Inorganica Chimica Acta, 170 (1990) 1–4

Inorganica Chimica Acta

LETTER

Formation of $Fe(bpy)(CN)_4{}^{3-}$ and $Fe(DMbpy)(CN)_4{}^{3-}$ in the Photo-induced Redox Reaction of $Fe(bpy)(CN)_4{}^{2-}$ and $Fe(DMbpy)(CN)_4{}^{2-}$

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(Received September 22, 1989; revised December 18, 1989)

The quantum yields for the photo-ionization of different coordination compounds with reducing transition metal centers have been shown to vary according to the ligand exchange and substitution on the coordinated ligands. The series of $[M(CN)_{6-2n}L_n]^{(4-2n)-}$ complexes (where M = Fe, Ru; n = 0, 1, 2, 3; and L = 2,2′-bipyridine, 1,10′-phenanthroline and their derivatives) are excellent candidates for photoredox studies because the energy level of the metal-to-ligand charge transfer (MLTC) and the ligand field (LF) states are altered by the replacement of ligands to such an extent that their order can even be reversed [1, 2]. Another remarkable feature of these mixed-ligand complexes is that they possess an extraordinary solvent sensitivity which has been attributed to donor–acceptor interactions between the lone pairs of the cyanide ligands and an acceptor solvent [3, 4]. The solvent tuning of the excited states of $[M(L)_2(CN)_2]$ and $[M(L)(CN)_4]^{2-}$ complexes has been recently studied [5, 6]. The transient spectra obtained by picosecond flash photolysis techniques following 532-nm excitation [5] clearly indicate that the lowest excited state of $Ru(bpy)_2(CN)_2$ is an MLCT state in methanol solution, while the replacement of another bpy with two CN^- ligands increases the LF state above the MLCT state of $Fe(bpy)(CN)_4{}^{2-}$ only in weakly accepting solvents such as acetone [6].

Here we report observations and results obtained for the UV-excited acidic and alkaline aqueous solutions of $Fe(bpy)(CN)_4{}^{2-}$ and $Fe(DMbpy)(CN)_4{}^{2-}$ (DMbpy = 4,4′-dimethylbipyridine).

Experimental

The potassium salts and the dihydrogen compound of $[Fe(L)(CN)_4]^{2-}$ as well as the $H[Fe(L)(CN)_4]\cdot 2H_2O$ complexes were prepared according to Schilt [3]. All the chemicals used were of reagent grade. The concentrations of the complexes in solutions to be irradiated varied between 1×10^{-4} M and 1×10^{-3} M. The concentration of the iron(II) complex acids was limited by their solubility, suggesting the weak acidity of $H_2[Fe(L)(CN)_4]$. The stability constants of the protonated species have been determined spectrophotometrically. The obtained values ($\log \beta_1 = 6.4 \pm 0.2$, $\log \beta_2 = 8.3 \pm 0.3$, and $\log \beta_1 = 6.3 \pm 0.1$, $\log \beta_2 = 8.2 \pm 0.2$ for bpy and DMbpy compounds respectively) show that the partial mole fraction of $HFe(L)(CN)_4{}^-$ is approximately one in 1×10^{-4} to 1×10^{-3} M solutions of the complex acids. The excitations of the samples were performed in a quartz cuvette with a volume of 4 cm^3 and an optical path length of 1 cm in anaerobic conditions. In the case of the steady-state experiments, a 16-W low-pressure mercury arc lamp (Applied Photophysics) was used as the light source which irradiated more than 90% of its energy at 254 nm. The light intensity was determined by the micro version of trioxalato ferrate(III) actinometry [7, 8]. The photo-oxidation was monitored spectrophotometrically at 480 nm. At this wavelength the difference between the molar absorption coefficients of the reduced and the oxidized forms of the tetracyano complexes have been determined from their visible spectra ($\Delta\epsilon$ = 2390 M^{-1} cm^{-1} and $\Delta\epsilon$ = 2360 M^{-1} cm^{-1} for bpy and DMbpy derivatives respectively).

The flash photolysis investigations were carried out using a laser kinetic spectrometer (Applied Photophysics K-347 with an SL 402 Nd:YAG laser for 1064, 532, 355 and 266 nm excitation). The transient signals were monitored with an 1P28 or an R955 Hamamatsu photomultiplier tube, the output of which was fed into a Philips PM 3320/A digitizing storage oscilloscope (250 Msample/s).

