Towards an understanding of organic processes in ionic liquids

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In the move towards so-called 'green' or 'sustainable chemistry', there has been much investigation of chemical processes in ionic liquids. However, differences in the rates and selectivities of these processes are often observed when compared to the corresponding reactions in molecular solvents and there are only limited reports detailing the origins of the changes. This contrasts with the extensive understanding of the effect on reaction outcome on changing from one molecular solvent to another. For ionic liquids to be considered as genuine alternatives, the equivalent understanding for these solvents is required.

Initial molecular dynamics studies on the origin of the solubility of aromatic compounds in ionic liquids indicated that one feature that was being consistently overlooked in considering organic processes in ionic liquid was the significance of the interactions between the components of the ionic liquid. Since these interactions are much greater than those present in molecular solvents, as is demonstrated by the negligible vapour pressures observed, it is reasonable to consider these as having a dramatic effect on reaction outcome.

The work described in this presentation will demonstrate how these electrostatic interactions can be used to explain the outcomes of a series of representative reactions, including unimolecular substitution (Scheme 1a), mixed unimolecular/bimolecular substitution (Scheme 1b) and nitrile oxide cycloaddition (Scheme 1c), where traditional measures of solvent properties cannot.

![Scheme 1](image)

Scheme 1: Representative reactions which have been investigated in ionic liquid. (a) Unimolecular substitution of a linalool derivative. (b) Menschutkin reaction of substituted benzyl bromides. (c) Nitrile oxide cycloaddition.