Mechanism of photoinduced redox reactions in aqueous solutions of $[Fe(bpy)(CN)_4]^{2-}$

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Abstract

The mechanism of redox reactions initiated by UV excitation of $[Fe(bpy)(CN)_4]^{2-}$ in aqueous solutions has been investigated by continuous photolysis, laser kinetic spectroscopy and pulse radiolysis. Hydrated electrons formed in the light induced reaction are shown to react with ground state $[Fe(bpy)(CN)_4]^{2-}$ to form $[Fe(bpy)(CN)_4]^{3-}$ characterized by its absorption spectra and reactions. The back reaction between $[Fe(bpy)(CN)_4]^{-}$ and $[Fe(bpy)(CN)_4]^{3-}$ takes place with $k=1.8 \pm 0.4 \times 10^{10}$ M^{-1} s^{-1}. The quantum yield of solvated electron formation determined by using nitrate ions as electron scavenger is 0.14 ± 0.01 and 0.068 ± 0.007 at $\mu \sim 0.01$ and $\mu \sim 1.0$, respectively. Addition of methylviologen (MV^{2+}) to the solution of iron(II) complex leads to production of MV^+ via direct electron scavenging and an electron transfer reaction from $[Fe(bpy)(CN)_4]^{3-}$. The latter process takes place with $k=9.0 \pm 0.6 \times 10^9$ M^{-1} s^{-1}. The decay of MV^+ occurs in reactions with both iron(III) and iron(II) complexes.

Introduction

The short-lived excited-states of the mixed ligand complex cyanides of iron(II) have been characterized recently [1–4]. The considerable interest is due to the fact that the photophysical properties and hence the photochemical reactivity of a solute molecule of this type can be widely modified. The coarse tuning of the low-lying metal to ligand charge transfer (MLTC) excited state can be realized by ligand exchange while the variation of solvent permits a fine tuning of MLTC state energies which has been attributed to donor–acceptor interactions between the solvent molecules and the cyanide ligands of the complex [5–7]. We have pointed out that the quantum yield of solvated electron formation from the higher energy charge transfer (CT) excited state also changes dramatically with modification of the ligands [8–10]. In our previous short communication [11], solvated electron and $[FeL(CN)_4]^{3-}$ (L = 2,2′-bipyridine and 4,4′-dimethyl-2,2′-bipyridine) as products of the electron scavenging reaction of the ground state iron(II) compound were identified in aqueous solution of $[FeL(CN)_4]^{2-}$ complexes excited at 266 nm. Here we report the results of detailed kinetic analysis of the photo-induced redox reaction of $[Fe(bpy)(CN)_4]^{2-}$ in the presence of different other solutes and the identification of short-lived intermediates by ns time resolved spectroscopy and pulse radiolysis.

Experimental

Materials

The potassium salt of $[Fe(bpy)(CN)_4]^{2-}$ was prepared according to the procedure detailed in ref. 12 and checked by elemental analysis and spectroscopic methods (UV–Vis, IR). All the other chemicals used were of reagent grade.

Photochemical investigations

The concentration of the complex in solution to be irradiated varied between 5×10^{-5} and 5×10^{-4} M, while that of the nitrate and methylviologen (MV^{2+}) ions used as electron scavengers changed up to 10^{-2} M, and between 10^{-5} and 5×10^{-4} M, respectively. The excitation of the samples was performed in a quartz cuvette with an optical path length of 1 cm and a volume of 4 cm^3 in anaerobic conditions. In the case of steady state experiments, a 16-W low pressure mercury arc lamp (Applied

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Photophysics) was used as light source, which irradiated more than 90% of its energy at 254 nm. The incident light intensity was determined by trioxalato ferrate(III) actinometry [13, 14]. The photooxidation was monitored spectrophotometrically at 480 nm. At this wavelength the difference between the molar absorption coefficients of the iron(II) and the iron(III) complexes was determined from their visible spectra ($\Delta\epsilon_{480} = 2390 \pm 20$ M^{-1} cm^{-1}).

The laser flash photolysis investigations were carried out by using an LKS-40 laser kinetic spectrometer (Applied Photophysics) consisting of a K-347 kinetic spectrometer and an SL-402 Nd:YAG laser source for 1064, 532, 355 and 266 nm excitation. The transient signals were detected with an 1P28 or an R955 Hamamatsu photomultiplier tube, the output of which was fed into a Philips PM 3320/A type digitizing storage oscilloscope (250 Msample/s). The data acquisition was carried out by an IBM compatible AT personal computer.

