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.

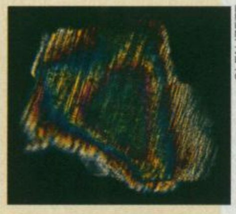
Finally, Tributsch and Pohlmann (p. 1891) review theoretical approaches to electron transfer reactions, which are important in a range of systems from photosynthesis to electrochemistry. They discuss the concepts of passive self-organization (involving strong molecular interactions and participation 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?

David E. Blockstein
Senior Scientist,
Committee for the National Institute for the Environment,
1725 K Street NW,
Washington, DC, 20006–1401, USA
E-mail: david@cnie.org

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The Paleobotanical Record

Richard A. Kerr's article "Comet shower hit, but life didn't blink" (News, 30 Jan., p. 652) reports on Kenneth Farley's interpretation of elevated helium-3 levels as an indicator of comet dust in Eocene ocean sediments and their temporal correlation to large impact craters and shocked quartz crystals. Helium values peaked at 35.5 million years ago (Ma) and tapered off over the 2 million years that followed. From these lines of evidence, experts are said to have concluded that, during this time, there was a terrestrial comet impact but, the article states, "What's missing is any sign that the shower affected life," for the biota was left "unscathed."

Although mass extinctions are not known from the paleobotanical record at this time, a major climatic cold snap—and consequent botanical change—did occur throughout North America about 34 to 33 Ma (*1*). This corresponds with the Eocene-Oligocene boundary (*2*) and the subsequent million years. The paleobotanical evidence thus suggests to me a climate-altering blow, with (i) an abrupt decrease in the mean annual temperature, (ii) an increase in the mean annual range of temperatures, and (iii) floras adapted to these colder temperature regimes (*1*).

Patrick F. Fields
Michigan State University,
Lansing, MI 48824–1312, USA
E-Mail: fieldspa@pilot.msu.edu

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Free Calcium Signals

The commentary "Calcium signaling: Up, down, up, down.... What's the point?" by James W. Putney Jr. (*Science*'s Compass, 9 Jan., p. 191) incorrectly states that free calcium signals were first seen within living cells just over a decade ago. In fact, they were first "seen" over three decades ago as transients from single, twitching barnacle muscle fibers (*1*) and first imaged two decades ago as intense waves or tsunami through fertilizing medaka fish eggs (*2*). In both cases, calcium was seen by means of chemiluminescent aequorin rather than the fluorescent reporters that are more widely used now. However, photoproteins like aequorin retain decisive advantages for the study of many key problems in developmental, cell, and neurobiology (*3*).

Lionel F. Jaffe
Calcium Imaging Lab,
Marine Biological Laboratory,
Woods Hole, MA 02543, USA
E-mail: ljaffe@mbl.edu

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CIMMYT Budget

I read with concern the article "Midlife crisis threatens center for semiarid crops" by Pallava Bagla (News & Comment, 2 Jan., p. 26). ICRISAT (the International Crops Research Institute for the Semi-Arid Tropics) is an important "sister" research institute that has made major contributions to ensuring food security for the poor in developing countries, and to see them having to cope with such budget difficulties is distressing. Other centers in the global research network have, as the article notes, been experiencing similar financial problems.

In the late 1980s, the management of CIMMYT (Centro Internacional de Mejoramiento de Maiz y Trigo—the Mexico-based maize and wheat research center) began a fundamental restructuring of the center in anticipation of the funding crisis that has since engulfed other international research centers. That restructuring involved significant streamlining and refocusing of our work, and phased staff reductions were a part of the repositioning strategy until late 1992. Even though our "core" funding has declined in the 1990s, we have more than made up for it by special-project fundraising, and we have experienced no layoffs or severe budget shortfalls in the last 5 years. Nor did CIMMYT impose layoffs in 1997 because of budget cuts, as the article states.

Tiffin D. Harris
Director of External Relations,
CIMMYT,
Apdo. Postal 6-641,
06600 México, D. F., México