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Photochemistry of iodo iron(III) complexes

Jozef Šima [a],*, Vlasta Brezová [b]

[a] *Department of Inorganic Chemistry, Slovak Technical University, Radlinského 9, SK-81237 Bratislava, Slovak Republic*
[b] *Department of Physical Chemistry, Slovak Technical University, Radlinského 9, SK-81237 Bratislava, Slovak Republic*

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Contents

Abstract

Photoredox reactions occurring in irradiated methanolic solutions of *trans*-[Fe(5-R-salen)(CH_3OH)I] or *trans*-[Fe(4-R-benacen)(CH_3OH)I] have been investigated and their mechanism proposed. In the formulae, 5-R-salen^{2-} and 4-R-benacen^{2-} symbolize *N,N′*-ethylenebis(5-R-salicylidene-iminate) and *N,N′*-ethylenebis(4-R-benzoylacetoneiminate) open-chain N_2O_2-Schiff bases, respectively, with R = H, F, Cl, Br, I, CH_3, OCH_3, CF_3 and NO_2 groups. Methanolic solutions of these complexes are redox-stable in the dark, however, ultraviolet and/or visible irradiation induces photoreduction of Fe(III) to Fe(II). Depending on the composition of the irradiated solutions, the formation of $^{\bullet}CH_2OH$ radicals or solvated electrons was indicated by the EPR spin trapping technique. The final products of the photoredox reaction represent Fe^{II} and formaldehyde with a molar ratio of $c_{Fe(II)}:c_{CH_2O} \sim 2:1$. The effectiveness of the photoredox processes is strongly wavelength-dependent, and is influenced by the peripheral substitutents R on the tetradentate ligands. In addition to the authors' results, a survey of the photochemistry of iodo complexes is given. © 2002 Elsevier Science B.V. All rights reserved.

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

1. Introduction

Iron(III) iodide and iodo iron(III) complexes are compounds not yet very familiar to inorganic chemists. Even in the fundamental inorganic compendia [1,2] few data are mentioned [3]. In one of the principal monographs on inorganic photochemistry [4] it is stated that "complexes between Fe(III) and strongly reducing ligands (e.g. I^-) are so black that they cannot exist". The main reason for such a statement and general belief derive from the known reducing effect of the anion I^- towards the cation Fe^{3+} expressed by means of the standard electrode potential values $E^\circ(Fe^{III}/Fe^{II}) = 0.771$ V and $E^\circ(I_2/I^-) = 0.536$ V [3].

A method to overcome the above thermodynamic barrier and stabilize the $Fe^{III}-I^-$ bond was documented for first time [5] by the synthesis of [FeI(S_2CNEt_2)] (where $S_2CNEt_2^-$ is diethyldithiocarbamate anion) in 1967. A single crystal X-ray investigation of the complex proved the direct coordination of iodide ion to the central atom Fe^{III} [6]. The Anion $[FeI_4]^-$ was prepared first in solution [7], and its slow redox decomposition was observed at room temperature. The primary information on iron(III) iodo complexes with Schiff base ligands, namely [Fe(salen)I], was published in 1971 [8]. Finally, applying low-temperature photochemical synthesis, pure FeI_3 was also prepared [9] in 1990. The

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* Corresponding author.
E-mail address: sima@chtf.stuba.sk (J. Šima).

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preparation of an iodo iron(IV) complex [10], demonstrated later the ability of some ligands to stabilize complexes with an iodide anion bound to the iron central atom in even a higher oxidation state.

The existence and ground-state redox stability of iodo iron(III) complexes are generally significantly influenced by the following factors:

i) Characteristics of solvent used, which may influence the electrode potentials of Fe^{III}/Fe^{II} and I_2/I^- couples and, in principle, change their relative position.
ii) The presence or absence of an energy impact (iron(III) iodo complexes are, in general, stable in the dark and when not heated).
iii) Ligand coordination to the central atom Fe^{III} stabilizing its oxidation state through forming complexes with high stability constant.

The photochemistry of iodo iron(III) complexes is an unexplored area and apart from the author's preliminary contribution [11] consists of few papers. The flash photolytic investigation of $[Fe([15]pydieneN_5)I_2]^+$ (where [15]pydieneN_5 represents 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene) was described in [12]. Here, as a primary photoredox step, the homolytic splitting of a $Fe^{III}–I^-$ bond from a LMCT state is postulated, followed by several secondary dark redox processes. Examples of the photochemistry of iron(III) tetrapyrrole complexes containing an iodo ligand are gathered in [13]. The correlation of spectral and photochemical properties was documented for [Fe(tpp)X] (tpp = 5,10,15,20-tetraphenylporphyrinate anion, X = Cl, Br or I) in [14], however, no photochemical data were, provided for the iodo complex.

Comparing the photoredox chemistry of other structurally similar halo iron(III) complexes, two specific and counteracting factors are representative for iodo complexes. The first is the thermodynamic factor, which, represents the facile oxidizability of the I^- ligand giving a chance to reach the highest photoredox efficiency. The second is the frequently confirmed observation that iodo complexes display the lowest net photoredox reactivity [15] compared with other halogeno analogues.

