

# Enhancement of magnetic field effect in $\text{Ru}(\text{bpy})_3^{2+}/\text{MV}^{2+}$ system by $\text{Ru}(\text{bpy})_3^{2+}\text{-Ag}^+$ exciplex formation

Lajos Fodor<sup>a</sup>, Attila Horváth<sup>a,1</sup>, Karsten A. Hötzer<sup>b</sup>, Stefan Walbert<sup>b</sup>,  
Ulrich E. Steiner<sup>b,\*</sup>

<sup>a</sup> Department of General and Inorganic Chemistry, University of Veszprém, Veszprém, H-8201, P.O.B. 158, Hungary

<sup>b</sup> Fakultät für Chemie der Universität Konstanz, D-78457 Konstanz, Germany

Received 12 July 1999; in final form 7 October 1999

## Abstract

The influence of ionic strength variation and of exciplex formation between silver ions and triplet excited  $\text{RuL}_3^{2+}$  ( $\text{L} = \text{bipyridine, phenanthroline}$ ) on the photo electron transfer kinetics of the complex with methylviologen and the magnetic field dependence of free radical formation efficiency has been studied by laser flash spectroscopy. The magnetic field effect consisting in a decrease of the efficiency of cage escape  $\eta_{\text{ce}}$  in the  $\text{Ru}(\text{bpy})_3^{2+}/\text{MV}^{2+}$  system is enhanced by 40% when exciplex formation between  $\text{Ag}^+$  ions and triplet excited  $\text{RuL}_3^{2+}$  complexes takes place. The relevant kinetic parameters have been determined by magnetokinetic model calculations. © 2000 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Light induced electron transfer reactions from *tris*-diimineruthenium(II) complexes to various electron acceptors such as methylviologen ( $\text{MV}^{2+}$ ) have been extensively studied because of their potential applicability in the design of artificial systems for conversion and storage of solar energy [1–7]. Particular attention has been paid to the kinetics of geminate backward electron transfer (GBET) representing an energy loss channel that competes with the formation of energy-rich free radicals. The discovery of a responsiveness of the yield of free redox products in

such reactions to high magnetic fields [8,9] has provided a useful technique in elucidating the mechanism of the GBET process [10–15].

In the  $\text{Ru}(\text{bpy})_3^{2+}/\text{MV}^{2+}$  system the magnetic field effect (MFE) becomes measurable in fields of some 0.1 T and reaches a saturation limit in fields of about 10 T. It consists in a decrease of the efficiency of free redox product formation by up to several 10%. MFE studies of  $\{^3[\text{RuL}_3]^{2+} \dots \text{MV}^{2+}\}$  reactions have revealed a high sensitivity of the MFE to ligand variation [10,15] and to solvent viscosity variation [16]. This type of MFE has been accounted for by the spin chemical radical pair mechanism [17,18] which is based on the rule of spin conservation in fast chemical reaction steps, demanding that a spin change has to occur before recombination can take place if the multiplicity of the spin state in which the

\* Corresponding author. Fax: +49-7531-88-3014; e-mail: steiner@chclu.chemie.uni.konstanz.de

<sup>1</sup> Also corresponding author. E-mail: attila@vegic.sol.vein.hu.

RP is created (here: triplet) and of the recombination product (here: singlet) are different. For the  $\{\text{Ru}^{3+} \dots \text{MV}^{+\cdot}\}$  redox pair both spin relaxation (which is essentially field independent [13]) and magnetic field induced coherent spin motion are dominated by the strong spin-orbit coupling in the  $\text{Ru}^{3+}$  complex. This situation necessitated a specific adaptation of the RP theory to this type of systems [11,13]. Recently, the validity of this adapted RP theory has been directly demonstrated for another transition metal system [19] by sub-picosecond time-resolved experiments.

Photoexcited ruthenium(II) and iridium(III)- $\alpha$ , $\alpha$ -diimine complexes show the interesting phenomenon of dynamic, reversible formation of binary (as  ${}^3\text{RuL}_3^{2+}|\text{Ag}^+$ ) and ternary (as  ${}^3\text{RuL}_3^{2+}|\text{Ag}_2^{2+}$ ) exciplexes in the presence of inorganic ground state species such as  $\text{Ag}^+$  [20–23] and  $\text{HgCl}_2$  [24], respectively. In aqueous solution, addition of silver ions up to 1.5 M at constant ionic strength (3 M) results in the decrease of the lifetime and the luminescence quantum yield of  ${}^3\text{RuL}_3^{2+}$  (L = bipyridine or phenanthroline) and a shift of the emission band to longer wavelengths [25]. With  $\text{MV}^{2+}$  these exciplexes undergo an electron transfer reaction similar to the parent Ru(II) complex. In case of the binary and ternary exciplexes mentioned above both the rate constant  $k_q$  of quenching by  $\text{MV}^{2+}$  and the efficiency  $\eta_{\text{ce}}$  of free radical formation in the quenching process decrease. Whereas the decrease of the quenching rate constant may be assigned to the higher positive charge of the exciplex, since it retards the approach of the  $\text{MV}^{2+}$  quencher dication, the origin of the decrease of the cage escape efficiency might be sought in a faster GBET and/or a slower cage escape process of the RP. In order to get more insight into this question the present MFE study was undertaken.

