

# Photoelectron transfer from excited-state ruthenium(II) tris(bipyridyl) to methylviologen in an ionic liquid

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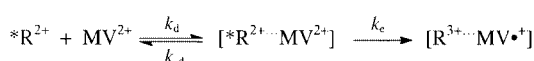
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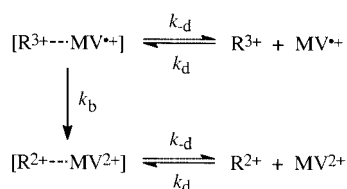
The temperature dependence of bimolecular rate constant and product cage escape yields for the photoelectron transfer reaction between  $[\text{Ru}(\text{bpy})_3]^{2+}$  and  $\text{MV}^{2+}$  in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate is reported.

Ionic liquids have been the subject of considerable interest in recent years. Potential applications include battery electrolytes,<sup>1</sup> solvents for homogeneous catalysis or other organic reactions,<sup>2</sup> novel extraction solvents<sup>3</sup> and liquid crystals.<sup>4</sup> The interest is stimulated in particular by their potential application as 'green' solvents in industrial processes.<sup>5</sup> However, there is very little quantitative information regarding their influences on chemical reactions. To date there are also only three papers that describe the use of ionic liquids as solvents for photochemical reactions.<sup>6</sup>

The simplest of all chemical reactions is electron transfer; this type of process occurred in the photochemical systems so far investigated in ionic liquids.<sup>6</sup> We decided to start a quantitative examination of the influence of ionic liquids on reaction rates in one of the most thoroughly investigated of photoinduced electron transfer systems: the ruthenium tris(4,4'-bipyridyl)/methylviologen ( $[\text{Ru}(\text{bpy})_3]^{2+}/\text{MV}^{2+}$ ) couple. The effects of the medium on this reaction have been studied extensively with variation in temperature, solvent, pH and ionic strength.<sup>7</sup> These results may be summarised with reference to Schemes 1 and 2.



Scheme 1



Scheme 2

First there is the forward electron transfer step (Scheme 1) involving the reaction between the photoexcited  $[\text{Ru}(\text{bpy})_3]^{2+}$ ,  ${}^*R^{2+}$ , and methylviologen,  $\text{MV}^{2+}$ , forming an encounter complex/excplex  $[{}^*R^{2+}\cdots MV^{2+}]$ . This occurs with a bimolecular rate constant corresponding to diffusion control,  $k_d$ . Once formed,  $[{}^*R^{2+}\cdots MV^{2+}]$  can either regenerate reactants with a unimolecular rate constant  $k_{-d}$ , or electron transfer may occur from  ${}^*R^{2+}$  to  $\text{MV}^{2+}$  with a rate constant  $k_e$ . The composite bimolecular rate constant for the overall luminescence quenching reaction,  $k_q$ , is given by eqn. (1)

$$k_q = k_d k_e / (k_{-d} + k_e) \quad (1)$$

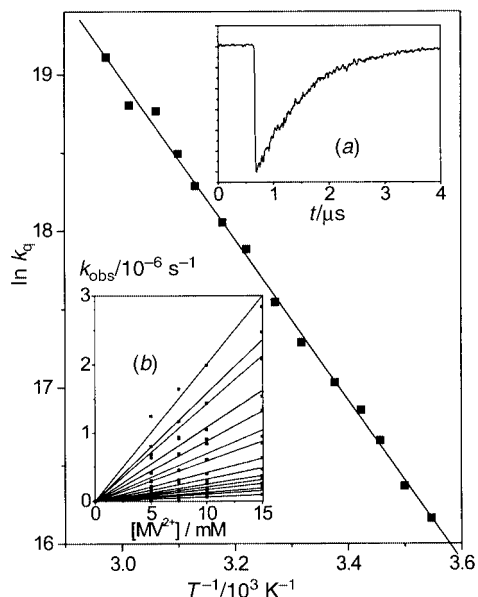
After forward electron transfer has occurred within the encounter complex, there are two competing reaction pathways as summarised in Scheme 2.

Back electron transfer within the  $[R^{3+}\cdots MV^{+}]$  cage, with a rate constant  $k_b$ , competes with diffusion apart of  $R^{3+}$  and  $MV^{+}$ , which occurs with a rate constant  $k_{-d}$ . The cage escape efficiency,  $\eta_{ce}$ , is given by eqn. (2)

$$\eta_{ce} = k_{-d} / (k_b + k_{-d}) \quad (2)$$

This photochemical system has a number of features that could be influenced by a purely ionic environment. It has previously been shown that ion pairing of the encounter complexes with a variety of solvated anions in aqueous solution increases  $k_q$  and decreases  $\eta_{ce}$ .<sup>8</sup> In an ionic liquid, there is the question as to the extent to which solvent anions will reduce electrostatic repulsion between the two reactant cations *via* a charge screening effect on formation of an encounter complex. Such effects may also reduce  $k_{-d}$ . Furthermore,  $k_b$  could be affected by alterations in electronic coupling between caged donor/acceptor pairs, or changes in  $\Delta G$  and solvent reorganisation energy. A combination of these effects would be expected to result in significantly different  $k_q$  and  $\eta_{ce}$  values in ionic liquids.