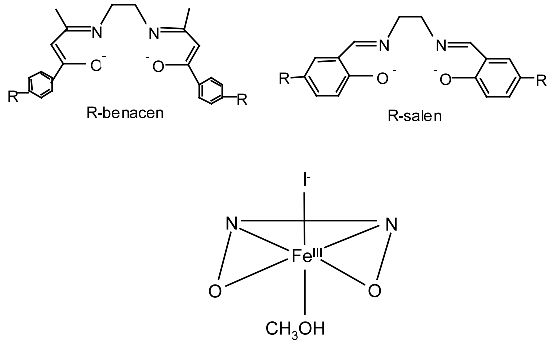

Fig. 1. Schematic representation of N_2O_2-ligands and the coordination of ligands in $[Fe(N_2O_2)(CH_3OH)I]$.

In this contribution, the results of photochemical investigations of the complexes *trans*-[Fe(5-R-salen)(CH_3OH)I] and *trans*-[Fe(4-R-benacen)(CH_3OH)I] (hereinafter abbreviated as $[Fe(N_2O_2)(CH_3OH)I]$) are presented. The structure of the tetradentate ligands and mode of their coordination to the central atom Fe^{III} are depicted in Fig. 1.

2. Experimental

The Schiff bases H_2(5-R-salen) and H_2(4-R-benacen) were synthesized by condensation of the corresponding 5-R-salicylaldehyde and 4-R-benzoylacetylacetone, respectively, with ethane-1,2-diamine in 2:1 molar ratio in methanol using a general procedure [16]. The purity of the ligands was checked by elemental analysis, melting point, ^{1}H-NMR, ^{13}C-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-1-pyrroline-N-oxide, (DMPO, Aldrich) was freshly distilled before use and stored under argon in a freezer. Potassium tris(oxalato)ferrate(III) (Oxford Organic Chemicals), nitrosodurene, (ND, Sigma), $[N(CH_3)_4]I$ and 1,10-phenanthroline, (phen, Aldrich) were used without further purification. The other chemicals were of analytical grade, purchased from Lachema and used as received.

Solid complexes $[Fe(N_2O_2)I]$ were synthesized as described in [17] and characterized by elemental analysis and electronic absorption spectra.

Solutions of $[Fe(N_2O_2)(CH_3OH)I]$ were prepared either from the solid $[Fe(N_2O_2)I]$, NMe_4I and methanol, or in situ from stock methanolic solutions of $Fe(NO_3)_3$, corresponding quantities of $H_2(N_2O_2)$ and NMe_4I so to obtain solutions with the initial concentrations of $c_{Fe}^{III} = 2.0 \times 10^{-4}$ mol dm^{-3} and $c_{I^-} = 2.0 \times 10^{-3}$ mol dm^{-3}.

Steady state photolysis was performed in a three-chambered tempered (20 ± 1 °C) quartz photoreactor. 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 as radiation sources. The irradiated solutions were thoroughly deoxygenated by purging with argon 30 min before and during irradiation. The intensity of the incident monochromatized radiation was determined with ferrioxalate or Reinecke salt actinometry [18].

The course of photoredox changes was monitored by electronic absorption spectroscopy as time evolution of $c_{Fe(II)}$ and c_{CH_2O}. Iron(II) was determined as $[Fe(phen)_3]^{2+}$, formaldehyde was determined as 3,5-diacetyl-2,6-dimethyl-dihydropyridine. The analytical procedures, as well as experimental data treatment are described in detail in our previous papers [19–21].

The EPR spectra were measured at 290 K using a Bruker 200D spectrometer (Germany) interfaced to an Aspect 2000 computer (Germany). The standard spectrometer settings are listed in our previous paper [11]. The freshly prepared solutions containing spin traps ($c_{\mathrm{DMPO}} = 0.01$ mol dm^{-3}; 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, UK), 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).

The electronic absorption spectra of solutions were recorded on a Specord 200 spectrophotometer using 1.00 or 0.20 cm quartz cells.

3. Results and discussion

The composition of the complexes present in methanol can be expressed as *trans*-[Fe(N$_2$O$_2$)(CH$_3$OH)I] based on three factors, namely

i) The known tendency of the high-spin Fe$^{\mathrm{III}}$ to form hexacoordinated complexes, both in the solid state and solution [22,23].
ii) The results of potentiometric titrations using an ion-selective electrode [24].
iii) The disposition of the N$_2$O$_2$-ligands to form the equatorial plane of complexes [25–27].

Typically, electronic absorption spectra of the complexes [Fe(N$_2$O$_2$)(CH$_3$OH)I] consist of several structured bands in the UV region and a broad band in the visible region as is demonstrated in the solution spectrum of *trans*-[Fe(salen)(CH$_3$OH)I] shown in Fig. 2(a and a′). For comparison, the solution spectrum of *trans*-[Fe(salen)(CH$_3$OH)$_2$]$^+$ is also presented (Fig. 2b and b′). The spectra given are rather similar due to the fact that they consist predominantly of the bands of IL transitions.

