

Spin-orbit coupling controlled spin chemistry of $\text{Ru}(\text{bpy})_3^{2+}$ photooxidation: Detection of strong viscosity dependence of in-cage backward electron transfer rate

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Abstract: The magnetic field dependence of η_{ce} , the cage escape yield of radicals generated by photoelectron transfer between $\text{Ru}(\text{bpy})_3^{2+}$ and methylviologen (MV^{++}) was investigated for a series of solvent mixtures of increasing viscosity, obtained by adding ethylene glycol (EGLY) to $\text{H}_2\text{O}/\text{ACN}$. From the experimental results the absolute values of the rate parameters characterizing the primary radical ion pair (k_{ce} for cage escape, τ_{s} for spin relaxation, and k_{bet} for spin-allowed backward electron transfer) have been obtained. Particularly noteworthy is the strong viscosity dependence of k_{bet} , which can be assigned to dielectric solvent relaxation as the rate limiting step of backward electron transfer in the EGLY containing solvents.

Introduction

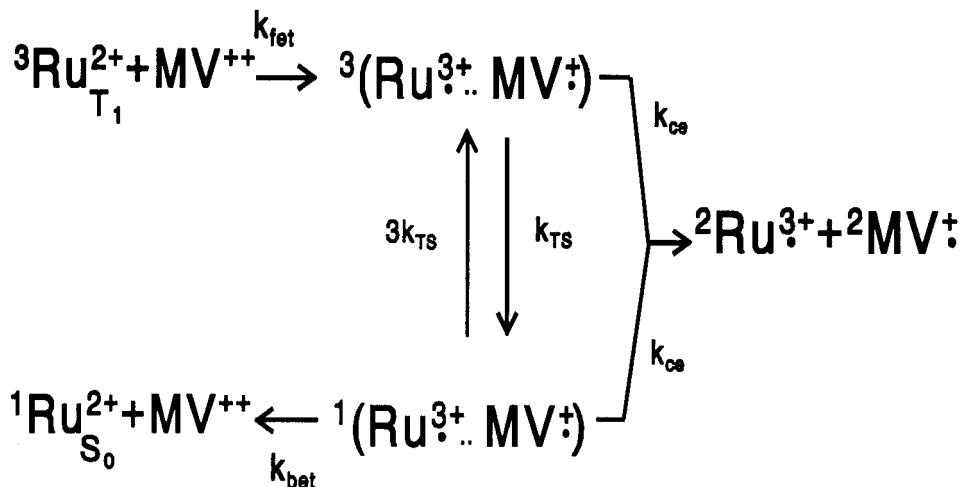
One of the main interests in photoelectron transfer reactions is their eminent potential for converting light energy into chemical energy. This potential is based on the general property of electron transfer processes to exhibit very fast rates while at the same time conserving most of the primary electronic excitation energy in the formation of energy rich radical ion pairs (RIPs). However, the thermodynamic potential of these primary RIPs can be utilized only if the primary charge separation is followed by further separation of the oxidized and reduced species (or- in a solid matrix- by a separation of the produced electron/hole pair through subsequent electron transfer steps), a process that has to compete with backward electron transfer (BET) regenerating the reactants in their ground states whereby all of the absorbed photon energy would be finally wasted.

Kinetically, the processes in the primary RIP are usually characterized by two rate constants: k_{ce} for cage escape (CE) and k_{bet} for the energy dissipating BET, from which the efficiency η_{ce} of CE is obtained as $\eta_{\text{ce}} = k_{\text{ce}} / (k_{\text{ce}} + k_{\text{bet}})$. For freely diffusing reactants only η_{ce} is usually observable from which k_{bet} may be estimated by employing a theoretical estimation of k_{ce} based e.g. on the Eigen-Debye equation (1). For chemically linked donor and acceptor systems (dyads) k_{bet} can be measured by time-resolved spectroscopy since the CE is blocked and the rate of the forward electron transfer is not limited by diffusion. In particular, such methods have been also applied to the reaction of photoexcited Ru-trisbipyridine ($\text{Ru}(\text{bpy})_3^{2+}$) with methylviologen (MV^{++}), a most popular photoelectron transfer system because of its potential to function as an efficient sensitizing system in the photochemical splitting of water (2). What has been disregarded, however, in most of the pertinent investigations, is the role of electron spin as a kinetically controlling factor, which can be unequivocally demonstrated through a magnetic field effect on the observed CE efficiency η_{ce} . In a series of investigations (3-8) we have shown how one can take advantage of this effect to determine the details of the BET/CE kinetics. In this paper we will report the first results of a spin chemical investigation studying the solvent viscosity dependence of the processes occurring in the photogenerated RIP ($\text{Ru}(\text{bpy})_3^{3+\bullet} \dots \text{MV}^{+\bullet}$).

