Aspects of Ligand and Electron-Acceptor Dependence of Magnetic Field Effects on Net Electron Transfer Efficiencies in Photooxidation of Ru(II)-trisbipyridyl Type Complexes

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The heteroleptic series of $\text{Ru}(\text{bpy})_n(\text{dce})_3^{2+}$, with $\text{bpy} = 2,2'$ -bipyridine, and $\text{dce} = 4,4'$ -diethoxycarbonyl-2,2'-bipyridine, has been investigated for the kinetic parameters of photo electron transfer, and for the magnetic field dependence of the net electron transfer efficiency (η_{ce}) in photooxidations with methylviologen and propylviologen sulfonate (the latter only in the case $n = 3$) using ns-laser-flash spectroscopy and stationary illumination methods. Whereas the electric charge of the electron acceptor had no influence on the magnetic field effect on η_{ce} , the variation of ligands was found to result in a strictly linear (with n) increase of the magnetic field effect on k_{bet} , the effective rate constant of backward electron transfer in the primary redox pair. The physical implications of these observations with respect to a previously developed magnetokinetic model are discussed.

Die heteroleptische Reihe der Komplexe $\text{Ru}(\text{bpy})_n(\text{dce})_3^{2+}$ mit $\text{bpy} = 2,2'$ -bipyridin, und $\text{dce} = 4,4'$ -diethoxycarbonyl-2,2'-bipyridin, wurde im Hinblick auf die kinetischen Parameter der photochemischen Elektronenübertragung und auf die Magnetfeldabhängigkeit der Nettoausbeute der Elektronenübertragung (η_{ce}) für die Photoreaktion mit Methylviologen und Propylviologensulfonat (letzteres nur für $n = 3$) mittels ns-Laserblitzspektroskopie und kontinuierlicher Belichtungsmethoden untersucht. Während die Ladung des Elektronenakzeptors keinen Einfluß auf den Magnetfeldeffekt auf η_{ce} hatte, bewirkte die Variation der Liganden eine streng lineare Zunahme (bezüglich n) des Magnetfeldeffektes auf k_{bet} , die effektive Geschwindigkeitskonstante der Elektronen-Rückübertragung im primären Redox-Paar. Die physikalische Bedeutung dieser Beobachtungen wird im Rahmen eines kürzlich entwickelten magnetokineticen Modells diskutiert.

1. Introduction

The field of magnetokinetics, dealing with external and internal magnetic field effects (MFEs) on the kinetics of chemical reactions, has received

growing interest in recent years [1–3]. Magnetokinetic effects, such as CIDNP, CIDEF, RYDMR, MARY, can provide powerful methods for gaining information on reaction mechanisms as a whole (only reactions in which unpaired electron spins are involved show the mentioned effects) as well as for the evaluation of rate constants of processes that cannot be observed directly, e.g. because they are too fast for usual detection methods.

A particularly interesting field of magnetokinetic applications are photoinduced electron transfer reactions. Usually there are several reaction channels available for the decay of a primary photochemical electron transfer product, one of them being fast backward electron transfer to the singlet ground state educts, a process that is spin-forbidden if the forward reaction occurs between a triplet excited donor or acceptor and a diamagnetic substrate.

The magnetokinetic effects that will be dealt with in this paper involve spin-orbit coupling (SOC) as the mechanism that is responsible for, in our case, triplet to singlet transitions in the primary redox pair of photochemically generated Ru(III)-trisbipyridyl type complexes and methylviologen radicals ($MV^{\cdot+}$), systems well known from model studies of photochemical water cleavage [4–9].

The reaction mechanism for oxidative quenching of Ru(II) complexes is represented in Scheme 1. The excited $\text{Ru}(\text{bpy})_3^{2+}$ (or derivative) complex undergoes fast intersystem crossing (ISC) into the lowest excited triplet state that is quenched by MV^{2+} (or derivative) with the rate constant k_q , yielding the primary redox pair ${}^3[{}^2\text{Ru}(\text{bpy})_3]^{3+} \dots {}^2\text{MV}^{\cdot+}$ furtheron denoted RP. This pair can escape from the solvent cage (rate constant k_{ce}) to form free radicals, or can undergo backward electron transfer (k_{bet}) to the ground state educts, the latter reaction being, in principle, spin-forbidden.

