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Bimolecular rate constants for diffusion in ionic liquids†

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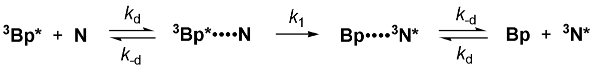
Received (in Cambridge, UK) 25th March 2002, Accepted 1st May 2002
First published as an Advance Article on the web 26th July 2002

The temperature dependence of the bimolecular rate constants for a diffusion controlled reaction involving neutral reactants have been directly determined in five commonly used ionic liquids over the temperature range 5–70 °C.

There is a paucity of reliable, quantitative information on reaction rates and rate constants in room temperature ionic liquids (RTILs) despite the recent widespread interest in developing their use as alternative solvents for a wide range of applications including synthesis,[1] biphasic catalysis,[2] electrochemistry,[3] and separations.[4] We have therefore undertaken a quantitative study of the detailed reaction mechanisms associated with examples of a bimolecular electron transfer,[5] cycloaddition and a fragmentation reaction in a variety of RTILs in order to redress this information shortage. It was obvious that we would initially have to investigate diffusion controlled processes in ionic liquids before looking at more complex bimolecular reactions. In this paper we report the results of an investigation on the temperature dependence of diffusion controlled rate constants and the solvent viscosity, η, of five structurally related RTILs based on the 1-alkyl-3-methylimidazolium cation.‡

We have selected the exothermic triplet energy transfer from triplet benzophenone (^{3}**Bp***) to naphthalene (**N**) as the probe of RTIL diffusional properties. According to Scheme 1 below, this irreversible energy transfer process can be broken down into a number of steps. Initially, an encounter complex is formed with a bimolecular rate constant k_d corresponding to diffusion control. This encounter complex can then undergo two competing unimolecular processes: reactants can be regenerated with a unimolecular rate constant k_{-d}, or irreversible energy transfer can occur with a unimolecular rate constant k_1. Finally, ^{3}**N*** and **Bp** can diffuse apart with a rate constant k_{-d}.



$$^3\mathrm{Bp}^* + \mathrm{N} \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} {}^3\mathrm{Bp}^*\cdots\mathrm{N} \xrightarrow{k_1} \mathrm{Bp}\cdots{}^3\mathrm{N}^* \underset{k_d}{\overset{k_{-d}}{\rightleftharpoons}} \mathrm{Bp} + {}^3\mathrm{N}^*$$

Scheme 1

The overall bimolecular rate constant for ^{3}**Bp*** quenching by **N** is given by $k_q = k_d\, k_1/(k_{-d} + k_1)$. Providing $k_1 \gg k_{-d}$, this expression further reduces to $k_q = k_d$, and the reaction is diffusion controlled. Confirmation that k_q values do reflect k_d should come from the comparison of the temperature dependence of k_q with the temperature dependence of viscous flow. Identical activation energies would indicate that both processes are driven by solvent viscous flow, and therefore that k_q does indeed reflect k_d.

The ^{3}**Bp***/**N** energy transfer system is extremely well characterised and is readily amenable to study by laser flash photolysis (LFP) methods.[6] Typically, an N_2 saturated 100 mM solution of **Bp** was excited using 355 nm pulsed laser excitation to form ^{3}**Bp***, the absorption of which was monitored at λ = 525 nm. The pseudo-first order rate constant for the decay of ^{3}**Bp***, k_2, was measured as a function of the concentration of **N**, and k_q determined over a temperature range of 5–70 °C from plots of k_2 *vs.* [**N**]. Arrhenius plots were then constructed and the parameters obtained are presented in Table 1 together with those for acetonitrile and toluene—solvents more typically associated with photochemical energy transfer studies. An example of the data obtained is shown in Fig. 1. In the absence of naphthalene, ^{3}**Bp*** decays *via* first order kinetics, forming a ketyl radical that is derived from a hydrogen-abstraction process involving the ionic liquid cation. We have recently commented on the unusually large temperature dependence of this process.[7] The treatment of the data reported here is not influenced by the unusual hydrogen abstraction results.

The viscosity measurements were carried out using a cone and plate viscometer on RTILs that had been dried by heating to 70 °C under vacuum for several hours. This treatment has previously been shown to provide ionic liquids that are 'operationally' dry.[8] Comparison of our viscosity data (Table 1) with those of other researchers shows good agreement.[10]

The information in Table 1 is presented in such a way as to allow the calculation of k_q and or η at any temperature between 3 and 70 °C. The error limits quoted on activation parameters are extremely conservative. Nevertheless, because of the very high activation energies determined and the consequently large errors in pre-exponential factors, we felt that limits should be quoted for ± 10% errors in E_a. Errors of no more than 5% in either η or k_q will arise if the quoted activation parameters are used to calculate these terms over the temperature range employed.