Spin Chemistry of BET

Since the photoreactive MLCT state of $\text{Ru}(\text{bpy})_3^{2+}$ is of predominant triplet character and electron spin is conserved as far as possible in a fast electron transfer reactions, the primary RIP ($\text{Ru}(\text{bpy})_3^{3+\bullet} \dots \text{MV}^{+\bullet}$) originates with predominant triplet spin. This is true in spite of the strong spin-orbit coupling

(SOC) at the Ru center (cf. ref. (4) for details). On the other hand, the product of the BET is the singlet ground state pair $^1(\text{Ru}(\text{bpy})_3^{2+}\cdots\text{MV}^{++})$. Therefore, a triplet to singlet spin conversion in the RIP has to occur prior to the BET step. The spin chemical reaction scheme thus introduces another step in order to account for the spin transition in the RIP. In zero field the $T \rightarrow S$ and $S \rightarrow T$ transitions can be described by a first order rate constant k_{TS} which is determined by the fast spin relaxation time τ_{S} at the Ru^{II} -center, whereby $k_{\text{TS}} = (4\tau_{\text{S}})^{-1}$. In an external magnetic field, the Larmor precession of the two unpaired spins at Ru^{III} (where an effective spin $S_{\text{eff}} = 1/2$ is used to account for the strong SOC) and at MV^{\bullet} occur around different axes and at different frequencies because the g -tensor at Ru^{III} is strongly anisotropic. In effect, this magnetic-field driven (coherent) spin motion accelerates the $T \rightarrow S$ transitions and thereby enhances the effectivity of BET with a concomitant decrease of η_{ce} , which is conveniently observed as a magnetic field dependence of the yield of free MV^{\bullet} radicals or of free Ru^{III} complex.



SCHEME 1

In previous work (4,6,7) we have described in detail the theory of this magnetic field effect and the method to determine the rate parameters k_{ce} , k_{bet} (here defined as the rate constant for a hypothetically pure singlet RIP state) and k_{TS} (or, equivalently, τ_{S}) from a set of experimentally accessible parameters comprising the value of η_{ce} , its magnetic field dependence and the g -tensor of the Ru^{III} -complex.

Experimental

The photoelectron transfer rate parameters were determined, as described previously (3,5,7) using ns-time resolved laser flash spectroscopy with an excimer laser pumped dye laser and exciting $\text{Ru}(\text{bpy})_3^{2+}$ at 455 nm. Solutions of the complex were made up from the chloride salt $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ obtained as a gift from Prof. T. Ohno, Osaka. It was synthesized according to ref.(9). Methylviologen (MV^{++}), as a dichloride trihydrate, was obtained from Aldrich. All measurements were carried out at room temperature. The solutions were deaerated by purging with solvent saturated suprapure N_2 . Solvent mixtures were made up from deionized water, acetonitrile (Merck p.A.), and ethylene glycol (EGLY, Merck p.A.). The actual solvent viscosities were measured using a Höppler viscosimeter. The ionic strength of the solutions was adjusted to 0.2 M by NaCl. For details of the experiments cf. ref. (8).

