RESEARCH: CHEMICAL REACTIONS

Selective Chemistry Redux

Izhack Oref

In a report published on page 847 of this issue, Diau *et al.* (*1*) present a novel way of influencing and following a chemical reaction on a time scale of femtoseconds (1 fs = 10^{-15} s). The work touches on basic, interrelated aspects of molecular dynamics: molecular dissociation and energy redistribution. Following Lindemann's suggestion in 1922 that excited molecules do not dissociate immediately but have finite lifetimes, Rice and Ramsperger in 1927 and Kassel in 1931 looked at the experimental results of dissociation of azomethane molecules and interpreted the findings by what is now called RRK theory. They assumed that the molecule behaves as an ensemble of identical classical oscillators in which the internal vibrational energy is statistically distributed.

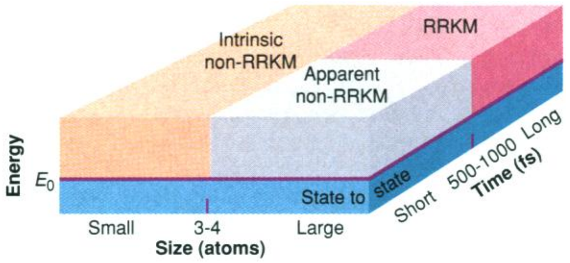
The statistical aspects of the RRK theory imply that the excited molecule can be assigned a vibrational temperature T_v. This results in a convenient Arrhenius-like expression for the rate coefficient of a homologous series (*2*) (that is, molecules that have identical reaction coordinates but different numbers of vibrational modes)

$$k(E) = K \exp(-E^*/k_B T_v) \qquad (1)$$

where K and E^* are constants that are unique for each series and k_B is the Boltzmann constant. In addition, the concept of vibrational temperature enables the estimation of the number of effective vibrational modes s (that is, the number of identical classical oscillators) in the RRK expression $s = E/RT_v$, where R is the gas constant.

In the early 1950s, Marcus provided the proper (RRKM) expression for $k(E)$. The underlying assumption in the RRKM theory is that the rate of intramolecular vibrational energy-redistribution (IVR) is much faster than the rate of dissociation of the molecule. The energy is distributed statistically among the vibrational rotational modes of the molecule, and there are no bottlenecks to the flow of energy in the molecule. It should be noted that, also in the 1950s, Slater developed an appealing unimolecular theory whereby the energy does not undergo IVR but remains in the active site associated with the reaction. Reaction occurs when there is constructive interference of the normal-mode amplitudes, leading to stretching of the dissociating bond. In series of key experiments done in the 1960s, mostly by Rabinovitch and co-workers, it was found that Slater's theory fails and RRKM theory holds. No internal bottlenecks were found for reactions of polyatomic molecules under normal conditions where the unimolecular rate coefficient was much smaller than the rate of IVR (*3*).

The statistical theory is bound to fail when the rate of reaction is of the same order of magnitude as the rate of IVR, which is estimated to be in the range of 500 fs to 1 ps. Some ion dissociation reactions (*4*) or collisionless reactions with low threshold energies (*5*, *6*) are so fast that IVR does not take place. Indeed, experimental (*5*) and theoretical (*7*) studies indicate that relaxation occurs stepwise among polyades (subsets of normal modes within the vibrational manifold). This mode of relaxation is akin to local bottlenecks for relaxation. The subject of IVR is related to coherent and incoherent dynamics in polyatomic molecules and its effects on the photophysics of such systems (*8*), but this topic will not be discussed further. In summary, large molecules, high energies, and long dissociation times exhibit RRKM behavior. Large molecules, high energies, and short dissociation times exhibit apparent non-RRKM behavior. Small molecules, or large molecules with bottlenecks (*9*), high energies, and long or short dissociation times exhibit intrinsic non-RRKM behavior (see figure).



Molecular breakups. At energies below the threshold for dissociation E_0, there is state-to-state photophysics. At energies above E_0, small molecules exhibit nonergodic, intrinsic non-RRKM behavior at all dissociation times. Large molecules with short dissociation times exhibit nonergodic, apparent non-RRKM behavior. Large molecules with long dissociation times exhibit ergodic RRKM behavior.

Early methods for testing various aspects of the RRKM theory—the statistical assumption, the rate of IVR, and nonrandom dissociation—used homologous series and high pressures of bath gases (*3*). Thus, the net effect of the number of modes on $k(E)$ can be studied without worrying about how it is affected by changes in the potential-energy surface. It is an elegant way of producing molecules with different values of T_v with the same excitation source. Systematic studies involving homologous series of substituted cyclopropane, cyclobutane, and alkyl azo compounds showed the validity of the statistical theories. However, at very high pressures of bath gases, other effects were found. These effects were explained by nonstatistical behavior (*3*). Generally, collisions deactivate the excited molecule and thus compete with dissociation. At very high pressures, however, they serve as an external clock, competing not only with dissociation but also with IVR. At 100 atm, there is about one collision every picosecond, a time scale approaching that of IVR. Experimental results show that even though the pressure was high enough to deactivate all of the excited molecules, some did dissociate. The products emanated from nonergodic molecules in which the excitation site was also the dissociation site. (Nonergodic here means that the molecule's energy was not capable of flowing to all vibrational modes.) The nonrandom contribution is small but it enables the calculations of IVR rates.

The dissociation of van der Waals molecules, a complex of inert gas atoms with a molecule formed at very low temperatures in a supersonic beam, shows distinct nonergodic behavior. It is found that the weak bond between the inert gas atom and the molecule dissociates (vibrational predissociation) nonstatistically (*10*). The atom-molecule bond strength is, at most a few hundred wave numbers, well below some of the molecular vibrations, so it is perhaps to be expected that IVR does not take place even if the excitation energy is larger than the van der Waals bond energy.