We have examined the temperature dependence of  $k_q$  and  $\eta_{ce}$  in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ( $[\text{bmim}][\text{PF}_6]$ ) using laser flash photolysis methods.<sup>9</sup> The value of  $k_q$  was determined from plots of the first order rate constant for the decay of  ${}^*R^{2+}$ ,  $k_{\text{obs}}$ , as a function of  $\text{MV}^{2+}$  concentration at a series of temperatures over the range 6–70 °C. The concentrations of  $\text{MV}^{2+}$  employed ranged from 5 to 15 mM. The results are shown in Fig. 1 together with the resulting Arrhenius plot. The Arrhenius behaviour fits the equation  $\ln k_q = 33.98 (\pm 1.7) - 5003 (\pm 480)/T$ , giving an activation energy ( $E_a$ ) of 41.6 ( $\pm 4$ ) kJ mol<sup>-1</sup> and a pre-exponential factor of  $5.72 \times 10^{14}$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup> for the luminescence quenching reaction. At 20 °C, this corresponds to a  $k_q$  value of  $2.19 \times 10^7$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>. This should be compared with values of  $1.7 \times 10^9$  and  $2.2 \times 10^7$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup> previously recorded at this temperature in water and acetonitrile respectively.<sup>10</sup> The viscosity of  $[\text{bmim}][\text{PF}_6]$  at 20 °C is 0.330 Pa s, compared with 0.001 and 0.00036 Pa s for water and acetonitrile, respectively. Given the high viscosity of  $[\text{bmim}][\text{PF}_6]$ , we would anticipate that this reaction becomes diffusion controlled, *i.e.*  $k_e \gg k_{-d}$ , and therefore  $k_q = k_d$ . To this end, we determined an  $E_a$  for viscous flow of 37.6 kJ mol<sup>-1</sup> in  $[\text{bmim}][\text{PF}_6]$  over the temperature range 10–70 °C. Clearly,  $E_a$  for the reaction between  $\text{MV}^{2+}$  and  ${}^*R^{2+}$  is very close to that of viscous flow. Electrostatic repulsions should result in an increase in the barrier to formation of an encounter complex/excplex between two divalent cations in a typical, non-ionic solvent. This leads us to conclude that such repulsions contribute no more than *ca.* 4 kJ mol<sup>-1</sup> to our observed activation energy in  $[\text{bmim}][\text{PF}_6]$ , which is effectively our estimated error in  $E_a$ . Finally, the pre-exponential factor is extremely large for a bimolecular reaction,



**Fig. 1** Arrhenius plot for the bimolecular rate constant for the reaction between  $^*[\text{Ru}(\text{bpy})_3]^{2+}$  and  $\text{MV}^{2+}$  in  $[\text{bmim}][\text{PF}_6]$ . Insert (a)  $^*[\text{Ru}(\text{bpy})_3]^{2+}$  emission recorded at  $\lambda = 630 \text{ nm}$  ( $\lambda_{\text{ex}} = 355 \text{ nm}$ ) and  $19^\circ \text{C}$  under  $\text{N}_2$ -saturated conditions; (b) plot of  $k_{\text{obs}}$  as a function of  $[\text{MV}^{2+}]$  over the temperature range  $5\text{--}70^\circ \text{C}$ .

and corresponds to a value of  $\Delta S^\ddagger = 29.3 (\pm 14) \text{ J K}^{-1} \text{ mol}^{-1}$  at  $298 \text{ K}$ . Such a positive  $\Delta S^\ddagger$  value suggests a structure-breaking process involving the freeing up of solvent ions on formation of the encounter complex. This in turn suggests that the solvent itself is a significantly ordered environment, as has previously been indicated from NMR studies on related ionic liquid systems.<sup>11</sup> We are currently investigating the influence of solute charges on diffusion-controlled reaction rates within ionic liquids and will report our results in due course.

