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Ligand dependence of magnetic spin effects on photooxidation of $[Ru(bpy)_{3-n}(CN)_{2n}]^{(+2-2n)}$ type complexes

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Abstract

Photoinduced electron transfer reaction from the series of $[Ru(bpy)_{(3-n)}(CN)_{2n}]^{(2+-2n)}$ complexes ($n = 0, 1, 2$) to methylviologen has been investigated using external magnetic field modulation in order to obtain relevant kinetic parameters for spin relaxation, backward electron transfer and cage escape of the geminate radical pair. The replacement of one bpy by two cyanide ligands results in an increase of the quenching rate constant and a decrease of the cage escape efficiency. The latter is decreased in a magnetic field and the sensitivity of this effect is weakened by introducing CN^- ligands. From the analysis of the magnetic field dependence it can be inferred that with increasing number of CN^- ligands, backward electron transfer rate and spin relaxation time in the geminate radical pair exhibit a moderate decrease but that the rate constant of cage escape decreases very strongly.

Keywords: Mixed ligand ruthenium(II) complexes; Electron transfer quenching; Magnetic field effects

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1. Introduction

Photophysics and photochemistry of d^6 polypyridyl complexes of transition metal ions such as Re(I) [1–3], Ru(II) [4–6] and Os(II) [7,8], in particular that of $Ru(L)_3^{2+}$ type, have figured prominently as leading compounds in numerous studies of light induced electron transfer reactions generally motivated by searching for systems capable of efficient chemical conversion of solar energy [9–19]. Mechanistic investigations have focussed on the rate parameters of three elementary processes: the rate constant k_{fet} of bimolecular forward electron transfer between the excited ^{3}MLCT state Ru(II) complex and some ground state electron acceptor or donor, the rate constant k_{bet} of geminate backward electron transfer regenerating the singlet ground state of the complex and the rate constant k_{ce} of cage escape from the radical pair [18,20–22]. On the other hand, it has not been generally considered that, due to the different spin multiplicity of photoreactive and ground states of the complex, a spin process becomes an essential step in the overall kinetics of geminate backward electron transfer [23–25]. This has been demonstrated by the magnetic field dependence of the quantum yield of radicals formed in photoinduced redox reactions of $Ru(L)_3^{2+}$ complexes [26–34].

The way that spin conversion enters the kinetics of the photoelectron transfer mechanism is shown in Scheme 1. The electron spin is conserved in an electron transfer process. Therefore, the primary geminate pair is generated with triplet multiplicity. A spin conversion has to occur before the backward electron transfer becomes allowed. Since the spin relaxation of Ru(III) is very fast [35a] spin flips at the Ru(III) center dominate the spin conversion of geminate radical pair and the pertinent rate constants k_{TS} and k_{ST} can be expressed through the spin relaxation time τ_S of the Ru(III) complex. Thus, in addition to k_{ce} and k_{bet}, τ_S becomes the third significant parameter necessary to characterize the geminate electron transfer process with Ru(III) complexes. The magnetic field dependence of the cage escape yield η_{ce} of radicals has been shown to provide unique information for evaluating all three parameters of the geminate

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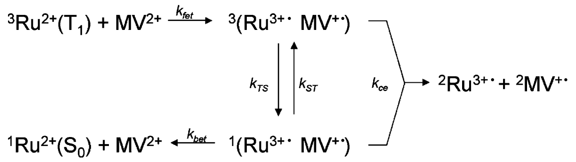

Scheme 1.

pair. Hence it can be used as an efficient tool for elucidating the structural effects on the photoinduced electron transfer mechanism.

A promising way to realize structural changes of the complex is to vary the coordination sphere systematically with the stepwise substitution of individual ligands. For example, the effects of such variations have been studied with the magnetic-field-effect method for the photooxidation of the series of $[Ru(bpy)_n(dce)_{3-n}]^{2+}$ [28] and $[Ru(bpy)_n(phen)_{3-n}]^{2+}$ [31,33] by methylviologen (MV^{2+}) (bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline and dce = 4,4′-diethoxycarbonyl-2,2′-bipyridine). It is important to note that the variations in the behavior and properties of the ligands in these series are fairly subtle. The aim of our study was to investigate a series of complexes in which the variation of ligand properties is much more pronounced. It has been achieved by the replacement of bpy with two cyanide ligands yielding a series of complexes $[Ru(bpy)_3]^{2+}$, $[Ru(bpy)_2(CN)_2]$ and $[Ru(bpy)(CN)_4]^{2-}$. The spectral, photophysical and electrochemical properties of these complexes are well characterized [36–40]. The more cyanide ions are coordinated to Ru(II) the lower is the oxidation potential of the complex and its ^{3}MLCT excited stated has a higher driving force ΔG°_{fet} in the photoinduced forward electron transfer, while the driving force of the backward electron transfer ΔG°_{bet} is smaller. Furthermore, the change in charge of the complex is expected to have a major impact on k_{ce}. Finally, the effect of CN^- ligands on spin relaxation in the Ru(III) complex is an open question to which answers can be expected from a magnetic field dependent study of the electron transfer mechanism.