Due to the strong SOC at the Ru center neither the excited triplet charge transfer state nor the RP (both with d^5 configuration at the Ru-center) are of pure triplet character, a fact that is indicated by the symbol $3'$. The singlet contamination and a pronounced SOC-induced spin relaxation process providing triplet $\rightarrow$ singlet transitions are responsible for quite efficient backward electron transfer in the RP, lowering the efficiency of net electron transfer η_{ce} (to be consistent with the literature, the subscript 'ce' will be used, denoting this quantity as an efficiency of cage escape from the primary

RP through which all the quenching reaction is assumed to proceed) to about 25% in the case of the $\text{Ru}(\text{bpy})_3^{2+}/\text{MV}^{2+}$ system.

As we reported previously [10] application of an external magnetic field decreases the yield of free radicals, but not the values of k_o (for the monomolecular deactivation process) and k_q , from which one has to conclude that it is η_{ce} that is decreased, and the MFE must be clearly due to changes in the spin and reaction dynamics of the primary RP. According to the sign of the MFE, the effective rate of backward electron transfer ($\bar{k}_{bet}$) must be concluded to increase in a magnetic field. For a detailed theoretical treatment of the mechanisms of spin relaxation and MFE the reader is referred to the paper by Steiner and Bürßner in this issue [11].

Here we will report some experimental results which characterize the way how chemical modifications of the species constituting the RP influence η_{ce} and its magnetic field dependence. These experiments have been carried out as part of a program set up to provide a broad empirical basis for this novel magnetokinetic situation, involving strongly SOC coupled transition metal complexes.

bpy

MV^{2+}

dce

PVS

In the series of complexes investigated the bpy ligands of the Ru complex were replaced in a stepwise fashion by 4,4'-diethoxycarbonyl substituted bpy (dce), affording the complete series $\text{Ru}(\text{bpy})_n(\text{dce})_{3-n}^{2+}$, with $n = 0-3$. On the acceptor side methylviologen (MV^{2+}) has been used in general. In the reaction with the parent $\text{Ru}(\text{bpy})_3^{2+}$ complex propylviologen sulfonate (PVS) has been also used, in order to study the effect of charge variation.

Although the present results have not yet been fully rationalized on the basis of our mechanistic model [11], they are remarkable in that they exhibit some regular empirical features of the chemical structure dependence of the magnetokinetic effect very clearly.

2. Experimental

4,4'-diethoxycarbonyl-2,2'-bipyridine (dce) was prepared in a 3-step synthesis: the 4,4'-dimethyl-2,2'-bipyridine according to Spritschnik *et al.* [12], the oxidation to the

dicarboxylic acid according to Elliott *et al.* [13], and the esterification according to Sprintschnik *et al.* [12]. The product was recrystallized from ethylacetate.

The homoleptic Ru complexes $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ and $\text{Ru}(\text{dce})_3(\text{PF}_6)_2$ were synthesized following a procedure by G. Furrer [14]. 2,2'-bipyridine (bpy) was purchased from Fluka (> 98%). The heteroleptic complexes $\text{Ru}(\text{bpy})_2(\text{dce})(\text{PF}_6)_2$ and $\text{Ru}(\text{bpy})(\text{dce})_2(\text{PF}_6)_2$ were prepared according to Ref. [12] via $\text{Ru}(\text{bpy})_2\text{Cl}_2$ and $\text{Ru}(\text{dce})_2\text{Cl}_2$, respectively. Propylviologen sulfonate (PVS) was obtained following the procedure of Nagamura *et al.* [15]. The compounds were characterized by elemental analysis, UV/VIS and NMR spectroscopy.

