Tracking State-to-State Bimolecular Reaction Dynamics in Solution

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ences in the isotopic composition of the two domains, and because of the precision of the measurements needed to resolve these issues. Now, investigations of core-mantle exchange can be extended using chromium isotopes.

A related question—What is the chromium isotopic composition of the Moon?—can also be explored. Lunar rocks have oxygen and tungsten isotopic compositions that are identical to that of Earth's mantle and, thus, Earth's distinctive chromium isotopic composition might also be found in lunar rocks. If not, would this imply that chromium isotopes were fractionated during lunar core formation or during the giant impact that is believed to have created the Moon?

Another stimulating issue arising from Moynier et al. is what chromium isotopes tell us about processes in the solar nebula and chondrite formation, which represents the least understood first step in planet formation (8). It appears that different types of chondrites, and even subgroups within these types, have different isotopic compositions. Major classes of chondrites can be distinguished by the oxidation state of their metal-loving elements. These may be dominant in the reduced, iron-nickel (Fe-Ni) alloy form (e.g., as in enstatite chondrites); in the oxidized forms, where iron almost always occurs as an oxide (e.g., as in most carbonaceous chondrites); or as a mixture of both (e.g., as in common ordinary chondrites, which represent ~90% of all chondrites). Moynier et al. show that the ordinary chondrites generally have heavier chromium isotopic compositions than carbonaceous chondrites. At the same time, they show that those subgroups of carbonaceous chondrites with greater amounts of refractory materials (known as the CO and CV types) also have increasingly heavier chromium isotopic compositions. The issue for cosmochemists and astrophysicists is how this information can be used to improve models of mixing in the solar nebula and chondrite formation.

For more than half a century, it has been observed that meteorites (9) and planets (10) are composed of both a refractory (and per-haps reduced) component and a volatile-rich, oxidized component. It is hoped that a certain brilliance will come from plating this story with chromium isotopes, which can contribute to unraveling where, in time and space, these components existed and were mixed together.

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CHEMISTRY

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A bimolecular reaction can produce a large fraction of highly vibrationally excited products despite the collision and confinement effects of the surrounding liquid.

Stephen Bradforth

If two reactant molecules collide with sufficient energy and the geometry between them is right, then the reactants can pass through a transition state to form new chemical products. A "state-to-state" study maps out how distributing energy (such as in different bond vibrations) in the reactant states affects the likelihood of reaction, as well as the corresponding state population of the products. For gas-phase reactions, the product states, rather than being populated statistically (with population falling off exponentially with increasing energy), can instead show higher population in excited states than the ground state. This so-called state inversion is the basis for the powerful HF chemical laser (1). But does this state-to-state behavior matter at all for bimolecular reactions run in liquids? The constant fluctuations of the solvent should randomize the state of the reactant right up to the transition state, and speed the relaxation of product excited states back to a statistical distribution. On page 1423 of this issue, Greaves et al. (2) show that a vibrational state inversion can in fact be achieved in a hydrogen transfer reaction in a common liquid solvent by tuning the time scales of the relaxation processes.

In the 1960s, Polanyi formulated a simple set of rules for what energy states in the reactants would enhance reaction, and in what states the energy released should appear (3). These rules, for example, explained why the reaction powering the HF chemical laser, the transfer of a hydrogen atom between molecular hydrogen and fluorine to produce hydrogen fluoride, exhibited a vibrational state inversion (1). Modern gas-phase reaction dynamics, aided by laser-assisted reactant-state preparation and product-state interrogation, now provides stunning detail on the bimolecular reactions of small molecules, revealing the detailed forces acting at the transition state (4, 5). Studies under vacuum conditions can ensure that the only collision between two molecules is the reactive event itself, and that all of the information encoded in the product state distribution is preserved.

In liquids, it is hard to observe such non-statistical product-state distributions precisely because the constant buffeting molecules suffer is acting to rapidly degrade this fingerprint into a statistical distribution (6). Indeed, energy released into translation and rotation is nearly always (7, 8) relaxed into the solvent on the time scale of the reactive event itself, but vibrations can relax much more slowly. High-frequency vibrations like those involving hydrogen atom stretches in diatomic and triatomic molecules can take hundreds of picoseconds to relax (9, 10), so it should be possible to observe a vibrational distribution for a solution-phase reaction (6). However, there are few examples for a bimolecular reaction where this state distribution has even been measured (11).

The Polanyi rules provide insight into the origin of nonstatistical energy distributions in

