Mechanistic studies of conformationally controlled ionic cycloadditions and state selective reactions

A. Kilaj[1], H. Gao[1], D. Rösch[1], U. Rivero[1], J. Küpper[2,3]*, S. Willitsch[1]*

[1]Department of Chemistry, University of Basel, Klingelbergstrasse 80, 4056 Basel, Switzerland, [2] Center for Free-Electron Laser Science, DESY, Notkestrasse 85, 22607 Hamburg, Germany, [3] Department of Physics, University of Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany

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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