

Abstract

Little is known about the mechanisms of reactions of lithium organic compounds. These compounds form aggregates, whose sizes and structures depend much on the solvent used. This complexity makes mechanistic studies in lithium organic chemistry extraordinary challenging.

The topic of this thesis is mainly computational studies of mechanisms of chiral lithium amide induced rearrangement reactions. A computational transition state model has been developed for the enantioselective reaction of a chiral lithium amide with cyclohexene oxide. In the model, solvation differences of the diastereoisomeric activated complexes are strongly influencing the enantioselectivity, together with non-bonded interactions between the epoxide and the lithium amide. The calculated and the experimentally determined enantioselectivities are in good agreement.

Based on the computational model, a highly enantioselective chiral lithium amide has been developed. The transition states for deprotonation of cyclohexene oxide with this lithium amide have been studied by both kinetics and computational chemistry. Improved stereoselectivity has been obtained using lithiated 1-methylimidazole or lithiated 1,2-dimethylimidazole as bulk base in catalytic deprotonations. The bulk base and the lithium amide form heterodimers, and the nature of these new reagents have been studied computationally.

Additives such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) have been used to increase the enantioselectivity in chiral lithium amide mediated epoxide deprotonations. It was found that DBU is lithiated under conditions normally used and that it forms heterodimers with the chiral lithium amide. Such heterodimers have been characterised by PM3 and DFT-computational studies.

The aggregation and solvation of the product formed in the epoxide deprotonation, an allylic alkoxide, has also been studied. It was found that distorted cubes and drum-shaped hexamers are the dominating aggregates of the lithium alkoxide. PM3-energies have been found not useful for evaluating stabilities of aggregates of lithium alkoxides.

The allylic alkoxide undergoes solvent induced rearrangement to a homoallylic alkoxide by a 1,3-proton transfer reaction. The reaction mechanism for this rearrangement has also been investigated.

New insights into the reaction mechanism of a protium/deuterium exchange between methane and $(^2\text{HF})_x$ -solvated $^2\text{H}_2\text{F}^+$ ions by both experimental and computational studies are reported. It is found that free protonated methane, the methonium ion, is likely not an intermediate in the reaction but rather part of the activated complexes as solvated by a $(^2\text{HF})_x$ -polymer.

Keywords: ab initio, aggregation, carbonium ions, catalytic, chiral lithium amides, computational chemistry, density functional theory, deprotonation reactions, enantioselectivity, heterodimers, methane activation, semiempirical, superacids, transition states.

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