# Mechanistic studies of conformationally controlled ionic cycloadditions and state selective reactions

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Despite their significance in organic synthesis, the mechanistic details of Diels-Alder cycloadditions, in which a diene and a dienophile react to form a cyclic product, still remain an unsolved and extensively discussed question. It has proven difficult to determine whether only the s-cis conformer (concerted mechanism) or both conformers (stepwise mechanism) of the involved diene react to form the cyclic product. Due to their high stereo- and regioselectivity, a concerted mechanism is generally assumed [1]. For polar Diels-Alder reactions, however, where one of the reactants contains a charge, the reaction may instead favor a stepwise mechanism [2].

In order to shed light on these questions we investigate the reactivities of individual conformers by employing molecular beam technology [3]. Owing to their different dipole moments, conformers can be spatially separated in an inhomogeneous electric field. Directing a molecular beam of spatially separated conformers into a cloud of sympathetically cooled molecular ions in an ion trap allows us to study highly conformationally selective reactions such as Diels-Alder cycloadditions. Previously, this method has been successfully applied to study reactive collisions of 3-aminophenol with a Coulomb crystal of $Ca^+$ ions [4][5]. As a representative example, we want to study the conformationally resolved ionic cycloaddition reaction of 2,3-dibromo-1,3-butadiene which exhibits two different conformers, s-cis and s-trans, with ionic maleic anhydride. The products of the reactive collisions are analyzed by an integrated high-resolution time-of-flight mass-spectrometer. The performance of the setup was recently confirmed by measuring the rate constant of the reaction between laser cooled $Ca^+$ ions with $N_2O$ [6]. This advancement will enable us to trace the complex mechanistic pathways of Diels-Alder reactions.

Besides conformers, our setup also enables us to study state selective reactions. In the presence of a strong inhomogeneous electric field, water molecules in a molecular beam can be separated into their two nuclear spin isomers ortho and para which correlate with different rotational states [7]. Currently we are investigating the reaction of rotational state selected $H_2O$ molecules with $N_2^+$ and $N_2H^+$ ions. The flexibility of our setup allows us to access the individual spin isomers and study their reactivities.

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