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RESEARCH ARTICLE

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The effects of using an ionic liquid as a solvent for a reaction that proceeds through a phenonium ion

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Abstract

A unimolecular reaction that proceeds predominantly through a phenonium ion intermediate was investigated in mixtures of an ionic liquid and methanol. Varying the proportion of the ionic liquid in the reaction mixture led to an increase in the rate constant compared with methanol when very small amounts of ionic liquid were present in the reaction mixture and a decrease when higher proportions of the salt were present. Activation parameters determined for the process showed that the effect of changing the solvent composition on the rate constant was due to a key interaction between the ionic liquid and the transition state of the process, similar to other unimolecular processes. Analysis of the stereochemistry of the products demonstrated that the ionic liquid had no effect on either the ratio of the stereochemistry of the substitution products, or the ratio of the substitution and eliminations mechanisms occurring in solution.

KEYWORDS

ionic liquids, kinetics, phenonium ion, unimolecular substitution

1 | INTRODUCTION

Ionic liquids (defined as salts with a melting point below 100°C[1]) have attracted much attention in recent decades as potential alternatives to traditional molecular solvents due to properties such as low flammability, negligible vapour pressure and the potential to recycle them after use.[2] In addition, their properties (such as melting point, density and viscosity) can be fine-tuned by varying the constituent ions, leading to them being described as 'designer solvents'.[3] There has been a significant amount of work undertaken investigating their effects as solvents for many reaction types, notably substitution mechanisms[4] and pericyclic processes.[5] These studies were prompted by early observations that the outcomes of these reactions in ionic liquids (including rates of reaction and selectivity in product formation) tend to differ from those outcomes in traditional solvents.[6] Importantly, it has subsequently been demonstrated that these outcomes vary with the proportion of ionic liquid in the reaction mixture and that these solvent effects can be rationalised by understanding key interactions in solution (see Hawker and Harper[7] and references cited therein). The result of this increased understanding is the potential to use a given ionic liquid in a specific solvent composition to control reaction outcome in a rational fashion.[8]

Unimolecular nucleophilic substitution (S_N1) reactions were initially relatively unexplored in ionic liquids[9]; these studies have been expanded upon recently.[10] In general, it has been found that using a small amount of ionic liquid in a mixture with a molecular solvent leads to an increase in the rate constant of the process compared with cases when molecular solvents are used alone. It has been found however that these effects are generally dependent on the nature of the carbocation intermediate; a process involving an intermediate with a greater degree of charge delocalisation will lead to an overall increase in the rate constant no matter

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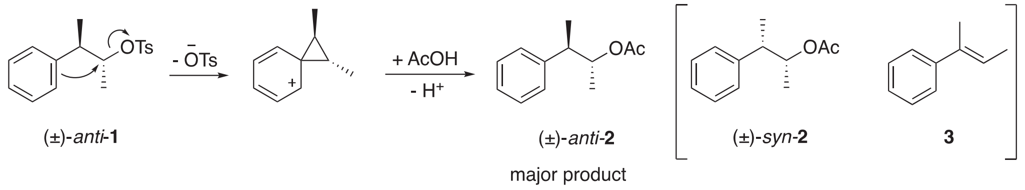

SCHEME 1 The solvolysis of the tosylate **1** in acetic acid, a major proportion of which proceeds through a phenonium ion intermediate

how much ionic liquid is present in the reaction mixture compared with the molecular solvent case,[9e,10a,b] whereas a process involving an intermediate with a more localised charge will generally lead to a decrease in the rate constant compared with the molecular solvent when a large amount of ionic liquid is present in solution.[9a,b,10c]* These results indicate that in order for ionic liquids to be used as solvents for S_N1 processes in a more predictable fashion, reactions involving intermediates that differ in nature to those considered previously need to be studied.

The solvolysis of the tosylate **1** in acetic acid was found to retain the stereochemistry in the product **2** when the *anti*-isomers of tosylate **1** were used, due to the reaction proceeding through a cyclic intermediate—a phenonium ion (Scheme 1).[11] While not the only mechanism occurring, this mechanism was the major reaction pathway, accounting for approximately 80% of the products. The other products were the isomer *syn*-**2**, which had inverted stereochemistry relative to the tosylate **1**, and the butyrene **3**, indicating the reaction was also proceeding through both traditional substitution and elimination mechanisms; the order of each additional mechanism was not investigated.