Methylviologen dichloride trihydrate (MV^{2+}) was purchased from Aldrich and used without further purification, but the purity was checked by elemental analysis and UV spectroscopy. The disodium salt of ethylene-diamine tetraacetic acid (EDTA, dihydrate, Merck, p.a.) was recrystallized from methanol/water as described by Blaedel *et al.* [16].

All measurements were carried out in water (distilled)/acetonitrile (Merck, p.a.) 1/1 (v/v) at room temperature; the solutions were deaerated by purging with solvent saturated supra pure N_2 . The concentration of the Ru complexes was 2×10^{-5} or 4×10^{-5} M, of the acceptor 5×10^{-3} to 0.1 M, depending on the k_q value. The ionic strength, μ , of the solutions was adjusted to 0.2 M by adding suitable amounts of NaCl, except in the case of $\text{Ru}(\text{dce})_3^{2+}$ where μ was 0.3 M, because of the high MV^{2+} concentration required.

For time-resolved experiments (determination of k_o , k_q , η_{ce} , MFE on η_{ce}) the ns-laser-flash equipment described in Ref. [17] has been used. With Coumarin 2 as laser dye the Ru complexes were excited at 455 nm.

The efficiency of net electron transfer, η_{ce} , was determined by the saturation method, detecting the generated MV^+ absorption at 600 nm as a function of the laser energy and extrapolating to saturation ($\Delta A_{\text{saturation}}^{600}$) [18].

$$\eta_{ce} = \frac{\Delta A_{\text{saturation}}^{600}}{\eta_q \times [\text{Ru(II)}]_0 \times \epsilon_{\text{MV}^+}^{600}} \quad (1)$$

The value of η_{ce} was obtained according to Eq. (1) with η_q the quenching efficiency, $k_q[\text{Q}]/(k_o + k_q[\text{Q}])$, $[\text{Ru(II)}]_0$ the total concentration of the Ru complex, and $\epsilon_{\text{MV}^+}^{600} = 12000 \text{ M}^{-1} \text{ cm}^{-1}$.

Magnetic fields up to 3.2 T were generated using a Bruker B-E15 magnet. The relative MFE on η_{ce} , $R_{\eta_{ce}}(B)$, defined as

$$R_{\eta_{ce}}(B) = \frac{\Delta A(B) - \Delta A(B=0 \text{ T})}{\Delta A(B=0 \text{ T})} \quad (2)$$

was measured at 600 and 395 nm, the two absorption maxima of the MV^+ (and PVS^-) radicals.

To measure $R_{\eta_{ce}}$ most accurately, especially at fields below 1 T, the continuous flow technique as described in Refs. [10, 19] was applied. In these experiments EDTA (1×10^{-2} M) was added as a sacrificial electron donor to reduce Ru(III) to Ru(II) , thus preventing the free acceptor radicals from recombination with the Ru(III) complex, and allowing for their detection by stationary absorption measurements. By adding suitable amounts of NaOH the pH of these EDTA containing solutions was adjusted to 6.2; at this pH EDTA acts as convenient buffer substance.

3. Results and discussion

The kinetic parameters determined for the systems investigated are listed in Table 1.

Table 1. Kinetic parameters of photo electron transfer and relative magnetic field effect, $R_{\eta_{ce}}$, on cage escape efficiency, η_{ce} , for $\text{Ru}(\text{bpy})_3^{2+}/\text{PVS}$ and $\text{Ru}(\text{bpy})_n(\text{dce})_3^{2+}/\text{MV}^{2+}$.

