Polish J. Chem., **77**, 1857–1865 (2003)

Bell-shaped Dependence of the Quantum Yield of Fe(II) Formation in Irradiated Methanolic Solutions of Iron(III) Azido Complexes with *N,N′*-Ethylenebis(benzoylacetoneiminato) Schiff Base Derivatives

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(Received July 21st, 2003; revised manuscript August 18th, 2003)

The complexes *trans*-[Fe(4-R-benacen)(CH_3OH)N_3], where 4-R-benacen^{2-} are tetradentate open-chain N_2O_2-Schiff base *N,N′*-ethylenebis(4-R-benzoylacetoneiminato) ligands (R = H, Cl, Br, OCH_3, CH_3) are redox stable in the dark. Under the impact of ultraviolet and/or visible radiation they undergo photochemical reactions, yielding Fe(II) and formaldehyde CH_2O as final products. As an intermediate, $^{\bullet}CH_2OH$ radicals were identified by EPR spin trapping technique. The efficiency of the photoredox processes, expressed by the quantum yield of Fe(II) formation, $\Phi_{Fe(II)}$ is strongly wavelength dependent and influenced by the peripheral groups R of the tetradentate ligands. It was found, that along with a frequently observed decrease in the quantum yield with decreasing the photon energy of incident radiation ($\Phi_{Fe(II)}$ at 313 nm < $\Phi_{Fe(II)}$ at 366 nm < $\Phi_{Fe(II)}$ at 436 nm), a substantial drop in $\Phi_{Fe(II)}$ was found, when shifting the wavelength of incident radiation from 313 nm to 254 nm. This drop is attributed to azido group decomposition competing with photoreduction of Fe(III) to Fe(II).

Key words: photolysis, iron(III) complexes, azide decomposition, mechanism, quantum yield, wavelength dependence

Three types of dependences of the quantum yield on the wavelength of incident radiation (further abbreviated as Φ/λ dependence) have been described so far (see Table 1). The first one, almost independent Φ on λ, may be exemplified by the well-known actinometer $[Fe^{III}(C_2O_4)_3]^{3-}$. The most frequent kind of the dependence is a gradual decrease in Φ with increasing λ and this may be represented by iron(III) complexes with kojic acid derivatives as ligands. In a third type of Φ/λ dependence, the quantum yield reaches a maximum value at a certain wavelength and its gradual decrease in both energy sides. All the three types have been rationalized in [1,2] taking into account the following aspects: (i) ratio of the rate of photophysical deactivations (internal conversion and intersystem crossing) and vibrational relaxation, (ii) single-channel vs. multi-channel chemical deactivations, (iii) efficiency of recombination of the products formed in the primary photochemical reactions, (iv) redox reversibility of oxidized ligands in instances of photoredox processes, (v) participation in chemical deactivations of different photoreactive excited states within a manifold of the states [3].

Table 1. Wavelength dependence of the quantum yield of the central atom photoreduction Φ in selected systems [8,9,14].

λ_{irr}, nm	229	254	313	366	436	510
Complex			Φ			
$[Fe(C_2O_4)_3]^{3-}$	1.25	1.25	1.24	1.21	1.11	0.86
$UO_2^{2+}(C_2O_4^{2-})_x$		0.60	0.56	0.50	0.58	
$[Fe(phen)_2(C_2O_4)]^+$	0.33	0.50	0.72	0.95	0.48	0.16
$[Fe(Hedta)(H_2O)]$	0.20	0.36	0.25	0.09	0.01	
$[Fe(salen)(CH_3OH)I]$		0.0024	0.00090	0.00060	0.00051	
$[Fe(benacen)(CH_3OH)I]$		0.0067	0.0039	0.0030	0.0018	
$[Fe(allomaltol)_3]$	0.024	0.011	0.0025	0.0010	0.00075	
$[Fe(koji)_3]$		0.16	0.10	0.029	0.018	0.0050

phen = 1,10-phenanthroline; $Hedta^{3-}$ = anion of ethylenediaminetetraacetic acid; $salen^{2-}$ = anion of *N*,*N*′-bis(salicylidene)ethylenediamine; $allomaltol^-$ = anion of 5-hydroxy-2-methyl-4*H*-pyran-4-one; $koji^-$ = anion of 5-hydroxy-2-hydroxymethyl-4*H*-pyran-4-one.