As ionic liquids have been shown to interact with the transition state of S_N1 processes, it is of interest to investigate how an ionic liquid may influence either the retention or the loss of stereochemistry for a reaction that proceeds through a phenonium ion. In addition, given that the reaction proceeds through multiple mechanisms in parallel, it is of interest to consider how an ionic liquid might affect the ratio of these mechanisms, as has been described previously.[8a,9d,10a] The overall aim of this study is therefore to investigate a reaction that proceeds through a phenonium ion intermediate using an ionic liquid as a solvent in order to identify any changes in both the stereochemistry and the major product of the process. This could, in turn, allow for ionic liquids to be used on a wider scale for this reaction type and extends the current understanding of the application of ionic liquids as solvents for organic reactions.

2 | EXPERIMENTAL

Analytical grade deuterated methanol was dried over 3 Å molecular sieves before use. Triethylamine was distilled over calcium hydride and stored over 3 Å molecular sieves at −20°C until use. The mesylate **4** was synthesised from the corresponding alcohol using methanesulfonyl chloride.[12] The alcohol was synthesised from the corresponding aldehyde by undergoing a Grignard reaction with methylmagnesium bromide.[11] The *syn*-isomers and *anti*-isomers of the alcohol were separated by converting the alcohol to the corresponding phthalate and carrying out recrystallisation using petroleum spirits (boiling point range 40°C to 60°C), followed by hydrolysis.[11] The ionic liquid **6** was synthesised by alkylating 1-methylimidazole with *n*-bromobutane to give the bromide salt, followed by a salt metathesis with lithium *bis*(trifluoromethanesulfonyl)imide.[13] The ionic liquid **6** was dried under reduced pressure (<0.3 mbar) prior to use and found to have <100 ppm of water present using Karl Fischer coulometry. Ion chromatography was used to determine the residual halide content of <5 ppm. Full synthetic procedures, characterisation of all synthesised compounds and diastereomeric ratios of substrates can be found in the Supporting Information.

Kinetic analyses were carried out in solutions containing the mesylate **4** (approximately 0.009 mol L^{-1}), triethylamine (approximately 0.02 mol L^{-1}) and the desired solvent mixture of methanol and the ionic liquid **6**. Nucleophile dependence studies were carried out using the same amounts of the electrophile **4** and triethylamine as above and different concentrations of methanol (approximately 0.1, 0.2, 0.3 and 0.4 mol L^{-1}) in formamide. Mole fraction dependence studies were performed at 42.0°C; temperature dependence studies were performed across a range of temperatures (31.7°C to 58.2°C). An aliquot (0.5 ml) of each stock solution was placed in an NMR tube and monitored using ^{1}H NMR spectroscopy either *in situ* with the spectrometer set to the desired

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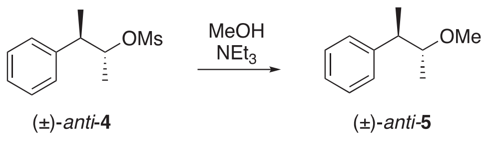
*A small amount of ionic liquid tends to lead to an increase in the rate constant but the magnitude of the increase varies with the nature of the substrate.

temperature or in a water bath set to the desired temperature with spectra taken periodically. Rate constants were obtained by following the depletion of the signal δ 3.0 corresponding to the proton adjacent to the mesylate group of the electrophile **4** over time, either to approximately 10% or 90% conversion of starting material, depending on the rate of reaction. All kinetic analyses were performed in at least triplicate. Further details of kinetic analyses, including rate constants and stock solution compositions, can be found in the Supporting Information. Activation parameters were determined by fitting obtained rate constants to the Eyring equation.[14] Diastereomeric ratios and product ratios were determined using ^{1}H NMR spectroscopy by normalising the sum of the integrals of key signals. Long relaxation times ($>5\ T_1$) were used to ensure accurate integrations of signals.