Pulse radiolysis investigations

The pulse radiolysis investigations were performed by a computer controlled system described elsewhere [15]. Its electron source, the Tesla Linac LPR-4 accelerator produces electron pulses with an average energy of 4 MeV. The electron beam has a peak value of 200 mA and the pulse duration is 2.6 μs. The value of dose/pulse was varied between 50 and 200 Gy.

Results and discussion

Identification of hydrated electron

Figure 1 shows the transient absorption spectra obtained immediately after excitation of 3.32×10^{-4} M $K_2[Fe(bpy)(CN)_4]$ in water by 266 nm laser pulses with beam energy of c. 40 mJ. The absorption peaking in the red around 700 nm decays at a rate proportional to the concentration of $[Fe(bpy)(CN)_4]^{2-}$ (Fig. 2). The disappearance of the intermediate obeys first order kinetics. The reaction becomes somewhat faster when the ionic strength is increased by addition of potassium chloride. It suggests that the intermediate disappears in a reaction which involves particles of similar charge. Addition of NO_3^- or methylviologen (MV^{2+}) ions significantly reduces the red absorption and results in a considerable increase of the decay rate. These observations led to the assignment of the red absorbing species as hydrated electron. The relative yields of e_{aq}^- as a function of incident laser energy are given in Table 1. The concentration of the hydrated electron was calculated from the absorption at 600 nm measured immediately after the laser pulse. The molar absorbance of e_{aq}^- was taken to be 13 000 M^{-1} s^{-1} according to the literature [16]. The linearity of the electron concentration with the laser energy suggests that the solvated electron is produced by a monophotonic mechanism.

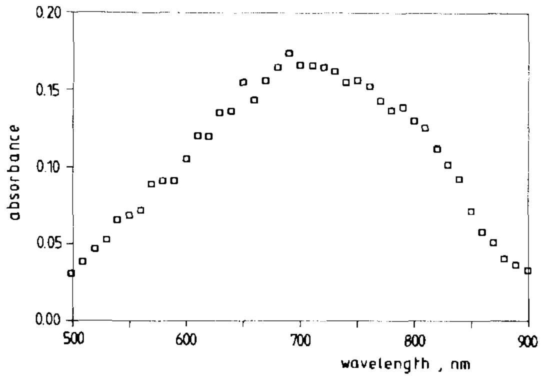

Fig. 1. Transient absorption spectrum observed immediately after 266 nm laser pulses in solution of 3.32×10^{-4} M $K_2[(Fe(bpy)(CN)_4]$ in deaerated water.

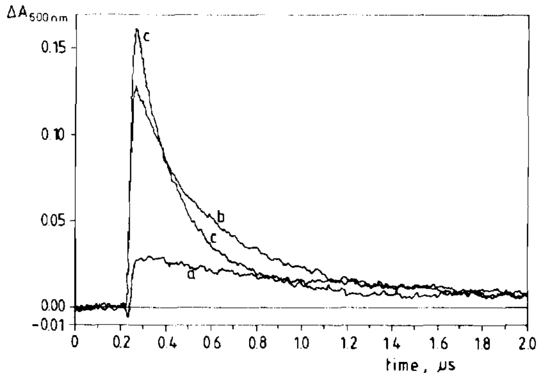

Fig. 2. Transient decays at 600 nm in aqueous solutions of $K_2[Fe(bpy)(CN)_4]$ (concentrations of the complex: 3.32×10^{-5} M (a), 1.66×10^{-4} M (b), 3.32×10^{-4} M (c)).

TABLE 1. Concentration of e_{aq}^- formed as a function of laser energy.

Laser energy (mJ)	Concentration of $e_{aq}^- \times 10^{-6}$ (M)
14	1.69
17.5	3.31
22	5.23
25	6.62
30	8.77
32.5	9.92
35	11.00
38	12.31

Linear *RS* = 0.9999.

$$[\mathrm{Fe(bpy)(CN)_4}]^{2-} \xrightarrow[266\ \mathrm{nm}]{h\nu} (\mathrm{CT})[\mathrm{Fe(bpy)(CN)_4}]^{2-} \quad (1)$$

$$(\mathrm{CT})[\mathrm{Fe(bpy)(CN)_4}]^{2-} \longrightarrow [\mathrm{Fe(bpy)(CN)_4}]^{-} + e^{-}_{aq} \quad (2)$$