2. Experimental

2.1. Materials and solutions

Analytical grade $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (Aldrich) was used without further purification. The mixed ligand complexes, $[Ru(bpy)_2(CN)_2]$ and $K_2[Ru(bpy)(CN)_4] \cdot 2H_2O$ were prepared by the methods described in the literature [36,41]. The purity of these compounds was checked by elemental analysis and spectroscopic methods (UV–Vis, IR). Methylviologen (MV^{2+} = 1,1′-dimethyl-4,4′-dipyridinium) was purchased as chloride from Aldrich and Fluka (purum quality). Water purified by a Millipore Super-Q system was used to prepare aqueous solutions while spectrograde MeOH and D_2O (99.9% grade) purchased from Aldrich and Deutero GmbH were used for photophysical and -chemical measurements without further purification. The concentration of Ru complexes varied between 2×10^{-5} and 8×10^{-5} M, while the concentration of MV^{2+} changed between 0 and 5×10^{-3}, 2×10^{-3} and 1×10^{-3} M for $[Ru(bpy)_3]^{2+}$, $[Ru(bpy)(CN)_2]$ and $[Ru(bpy)(CN)_4]^{2-}$, respectively.

2.2. Equipment and methods

Transient emission and absorption signals in the nanosecond to microsecond range were measured using the Nd-YAG/dye-laser based flash photolysis equipment described previously [42]. The laser dye employed for exciting the Ru(II) complexes was stilbene 3, yielding a laser wavelength of 420 nm. The dye was pumped by the third harmonic of the NdYAG laser. Luminescence lifetimes were obtained by a single-exponential fitting to the emission decay ($\lambda_{em} = 600$ nm). The quenching constants in various solutions were measured by luminescence quenching method using the well-known Stern–Volmer equation:

$$\frac{1}{\tau} = \frac{1}{\tau_0} + k_q[Q] \tag{1}$$

where τ_0 is the lifetime of the luminescent species at $[Q] = 0$, k_q is the rate constant of quenching and $[Q]$ is the quencher concentration. The cage escape efficiency η_{ce} of radicals, i.e. the net efficiency of electron transfer, was determined by the saturation method, detecting the $MV^{+\bullet}$ absorption at 395 nm as function of laser energy and extrapolating to saturation [43].

$$\Delta A_{395} = \Delta A_{395,sat}[1 - \exp(bI_L)] \tag{2}$$

where I_L denotes the relative energy of the laser pulse and b is a fit parameter that should be proportional to the molar absorption coefficient of the irradiated complex at the wavelength of the laser. From $\Delta A_{395,sat}$, the saturation value of the absorbance changed at 395 nm, η_{ce} was obtained by the expression:

$$\eta_{ce} = \Delta A_{395,sat}/(\eta_q[Ru(II)]_o\Delta\varepsilon_{395}), \tag{3}$$

where η_q is the quenching efficiency, given by

$$\eta_q = \frac{k_q[Q]}{1/\tau_0 + k_q[q]}, \tag{4}$$

$[Ru(II)]_o$ is the total concentration of Ru complexes, and $\Delta\varepsilon_{395}$ is the change of molar absorbance at 395 nm given by $\varepsilon_{MV^+} - \varepsilon_{MV^{2+}} + \varepsilon_{Ru(III)} - \varepsilon_{Ru(II)}$. The main contribution to $\Delta\varepsilon_{395}$ is from the $MV^{+\bullet}$ radical cation exhibiting an absorption maximum at this wavelength with $\varepsilon_{395} =$

39 100 M^{-1} cm^{-1} [44] whereas for MV^{2+} $\varepsilon = 0$ at this wavelength. The ε values of the complexes were determined in aqueous solutions. To generate Ru(III) complexes, Ru(II) complexes were oxidized in acidified solutions ($[H_2SO_4] \sim 0.25$–0.5 M) by PbO_2 in the case of $[Ru(bpy)_3]^{2+}$ and by BrO_3^- in the case of the mixed cyano complexes. The following values (in M^{-1} cm^{-1}) were obtained: $[Ru(bpy)_3]^{2+/3+}$ (5700/1800), $[Ru(bpy)_2(CN)_2]^{0/+}$ (4370/1690) $[Ru(bpy)(CN)_4]^{2-/-}$ (3080/1520). The same values were used for Ru(III) complexes in H_2O, D_2O, and MeOH. The uncertainty of $\Delta\varepsilon$ introduced by a weak variation between these solvents is probably less than ± 1000 M^{-1} cm^{-1}, i.e. less than $\pm 3\%$.

The cuvette of the laser flash spectrometer was positioned between the pole pieces of a Bruker B-E 15 electromagnet. The relative magnetic field dependence of η_{ce} was measured by comparing the ΔA values at field values in the range between 0 and 3.3 T with the ΔA value at zero field.

3. Results

Excitation of the three types of Ru(II) complexes leads to formation of the triplet MLCT state within several hundreds of fentoseconds [45]. These excited species have similar absorption spectrum possessing a very strong and a strong absorption bands peaking at 370 and 430 nm, respectively that are characteristic of a species containing the bpy^- chromophore [46,47]. In the presence of MV^{2+} the excited species is quenched by electron transfer reaction. This process results in the $MV^{+\bullet}$ radical that has a very strong and sharp absorption band peaking at 395 nm and another band showing fine structure between 500 and 700 nm [48,49] as is demonstrated by Fig. 1.