On the basis of previously published results [17,28,29], the absorption of a photon in the visible region occurs mainly through a ligand-to-metal charge transfer (LMCT) transition O2p or I5p → Fe3d (Eq. (1)), and the ultraviolet bands centered at 230–260 and 270–380 nm to the intraligand transitions IL ($\pi \rightarrow \pi^*$) localized predominantly on the benzene rings and on the azomethine C=N fragment of the N$_2$O$_2$-ligands, respectively (Eq. (2)).

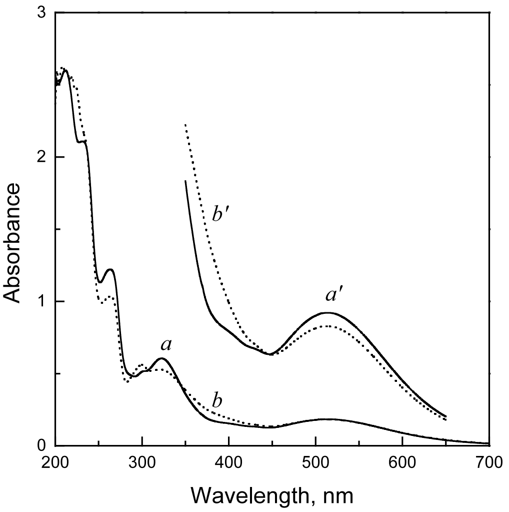

Fig. 2. Electronic absorption spectra of 2.0×10^{-4} [Fe(salen)(CH$_3$OH)I] in methanolic 2.0×10^{-3} NMe$_4$I (solid line), 2.0×10^{-4} [Fe(salen)(CH$_3$OH)$_2$]$^+$ (dotted line) measured in 0.2 cm (a, b) and 1.0 cm (a′, b′) cells.

Photons with $\lambda \leq 250$ nm are absorbed predominantly by I$^-$ anions and a photochemically populated charge transfer-to-solvent (CTTS) state is deactivated by solvated electron formation with a high quantum yield. In order to avoid such a process, only irradiation wavelengths $\lambda \geq 254$ nm were applied. 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(N$_2$O$_2$)(CH$_3$OH)I] did not exhibit spontaneous redox changes in methanolic solutions in the dark at 20 °C.

Irradiation of methanolic solutions of the investigated complexes with ultraviolet radiation or visible light leads to the photoreduction of Fe$^{\mathrm{III}}$ to Fe$^{\mathrm{II}}$. The integral quantum yield values of Fe$^{\mathrm{II}}$ formation, $\Phi_{\mathrm{Fe(II)}}$, are listed in Table 1.

The following conclusions, to be discussed later, can be extracted from the data in Table 1:

i) The tendency to undergo photoredox changes, expressed by means of integral quantum yields, $\Phi_{\mathrm{Fe(II)}}$, is strongly dependent on the wavelength of the incident radiation.
ii) The R peripheral groups of the tetradentate ligands influence $\Phi_{\mathrm{Fe(II)}}$, however, no correlation between $\Phi_{\mathrm{Fe(II)}}$ and any available relevant parameter of the R peripheral groups was found.
iii) Complexes containing R-benacen ligands exhibit a higher phoredox reactivity than their salen-containing analogues.

Table 1
Wavelength dependence of integral quantum yields of Fe^{II} formation, $\Phi^{II}_{Fe} \times 10^3$, for 2.0×10^{-4} mol dm^{-3} methanolic solutions of $[Fe^{III}(N_2O_2)(CH_3OH)X]$ irradiated at 20 °C, and Hammett constants σ(R) of the groups R of the R-salen-containing complexes [30–32]

λ_{irr}	Axial X^-	$\Phi_{Fe(II)} \times 10^3$				σ(R)
N_2O_2		254 (nm)	313 (nm)	366 (nm)	546 (nm)	
Salen	F^-	0.20	0.01	< 0.01	< 0.01	0.00
Salen	Cl^-	0.78	0.53	0.20	< 0.01	0.00
Salen	Br^-	0.36	0.31	0.09	< 0.01	0.00
Salen	I^-	2.3	0.90	0.60	0.51	0.00
5-NO_2-salen	I^-	1.8	1.1	0.85	0.30	0.78
5-CF_3-salen	I^-	0.90	0.75	0.55	0.20	0.54
5-I-salen	I^-	1.9	1.5	1.0	0.65	0.24
5-Br-salen	I^-	2.1	1.5	0.37	0.32	0.23
5-Cl-salen	I^-	1.9	0.80	0.52	0.41	0.22
5-F-salen	I^-	3.6	2.8	2.2	1.1	0.06
5-CH_3-salen	I^-	2.2	2.0	1.4	0.90	−0.17
5-CH_3O-salen	I^-	1.8	1.3	1.1	0.40	−0.31
benacen	I^-	27	10	5.5	3.0	–
benacen	F^-	0.49	0.06	< 0.01	< 0.01	–
benacen	Cl^-	14	4.8	1.3	0.2	–
benacen	Br^-	6.6	3.1	0.8	< 0.01	–
4-Cl-benacen	I^-	35	22	9.0	5.0	–
4-Br-benacen	I^-	20	17	6.5	2.5	–
4-CH_3-benacen	I^-	48	40	25	9.0	–
4-OCH_3-benacen	I^-	32	20	15	7.0	–
4-NO_2-benacen	I^-	64	52	27	10	–

iv) Iodo complexes are substantially more photoreactive then, their fluoro, chloro, or bromo analogues and exhibit photosensitivity also in the visible region.