Type of complex n	Acceptor	λ_{em}^{max} , nm	$k_o \times 10^{-6}$, s^{-1}	$k_q \times 10^{-7}$, $M^{-1} s^{-1}$	ΔG_{et}^a , eV	η_{ce} ($B = 0\text{ T}$)	$R_{\eta_{ce}}$ % ($B = 3.2\text{ T}$)
3	PVS	610	1.21	85.0	-0.37 ^b	0.09	-22.5
3	MV^{2+}	610	1.21	73.6	-0.33 ^c	0.19	-22.8
2	MV^{2+}	660	1.86	3.5	-0.04 ^d	0.12	-18.9
1	MV^{2+}	680	1.05	1.4	^e	0.18	-13.4
0	MV^{2+}	640	0.66	0.5	+0.06 ^f	0.31	-5.9

^a The ΔG_{et} values are calculated from the redox potentials of the ground state reactants (in CH_3CN , unless otherwise denoted) and the luminescence maximum of the respective Ru complex [in $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ 1/1 (v/v) at room temperature]

^b in H_2O , using data from Refs. [20, 21]

^c in CH_3CN and H_2O , using data from Refs. [7, 22], and Refs. [20, 21], respectively

^d using data from Refs. [7, 13]

^e not available

^f using data from Refs. [7, 22].

Fig. 1. Magnetic field effect on radical yield in the quenching of photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ by MV^{2+} . The transient absorption signals were observed at 395 nm. Magnetic fields (from top to bottom): 0, 0.5, 1, 1.5, 2, 2.5, 3.2 T.

Figure 1 gives a demonstration of the MFE as measured by ns-laser-flash spectroscopy. At the observation wavelength of 395 nm there is a strong absorption maximum of the MV^+ radical, but there is also some excited state absorption of the photoreactive $\text{Ru}(\text{II})$ complex produced by the laser pulse. Thus we see a fast rise of the absorption during the laser

Fig. 2. Magnetic field dependence of cage escape efficiency in the series $\text{Ru}(\text{bpy})_n(\text{dce})_3^{3+}/\text{MV}^+$ ($\bullet$ $n=0$, $\blacksquare$ $n=1$, $\square$ $n=2$, $\circ$ $n=3$), and for $\text{Ru}(\text{bpy})_3^{3+}/\text{PVS}^-$ (Δ). The curves shown are drawn to aid the viewer.

pulse of about 30 ns, corresponding to the population of the photoreactive state and, subsequently, a slower grow-in of the radical absorption as a consequence of the electron transfer reaction, reaching a plateau on the ns time scale, but decaying on the μs time scale due to the second order recombination process between the $\text{Ru}(\text{III})$ complex and the MV^{2+} radical. The grow-in time constant depends on the MV^{2+} concentration and matches the luminescence decay constant of the $\text{Ru}(\text{II})$ complex exactly.

The Figure shows that the plateau of radical absorption is lowered by a magnetic field, but the fields to be applied must be fairly strong. We have made sure that neither the lifetime of the excited complex nor the quenching rate constant show a significant magnetic field dependence ($< \pm 1\%$). Thus it has been established that the MFE observed is due to changes in η_{ce} , and that its explanation must be sought in terms of the magnetokinetics of the RP.

The magnetic field dependence of η_{ce} is shown in Fig. 2. All curves have the same characteristics: the MFEs show their steepest increase between 0.4 and 1 T. The slope of the curves decreases at higher fields, but at 3.2 T the effect is still far away from saturation. The amplitude of the MFE is highest for the $\text{Ru}(\text{bpy})_3^{3+}$ complex ($n=3$) and decreases in rather regular steps as bpy is replaced by dce.

Table 2. Kinetic parameters of in-cage backward electron transfer for $\text{Ru}(\text{bpy})_3^{3+}/\text{PVS}^-$ and $\text{Ru}(\text{bpy})_n(\text{dce})_3^{3-n}/\text{MV}^{2+}$.

