EPR spectrum depicted in Fig. 3b was simulated as a superposition of three individual EPR spectra, those of the $ND^{-\bullet}$ anion radical, and the $^{\bullet}ND{-}CH_2C_6H_5$ adduct (g = 2.0054, a_N = 1.448 mT, $2a_H$ = 0.897 mT)[19,20], and of low-intensity spectrum of $^{\bullet}ND{-}CH_2OH$ adduct (g = 2.0054, a_N = 1.390 mT, $2a_H$ = 0.7725 mT)[21]. The addition of high concentration of benzyl chloride probably substantially changed the kinetics of reactions for both solvated electrons and $^{\bullet}CH_2OH$ radicals. Consequently, the addition of photo-produced hydroxymethyl radicals to the ND spin trap was possible, and the low-intensity signal of the $^{\bullet}ND{-}CH_2OH$ adduct could be observed (Fig. 3b).

The relative intensity of $ND^{-\bullet}$ increased upon irradiation of $[Fe^{III}(salen)(CH_3OH)I]$ solutions; after the irradiation source was removed, the EPR signal of the anion-radical disappeared by the formal first-order kinetics, with the rate constant of $k = 5.3 \cdot 10^{-3}$ s^{-1}.

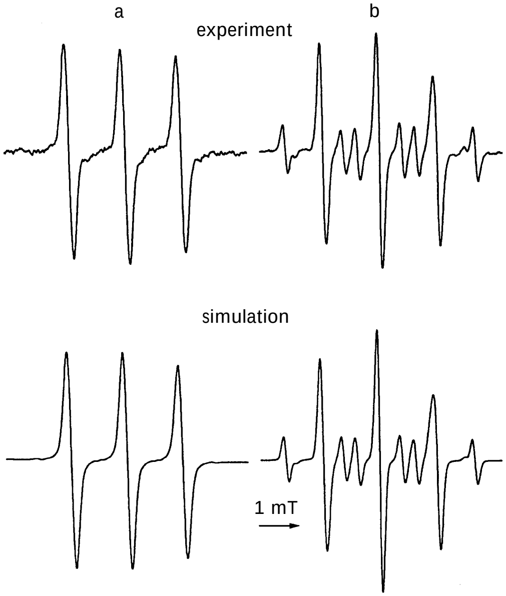


FIG. 3

Experimental and simulated EPR spectra measured upon continuous wave-irradiation (λ > 300 nm) in: a $[Fe^{III}(salen)(CH_3OH)I]$ in methanol ($c = 1 \cdot 10^{-3}$ mol l^{-1}) saturated with nitrosodurene spin trap; b $[Fe^{III}(salen)(CH_3OH)I]$ in methanol ($c = 5 \cdot 10^{-4}$ mol l^{-1}) saturated with nitrosodurene spin trap in the presence of benzyl chloride (c = 6 mol l^{-1})

Upon irradiation of [Fe^{III}(salen)(CH$_3$OH)I] in the concentration range of $5 \cdot 10^{-4}$–10^{-3} mol l^{-1} in the presence of DMPO spin trap, no EPR signals were observed. It is beyond the aim of the present paper to offer an explanation of the concentration dependence of EPR spectra, as this requires values of the rate constants for all actual consecutive and parallel reaction steps involved, that are not known at present.

As the final products of the photoredox processes, formaldehyde and Fe(II) were formed in the 1 : 2 molar ratio. No sign of accumulation of I_3^- anions during irradiation was observed in electronic absorption spectra.

Introducing oxygen into the systems after switching off the irradiation led to a reappearance of the parent iron(III) complex spectra (Eq. (*16*)).

Based on the above spectra interpretation, identification of radicals, determination of molar ratio for the final products and on the literature data[22,23], a plausible mechanism for the processes occurring in irradiated systems of the iodo complexes can be proposed. (GS, IL, and LMCT mean the corresponding ground state, intraligand, and ligand-to-metal charge transfer excited states of Fe(III) complexes, respectively. Left superscripts denote the multiplicity of a given state.) Composition of the complexes is tentatively proposed to satisfy the stoichiometry requirements; for the sake of simplicity, non-redox reactions are not presented.