In accord with our previous experience with the photoredox reactions of Fe^{III} complexes in methanolic solutions [33], we proposed that by using the EPR spin trapping technique with DMPO and ND spin traps we could obtain evidence for the formation of free radical species in the irradiated systems.

The application of DMPO in solution of 10^{-3} mol dm^{-3} $[Fe(benacen)(CH_3OH)I]$ led to the formation of a low intensity EPR spectrum, however, the characteristic features of the $^{\bullet}$DMPO-CH_2OH adduct ($a_N = 1.52$ mT; $a_H = 2.14$ mT; $g = 2.0059$ [34]) was measured upon continuous irradiation ($\lambda > 300$ nm) Fig. 3.

Irradiation of 10^{-3} mol dm^{-3} $[Fe(benacen)(CH_3OH)I]$ in the presence of the ND spin trapping agent resulted in the formation of an EPR spectrum, which is compatible with the hyperfine splitting of the $^{\bullet}$ND–CH_2OH adduct ($a_N = 1.444$ mT; $a_H(2H) = 1.188$; $g = 2.0054$ [34]).

EPR spectra monitored during in situ photochemical experiments for solutions with different concentrations of free iodide anions showed that the higher c_{I^-}, the lower the intensity of the $^{\bullet}$DMPO–CH_2OH and $^{\bullet}$ND–CH_2OH signals. In agreement to the analysis of photoredox mechanism we propose that the excess of iodide in the irradiated systems is reflected in the fast consumption of $^{\bullet}CH_2OH$ radicals (Eq. (9)), which resulted in a lower yield of $^{\bullet}$DMPO–CH_2OH and $^{\bullet}$ND–CH_2OH adducts.

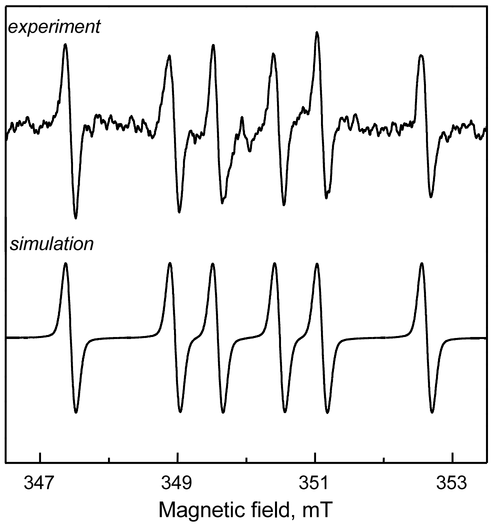

Fig. 3. EPR spectrum measured upon continuous irradiation ($\lambda > 300$ nm) of $[Fe(benacen)(CH_3OH)I]$ methanol solution ($c = 10^{-3}$ mol dm^{-3}) in the presence of DMPO ($c_{DMPO} = 0.01$ mol dm^{-3}). The simulated EPR spectrum was calculated using Hamiltonian parameters $a_N = 1.52$ mT; $a_H = 2.14$ mT; $g = 2.0059$).

Evidence for the formation of solvated electrons was obtained by the addition of a large amount of benzylchloride into the experimental systems. The reaction of benzylchloride with electrons lead to the forma-

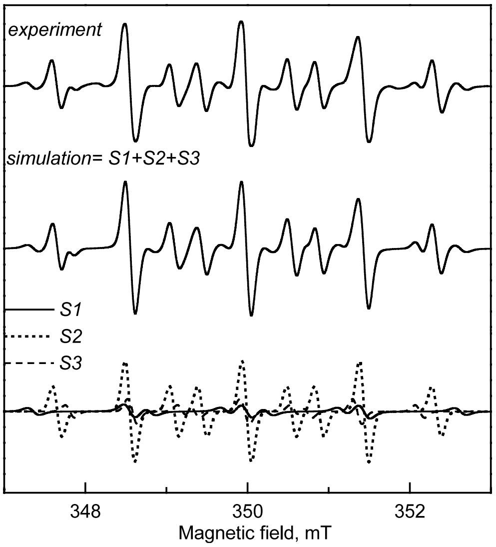

Fig. 4. Experimental and simulated EPR spectra measured upon continuous irradiation ($\lambda > 300$ nm) of [Fe(benacen)(CH_3OH)I] methanol/benzylchloride (1:1; v/v) solution ($c = 10^{-3}$ mol dm^{-3}) in the presence of excess of iodide ($c_{I^-} = 0.01$ mol dm^{-3}) saturated with ND spin trap. The simulated EPR spectrum was calculated as a linear combination of three individual calculated EPR spectra corresponding to $^{\bullet}$ND–CH_2OH (***S1***), $^{\bullet}$ND–$CH_2C_6H_5$ (***S2***) and $^{\bullet}$ND–CH_2R (***S3***).

