Conformational effects in radical reactions

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Revealing the dynamics of hydrocarbons reacting with free radicals is of major relevance for understanding atmospheric processes and combustion chemistry [1]. Despite their significance demonstrated by the vast body of literature, the conformational dependence of radical reactions still remains largely unexplored. Only a few studies demonstrate conformational effects in these reactions [2, 3]

To gain detailed insights into reaction dynamics, a crossed-molecular-beam apparatus with integrated conformer-selector is being built. The molecular beam technique allows us to study single-collision events under well controlled initial conditions. Due to different dipole moments, conformers can be spatially separated in a molecular beam using an inhomogeneous electric field. This technique of separation has been previously successfully implemented to study conformationally resolved reactions of 3-aminophenol with Ca^+ ions [4].

We are now extending this approach to neutral reactions. Our first target is the reaction of conformationally selected 1,2-bis(trifluorosilyl)ethane with chlorine radicals [5]. Calculations of the potential energy surface suggest that the abstraction of hydrogen by chlorine is more favourable from the gauche-conformer because of the sterical hinderance exerted by the SiF_3 groups. In a first stage, we aim to measure conformer-specific reaction rates which yield information about the activation energies of different conformational reaction pathways. At a later stage, the experiments will be extended for measurements of product state and angular distributions and different radical species, e.g., fluorine.

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