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PERSPECTIVES

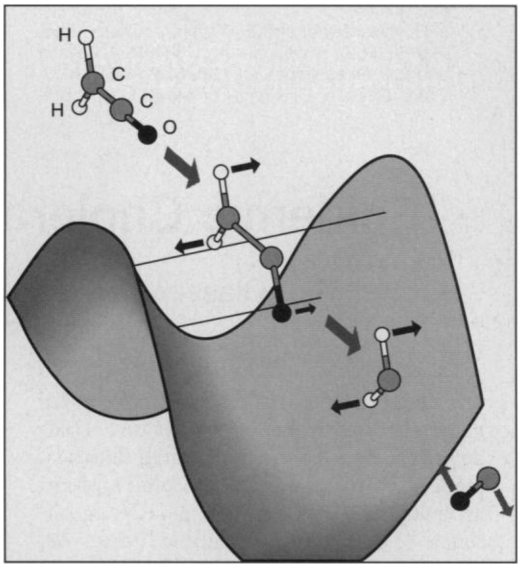
Skiing the Reaction Rate Slopes

R. A. Marcus

On the way from reactants to products, a chemical reaction passes through what chemists term the transition state—for a brief moment, the participants in the reaction may look like one large molecule ready to fall apart. The nature of this elusive state is the subject of a number of exciting recent developments that involve theory and experiment in the study of chemical reaction rates (*1–6*). They include time-resolved studies of molecules in the transition state region (*3*), spectroscopic observations of that region (*4*), reactive scattering state-to-state cross sections for reactions such as $H + H_2 \rightarrow H_2 + H$ (*5*), and experimental/theoretical studies of electron transfer processes in the condensed phase (*6*). The experiments of Lovejoy *et al.* described in this issue of *Science* (*7*) involve the fundamental question of the quantization of vibrational energy levels of the transition state and its implications for unimolecular reaction rate theory.

The most commonly used treatment of chemical reaction rates is transition state (TS) theory (*8*). In the latter, it is assumed [explicitly or, better still, as a consequence of a dynamical approximation attributable to Wigner (*9*)], that there is a quasi-equilibrium between reactant (or reactants) and systems crossing the TS in the forward direction along the reaction coordinate q, that is, from reactants to products. Equilibrium statistical mechanics is then used to calculate the density of systems (number per unit length) along q in the TS region, and from it, using a distribution of velocities $\dot{q}$ consistent with the given conditions, the reaction rate is obtained. In the most frequently used form of TS theory, the motion along q is treated with classical mechanics, and the transverse motions, particularly the vibrations of the TS, are treated quantum mechanically, the latter resulting in quantized vibrational energy levels for the TS. There may also be additional quantum mechanical effects, such as nuclear tunneling through a barrier along q, and there is also the question of dynamical separability of q from the other coordinates in such a case, a question that has been and is being addressed to various degrees of sophistication in current and older literature [for example, in (*1*) and (*2*)].

In the early days of TS theory (the mid-1930s), Kassel (*10*) pointed out that the "quantized" vibrational energy states of the TS might be considerably broadened. He based his idea on Heisenberg's uncertainty principle, $\Delta E\ \tau \geq \hbar$: when the TS exists only for a very short time τ (the time to "pass" through the TS region), the broadening ΔE of each relevant vibrational state of the TS could become so large that "quantization" of these levels would tend to be washed out (*10*).



Over the hump. Schematic diagram of the unimolecular dissociation of ketene (CH_2CO) (see cover illustration also). The ketene molecule is prepared in a vibrationally excited state by absorption of laser light, which is followed by a localization of energy in the C-C bond. At the transition state (the saddle point of the energy surface) the CH_2 and CO repel, converting potential energy into translational and rotational energy of the fragments, which can be observed with laser-induced fluorescence. As more energy is pumped into the transition state complex, stepwise increases in dissociation rate are observed. This is consistent with RRKM theory, which assumes that the dissociation rate is controlled by quantized transition state thresholds. [Figure is adapted from Lovejoy *et al.* (*7*)]

Later it was recognized that the dynamics of the reaction might permit the system to exist for a longer time τ in a given vibrational quantum state of the transverse coordinates; that is, the transverse vibrational quantum numbers might indeed be approximate constants of the motion. Such behavior has been termed vibrational adiabatic (*11*), and has since been used to compare with the results of experiments or dynamical calculations on reaction rates.

This vibrational adiabaticity might be either *global*, that is, the vibrational quantum numbers might remain "good" all the way from reactants to products (*12*), or *local*, that is, good only in some limited region along q around the TS region (*11*). If that region of "goodness" is large enough, then τ is large, ΔE is small, and the quantization of the TS is sharp. Experimental or quantum mechanical tests of global adiabaticity have been made with state-to-state experiments or calculations, which compare the initial vibrational quantum states of reactants with the final vibrational quantum states of products. In this way, global vibrational adiabaticity has been seen to be approximately obeyed for a thermoneutral reaction such as $H + H_2 \rightarrow H_2 + H$, but is frequently violated for reactions which are highly exothermic in the forward or reverse direction.