## 2. Experimental

### 2.1. Materials and solutions

Analytical grade  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  and  $[\text{Ru}(\text{phen})_3]\text{Cl}_2 \cdot x\text{H}_2\text{O}$  (Aldrich),  $\text{AgNO}_3$  (Reanal),  $\text{NaNO}_3$  (Reanal) were used without further purification.

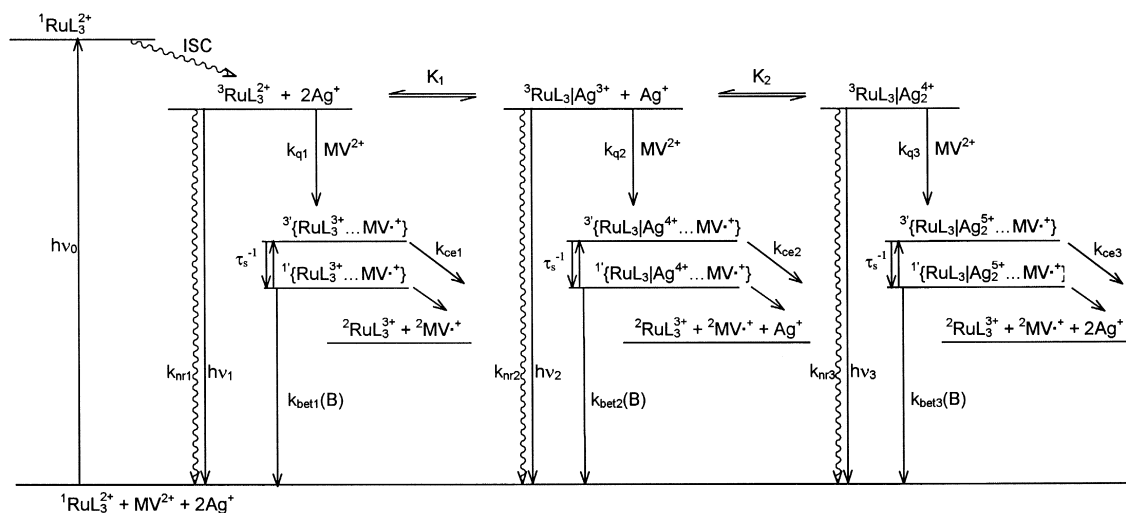
The methylviologen dichloride (Aldrich) as well as the ruthenium(II) complexes were converted to diperchlorate salts by the method described in Ref. [26]. Water purified by a Millipore Super-Q system was used to prepare aqueous solutions. The concentration of the ruthenium complex varied between  $2 \times 10^{-5}$  and  $8 \times 10^{-5}$  M and the concentration of methylviologen changed between 0 and  $3 \times 10^{-3}$  M, while the concentration of  $\text{Ag}^+$  was varied between 0 and 1.5 M. Suitable amounts of  $\text{NaNO}_3$  were added to the reaction mixtures to adjust the required ionic strength. Laser flash photolysis of the samples was performed in a flow-through cuvette of optical path length 1 cm under anaerobic conditions.

### 2.2. Equipment and methods

Transient emission and absorption signals in the nanosecond to microsecond range were measured in different external magnetic fields up to 3.3 T magnetic flux density using the laser flash photolysis equipment described previously [27]. Coumarin 47 was used as laser dye to obtain a wavelength of 470 nm for exciting the ruthenium complexes. The dye was pumped by the third harmonic of a Nd:YAG laser (Spectra Physics, Quanta Ray GCR 150). Luminescence lifetimes were obtained by a single-exponential fitting to the emission decay ( $\epsilon_{\text{em}} = 600$  nm). The efficiency of net electron transfer,  $\eta_{\text{ce}}$  was determined by the saturation method, detecting the  $\text{MV}^{+\cdot}$  absorption at 395 nm as a function of the laser energy and extrapolating to saturation [28]. The efficiency of net electron transfer was obtained using the following equation.

