

Dynamics of the reaction between fluoride and various organochlorines

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Halogenated hydrocarbons play a very important role in organic synthesis both as solvents and as reaction intermediates. The bimolecular nucleophilic substitution (S_N2) is one of the most common processes of these compounds. The reaction type is of fundamental importance in physical organic chemistry due to its underlying simplicity, nevertheless its dynamics has not been understood in complete detail. In the past, understanding of the reaction dynamics relied strongly on chemical trajectory simulations. However, advancements in the crossed beam scattering and velocity map imaging (VMI) techniques in the previous decade have led to new insights into the reaction dynamics from measurements of correlated energy and angle differential cross sections.

The simplest case of a nucleophilic substitution reaction consists of a methyl halide colliding with a mono atomic nucleophile. Using a crossed beam setup and a velocity map imaging spectrometer [1], our group has extensively studied exothermic S_N2 -reaction systems [2]. The present study focuses on the reaction between fluoride ions and three different organochlorines: CH_3Cl , CD_3Cl and CH_3CH_2Cl . The low energy F^- ions are produced from a mixture of NF_3 and Argon in an electron impact supersonic expansion source via dissociative electron attachment. In the interaction region a pulsed supersonic neutral beam is crossed with the ion beam and the complete velocity vector of the product anion is measured using velocity map imaging.

We have performed experiments on the S_N2 reaction of F^- with methyl chloride at six different relative collision energies ranging from 0.4 eV to 2.0 eV. The direct S_N2 pathway is the dominant channel at high energy, with an increasingly strong contribution from the complex mediated channel at lower energies. We have also investigated the effect of deuteration on the reaction dynamics by performing the experiment with CD_3Cl at a single collision energy of 0.9 eV and looking for the relative importance of the direct and complex mediated channels. In this contribution we present the experimental technique in detail along with the analysis of the scattering images. A comparison of the present results with previous studies by our group on similar systems like $F^- + CH_3I$ and $Cl^- + CH_3I$ [2,3], will provide better understanding of the dynamics of S_N2 reactions. As an outlook, we shall also discuss our efforts towards investigating the difference and relative importance between the S_N2 and $E2$ mechanisms by performing the experiments with CH_3CH_2Cl [4].

[1] J. Mikosch, U. Frühling, S. Trippel, D. Schwalm, M. Weidemüller and R. Wester, *Phys. Chem. Chem. Phys.* 2006, **8**, 2990.

[2] J. Mikosch, S. Trippel, C. Eichhorn, R. Otto, U. Lourderaj, J. X. Zhang, W. L. Hase, M. Weidemüller, M and R. Wester, *Science* 2008, **319**, 183.

[3] J. Mikosch, J. Zhang, S. Trippel, C. Eichhorn, R. Otto, R. Sun, W. DeJong, M. Weidemüller, W. L. Hase and R. Wester, *J. Am. Chem. Soc.*, **in press**.

[4] M. Mugnai, G. Cardini and V. Schettino, *J. Phys. Chem. A* 2003, **107**, 2540.

