

Do Highly Excited Reactive Polyatomic Molecules Behave Ergodically?

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The last several years have been ones of great effort and considerable controversy on the subject of intramolecular vibrational relaxation in reacting molecules. We consider only complex, polyatomic species at the high levels of internal excitation characteristic of unimolecular reaction. Most molecules of recent concern have thresholds in excess of 30–40 kcal mol⁻¹. The contemplation of the nature of their relaxation behavior has brought together the interests of physicists, chemists, spectroscopists, molecular dynamicists, quantum chemists, photochemists, and chemical kineticists.

The question posed is this: Do reacting molecules display ergodic or nonergodic behavior? That is to say, does an ensemble of reacting molecules explore uniformly all regions of its available internal energy-coordinate hypervolume (statistical behavior) prior to decomposition? Or is only a portion of phase space visited during the lifetimes of the molecules (nonstatistical behavior)? Considerable effort has been devoted in the past several decades to the clarification of this question. The dilemma was phrased during the 1950s as follows. Which is the more correct theory of unimolecular reaction—that of R. A. Marcus and O. K. Rice or that of N. B. Slater?¹ The theory of Marcus and Rice (RRKM) employs a statistical model which postulates that coupling of the internal motions leads to rapid intramolecular energy randomization on a time scale short relative to the mean lifetime of decomposing species (ergodic behavior). The Slater theory characterizes a molecule by a potential function having only quadratic terms and internal normal modes of motion which are orthogonal to each other, so that the system does not relax throughout its vibrational manifold before decomposing (nonergodic behavior).

Indeed, this problem was subsequently resolved in favor of statistical models for molecules having lifetimes longer than $\sim 10^{-10}$ s². A variety of evidence obtained in the '50s and '60s supported the ergodic proposition. Notwithstanding, the contrary view has been advanced

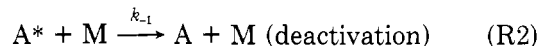
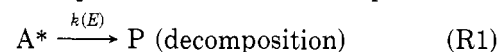
and the generality of the conclusions based on conventional thermal or chemical activation data has been contested.^{3,4} Especially in recent years, a variety of calculational and experimental studies including trajectory calculations, crossed beam experiments, and multiphoton laser excitation work have raised anew the question of the validity of statistical models.

Interestingly, the ergodic question also appears in collisional phenomena. Intermolecular vibrational energy transfer between highly excited polyatomic molecules and bath molecules involves some type of accommodation in a short-lived complex.⁵ Thus, the extent of intramolecular relaxation within the loosely bound compound species is a related problem.

We first sketch briefly some background related to unimolecular rate formulations and experimental studies. Then we take up some of the types of experimentation that lead to useful conclusions with regard to the controversial propositions at hand. In the spirit of these Accounts, the treatment represents particular viewpoints of the authors rather than a comprehensive review.⁶

Models for Unimolecular Decomposition

An activated species A* at the internal energy level E undergoes two processes. R1 is decomposition to



products P with rate coefficient $k(E)$; R2 is collisional deactivation by a bath molecule, M. The rate coefficient for deactivation k_{-1} can be calculated from kinetic theory with varying degrees of sophistication. In the simplest case (strong collision), A* is deactivated below the threshold energy for decomposition, E_0 , by a single collision. If more than one collision is needed on the average to deactivate A*, then M is a weak collider with relative efficiency $\beta < 1$. Deactivation can encompass all aspects of intermolecular energy transfer $V \rightarrow V$, $V \rightarrow R$, $V \rightarrow T$, where V indicates vibrational, T translational, and R rotational energy. The subject has been

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reviewed recently^{5,7} and need not be elaborated.

As mentioned in the introduction, Slater's model¹ for $k(E)$ postulates nonergodic behavior in which decomposition occurs when a critical coordinate q extends beyond a critical length q_c . The molecule does not sample the whole of phase space, and q is obtained by a superposition of various normal coordinates closely associated with the breaking bond. The RRKM transition-state model^{1,8-10} applies in simplest form to reactions having a large potential barrier in both directions; internal energy is statistically distributed among the vibrational modes both in the excited polyatomic molecule and in the activated complex located at the saddle point of the hyperpotential surface. Then

$$k(E) = \sum P(E^+) / hFN(E) \quad (1)$$

$N(E)$ is the density of states of the excited molecule; $\sum P(E^+)$ is the number of accessible internal states of the complex; $E^+ = E - E_0$; h is Planck's constant; F is a correction for centrifugal energy effects.

When the vibrational frequencies of the molecule are known, $N(E^*)$ can be calculated quite accurately by various algorithms.^{9,10} $\sum P(E^+)$ is harder to evaluate since the frequencies of the complex are not known; however, certain procedures, such as reproducing the thermal Arrhenius A factor, ensure that reasonable values are assigned. A molecule for which $k(E)$ can be evaluated by the above procedure is called an RRKM molecule. There are conjectural, as well as known cases, however, where $k(E)$ may not fit the experimental magnitude.^{3,11-16} This could come about because of a "bottleneck" in phase space or because of a time scale for reaction which prevents statistical redistribution of the internal energy prior to decomposition. Such behavior is called, respectively, "intrinsic" and "apparent" non-RRKM behavior.¹⁶

Techniques of Excitation

There are basically two ways to produce the excited species A^* . One way is in a thermal Boltzmann system^{9,10} in which a fraction of the molecules of the ensemble are transported above the threshold E_0 by collisions.^{9,10,16-27} The second way of producing A^* is by some "external" energy source or mechanism not subject to the equilibrium distribution law of canonical ensembles. Such sources include chemical activation,^{11-13,28-42} multiphoton excitation,⁴³⁻⁷² molecular beams,⁷³⁻⁹² single photon excitation,⁹³⁻¹⁰⁶ and photosensitized reaction.¹⁰⁷⁻¹¹² The hot molecules produced

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are subject to collisional intervention unless collision-free conditions are maintained.