3 | RESULTS AND DISCUSSION

Initial considerations in this work involved appropriate choice of substrate for this study. Previous reports have shown the significance of interactions involving aromatic species in ionic liquids (particularly in determining solubility[15]). As such, in order to focus on the nature of the carbocation intermediate, it was deemed necessary to replace the tosylate group of reagent **1** with a leaving group with less potential for additional interactions with the ionic liquid. Initially, a bromide leaving group was considered due to its use in previous systems,[10a,c] which would allow for comparison with other studies. However, it was necessary to obtain a starting material with a high diastereomeric ratio of the *anti*-isomer in order to readily follow the proportion of the reaction proceeding through a phenonium ion intermediate; attempts to synthesise the corresponding bromide resulted in mixtures of the *anti*-isomers and *syn*-isomers that were not readily separable (see the Supporting Information for full details). Therefore, a mesylate leaving group was considered; the appropriate starting material (±)-*anti*-**4** was prepared with a diastereomeric ratio of 91:9 *anti*:*syn*. The reaction shown in Scheme 2 was therefore selected for further study.



SCHEME 2 The reaction of the mesylate *anti*-**4** in methanol to give the ether **5**, which will be the focus of this study

Initial studies found that the diastereomeric ratio of the substitution product **5** was found to be 80:20.[†] Given that the diastereomeric ratio of the starting mesylate *anti*-**4** was 91:9, if the reaction proceeded solely through a phenonium ion, the ratio of isomers would be expected to be 95.5:4.5.[‡] Therefore, there must be an additional substitution mechanism through which the reaction is proceeding. In order to identify the order of the additional substitution mechanism, nucleophile dependence studies were performed for the reaction shown in Scheme 2 by varying the concentration of methanol in formamide (Figure S3). These studies found that there was no significant change in the rate constant as the concentration of methanol was varied, indicating that the reaction proceeds exclusively through a unimolecular process[§]; this demonstrates that the substitution mechanism occurring in addition to the mechanism proceeding through a phenonium ion intermediate is a typical S_N1 mechanism. Given the diastereomeric ratio above and taking into account the loss of stereochemistry that would occur when the reaction proceeds through a typical S_N1 mechanism, the actual ratio of the two substitution mechanisms is 65:35 phenonium ion mechanism/typical S_N1 mechanism.

3.1 | Kinetic analyses

With the desired reaction selected and the mechanisms through which it proceeds confirmed, the effect of an ionic liquid on this reaction was considered. The ionic liquid 1-butyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide **6** ([bmim][N(SO_2CF_3)$_2$], Figure 1) was selected given its ease of synthesis,[13]

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FIGURE 1 The ionic liquid [bmim][N(SO_2CF_3)$_2$] **6**, which is used in this study

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[†] The elimination product **3** was also observed (approximately 15% of converted starting material **1**). This will be discussed in detail below.

[‡] A conservative estimate of the uncertainties in the NMR determination of the diastereomeric ratio in the starting material *anti*-**4** and the product **5** is ±2; the expected value here lies well outside those limits.

[§] Subtle variations in the rate constant of the nucleophile dependence studies are likely due to the change in the nature of the solvent on changing the concentration of methanol in formamide.

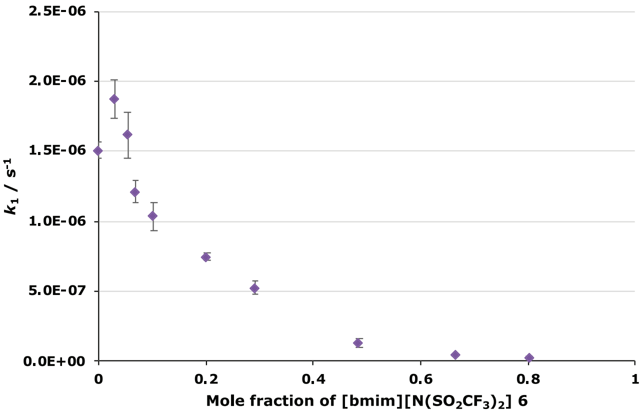

FIGURE 2 The dependence of the overall unimolecular rate constant, k_1, for the reaction of the mesylate *anti*-**4** in methanol at 42.0°C on the proportion of [bmim][$N(SO_2CF_3)_2$] **6** in the reaction mixture. Uncertainties are obtained from the standard deviation of triplicate measurements

low viscosity[16] and use in a large number of previous studies.[7]

