

Exploring a Non-Polar Cope Rearrangement in (Polar) Ionic Liquids

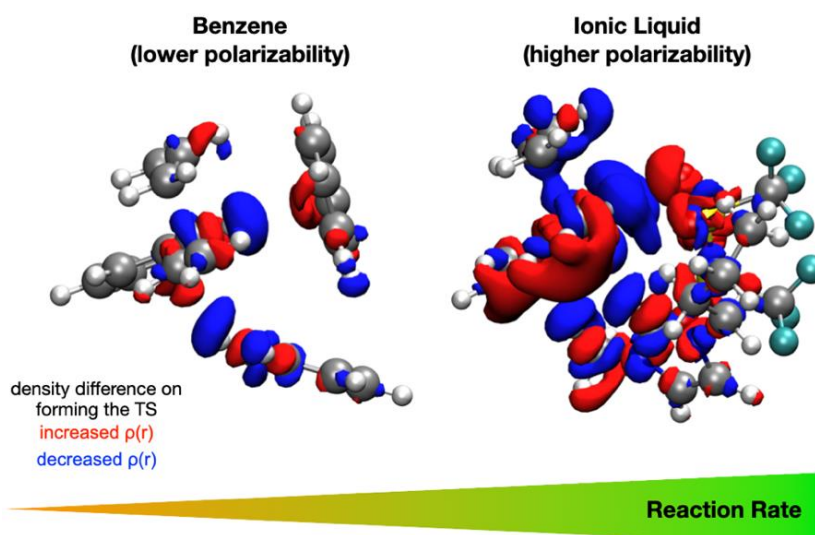
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Ionic liquids (ILs) are a novel class of solvent composed entirely of ions that are (typically) liquid below 100°C. The ions are larger and more chemically complex than traditional molten salt ions. As a group ILs exhibit a variety of properties which set them apart from traditional molecular liquids. Many ILs are non-volatile, non-flammable, conductive, have good solubility / miscibility characteristics and exhibit a high thermal stability. These characteristics make ILs re-useable, and lead to ILs being considered as green reaction solvents. However, critically, we still lack a robust molecular level understanding of how ILs impact reactivity.

The impact of ionic liquids on polar reactions is well recognised, however the impact of ILs on non-polar reactions is less well explored. Pericyclic Cope rearrangements are highly concerted, exhibit minimal charge localisation and pass through an uncharged but structurally well-defined transition state, and thus provide a good mechanism for exploring the impact of IL polarity/polarizability on chemical reactivity. Recently, a 10x rate enhancement has been observed for the Cope rearrangement of hexa-1,5-dien-3-ylbenzene in the IL 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)-imide [C₄C₁im][NTf₂] compared to benzene.^[1]

Why this non-polar Cope rearrangement is substantially accelerated within a (polar) IL is not obvious. We have undertaken a DFT based computational study of the hexa-1,5-dien-3-ylbenzene Cope rearrangement comparing molecular solvents with the IL [C₄C₁im][NTf₂].^[2] We have evaluated a volume of activation and identified two potential volume effects that could contribute to the rate enhancement. Specific solvent interactions for benzene and the IL are also explored. We find that the IL ions can form a Van der Waals pocket in which the TS sits, and that the TS electron density can be significantly more polarised for the IL. Overall, we provide a deeper molecular level insight into the impact of ILs on non-polar reactions.



[1] S. Keaveney, R. Haines, and J. Harper, *ChemPlusChem* **2017**, *82* (3), p449–457, doi 10.1002/cplu.201600585

[2] G. Smith, S. Koutsoukos, B. Lancaster, J. Becker, T. Welton and P.A. Hunt, *Phys. Chem. Chem. Phys.*, **2024**, *26*, 12453-12466, doi: 10.1039/D4CP00156G.