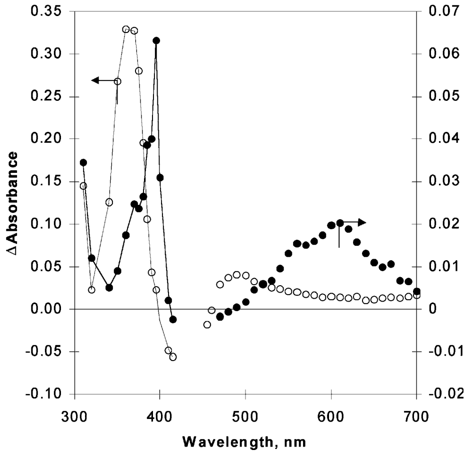

Fig. 1. Transient absorption spectra detected in aqueous solution of $Ru(bpy)_2(CN)_2$ and MV^{2+} at room temperature with excitation at 420 nm and with time delay of 50 ns (○) for 2×10^{-5} M $Ru(bpy)_2(CN)_2$ and with time delay of 1500 ns (●) for 2×10^{-5} M $Ru(bpy)_2(CN)_2$ and 2×10^{-3} M MV^{2+}.

Table 1
Characteristic parameters determined in various Ru(II)–MV^{2+} systems

Parameter	$Ru(bpy)_3{}^{2+}$	$Ru(bpy)_2(CN)_2$	$Ru(bpy)(CN)_4{}^{2-}$
ΔG°_{fet} (eV) [a]	-0.48	-0.89	-1.19
ΔG°_{bet} (eV) [a]	-1.67	-1.31	-1.19
In H_2O, ionic strength = 0.1 M ($NaNO_3$)			
$k_q \times 10^{-9}$ (M^{-1} s^{-1})	1.13	3.7	7.0
η_{ce} (%)	14.6	4.8	4.8
MFE (2.7 T) (%)	-17.3	-8.9	-0.7
τ_S (ps)	20.5 ± 0.6	17.2 ± 0.7	12
$k_{TS} = 1/4\tau_S$ (ns^{-1})	12.2	14.5	20.8
k_{ce} (ns^{-1})	1.9 ± 0.15	0.23 ± 0.01	0.08
$k_{ce,diff}$ (ns^{-1})	4.43	3.94	3.18
k_{bet} (ns^{-1})	88 ± 8	22.4 ± 0.5	6.5
In D_2O, ionic strength = 0.1 M ($NaNO_3$)			
$k_q \times 10^{-9}$ (M^{-1} s^{-1})	1.04	3.5	6.2
η_{ce} (%)	11.3	3.6	2.6
MFE (2.7 T) (%)	-19.8	-10.5	-2.8
τ_S (ps)	23.0 ± 1.5	17	12
$k_{TS} = 1/4\tau_S$ (ns^{-1})	10.9	14.7	20.8
k_{ce} (ns^{-1})	1.25 ± 0.2	0.18	0.05
$k_{ce,diff}$ (ns^{-1})	3.49	3.1	2.5
k_{bet} (ns^{-1})	81 ± 15	25	7.5
In MeOH, ionic strength = 0.1 M ($NaNO_3$)			
$k_q \times 10^{-9}$ (M^{-1} s^{-1})	1.22	4.15	9.4
η_{ce} (%)	19.6	7.7	5.5
MFE (2.7 T) (%)	-19.6	-12.7	-4.2
τ_S (ps)	25 ± 0.6	16.5 ± 1.5	12
$k_{TS} = 1/4\tau_S$ (ns^{-1})	10.0	15.2	20.8
k_{ce} (ns^{-1})	2.8 ± 0.3	0.75 ± 0.10	0.15
$k_{ce,diff}$ (ns^{-1})	9.07	7.24	4.69
k_{bet} (ns^{-1})	110 ± 15	56.5 ± 9.0	11.5

The rate coefficients of the quenching reaction determined by using Stern–Volmer plots are summarized in Table 1. These data clearly indicate that the exchange of one bpy with two cyanide ligands leads to a considerable increase in the rate of the electron transfer quenching. According to the semi-classical formulation of Marcus theory the rate constant of an outer-sphere electron-transfer reaction depends on the electronic coupling coefficient, the reorganization energy and the activation energy of the reaction. The activation energy is determined by the reorganization energy and the driving force of the reaction ΔG°. Values of ΔG° for an electron transfer reaction can be calculated with Eq. (5)

$$\Delta G^\circ = E^\circ(D^+/D) - E^\circ(A/A^-) + w_p - w_r, \qquad (5)$$

where $E^\circ(D^+/D)$ and $E^\circ(A/A^-)$ are the standard potentials of the donor and acceptor couples, respectively, and w_p and w_r are the coulombic work terms for the products and the reactants, respectively, which correct for the work involved in bringing ionic species together. The coulombic terms are usually small (approximately 10^{-2} eV). Hence the standard free energies $\Delta G^\circ_{\text{fet}}$ for the forward and $\Delta G^\circ_{\text{bet}}$ for the backward electron transfer reaction, respectively, of a system containing the ^{3}MLCT excited state of the Ru(II) complex and the electron acceptor MV^{2+} can be estimated as