The effects of the proportion of ionic liquid in the reaction mixture on the rate constant of the process shown in Scheme 2 were first considered; these results are shown as a mole fraction dependence plot (Figure 2). These studies show that on addition of a small amount of ionic liquid **6** to the molecular solvent, there is an increase in the rate constant, k_1, compared with the methanol case; the maximum increase is approximately 20% greater than the methanol case and is observed at χ_6 approximately 0.03.[¶] Above $\chi_6 = 0.05$, k_1 decreases below that of the methanol case, to the point where it is over a magnitude lower at χ_6 approximately 0.50. The shape of the plot shown in Figure 2 and the trend in the rate constant are similar to previous S_N1 systems where the positive charge on the intermediate is relatively localised (*i.e.*, alkyl systems[9b,10c]) as opposed to the delocalisation of the charge across aromatic rings.[9e,10a,b] In particular, the relative magnitudes of the rate constants at different mole fractions compared with the methanol case are comparable to those seen for a system containing an oxocarbenium intermediate,[10c] suggesting that a similar extent of delocalisation of the positive charge in each case leads to a comparable trend in the ionic liquid effects on the rate constant for the process. This result indicates that the effect of an ionic liquid can potentially be predicted for unimolecular substitutions where the nature of the intermediate, particularly the extent of charge delocalisation, is known.

TABLE 1 The activation enthalpy and entropy determined for the reaction of the mesylate *anti*-**4** in either methanol or a mixture of methanol and the ionic liquid [bmim][$N(SO_2CF_3)_2$] **6** at χ_6 approximately 0.20

Solvent	$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / J K^{-1} mol^{-1}
Methanol	122.6 ± 1.4	14 ± 5
[bmim][$N(SO_2CF_3)_2$] **6**	95.5 ± 2.5	-77 ± 8

Given the dependence of the rate constant on the mole fraction of ionic liquid **6** in the reaction mixture, it was of interest to determine the interactions responsible for these trends in solvent effects. Temperature-dependent kinetic analyses were used to determine the enthalpy and entropy of activation, calculated using the Eyring equation.[14] These parameters were determined for the methanol case and at χ_6 approximately 0.20. This solvent composition was selected given that the change in rate constants between the two cases was deemed large enough to observe a difference in the parameters.[#] The results are outlined in Table 1.

The activation parameters determined for the methanol case are characteristic of a unimolecular mechanism: a large enthalpy of activation is consistent with a significant degree of bond breakage and charge localisation in the transition state; likewise, the positive value of the entropy of activation is a characteristic of solvent organisation around the transition state, which overcomes any increase in disorder of the system as the mesylate group departs.[17] Comparing these values with those seen for the ionic liquid case at χ_6 approximately 0.20 shows that both the enthalpy and entropy of activation decrease on moving to the ionic liquid case. These results are indicative of the ionic liquid interacting to a greater degree than methanol with the transition state: the enthalpy of activation decreases as the transition state is more stabilised than in the methanol case; the entropy of activation decreases as the ionic liquid organises around the transition state to a greater extent than in the methanol case. Given that the rate constant decreases compared with the molecular solvent case when anything more than a little ionic liquid **6** ($\chi_6 > 0.05$) is added to the reaction mixture, it is clear that the process is entropically constrained at

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[¶] It is important to note that k_1 includes contributions from both the mechanism that proceeds through the phenonium ion and the typical S_N1 mechanism; additional contributions from elimination processes make separation of the rate contributions to those proceeding through different intermediates difficult. The relative effects of the ionic liquids on these processes will be explicitly discussed below.