Excited states population:

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

$$ {}_{\mathrm{GS}}^{6}[\mathrm{Fe^{III}(R,R'\text{-}salen)(CH_3OH)I}] \xrightarrow{h\nu\ (\mathrm{VIS})} {}_{\mathrm{LMCT}}^{6}[\mathrm{Fe^{III}(R,R'\text{-}salen)(CH_3OH)I}] \quad (2)$$

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

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

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

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

Primary photoredox step(s):

$${}^{6\text{ or }4}_{\text{LMCT}}[\text{Fe}^{\text{III}}(\text{R,R}'\text{-salen})(\text{CH}_3\text{OH})\text{I}] \rightarrow [\text{Fe}^{\text{II}}(\text{R,R}'\text{-salen})\text{I}]^- + \text{H}^+ + {}^{\bullet}\text{CH}_2\text{OH} \tag{6}$$

$${}^{6\text{ or }4}_{\text{LMCT}}[\text{Fe}^{\text{III}}(\text{R,R}'\text{-salen})(\text{CH}_3\text{OH})\text{I}] \rightarrow [\text{Fe}^{\text{II}}(\text{R,R}'\text{-salen})(\text{CH}_3\text{OH})] + \text{I}^{\bullet} \tag{7}$$

$$\text{I}^- \xrightarrow{h\nu\ (\lambda \leq 254\text{ nm})} \text{I}^{\bullet} + \text{e}^-\ (\text{solv}) \tag{8}$$

Back reactions of the products formed in the primary process(es):

$$[\text{Fe}^{\text{II}}(\text{R,R}'\text{-salen})\text{I}]^- + \text{H}^+ + {}^{\bullet}\text{CH}_2\text{OH} \rightarrow {}_{\text{GS}}[\text{Fe}^{\text{III}}(\text{R,R}'\text{-salen})(\text{CH}_3\text{OH})\text{I}] \tag{9}$$

$$[\text{Fe}^{\text{II}}(\text{R,R}'\text{-salen})(\text{CH}_3\text{OH})] + \text{I}^{\bullet} \rightarrow {}_{\text{GS}}[\text{Fe}^{\text{III}}(\text{R,R}'\text{-salen})(\text{CH}_3\text{OH})\text{I}] \tag{10}$$

Secondary thermal redox steps:

$$\begin{aligned}[\text{Fe}^{\text{III}}(\text{R,R}'\text{-salen})(\text{CH}_3\text{OH})\text{I}] + {}^{\bullet}\text{CH}_2\text{OH} \rightarrow {} & [\text{Fe}^{\text{II}}(\text{R,R}'\text{-salen})(\text{CH}_3\text{OH})\text{I}]^- + \\ & + \text{H}^+ + \text{CH}_2\text{O}\end{aligned} \tag{11}$$

$$\text{I}^{\bullet} + \text{I}^- \rightarrow \text{I}_2^- \tag{12}$$

$$\text{I}_2^- + \text{I}^{\bullet} \rightarrow \text{I}_3^- \tag{13}$$

$$\text{CH}_3\text{OH} + 2\ \text{I}^{\bullet}\ (2\ \text{I}_2^-\ \text{or}\ \text{I}_3^-) \rightarrow \text{CH}_2\text{O} + 2\ \text{HI}\ (2\ \text{HI} + 2\ \text{I}^-\ \text{or}\ \text{I}^-) \tag{14}$$

$${}_{\text{GS}}[\text{Fe}^{\text{III}}(\text{R,R}'\text{-salen})(\text{CH}_3\text{OH})\text{I}] + \text{e}^- \rightarrow [\text{Fe}^{\text{II}}(\text{R,R}'\text{-salen})(\text{CH}_3\text{OH})\text{I}]^- \tag{15}$$

