Effect of ionic liquids in unimolecular solvolysis reactions involving carbocationic intermediates

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ABSTRACT

Solvolysis studies of pivaloyl triflate were performed using ionic liquid/methanol solvent mixtures. The rearranged carbocation intermediate reacts with methanol via nucleophilic attack or elimination of a proton. Relative amounts of products were determined through ^{1}H NMR analysis. For most ionic liquids, increasing the ionic liquid:methanol ratio leads to increased yields of elimination product. Product ratios vary based on Kamlet–Taft solvatochromic parameters of hydrogen bond donating and accepting ability of the ionic liquid.

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Introduction

Many studies have been undertaken of late in an effort to understand nucleophilic substitution reactions in ionic liquids (ILs) and how they vary from similar reactions in 'traditional' organic solvents. Most of these studies to date have focused on bimolecular substitution reactions and have found that these reactions occur more rapidly and generate smaller amounts of undesirable elimination products in ionic liquids than in traditional solvents.[1–3] Welton has demonstrated that these results are actually expected based on Hughes–Ingold rules of solvent effects, specifically hydrogen-bond accepting and donating ability of the ionic liquid anion and cation, respectively.[4–7] In fact, very few examples of novel 'IL effects' have been convincingly demonstrated in the literature.[8,9] Excellent reviews of this topic have been published by Lancaster[10] and Hallett & Welton.[11]

A marked gap in the study of these reactions is in the area of unimolecular solvolysis reactions, that is, those involving carbocationic intermediates. We have previously shown that ionic liquids do support carbocation formation.[12] It should also be noted that the ionic liquid solvents investigated do not react with the carbocation intermediate in such reactions as the anions used are non-nucleophilic. Rather, the carbocation reacts either with cosolvent, or with trace amounts of water present to form both substitution and elimination products.

Some studies of unimolecular solvolysis reactions in ionic liquids have been reported,[13,14] but these reactions are still extremely understudied. Such studies have focused on reaction rates and have limited their focus to a single ionic liquid. These studies have also taken great care in their choice of substrates in order to exclude the elimination pathway. For the present study, we have chosen to analyze product ratios in order to study the competition between substitution and elimination in unimolecular solvolyses. Indeed to our knowledge, this is the first study to involve a system where the ability to observe this competition is possible. We also chose to investigate a variety of ionic liquids to better understand the effect that variations in ionic liquids have on these reactions.
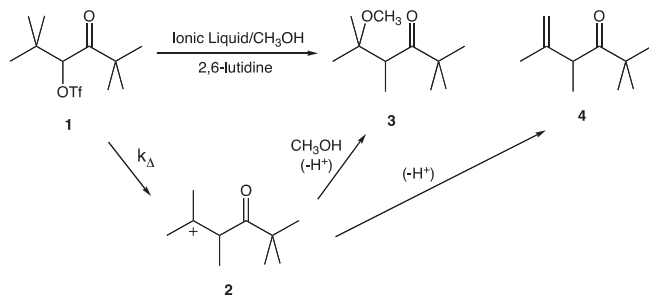
Our group recently undertook a preliminary study of the effect of ionic liquids on unimolecular substitution reactions.[15] In this study we discovered that increasing the concentration of the ionic liquid 1-butyl-3-methylimidazolium bistrifluoromethanesulfonamide ([C$_4$C$_1$im][NTf$_2$]) appeared to increase the favorability of an elimination pathway versus a substitution pathway. The present study focuses on a single cosolvent, methanol, while investigating the effects of different ionic liquids on this solvolysis reaction.

Results and discussion

The solvolysis reaction under investigation is the methanolysis of α-keto triflate **1**. 2,6-Lutidine is used as a non-nucleophilic buffering agent to absorb the acid produced in the reaction. Ionization of **1** occurs concurrently with a methyl shift, a k_Δ process, to give rearranged carbocation **2**. Once formed, this carbocation can then either undergo attack by methanol to give substitution product **3** or deprotonation by methanol to give elimination product **4** (Scheme 1).[16] This reaction is known to proceed by a similar

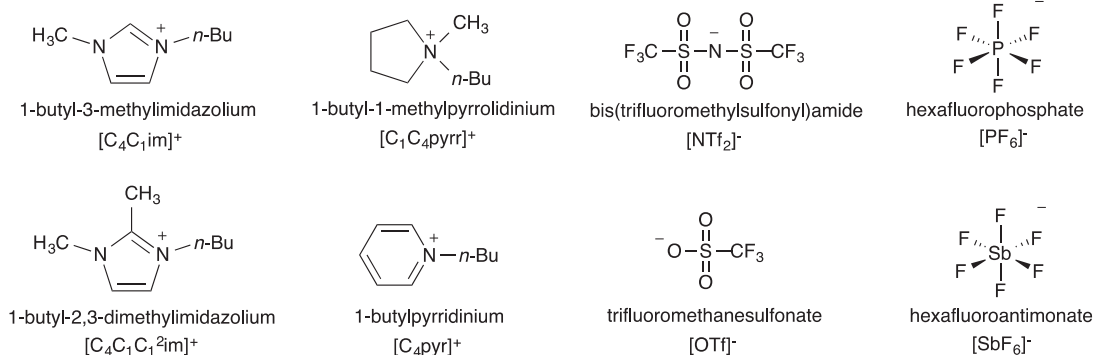* Corresponding author. Tel.: +1 510 430 2085.
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Scheme 1. Mechanism for solvolysis of triflate **1**.