Table 1 Arrhenius parameters for the reaction between ^{3}**Bp*** and **N** in a range of ionic liquids and conventional solvents, along with Andrade parameters for the same solvents

Solvent	η^a/cP	ln η	E_η	$k_q{}^a$/dm^3 mol^{-1} s^{-1}	ln A	E_a/kJ mol^{-1}
[omim][PF_6]	690.6	−18.79	45.6	1.10×10^8	38.09	48.6
[bmim][PF_6]	257.1	−16.52	37.6	1.26×10^8	33.87	37.7
[omim][Tf_2N]	92.7	−14.62	30.3	2.96×10^8	33.23	34.0
[bmmim][Tf_2N]	97.1	−14.91	31.2	2.39×10^8	31.28	29.7
[bmim][Tf_2N]	51.5	−13.21	25.4	3.83×10^8	29.41	23.9
Acetonitrile	0.345[b]	−8.42	6.8	6.83×10^9	26.6	9.8
Toluene	0.556[b]	−8.79	9.1	8.53×10^9	26.5	9.0

[a] At 298 K; 1 cP = 10^{-3} Pa s. [b] Taken from *CRC Handbook of Chemistry and Physics*, ed. R.C. Weast, CRC Press, Inc., Boca Raton, FL, 68th edn., 1987–1988

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† Electronic supplementary information (ESI) available: Fig. S1: isokinetic plot obtained for the energy transfer reaction of ^{3}BP* and N in five ionic liquids, toluene and acetonitrile. See http://www.rsc.org/suppdata/cc/b2/b202944h/

DOI: 10.1039/b202944h

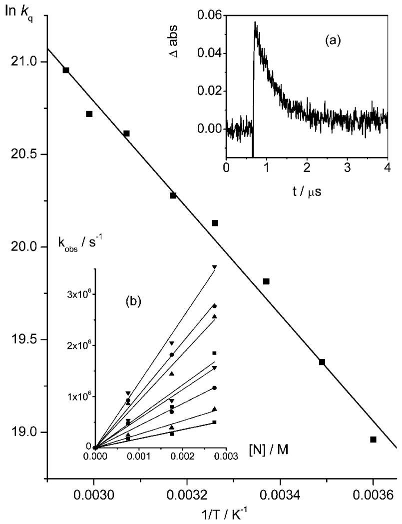

Fig. 1 An Arrhenius plot for the bimolecular rate constant k_q for triplet energy transfer from ^{3}**Bp*** to **N** in [bmim][Tf_2N]. Inset (a) shows a typical transient decay recorded at 525 nm and 33.8 °C, [**N**] = 2.73 mmol dm^{-3}; inset (b) shows plots of k_2 as a function of [**N**] over the temperature range 5–67 °C.

It is clear from Table 1 that all k_q values in RTILs have activation energies within 10% of that for viscous flow. We therefore conclude that these k_q values and the corresponding activation parameters are those of a diffusion controlled process in all RTILs employed here. It should be noted that the room temperature k_q values observed in RTILs are up to an order of magnitude *larger* than those k_d values estimated by eqn. (1)[9] which has recently been used by other workers in the field.[10]

$$k_{\text{diff}} = 8000RT/3\eta \qquad (1)$$

The only direct comparison available is that with our own result for the diffusive electron transfer quenching of excited state tris(bipyridyl)ruthenium by methylviologen in [bmim][PF_6].[5] A k_q value of 2.92×10^7 dm^3 mol^{-1} s^{-1} was determined for the electron transfer quenching process at 298 K, compared with 1.26×10^8 dm^3 mol^{-1} s^{-1} obtained in the present study. The lower k_q obtained in the former study originates from a slightly higher activation energy than that observed in the energy transfer process (41.6 *vs.* 37.7 kJ mol^{-1}, respectively). Electrostatic repulsion between the two dipositive reactants in the electron transfer process may be responsible for the slightly larger activation energy. The *A* factors are essentially identical for both reactions in this solvent. We had previously attributed the difference between E_η and E_a for the electron transfer process to experimental error[5] and are presently extending our investigation into charge effects in RTILs. The results will be reported in more detail in a full treatment of k_d values in RTILs.

The k_q values listed in Table 1 are up to an order of magnitude greater than those estimated using eqn. (1). As discussed below, this is mostly due to the very large, solvent dependent pre-exponential factors, *A*, which compensate for the large E_a values seen in RTILs. The values obtained for k_q, *A* and E_a in acetonitrile and toluene are in good agreement with those reported previously for diffusional processes in these solvents.[11]

Attention should be drawn to a striking correlation between pre-exponential factors and activation energies for both η and k_q. This correlation gives rise to isokinetic behaviour in RTILs and remains even when the conventional solvent data is included (see ESI†). Such correlations are relatively commonplace in organic chemistry, but caution is required in their interpretation. Taken at face value our data indicate that the probability of diffusional jump, given that a solvent hole has been created, is correlated with the amount of energy required to create the hole. As discussed below, this energy depends on structural aspects of both the anion and cation constituting the RTIL.