Results and Discussion

Excitation of the aqueous solution of $Fe(L)(CN)_4{}^{2-}$ complexes by a 266-nm laser pulse results in an immediate absorption peak around 700 nm, which decays more rapidly in acidic solutions than in alkaline media (Fig. 1). Saturation of the sample with O_2 or by addition of $NO_3{}^-$ ions to the solutions was found to remove this red absorption. These observations lead to the assignment of the red absorbing species as a hydrated electron. For the

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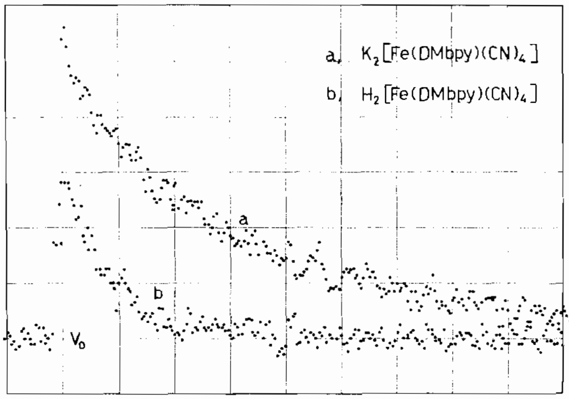

Fig. 1. Decay of e_{aq}^- at 600 nm for (a) 3.33×10^{-4} M $K_2[Fe(DMbpy)(CN)_4]$ and (b) 3.33×10^{-4} M $H_2[Fe(DMbpy)(CN)_4]$ in deaerated water recorded after 266-nm laser excitation (horizontal scale, 100 ns/div; vertical scale, 20 mV/div; $V_0 = 500$ mV).

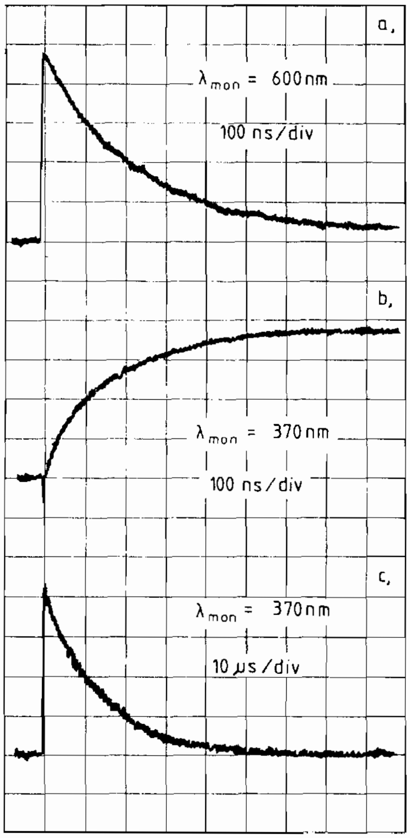

Fig. 2. (a) Decay of e_{aq}^- at 600 nm; (b) growth and (c) decay of $Fe(bpy)(CN)_4^{3-}$ at 370 nm for $3 \times 33 \times 10^{-4}$ M $K_2[Fe(bpy)(CN)_4]$ in deaerated water (horizontal scales, 100 ns/div (a, b) and 10 μs/div (c); vertical scale, 20 mV/div; $V_0 = 500$ mV).

systems of 3.33×10^{-4} M $K_2[Fe(bpy)(CN)_4]$ and 3.33×10^{-4} M $K_2[Fe(DMbpy)(CN)_4]$ in water, the decay of the hydrated electron monitored at 600 nm obeys first-order kinetics with a lifetime of ~200 and ~250 ns, respectively. Considering the molar absorbance of the hydrated electron at 600 nm [9], the concentration of e_{aq}^- is $\sim 7 \times 10^{-6}$ M immediately after the laser pulse. It is nearly two orders of magnitude smaller than that of the iron(II) complex. The excitation of a solution containing 3.33×10^{-4} M $K_2[Fe(bpy)(CN)_4]$ and 10^{-2} M KNO_3 as an electron scavenger leads to a decrease of the absorbance in the visible range (330–550 nm) that corresponds to the formation of $Fe(bpy)(CN)_4^-$, but no electron is detected. The concentration of the iron(III) complex immediately after the pulse is equivalent to that of the hydrated electron in solution without a scavenger. The decay of the hydrated electron in the latter solution occurs in the same time scale as the growth of the absorption at 370 nm (Fig. 2). In the case of $Fe(bpy)(CN)_4^{2-}$,