Results and Discussion

Setting out from investigations of the $\text{Ru}(\text{bpy})_3^{2+}/\text{MV}^{++}$ photoreaction in $\text{H}_2\text{O}/\text{ACN}$ (1:1,v:v) solutions (6) we chose to vary the solvent viscosity by the addition of ethylene glycol (EGLY). Thereby a range of dynamic solvent viscosities η between 0.834 cP and 13.40 cP was covered (cf. Table 1.). The dielectric properties, too, (cf. the ϵ values in Table 1) are affected to some extent by changing the composition of the solvent, but to a much lesser degree. Below, we will discuss to what extent the observed solvent effect might be assigned to a variation of solvent polarity. In any case, as may

TABLE 1. Spectroscopic and photoelectron transfer rate parameters of the Ru(bpy)₃²⁺/MV²⁺ reaction system in solvent mixtures of varying viscosity a)

%(vol.) EGLY		0	20	40	60	80	95 a)
η_{25} , cP	(b)	0.834	1.295	2.150	3.884	7.680	13.40
ϵ	(c)	57.8	53.5	49.1	44.8	40.5	38.3
λ_{\max} , nm	(d)	610	610	610	610	610	610
k_0 , 10^6 s^{-1}	(e)	1.21	1.21	1.21	1.21	1.21	1.21
k_q , $10^8 \text{ l mol}^{-1} \text{ s}^{-1}$	(f)	7.36	6.60	5.19	3.65	2.28	1.16
k_{rec} , $10^9 \text{ l mol}^{-1} \text{ s}^{-1}$	(g)	3.7	2.8	2.1	1.6	1.1	0.6
η_{ce}	(h)	0.19	0.16	0.13	0.09	0.06	0.05
$R(\eta_{\text{ce}}, 3.3 \text{ T})$	(i)	-0.228	-0.229	-0.227	-0.208	-0.181	-0.140
k_{ce} , 10^9 s^{-1}	(j)	3.5	1.4	0.9	0.45	0.2	0.1
k_{bet} , 10^{11} s^{-1}	(k)	1.68	0.59	0.45	0.30	0.18	0.10
τ_s , ps	(l)	24.7	31.3	33.9	37.0	40.8	47.6
τ_ℓ , ps	(m)	0.3 ⁽ⁿ⁾	3.6	5.2	8.6	15.0	28.6
$k_{\text{bet,eff}}$, 10^{11} s^{-1}	(o)	0.15	0.074	0.060	0.046	0.031	0.019

a) solvent H₂O/CH₃CN (1/1 by volume) mixed with ethylenglycol (EGLY) of given % (by volume); no CH₃CN was contained in the 95% EGLY solution. In all solutions the ionic strength was adjusted to 0.2 M by NaCl. b) dynamic viscosity c) dielectric constant, interpolated from literature data (cf. ref. (8)) d) maximum of luminescence band e) decay time of ³Ru(bpy)₃²⁺ in quencher-free solution f) reaction rate constant of forward electron transfer g) rate constant of bulk recombination of Ru^{III} and MV^{+•}. h) efficiency of cage escape i) relative magnetic field effect on η_{ce} at 3.3 T j) rate constant of cage escape k) rate constant of spin-allowed BET in the primary RIP l) time constant of electron spin relaxation at the Ru^{III} centre (the parameters k_{ce} , k_{bet} , τ_s result from the analysis of the magnetic field effect) m) longitudinal dielectric relaxation time evaluated according to eq.(7) n) this value was adopted as a reference value o) apparent rate constant of BET in a reaction scheme without consideration of spin processes, defined as $k_{\text{bet,eff}} = k_{\text{ce}}(1 - \eta_{\text{ce}})/\eta_{\text{ce}}$.