The work reported by Diau *et al.* (*1*) shows directly for the first time that nonrandom dissociation exists in polyatomic molecules on the femtosecond time scale. It circumvents IVR by exciting the reactant to high energies, well above the threshold energy E_0, and sampling the products on time scales shorter than that of IVR. Short (~50 fs) pulses excite a homologous series of cyclic ketones, breaking a C–C bond and producing a series of hot carbonyl biradicals

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The author is in the Department of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel. E-mail: chroref@aluf.technion.ac.il

$CH_2 - (CH_2)_{n-2} - C = O^\dagger$. A 100-fs delayed probing pulse follows the dissociation of the hot carbonyl biradicals. The rate is practically independent of molecular size. This result is contrary to the prediction of the statistical theory and indicates non-ergodic behavior. It is in contrast with previous work on the photolysis of cyclobutanone, which was done with conventional photolytic sources (*11*) and could be interpreted by assuming a statistical distribution of energy in the excited carbonyl biradical.

The long-sought goal of selective chemistry is related to the question of ergodicity. By this, it is meant that under unusual experimental or molecular conditions, a given moiety in a molecule can be selectively (*12*) photoexcited or chemically activated and made to dissociate into products different from those obtained under normal thermal or photochemical conditions. In this way, it is possible to "tailor" a reaction to yield specific products. Working against selective chemistry is IVR, which drains the energy from the excited moiety at a rate greater than the rate of reaction and leads to products obtained from the RRKM mechanism. Early attempts to produce selective chemistry with infrared multiphoton excitation failed precisely because the rate of pumping was slower than the rate of IVR. The work of Diau *et al.* (*1*) shows that by using highly energetic but sufficiently short light pulses, it is possible to obtain selective nonergodic behavior in reacting systems at high energies.

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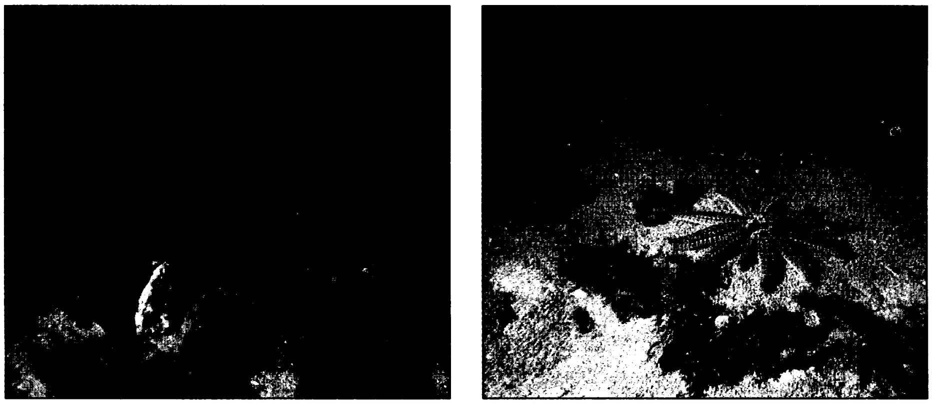
ECOLOGY

Reversal of the Burden of Proof in Fisheries Management

Paul K. Dayton

Traditional management of fisheries aims to optimize the catch of certain economically important species by commercial fishing boats, but this goal often eventually results in the collapse of the targeted species itself. We have excellent long-term data documenting this process for some fisheries. (See report on page 860 and news story on page 809.) But what is happening to the hundreds of noncommercial species taken incidentally or by poaching or ghost fishing by lost or abandoned gear? There is virtually no information. In addition, thousands of square kilometers of benthic habitat and invertebrate communities have been obliterated by trawling (see the figure), and recreational fishing and poaching have massively altered many coastal marine communities.

One irreparable consequence of this widespread damage is the loss of the opportunity to study and understand intact communities: In most cases there are no descriptions of the pristine habitats. The damage is so pervasive that it may be impossible ever to know or reconstruct the ecosystem. In fact, each succeeding generation of biologists has markedly different expectations of what is natural, because they study increasingly altered systems that bear less and less resemblance to the former, preexploitation versions. This loss of perspective is accompanied by fewer direct human experiences (or even memories) of once undisturbed systems. The effects of humans sometimes result in cascading ecological changes—a void often in part filled with introduced or inappropriate impostors that replace and mask the traces of the former natural system—but the species often simply disappear, leaving no conspicuous effect on the community. As with the loss of human cultures and languages after the passing of the elders with their wisdom, so too is humanity losing the evolutionary wisdom found in intact ecosystems.



A type II error? An extensive bed of *Atrina zealandica* (a pinniad bivalve) (**left**) was decimated by commercial dredging for scallops (**right**).

How can society stop the alteration of these previously diverse and productive habitats? It is first necessary to recognize a fundamental problem: Unlike other effects of private interests on the resources of the general public, fishing often is considered a right not a privilege. Regulations often are barely tolerated by the fishing community, and poaching is rampant and minimally penalized. Management of fisheries has typically aimed to maximize the number of fish caught, while allowing little safety margin for assessment error, interannual variability in recruitment of young fish, or other factors such as El Niño and diseases. The countless species incidentally killed are usually ignored—unless they are also of commercial or recreational value, or are protected by the Endangered Species Act or the Marine Mammal Protection Act. Even the marginal protection afforded by these regulations are impeded by controversies and may take more than a decade to implement.

The challenge to management of any wild resource is to provide a buffer for uncertainties to safeguard the future health of the population or ecosystem. Appropriate application of available statistical techniques could allow

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The author is at the Scripps Institution of Oceanography, La Jolla, CA 92093-0201, USA. E-mail: pdayton@ucsd.edu