Further reactions of hydrated electron

The decay of the hydrated electron absorption at 600 nm is accompanied by a concomitant growth of absorption in the near UV as given in Fig. 3. The optical density of the iron(III) complex at 370 nm is smaller than that of the iron(II) compound, hence the bleaching under the pulse is attributed to the formation of $[\mathrm{Fe(bpy)(CN)_4}]^{-}$. The growth of the absorption depends on the concentration of $[\mathrm{Fe(bpy)(CN)_4}]^{2-}$ and the ionic strength adjusted by potassium chloride. Both compounds increase the rate of the development in the absorption at 370 nm. In the presence of the nitrate ion as an electron scavenger the yield of this transient species decreases. Comparing these with the electron decay kinetics it is reasonable to assume that the increasing optical density in the UV is due to the formation of $[\mathrm{Fe(bpy)(CN)_4}]^{3-}$ as a product of the electron scavenging.

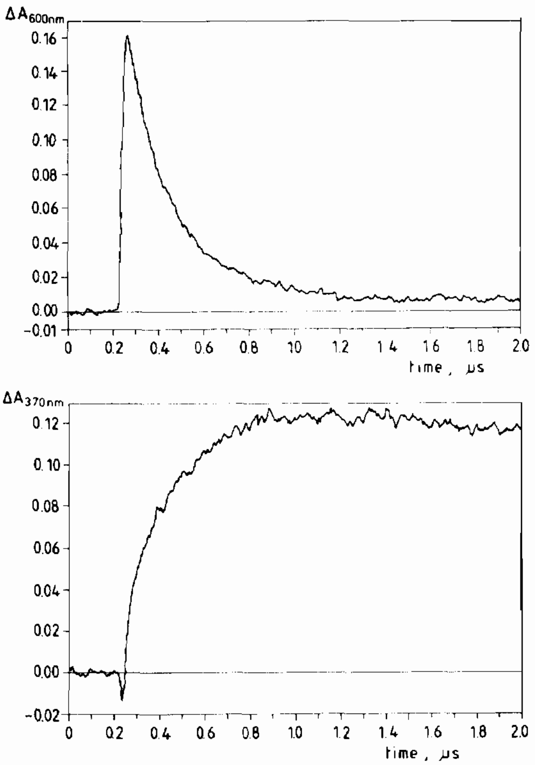

Fig. 3. Decay of e^{-}_{aq} at 600 nm and growth of $[\mathrm{Fe(bpy)(CN)_4}]^{3-}$ at 370 nm for 3.32×10^{-4} M $\mathrm{K_2[Fe(bpy)(CN)_4]}$ in deaerated water.

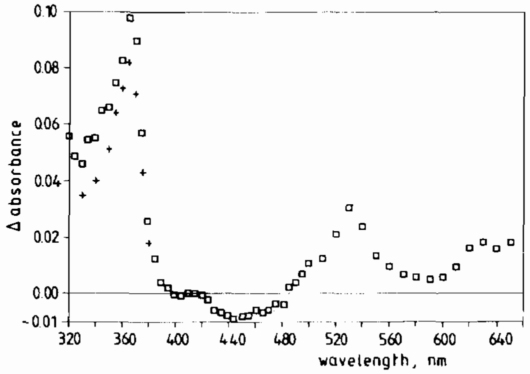

Fig. 4. Spectrum (□) obtained 1 μs after a 266 nm laser pulse delivered to an aqueous solution of 3.32×10^{-4} M $\mathrm{K_2[Fe(bpy)(CN)_4]}$ and 1 M KCl; spectrum (+) taken 1 μs after an electron pulse is delivered to 2×10^{-4} M $\mathrm{K_2[(Fe(bpy)(CN)_4]}$ in water containing 2% tert-butyl alcohol.

The spectrum obtained 1 μs after the laser pulse in aqueous solution of $[\mathrm{Fe(bpy)(CN)_4}]^{2-}$ is shown in Fig. 4 together with that produced by pulse radiolysis of a solution containing 2% tert-butyl alcohol as well to scavenge OH radicals. The comparison of spectra lends support to the assumption mentioned above, the ground state $[\mathrm{Fe(bpy)(CN)_4}]^{2-}$ acts as an effective electron scavenger.

$$e^{-}_{aq} + [\mathrm{Fe(bpy)(CN)_4}]^{2-} \longrightarrow [\mathrm{Fe(bpy)(CN)_4}]^{3-} \quad (3)$$