A local vibrational adiabaticity in the TS region for a sufficiently broad region implies a quantization of the vibrational energy of the TS. The experiments of Lovejoy *et al.* (*7*) address this quantization, using a high resolution study of a unimolecular reaction (see figure and cover). In the theory for unimolecular reactions, the rate constant is given as a function of the energy E of the reacting (dissociating or isomerizing) molecule by the RRKM (Rice-Ramsperger-Kassel-Marcus) (*13, 14*) expression

$$k_{EJ} = N^{\ddagger}_{EJ}/h\rho_{EJ} \qquad (1)$$

where $N^{\ddagger}_{EJ}$ is the number of vibrational-rotational quantum states of the TS with energy equal to or less than E, ρ_{EJ} is the number of such states of the parent molecule per unit energy at the same total energy, J is the angular momentum, and h is Planck's constant. RRKM theory (*13*) is a TS theory that treats the molecule as a microcanonical system (a system statistically distributed among all possible states at the given energy). The theory drew upon the early ideas of the RRK theory (Rice-Ramsperger-Kassel) of the late 1920s (*15*) and upon TS theory (*8*).

When the vibrational energy of the reacting molecule is systematically increased, for example by exciting a molecule optically with a laser of the appropriate frequency and increasing the photon energy, the RRKM rate constant k_{EJ} is predicted in Eq. 1 to increase in steps of magnitude $1/h\rho_{EJ}$, the steps occurring when each new vibrational quantum state of the TS becomes energetically accessible.

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Two effects would tend to round off or otherwise modify these steps: (i) when there is a breakdown of local adiabaticity for the vibrational motion near the TS during the motion of the system along q, and (ii) when there is sufficient nuclear tunneling (*16*) through the energy barrier along q in the TS region. Examples of (ii) are seen in quantum mechanical calculations for reactions involving the transfer of an H atom, reactions where nuclear tunneling is expected because of the lightness of the H atom. In the reaction studied by Lovejoy *et al.* (*7*), the dissociation of the triplet state of ketene, $CH_2CO \rightarrow CH_2 + CO$, the motion along q is that of nuclei substantially heavier than H, so the reaction would be less prone to a tunneling through the potential energy barrier.

The report of Lovejoy *et al.* (*7*) provides evidence for stepwise increases in k_{EJ}, which indicates that quantization is maintained. The question of "what next" naturally arises. Two ingredients are present in RRKM theory: (i) a statistical treatment which samples all parts of the "phase space" of the molecule and which leads to the underlying monotonic increase of the rate constant k_{EJ} as a function of energy; and (ii) a quantization of the TS, which leads to steps in k_{EJ} of size $1/h\rho_{EJ}$ imposed by the quantization of the TS upon this monotonic increase. When the statistical assumption (i) breaks down (a search for "non-RRKM" behavior is actively pursued in the literature) one expects an underlying behavior of k_{EJ} versus E to be more highly structured, that is, one would obtain nonmonotonic behavior of k_{EJ} versus E, as was found in the dissociation of CH_2O under extremely high resolution (Stark level-crossing spectroscopy) conditions (*17*). If there is sufficient averaging over an energy range in the ensemble prepared, such local structure would disappear in the averaging (*18*). Regardless of whether or not this averaging has occurred in the experiments of Lovejoy *et al.* (*7*), a question which remains concerns the size of the steps and how closely they match the expected value of $1/h\rho_{EJ}$. Estimates of ρ_{EJ} have been made, but as Lovejoy *et al.* (*7*) point out, more accurate values would be useful.

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Epidemic Cholera in the Americas

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In January 1991, cholera, the most feared epidemic disease of the 19th century, characterized by severe, often fatal diarrhea, made a dramatic and unexpected reappearance in the Americas after a 100-year absence (*1*). The first confirmed cases occurred in Peru, and by mid-February more than 10,000 patients were being treated weekly. The epidemic spread to involve a new country almost every month, and by year's end 391,000 cases and nearly 4,000 deaths had been reported to the Pan American Health Organization, more cases than reported worldwide during the previous 5 years.

Much of our knowledge of epidemic cholera comes from experience with the six previous pandemics of the 1800s and early 1900s (*2*). Each pandemic began in Asia, swept through Europe, and some went on to the Americas. All went away within a few years for reasons still unknown. During the epidemic in London in the 1850s, John Snow laid the groundwork for control by linking the transmission of disease with consumption of fecally contaminated water. By 1883, when Robert Koch discovered the causative organism, *Vibrio cholerae* 01, cholera was on the decline in Europe. In the 1900s, cholera persisted as a seasonal endemic disease in many areas of Asia until 1961 when a new pandemic began in the Celebes Islands heralded by the novel El Tor biotype of *V. cholerae* 01 (*3*). This seventh pandemic spread in Asia and the Middle East and reached Africa in 1970 where it invaded 29 countries in 2 years. Unlike previous pandemics, this pandemic has not gone away.

The extension of the seventh pandemic to the Americas has raised many questions: How was *Vibrio cholerae* 01 introduced? Why did it spread so rapidly? What can be done in each country to control the epidemic? Its reemergence has breathed new life into issues both of public health—the need to provide quality water and sewage treatment and address food hygiene—and of science—the need to apply epidemiologic and molecular techniques to examine disease transmission, identify environmental reservoirs, and develop improved vaccines.

We may never know how *V. cholerae* 01, El Tor, was introduced into the Americas, but characterization of early isolates with new techniques such as ribotyping or se-

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