Values of  $\eta_{\text{ce}}$  were calculated by measuring the intensity of the signal observed for  $\text{MV}^{+}$  at  $605 \text{ nm}$  relative to that of  $^*\text{R}^{2+}$  at  $450 \text{ nm}$  (values previously reported in acetonitrile of  $1.37 \times 10^4$  and  $-1.0 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$  respectively were used for the difference molar absorptivities).<sup>10</sup> The rate of formation of  $\text{MV}^{+}$  was always the same as the rate of decay of  $^*\text{R}^{2+}$  fluorescence. The calculated values of  $\eta_{\text{ce}}$  range from  $0.35$  at  $25^\circ \text{C}$  to  $0.8$  at  $60^\circ \text{C}$ , compared with  $0.29$  at  $20^\circ \text{C}$  and  $0.45$  at  $65^\circ \text{C}$  in acetonitrile.<sup>10</sup> Such large values of  $\eta_{\text{ce}}$  are unexpected in a viscous ionic solvent due to the much larger  $E_a$  reducing  $k_{-d}$  in the ionic liquid with respect to that a non-viscous solvent such as acetonitrile. Previous studies have clearly shown that  $\eta_{\text{ce}}$  decreases with increasing ionic strength, primarily because of the anionic counter ions counteracting the electrostatic repulsion between  $\text{R}^{3+}$  and  $\text{MV}^{+}$  within the encounter complex. This leads to  $k_{-d}$  decreasing with respect to  $k_b$  as ionic strength increases, which in turn results in a decrease in  $\eta_{\text{ce}}$ .<sup>8</sup> Clearly, our results are in complete contrast to these earlier studies. Our assumption that the relative molar absorptivities of  $^*\text{R}^{2+}$  and  $\text{MV}^{+}$  are independent of solvent may of course be incorrect; nonetheless we do not expect such ratios to alter greatly in different solvents. For comparable cage escape yields to be observed in  $[\text{bmim}][\text{PF}_6]$  and acetonitrile at room temperature (assuming Schemes 1 and 2 are valid),  $k_b$  must decrease in the ionic liquid relative to acetonitrile in order to compensate for the lower  $k_{-d}$  value in the former solvent. Back electron transfer from  $\text{MV}^{+}$  to  $\text{R}^{3+}$  is thought to occur in the so-called Marcus inverted region.<sup>12</sup> Therefore reduction in  $k_b$  in  $[\text{bmim}][\text{PF}_6]$  with respect to acetonitrile must either be due to  $\Delta G$  becoming more negative, or else a smaller solvent reorganisation energy in  $[\text{bmim}][\text{PF}_6]$ , or a combination of both. At this stage we do not have reliable estimates of  $\Delta G$  in this solvent, nor can we reliably estimate the reorganisation energies; these are usually estimated using the dielectric continuum model. Using pyrenecarbaldehyde fluorescence as a probe of solvent di-

electric,  $\epsilon$ , we estimate  $\epsilon < 10$  for  $[\text{bmim}][\text{PF}_6]$  at  $20^\circ \text{C}$ .<sup>13</sup> It is quite possible that  $\Delta G$  is more negative and the solvent reorganisation energy is smaller in  $[\text{bmim}][\text{PF}_6]$  than acetonitrile, given such a low dielectric in the former solvent. We are currently determining the temperature dependence of  $\Delta G$  in a range of ionic liquids, and will report our results in full at a later date.

However, there may be a non-electrochemical explanation for the large  $\eta_{\text{ce}}$  values in the ionic liquid. A weak dependence of  $k_b$  on  $\Delta G$  has been reported for a number of  $[\text{Ru}(\text{diimine})_3]^{2+}/\text{MV}^{2+}$  systems;<sup>12</sup> a suggested explanation is that significant molecular reorientation is required within the solvation sphere prior to back electron transfer. In such a situation the reorientation step is rate determining and competes with diffusion apart of the products. Our results are consistent with this hypothesis: both the diffusion apart of the charge separated pair and geometric reorganisation could be expected to require significant contributions from those processes driving viscous flow. The activation energies of both  $k_{-d}$  and  $k_b$  would then be affected by  $[\text{bmim}][\text{PF}_6]$  solvation to a similar extent, and therefore cage escape yields are not greatly altered with respect to less viscous solvents such as acetonitrile.

In conclusion, we have been able to show that the photoelectron transfer reaction between  $^*\text{R}^{2+}$  and  $\text{MV}^{2+}$  in  $[\text{bmim}][\text{PF}_6]$  occurs, within experimental error, at a diffusion-controlled rate. We believe this is the first detailed report of quantified reaction kinetics in an ionic liquid, and also the first indication of the magnitude of diffusion-controlled rate constants in such media. The yield of  $\text{MV}^{+}$  is surprisingly larger than expected for such a viscous medium. We are currently investigating the influence of solvent viscosity on diffusion-controlled processes and cage escape yields with a range of ionic liquids, and will report our results in due course.

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## Notes and references

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- Experimental details:*  $[\text{bmim}][\text{PF}_6]$  was prepared according to literature procedures, and dried thoroughly under vacuum before use.<sup>3</sup> In all experiments the concentration of  $[\text{Ru}(\text{bpy})_3]^{2+}$  was  $4 \times 10^{-5} \text{ M}$ . The laser flash photolysis setup is based around a Spectron Nd-YAD laser, combined with an Applied Photophysics optical bench.
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