[#] Previous studies have found that a small change in the rate constant is not always significant enough to observe a change in the activation parameters; hence, the solvent composition in which the maximum rate constant was observed (χ_6 approximately 0.03) was not considered here.

these higher proportions of salt **6** in the reaction mixture. That is, the decrease in the rate constant above χ_6 approximately 0.05 is due to significant ordering of the components of solution about the transition state. These solvent effects of ionic liquids are, again, similar to those seen in previously studied reactions that proceed through S_N1 mechanisms,[9c,e] particularly those where the major interactions leading to the change in the rate constant are non-specific in nature[10c] (*e.g.*, charge–charge interactions), which would likely be similar in this case. It should be noted that the exact site of interaction in the transition state has not been identified (vide infra).

3.2 | Product analyses

As mentioned, it was of interest to investigate how the ionic liquid **6** may influence the stereochemistry of the substitution product **5.** The percentage of each isomer of the substitution product was calculated across the range of solvent compositions considered for the kinetic analyses (Figure 3). These results show that there is no change in the ratio of the isomers of the ether **5** on the addition of any amount of the ionic liquid **6** to the reaction mixture (the proportion of the *anti*-**5** isomer is always 80%, with the uncertainty of the measurement). An outcome of this observation is that, as in the methanol case, the ratio of the proportion of the reaction proceeding through a phenonium ion and a typical S_N1 reaction is 65:35 for all of the solvent systems considered. As mentioned above, the reaction of the tosylate **1** proceeded through both a phenonium ion and another substitution mechanism at a ratio of 80:20; given the differences in the substrate studied in this work, and the uncertainties in the data for the proportion of each isomer of the product **5** in this case, these results show no significant variation across all mole fractions of ionic liquid **6**.

These results indicate that the interaction between the ionic liquid **6** and the transition state of this process either does not influence which substitution mechanism dominates *or* influences both to the same degree; that is, if the ionic liquid favours/disfavours the formation of the phenonium ion intermediate more so than methanol, it must also favour/disfavour the typical S_N1 mechanism to the same degree; otherwise, there would be an obvious change in the ratio of the isomers of the product **5**. Given that the overall rate constant for the process differs with the amount of ionic liquid **6** present in solution, the implication of this result is that both substitution mechanisms are affected similarly.

As the reaction also showed evidence of an elimination product **3** appearing in the methanol case, any effect of the ionic liquid on the ratio of this product to the substitution product **5** was investigated. These results are shown in Figure 4 with the value for the substitution product **5** being the sum of both *anti*-isomers and *syn*-isomers.

Similar to the case above, it is immediately clear that there is no significant change in the ratio of the substitution and elimination products as the amount of ionic liquid is varied in the reaction mixture. Although there is some degree of scatter in the data and some points lie outside of uncertainty compared with the methanol case, the lack of a clear trend and the uncertainty in the data indicates that there is no obvious change in the proportion of each mechanism through which the reaction proceeds as the ionic liquid **6** is added to the reaction mixture. These results are perhaps surprising given

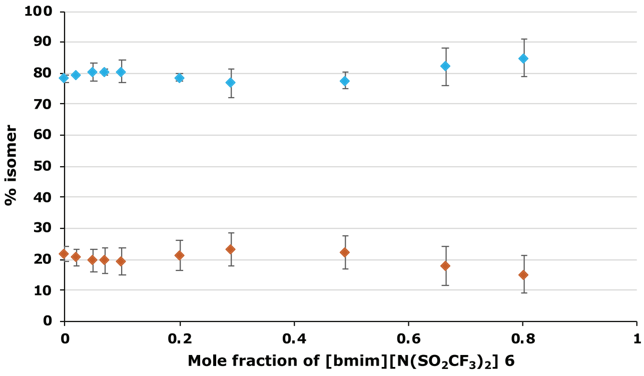

FIGURE 3 The percentage of the *anti*-isomers (◆) and *syn*-isomers (◆) of the ether **5** produced in the reaction of the mesylate *anti*-**4** in methanol in mixtures containing different proportions of $[bmim][N(SO_2CF_3)_2]$ **6**. Uncertainties are obtained from the standard deviation of triplicate measurements