$$\eta_{\text{ce}} = \Delta\text{OD}_{395, \text{sat}} / (\eta_q [\text{Ru}(\text{II})]_o \Delta\epsilon), \quad (1)$$

where  $\Delta\text{OD}_{395, \text{sat}}$  is the saturation value of absorption at 395 nm,  $\eta_q = k_q[\text{Q}] / (1/\tau_o + k_q[\text{Q}])$  is the quenching efficiency,  $[\text{Ru}(\text{II})]_o$  is the total concentration of ruthenium complexes,  $\Delta\epsilon$  is the change of molar absorbance ( $\Delta\epsilon = \epsilon_{\text{MV}^{+\cdot}} + \epsilon_{\text{Ru}(\text{III})} - \epsilon_{\text{Ru}(\text{II})}$ ). The quenching constant  $k_q$  at various ionic strengths and  $\text{Ag}^+$  concentrations was measured by the luminescence quenching method using the Stern–Volmer equation:  $1/\tau = 1/\tau_o + k_q[\text{Q}]$ , where  $\tau_o$  is the lifetime of the luminescent species at  $[\text{Q}] = 0$ ,  $k_q$  is the



Scheme 1.

rate coefficient of the quenching reaction and  $[Q]$  is the concentration of the quencher.

### 3. Results

The reaction scheme describing the system investigated is presented in Scheme 1. Association between  $\text{Ag}^+$  ions and the Ru(II) complex occurs only when the complex is in the excited state, whereupon bimolecular and termolecular exciplexes are formed.

In order to achieve high efficiencies of exciplex formation 1.5 M solutions of  $\text{Ag}^+$  were employed, yielding equilibrium concentrations of 7, 35, and 58% of free ruthenium complex, bimolecular and termolecular exciplex, respectively. It is important to note that due to the high silver ion concentration the time to establish the exciplex equilibrium is much shorter than the quenching reaction with  $\text{MV}^{2+}$  at any quencher concentration employed [25].

The results of our measurements of the parameters of the electron transfer reaction with  $\text{MV}^{2+}$ , viz.

Table 1

Characteristic reaction parameters measured and evaluated for the primary radical pair formed in the electron transfer reaction  ${}^3\text{Ru}(\text{bpy})_3^{2+} + \text{MV}^{2+}$  in aqueous solution at different ionic strength for  $[\text{Ag}^+] = 0$  and  $[\text{Ag}^+] = 1.5 \text{ M}$

System parameter	$\text{Ru}(\text{bpy})_3^{2+} - \text{MV}^{2+}$ IS = 0.1 M	$\text{Ru}(\text{bpy})_3^{2+} - \text{MV}^{2+}$ IS = 3.0 M	$\text{Ru}(\text{bpy})_3^{2+} - \text{Ag}^+ - \text{MV}^{2+}$ IS = 3.0 M, $[\text{Ag}] = 1.5 \text{ M}$
measured quantities			
$k_q \times 10^{-9}, \text{M}^{-1}\text{s}^{-1}$	0.85 (0.48) <sup>b</sup>	2.7	1.5
$\eta_{\text{ce}}, \%$	15.5 (14.7) <sup>b</sup>	6.4	2.9
$R_{\eta_{\text{ce}}}, \%$ measured at B = 3.3 T	19 (23) <sup>b</sup>	17.5	25
evaluated quantities			
$\tau_s, \text{ps}$	21 (24.4) <sup>b</sup>	23	27
$k_{\text{ce}}, \text{ns}^{-1}$	2.1 (1.7) <sup>b</sup>	0.45	0.29
$k_{\text{bet}}, \text{ns}^{-1}$	83 (65) <sup>b</sup>	42	87

<sup>a</sup>The values given are average values referring to a mixture of species  ${}^3\text{Ru}(\text{bpy})_3^{2+}(\text{Ag}^+)_n$  with 7, 35, and 58% for  $n = 0, 1, 2$ .

<sup>b</sup>Data from Ref. [27].

quenching constant  $k_q$  and cage escape efficiency  $\eta_{ce}$  and the relative magnetic field effect,  $R(B_0) = [\eta_{ce}(B_0) - \eta_{ce}(B_0 = 0)] / \eta_{ce}(B_0 = 0)$ , on the latter quantity, are given in Table 1. The field dependence of the magnetic field effect is shown in Fig. 1. Because the high concentration of the silver salt gives rise to a high ionic strength it seemed appropriate to investigate first the influence of ‘inert’ ionic strength as established by  $\text{NaNO}_3$ . Under such conditions the quenching rate constant was found to increase by about a factor of 3, while the efficiency  $\eta_{ce}$  of geminate cage escape was reduced by a factor of about 2.5. The MFE on  $\eta_{ce}$  showed little sensitivity towards variation of ionic strength. Still there is a slight increase of the (absolute) value of the MFE at low fields and a slight decrease at high fields. Upon exciplex formation with silver ions  $k_q$  slightly decreases whereas  $\eta_{ce}$  is reduced by a factor of about 2. The MFE on  $\eta_{ce}$  is considerably enhanced at all fields investigated, its increase amounting to about 40% at 3.3 T.