$$\Delta G^\circ_{\text{fet}} = E^\circ[\text{Ru(III)}/{}^*\text{Ru(II)}] - E^\circ[\text{MV}^{2+}/\text{MV}^{+\bullet}] \qquad (6)$$

and

$$\Delta G^\circ_{\text{bet}} = E^\circ[\text{MV}^{2+}/\text{MV}^{+\bullet}] - E^\circ[\text{Ru(III)}/\text{Ru(II)}] \qquad (7)$$

respectively (Table 1). The driving force of the forward electron transfer increases with the number of the cyanide ligands coordinated to the Ru(II) center which, in accordance with the measured data, predicts an increase in the rate of the forward electron transfer reaction.

The variation of the transient absorption detected at 395 nm after excitation of Ru(II)–MV^{2+} systems in aqueous solution as a function of the laser pulse energy is presented in Fig. 2.

The representative plots for the tris- and bis-bpy complexes clearly indicate the saturation at high laser energy, from which the η_{ce} values have been calculated (Eq. (3)). However, the curvature of the laser energy dependence of ΔA for mono-bpy complex was too weak. Hence the saturation value could not assessed without further assumptions. The values given in Table 1 were obtained by fixing b in Eq. (2) to a value that reduces the value used for $Ru(bpy)_2(CN)_2$ complex in proportion to the respective molar absorption coefficients at the wavelength of the laser. As it is demonstrated by the data given in Table 1, the cage escape efficiency dramatically decreases by the replacement of one and two bpy, respectively with cyanide ligands. This is expected by considering the change in the electric charge of the Ru(III) constituent of the radical pair. The lowest cage escape efficiencies were obtained in D_2O while the cage escape was found to be most efficient in methanol.

The observed magnetic field effect (MFE) on the quantum yield of light induced $MV^{+\bullet}$ radical formation $R(B) = [\eta_{\text{ce}}(B) - \eta_{\text{ce}}(0)]/\eta_{\text{ce}}(0)$ for the three complexes in aqueous solution is depicted in Fig. 3. It clearly indicates that the magnetic field sensitivity regularly decreases by every replacement of a bpy with two CN^- ligands. Although the same tendency is observed in H_2O, D_2O and MeOH solvents for the complexes studied, the magnetic field modulation is most efficient in MeOH (cf. Table 1).

Based on the theoretical simulation of this MFE, these experimental data provide access to the rate parameters k_{ce}, k_{bet}, k_{TS} and k_{ST} defined in Scheme 1. The reason why η_{ce} is magnetic-field sensitive, lies in the rate-determining role of the triplet/singlet spin conversion in the primary RP. For one, the rate of this process is determined by the (magnetic-field independent) spin relaxation time τ_S of the $Ru(bpy)_3{}^{3+}$ complex. This relaxation parameter is related to the rate constants k_{TS} and k_{ST} by the equations:

$$k_{\text{TS}} = \frac{1}{3}\,k_{\text{ST}} = \frac{1}{4\tau_S} \qquad (8)$$

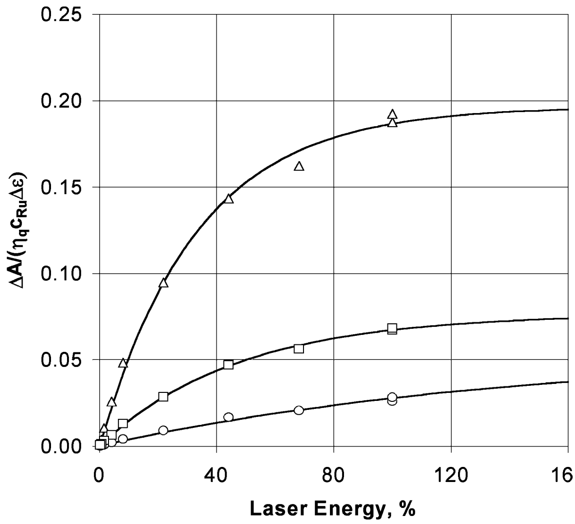

Fig. 2. Variation of produced absorbance of free radicals at 395 nm as a function of relative laser energy for the photoreaction of complexes $[Ru(bpy)_{3-n}(CN)_{2n}]^{2+-2n}$ with MV^{2+} in MeOH (△, $n=0$; □, $n=1$; and ○, $n=2$). The solid lines represent fits according to Eq. (2), from which the absolute efficiencies of radical formation can be extrapolated [43].