Type of complex n	Acceptor	$k_{\text{ce}} \times 10^{-9},^{\text{a}}$ s^{-1}	$\bar{k}_{\text{bet}} \times 10^{-10},^{\text{b}}$ s^{-1} ($B = 0 \text{ T}$)	$\Delta G_{\text{bet}},^{\text{c}}$ eV	$R_{\bar{k}_{\text{bet}}},$ % ($B = 3.2 \text{ T}$)
3	PVS	2.11	2.13	-1.66 ^d	+31.5
3	MV^{2+}	5	2.13	-1.70 ^e	+36.2
2	MV^{2+}	5	3.67	-1.84	+26.7
1	MV^{2+}	5	2.28	^f	+18.9
0	MV^{2+}	5	1.11	-2.00	+9.0

^a calculated from the Debye-Eigen equation (except for PVS, cf. text)^b effective rate constant of in-cage backward electron transfer, calculated according to Eq. (4)^c calculated from the redox potentials of the ground state reactants (in CH_3CN , unless otherwise denoted) from the Refs. cited in Table 1^d in H_2O ^e in CH_3CN and H_2O ^f not available.

When PVS is used as electron acceptor (so far we have only investigated its reaction with the parent $\text{Ru}(\text{bpy})_3^{2+}$ complex), the magnetic field dependence is the same as with MV^{2+} within the accuracy of the experiment.

There is only a slight increase in the quenching rate constant when the electron acceptor MV^{2+} is replaced by the (overall uncharged) acceptor PVS. Since the ΔG_{et} values of the forward electron transfer are almost the same (cf. Table 1), this indicates that at an ionic strength of 0.2 M there is not much electrostatic repulsion between the two doubly charged species $\text{Ru}(\text{bpy})_3^{2+}$ and MV^{2+} , because the formally neutral species PVS does not react much faster. On the other hand, the net electron transfer with PVS is only about half as efficient as in the MV^{2+} case. This is plausible, because with PVS there is a Coulombic attraction in the RP between $\text{Ru}(\text{bpy})_3^{3+}$ and PVS^- radical ion, causing a reduction of the rate and efficiency of cage escape.

Examining the data in Table 1 we note that in the series of complexes $\text{Ru}(\text{bpy})_n(\text{dce})_3^{2-n}$ the k_0 values differ by more than a factor of 2, but the change is not monotonic. The k_q values do decrease monotonically, but there is a dramatic fall from $n = 3$ to $n = 2$, and only a rather moderate one for $n < 2$. This is in correspondence with the change in ΔG_{et} , the thermodynamic driving force of the forward electron transfer.

The efficiency of net electron transfer (η_{ce}) is not independent of n , but its change is neither a dramatic nor a systematic one. It does not exhibit a correlation with ΔG_{bet} , the driving force of the backward electron transfer reaction (cf. Table 2).

Fig. 3. Relative magnetic field effect ($B = 3.2$ T) on the cage escape efficiency ($R_{\eta_{ce}}$, ○, left hand scale) and on the effective rate constant of backward electron transfer ($R_{k_{bet}}$, ■, right hand scale) as a function of the number of bpy ligands n in the primary redox pairs $\text{Ru}(\text{bpy})_n(\text{dce})_3^{3+}/\text{MV}^+$.

There is a pronounced decrease (by about a factor of 4) of $R_{\eta_{ce}}$ (3.2 T) with decreasing n . Really surprising, because all the other parameters listed in Table 1 do not at all exhibit such a regular variation, is the observation of a close to linear correlation between $R_{\eta_{ce}}$ and n (cf. Fig. 3). From a phenomenological point of view each type of ligands seems to have its specific increment contributing to the overall MFE on η_{ce} , but it is clear that a mechanistic explanation must be sought in terms of the RP-dynamics which obviously involves a magnetokinetic feature that is quite regularly affected by the ligand variation.

Since η_{ce} is not a basic quantity of the RP decay mechanism, it will be sensible to analyze the MFE on the level of more elementary quantities, as are the rate constants of cage escape k_{ce} and an effective rate constant $\bar{k}_{bet}$ of backward electron transfer, the latter being defined through Eq. (3):

$$\eta_{ce} = \frac{k_{ce}}{k_{ce} + \bar{k}_{bet}} \quad (3)$$

leading to

$$\frac{\bar{k}_{bet}}{k_{ce}} = \frac{1}{\eta_{ce}} - 1. \quad (4)$$

Since $\bar{k}_{\text{bet}}$ refers to an overall spin-forbidden process, involving the change of multiplicity as an implicit step, it should exhibit a MFE in a more directly explicable way than η_{ce} . Relative values of $\bar{k}_{\text{bet}}$ for the various RPs can be obtained from η_{ce} according to Eq. (4), if the constancy of k_{ce} may be assumed. We think that such an assumption is reasonable for the RPs involving MV^+ as the common acceptor radical.