Both E_a and *A* values show a significant, systematic dependence on the identity of the anion and the nature of the alkyl substituents on the cation constituting the RTILs. For any particular cation, the E_a and E_η values are 12–15 kJ mol^{-1} higher for the [PF_6]$^-$ salts than the [Tf_2N]$^-$ salts. This is readily accounted for on the basis of the differences in charge distribution between these two anions. The more symmetrical distribution of the negative charge on [PF_6]$^-$ permits interaction with several of the surrounding cations whereas the more directional charge on [Tf_2N]$^-$ restricts the degree of interaction with the surrounding cations.[12] Consequently, the greater E_a values in the [PF_6]$^-$ salts may simply reflect the greater extent of ionic cross-linking possible in RTILs with this anion compared to [Tf_2N]$^-$. The relative magnitudes of the pre-exponential factors may also reflect this as enhanced ionic cross-linking would result in a greater effective diffusing mass. The movement of larger solvent masses requires the breaking of significant interionic bonding, whilst creating large cavities for solutes to jump into. This enhanced cross-linking may explain the apparent contradiction that the [PF_6]$^-$ salts display larger *A* factors than the [Tf_2N]$^-$ salts, despite the larger molar mass of the latter.

Finally, it is interesting to note the significant (*ca.* 10 kJ mol^{-1}) increase in E_a values associated with octyl *vs.* butyl substitution on the cation. Clearly the breakdown of van der Waals forces play a significant part in facilitating diffusion processes in these liquids despite the presence of strong electrostatic interactions between ions. The apparent strength and significance of the van der Waals interactions is supported by the very large molar mass of ionic liquids. We are currently investigating diffusional processes in RTILs in greater detail and will report our results, in full, shortly.

We would like to thank the EPSRC (Grant No. GR/M56852) for financial support and the award of a studentship (M. J. M), the Royal Society of Edinburgh for the award of a BP Research Fellowship (C. M. G.), and 3M (Minneapolis, MN) for a gift of Li(Tf_2N). We would also like to thank Mr Jim Morrow (US) for carrying out the viscosity measurements and Mr David Stirling for assistance with the laser flash photolysis measurements.

Notes and references

‡ In this study, the three cations used were 1-butyl-3-methylimidazolium ([bmim]$^+$), 1-octyl-3-methylimidazolium ([omim]$^+$), and 1-butyl-2,3-dimethylimidazolium ([bmmim]$^+$). The anions were [PF_6]$^-$ and [Tf_2N]$^-$ (Tf = CF_3SO_2). The ionic liquids were prepared following the procedure outlined in ref. 7.

1 J. D. Holbrey and K. R. Seddon, *Clean Prod. Processes*, 1999, **1**, 223; T. Welton, *Chem. Rev.*, 1999, **99**, 2071.

2 (*a*) C. M. Gordon, *Appl. Cat. A, General*, 2001, **222**, 101; (*b*) R. A. Sheldon, *Chem. Commun.*, 2001, 2399; (*c*) P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3772.

3 See *e.g.*, C. L. Hussey, in *Chemistry of Nonaqueous Solutions*, ed. G. Mamantov and A. I. Popov, VCH, Weinheim, 1994, pp. 227–276.

4 See *e.g.*, A. E. Visser, R. P. Swatloski and R. D. Rogers, *Green Chem.*, 2000, **2**, 1.

5 C. M. Gordon and A. J. McLean, *Chem. Commun.*, 2000, 1395.

6 A. A. Gorman, I. Hamblett, C. Lambert, A. Prescott and M. A. J. Rodgers, *J. Am. Chem. Soc.*, 1987, **109**, 3091.

7 M. J. Muldoon, A. J. McLean, C. M. Gordon and I. R. Dunkin, *Chem. Commun.*, 2001, 2364.

8 M. J. Muldoon, C. M. Gordon and I. R. Dunkin, *J. Chem. Soc., Perkin Trans 2*, 2001, 433.

9 J. H. Espenson, *Chemical Kinetics and Reaction Mechanisms*, McGraw-Hill, New York, 2nd edn., 1995, pp. 201–202.

10 D. Behar, C. Gonzalez and P. Neta, *J. Phys. Chem. A*, 2001, **105**, 7607.

11 J. Saltiel, P. T. Shannon, O. C. Zafirou and A. K. Uriarte, *J. Am. Chem. Soc.*, 1980, **102**, 6799.

12 J. J. Golding, D. R. MacFarlane, L. Spiccia, M. Forsyth, B. W. Skelton and A. H. White, *Chem. Commun.*, 1998, 1593.