tion of $^{\bullet}CH_2C_6H_5$ radicals, which are trapped by ND and easily identified ($a_N = 1.44$ mT; $a_H(2H) = 0.89$ mT [34–36]). The experimental EPR spectrum obtained upon continuous irradiation ($\lambda > 300$ nm) [Fe(benacen)(CH_3OH)I] methanol–benzylchloride (1:1; v/v) solution ($c = 10^{-3}$ mol dm^{-3}) containing excess of iodide ($c_{I^-} = 10^{-2}$ mol dm^{-3}) and saturated with nitrosodurene spin trap is depicted in Fig. 4. The experimental EPR spectrum was simulated as a superposition of three individual EPR spectra simulations (***S1***, ***S2***, ***S3***), namely $^{\bullet}$ND–CH_2OH adduct ($a_N = 1.444$ mT; $a_H(2H) = 1.188$ mT, $g = 2.0054$; ***S1***), $^{\bullet}$ND–$CH_2C_6H_5$ adduct ($a_N = 1.444$ mT; $a_H(2H) = 0.894$ mT, $g = 2.0054$; ***S2***) and additionally of the $^{\bullet}$ND–CH_2R radical ($a_N = 1.385$ mT; $a_H(2H) = 0.772$ mT; $g = 2.0056$; ***S3***), which corresponds probably to a photoproduct of ND in methanol [34].

The spin adduct yields monitored in irradiated solutions of Fe^{III}(salen)(CH_3OH)I] complexes were significantly lower probably due to their lower photoredox reactivity. Surprisingly, for these complexes, electron transfer to nitrosodurene spin trap generating $ND^{-\bullet}$ was observed upon irradiation [11].

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

Introducing oxygen into the systems after switching off the irradiation led to a slow reappearance of the parent iron(III) complex spectra (Eq. (14)).

Based on the above spectra interpretation, free radical species identification, determination of molar ratio of the final products and literature data [37,38] a mechanism of the processes occurring in the irradiated systems of the iodo complexes can be proposed, and is summarized in the following equations (GS, IL and LMCT mean the corresponding ground and excited states of Fe^{III} complexes, respectively, left superscripts denote the multiplicity of a given state). The composition of the complexes is tentatively proposed to satisfy the stoichiometry requirements; for simplicity, non-redox reactions are not presented. For better orientation, oxidation states of the central iron atom are given in equations.

Excited state population:

$$ {}^{6}_{\text{GS}}[Fe^{III}(N_2O_2)(CH_3OH)I] \xrightarrow[\text{LMCT}]{h\nu(\text{vis})} {}^{6}[Fe^{III}(N_2O_2)(CH_3OH)I] \quad (1)$$

$$ {}^{6}_{\text{GS}}[Fe^{III}(N_2O_2)(CH_3OH)I] \xrightarrow[\text{IL}]{h\nu(\text{UV})} {}^{6}[Fe^{III}(N_2O_2)(CH_3OH)I] \quad (2)$$

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

$$ {}^{6}_{\text{IL}}[Fe^{III}(N_2O_2)(CH_3OH)I] \xrightarrow[\text{LMCT}]{\text{ic/isc}} 6 \text{ or } 4[Fe^{III}(N_2O_2)(CH_3OH)I] \quad (3)$$

$$ {}^{6}_{\text{LMCT}}[Fe^{III}(N_2O_2)(CH_3OH)I] \xrightarrow[\text{LMCT}]{\text{isc}} {}^{4}[Fe^{III}(N_2O_2)(CH_3OH)I] \quad (4)$$

$$ {}^{6\text{ or }4}_{\text{LMCT}}[Fe^{III}(N_2O_2)(CH_3OH)I] \xrightarrow{\text{ic/isc}} {}_{\text{LF or GS}}[Fe^{III}(N_2O_2)(CH_3OH)I] \quad (5)$$

Primary photoredox step(s):

$$ {}^{6\text{ or }4}_{\text{LMCT}}[Fe^{III}(N_2O_2)(CH_3OH)I] \rightarrow [Fe^{II}(N_2O_2)I]^- + H^+ + {}^{\bullet}CH_2OH \quad (6)$$

$$ {}^{6\text{ or }4}_{\text{LMCT}}[Fe^{III}(N_2O_2)(CH_3OH)I] \rightarrow [Fe^{II}(N_2O_2)(CH_3OH) + I^{\bullet} \quad (7)$$

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

$$[Fe^{II}(N_2O_2)I]^- + H^+ + {}^{\bullet}CH_2OH \rightarrow_{\text{GS}} [Fe^{III}(N_2O_2)(CH_3OH)I] \quad (8)$$

$$[Fe^{II}(N_2O_2)] + I^{\bullet} \rightarrow_{\text{GS}} [Fe^{III}(N_2O_2)(CH_3OH)I] \quad (9)$$

