

CHEMISTRY

Not So Simple

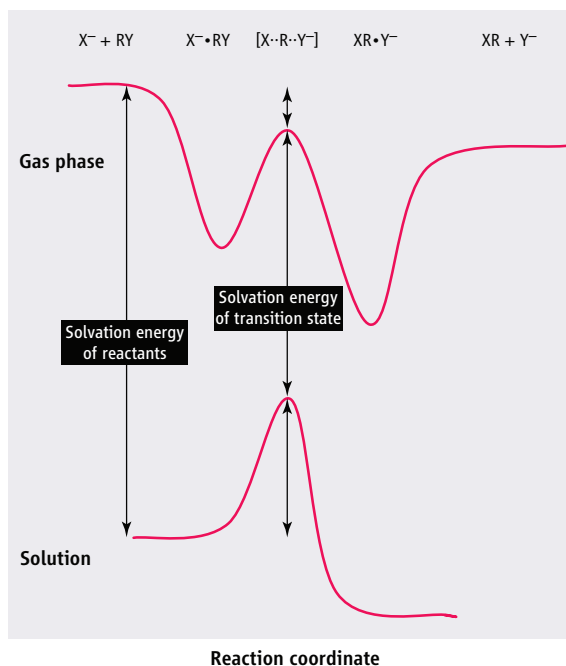
John I. Brauman

The details of molecular transformations are often referred to as chemical reaction mechanisms. These mechanisms can be characterized in terms of the number of molecules involved, geometric and structural features (including stereochemistry), the presence or absence of intermediates, and the timing of individual steps. Knowledge of mechanism is critical for predicting how molecules may react and for inventing or developing new reactions. On page 183 of this issue, Mikosch *et al.* (1) reveal details of the timing, structural changes, and energy exchange in a paradigmatic reaction: the displacement reaction $\text{Cl}^- + \text{CH}_3\text{I} \longrightarrow \text{CH}_3\text{Cl} + \text{I}^-$. The work elegantly combines experiment and theory.

The reaction studied by the authors is a simple example of a nucleophilic displacement ($\text{S}_{\text{N}}2$) reaction, which has an exceptional place in organic chemistry because of its apparent simplicity and its utility. In this reaction, the nucleophile X^- reacts with RY , which can be any of a wide variety of organic chemical structures, giving the products RX and the leaving group Y^- .

The $\text{S}_{\text{N}}2$ reaction is sensitive to the conditions under which it is carried out (2), such as whether it is performed in solution or in the gas phase (see the figure). Because the gas-phase reaction occurs at low pressure, there is enough energy to cross the reaction barrier. The solution reaction is much slower, because the reactants are stabilized by solvation more than the transition state is; only a small fraction of the reactants has enough energy to proceed to products at any given time (3).

Mikosch *et al.* now use molecular beams to provide a detailed analysis of this reaction in the gas phase. In these experiments, the temperature and collision velocity of the reacting molecules can be controlled separately. The directional distribution and velocity of the products reveals much about the times involved in the reaction and—from considerations of conservation of energy—the distribution of energy in



Images and insights. The ability to image the dynamics of ion-molecule reactions in the gas phase allows new insights into the details of a classic organic chemical reaction, as reported by Mikosch *et al.* in this issue.

the products as kinetic energy or internal (vibrational) energy. Recent advances in detection allow the data to be accumulated and displayed as images that reflect the relative amounts of product produced at each energy in every direction (4). This technique has been used to study reactions of neutral molecules (5, 6). The authors now apply it to reactions of ions with molecules.

The details of solution reactions are often inferred rather than directly observed, because collisions with solvent control the trajectories of the molecules, so that the behavior of the initially formed products cannot be determined. In the current case, the solution reaction is essentially a simple, one-step process in which the nucleophile attacks the neutral substrate from the back side and gives a product with stereochemical inversion of configuration relative to the starting material. Molecular dynamics simulations show, however, that interactions with solvent can cause products to return to reactants and cross back and forth many times before finally completing the reaction (7).

Mikosch *et al.* now provide considerable detail about the reaction in the gas phase. At

A molecular-beam study of a classic organic reaction shows that its mechanism is more complex than previously assumed.

low collision energy, the reaction products are distributed isotropically—that is, equally probable in all directions—showing that intermediate $\text{X} \cdots \text{R} \cdots \text{Y}$ complexes persist long enough to undergo many rotations.

At higher collision energies, a new mechanism appears: The I^- departs directly along the axis from which the Cl^- enters, and most of the energy is retained as kinetic energy in the I^- product. In this “direct” reaction, the complexes do not last long enough to rotate before the reaction occurs. Depending on the collision energy, the original process and the new processes compete, with the direct reaction becoming increasingly important as the collision energy is increased.

Direct dynamics trajectory simulations also reported by Mikosch *et al.* are consistent with the experiments in terms of energetics, but also show important details that the experiments do not completely reveal. At even higher collision energy, the indirect reaction reappears, but with an unexpected twist: The incoming Cl^- collides

with and induces a rotation of CH_3I , followed by backside attack and displacement. This process can involve multiple rotations of the CH_3I , and a small fraction of the trajectories show transient trapping in the postreaction complex. The study by Mikosch *et al.* illustrates the exceptional insights into details of reaction dynamics that can be obtained with molecular beams. As more reactions are studied with this technique, it should become possible to generalize and make predictions prior to detailed experiments or calculations.

References

1. J. Mikosch *et al.*, *Science* **319**, 183 (2008).
2. E. V. Anslyn, D. A. Dougherty, *Modern Physical Organic Chemistry* (University Science Books, Sausalito, CA, 2006), chap. 11.
3. M. L. Chabiniy, S. L. Craig, C. K. Regan, J. I. Brauman, *Science* **279**, 1882 (1998).
4. J. Mikosch *et al.*, *Phys. Chem. Chem. Phys.* **8**, 2990 (2006).
5. K. Liu, *Annu. Rev. Phys. Chem.* **52**, 139 (2001).
6. M. S. Elioff, J. J. Valentini, D. W. Chandler, *Science* **302**, 1940 (2003).
7. J. P. Bergsma, B. J. Gertner, K. R. Wilson, J. T. Hynes, *J. Chem. Phys.* **86**, 1356 (1987).

The author is in the Department of Chemistry, Stanford University, Stanford, CA 94305, USA. E-mail: brauman@stanford.edu

10.1126/science.1152387