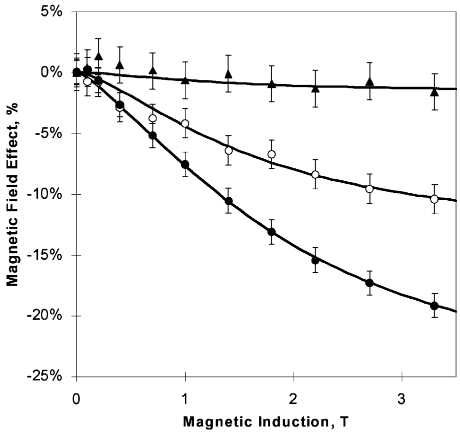

Fig. 3. Relative MFE R(B) on the quantum yield of $MV^{+\bullet}$radical formation upon quenching of photoexcited $[Ru(bpy)_{3-n}(CN)_{2n}]^{2+-2n}$ complexes in water; $n=2$ (▲), $n=1$ (○) and $n=0$ (●). The solid lines represent the results of theoretical simulations of magnetic field dependence using parameters given in Table 1.

On the other hand, due to the large difference of g values of Ru(III) and $\mathrm{MV}^{+\bullet}$, the magnetic field induces a coherent mixing of triplet and singlet of the RP, the frequency of which is proportional to the magnetic field B_o. The full kinetics of the geminate RP is properly described by a Stochastic Liouville Equation, from the numerical solution of which the MFE on η_{ce} can be predicted [29,31,33]. The parameters of the kinetic model are the g tensor values of the radical species and the three rate parameters k_{ce}, k_{bet} and τ_S. Since the g tensors are known from EPR spectra, the fit of the theoretical dependence $\eta_{ce}(B_o)$ to the experimental one can be used to assign the values of k_{ce}, k_{bet} and τ_S. A fully computerized optimization routine has been developed to obtain the best three-parameter fits [50].

The g values employed in the calculations were $g = 2.00$ for $\mathrm{MV}^{+\bullet}$ and $g_{\parallel} = 1.18$ and $g_{\perp} = 2.65$ for $\mathrm{Ru(bpy)_3}^{3+}$ [33]. No g tensor values are available in the literature for the complexes $[\mathrm{Ru^{III}(bpy)_2(CN)_2}]^+$ and $[\mathrm{Ru^{III}(bpy)(CN)_4}]^-$. However, for the corresponding Fe complexes it is known that there is little effect on the g tensor components when replacing one ore two bpy ligands by pairs of CN^- ligands [51]. Therefore, it seemed reasonable that the values $g_{\parallel} = 1.18$, $g_{\perp} = 2.65$ for $\mathrm{Ru(bpy)_3}^{3+}$ could be used for the two mixed ligand complexes, too.

Values of the kinetic parameters k_{ce}, k_{bet} and τ_S obtained by the described fitting procedure are listed in Table 1. For $[\mathrm{Ru(bpy)_3}]^{2+}$ and $[\mathrm{Ru(bpy)_2(CN)_2}]$ the parameter sets correspond to well defined global minima of the fitting procedure. However, no unique fits were obtained for the tetracyano complex because of the small MFEs and the weak curvature. Hence in this case, instead of the automatic three-parameter fitting routine, a corresponding two-parameter optimization was performed keeping τ_S constant. The procedure was repeated with stepwise changes of τ_S in the range between 4 and 20 ps. The variations of the optimized fit parameters k_{ce} and k_{bet} as a function of τ_S are illustrated in Fig. 4. The values of k_{bet} and k_{ce} entered in Table 1 correspond to a τ_S value chosen by an educated guess based on the following observations. When replacing the first bpy ligand by two CN^- ligands, the τ_S value is decreased by approximately 6 ps (average of the three solvents). This observation is in line with the same trend in the series $[\mathrm{Fe(bpy)}_{3-n}(\mathrm{CN})_{2n}]^{3-2n}$ [52], where it is seen to hold true also for the replacement of the second bpy ligand by two CN^- groups. Thus it seemed reasonable to apply the same principle to the analogous series of Ru complexes and to assume that τ_S decreases by another 6 ps from $\mathrm{Ru(bpy)_2(CN)_2}^+$ to $\mathrm{Ru(bpy)(CN)_4}^-$.

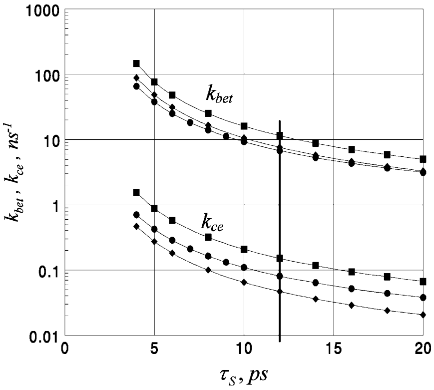

Fig. 4. Sets of parameters k_{bet} and k_{ce} that for a given τ_S, produce equally acceptable fits of the magnetic field dependent cage escape efficiency η_{ce} for the photoreaction of complex $[\mathrm{Ru(bpy)(CN)_4}]^{2-}$ with MV^{2+}. The upper set of curves refers to k_{bet}, the lower set to k_{ce}. (■) in MeOH, (●) in H_2O, (◆) in D_2O. The vertical bar marks the values adopted for Table 1.