Comparing to their structurally similar halogeno complexes, a significantly richer photochemistry of azido complexes lies in a possible conversion of azido group to a six-electron triplet [4] or singlet [5] nitrene intermediates, azidyl radical [6], radical $N_3^{\bullet}$ [7], dinitrogen molecules [8] or a nitrido ligand coordinated to the central atom by a triple bond [9]. Of the radical primary photoproducts, radicals $N_3^{\bullet}$ were identified by spin trapping EPR [10], the formation of nitrene and azidyl intermediates was only suggested, based on the products of subsequent secondary reactions. Photochemistry of iron(III) azido complexes has been limited so far to compounds with tetrapyrrole or cyclam macrocyclic ligands [9,11]. Prolonged low-temperature irradiation of such complexes has led to the formation of iron(V) nitrido compounds.

The ability of azido ligand or of the free anion to undergo decomposition, not involving the central atom, opens a possibility to provide a "bell-shaped" dependence of the quantum yield of the central atom reduction on the wavelength of incident radiation [12]. Due to their photoreactivity independent on the central atom, azido complexes seem to be a suitable candidate of such behaviour. A similar dependence was observed within the study of photoredox chemistry of iron(III) cytochrome *c* and its azide derivative, where the quantum yield reached a maximum at about pH 6 and gradually decreased to zero, when both increasing and decreasing pH. Based on the Φ/pH curve, the dependence was named "bell-shaped" [10].

In this contribution, the results on photochemical properties of the complexes *trans*-[Fe(4-R-benacen)(CH_3OH)N_3] are presented. The structure of the complexes is depicted in Fig. 1.

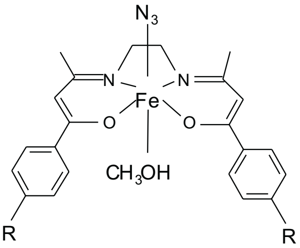

Figure 1. Schematic representation of the complexes *trans*-[Fe(4-R-benacen)(CH_3OH)N_3].

EXPERIMENTAL

The Schiff bases H_2(benacen), H_2(4-Cl-benacen), H_2(4-Br-benacen), H_2(4-CH_3O-benacen), and H_2(4-CH_3-benacen) were synthesized using a general procedure [13] by condensation of the corresponding 4-R-benzoylacetone with ethane-1,2-diamine in 2:1 molar ratio in methanol. The purity of the ligands was checked by elemental analysis, melting point, ^{13}C-NMR and ^{1}H-NMR spectra.

Ethane-1,2-diamine (Lachema) was distilled at a reduced pressure prior to use. 5,5-Dimethyl-1-pyrrolidine-N-oxide, (DMPO, Aldrich) was freshly distilled before use and stored under argon in a freezer. Methanol (Lachema, reagent grade) was dried before use by distillation from $Mg(OCH_3)_2$. Potassium tris(oxalato)ferrate(III) (Oxford Organic Chemicals), nitrosodurene, (ND, Sigma), NaN_3 (Sigma), 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.

Solutions of [Fe(4-R-benacen)(CH_3OH)N_3] were prepared *in situ* from stock methanolic solutions of $Fe(NO_3)_3$, corresponding solid H_2(4-R-benacen) and NaN_3 so as to obtain solutions with the initial concentration ratio $c(\mathrm{Fe^{III}}) : c(\mathrm{H_2}$(4-R-benacen)): $c(N_3^-) = 1 : 1.02 : 10$.

Solutions of investigated complexes were photolysed by radiation of 254 nm in a two-chambered quartz photoreactor equipped with a low pressure Germicidal Lamp G8T5; at 313 nm, 366 nm or 436 nm in a three-compartment temperature-controlled (20± 1°C) quartz photoreactor (Applied Photophysics), radiation of the high-pressure 150 W Hg-lamp being monochromatized by solution filters [10]. The irradiated solutions were deoxygenated by purging with argon 30 minutes prior and during irradiation. The intensity of the incident monochromatized radiation was determined with ferrioxalate actinometry [14].

