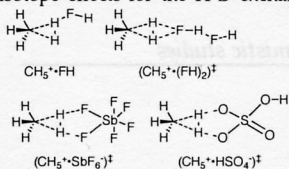


ABSTRACT

This thesis deals with structural and mechanistic investigations of alkane activation by superacids, and enantioselective reactions using chiral lithium amides.

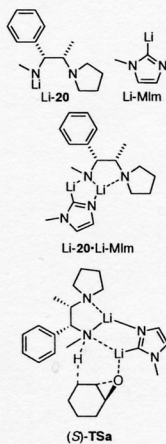
In the activation of methane in liquid superacids, the methonium ion CH_5^+ has been postulated to be an intermediate or a transition state. Using NMR, the secondary kinetic isotope effects for the H-D exchange of methane in DF/SbF_5 were measured. In order to



interpret the experimental results, a DFT investigation of the superacids and the activated complexes was performed. The computational results show that only the H_2F^+ superacid is strong enough to protonate methane, forming a strongly hydrogen-bonded intermediate, $\text{CH}_5^+\cdot\text{FH}$. In all other superacids, CH_5^+ shows up as a part of the activated complexes $((\text{CH}_5^+\cdot(\text{FH})_2)^\ddagger, (\text{CH}_5^+\cdot\text{SbF}_6^-)^\ddagger)$ in the hydrogen exchange.

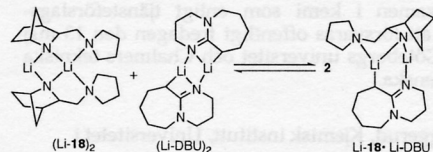
The H-D exchange has also been investigated for sulfuric acid by kinetics and DFT calculations. The CH_5^+ -part of the transition states for the H-D exchange in sulfuric acid also resembles the CH_5^+ , but the barrier for exchange is higher.

The chiral lithium amide Li-20, in the presence of the bulk base Li-MIm, catalytically deprotonates cyclohexene oxide with high enantioselectivity. The bulk base, Li-MIm, forms a mixed dimer, Li-20•Li-MIm, together with Li-20. The reaction orders have been determined by kinetics, showing that the activated complex is built from one molecule of cyclohexene oxide and one molecule of the mixed dimer. The structures and energies of the activated complexes and the intermediates have been investigated using DFT.



The site selectivity of the deprotonation of cyclohexene oxide by Li-20•Li-MIm, and other chiral and achiral lithium amides, has been determined using ^2H NMR, isotopic stereoisomers at natural abundance, and kinetic isotope effects. The reactions proceed via β -*syn* mechanisms.

In the catalytic, highly stereoselective deprotonation of epoxides by Li-18, DBU has been used as an additive to increase the reactivity and the



enantioselectivity. In order to elucidate the function of DBU, the solution structure of Li-18 and the influence of additions of DBU, have been studied using multinuclear NMR. Li-18 is mainly present as a non-equivalent dimer, $(\text{Li-18})_2$, in THF. In solution with equivalent amounts of Li-18 and Li-DBU, an equilibrium between $(\text{Li-18})_2$, Li-DBU, and the heterodimer Li-18•Li-DBU is present. This shows that DBU plays a more intricate role than just as an additive.

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Keywords: alkane activation, carbonium ions, H-D exchange, superacids, sulfuric acid, chiral lithium amides, deprotonation, DFT, *ab initio*, activated complexes.