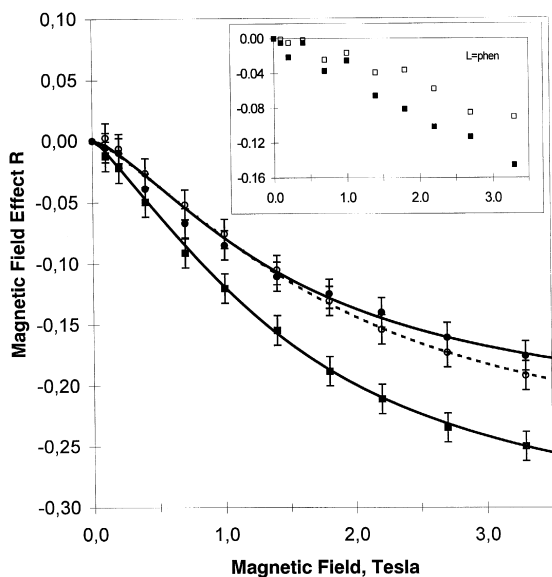


Fig. 1. Relative magnetic field effect  $R(B_0)$  on the quantum yield of  $\text{MV}^{+\cdot}$  radical formation upon quenching of photoexcited  $\text{RuL}_3^{2+}$  complexes: (○) L = bpy,  $\mu = 0.1$  M,  $[\text{Ag}^+] = 0$  M; (○) L = bpy,  $\mu = 3.0$  M,  $[\text{Ag}^+] = 0$  M; (■) L = bpy,  $\mu = 3.0$  M,  $[\text{Ag}^+] = 1.5$  M. Inset represents  $R(B_0)$  data obtained for the L = phen complex: (□)  $\mu = 3.0$  M,  $[\text{Ag}^+] = 0$  M, (■)  $\mu = 3.0$  M,  $[\text{Ag}^+] = 1.5$  M.

#### 4. Discussion

The present kinetic investigations were undertaken in order to explore the effects of  $^3\text{Ru}(\text{II})\text{L}_3^{2+}|\text{Ag}_1^{+(2+)}$  exciplex formation on the photo-induced electron transfer kinetics of Ru(II) complexes. As has been pointed out above and is indicated in Scheme 1, the system does not allow to observe the individual binary or ternary exciplex, but only mixtures that are rich in at least two components, either the free Ru-complex with the binary exciplex or the binary and ternary exciplex with a small admixture of the free Ru-complex [25]. For the present experiments a mixture with a small fraction of free Ru-complex was chosen. Since it contains binary and ternary exciplex in similar amounts the results obtained represent averages (below denoted by  $\langle \rangle$ ) of the behavior of binary and ternary exciplex. At the present stage of investigation, no attempt has been made yet at differentiating the two exciplex species, although, in principle, this is possible by investigating in detail the  $\text{Ag}^+$  concentration dependence.

As shown in Scheme 1 electron transfer quenching of the  $^3\text{Ru}(\text{II})$  species generates pairs of redox products each with an overall triplet alignment of the unpaired spins. Before the redox pairs can undergo geminate recombination occurring with rate constant  $k_{bet}$  they have to undergo spin transitions generating singlet spin alignment. In zero magnetic field such spin transitions occur only incoherently through spin relaxation at the Ru(III) centers. (The primes used with the multiplicity symbols  $3'$  and  $1'$  denote some spin-orbit-coupling induced contamination with components of the other multiplicity). Spin equilibrium is established with a rate constant of  $\tau_s^{-1}$ ,  $\tau_s$  denoting the (transversal = longitudinal and field independent) relaxation time of the Ru(III) complex. In an external magnetic field an additional (coherent) mechanism of T-S transitions based on the different  $g$  tensors of the two types of redox species comes into effect. In competition with spin-dependent backward electron transfer the geminate pairs of redox products may dissociate ( $k_{ce}$ ) into the free redox products. The efficiency  $\eta_{ce}$  of this ‘cage escape’ process is measured in the experiment. It should be noted that in Scheme 1 the energetic separation of the different spin multiplicities of the redox-pairs and the free redox products is not drawn to scale. It is important

to note that these states have practically the same energies.

First we discuss the observed effects on  $k_q$ . As has been shown by Clark and Hoffman [29–31] electron transfer rate constants in the  $\text{Ru}(\text{bpy})_3^{2+}/\text{MV}^{2+}$  system are enhanced by ion-pairing of these cations with anions of the added salts. This enhancement was reported to correlate with the free enthalpy  $\Delta G_{\text{hydr}}^0$  of hydration of the anion: the less negative  $\Delta G_{\text{hydr}}^0$  the faster the electron transfer with ruthenium complexes paired with these ions. This correlation was suggested to be due to a smaller reorganization energy  $\lambda_{\text{solv}}$  associated with anions of higher hydrophobicity (less negative  $\Delta G_{\text{hydr}}^0$ ). The  $\Delta G_{\text{hydr}}^0$  values of  $\text{NO}_3^-$  (not investigated by Clark and Hoffman) of  $-1362$  kJ/mol is very close to the value of  $\text{Br}^-$  ( $-1377$  kJ/mol) [29,32]. In agreement with the correlation noted by Clark and Hoffman the  $k_q$  values for  $\mu = 0.1$  M and 3.0 are compatible in order of magnitude and trend of concentration dependence with the values reported for NaBr ( $1.88 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for  $\mu = 0.1$  and  $3.96 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for  $\mu = 1.0$ , the highest concentration investigated by these authors. But here the salt concentration dependence of  $k_q$  seems close to saturation [29]).

