10th Australian Symposium on Ionic Liquids

Investigating the rate increase of Cope and Claisen rearrangements in $[C_4C_1Im][NTf_2]$

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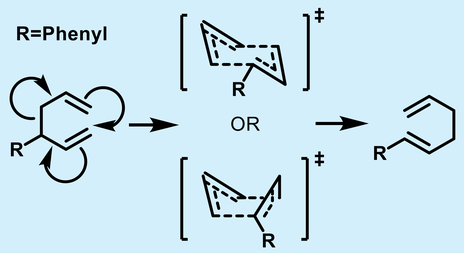
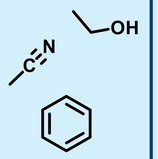
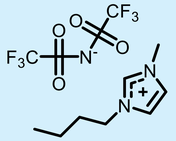
1. Literature Cope reaction



Molecular solvent



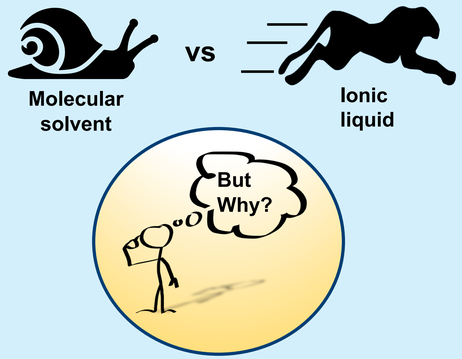
Ionic liquid $[C_4C_1Im][NTf_2]$



10x faster[1]

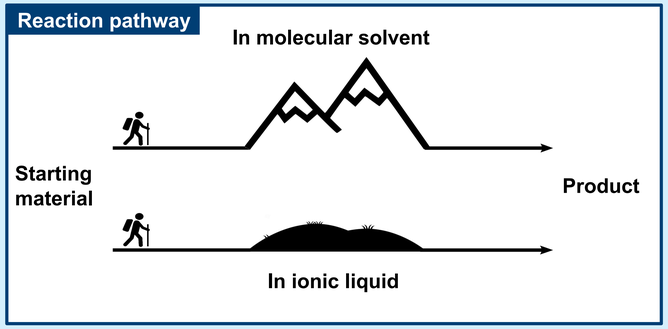
[1] S. T. Keaveney, R. S. Haines, and J. B. Harper, *ChemPlusChem* **2017,** *82*, 449-457

2. Our work



3. Is the ionic liquid lowering the transition state?

Reaction pathway

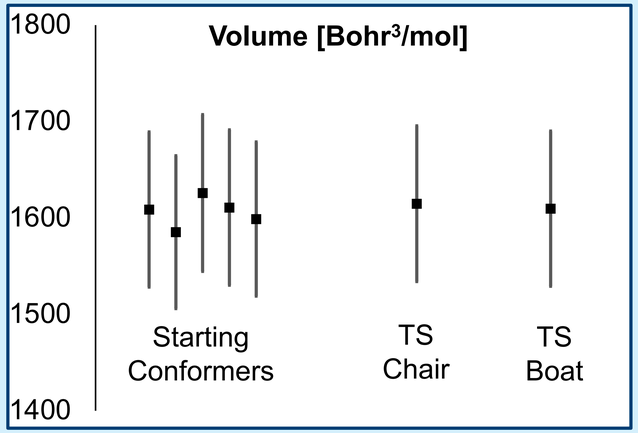


	Gas Phase	MeCN	Benzene	Ethanol	$[C_4C_1Im][NTf_2]$
Act. E. [kJ/mol]	108	105	106	105	105

- Calculation with a solvent environment (SMD)
- No difference in activation energy between solvents

not the answer

4. Are low-volume transition states favoured in high internal pressure ILs?

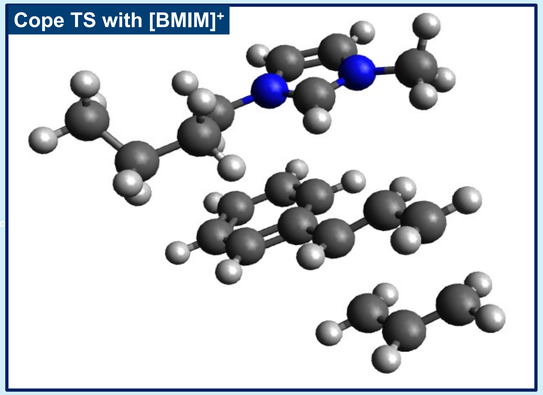


- Accuracy of calculations do not allow for definitive predictions
- No indication of lower volume TS

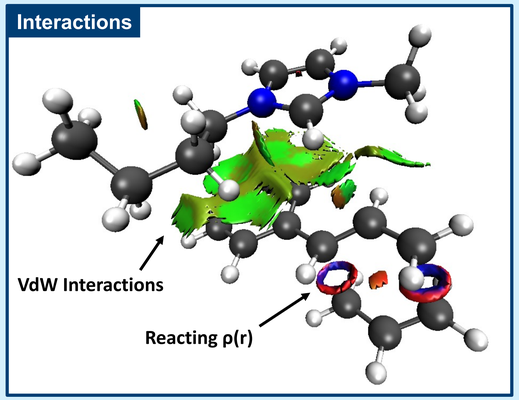
not the answer

5. Are ion-π interactions stabilising transition states?

Cope TS with [BMIM]+



Interactions



- BOTH starting material and TS interact with $[C_4C_1Im]^+$
- Activation energy is unchanged

not the answer

6. Conclusions

- Energy calculations do not show a reduction in TS barrier for IL
- Volume calculations do not show a smaller TS, but variation is large, may not be accurate
- Specific solvent interactions do not change activation energy as starting materials and TS are equally affected

7. Future Work

- Experimental approach is needed
- Is there an increased reaction rate in neutral mimics under high pressure?