Dark reoxidation of Fe(II):

$$\begin{aligned}4\ [\text{Fe}^{\text{II}}(\text{R,R}'\text{-salen})\text{I}]^- + \text{O}_2 + 4\ \text{H}^+ + 4\ \text{CH}_3\text{OH} \rightarrow {} & 4\ [\text{Fe}^{\text{III}}(\text{R,R}'\text{-salen})(\text{CH}_3\text{OH})\text{I}] + \\ & + 2\ \text{H}_2\text{O}\end{aligned} \tag{16}$$

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

Fe(III) to Fe(II) (refs[4,22]). One of the LMCT state deactivations is a redox decomposition of the complexes leading to the formation of Fe(II) and $^{\bullet}CH_2OH$ or $I^{\bullet}$ (Eqs (*6*), (*7*)). As documented by the value $E^0(^{\bullet}CH_2OH/CH_2O)$ = –1.180 V (ref.[24]), the radical $^{\bullet}CH_2OH$ is a strong reducing agent capable of reducing further Fe(III) (Eq. (*11*)).

Reactions of iodine atoms (Eqs (*12*), (*13*)) are characterized by nearly diffusion-limited rate constants. Given its characteristic spectrum[25] (ε_{353} = 26 400 mol^{-1} l cm^{-1}), formation of I_3^- can be followed by absorption spectroscopy in the absence of a potential reaction partner. In the presence of a scavenger such as aliphatic alcohols (including methanol), iodine-atom based radicals react to produce aldehydes (Eq. (*14*)).

The ratio $c(Fe^{II}) : c(CH_2O) = 2 : 1$, determined in the systems investigated in this work, shows that, along with the reverse reaction (Eq. (*9*)), the reduction of Fe(III) with $^{\bullet}CH_2OH$ is the main (if not the only) reactivity mode of $^{\bullet}CH_2OH$. Its transformation to $HOCH_2–CH_2OH$ or other products would increase the mentioned ratio. Moreover, no such product has been found so far in irradiated methanolic solutions of Fe(III) complexes[22,23].

Based on the rationalization published in ref.[10], the observed wavelength dependence of the quantum yield $\Phi_{Fe(II)}$ can be understood and summarized in four points:

1) The communication between the populated IL and photoredox reactive LMCT states (Eq. (*3*)) is very effective.

2) The photoreduction of Fe(III) to Fe(II) (Eqs (*6*), (*7*)) is the most significant (if not the only) mode of photoredox deactivation of the Fe(III) complexes.

3) The content of vibrational energy of the photoreactive LMCT states is proportional to the energy of an absorbed photon. The higher the difference between the vibrational energy of a given LMCT state and the threshold energy of the primary photoproducts formation (Eqs (*6*), (*7*)), the higher probability of their separation, *i.e.* the lower the probability of their recombination (Eqs (*9*), (*10*)) and, consequently, the higher $\Phi_{Fe(II)}$.

4) Since the investigated complexes provide no luminescence, continuous photolysis does not allow to distinguish between the photoredox reactivity of the quartet and sextet LMCT states.

Contrary to the electrochemical measurements, where a good correlation of the electrode potential $E_{1/2}(Fe^{III}/Fe^{II})$ was observed for systems containing analogous fluoro complexes $[Fe^{III}(R,R'\text{-salen})(CH_3OH)F]$ (ref.[26]), no $\Phi_{Fe(II)}/\sigma(R)$ correlation was observed in photochemistry of the studied complexes. The reasons for this phenomenon are well understood and explained in detail elsewhere[23].

A comparison of quantum yields $\Phi_{Fe(II)}$ for [Fe^{III}(R,R′-salen)(CH_3OH)I] and those for their structural analogues with axial F^-, Cl^- or Br^- ligands[23,26] has documented a substantially higher photoredox reactivity of the former complex. While complexes with the other halogeno ligands underwent photoreduction of Fe(III) only under ultraviolet radiation, redox decomposition of iodo complexes was also initiated by visible light.

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