residues and one glutamate (E) residue located at strategic positions in these transposases bind a divalent cation necessary for DNA strand scission in the transposition reaction. The D residues are typically separated by more than 90 amino acids and the final D and E residues by 34 or 35 amino acids. The D, D(35)E superfamily also includes retrovirus transposases such as those of the human immunodeficiency virus (HIV) and Rous sarcoma virus (RSV), retrotransposons of the *copia* and *gypsy* class, *Tc1*-like transposable elements, and various bacterial insertion sequences (6). The MLEs are a unique lineage in having a D, D(34)D signature in the transposase. The final D is essential for MLE activity and cannot be replaced by E (7). Transposition in the superfamily occurs by a cut-and-paste mechanism: A staggered double-strand scission at each end of the element releases it from the donor molecule, and the element is ligated into a staggered cut at the target site (8).

The widespread phylogenetic distribution of *mariner* elements reflects an evolutionary history in which the elements have been transmitted horizontally between diverse hosts repeatedly. Many examples of horizontal transmission have been inferred from the close sequence similarity between *mariner* elements in otherwise highly divergent species. Horizontal transmission has occurred between insect families within the Diptera (9), between orders within Insecta (10), and between phyla within Animalia (11), including at least two horizontal transmissions into the human genome (12).

The extraordinary host range of MLEs implies that few host functions are required for transposition. In their *Leishmania* experiments, Gueiros-Filho and Beverley (1) used a *mariner* element called *Mos1*, known to encode a functional transposase in *Drosophila* (13, 14). They transfected *L. major* cells with two types of plasmid, one containing an intact *Mos1* element and the other containing the *Mos1* transposase-coding region fused with DNA sequences allowing trans-RNA spicing and gene expression in *Leishmania*. (The organism is unusual in that a mini-exon of 39 nucleotides must be trans-spliced onto the 5′ end of every messenger RNA.) Among transfected cells chosen at random, without selection for *Mos1* integration, 23% of the cells had *Mos1* inserted into the genome. Further studies showed that *Mos1* insertions could be used to obtain insertional inactivation of the gene for dihydrofolate reductase–thymidylate synthase—and that a modified *Mos1* element could be used to identify *Leishmania* genes by insertions that fuse *Mos1* and the hygromycin-resistance gene to an RNA-splice acceptor, allowing expression of antibiotic resistance.

The demonstration that *mariner* functions in *Leishmania* adds insertional mutagenesis and transposon tagging to an already impressive set of tools developed for genetic analysis in this organism, including expression vectors, gene knockouts, artificial chromosomes, and inducible expression systems. Of wider significance is that these experiments will inevitably encourage attempts to use *mariner* in developing genetic tools for use with other pathogens, pest species, and organisms of genetic interest. (Judging from the volume of my e-mail requesting *Mos1* vectors, there is already considerable interest.) There is no obvious reason why such experiments should be restricted to lower eukaryotes and invertebrates, because *mariner* can evidently function in at least some vertebrate genomes. Preliminary evidence indicates that the *Mos1* element can integrate into the genome of *Danio rerio*, the zebrafish (15). For *mariner* researchers, the *Leishmania* findings are exceptionally exciting because they emphasize the importance of understanding the evolution, molecular genetics, and self-regulation (16) of this remarkable traveler among animal genomes. Although we did not know it at the time (17), *mariner* was an apt name for this wide-ranging transposable element.

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CHEMISTRY

Ultrafast Reaction Dynamics in Molecular Cluster Ions

Robert Parson and James Faeder

In most chemical reactions, the reactants and products are not isolated but are in contact with their surroundings. Even a solvent that only weakly perturbs the reactants can profoundly influence the course of the reaction by blocking the path of a departing atom or by removing excess energy from products or reactive intermediates. A celebrated example is the photodissociation and recombination of the iodine molecule in nonpolar solvents (1), clusters (2), and solid matrices (3). Solvent effects become still more important when the reaction involves charged species, because the forces between an ionic solute and a polar or polarizable solvent can be as strong as the chemical binding forces between the reactants themselves. The solvent then does not merely interrupt and redirect motion on the potential energy surface of the isolated solute, it actually changes the topography of that surface. This is not news to chemists, who have long appreciated that a solvent will stabilize the transition state of a reaction differently than it does the reactants or products. Understanding the full impact of strong solvent-solute interactions on reaction dynamics has nevertheless proved to be a demanding task.

New experimental techniques, capable of probing molecular dynamics in well-characterized solvent environments on extremely short time scales, are now being brought to bear on these problems. By stimulating molecules with laser pulses having a duration of a few tens of femtoseconds, physical chemists can watch chemical bonds break and reform in real time. By studying reactions in small gas-phase clusters, they can examine the effect of the solvent on a molecular scale. Clusters are particularly well suited for the study of ionic systems because systems of a desired size can be selected with a mass spectrometer.