4. Discussion

4.1. Electron transfer quenching

In the presence of electron acceptors such as MV^{2+}, an electron is transferred from the ^{3}MLCT state of the complex to the quencher. The first step of this process is the diffusional formation of a precursor complex followed by the diffusional breakup of the complex in competition with the electron transfer step generating a radical pair consisting of ^{2}Ru(III) and $^2\mathrm{MV}^{2+}$ constituents.

$$^{*3}\mathrm{Ru(II)} + {}^1\,\mathrm{MV}^{2+} \underset{k_{-d}}{\overset{k_d}{\rightleftarrows}} \{^{*3}\mathrm{Ru(II)} \cdots {}^1\,\mathrm{MV}^{2+}\} \qquad (9)$$

(diffusional processes)

$$\{^{*3}\mathrm{Ru(II)} \cdots {}^1\,\mathrm{MV}^{2+}\} \xrightarrow{k_{\mathrm{fet}}} 3\{^2\mathrm{Ru(II)} \cdots {}^1\,\mathrm{MV}^{-\bullet}\} \qquad (10)$$

(forward electron transfer)

The steady state treatment of reactions (9) and (10) yields

$$k_q = k_d k_{\mathrm{fet}}/(k_{-d} + k_{\mathrm{fet}}). \qquad (11)$$

The rate constant of diffusion-controlled reaction k_d can be calculated from the Debye–Smoluchowski equation (Eq. (12)) [53,54] and k_{-d} can be estimated by the Eigen equation (Eq. (13)) [55]:

$$k_d = \frac{2kTN}{3\eta}\left(\frac{1}{r_a} + \frac{1}{r_b}\right) \frac{1}{\int_a^{\infty} r^{-2} \exp[w(r,\ \mu)/kT]\,\mathrm{d}r} \qquad (12)$$

$$k_{-d} = \frac{kT}{2\pi\eta a^2}\left(\frac{1}{r_a} + \frac{1}{r_b}\right) \frac{\exp[w(a,\ \mu)/kT]}{a\int_a^{\infty} r^{-2} \exp[w(r,\ \mu)/kT]\,\mathrm{d}r} \qquad (13)$$

Here, k is Boltzmann's constant, N is Avogadro's number, η is the viscosity of the solution, and r_a and

r_b are the radii of the reactants; $a = r_a + r_b$. The terms $w(\mu, r)$ and β are given by Eqs. (14) and (15):

$$w(\mu,\ r) = \frac{z_a z_b e^2}{\varepsilon r}\ \exp(-\beta r\sqrt{\mu}), \tag{14}$$

$$\beta = \left(\frac{8\pi N e^2}{\varepsilon k T}\right)^{1/2}, \tag{15}$$

where z_a and z_b are the ionic charges of the reactants, ε is the static dielectric constant of the solution, e is the electron charge and μ is the ionic strength of the solution. Note that in Eqs. (12)–(15) all quantities are in cgs units.

In Table 2, the observed values of k_q are compared with the theoretical values of k_d. In its trend, the increase of k_d in the series Ru(bpy)$_3^{2+}$ to Ru(bpy)(CN)$_4^{2-}$, which is most pronounced in methanol, reflects the change of charge in this series of complexes. Furthermore, the effect of solvent viscosity, which is decreasing from D_2O trough H_2O to methanol [56,57], is borne out in these values. The observed k_q values are not much less than the diffusion-controlled values. However, the difference is sufficient to evaluate a meaningful value of k_{fet}, the first-order rate constant of forward electron transfer in the encounter pair. In H_2O and D_2O these values show a general tendency to increase with the number of CN$^-$ ligands, which parallels the trend in the increasing driving force ($-\Delta G^\circ_{fet}$, cf. Table 1). In methanol, the middle one of the k_{fet} values is the highest, although the difference between the values of the three complexes is rather small.

Table 2
Rate constants of diffusional electron transfer components estimated by Debye–Smoluchovski and Eigen equations using the measured quenching rate constants at room temperature in solutions of 0.1 M ionic strength [a]

	Ru(bpy)$_3^{2+}$ [b]	Ru(bpy)$_2$(CN)$_2$ [c]	Ru(bpy)(CN)$_4^{2-}$ [d]
In H_2O, ionic strength adjusted with $NaNO_3$			
$k_q \times 10^{-9}$ (M^{-1} s^{-1})	1.13	3.70	7.00
$k_d \times 10^{-9}$ (M^{-1} s^{-1})	5.51	7.29	9.69
$k_{-d} \times 10^{-9}$ (s^{-1})	5.31	3.22	1.55
$k_{fet} \times 10^{-9}$ (s^{-1})	1.32	3.01	4.03
In D_2O, ionic strength adjusted with $NaNO_3$			
$k_q \times 10^{-9}$ (M^{-1} s^{-1})	1.04	3.50	6.20
$k_d \times 10^{-9}$ (M^{-1} s^{-1})	4.34	5.74	7.63
$k_{-d} \times 10^{-9}$ (s^{-1})	4.04	2.57	1.22
$k_{fet} \times 10^{-9}$ (s^{-1})	1.27	2.83	5.28
In MeOH, ionic strength adjusted with $NaNO_3$			
$k_q \times 10^{-9}$ (M^{-1} s^{-1})	1.22	4.15	9.40
$k_d \times 10^{-9}$ (M^{-1} s^{-1})	8.63	12.2	16.8
$k_{-d} \times 10^{-9}$ (s^{-1})	11.1	5.47	1.50
$k_{fet} \times 10^{-9}$ (s^{-1})	1.83	3.36	1.91

[a] The following values of dielectric constant and viscosity at 20 °C were used: 80.1 [56a], 1.00 cP [56b] (H_2O); 79.75 [56a], 1.24 [57] (D_2O); 32.62 [56c], 0.597 [56d] (MeOH).