The course of photoredox changes was monitored by electronic absorption spectroscopy as time evolution of $c(\mathrm{Fe^{II}})$ and $c(\mathrm{CH_2O})$. Iron(II) was determined in the form of $[\mathrm{Fe(phen)_3}]^{2+}$, formaldehyde CH_2O as 3,5-diacetyl-1,4-dihydrolutidine. Details on the experiments performed, analytical procedures and experimental data processing are described elsewhere [15,16].

The EPR spectra were measured on a Bruker 200D spectrometer (Germany) interfaced to an Aspect 2000 computer (Germany) using freshly prepared solutions containing spin traps DMPO or ND. Measurement conditions and a mode of the EPR spectra simulations are given in our previous paper [16].

Electronic absorption spectra were recorded on a Specord 200 spectrophotometer using 1.00 or 0.10 cm quartz cells. IR spectra were scanned on a FT spectrometer Nicolet, Magna 750 in Nujol mulls.

RESULTS AND DISCUSSION

Given the known tendency of the high-spin Fe(III) to form hexacoordinated complexes, both in the solid state and solutions, that of benacen-type ligands to form their equatorial plane, and stemming from the previous potentiometric determination of a number of coordinated acido ligands [17], the composition of the complexes present in methanol at our conditions can be expressed as *trans*-[Fe(4-R-benacen)(CH_3OH)N_3].

Typically, the electronic absorption spectra of the complexes [Fe(4-R-benacen)(CH_3OH)N_3] consist of several broad bands and shoulders. As an example, a spectrum of [Fe(benacen)(CH_3OH)N_3] and for comparison that of [Fe(benacen)$(CH_3OH)_2]^+$ are shown in Fig. 2.

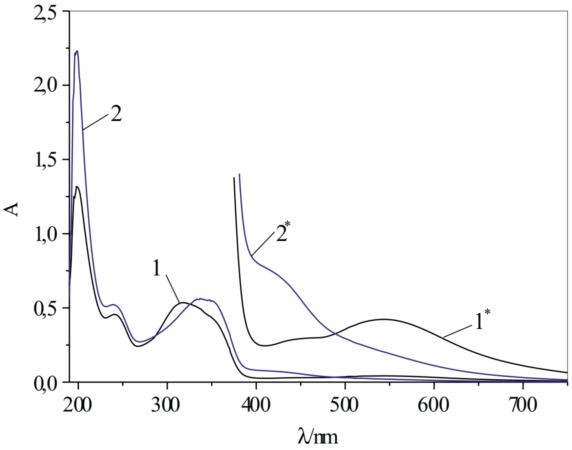

Figure 2. Electronic absorption spectra of 2.0×10^{-4} mol dm^{-3} [Fe(benacen)$(CH_3OH)_2]^+$ (1, 1^*) and [Fe(benacen)(CH_3OH)N_3] (2, 2^*) in methanol measured in 0.1 cm (1, 2) or 1.0 cm (1^*, 2^*) cells.

Based on previously published results [18–21], bands in the visible region can be attributed to ligand-to-metal charge transfer (*LMCT*) transitions O2p or N(2p) → Fe3d, the ultraviolet bands in the regions of 210–280 nm and 300–360 nm to the intraligand transitions $IL(\pi\rightarrow\pi^*)$ localized predominantly on the phenyl rings and on the azomethine C=N fragment of the 4-R-benacen-ligands, respectively. Photons with $\lambda \leq 270$ nm are absorbed also by N_3^- anions, $\varepsilon_{254\ \mathrm{nm}}(N_3^-) \cong 100$ mol^{-1} dm^3 cm^{-1} in methanol [22]. Owing to their spin-forbidden nature, bands of ligand field (*LF*) states were not observed in solution spectra.

Control experiments confirmed that the complexes [Fe(4-R-benacen)(CH_3OH)N_3] do not undergo spontaneous redox changes in methanolic solutions in the dark.

Irradiation of methanolic solutions of the investigated complexes by ultraviolet or visible radiation leads to the photoreduction of Fe(III) to Fe(II). The quantum yields of net Fe(II) formation $\Phi_{Fe(II)}$ depend on the wavelength of the incident radiation and on the peripheral groups R of the 4-R-benacen-ligands (Table 2).

