Editorial & Letters

EDITORIAL

Reaction Dynamics

The outcome of a reaction—that is, the products that are ultimately formed—depends on a complex set of conditions such as temperature, pressure, the reaction medium, and the presence of a catalyst, all of which influence the energetics of the reacting molecules. The study of reaction mechanisms thus lies at the heart of chemistry: If we understand how molecules react, then we can think of new reactions, tailor reactions to avoid unwanted side products, and make new products through rational synthesis. Modern approaches have evolved from early gas-phase photochemistry studies and transition state theories to allow us to look directly at the events that make up a reaction mechanism and the electronic and structural factors that determine the reaction's outcome. The dynamics of simple reactions in the gas phase are now understood at an impressive level of detail, not least thanks to advances in laser technology and computer power. Attention is now turning to more complex reactions such as those at surfaces, in free solution, or in proteins, where important advances have been made in recent years. In this issue of *Science*, we bring together five Articles, a News story, and two Reports that provide a glimpse of the state of the art in the study of reaction dynamics.

Focusing on uni- and bimolecular gas-phase and surface reactions, Zare (p. 1875) discusses how reaction outcomes can be controlled in sophisticated laser and molecular beam experiments. Control can be exercised through selecting the internal energy states of the reactants before their collision or through guiding the reactants during the reaction by controlling the phase of their motions. Clary (p. 1879) emphasizes that progress in this field depends on close collaboration between experimental and theoretical researchers. He illustrates the high level of theoretical understanding and computational power required to interpret experimental observations. For simple gas-phase reactions, theoretical predictions now rival experiments in their accuracy. Attempts are under way to extend such high-accuracy predictions to more complicated gas-phase and even surface reactions. A News story (p. 1847) discusses recent advances in the coherent control of reactions, using optimized laser pulse sequences, and a Report by Besenbacher *et al.* (p. 1913) shows how combined experimental and modeling studies have led to the rational design of an improved alloy catalyst for the steam reforming process that converts hydrocarbons and water into hydrogen and carbon monoxide molecules.

Moving on to more complex reactions and the influence of microsolvation, Chabinyc *et al.* (p. 1882) concentrate on the relations among kinetics, structure, and reactivity, and the effect of small numbers of solvent molecules in nucleophilic displacement reactions of ions. The dynamics of this prototypical organic reaction (often the first reaction presented in elementary organic chemistry courses) differ substantially between the gas phase and the solution phase. Insights from gas-phase studies, however, are critical in understanding the solution process.

Enzymes provide organized reaction sites that have been optimized to lead to the desired products; this may involve a transition state and a product distribution different from those in free solution. Gai *et al.* (p. 1886) use the photoisomerization reaction in bacteriorhodopsin as an example to illustrate the complexity of such reactions and discuss the approaches used today to gain structural insights. Ultrafast time-resolved spectroscopic techniques have to date provided most of the information, but time-resolved crystallography is beginning to provide direct structural information complementing these techniques. In the Report by Perman *et al.* (p. 1946), time-resolved crystallography is used to characterize the early structural events in the photocycle of photoactive yellow protein. The structure of a short-lived intermediate is characterized at nanosecond time resolution.

Finally, Tributsch and Pohlmann (p. 1891) review theoretical approaches to electron transfer reactions, which are important in a range of systems from photosynthesis to electrochemistry. They discuss the concepts of passive self-organization (involving strong molecular interactions and participation of the surrounding medium in the electron transfer process through transient chemical bonding) and dynamic self-organized electron transfer (involving an active molecular environment cooperating in the reaction). Inspired by biological reactions, these concepts may be exploited in the design of molecular chemical environments that enable chemical syntheses under mild conditions.

Julia Uppenbrink

LETTERS

From the past

A reader asks whether the extinction of the passenger pigeon might be related to outbreaks of Lyme disease in the late 20th century. Could comet showers that peaked 35.5 million years ago (and which caused the stressed quartz at right) have caused changes in the flora of North America 1 million years later? What role do collagen repeats play in bacteriophages? And could the long life of Jeanne Calment (more than 120 years) have been inherited from her ancestors?

GLEN IZETT

Lyme Disease and the Passenger Pigeon?

There is another possible twist to the complicated ecological chain of events presented by Clive G. Jones *et al.* (Reports, 13 Feb., p. 1023) whereby the incidence of Lyme disease might increase following population increases of mice allowed by a big mast year of acorns. A major competitor of deer and mice for these bumper crops has been absent from the eastern deciduous forests for a century. The extinct passenger pigeon (*Ectopistes migratorius*) was a nomadic wanderer that specialized on a diet of the superabundant, but unpredictable, crops of mast (*1*). With a population estimated at 2 to 5 billion (*2*), concentrated in enormous flocks, passenger pigeons congregated wherever there were huge crops of mast. The birds were so efficient at denuding the woods of nuts that many observers noted that native wildlife and feral hogs could not find sufficient food after a pigeon flock had passed through (*2*). Is it possible that, in the presence of passenger pigeons, the population explosions of mice in mast years, reported by Jones *et al.*, would have been less likely. Could the outbreaks of Lyme disease in the late 20th century have been a delayed consequence of the extinction of the passenger pigeon a century earlier?

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