Subsequent secondary thermal redox steps:

$$I^{\bullet} + CH_3OH \rightarrow_{\text{CT}} \{I^{\bullet}/CH_3OH\} \rightarrow HI + {}^{\bullet}CH_2OH \quad (10)$$

$${}^{\bullet}CH_2OH + I^- \rightarrow ICH_2OH + e^- \rightarrow HI + CH_2O + e^- \quad (11)$$

$$_{\mathrm{GS}}[\mathrm{Fe^{III}(N_2O_2)(CH_3OH)I}] + {}^{\bullet}\mathrm{CH_2OH} \rightarrow [\mathrm{Fe^{II}(N_2O_2)(CH_3OH)I}]^- + \mathrm{H}^+ + \mathrm{CH_2O} \quad (12)$$

$$_{\mathrm{GS}}[\mathrm{Fe^{III}(N_2O_2)(CH_3OH)I}] + \mathrm{e}^- \rightarrow [\mathrm{Fe^{II}(N_2O_2)(CH_3OH)I}]^- \quad (13)$$

Dark reoxidation of $\mathrm{Fe^{II}}$:

$$4[\mathrm{Fe^{II}(N_2O_2)I}]^- + \mathrm{O_2} + 4\mathrm{H}^+ + 4\mathrm{CH_3OH} \rightarrow 4[\mathrm{Fe^{III}(N_2O_2)(CH_3OH)I}] + 2\mathrm{H_2O} \quad (14)$$

It is obvious that the populated IL states (Eq. (2)) cannot be responsible for the observed redox process as the corresponding change in orbitals occupation is localized far from the central atom.

Of all accessible excited states, only the spin-allowed sextet and spin-forbidden quartet LMCT states (Eqs. (1), (3) and (4)) possess the electron distribution suitable for an inner-sphere electron transfer leading to the observed photoreduction of $\mathrm{Fe^{III}}$ to $\mathrm{Fe^{II}}$ [4,37]. This infers that the energy higher IL states are deactivated to LMCT states (Eq. (3)).

The excited states of iron(III) complexes are non-luminescent due to their extremely short lifetimes. Until now, evidently no data on the kinetics of transient decay processes have been available in the literature. The missing possibility to scan any phosphorescence or fluorescence spectra strongly preclude a more detailed characterization of the actual photophysical deactivation steps.

One of the deactivation modes of the LMCT states is redox decomposition of the complexes involving the central atom, leading to formation of $\mathrm{Fe^{II}}$ and ${}^{\bullet}\mathrm{CH_2OH}$ or $\mathrm{I}^{\bullet}$ (Eqs. (6) and (7)). The $\mathrm{I}^{\bullet}$ radicals usually convert in the presence of I^- to the stable I_3^- anions and identification of I_3^- in a system is generally accepted as an undoubted proof of $\mathrm{I}^{\bullet}$ radical formation. Given its characteristic spectrum, the formation of I_3^- may readily be followed by electronic absorption spectroscopy ($\lambda_{\max} = 353$ nm). In our systems no sign of I_3^- anion formation, as a final product, was found. One of the reasons for this fact may be a very effective recombination (Eq. (9)). Another reason can lie in the electron transfer and/or hydrogen atom abstraction from a methanol molecule to iodine atom $\mathrm{I}^{\bullet}$ within a CT complex (Eq. (10)) since alcohols are efficient traps of halogen atoms yielding aldehydes. The room temperature lifetime of such CT complex is less than 10^{-6} s [39]. This process (Eq. (10)) is also supported by the electrode potential values $E^{\circ}(\mathrm{I}^{\bullet}/\mathrm{I}^-) = 1.380$ V and $E^{\circ}({}^{\bullet}\mathrm{CH_2OH}/\mathrm{CH_3OH}) = 1.290$ V showing that $\mathrm{I}^{\bullet}$ may act as an oxidant towards $\mathrm{CH_3OH}$. It should, however, be mentioned that in the absence of other suitable reaction partners, such as anions I^-, iodine atoms $\mathrm{I}^{\bullet}$ recombine to $\mathrm{I_2}$ in methanol with a rate constant $k = 2.4 \times 10^{10}$ $\mathrm{mol^{-1}\ dm^3\ s^{-1}}$ [40]. A higher photoreactivity of iodo complexes, when compared with their structurally similar fluoro, chloro or bromo analogues, indicates that iodo ligands participate in and/or stimulate the photoredox processes. The mode of this participation is not, however, definitely resolved.

In general, preferential photooxidation of another coordinated ligand cannot be excluded. Such a preference for photooxidation of coordinated methanol was observed in many cases, e.g. in the case of irradiated methanol-containing solutions of [Fe(OEP)I] where OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato(2-) anion [41]. Given the shown electrode potential values above of the $\mathrm{I}^{\bullet}/\mathrm{I}^-$ and ${}^{\bullet}\mathrm{CH_2OH}$–$\mathrm{CH_3OH}$ couples it is obvious that from the viewpoint of thermodynamics methanol molecule is more easily oxidizable than the iodide anion. It should be kept in mind, however, that redox properties of I^- and $\mathrm{CH_3OH}$ will change upon coordination and solvent used, and the electrode potentials should used with care.