Table 2. Quantum yields of Fe(II) formation, $\Phi_{Fe(II)}$ in irradiated methanolic solutions of 2.0×10^{-4} mol dm^{-3} [Fe(4-R-benacen)(CH_3OH)N_3].

4-R-benacen/λ_{irr}, nm	254	313	366	436
		$\Phi_{Fe(II)} \times 10^3$		
benacen	1.83	18.1	0.90	0.47
4-Cl-benacen	2.17	20.2	2.47	0.95
4-Br-benacen	2.25	15.7	3.25	1.45
4-CH_3O-benacen	0.70	27.3	1.18	0.49
4-CH_3-benacen	3.15	17.5	2.95	1.00

In accord to our previous experience with the photoredox reactions of Fe(III) complexes in methanolic solutions [15,16,21,23], we proposed that using DMPO and ND spin traps we could obtain evidences on the formation of radicals in the irradiated systems. Similarly as in case of iodo complexes [16], using ND in saturated ($c \sim 10^{-2}$ mol dm^{-3}) solutions of [Fe(benacen)(CH_3OH)N_3] complex, only poor-quality low-intensity EPR spectra of $^{\bullet}CH_2OH$-ND adduct were obtained.

Upon irradiation of 5×10^{-3} mol dm^{-3} [Fe(benacen)(CH_3OH)N_3] in the presence of DMPO spin trap, an EPR signal of $^{\bullet}CH_2OH$-DMPO was observed (Fig. 3). It should be noted that phenyl-*N*-*tert*-butylnitrone (PBN) spin trap, which was successfully applied in aqueous systems azido complexes of cytochrome *c* [10], could not be used in our system, due to its reaction with the investigated complexes.

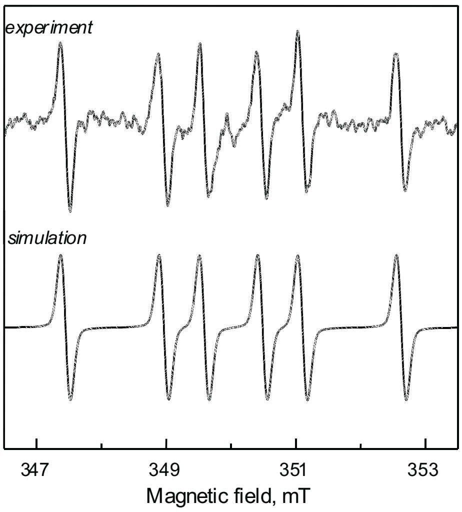

Figure 3. Experimental and simulated room temperature EPR spectrum measured at irradiation of methanolic solution of 5×10^{-3} mol dm^{-3} [Fe(benacen)(CH_3OH)N_3] in the presence of 1.0×10^{-2} mol dm^{-3} DMPO by radiation with $\lambda_{irr} \geq 300$ nm. The EPR spectrum was simulated using the following parameters: $a_N = 1.50$ mT, $a_H = 2.115$ mT; $g = 2.0057$.

As the final products of photoredox processes, formaldehyde and Fe(II) were formed. When irradiating the solutions at 313 nm, 366 nm or 436 nm, CH_2O and Fe(II) were formed in a 1 : 2 molar ratio. At irradiation by 254 nm, the ratio was 2.1 : 1. Within irradiation of 2.0×10^{-3} mol dm^{-3} NaN_3 in methanol in the absence of any Fe(III) complex, formaldehyde was formed with the quantum yield approaching 1×10^{-2}. Introducing oxygen into the systems after switching off the irradiation led to a slow reappearance of the parent iron(III) complex spectra.