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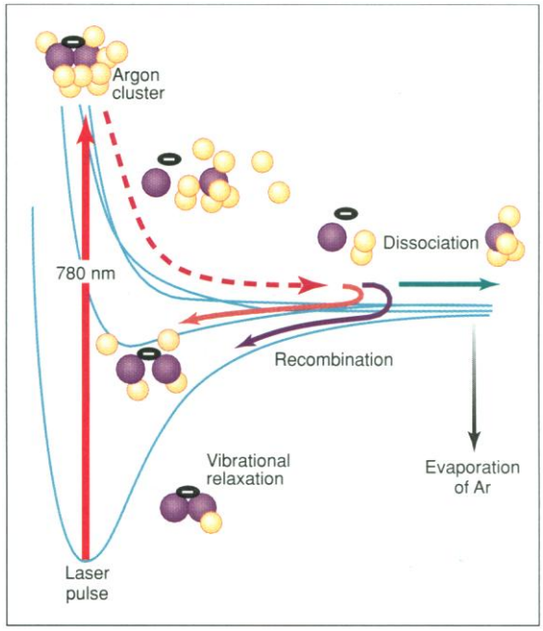
On page 1675 of this issue, Greenblatt *et al.* (4) describe the use of these techniques to unravel the influence of a solvent on the photodissociation of a molecular ion.

Greenblatt *et al.* build on pioneering experiments by Lineberger and co-workers (5, 6). Of particular relevance here are two recent studies of I_2^- clustered with argon (6). In the first, cluster ions are generated in an expansion, and ions of specified size are selected with a mass spectrometer. A laser pulse having a duration of several nanoseconds then dissociates the solutes within those clusters, and a mass spectrometer determines the size distribution of the photodissociation products. By sorting out those fragments whose masses correspond to clusters built around either I^- or I_2^- ions, the experiment determines the extent to which the solvent "cage" is able to force the dissociated atoms together again. The onset of caging as a function of cluster size was found to be remarkably rapid, reaching 100% in clusters having less than a single solvent shell around the ion. Further examination of the photofragment mass distribution led Vorsa *et al.* (6) to conclude that some of the "caged" products contain not I_2^- in its ground electronic and vibrational state, but rather some sort of metastable species. The identity of this species cannot be determined from the mass spectrum alone, although molecular dynamics simulations (7, 8) suggest that the I_2^- has recombined into a weakly bound but long-lived excited electronic state (see figure). In the second experiment, a femtosecond laser pulse dissociates the solute, and a second, delayed femtosecond pulse probes for the reappearance of I_2^- near the bottom of the ground-state well. Vorsa *et al.* (6) inferred that the time scale for the overall process of photodissociation, recombination, and relaxation was 100 to 200 ps.

Greenblatt *et al.* (4) also begin by dissociating size-selected I_2^--Ar_n clusters with a femtosecond laser pulse, but they follow this with a second femtosecond pulse in the ultraviolet that detaches the excess electron from the anion. By measuring the kinetic energy of the ejected electrons, they determine the electron affinity of the transient species. This technique, which is called femtosecond photoelectron spectroscopy (FPES), is a direct probe of the local environment of the detached electron, sensitive both to chemical bonding interactions within the solute and to interactions between the solute and the solvent.

When this experiment is carried out on the isolated solute, the photoelectron spectrum evolves smoothly from a shape characteristic of I_2^- to one characteristic of I^- over a period of 200 fs, indicating that by this time the electron has become localized on a single atom. When the solute is embedded in a cluster of six argon atoms, the transient photoelectron spectrum reveals that after the charge localizes it continues to feel the influence of several solvent atoms for about 1 ps, the time required for the I^- ion to escape from the cluster. Molecular dynamics calculations that model how the solvent interacts with the localizing solute charge predict shifts in electron affinity that agree well with this experiment (8).



Chemical dynamics in clusters. An ultrashort laser pulse at a wavelength of 780 nm photodissociates an I_2^- ion (purple) embedded in an argon cluster (yellow). The strong attraction between the ion and the polarizable solvent can make the dissociated atoms recombine into either the ground electronic state (black path) or a metastable excited state (red path). Subsequent vibrational relaxation is accompanied by evaporation of the solvent. These processes leave identifiable signatures in the time-resolved photoelectron spectrum of the transient species.

In larger clusters, the transient photoelectron spectrum develops in a more complicated fashion. During the first picosecond, it qualitatively resembles that of the small cluster, but at longer times, additional features appear, which Greenblatt *et al.* attribute to the formation of recombined I_2^- in both ground and excited electronic states. Excited-state recombination begins about 1 ps after excitation and is complete in 35 ps, whereas features attributable to ground-state I_2^- appear between 4 and 10 ps after excitation and continue to evolve out to 200 ps as the molecule gives up energy to the cluster. This lifetime is much longer than the 3- to 6-ps vibrational relaxation time of I_2^- in polar and nonpolar liquids (9). Although one expects argon to be less effective at inducing vibrational energy transfer than a polyatomic molecule, another factor comes into play in the cluster that has no analog in the liquid phase: the solvent evaporates during the relaxation process. At very long times the solvent is completely lost and further relaxation is impossible. The long time scale thus results from the interplay between vibrational relaxation and evaporative cooling, rather than vibrational relaxation alone. By following the evolution in time of the transient photoelectron spectrum, Greenblatt *et al.* have confirmed that the two classes of photodissociation products observed by Vorsa *et al.* correspond to two different electronic states of the solute, and they have determined the time scales for recombination and relaxation in each of these states.

In a single experiment, Greenblatt *et al.* (4) have presented a comprehensive picture of the recombination, relaxation, and evaporation processes that follow photodissociation of a diatomic molecular ion in a cluster. Similar experiments with more complex solvents would be of great interest; whereas argon atoms perturb an ionic solute much more strongly than they do a neutral molecule, the interactions are still much weaker than those between an ion and polar molecules. More challenging would be the study of polyatomic solutes, for which multiple reaction pathways already exist in the isolated molecule. From cluster experiments like these, we can expect to learn not only about molecular interactions and dynamics in condensed phases but also about processes that are unique to this intermediate state of matter.

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