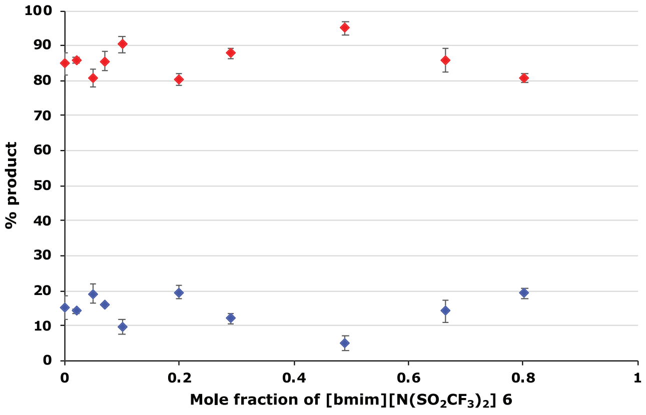

FIGURE 4 The percentage of the substitution product **5** (◆) and elimination product **3** (◆) for the reaction of the mesylate **4** in methanol in mixtures containing different proportions of $[bmim][N(SO_2CF_3)_2]$ **6**. Uncertainties are obtained from the standard deviation of triplicate measurements

previous studies that have found that changing to an ionic liquid solvent can have a significant change on the ratio of the mechanisms occurring in solution compared with a molecular solvent[8a,d,9e,10a,c]; these ratios were also shown to differ across mole fractions of ionic liquid.

Both the ratio of *anti*-isomers to *syn*-isomers of the substitution product **5** and the ratio of the substitution **5** to elimination product **3** in the methanolysis of the mesylate 4 indicate that the interactions between the ionic liquid and the transition state do not influence the mechanisms occurring in solution to any significant degree. There is the potential that these results are due to the structure of the transition state that precedes the phenonium ion intermediate, which may not allow for any change in the mechanism as the reaction proceeds. Given that there is an effect on the rate constant of the process, this outcome is interesting as it suggests that the -site(s) of the key interactions in mixtures containing the ionic liquid that affect the rate constant do not lead to a change in the mechanism. That is, the interactions responsible for affecting the rate determining step do not affect the product determining step(s).

4 | CONCLUSIONS

The work described herein has investigated the effect of using an ionic liquid as a solvent for a reaction that proceeds predominantly through a phenonium ion intermediate. Mole fraction dependence studies show that at very low proportions of the ionic liquid in the reaction mixture there was an increase in the rate constant relative to the molecular solvent case; the rate constant was then found to decrease significantly as more ionic liquid was added. Temperature dependence studies determined the activation parameters for this process and found that an interaction between the ionic liquid and the transition state was driving the changes in the rate constant compared with the molecular solvent case with the decrease being the result of an entropic cost.

These trends in both the rate constant across differing proportions of ionic liquid in the reaction mixture and the activation parameters for the process in an ionic liquid are remarkably similar to those seen in a previous case where the nature of the intermediate is comparable.[10c] This study therefore highlights the ability to be able to predict ionic liquid effects for unimolecular reactions where the nature of the intermediate is well understood. Such an outcome is important for the increased application of ionic liquids as solvents in preparative chemistry, where solvent effects must be well-defined.

Analysis of the stereochemistry of the substitution product **5** for the reaction studied here found that there was no change in the relative proportions of each substitution mechanism as the amount of ionic liquid in the reaction mixture varied. In addition, no significant change was observed in the ratio between the substitution and elimination mechanisms as ionic liquid was added to the reaction mixture. While perhaps surprising given previous cases,[8a,d,9e,10a,c] this case highlights the potential to use an ionic liquid for a reaction of a similar substrate to increase the rate constant of the process without influencing the relative proportions of each mechanism through which the reaction proceeds. As an illustrative example, in this case, a small amount of ionic liquid could be used to increase the rate of reaction without affecting the relative stereochemistry of the products. Overall, this study shows that an ionic liquid can be used to control the reaction outcome for a unimolecular process that proceeds through a phenonium ion intermediate.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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