The rate constant ($k_3 = 1.3\pm0.3\times10^{10}\ \mathrm{M^{-1}\,s^{-1}}$) calculated from oscilloscope traces detected at 600 nm for aqueous solutions of the iron(II) complex of various concentrations indicates that the rate of reaction (3) is controlled by diffusion. As the difference spectrum detected 1 μs after the laser pulse is reminiscent of that of the 2,2′-bipyridine radical ion [17, 18] and the excited $[\mathrm{Fe(bpy)(CN)_4}]^{2-}$ [4] it is tempting to suggest that reaction (3) leads to the population of the empty π^* orbital of the coordinated bpy ligand. The molar absorption of $[\mathrm{Fe(bpy)(CN)_4}]^{3-}$ was estimated from the transient spectra, considering the absorption of the iron(III) complex and the amount of scavenged electrons.

Reaction of $[Fe(bpy)(CN)_4]^{3-}$

The product of reaction (3) must be a highly reducing compound therefore it should disappear in a fast redox reaction with the iron(III) complex formed in reaction (2). The observations are in accordance with this assumption. The decay of the absorption at 370 nm (Fig. 5) obeys second order kinetics with $k_4 = 1.8\pm0.4\times10^{10}\ \mathrm{M^{-1}\,s^{-1}}$ rate constant. The pulse radiolysis investigations in aqueous

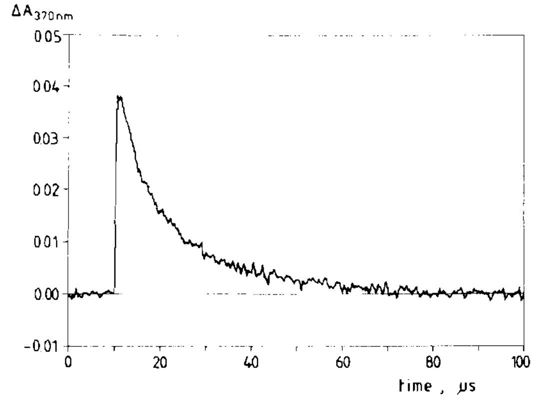

Fig. 5. Decay of $[Fe(bpy)(CN)_4]^{3-}$ at 370 nm for laser excited solution of 3.32×10^{-4} M $K_2[Fe(bpy)(CN)_4]$.

TABLE 2. Relative rate constants of reactions (3) and (4) as a function of potassium chloride concentration (L=bpy), $k_r=k([KCl]\neq0)/k([KCl]=0)$[a]

Concentration of KCl (M)	k_r (3)	k_r (4)
0.01	1.21	1.31
0.10	1.49	1.58
1.00	1.71	2.35

[a]The dependence on ionic strength is different from that predicted. This is due to the less effective charge acting than the formal charge because of the relatively large ionic radius of the complex and the association of K^+ ions with the complexes.

solution of the tetracyano iron(II) complex give similar results. Although the decay of absorption at 370 nm does not fit to a pure second order kinetics, the calculation for the second order stage of the curve leads to $k=2.2\pm0.6\times10^{10}$ M^{-1} s^{-1} which is in good agreement with the value obtained above. The rate constants of this reaction and that of reaction (3) were determined at various ionic strengths adjusted by potassium chloride. The relative rate constants of reactions (3) and (4) are given in Table 2. These indicate that the repulsion between the reactants is larger in the case of reaction (4) than in the electron scavenging, reaction (3). These observations also confirm that the iron(I) complex disappears via conproportionation to the iron(II) compound.

$$[Fe(bpy)(CN)_4]^{3-}+[Fe(bpy)(CN)_4]^{-}\longrightarrow 2[Fe(bpy)(CN)_4]^{2-} \qquad (4)$$

Determination of molar absorbances of $[Fe(bpy)(CN)_4]^{3-}$

In order to determine the accurate molar absorbances of $[Fe(bpy)(CN)_4]^{3-}$ a fitting to both the decay at 600 nm and the growth followed by disappearance of the absorption at 370 nm was carried out. The absorption around 600 nm originates from the hydrated electron and $[Fe(bpy)(CN)_4]^{3-}$ only, hence $\Delta D_{600\,nm}=\{\epsilon_{e^-}[e^-]+\epsilon_{Fe^+}[Fe^+]\}\times l$. The molar absorbance of the former (ϵ_{e^-}) is well known from the literature while the other was estimated from the spectra obtained 1 µs after the laser pulse (Fig. 4).