be assessed from the wavelength λ_{\max} of luminescence from the photoexcited complex and its decay rate constant k_0 , there is little effect of the solvent on the excited state properties of the photoreactive Ru-complex. On the other hand, as expected, the kinetic parameters characterizing *intermolecular* reaction show a significant change with increasing percentage of EGLY: the rate constant k_q at which the photoexcited complex is quenched by MV⁺⁺, the efficiency η_{ce} of cage escape, leading to observable long-lived free radicals MV^{+•} and Ru^{III}-complex, and the second order rate constant k_{rec} at which they recombine. Their viscosity dependence is approximately proportional to $\eta^{-0.5}$ (cf. Figure 1 for k_q and η_{ce}). Similar viscosity dependences which, as far as k_q and k_{rec} are concerned, probably reflect the non-Stokes-Einstein behaviour of the diffusion coefficient, have been observed for several systems by other authors, too (10). Of course, regarding the kinetic processes in the primary radical pair, the parameter η_{ce} is of foremost importance. Traditionally, it has been analyzed in terms of the expression

$$\eta_{\text{ce}} = \frac{k_{\text{ce}}}{k_{\text{ce}} + k_{\text{bet,eff}}} \quad (1)$$

involving two rate constants, k_{ce} for the cage escape process, and $k_{bet,eff}$ a "rate constant of BET" which we characterize here as an effective or apparent rate constant, since in the light of our spin chemical findings the overall BET process is a combination of spin process and genuine BET step, and it must be described by at least two rate constants. Within the traditional view, one would probably argue that $k_{bet,eff}$ is not affected by solvent viscosity, so that the variation of η_{ce} uniquely reflects the viscosity dependence of k_{ce} since for small η_{ce} the denominator of eq.(1) must be largely determined by $k_{bet,eff}$. This interpretation seems to receive support from the parallelity of k_q , k_{rec} and η_{ce} . However, as will be shown in the following, this simple interpretation would, in fact, miss the most spectacular features in the solvent viscosity dependence of the primary radical pair kinetics.

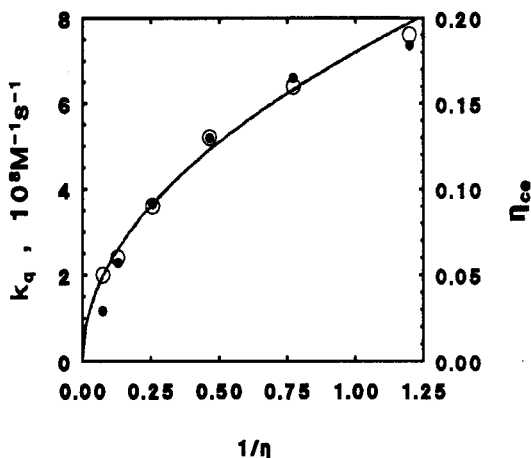


Fig. 1 Viscosity dependence of k_q (filled circles) and η_{ce} (open circles).

The additional information to resolve the overall BET process into the spin process and the true BET step and, furthermore, to obtain the absolute values of the rate constants of the processes in the primary radical ion pair ($\text{Ru}(\text{bpy})_3^{3+ \cdot}$.. $\text{MV}^{+\cdot}$), is encoded in the magnetic field dependence of η_{ce} . Signals demonstrating the magnetic field effect and the solvent effect on η_{ce} are shown in Figure 2. The magnetic field dependence of η_{ce} in the different solvents is represented in Figure 3. It is interesting to note that the way a change of solvent viscosity affects the magnetic field sensitivity of η_{ce} , depends on the strength of the magnetic field (cf. Fig. 4). At low fields, increasing the viscosity enhances the (negative) magnetic field effect, but at higher viscosities this trend is reversed, so that a maximum of the (absolute value of the) field effect is observed as a function of solvent viscosity. Towards higher fields, the viscosity value of the maximum effect decreases until, at the highest field applied (3.3 Tesla), a maximum

is not any more observed within the viscosity range investigated.