[b] The radii of Ru(bpy)$_3^{2+}$ and MV^{2+} were estimated to be 700 and 330 pm.

[c] The radius of Ru(bpy)$_2$(CN)$_2$ was estimated to be 630 pm.

[d] The radius of Ru(bpy)(CN)$_4^{2-}$ was estimated to be 560 pm.

The k_{fet} values may be discussed in the framework of the semiclassical Marcus theory of non-adiabatic electron transfer, according to which they should be given by

$$k_{fet} = (4\pi^2 V^2/[h(4\pi\lambda RT)^{1/2}]\exp(-\Delta G^{\neq}/RT) \tag{16}$$

Here V is the electronic coupling coefficient, λ is the reorganization energy and $\Delta G^{\neq}$ is the free energy of activation of the electron transfer [58], for which the relation

$$\Delta G^{\neq} = \lambda/4(1 + \Delta G^\circ_{fet}/\lambda)^2 \tag{17}$$

is expected to hold. The reorganization energy λ is a sum of the solvent reorganization energy λ_{out} and the intramolecular reorganization energy λ_{in}. For λ_{out} the following equation is generally used:

$$\lambda_{out} = e_0^2\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r_{12}}\right)\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right) \tag{18}$$

with a_1 and a_2, the radii of the two reactants; r_{12}, the reaction distance; and ε_{op}, the dielectric constant in the optical frequency range (which equals the square of the refraction index). For λ_{out} a value close to 1.0 eV is obtained for all reaction systems and solvents investigated. For Ru(bpy)$_3^{2+}$/MV^{++} a reasonable order of magnitude for λ_{in} is 0.3–0.5 eV [42]. Assuming the electronic coupling V equal for the three complexes, Eq. (15) yields a ratio of 1:81:500 ($\lambda = 1.5$ eV) or 1:46:150 ($\lambda = 1.3$ eV) in the series Ru(bpy)$_3^{2+}$ to Ru(bpy)(CN)$_4^{2-}$, whereas the experimental values are approximately in a ratio of 1:3.3:7. Thus, the trend in k_{fet} cannot be understood in terms of a change of the free energy of activation alone. It appears as if a trend of decreasing V counterbalances the trend of increasing driving force of the electron transfer as the number of CN$^-$ ligands is increased. A rationale of this hypothesis may be that the photoelectron has to be donated from a bpy$^-$ ligand created in the MLCT excitation of the complex. The statistical factors of 3:2:1 are, however, not sufficient to account for the deviation of the observed ratios from the ratios predicted by the free energy term of the Marcus expression. The argument of a reduction of V by reducing the number of byp ligands might be enhanced by postulating that the MV^{2+} ions have a strong tendency to associate with that side of the complex where the CN^- groups are located.

4.2. Cage escape

As described in Section 3, k_{ce} like k_{bet} and τ_S has been evaluated from the analysis of the magnetic field dependence of η_{ce}. No assumption regarding the suitability of the Eigen–Debye equation (Eq. (13)) that follows from the model of unhindered diffusion, has been made to predict k_{ce}. Thus it is of interest to compare the magnetic-field-effect derived k_{ce} values with the diffusion-controlled ones (cf. $k_{ce,diff}$ in Table 1). For $Ru(bpy)_3{}^{2+}$ the k_{ce} values reproduce the solvent viscosity dependence predicted for $k_{ce,diff}$ by the Eigen–Debye equation. However, the absolute values are only about 1/3 of the $k_{ce,diff}$ values. Such behavior has been also observed for the temperature dependence of k_{ce} with this complex in water [50]. As was pointed out in that reference, the factor 3 of deviation from the result according to the Eigen–Debye equation should not be taken too dogmatic because there is some arbitrariness, in principle, in assigning a first-order rate constant to the diffusional separation process of a pair of reactants. Indeed, alternative theoretical results have been presented in the literature that differ from the Eigen–Debye result by a factor of 2–3 [59,60,50]. Hence we do not hesitate to take the k_{ce} results for the $[Ru(bpy)_3]^{3+}/MV^{+\bullet}$ pairs as indicating diffusion-controlled separation. The same is definitely not true, however, for the RIPs with the cyano complexes. Even if we allow for the factor of 3 the Eigen–Debye equation might overestimate $k_{ce,diff}$, the dissociation is 3–6 times slower than diffusion-controlled for the RIP derived from the $[Ru(bpy)_2(CN)_2]$ complex and 10–20 times slower for that from the $[Ru(bpy)(CN)_4]^{2-}$ complex. These observations bear evidence of some attractive interaction in the RIPs between $MV^{+\bullet}$ and the mixed bpy/cyano Ru(III) complexes that may be due to a specific ion pairing effect (note that the net Coulomb interaction is included in the calculation of $k_{ce,diff}$). While, at present, it is difficult to characterize this specific interaction more precisely, we note that the free energy ΔG of this specific interaction, if assessed by the factor $\exp(-\Delta G/RT)$, is only on the order of 3–5 kJ mol^{-1}, i.e. 1–2 times kT.