All the iron complexes appearing in these solutions absorb the light at $\lambda<500$ nm, therefore their absorptions are involved in the transient spectra and the decay curves at this spectral range. The molar absorbances of iron(II) and iron(III) complexes were measured from their freshly prepared solutions. Using these values $\Delta D(t)=\{\Delta\epsilon_{Fe^+}[Fe^+](t)+\Delta\epsilon_{Fe^{3+}}[Fe^{3+}](t)\}\times l$ is obtained for transient traces, where $[Fe^+]$ and $[Fe^{3+}]$ are the concentrations of the iron(I) and iron(III) complexes, $\Delta\epsilon_{Fe^+}$ and $\Delta\epsilon_{Fe^{3+}}$ are the differences of molar absorbances between iron(I) and iron(II) and between iron(III) and iron(II) compounds, respectively, and l is the optical path length. The initial value of $\Delta\epsilon_{Fe^+}$ was estimated from the transient spectra by the procedure described above. The concentration change of the hydrated electron and that of the iron complexes of different oxidation states initiated by a laser pulse can be given by differential equations involving reactions (1)–(4). The best fitting to the transients measured at both wavelengths (600 and 370 nm) was performed by changing the molar absorbances ϵ_{Fe^+}(370 nm) and ϵ_{Fe^+}(600 nm). The procedure involved the solution of differential equations with a modified step size Runge–Kutta method of order four [19]. The iteration led to the corrected molar

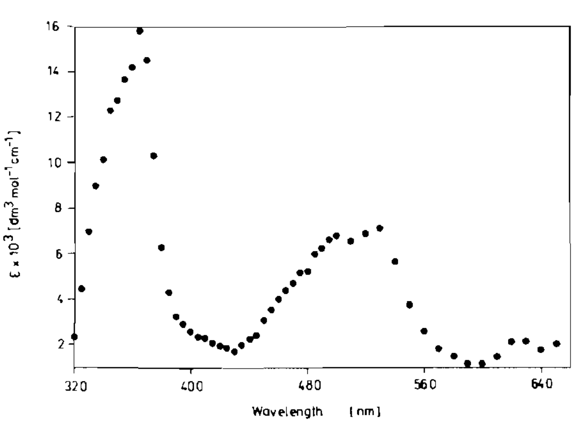

Fig. 6. Absorption spectrum of $[Fe(bpy)(CN)_4]^{3-}$

absorbances of the short-lived iron(I) complex in UV and in visible ranges (see Fig. 6).

Reactions in the presence of NO_3^- ions

The electron scavenging with nitrate ions is also a diffusion controlled process [20], hence the formation of iron(I) complex takes place with smaller efficiency when the concentration of the nitrate ions is increased, as illustrated in Fig. 7. The reaction of the hydrated electron with nitrate ion leads to the formation of the NO_2 radical [21].

$$NO_3^- + e_{aq}^- + H_2O \longrightarrow {}^{\cdot}NO_2 + 2OH^- \qquad (5)$$

The nitrite radical disappears via dimerization followed by disproportionation [20] or oxidizes the iron(II) complex.

$$[Fe(bpy)(CN)_4]^{2-} + {}^{\cdot}NO_2 \longrightarrow [Fe(bpy)(CN)_4]^- + NO_2^- \qquad (6)$$

Reaction (6) was monitored by both pulse radiolysis and laser flash photolysis at 475 nm, where the bleaching of the solution is assigned to the formation of the iron(III) compound from the iron(II) complex. The analysis of the oscilloscope traces gives $k_6 = 3.3 \pm 0.2 \times 10^6\ M^{-1}\ s^{-1}$ for the bimolecular rate constant. This value is rather similar to those obtained for the reaction of the NO_2 radical with other iron(II) complex cyanides [9, 21]. The excitation of a solution of $[Fe(bpy)(CN)_4]^{2-}$ containing nitrate ions results in the oxidized complex only if the electron scavenging reaction of the nitrate ions competes effectively with reaction (3). It is realized when the concentration of the nitrate ion exceeds 10^{-2} M. Under these conditions the rate of the iron(III) complex formation is proportional to the quanta of photons absorbed by the iron(II) compound. Hence the quantum yield for solvated electron formation, φ_e, can be determined by this method using the continuous irradiation technique. It is interesting to note that a very slow thermal reduction of $[Fe(bpy)(CN)_4]^-$ also takes place, especially in alkaline media, however, it can be neglected at the initial stage of the photooxidation of $[Fe(bpy)(CN)_4]^{2-}$. The quantum yields (φ) determined at various concentrations of NO_3^- and at different ionic strengths are given in Table 3. Since reaction (4) can be neglected, the limiting quantum yield, φ_e (φ at infinite concentration of scavenger) can be obtained by the steady state assumption

$$1/\varphi = 1/\varphi_e \left\{ 1 + \frac{k_3[Fe(bpy)(CN)_4{}^{2-}]}{k_4[NO_3{}^-]} \right\} \qquad (7)$$