The magnetic field dependences observed in the various solvents can be quantitatively accounted for by our spin chemical mechanism. This is demonstrated by the theoretical curves in Figure 3 obtained by suitably adapting the three kinetic parameters k_{ce} , k_{bet} , and τ_s . (For details of the calculations cf. refs. (6,8)). It should be noted that, in addition to yielding a good theoretical fit to the experimental magnetic field dependence, the assigned sets of parameter values are subject to the constraint that they must also yield the correct absolute value measured for the cage escape efficiency η_{ce} . Thereby, fitting the

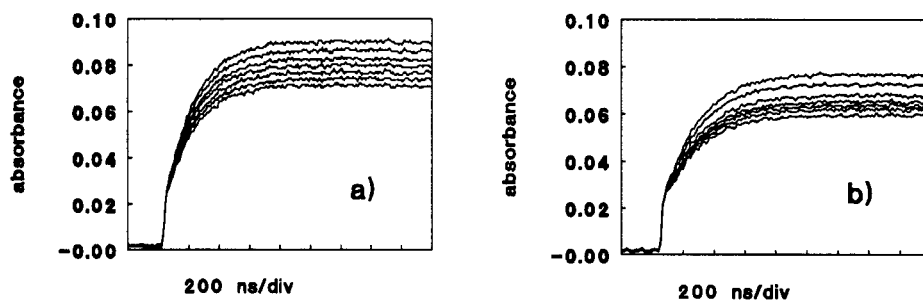


Fig. 2 Laser flash induced transient absorption signals observed at 395 nm, the main absorption band of $\text{MV}^{+\cdot}$, in solutions with 0% EGLY (a) and 20% EGLY (b) at different fields. Field values from above: are 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.2 T. The concentrations were 2×10^{-5} M for $\text{Ru}(\text{bpy})_3^{2+}$ and 5×10^{-3} M for $\text{MV}^{+\cdot}$. The absorbance plateau reached at the end of each signal trace is proportional to η_{ce} .

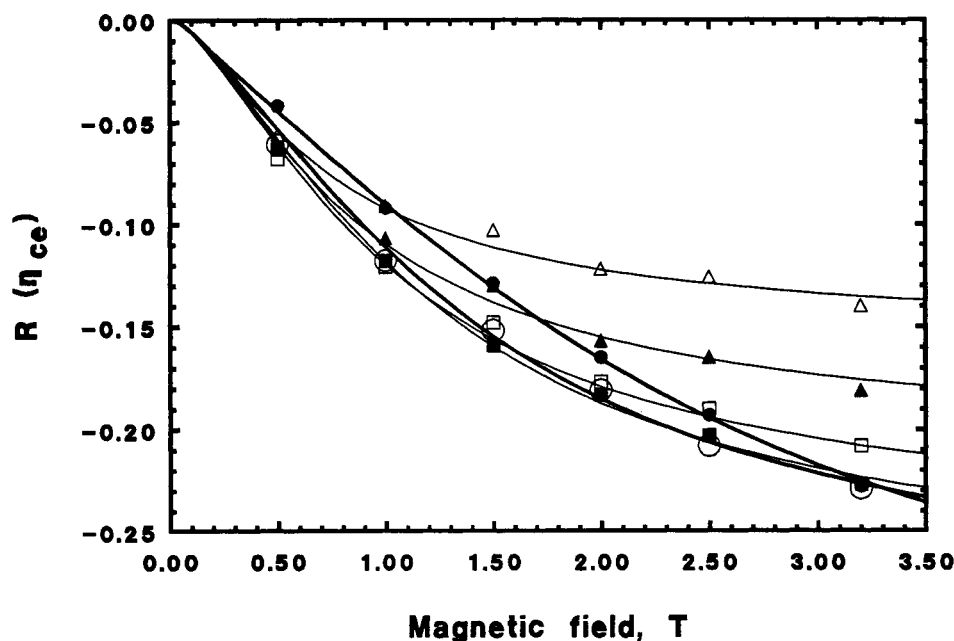


Fig 3. Relative magnetic field dependence $R(B) = (\eta_{ce}(B) - \eta_{ce}(0))/\eta_{ce}(0)$ for different solvent mixtures. The percentage of EGLY (cf. Table 1) is: ● 0%, ○ 20%, ■ 40%, □ 60%, ▲ 80%, △ 95%. The lines shown result from theoretical simulations of the magnetic field effect.

magnetic field dependence curves becomes a two-variant parameter fit problem yielding stable solutions with a reliability for k_{ce} and τ_s of $\pm 20\%$ and of $\pm 40\%$ for k_{bet} in the final result. As recently shown with our experiments in the field range up to 17.5 T carried out at a high magnetic field laboratory (7) extension of the field range to observe the saturation limit, would improve the reliability of the fits. However, the solvent effects on k_{ce} and k_{bet} we are dealing with here, are so pronounced that the accuracy of the present results derived from the 0 - 3.3 T range still provide a safe basis for our conclusions.