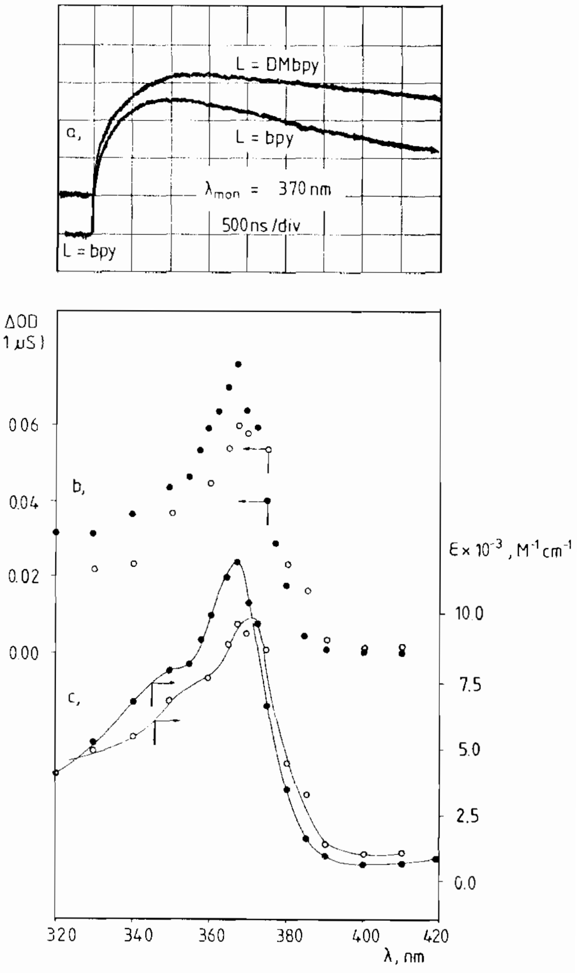

Fig. 3. (a) Build-up and decay of $Fe(L)(CN)_4^{3-}$ complexes, 500 ns/div; (b) the difference spectra determined 1 μs after 266-nm excitation for $Fe(L)(CN)_4^{2-}$ complexes; and (c) the corrected spectra of $Fe(L)(CN)_4^{3-}$, (●) L = bpy, (○) L = DMbpy.

the feature of the difference spectrum (Fig. 3(b)) is reminiscent of the spectrum of the 2,2'-bipyridine radical anion [10, 11] and the π–π^* absorption of the MLCT excited state of the complex [6]. The solution of the 4,4'-dimethylbipyridine derivative exhibits a rather similar transient spectrum. It is reasonable to assume that the growth of absorptions at 370 nm is due to the formation of $Fe(bpy)(CN)_4^{3-}$ and $Fe(DMbpy)(CN)_4^{3-}$ anions, respectively. Since all electron decay is complete 1 μs after the laser pulse, these spectral changes are considered to be a result of the formation of $Fe(L)(CN)_4^{3-}$ and $Fe(L)(CN)_4^-$ ions, according to the following reactions

$$Fe(L)(CN)_4^{2-} \xrightarrow{h\nu} (CT)Fe(L)(CN)_4^{2-} \tag{1}$$

$$(CT)Fe(L)(CN)_4^{2-} \longrightarrow Fe(L)(CN)_4^- + e_{aq}^- \tag{2}$$

$$e_{aq}^- + Fe(L)(CN)_4^{2-} \longrightarrow Fe(L)(CN)_4^{3-} \tag{3}$$

The rate constants of reaction (3) obtained from the decay curves of e_{aq}^- ($k = 1.4 \pm 0.4 \times 10^{10}$ M^{-1} s^{-1} and $k = 1.1 \pm 0.4 \times 10^{10}$ M^{-1} s^{-1} for L = bpy and L = DMbpy respectively) suggest that these reactions are diffusion controlled. Considering the concentration of the iron(II) and iron(III) complexes immediately after the laser pulse, it is assumed that more than 95% of the electrons are scavenged by $Fe(L)(CN)_4^{2-}$ ions.