While  $k_q$  the rate constant of the bimolecular forward electron transfer is obtained as a direct result of the kinetic experiment, the rate constants  $k_{\text{bet}}$  and  $k_{\text{ce}}$  are not directly observable but can only be recovered from the actual observable  $\eta_{\text{ce}}$  and its magnetic field dependence  $R(B_0)$ . The procedure for this evaluation is based on kinetic simulations employing the time-integrated solution of the Stochastic Liouville equation for the spin density matrix  $\rho$  of the geminate radical pair as described in detail in Refs. [11,13,19]. Apart from the  $g$ -tensor values of the radical, known from ESR data (for the  $\text{Ru}(\text{III})$  complex  $g_{\parallel} = 1.18$ ,  $g_{\perp} = 2.60$  [15], for  $\text{MV}^{2+}$  a value of  $g = 2.00$  can be used) the spin chemical model involves three kinetic parameters,  $k_{\text{ce}}$ ,  $k_{\text{bet}}$  and  $\tau_s$  corresponding to the rate constants of cage escape, fully spin-allowed backward electron transfer and (transversal equal to longitudinal [13]) spin relaxation time of the  $\text{Ru}(\text{III})$  complex, respectively.

For the details of the spin chemical theory and the numerical calculations we are referring to previous work [11–13,19]. Here we will only briefly describe

and rationalize the influence the three kinetic parameters have on the observable quantities  $\eta_{\text{ce}}$  and  $R(B_0)$ . For situations where  $\eta_{\text{ce}} \ll 1$ , the case prevailing here, the geminate radical pairs mainly decay through backward electron transfer. Therefore it is clear that in this case  $k_{\text{ce}} \ll k_{\text{bet}}, 1/\tau_s$ . In such a situation any change of  $k_{\text{ce}}$  will be strongly reflected in the relative change of  $\eta_{\text{ce}}$ , but have only little effect on the magnetic field dependence  $R(B_0)$ . The latter conclusion follows from the fact that a magnetic field can only exhibit its effect during the lifetime of the geminate pair on which, however,  $k_{\text{ce}}$  has little influence if  $k_{\text{ce}} \ll k_{\text{bet}}, 1/\tau_s$ . On the other hand, for this kinetic situation  $k_{\text{bet}}$  and  $\tau_s$  do have a strong effect on the lifetime of the geminate radical pair and hence on the magnetic field effect. From these general dependences the following strategy can be derived for obtaining a unique set of parameters  $k_{\text{ce}}$ ,  $k_{\text{bet}}$  and  $\tau_s$  to fit the observed  $\eta_{\text{ce}}$  and  $R(B_0)$ .

First  $k_{\text{ce}}$  is set to a limiting small value, such that the MFE is essentially independent of any further reduction of  $k_{\text{ce}}$ . Then  $k_{\text{bet}}$  and  $\tau_s$  are varied subject to the restraint that the observed  $R$  value for the highest field is correctly reproduced (cf. Fig. 2). Thereby a family of curves is obtained differing in shape but all crossing in a common point. The suitability criterion of the model requires that one of

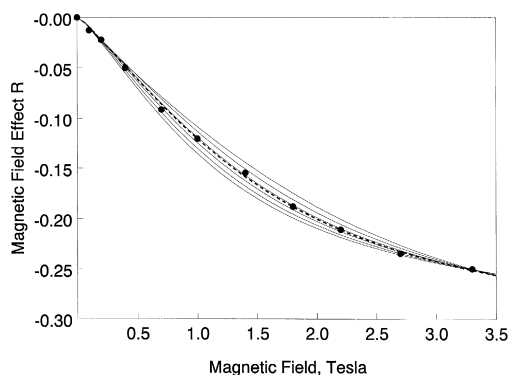


Fig. 2. Theoretical curves representing the influence of  $\{k_{\text{bet}}, \tau_s\}$  on  $R(B_0)$ . Parameter  $k_{\text{ce}}$  was kept constant at  $0.45 \text{ ns}^{-1}$ . The sets of  $\{k_{\text{bet}}, \tau_s\}$  values were selected with the restraint to reproduce the experimental value of  $R(3.3 \text{ T})$ . The pertinent values for curves 1–6 (numbering from above) are: 1: {153, 23}, 2: {111, 25}, 3: {90, 27}, 4: {76, 29}, 5: {67, 31}, 6: {60, 33}. The dashed curve represents the (negligible) change of curve 3 after setting  $k_{\text{ce}}$  to  $0.29 \text{ ns}^{-1}$ , yielding the experimental  $\eta_{\text{ce}}$  value of 2.9%; (•) are the measured data for  $L = \text{bpy}$ ,  $\mu = 3.0 \text{ M}$ ,  $[\text{Ag}^+] = 1.5 \text{ M}$ .