Based on the above spectra interpretation, radicals identification, molar ratio of the final products determination and literature data [24,25], processes occurring in irradiated systems of azido complexes may be expressed (in the following equations, *GS*, *IL* and *LMCT* mean the corresponding ground state, intraligand and ligand-to-metal charge-transfer excited states, respectively). At irradiation of investigated systems by ultraviolet or visible radiation, spin-allowed excited sextet states of complexes (1, 2) or singlet state of azide anions (3) are populated:

$$_{GS}[Fe^{III}(\text{4-R-benacen})(CH_3OH)N_3] \xrightarrow{h\nu(UV)} {}_{IL}[Fe^{III}(\text{4-R-benacen})(CH_3OH)N_3] \tag{1}$$

$$_{GS}[Fe^{III}(\text{4-R-benacen})(CH_3OH)N_3] \xrightarrow{h\nu(VIS)} {}_{LMCT}[Fe^{III}(\text{4-R-benacen})(CH_3OH)N_3] \tag{2}$$

$$N_3^- \xrightarrow{h\nu(UV, \lambda=254\ nm)} {}_{(n \rightarrow \pi^*)}N_3^- \tag{3}$$

Excited molecules can undergo physical deactivations from their energy higher to energy lower states by intersystem crossing (isc) or internal conversion (ic).

Of all accessible excited states of the complexes, only the spin allowed sextet *LMCT* states (populated directly by visible light absorption) and spin forbidden quartet *LMCT* states (reached by intersystem crossing from energy higher IL states) have the electron distribution suitable for an inner-sphere redox decompostion, due to an electron density transfer to the orbitals localized predominantly on the central atom. Decomposition of such excited complexes can lead to the formation of Fe(II) and ${}^{\bullet}CH_2OH$ or $N_3^{\bullet}$ (4, 5).

$$_{LMCT}[Fe^{III}(\text{4-R-benacen})(CH_3OH)N_3] \rightarrow [Fe^{II}(\text{4-R-benacen})N_3]^- + H^+ + {}^{\bullet}CH_2OH \tag{4}$$

$$_{LMCT}[Fe^{III}(\text{4-R-benacen})(CH_3OH)N_3] \rightarrow [Fe^{II}(\text{4-R-benacen})(CH_3OH)] + N_3^{\bullet} \tag{5}$$

Along with back reactions of the products formed within the primary processes, the radical product(s) can participate in subsequent processes.

In spite of the fact, that only ${}^{\bullet}CH_2OH$ was detected in irradiated systems, the primary formation of $N_3^{\bullet}$ radical (5) cannot be definitely excluded, since it can react with methanol molecules forming the observed ${}^{\bullet}CH_2OH$ radical

$$N_3^{\bullet} + CH_3OH \rightarrow HN_3 + {}^{\bullet}CH_2OH \qquad (6)$$

The course of this reaction was investigated [26] and is supported also by the electrode potentials $E^o({}^{\bullet}CH_2OH/CH_3OH) = 1.29$ V and $E^o({}^{\bullet}N_3/N_3^-) = 1.32$ V [27]. As documented by the value $E^o({}^{\bullet}CH_2OH/CH_2O) = -1.180$ V [28], the radical ${}^{\bullet}CH_2OH$ is a strong reducing agent able to reduce further Fe(III) in subsequent secondary thermal redox steps (7), forming thus the final products Fe(II) and CH_2O.

$$[Fe^{III}(4\text{-R-benacen})(CH_3OH)N_3] + {}^{\bullet}CH_2OH \rightarrow [Fe^{II}(4\text{-R-benacen})N_3]^- + H^+ + CH_2O \qquad (7)$$

The ratio of $c(Fe^{II}) : c(CH_2O) = 2 : 1$ determined in the systems irradiated by 313 nm, 365 nm or 436 nm in this work shows that the reduction of Fe(III) by ${}^{\bullet}CH_2OH$ (7) is the main (if not the only) reactivity mode of ${}^{\bullet}CH_2OH$. Its transformation to $HOCH_2$-CH_2OH or to other products would increase the mentioned ratio. It is worth noting that no such products have been found so far in irradiated methanolic solutions of Fe(III) complexes [24]. Based on the rationalization published in [1], the observed decrease in the quantum yield $\Phi_{Fe(II)}$ with increasing incident radiation wavelength in the region 313 nm to 436 nm for the systems investigated in this work may be understood and summarized in four points: 1) The communication between the populated *IL* and photoredox reactive *LMCT* states of the complexes is very effective. 2) The photoreduction (4, 5) of Fe(III) to Fe(II) is the most significant (if not the only) mode of photoinduced redox deactivation of the Fe(III) complexes at irradiation with 313 nm, 366 nm or 436 nm. 3) The content of rovibrational energy of the photoreactive *LMCT* states is proportional to the energy of the photon absorbed. The higher the difference between the rovibrational energy of a given *LMCT* state and the threshold energy of the primary photoproducts formation (4, 5), the higher the probability of their separation, *i.e.* the lower the probability of their recombination 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 and, thus, to determine, which of the states, forming the manifold of *LMCT* states, participate in the redox deactivation processes.