The photooxidation of methanol also may occur when coordination of a spin trap (as documented [42] for DMPO) itself to the iron(III) central atom is followed by addition of a $\mathrm{CH_3OH}$ molecule to a coordinated DMPO. In such cases, however, $\mathrm{CH_3O}^{\bullet}$ are exclusively trapped [42]. In systems investigated by us this situation can be excluded based on two observations, namely (a) it follows from the electronic absorption spectra that DMPO did not coordinate to the iron(III) central atom, (b) in our systems only ${}^{\bullet}\mathrm{CH_2OH}$ radical species (and not $\mathrm{CH_3O}^{\bullet}$) was found. Moreover, the formation of $\mathrm{CH_3O}^{\bullet}$ radical is supposed to be a consequence of the primary photoelectron transfer in complexes with coordinated $\mathrm{CH_3O}^-$ anion [42,43] or in outer sphere from an uncoordinated solvent molecule [$\mathrm{CH_3OH}$] [44]. Irradiation of complexes containing a coordinated molecule $\mathrm{CH_3OH}$ leads to the formation of ${}^{\bullet}\mathrm{CH_2OH}$ radical [44].

For the formation of solvated electrons, processes described by Eq. (11) are tentatively proposed. The energy demand for the abstraction of an electron from I^- is compensated, at least partially, by the energy released at C–I bond formation.

As documented by the value of $E^{\circ}(\mathrm{CH_2O}/{}^{\bullet}\mathrm{CH_2OH}) = -1.180$ V [45], the radical ${}^{\bullet}\mathrm{CH_2OH}$ is a strong reducing agent capable of reducing $\mathrm{Fe^{III}}$ (Eq. (12)). Similarly, $\mathrm{Fe^{III}}$ is the best reaction partner for generated solvated electrons (Eq. (13)).

The ratio $c_{\mathrm{Fe(II)}}{:}c_{\mathrm{CH_2O}} = 2{:}1$ determined in systems investigated in this work shows that, along with the recombination (Eq. (9)), the reduction of $\mathrm{Fe^{III}}$ with ${}^{\bullet}\mathrm{CH_2OH}$ is the main (if not the only) reactivity mode of ${}^{\bullet}\mathrm{CH_2OH}$ transformation. Its dimerization to $\mathrm{HOCH_2}$–$\mathrm{CH_2OH}$ or other processes would increase the above mentioned ratio. Moreover, no such product has been found so far in irradiated methanolic solutions of $\mathrm{Fe^{III}}$ complexes [37,38,43].

The complexes do not undergo any photochemical bond splitting process from their IL states, i.e. N_2O_2-ligands behave as innocent ligands. This fact is in accordance with previous observations [19,24,37,38].

Stemming from the ideas published in [20], the observed wavelength dependence of the quantum yield $\Phi_{Fe(II)}$ can be understood and summarized in four points:

i) The communication between the populated IL and photoredox reactive LMCT states is very effective (Eq. (3)).
ii) The photoreduction of Fe^{III} to Fe^{II} (Eqs. (6) and (7)) is the most significant (if not the only) mode of photoredox deactivation of the Fe^{III} complexes. Photoredox processes not including the central atom, such as decomposition of tetradentate ligand, may be definitely excluded.
iii) The vibrational energy content 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) and (7)), the higher the probability of their separation, i.e. the lower the probability of their recombination (Eqs. (8) and (9)) and, consequently, the higher $\Phi_{Fe(II)}$.
iv) Since the complexes investigated are not luminescent, continuous photolysis does not allow one to distinguish between the photoredox reactivity of the quartet and sextet LMCT states.

The statement given in paragraph (iii) deserves more detailed explanation. For some iron(II) complexes it was experimentally proved [46] that electronic transitions (e.g. a strongly spin-forbidden singlet-to-quintet intersystem crossing) were considerably faster processes (completing in less than 0.8 ps) than vibrational relaxation (lasting 2–3 ps). It is tacidly supposed that electronic deactivation processes in Fe^{III} complexes are even faster. For our complexes this means that a photoredox reactive LMCT state populated from an IL state may contain a larger amount of vibrational energy than the same electronically excited LMCT state populated directly by photoexcitation with visible light.

In our previous papers [21,48] a fair correlation of the Hammett constants $\sigma(R)$ of the ligand peripheral groups R and the electrode potential values $E^\circ(Fe^{III}/Fe^{II})$ of the complexes was found and rationalized. The reaction constant ρ expressed for complexes investigated by us as:

$$\rho = \frac{dE^\circ(Fe^{III}/Fe^{II})}{d\sigma(R)} \tag{15}$$

reached relatively large values, for example for [Fe(R-salen)$(CH_3OH)F$], $\rho = 0.183 \pm 0.008$ V [21], i.e. the redox orbital of the Fe^{III} central atom is influenced by the substituents R. In accordance with data published for other iron complexes [13], axial halogeno ligand exhibits only a one slight influence on the electrode potential. Such a correlation enables us one to purposefully modify and optimize the electrode potential for a structurally similar family of complexes based on the Hammett constant of the peripheral groups.