these curves must fit with the observed magnetic field dependence  $R(B_0)$  for all fields. Thereby a first approximation of  $k_{\text{bet}}$  and  $\tau_s$  is determined. Next the parameter  $k_{\text{ce}}$  is adjusted such that the experimental value of  $\eta_{\text{ce}}$  is reproduced. With this value of  $k_{\text{ce}}$  the MFE curve may change somewhat. Then  $k_{\text{bet}}$  and  $\tau_s$  are adjusted for adequate agreement of the calculated  $R(B_0)$  with the experimental one to within experimental accuracy by iterating the procedure to full self consistency. Usually only one further iteration step is sufficient.

For an ionic strength of  $\mu = 0.1$  M our  $\eta_{\text{ce}}$  value of 0.155 is in exact agreement with the value reported by Clark and Hoffman for a solution with NaCl and close to a value (0.147) observed earlier for NaCl solution in one of our laboratories [27]. The magnetic field effect curve  $R(B)$  in  $\text{NaNO}_3$  solution is also similar to what has been found earlier in NaCl solution (cf. Table 1). Accordingly, the resulting values for  $\tau_s$ ,  $k_{\text{ce}}$  and  $k_{\text{bet}}$  are similar to those in previous work with NaCl solutions. Comparing our  $k_{\text{ce}}$  and  $k_{\text{bet}}$  values with those published by Clark and Hoffman it is important to note how their values were assessed. Clark and Hoffman estimated  $k_{\text{ce}}$  by employing the Eigen–Debye (ED) equation which yielded a value of  $k_{\text{ce}}(\text{ED}) = 5.8 \times 10^9 \text{ s}^{-1}$ . Albeit on the same order of magnitude as our value it still differs from it by a factor of almost 3. For the understanding of this discrepancy it is interesting to note that there is some principal ambiguity in relating results from continuous diffusion theory to the parameters of a kinetic model comprising only first order rate processes [33]. For example, in theoretical simulations comparing the two types of models (diffusional and ‘exponential’) for redox pair recombination processes with the same spin characteristics as in the present systems [27] it was found that the equivalent first order rate constant of cage escape was typically 2 times smaller than the ED value.

Using the  $k_{\text{ce}}(\text{ED})$  value given above Clark and Hoffman evaluated  $k_{\text{bet}}$  from  $\eta_{\text{ce}}$  by employing the relation:

$$\eta_{\text{ce}} = k_{\text{ce}} / (k_{\text{ce}} + k_{\text{bet}}) . \quad (2)$$

In doing so the role of spin processes (cf. Scheme 1) is completely neglected. Therefore the resulting  $k_{\text{bet}}$  value should be considered as an ‘apparent’ value  $k_{\text{bet,app}}$ . Their result of  $3.2 \times 10^{10} \text{ s}^{-1}$  is 2.5 times

smaller than our value of the ‘true’  $k_{\text{bet}}$  of  $8.3 \times 10^{10} \text{ s}^{-1}$  obtained from the spin chemical analysis. Had they used the spin-chemically consistent  $k_{\text{ce}}$  value of  $2.1 \times 10^9 \text{ s}^{-1}$  an even smaller  $k_{\text{bet,app}}$  value of  $1.14 \times 10^{10} \text{ s}^{-1}$  would have ensued. The reason for the large difference to the spin-chemically evaluated  $k_{\text{bet}}$  value lies in the fact that the back electron transfer process involves the triplet to singlet process of the geminate redox pair  $\text{Ru}^{\text{III}}/\text{MV}^+$ . Actually the spin relaxation time  $\tau_s$  of 21 ps (evaluated from the present magnetic field effect but for which we have independent experimental evidence from NMR data) corresponds to a triplet to singlet conversion rate constant of  $k_{\text{TS}} = (4\tau_s)^{-1} = 1.19 \times 10^{10} \text{ s}^{-1}$  which represents an upper limit to the  $k_{\text{bet,app}}$  value. Indeed it is close to the  $k_{\text{bet,app}}$  value estimated from Eq. (2) when our spin-chemically consistent  $k_{\text{ce}}$  value is used. This agreement demonstrates that the BET process is actually spin-conversion controlled. The true  $k_{\text{bet}}$  value is about 8 times larger and can only be assessed with the help of the MFE.