Department of Chemistry, University of Southern California, Los Angeles, CA 90089–0482, USA. E-mail: stephen.bradforth@usc.edu
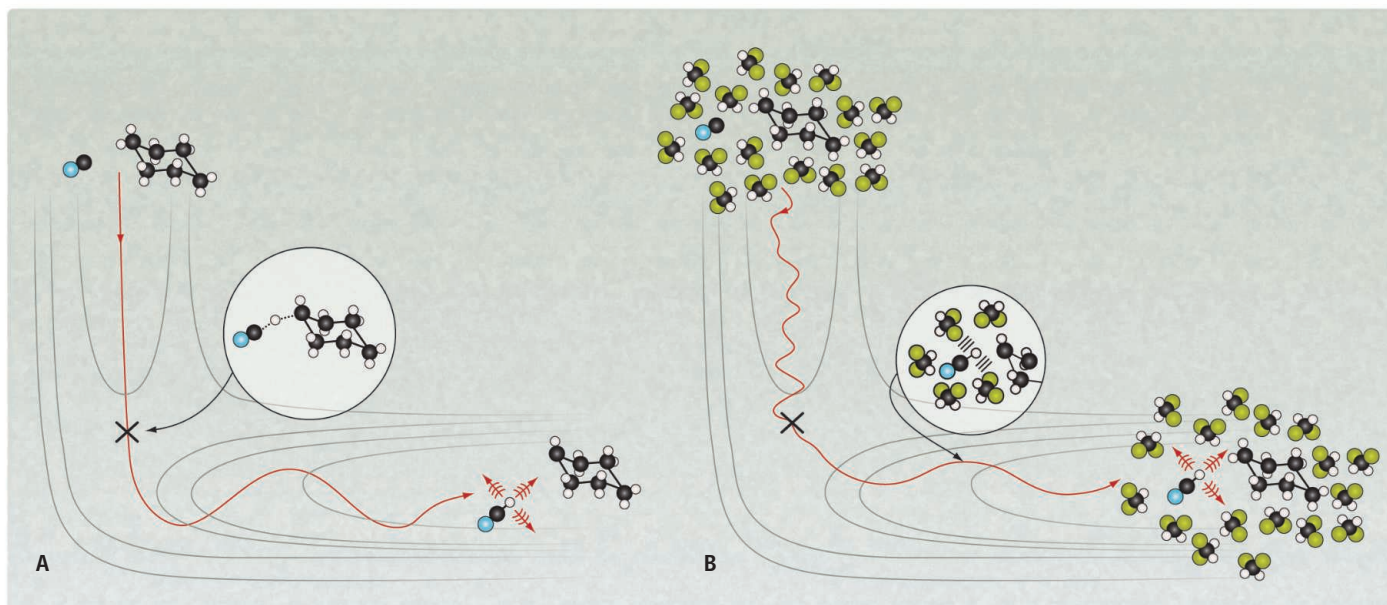
Crossing crowded dance floors. In the dance that makes up a chemical reaction, an existing bond is broken (here, the C-H of the ring-shaped cyclohexane molecule) and a new one formed (a new C-H in the HCN product). The hydrogen atom (white sphere) is transferred to the CN radical, $CN^{\bullet} + HC_6H_{11} \rightarrow HCN + C_6H_{11}^{\bullet}$. (**A**) In the gas phase, the reactants collide unimpeded (the dance floor is clear). The straight red arrow shows a classical reactive trajectory superimposed on the potential energy surface. The contour map is a function of the lengths of the C-H bond being formed (vertical axis) and the one being broken (horizontal axis). Because the transition state (×) is early, the downhill descent directs kinetic energy into the newly forming H-CN bond. (**B**) In solution, the reactants move more chaotically across a crowded dance floor. Greaves *et al*. show that despite solvent friction, much of the energy released is still directed into the H-CN bond.

terms of the location of the transition state (×) on the potential energy surface (see the figure, panel A), a map showing how the internal energy of the molecules changes with the position of the atoms. For a reaction where this barrier occurs "early"—the transition state looks more like the reactants—translational (rather than internal) energy is most effective at getting over the barrier. Downhill from the barrier, energy is released first into compressing the newly formed bond before the old bond is broken so the products are born with high stretching excitation. If the reaction releases a lot of energy and the barrier is early enough, an inverted population (like that created in the HF laser) will occur.

When solvent is added to this gas-phase picture, the frequent collisions between solvent and reactant in the entrance channel lead to more chaotic trajectories that might deprive the nascent products of state-specific energy disposal (see the figure, panel B). The close packing of the solvent should also provide mechanical and electrostatic friction (inset in the figure, panel B) that prohibits the reaction from delivering so much of its initial energy release into one specific mode. Greaves *et al*. build on pioneering experiments by Hochstrasser and co-workers where a free radical, $CN^{\bullet}$, strips a hydrogen atom from a solvent molecule (*11*). They replaced the reaction partner with cyclohexane, and by capturing broad sections of the infrared spectrum as a function of time after preparing the radical, they showed that the energy content in the C-H stretching vibration of the newly formed bond is not just slightly nonstatistical, as in the earlier work (*6, 11*), but has a strong population inversion (*3*). The time-resolved spectra also reveal excitation channeled into bending excitation of the product.

Although the solvent damped to some extent the channeling of energy into product vibration, for this particular reaction, the basic picture is little changed from that of the gas phase. The authors' selection of a reaction with an isolated high-frequency stretching mode in the product, a very low barrier, and a flat energy landscape near the transition state were likely crucial in revealing Polanyi-type reaction behavior. This choice separates the time scales between reaction and slow product relaxation and may lead to insensitivity to the direction of approach to the transition state. The downhill descent driving energy into the newly formed H-CN bond must be faster than any friction can be developed by the solvent. Finally, contrary to what was inferred for the $CN + HCCl_3$ reaction (*6, 11*), solvation has not pushed the barrier any later along the reaction coordinate. Calculations presented by Greaves *et al*. support rather small changes to the reaction potential energy surface on solvation.

It remains to be seen then whether state-specific energy disposal in the liquid phase is more general. Another intriguing possibility arising from this work is that rotational excitation surviving from the laser-induced dissociation (*8*) used to generate (*12*) the CN radicals here might be transmitted through the transition state and into the HCN bend, as Greaves *et al*. speculate. Perhaps other manifestations of the Polanyi rules, i.e., state-specific effects in the entrance channel of a reaction with a late barrier, may also be accessible with suitable preparation (*13*) for solution-phase bimolecular reactions.

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