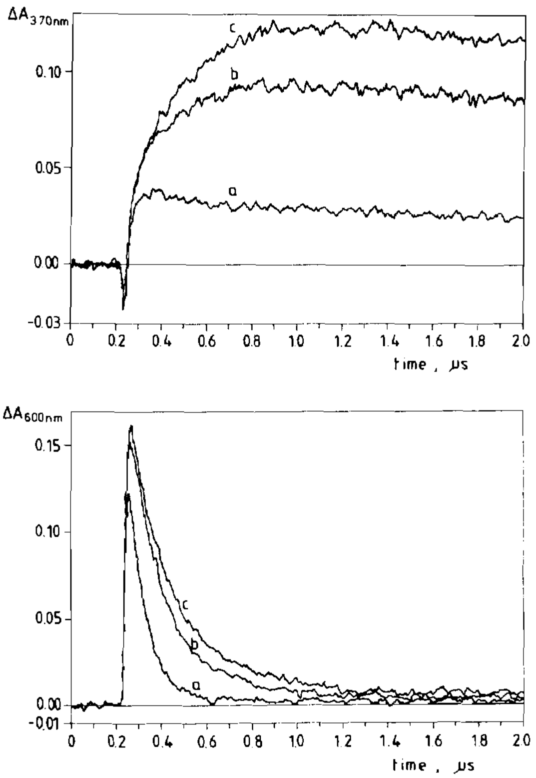

Fig. 7. Decay of e_{aq}^- at 600 nm and growth of $[Fe(bpy)(CN)_4]^{3-}$ at 370 nm in laser excited solutions of 3.32×10^{-4} M $K_2[Fe(bpy)(CN)_4]$, 10^{-3} M KNO_3 (a), 10^{-4} M KNO_3 (b) and 0 M KNO_3 (c).

TABLE 3. Dependence of quantum yield on the initial concentration of scavenger (NO_3^-)

Concentration of NO_3^- (M)	Quantum yield	
	0 M KCl	1 M KCl
1.00×10^{-2}	0.150	0.073
8.00×10^{-3}	0.144	0.077
6.00×10^{-3}	0.150	0.059
5.00×10^{-3}	0.145	0.057
4.00×10^{-3}	0.131	0.057
3.00×10^{-3}	0.155	0.060
2.00×10^{-3}	0.125	0.063
1.60×10^{-3}	0.119	0.062
1.30×10^{-3}	0.110	0.054
1.00×10^{-3}	0.113	0.057
6.40×10^{-4}	0.107	0.044
5.40×10^{-4}	0.107	0.046
4.30×10^{-4}	0.109	0.042
3.20×10^{-4}	0.099	0.036
2.10×10^{-4}	0.101	
1.80×10^{-4}	0.055	
1.40×10^{-4}	0.068	
1.00×10^{-4}	0.060	
Limiting quantum yield, φ_e	0.14 ± 0.01	0.068×0.007

The incident light intensity was 3.54×10^{-5} M photon min^{-1}. The quantum yields were determined by the initial slope of a polynome fitted by Marquardt's method [25] to the absorbance vs. time plots consisting of 25 points.

The figures indicate that the quantum yields are smaller at higher ionic strengths. This suggests that the primary recombination of the geminate pair (GP) constituents (hydrated electron and oxidized complex) is more effective at higher ionic strengths due to the increased shielding on the two negatively charged species.

Reactions in the presence of MV^{2+}

The transient spectrum detected 2 μs after the laser pulse in the aqueous solution of 3.32×10^{-4} M $[\mathrm{Fe(bpy)(CN)_4}]^{2-}$ and 4.23×10^{-4} M $\mathrm{MV^{2+}}$ is given in Fig. 8. It corresponds to the spectrum of $^{\bullet}\mathrm{MV^+}$ [23]. The appearance of this well-characterized radical is attributed to the electron scavenging reaction

$$\mathrm{MV^{2+}} + e^-_{aq} \longrightarrow {}^{\bullet}\mathrm{MV^+} \qquad (8)$$

