Disentangling the competition of elimination and nucleophilic substitution dynamics

Content

Base induced elimination (E2) and nucleophilic substitution (S_N2) reactions often appear in competition. We chose to study the reaction of F^- with CH_3CH_2Cl, as it represents one of the smallest model systems in which both pathways compete. In this reaction they lead to the same Cl^- product, which makes experimental approaches purely based on product mass very challenging.
Here we present a study combining angle- and energy-differential cross sections, obtained in a crossed-beam velocity map imaging experiment, with quasi-classical trajectory (QCT) calculations on an accurate 21-dimensional hypersurface [1]. The close agreement of the calculations with the experimental total cross sections allows us to disentangle the individual contributions and extract detailed information of the underlying atomistic reaction mechanisms.
We find that the anti-E2 pathway dominates over the whole investigated collision energy range with increasing contributions of S_N2 towards higher energies. The identified reaction mechanisms also match previously identified "dynamic fingerprints" of the two pathways [2].
Additionally we present recent experimental results on steering this reaction by fully substituting the beta-hydrogens with fluorine atoms to suppress the E2 pathway.

[1] J. Meyer, V. Tajti, E. Carrascosa et al., "Atomistic Dynamics of Elimination and Nucleophilic Substitution Disentangled for the F^- + CH_3CH_2Cl Reaction" Nature Chemistry 13, 977981 (2021)
[2] E. Carrascosa, et al., "Imaging dynamic fingerprints of competing E2 and S_N2 reactions" Nature Communications, 8:25 (2017)

Primary author: MICHAELSEN, Tim (Universität Innsbruck, Angewandte und Ionenphysik)

Co-authors: Dr MEYER, Jennifer (Universität Innsbruck, Angewandte und Ionenphysik/Technische Universität Kaiserslautern); Prof. WESTER, Roland (Universität Innsbruck, Angewandte und Ionenphysik); Dr CARRASCOSA, Eduardo (Universität Innsbruck, Angewandte und Ionenphysik); Mr TAJTI, Viktor (MTA-SZTE Lendület Computational Reaction Dynamics Research Group, Interdisciplinary Excellence Centre and Department of Physical Chemistry and Materials Science, University of Szeged); GYŐRI, Tibor (MTA-SZTE Lendület Computational Reaction Dynamics Research Group, Interdisciplinary Excellence Centre and Department of Physical Chemistry and Materials Science, University of Szeged); CZAKÓ, Gábor (MTA-SZTE Lendület Computational Reaction Dynamics Research Group, Interdisciplinary Excellence Centre and Department of Physical Chemistry and Materials Science, University of Szeged); Dr BASTIAN, Björn (Universität Innsbruck, Angewandte und Ionenphysik/Aarhus University Department of Physics and Astronomy); Dr STEI, Martin (Universität Innsbruck, Angewandte und Ionenphysik)

Presenter: MICHAELSEN, Tim (Universität Innsbruck, Angewandte und Ionenphysik)

Contribution Type: Hot topic contribution