

Novel Nucleophilic Trapping Reactions of Carbocations in Ionic Liquids

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Our current project is an investigation of the effect of ionic liquids on solute nucleophilicity. We are studying the solvolysis of pivaloyl triflate in binary solvent systems of ionic liquid and various organic alcohols. It is well known that pivaloyl triflate **1** solvolyzes via a k_A process to yield rearranged products **2** and **3**. Upon formation of the rearranged carbocation, **4**, the solute acts either as a nucleophile or a base forming two potential products: substitution and elimination. We are working to determine whether the presence of ionic liquid would affect the product ratio. The solvolysis reaction was carried out in solvent mixtures of bmimNTf₂ with a variety of organic alcohols, "HOS". It was found in all cases that as the percentage of alcohol co-solvent was decreased, more elimination product was observed. Or, stated differently, more ionic liquid led to more elimination product. Our studies suggest that the alcohol co-solvent becomes more basic (rather than more nucleophilic) in the presence of ionic liquid. This would appear to challenge the claim that ionic liquids increase the nucleophilicity of solutes. These studies are improving our understanding of both ionic liquids and solute/solvent interactions.

