Quantifying nucleofugality in ionic liquids – extending the range of nucleofuges

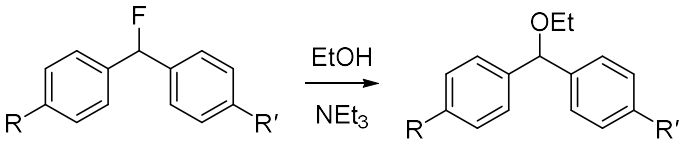
William J. Gaul,[a,*] Ronald S. Haines,[a] and Jason B. Harper[a]

[a]*School of Chemistry, University of New South Wales, Sydney, Australia*
**w.gaul@student.unsw.edu.au*

Ionic liquids have the potential to solve issues associated with current molecular solvents (volatility, flammability and toxicity).[1] However, these ionic solvents often change reaction outcomes, especially rate and selectivity, when compared to molecular solvents and in an unpredictable fashion.[2] Much work has been undertaken and it is now understood that these effects vary based on the nature of the ions present and the proportion of ionic liquid in the mixture, with these effects being explainable via microscopic interactions in solution.[3]

The understanding of solvent effects to this point has been qualitative. Initial attempts to quantify reaction outcomes was case specific and non-transferable.[4] More recently, the nucleofugality ("leaving group ability") of a range of nucleofuges (chloride[5], bromide[6] and dimethyl sulfide[7]) has been determined in mixtures containing ionic liquids, showing that quantifying these effects is possible. Importantly, these data can be used to accurately predict reaction outcomes in ionic liquids.[8]

The work presented here covers our initial attempts to extend these studies (Scheme 1). Fluoride will be considered as a leaving group as it will allow trends in nucleofugality down a group of monatomic nucleofuges to be evaluated. This is the first time the solvolysis of a fluoride leaving group as the rate determining step has been considered in an ionic liquid, so initial qualitative data will be of interest. Comparison with data in molecular solvents and trends of solvent effects with other nucleofuges is anticipated to provide a physical origin for these effects, allowing for additional quantitative predictive power.



Scheme 1. The solvolysis process of interest in this project. Substituents R and R′ are chosen to allow reaction to be followed in a reasonable timeframe.

References

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William is currently a Ph.D. student in the Harper group at UNSW Sydney, researching ionic liquid solvent effects. Specifically, he is investigating microscopic interactions of ionic liquid components with species along the reaction coordinate of organic processes, relating observations to quantitative predictions of reaction outcomes.