The growth of absorption at 370 nm (Fig. 2(b)) does not obey pure first-order kinetics because the formation of the intermediate is followed by its disappearance (Fig. 2, curve c, and Fig. 3(a)). Hence $t_{1/2}$ for curve b of Fig. 2 seems to be slightly shorter than that of curve a of Fig. 2. The decay of $Fe(L)(CN)_4^{3-}$ follows second-order kinetics with $k = 1.8 \pm 0.4 \times 10^{10}$ M^{-1} s^{-1} and $k = 1.2 \pm 0.4 \times 10^{10}$ M^{-1} s^{-1}. The molar absorbances ($\epsilon = 1.30 \times 10^4$ M^{-1} cm^{-1} and $\epsilon = 10^4$ M^{-1} cm^{-1} at 370 nm for $Fe(bpy)(CN)_4^{3-}$ and $Fe(DMbpy)(CN)_4^{3-}$ respectively) have been estimated on the basis of the concentration of the electron scavenged and the difference between the spectra of the iron(II) and iron(III) compounds. The corrected spectra of the iron(I) complexes are also given in Fig. 3(c).

The transients of $Fe(L)(CN)_4^{3-}$ have not been found in the solution of $H_2[Fe(L)(CN)_4]$ complexes. The absorption of the hydrated electron immediately after the laser pulse was smaller and the decay of e_{aq}^- was completed more rapidly than in alkaline solutions (Fig. 1). These observations, coupled with the fact that the $H[Fe(L)(CN)_4]^-$ complexes are the dominant species in solutions of 10^{-3} to 10^{-4} M, suggest that the excitation leads to the following reactions

$$(CT)H[Fe(L)(CN)_4]^- \longrightarrow H^+ + Fe(L)(CN)_4^- + e_{aq}^- \tag{4}$$

TABLE 1. Variation of quantum yields with temperature for the photo-oxidation in aqueous solution of 1×10^{-4} M $H_2Fe(L)(CN)_4$ complexes[a]

Temperature (°C)	Quantum yields, $\varphi_{Fe(III)} \pm 0.005$	
	L = bpy	L = DMbpy
20	0.060	0.064
22.5	0.063	0.063
25	0.065	0.070
30	0.074	0.081
35	0.083	0.091
40	0.097	0.103

[a] The incident light intensity was 3.39×10^{-5} M photon min^{-1}. The quantum yields were determined by the initial slope of a polynom fitted by Marquardt's method [13] to the absorbance vs. time plots consisting of 25 points.

$$(CT)H[Fe(L)(CN)_4]^- \longrightarrow H^{\bullet} + Fe(L)(CN)_4^- \tag{5}$$

$$H_3O^+ + e_{aq}^- \longrightarrow H^{\bullet} + H_2O \tag{6}$$

The rate constant of reaction (6) estimated from the transient trace of the electron (Fig. 1, curve b) is $\sim 2 \times 10^{10}$ M^{-1} s^{-1}, which is in good agreement with the value given in the literature [12]. It is not unreasonable to assume that the hydrogen radical disappears via radical recombination or in the following reaction

$$H[Fe(L)(CN)_4]^- + H^{\bullet} \longrightarrow H_2 + [Fe(L)(CN)_4]^- \tag{7}$$

The oxidation of iron(II) complexes has been found to be accompanied by a slight increase of pH upon prolonged steady-state irradiation at 254 nm. The quantum yield of iron(III) formation has been determined at different temperatures (Table 1). The figures show a positive temperature dependence. This observation suggests that the mechanism involves thermal reaction too, which leads to the formation of an iron(III) complex. The increase of pH can be interpreted by formation of the $HFe(L)(CN)_4$ complex which releases hydrogen cyanide under irradiation, consuming H^+ ions.

The results clearly indicate that excitation at both 254 and 266 nm leads to the formation of the hydrated electron, suggesting a CTTS character for the absorption band appearing as a shoulder in the UV spectrum of $Fe(bpy)(CN)_4^{2-}$ and $Fe(DMbpy)(CN)_4^{2-}$ at 38 800 cm^{-1} ($\epsilon = 7000$ M^{-1} cm^{-1}) and 38 500 cm^{-1} ($\epsilon = 8700$ M^{-1} cm^{-1}), respectively.

Investigations on the series of $FeL(CN)_4^{2-}$ complexes with other derivatives of bpy and 1,10-phenanthroline are in progress. The preliminary results suggest that the quantum yields for solvated electron formation are higher in alkaline than in acidic solutions.

Acknowledgement

This research was supported by the Ministry of Education of Hungary.

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