The transient traces at 395 and 600 nm show rather different features (Fig. 9). The molar absorbance of the methylviologen radical at 395 nm is approximately 4×10^4 $\mathrm{M^{-1}\ cm^{-1}}$ [23–25], hence it is at least one order of magnitude higher than that of other compounds formed after the laser pulse. The absorption increases up to ~2 μs then decreases. The setting up of the absorption and the maximum (value and position) of the $^{\bullet}\mathrm{MV^+}$ concentration depend on the initial concentration of methylviologen and the iron(II) complex. The decrease of the former component leads to the decreases of the concentration of the methylviologen radical and a shift in its maximum to a longer time. A similar trend in the concentration of the iron(II) complex results in a decrease of radical formation due to the smaller amount of absorbed light and a significant reduction in the rate of the disappearance of the radical. The decay of the methylviologen radical at $t>5$ μs after the laser pulse obeys first order kinetics. These observations anticipate that $^{\bullet}\mathrm{MV^+}$ reacts with the iron(II) complex.

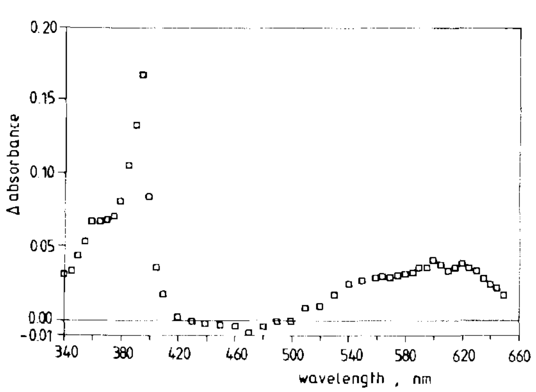

Fig. 8. Transient absorption spectrum observed 2 μs after the laser pulse in aqueous solution of 3.32×10^{-4} M $\mathrm{K_2[Fe(bpy)(CN)_4]}$ and 4.35×10^{-5} M $\mathrm{MV^{2+}}$.

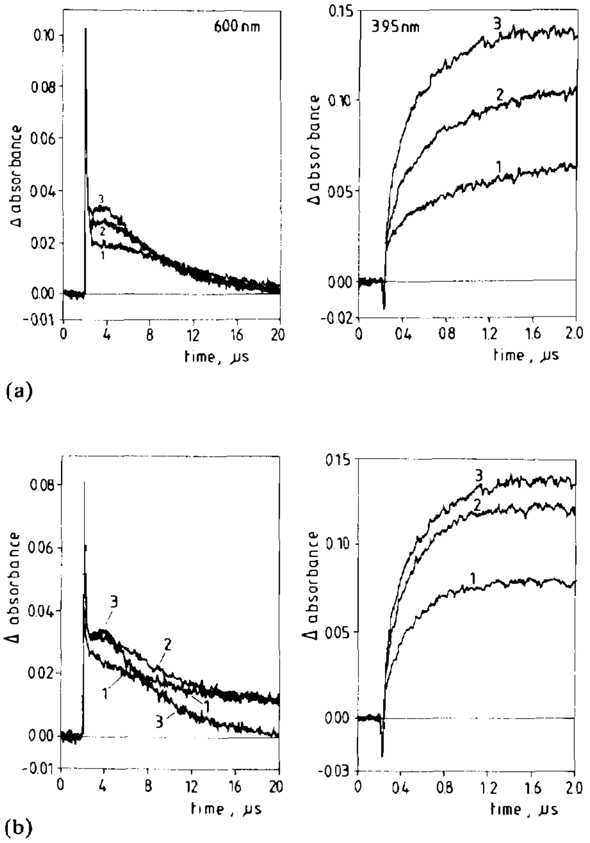

Fig. 9. Transient absorption traces detected at 395 and 600 nm in laser excited solutions of $\mathrm{K_2[Fe(bpy)(CN)_4]}$ and $\mathrm{MV^{2+}}$: (a) 3.32×10^{-4} M complex and 1.45×10^{-5} (1), 2.90×10^{-5} (2), 4.34×10^{-5} (3) M $\mathrm{MV^{2+}}$; (b) 4.34×10^{-5} M $\mathrm{MV^{2+}}$ and 6.64×10^{-5} (1), 1.66×10^{-4} (2), 3.32×10^{-4} (3) M complex.