Adopting a value of $k_{\text{ce}} = 5 \times 10^9 \text{ s}^{-1}$, following from the application of the Debye-Eigen equation to diffusion controlled dissociation of a pair of charged particles [23], the values of $\bar{k}_{\text{bet}}$ listed in Table 2 are obtained from η_{ce} . Correspondingly, with the reasonable assumption that k_{ce} is independent of a magnetic field, the relative MFE on η_{ce} ($R_{\eta_{\text{ce}}}$) may be converted into the relative MFE on $\bar{k}_{\text{bet}}$ ($R_{\bar{k}_{\text{bet}}}$). These values are also listed in Table 2.

As demonstrated in Fig. 3 the effect of transforming $R_{\eta_{\text{ce}}}$ to $R_{\bar{k}_{\text{bet}}}$ is gratifying because in the latter representation the MFE exhibits an almost perfectly linear dependence on the number n of bpy (or dce) ligands. We take this as convincing evidence (i) that the assumption of a constant k_{ce} , leading to these $\bar{k}_{\text{bet}}$ values, is well founded and (ii) that $\bar{k}_{\text{bet}}$ is in fact a most suitable parameter for a further analysis of the MFE.

The absolute values of $\bar{k}_{\text{bet}}$ exhibit a non-monotonic dependence on the number of bpy ligands, whereas the change in the thermodynamic driving force ΔG_{bet} is probably monotonic (the value for $n = 1$ is not yet available). A possible explanation of this relation would be that the change of systems scans just the top of the $\lg(k_{\text{bet}})$ vs. ΔG_{bet} Marcus parabola that has been confirmed experimentally in a number of recent publications [24, 25].

In discussing the dependence of $\bar{k}_{\text{bet}}$ on chemical changes of the RP, this parameter should be quantitatively related to the parameters of the explicit model suggested for the mechanism of backward electron transfer in Ref. [11]. Here we will confine ourselves to some qualitative arguments.

The parameters of the model are: k_{bet} , the rate constant of hypothetically spin-allowed backward electron transfer, P_i ($i = T'_{\pm}, T'_o, S'$), the initial populations of the spin substates of the RP (where S' is predominant singlet, $T'_{\pm}$ are appreciably singlet contaminated triplets, and T'_o is pure triplet), $\Delta g = g_{\text{Ru}} - g_{\text{free el.}}$, the deviation of the g tensor of the Ru complex from that of a free electron, and D_r , a parameter determining an effective rate constant for establishing equilibrium between the T' group of RP substates and the S' substate.

From model calculations it follows that the absolute value of $\bar{k}_{\text{bet}}$ is mainly determined by k_{bet} and the singlet character s of the RP at the instant of its creation. The MFE $R_{\bar{k}_{\text{bet}}}$ strongly depends on the initial singlet character s (decrease with increasing s), on the value of Δg , and on D_r (decrease with increasing D_r).

In the explanation given above the variation of $\bar{k}_{\text{bet}}$ has been implicitly attributed to an expected correlation $k_{\text{bet}}(\Delta G_{\text{bet}})$ for the spin-allowed pro-

cess. Alternatively, one could argue that a change of $\bar{k}_{\text{bet}}$ over the series of complexes might be due to a corresponding change in s . Then, however, the non-monotonic behavior of $\bar{k}_{\text{bet}}$ with n , the number of bpy ligands, should be paralleled by a non-monotonic behaviour of the MFE, $R_{\bar{k}_{\text{bet}}}$, which is at variance with the experimental results.