When increasing the ionic strength from  $\mu = 0.1$  to 3.0 M a significant decrease of  $\eta_{\text{ce}}$  is observed (cf. Table 1). On the other hand, the MFE curve changes only little with a minor enhancement of the MFE at lower fields and a minor attenuation of the MFE at higher fields. From our general reasoning given above on the dependence of the MFE curves on the various kinetic parameters it should be qualitatively clear that  $k_{\text{ce}}$  must undergo a major change. It decreases by a factor of 4.5 while  $k_{\text{bet}}$  is halved and  $\tau_s$  is nearly constant. In solutions with salt concentrations as high as 3.0 M, which are clearly out of the validity range of Debye–Hueckel theory, it is questionable to apply the ED equation for the interpretation of  $k_{\text{ce}}$ . Employing this equation nevertheless and accounting for the 23% higher viscosity [34] leads us to expect that  $k_{\text{ce}}$  should drop by no more than a factor of 2. On the other hand, in highly concentrated salt solutions the Coulombic shielding effect on the ionic cloud which leads to a decrease of  $k_{\text{ce}}$  for reactants of like charge, as in the case of  $\text{Ru}^{3+}/\text{MV}^+$ , is counteracted by short distance forces between ions in contact. Furthermore the dielectric constant is somewhat depressed by the salt [35]. Both these effects should lessen the decrease of  $k_{\text{ce}}$ . Therefore we do not favor the possibility to explain the assessed  $k_{\text{ce}}$  effect by the bulk properties of the

solution. A specific binding of  $\text{Ru}^{3+}$  and  $\text{MV}^{+\cdot}$  moiety by microscopic structural changes of their solvent and ionic spheres seems more reasonable. These structural changes must be adverse to electron transfer, too, as to be concluded from the evaluated decrease of  $k_{\text{bet}}$ . To which of the three basic parameters of electron transfer theory (thermodynamic driving force, reorganization energy, and electronic coupling matrix element) this change of  $k_{\text{bet}}$  should be assigned is difficult to assess, however, with the information at hand.

The fair constancy of  $\tau_s$  is in line with the previous notion [13] that the spin relaxation of the  $\text{Ru}^{\text{III}}$  complex is rather due to an intramolecular perturbation (vibrational fluctuations of the ligand field, indirectly modifying the spin-orbit coupling) involving primarily the inner ligand sphere of  $\text{Ru}^{\text{III}}$  ion.

Finally we have to discuss the effects introduced by exciplex formation of  ${}^3\text{Ru}(\text{bpy})_3^{2+}$  with  $\text{Ag}^+$  ions. Replacing 1.5 M  $\text{Na}^+$  ions in the solution by  $\text{Ag}^+$  ions leads to a further decrease in  $\langle \eta_{\text{ce}} \rangle$  by a factor of 2 and a clear enhancement of the MFE. According to the spin chemical analysis these changes are related to a further decrease of  $\langle k_{\text{ce}} \rangle$ , a doubling of  $\langle k_{\text{bet}} \rangle$  and a slight increase of  $\langle \tau_s \rangle$ . Since there is unequivocal indication of exciplex formation,  $\text{Ag}^+$  must be in specific association with the MLCT excited  $\text{Ru}(\text{bpy})_3^{2+}$  species. It is likely [25] that the electron promoted to a bpy ligand in the MLCT transition is delocalized to some degree over the  $\text{Ag}^+$  ion in the exciplex. This will certainly lower the LUMO (bpy  $\pi^*$ ) energy thereby reducing the thermodynamic driving force of the forward electron transfer which qualitatively explains the observed decrease of  $\langle k_{\text{q}} \rangle$ . While it will not directly affect the driving force of the backward electron process, the lowering of the LUMO might be still favorable for a faster backward electron transfer by enhancing the backward electron transfer related electronic coupling via an enhancement of the  $\text{MV}^+(\text{SOMO}) \rightarrow \text{bpy}(\pi^*) \rightarrow \text{Ru}(\text{d})$  superexchange mechanism.

## 5. Conclusion

We have shown that magnetic field effects are indispensable for unravelling the details of backward electron transfer and cage escape kinetics in

$\text{Ru}(\text{L})_3^{3+}/\text{MV}^{+\cdot}$  type redox pairs characterized by very fast spin relaxation. The spin chemical analysis of the cage escape efficiency and its magnetic field dependence has revealed that exciplex formation between  $\text{Ag}^+$  and  ${}^3\text{Ru}(\text{L})_3^{2+}$  (L = bipyridine, phenanthroline) significantly reduces the rate constant of cage escape and increases the rate constant of backward electron transfer in the photo-induced reaction of the Ru-complex with methylviologen.

## Acknowledgements

Financial support by the Hungarian National Science Foundation (OTKA No. T23760) and by the priority program Inter- and Intramolecular Electron Transfer of the Volkswagenstiftung is gratefully acknowledged.