4.3. Spin relaxation and backward electron transfer within the cage

Since the geminate backward electron transfer can only take place after the spin conversion of the RIP from triplet to singlet, the latter process may become rate determining for the whole process [50] and therefore is of significant kinetic interest. A trend of decreasing τ_S (i.e. increasing k_{TS}) was noted for the replacement of each bpy ligand by two CN^- ligands. This followed directly from the analysis of the MFE for the shift from $[Ru(bpy)_3]^{3+}$ to $[Ru(bpy)_2(CN)_2]^+$ and (by reference to the case of the analogous Fe complexes) was further extrapolated to the shift from $[Ru(bpy)_2(CN)_2]^+$ to $[Ru(bpy)(CN)_4]^-$. The experimental and theoretical study of the Fe(III) complexes provided some clues for understanding such a behavior [52] and the same reasoning can be applied to the Ru(III) complexes. The three lowest Kramers' doublets of such complexes with nearly octahedral coordination are derived from d^5 configurations of the three t_{2g} orbitals that are weakly split by the trigonal distortion of the ligand positions from ideal octahedral symmetry. From the analysis of the (slight) variation of the g tensor components with $n = 1$, 2, 3 in the series of complexes $[Fe(bpy)_n(CN)_{6-2n}]^{2n-3}$ it could be deduced that the energetic separation of the two lowest Kramers' doublets decreases as the number of CN^- ligands increases. Independent evidence of this behavior resulted from an observed trend in the activation energies of spin relaxation that parallels the trend of the lowest electronic excitation energy inferred from the g tensor analysis. The observed temperature dependence provides strong evidence that spin relaxation in these complexes is brought about by an Orbach mechanism [35b,61] wherein thermal excitation of the lowest excited electronic state is involved. By using calculations with the angular overlap model (AOM [62]) it could be shown that the influence of the geometric changes (the angle between the central metal atom and two CN^- ligands is closer to the octahedral angle of 90° than that between the central atom and the two nitrogen atoms of a bpy ligand; therefore the trigonal splitting is smaller in the complexes with CN^- ligands) dominates over the change in the ligand field parameters (CN^- is a stronger σ-donor and π-acceptor than the bpy nitrogen, which would tend to increase any ligand field splitting).

The values determined for k_{bet} follow the trend in the thermodynamic driving force $-\Delta G_{bet}$, i.e. they decrease from $[Ru(bpy)_3]^{2+}$ to $[Ru(bpy)_2(CN)_2]$, their ratios corresponding to approximately 10:4:1. Qualitatively, the observed ΔG dependence is a behavior typical for the normal Marcus region. From this observation one may infer that the reorganization energy $\lambda \lesssim 1.6$ eV. The solvent effect on k_{bet} is not very large as might have been anticipated from a calculation of λ_s by Eq. (18). Calculating the ratio of the theoretical values of k_{bet} according to Eq. (16) and assuming the coupling energy V to be constant, the result for the ratios of rate constants is 2.7:1.7:1, i.e. a somewhat weaker variation than evaluated from the experiments. To account for the difference one would, again, have to assume that the trend in V has a complementary effect to that of the ΔG dependent factor, i.e. it increases from $[Ru(bpy)_3]^{2+}$ to $[Ru(bpy)(CN)_4]^{2-}$. This conclusion is opposite to what has been discussed in relation with the ligand dependent trend in k_{fet}. However, one has to be aware of the fact that forward and backward transfer involve different orbitals in the complex: in the forward reaction the electron is transferred between the π* orbital of a bpy ligand to a π* orbital of MV^{2+}, whereas in the backward reaction the electron returns to a d-orbital of the central Ru ion. It has been suggested above that in the forward electron transfer V decreases because the MV^{2+} acceptor might be preferentially associated with the CN^- site of the complex. It does not seem implausible that the return of the electron from $MV^{+\bullet}$ to the Ru(III) centre is more favorable with the $MV^{+\bullet}$ moiety near the CN^- sites because of better overlap between donor and (Ru-localized) acceptor orbital.

5. Conclusions

The spin chemical analysis of the cage escape efficiency and its dependence on magnetic field strengths has revealed that each replacement of one bpy with two cyanides results in considerable decrease in the rate coefficient of cage escape, a moderate decrease of k_{bet} and an increase of the spin relaxation rate of geminate radical pair. It has been demonstrated that the magnetic field modulation of the photo induced electron transfer from Ru(II) complexes to MV^{2+} is a very useful technique for analyzing and understanding the intrinsic nature of the processes in the geminate radical ion pair, which is strongly influenced by the properties of the ligands coordinated to the Ru(II) center.

6. Supplementary material

The material is available from the authors on request.

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