Table 1
Kamlet–Taft solvatochromic parameters of ionic liquids and methanol, and product ratio data[11,17,18]

Solvent	α	β	π^*	Slope[a] (error)	R value
CH$_3$OH	0.93	0.62	0.60	–	–
[C$_4$C$_1$im][SbF$_6$]	0.64	0.15	1.04	−14.66 (7.71)	0.647
[C$_4$C$_1$im][PF$_6$]	0.63	0.21	1.03	12.35 (2.33)	0.882
[C$_4$C$_1$im][NTf$_2$]	0.61	0.24	0.98	19.08 (8.48)	0.622
[C$_4$C$_1$im][OTf]	0.63	0.46	1.01	36.12 (3.76)	0.964
[C$_4$C$_1$C$_1^2$im][NTf$_2$]	0.38	0.24	1.01	37.78 (1.60)	0.994
[C$_4$C$_1$pyrr][NTf$_2$]	0.43	0.25	0.95	37.09 (2.34)	0.983
[C$_4$pyr][NTf$_2$]	0.51	0.28	0.98	27.82 (4.09)	0.915
[C$_4$C$_1$im][NTf$_2$]	0.61	0.24	0.98	19.08 (8.48)	0.622

[a] Slope corresponds to rate of increase of product **4** with change in ionic liquid concentration.

mechanism in 'pure' ionic liquid solvents; the only difference being that the carbocation reacts with trace amounts of water present.[12] Because the rate-limiting step of unimolecular solvolysis reactions is carbocation formation, we chose not to study the reaction kinetics, but rather reaction product ratios. Reaction kinetics can only provide information about the ionization step of the mechanism, with any differences in reaction rates being attributable mostly to differences in solvent polarity. Alternatively, product ratios provide information about the second step in the mechanism: both about the reactivity of the methanol cosolvent (as affected by the ionic liquid) and the environment of the carbocationic intermediate.

Ionic liquids are unique among solvents in that their properties can be fine-tuned by careful selection of the cationic and anionic components. We chose to take advantage of this feature by investigating two series of ionic liquids: one series in which the cation remains constant and the anion is varied, and one series in which the anion remains constant and the cation is varied. The structures of the cationic and anionic components of the ionic liquids used for this study, along with their common abbreviations, are shown below.

each of the ionic liquids studied has both smaller α and β values than the methanol cosolvent. Adding ionic liquid to the methanolysis therefore reduces the overall α and β values of the solvent system, though some studies have shown that this does not happen in a linear fashion.[19–21]

Because trace amounts of water present in an ionic liquid could potentially give undesirable side products,[12] great care was taken to ensure that each of the ionic liquids and the methanol be extremely dry. Methanolysis of **1** was carried out in the presence of each of these ionic liquids at various concentrations. For each ionic liquid, the mole fraction was varied from near zero to approximately 0.5. It should be noted that in most cases, mole fractions of greater than 0.5 were unable to be tested due to the large difference in molecular weight between methanol and the ionic liquids. It simply is not feasible to weigh out milligrams of methanol to the exclusion of water. It should also be noted that reactions were not carried out in pure ionic liquid as the ionic liquid components do not react with the carbocation intermediate.[12] Reaction solutions were worked up and crude product mixtures analyzed by ¹H

The seven ionic liquids chosen for this study are listed in Table 1 along with the Kamlet–Taft solvatochromic parameters of hydrogen bond donating and accepting ability, α and β, respectively, and dipolarity/polarizability, π^*.[17,18] Though π^* values are consistently high, there is not much variation between individual ionic liquids. The α and β values, however, differ widely across ionic liquids. In any given ionic liquid, the cationic component is primarily responsible for the hydrogen bond donating ability (α) of the solvent system. Conversely, the anion is primarily responsible for the hydrogen bond accepting ability (β) of the solvent system. Indeed, ionic liquids with the same cationic component show only very small variations in α values ($\leqslant$5%) and ionic liquids with the same anionic component show only small variations in β values ($\leqslant$15%) (Table 1). Varying just one component of the ionic liquid therefore allows observation of the individual effects of each of these properties on the reaction in question. It should be noted that

NMR spectroscopy. Product ratios were determined by integration of the ¹H NMR signals corresponding to the α-carbonyl protons in **3** and **4**.

Figure 1 shows a typical graph of the percentage of elimination product, **4**, versus mole fraction of ionic liquid solvent (in this case, [C$_4$C$_1$C$_1^2$im][NTf$_2$]). Note that an increase in the ionic liquid cosolvent results in an increase in elimination product. This result is consistent for almost all of the ionic liquids studied. The exception, [C$_4$C$_1$im][SbF$_6$], will be discussed shortly. Slope and correlation data for the remaining ionic liquids are found in Table 1. Linear correlation of the data provides a good fit in each case with R values averaging 0.85 and most error values under 20%.

Two distinct observations are made from the data: (1) nearly all plots have positive slopes, meaning that for most ionic liquids, increasing the amount of ionic liquid increases the amount of elimination product **4**, and (2) for a series of ionic liquids in which one