The values determined as a function of solvent viscosity for the rate parameters k_{ce} , k_{bet} , and τ_s are listed in Table 1. While the value of the spin relaxation time at the Ru-centre changes by less than a factor of 2 through the solvent series, the changes of k_{ce} and of k_{bet} are very pronounced with an overall decrease by a factor of 35 (k_{ce}) and 17 (k_{bet}), respectively.

As is shown in Figure 5 the viscosity dependence of k_{ce} is approximately linear with $1/\eta$, although it must be noted that the data point for the lowest viscosity, viz. the EGLY free solution, considerably exceeds the value expected for the respective correlation line. The linear variation of k_{ce} versus $1/\eta$ clearly differs from that of other diffusion dependent processes in the system (cf. k_q , k_{rec}) where two particles have to approach each other from the bulk. The rate constant k_{bet} for the process of spin-allowed

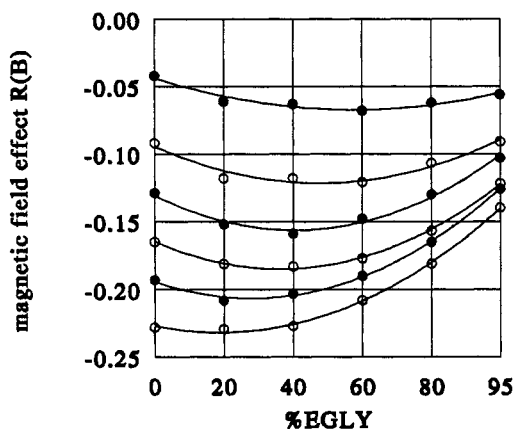


Fig. 4 Magnetic field effect $R(B)$ on η_{ce} (for definition cf. Fig. 3) plotted as a function of solvent composition. The curves from above are for magnetic fields of 0.5, 1.0, 1.5, 2.0, 2.5, 3.2 T. The lines are fitted to 2nd order polynomials drawn to aid the viewer.

BET in the primary radical ion pair ($\text{Ru}(\text{bpy})_3^{3+}\cdot\text{MV}^+\cdot$). follows an approximate square root dependence ($\eta^{-0.65}$) although in this case, too, the data point for $\text{H}_2\text{O}/\text{ACN}$ is located significantly above the correlation line. In the remainder of this paper we will focus on the possible origin of the strong variation of k_{bet} in the solvent series investigated.

In classical Marcus theory of nonadiabatic electron transfer, the rate constant k_{bet} is expressed as (11):

$$k_{\text{bet}} = \frac{2\pi}{\hbar} \frac{1}{\sqrt{4\pi\lambda k_{\text{B}}T}} V^2 \exp\left(\frac{-\Delta G_{\text{bet}}^{\ddagger}}{k_{\text{B}}T}\right) \quad (2)$$

with V the electronic coupling matrix element, λ the reorganization energy composed of the contributions of solvent polarization (λ_{out}) and internal vibrations (λ_{in}), and $\Delta G_{\text{bet}}^{\ddagger}$ the activation free enthalpy related to the standard reaction free enthalpy ΔG_{bet}^0 by

$$\Delta G_{\text{bet}}^{\ddagger} = \frac{(\Delta G_{\text{bet}}^0 + \lambda)^2}{4\lambda} \quad (3)$$

It seems unlikely that the present type of solvent variation causes changes in the reaction distance or in