At 600 nm the absorptions of the hydrated electron and the iron(II) complex overlap with that of the methylviologen radical. Therefore one can detect the resultant of three components at least at this wavelength. Because the electron has the highest molar absorption, a monotonous decreasing in absorption is expected if $^{\bullet}\mathrm{MV^+}$ is formed only in reaction (8). However, the sharp decay is followed by a growth in optical density and finally the blue colour disappears. The phenomenon can be interpreted by another electron transfer reaction resulting in the $^{\bullet}\mathrm{MV^+}$ radical ion. It has been proved that $[\mathrm{Fe(bpy)(CN)_4}]^{2-}$ scavenges the electron in a diffusion controlled reaction, hence reaction (3) must compete effectively with reaction (8). The iron(I) complex formed in reaction (3) should be a highly reducing anion therefore it seems to be reasonable to assume that the reaction of this species also leads to the methylviologen radical.

$$[\mathrm{Fe(bpy)(CN)_4}]^{3-} + \mathrm{MV}^{2+} \longrightarrow [\mathrm{Fe(bpy)(CN)_4}]^{2-} + {}^{\cdot}\mathrm{MV}^{+} \quad (9)$$

The disappearance of the methylviologen radical can be attributed to the following reaction

$$ {}^{\cdot}\mathrm{MV}^{+} + [\mathrm{Fe(bpy)(CN)_4}]^{-} \longrightarrow \mathrm{MV}^{2+} + [\mathrm{Fe(bpy)(CN)_4}]^{2-} \quad (10)$$

and a reaction of ${}^{\cdot}\mathrm{MV}^{+}$ with the iron(II) complex of ground state has been suggested

$$ {}^{\cdot}\mathrm{MV}^{+} + [\mathrm{Fe(bpy)(CN)_4}]^{2-} \longrightarrow \mathrm{A} \quad (11)$$

'A' is an unidentified intermediate of relatively long lifetime, which has an intensity absorption around 310 nm in UV. We have found that the absorption at 310 nm and the residual bleaching at 475 nm due to $[\mathrm{Fe(bpy)(CN)_4}]^{-}$ formed in reaction (2) decrease simultaneously in the ms time scale. These observations suggest that a reaction between these two species takes place, resulting in the original iron(II) complex.

In order to determine the rate constants of reactions (8)–(11) the fitting procedure described above was adapted to this system. All the transients detected at 395 and 600 nm in solutions of different compositions were used for the calculation. The best fitting was obtained with the following rate constants; $k_8 = 3.6 \pm 0.5 \times 10^{10}$ M^{-1} s^{-1}, $k_9 = 9.0 \pm 1.2 \times 10^{9}$ M^{-1} s^{-1}, $k_{10} = 1.8 \pm 0.4 \times 10^{10}$ M^{-1} s^{-1} and $k_{11} = 6.2 \pm 1.5 \times 10^{8}$ M^{-1} s^{-1}.

The reduced methylviologen has the capacity, under suitable conditions, to reduce water, hence it may be an important species in light energy conversion systems [26]. In this regard the yield of MV^{+} is essential among the factors determining the efficiency of this photochemical system. It depends on the concentration of the iron(II) complex and that of methylviologen and can be determined by the kinetical model presented here. Our calculation leads to concentrations $[\mathrm{MV}^{2+}] = 9 \times 10^{-4}$ M and $[\mathrm{Fe(bpy)(CN)_4}^{2-}] = 5 \times 10^{-4}$ M as the optimum values at fixed pulse energy ($\sim$40 mJ).

Conclusions

Efficient hydrated electron formation from UV excited $[\mathrm{Fe(bpy)(CN)_4}]^{2-}$ has been observed. The hydrated electrons formed have been shown to be scavenged by $[\mathrm{Fe(bpy)(CN)_4}]^{2-}$ of ground state or by other electron scavengers ($\mathrm{NO_3}^{-}$, MV^{2+}) to yield oxidizing (${}^{\cdot}\mathrm{NO_2}$), and reducing (${}^{\cdot}\mathrm{MV}^{+}$) intermediates, respectively. It has been pointed out that methylviologen radical is also produced by an electron transfer reaction from $[\mathrm{Fe(bpy)(CN)_4}]^{3-}$, and disappears in reactions with the ground state iron(II) and iron(III) complexes. Using the established kinetic model we can optimize the yield of reduced methylviologen, the species which can transform the light to chemical energy.

Although the present system cannot be considered as a useful tool for solar energy conversion since sunlight does not contain UV radiation of high intensity at the Earth's surface, the mechanisms in which photoexcitation leads to production of energy rich species such as reduced viologen are interesting.

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