Contrary to the electrochemical measurements, no $\Phi_{Fe(II)}/\sigma(R)$ correlation was observed in the photochemistry of the complexes studied. On the one hand, the peripheral groups, R, influence the efficiency of the central atom photoreduction (see data in Table 1), while on the other hand no relevant ground state property of the ligands or their peripheral groups allow to purposefully tune and optimize this efficiency.

Based on the rationalization offered in [38], the reasons for this phenomenon can be, in general, summarized as follows:

i) The central atom and ligands lose their original (usually free molecular) ground state properties upon coordination and excitation. Thus, ground state parameters may not be suitable to relate to excited state processes.
ii) The lifetimes of excited iron(III) complexes are very short which prevents some kinds of photoreactions (mainly bimolecular) from occurring. An excited complex itself may have a strong intrinsic tendency to undergo a photoredox deactivation process but it is deactivated in a faster competitive process (e.g. photosubstitution).
iii) Integral quantum yields are often negligible due to the fast recombination of ground state products formed in the primary photoredox step. The efficiency of such recombinations is driven both thermodynamically (the more negative ΔG of the recombination, the higher its rate constant) and kinetically (the higher kinetic energy of the redox changed partners, the lower the probability of their recombination).
iv) The kind of observed net photochemical reaction can differ from that of the primary photochemical step (e.g. a photosubstitution reaction can be a consequence of two subsequent redox steps).

A comparison of quantum yields $\Phi_{Fe(II)}$ for $[Fe^{III}(N_2O_2)(CH_3OH)I]$ and those for their structural analogues with axial F^-, Cl^- or Br^- ligands [38,48] documented a substantially higher photoredox reactivity for the former. While complexes with the other halogeno ligands underwent photoreduction of Fe^{III} only under the influence of ultraviolet radiation, redox decomposition of iodo complexes was also initiated by visible light. Similarly as observed for other families of iron(III) complexes containing salen-type and benacen-type ligands, the former undergo photoreduction of Fe^{III} to Fe^{II} with a substantially lower integral quantum yield than the latter (Table 1). The present knowledge does not permit one to quantify discrete contributions influencing the photoredox reactivity of the complexes studied arising from the differences in the stability constants of the complexes, flexibility of their tetradentate ligands, degree of π-conjugation in individual excited states, and/or further factors.

4. A survey of photochemical properties of iodo complexes

Based on the course of their reactions, the photochemical properties of iodo complexes can be classified into six groups.

i) Photosubstitution of iodo ligand, investigated mainly for inert complexes, such as $[Cr^{III}NH_3)_5I]$ [49–51], $[Rh^{III}(NH_3)_5I]$ [50,51], $[Rh^{III}(pc))(CH_3OH)I]$ where pc = phthalocyaninate(2-) anion [52] and their halogeno analogoues. Usually, the integral quantum yield of iodide photosubstitution is the lowest of all structurally similar halides.
ii) Inner-sphere photooxidation of iodo ligand to $I^{\bullet}$ atom associated with the central atom photoreduction, observed for $[Fe^{III}([15]pydieneN_5)I_2]^+$ [13], $[Pt^{IV}I_6]^{2-}$ [15], $[Bi^{III}I_x]^{x-3}$ [47], $[Mn^{III}(tpp)I]$ [53], $[Sn^{IV}(CH_3)_3(ROH)I]$ [54]. Along with the above mentioned photoprocess occurring from LMCT states, the photooxidation of iodo ligand can also be induced by LLCT excitation similar to that induced by electron transfer from an occupied 5p orbital of I^- to a π* orbital of bpy in $[Mn^I(bpy)(CO)_3I]$ [55].
iii) Inner-sphere photooxidation of a ligand other than the iodo ligand accompanied by central atom photoreduction, exemplified by $[Pt^{IV}(CH_3)_3I]$, $[Pt^{IV}(bpy)(CH_3)_3I]$ [56] where the photoreduction of Pt^{IV} to Pt^{II} is associated with the radical $^{\bullet}CH_3$ formation or by [Fe(OEP)I] [41] where no Fe^{III} is photoreduced in the absence of methanol that is the photooxidized ligand.
iv) Outer-sphere photooxidation of iodide anion in ion pairs, exemplified by sepulchrate complexes $[Co^{III}(sep)]^{3+}/I^-$ [57] or $[Co^{III}(NH_3)_6]^{3+}/X^-$ (X = Cl, Br, I) with the lowest quantum yield being that of X = I [58].
v) Apparently no photochemical process occurring, as observed in the above mentioned systems of [Fe(OEP)I] [41].
vi) Exciplex formation, such as those long-lived metal-centered highly luminescent exciplexes described for the systems of $[Cu^I(CN)_2]^-$ and anions X^- (X = Cl, Br, I) [59].

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