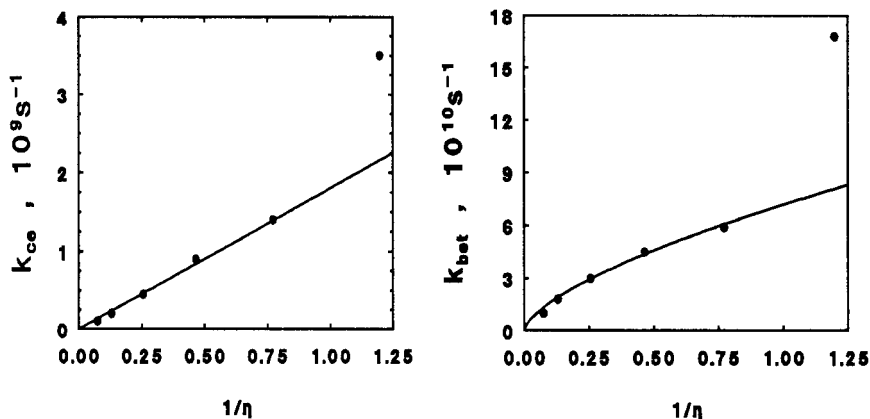


Fig. 5 Viscosity dependence of k_{ce} and k_{bet} as evaluated from the magnetic field dependence of the cage escape efficiency η_{ce} , with η^{-1} and $\eta^{-0.65}$ regression lines for k_{ce} and k_{bet} , respectively.

the internal vibrations of the reactants or products. Hence we discard changes of V and λ_{in} as possible reasons for the observed solvent effect on k_{bet} . On the other hand, since there is some change in solvent polarity, changes in λ_{out} and ΔG_{bet}^0 must be considered in more detail.

The solvent polarity effect on ΔG_{bet}^0 may be estimated on the basis of the Born equation (12) to be on the order of

$$\Delta G_{\text{bet}}^0(\epsilon_2) - \Delta G_{\text{bet}}^0(\epsilon_1) = \frac{e_0^2}{r_{12}} \left(\frac{1}{\epsilon_1} - \frac{1}{\epsilon_2} \right) \quad (4)$$

where ϵ_1 and ϵ_2 are the static dielectric constants of solvents 1 and 2, respectively, and r_{12} is the reaction distance in the radical ion pair. Using $r_{12} \approx 10 \text{ \AA}$, this expression predicts that in Egly ΔG_{bet}^0 is by 0.012 eV more negative than in the $\text{H}_2\text{O}/\text{ACN}$ mixture.

For assessing the probable change in λ we may apply the following equation derived by Marcus (11):

$$\lambda_{\text{out}} = e_0^2 \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r_{12}} \right) \left(\frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon_{\text{s}}} \right) \quad (5)$$

with a_1 and a_2 the radii of the two reactants and ϵ_{op} the dielectric constant in the optical frequency range. Using $a_1 = 6 \text{ \AA}$ for the Ru complex and $a_2 = 4 \text{ \AA}$ for MV⁺⁺, a decrease of 0.14 eV is expected for λ between H₂O/ACN and EGLY. In order to calculate the kinetic effects of the changes in λ and ΔG_{bet}^0 according to eq.(3), the absolute values of λ and ΔG_{bet}^0 must be known. For ΔG_{bet}^0 a value of -1.70 eV as previously assessed for ACN (5) can be used. For λ a value of 1.3 eV will be applied, which can be derived from the ΔG_{bet}^0 dependence of k_{bet} in a series of Ru(bpy)₃²⁺-type complexes (8). This value seems reasonable because, from eq.(3), a value of ca 1.0 eV is obtained for λ_{out} and 0.3 eV is acceptable for the contribution of λ_{in} .

Using the specified values for λ and ΔG_{bet}^0 and their solvent related variation estimated above, we can conclude that the polarity effect on $\Delta G_{\text{bet}}^\ddagger$ amounts to about 0.027 eV corresponding to a decrease of k_{bet} by a factor of 2.9 from H₂O/ACN to EGLY. Thus, since the observed reduction of k_{bet} amounts to a factor of 17, it is clear that a change of solvent polarity cannot be considered the main reason for the observed solvent effect on k_{bet} .