Excluding major changes in s along the series of Ru complexes, only variations in Δg and D_r seem to remain for explaining the variations of the magnetokinetic effects. So far, no independent experimental information is available on the Δg and D_r variation. To our knowledge ESR spectra of the Ru(III) complexes at room temperature have not been reported. Obviously, spin relaxation is too fast. Experiments at low temperature in glassy or highly viscous solvents are in progress in our laboratory to obtain the Δg tensors of the whole series of complexes and information on spin relaxation that might be extrapolated to the room temperature situation of the magnetokinetic experiments. At the present stage of analysis it appears as if the MFE observed might serve as a unique source of information on the dynamic and magnetic properties of such paramagnetic complexes under conditions that are out of reach of the present state ESR techniques.

For analyzing the results with PVS as electron acceptor (cf. Table 2) we have assumed $\bar{k}_{\text{bet}}$ to be the same as with MV^{2+} , since ΔG_{bet} differs only little between these two cases. From η_{ce} and Eq. (4) we thus obtain $k_{\text{ce}} = 2.1 \times 10^9 \text{ s}^{-1}$, a value significantly smaller than with MV^{2+} . This decrease of k_{ce} qualitatively reflects the difference in Coulomb interaction between the RPs $[\text{Ru}(\text{bpy})_3^{3+} \dots \text{MV}^+]$ and $[\text{Ru}(\text{bpy})_3^{3+} \dots \text{PVS}^-]$. On the basis of the Debye-Eigen equation, assuming the model of solvated charged spheres for the ions, one would expect k_{ce} in the case of PVS^- as counter radical ion to be about 10 times slower than in the case of MV^+ . The evaluated ratio is only 2.5, however, indicating either that the attached $-(\text{CH}_2)_3-\text{SO}_3^-$ groups do not completely overcompensate the effect of the positively charged bipyridyl system in PVS^- , or that the effect of ionic strength reduces the Coulomb interaction.

For $R_{\eta_{\text{ce}}}$ no change is observed when replacing MV^{2+} by PVS. It should be pointed out here that according to model calculations as described in Ref. [11] a decrease of k_{ce} at constant $\bar{k}_{\text{bet}}$ is expected to increase the MFE $R_{\eta_{\text{ce}}}$. It seems difficult to explain the observed constancy of $R_{\eta_{\text{ce}}}$ when changing k_{ce} by more than a factor of 2 without modifying the above mentioned model.

4. Conclusion

As the main result of the present investigations it has been found that the magnetic field effect $R_{\bar{k}_{\text{bet}}}$ on the effective rate constant of backward electron transfer in the primary redox pair varies linearly with the number of ligands

in the heteroleptic series with bpy and dce ligands. No obvious correlation of the magnetic field effect with absolute values of the rate constants $\bar{k}_{\text{bet}}$ and k_{ce} has been observed.

A qualitative magnetokinetic analysis of these findings seems to indicate that the magnetic field effect on $\bar{k}_{\text{bet}}$ mainly reflects changes in magnetic properties (Δg , spin relaxation) of the corresponding Ru(III) complexes. Since, so far, no independent experimental information is available how these properties change with the chemical variations studied here, pertinent ESR work is in progress in this laboratory now.

The lack of correlation between the magnetic field effect and the absolute values of $\bar{k}_{\text{bet}}$ and k_{ce} , observed with the present variation of Ru ligands and electron acceptors, is difficult to understand in terms of the mechanistic model worked out theoretically in Ref. [11]. This discrepancy meets somehow with the physical inconsistencies arising in the parameter values, required for obtaining a quantitative fit to the experimental magnetic field dependence with the parent system $\text{Ru}(\text{bpy})_3^{2+}/\text{MV}^{2+}$ [11]. In such a fit a very high D_r -value, incompatible with the explicit model assumption of rotational diffusion as the basic source of spin relaxation, has to be adopted. We expect that further progress in the proper understanding of these magnetic field effects will critically depend on the correct model of spin relaxation.

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