A different situation was found when applying 254 nm radiation. In this case, part of the photons is absorbed by anion N_3^- (3) and one of its possible deactivation modes is its decomposition, producing the nitrene anion N^-.

$${}_{(n \rightarrow \pi^*)}N_3^- \rightarrow N_2 + N^- \qquad (8)$$

As rationalized previously in [29], this electronically unsaturated anion is a very strong two-electron oxidant, able to abstract electrons and/or atoms from surrounding molecules. In our systems it reacts with methanol, producing additional formaldehyde following the stoichiometry

$$N^- + 2CH_3OH \rightarrow CH_2O + CH_3O^- + NH_3 \qquad (9)$$

The sequence, initiating by azide excitation (3) and terminating by formaldehyde formation (9), was proved independently by 254 nm irradiation of a methanolic solution of 2.0×10^{-3} mol dm^{-3} NaN_3 in the absence of iron(III) complex. Within such an irradiation, formaldehyde was formed. This "extra-produced" formaldehyde causes the observed high molar ratio $n(CH_2O) : n(Fe^{II}) = 2.1 : 1$ in the system of [Fe(benacen)(CH_3OH)N_3] irradiated by incident radiation with 254 nm.

A decrease in $\Phi_{Fe(II)}$ with decreasing incident radiation wavelength is a consequence of opening a new chemical deactivation channel, not involving the central atom and competing with a routine Fe(III) photoreduction. This channel is a decomposition of azido group, which occurs only using 254 nm incident irradiation, populating directly an excited state of this group. As documented by a relatively high quantum yield of CH_2O formation ($\Phi \cong 10^{-2}$) at irradiation of methanolic solution of NaN_3, this can be one mode to open the new channel. The other possibility lies in an indirect population of ($n\rightarrow\pi^*$) excited state, localized on the azide ligand/anion from energy higher IL excited state of the complex. Irrespective of the mode of excited azide formation, its reaction does not involve the central atom Fe(III) and, thus, reduces the quantum yield of its reduction to Fe(II). Moreover, oxidation of the photochemically produced Fe(II) by nitrene intermadiates cannot be excluded either. A significant drop in quantum yield of Fe(II) formation in changing the incident radiation wavelength from 313 nm to 254 nm was observed for all investigated complexes and is, therefore, of general nature.

Tetradentate Schiff base 4-R-benacen-ligands behave as "redox innocent" ligands, obviously not participating in the occurring redox processes. This conclusion is supported by dark reoxidation of Fe(II) expressed by stoichiometry

$$4[Fe^{II}(4\text{-R-benacen})N_3]^- + O_2 + 4H^+ + 4CH_3OH \rightarrow 4[Fe^{III}(4\text{-R-benacen})(CH_3OH)N_3] + $$
$$+ 2H_2O \qquad (10)$$

IR spectra of solid residues, obtained by vacuum room-temperature evaporation of methanol from solutions of [Fe(benacen)(CH_3OH)N_3] irradiated at 254 nm or 313 nm, showed no characteristic band attributable to a triple Fe(V)≡N bond, *i.e.* Fe(V) nitrido complexes were not formed. This is in agreement with the observation that such complexes are stable only at low temperature and in the case of complexes with macrocyclic (cyclam, porphyrin) ligands [9,11].

A comparison of the quantum yields $\Phi_{Fe(II)}$ for [Fe(4-R-benacen)(CH_3OH)N_3] and those for their structural analogues with axial F^-, Cl^-, Br^- or I^- ligands [21,25] documented a different wavelength dependence of the integral quantum yield of Fe(III) photoreduction, due to involvement of azido group decomposition, initiated by absorption of photons with 254 nm.

Acknowledgment

This work was supported by Science and Technology Assistance Agency under the contract No. APVT-20-010902.

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