Therefore, finally, we have to consider whether the solvent effect observed here could be a dynamic one, with the dielectric relaxation of the solvent determining the BET kinetics (13,14). The combined kinetic effects of activated nuclear tunneling and solvent relaxation are conveniently expressed by a rate constant (13)

$$k_{\text{bet}} = \left(\frac{1}{k_{\text{bet}}^0} + \frac{1}{k_l} \right)^{-1} \quad (6)$$

where k_{bet}^0 , obeying eq.(2), represents the rate constant in the case of infinitely fast solvent relaxation and k_l is the rate constant if the process is exclusively controlled by solvent relaxation. It can be calculated according to (13)

$$k_l = \sqrt{\frac{\lambda}{16\pi k_B T}} \frac{1}{\tau_l} \exp\left(\frac{-\Delta G_{\text{bet}}^\ddagger}{k_B T} \right) \quad (7)$$

Here τ_l is the longitudinal dielectric relaxation time of the solvent. For H₂O and ACN values of τ_l between 0.2 and 0.5 ps have been reported (13, 14). Using for a H₂O/ACN mixture an average value of 0.3 ps, and the values of λ (1.3 eV) and ΔG_{bet}^0 (-1.7 eV) given above, eq. (7) yields k_l (H₂O/ACN) $\approx 1 \times 10^{12} \text{ s}^{-1}$. This value is several times larger than the observed value of k_{bet} in this solvent implying that in H₂O/ACN the rate constant of electron transfer is approximately independent of solvent dynamics. In fact, inserting the values of k_l and k_{bet} in eq. (6) and solving for k_{bet}^0 , yields k_{bet}^0 (H₂O/ACN) = $2 \times 10^{11} \text{ s}^{-1}$, a value close to that of k_{bet} . If it is assumed now, that k_{bet}^0 is constant through the series of solvents (which above has been shown to be the case within a factor of about 3), using eqs. (6) and (7) we can determine k_l and τ_l for the EGLY mixtures from the value of k_{bet} , evaluated from the magnetic field effect. The resulting τ_l -values thus obtained are listed in Table 1. Although, at present, we have no direct experimental knowledge of τ_l for the solvent mixtures investigated here, our values ranging from 3.6 to 28.6 ps can be considered as of a very reasonable order of magnitude. For comparison, the τ_l values for methanol and propanol range around 6 ps and 33 ps, respectively (cf. ref. 13). For neat EGLY a double-Debye type dielectric relaxation has been observed with relaxation times of $\tau_{l,1} = 26 \text{ ps}$ and $\tau_{l,2} = 5.2 \text{ ps}$ (15,16). Thus our kinetic analysis strongly supports the conclusion that in the EGLY mixtures the (spin-allowed) BET in the (Ru(bpy)₃³⁺...MV⁺•) RIP is controlled by solvent dynamics. It must be emphasized that a neglect of the kinetic role of spin processes in the overall BET scheme, i.e. determining the "effective" rate constant of BET according to eq. (1) leads to values of $k_{\text{bet,eff}}$ (cf. Table 1) about one order of magnitude lower than for k_{bet} . On the basis of these $k_{\text{bet,eff}}$ values it would not have been possible to establish a relation with solvent relaxation dynamics because they are lower than reasonably expected for k_l values. These arguments emphasize how important it is that the spin processes are taken into account in order to arrive at a physically consistent interpretation.

As a final comment, we note that, although we believe that our kinetic treatment regarding the combination of three processes, viz. spin relaxation, solvent dynamics and BET, has led to at least qualitatively correct conclusions, the applicability of eq.(6), which in effect clamps together solvent dynamics and electron transfer (nuclear tunneling) into one formal process, should be investigated in more depth. In a more rigorous treatment all three processes, i.e. spin conversion, electron transfer through nuclear tunneling and dielectric solvent relaxation, should be dealt with on the same footing by integrating them into a suitable coupled transport equation for the spin density matrix, or at least the populations of the RIP spin substates, in the space of the relevant solvent coordinates.

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