## References

- [1] N. Sutin, C. Creutz, *Pure Appl. Chem.* 52 (1980) 2717.
- [2] K. Kalyanasundaram, *Coord. Chem. Rev.* 46 (1982) 159.
- [3] K. Kalyanasundaram, in: M. Grätzel (Ed.), *Energy Resources through Photochemistry and Catalysis*, Academic Press, New York, 1983.
- [4] V. Balzani, F. Scandola, in: M. Grätzel (Ed.), *Energy Resources through Photochemistry and Catalysis*, Academic Press, New York, 1983.
- [5] M. Venturi, Q.G. Mulazzani, M.Z. Hoffman, *J. Phys. Chem.* 88 (1984) 912.
- [6] C. Chiorboli, M.T. Indelli, M.A. Rampi, F. Scandola, *J. Phys. Chem.* 92 (1988) 156.
- [7] M.Z. Hoffman, *J. Phys. Chem.* 92 (1988) 3464.
- [8] G. Ferraudi, G.A. Argüello, *J. Phys. Chem.* 92 (1987) 1846.
- [9] U.E. Steiner, H.-J. Wolff, T. Ulrich, T. Ohno, *J. Phys. Chem.* 93 (1989) 5147.
- [10] H.-J. Wolff, U.E. Steiner, *Z. Phys. Chem. N.F.* 169 (1990) 147.
- [11] U.E. Steiner, D. Bürßner, *Z. Phys. Chem. N.F.* 169 (1990) 159.
- [12] U.E. Steiner, W. Haas, *J. Phys. Chem.* 95 (1991) 1880.
- [13] D. Bürßner, H.-J. Wolff, U.E. Steiner, *Z. Phys. Chem. N.F.* 182 (1993) 297.
- [14] M. Mukai, H. Tanaka, Y. Fujiwara, Y. Tanimoto, *Bull. Chem. Soc. Jpn* 67 (1994) 3112.
- [15] D. Bürßner, H.-J. Wolff, U.E. Steiner, *Angew. Chem. Ed. Engl.* 33 (17) (1994) 1772.
- [16] H.-J. Wolff, D. Bürßner, U.E. Steiner, *Pure Appl. Chem.* 67 (1995) 167.
- [17] K.M. Salikhov, Y.N. Molin, R.Z. Sagdeev, A.L. Buchachenko, *Spin Polarization and Magnetic Effects in Radical Reactions*, Elsevier, Amsterdam, The Netherlands, 1984.

- [18] U.E. Steiner, T. Ulrich, *Chem. Rev.* 89 (1989) 51.
- [19] P. Gilch, F. Pöllinger-Dammer, C. Musewald, M.E. Michel-Beyerle, U.E. Steiner, *Science* 281 (1998) 982.
- [20] N.P. Ayala, J.N. Demas, B.A. DeGraff, *J. Am. Chem. Soc.* 110 (1988) 1523.
- [21] A.B.P. Lever, P. Seymour, P.R. Auburn, *Inorg. Chim. Acta* 145 (1988) 43.
- [22] N.P. Ayala, J.N. Demas, B.A. DeGraff, *J. Phys. Chem.* 93 (1989) 4104.
- [23] T. Tsubomura, O. Igarashi, M. Morita, *Chem. Lett.* (1992) 385.
- [24] N.P. Ayala, C.M. Flynn Jr., L.-A. Sacksteder, J.N. Demas, B.A. DeGraff, *J. Am. Chem. Soc.* 112 (1990) 3837.
- [25] L. Fodor, A. Horváth, *J. Photochem. Photobiol. A.: Chem.* 112 (1998) 213.
- [26] M.G. Kinnaird, D.G. Whitten, *Chem. Phys. Lett.* 88 (1982) 275.
- [27] M. Linsenmann, *Doctoral Dissertation*, University of Konstanz, 1997.
- [28] G. Orellana, A.M. Braun, *J. Photochem.* 48 (1989) 277.
- [29] C.D. Clark, M.Z. Hoffman, *J. Phys. Chem.* 100 (1996) 7526.
- [30] C.D. Clark, M.Z. Hoffman, *J. Photochem. Photobiol. A.: Chem.* 111 (1997) 9.
- [31] C.D. Clark, M.Z. Hoffman, *Coord. Chem Rev.* 159 (1997) 359.
- [32] Y. Marcus, *Ion Solvation*, Chap. 5, Wiley, New York, 1985.
- [33] A.I. Burshtein, E. Krissinel, *J. Phys. Chem.* 100 (1996) 3005.
- [34] R.H. Stokes, A. Mills, *Viscosity of Electrolytes and Related Properties*, Pergamon, Oxford, 1965.
- [35] R.A. Robinson, R.H. Stokes, *Electrolyte Solutions*, Butterworths, London, 1959.