The overall unimolecular rate coefficient is¹⁰

$$k = \int_{E_0}^{\infty} \frac{I(E)k(E)}{k(E) + k_{-1}[M]} dE \quad (2)$$

where $E = E' + E_{th}$; E' is the effective energy introduced into the molecule by the non-Boltzmann excitation process; E_{th} is the original thermal energy content of the molecule; $f(E)$ is the energy distribution function, such as the light source profile in the case of photochemical reaction; I is the flux of the excitation source.

For an equilibrium thermal system, $E' = 0$, $E = E_{th}$, $f(E) = B(E_{th})$, $I = \beta k_{-1}(M)$, and

$$B(E)dE = \frac{N(E) e^{-E/RT} dE}{\int_0^{\infty} N(E) e^{-E/RT} dE} \quad (3)$$

For a weak collider bath there is depletion of substrate populations below E_0 ; $B(E)$ is replaced by its steady-state value $B_{ss}(E)$ which can be found by an iteration method⁹ or by eigenvalue solution of the steady-state matrix. According to eq 2, the decomposition behavior of the excited molecule is independent of the origin of excitation and responds only to the energy relaxation process and to collisional deactivation.

Thermal Systems

This method of experimentation is the oldest that has been applied to unimolecular systems. The resolution of the question of ergodicity of molecules prepared for reaction by collisions is not necessarily one of simple test. Both the Slater and the statistical Rice-Ramsperger-Kassel (RRK) theory lead to classical expressions for the rate coefficient that are similar in form:

$$k_S = \frac{k_{\infty}}{\Gamma[(n+1)/2]} \int_0^{\infty} \frac{x^{(n-1)/2} \exp(-x) dx}{1 + x^{(n-1)/2} \theta^{-1} \omega^{-1}} \quad (4)$$

and

$$k_{RRK} = \frac{k_{\infty}}{\Gamma(s)} \int_0^{\infty} \frac{x^{s-1} \exp(-x) dx}{1 + [x/(x+b)]^{s-1} A \omega^{-1}}$$

where θ is a quantity related to molecular parameters; A is a constant; ω is the specific collision rate; $b = E_0/RT$; $x = E/RT$; and n and s designate relevant internal degrees of freedom. It is seen from eq 4 that distinction between the two formulations could be difficult for a random ensemble of excited molecules: sufficient flexibility may be provided by the choice of n and θ in the first expression, or of s in the second, so as to bring about near-coincidence in the predicted magnitudes of k and of the falloff behavior (the decline of k with decreasing pressure).

However, for suitable choice of substrates certain consequences of the Slater formulation make a distinction unequivocal.² Consider the isomerization of cyclopropane to propylene. Cyclopropane has C_{3v} symmetry and 7 of the 21 normal vibrational modes are degenerate. The Slater treatment predicts¹ that the maximum number of modes that can contribute to the reaction coordinate is $n \leq 21 - 7 \leq 14$; the experimentally observed number is^{1,2} $n \approx 13$, in good

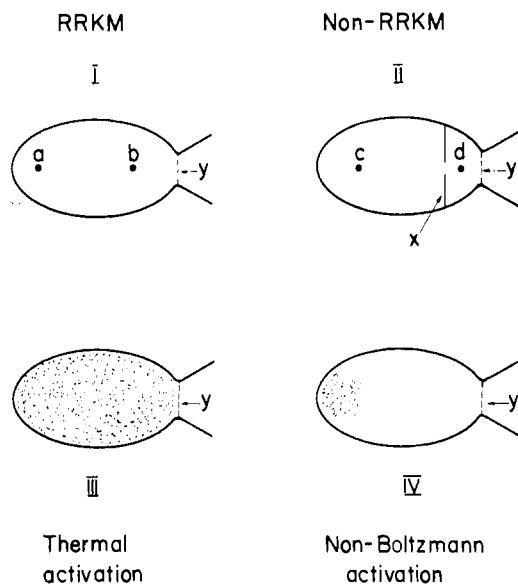


Figure 1. (I) RRKM molecule: Injection into phase space far away from point a, and close to point b, the critical bounding plane for decomposition, y. Injection into (b) can cause apparent non-RRKM behavior under appropriate experimental conditions. (II) Non-RRKM molecule: Injection into (c) is the reason for "false" high-pressure limit caused by the "bottleneck", x. Injection into (d) causes the "part" molecule behavior. All points at constant energy. (III) Thermal activation of an RRKM molecule. (IV) Non-Boltzmann activation (chemical, photoactivation) into part of phase space. See ref 16a.

agreement. However, if the symmetry of cyclopropane is reduced by substitution, as in 1,2-cyclopropane- d_2 , then the allowed maximum value of n should rise to $n \approx 17-18$. Instead, no increase above $n = 13$ other than a slight change due to quantum statistical effects predicted by RRKM theory was found.^{17b}

Similarly, for the isomerization of methyl isocyanide to acetonitrile, a molecule with C_{3v} symmetry in which 4 of the 12 vibrational modes are degenerate, the observed value of $n \approx 4$ is not essentially changed¹⁸ as the progressive substitutions are made: $\text{CH}_3\text{NC}(C_{3v}) \rightarrow \text{CH}_2\text{DNC}(C_1) \rightarrow \text{CD}_3\text{NC}(C_{3v})$. Indeed, for a number of reactions, e.g., cyclobutane¹⁹ and olefin isomerization,²⁰ symmetry restrictions cause failure of the Slater theory predictions for the falloff behavior. Good agreement exists with statistical theory. The above systems illustrate one way that ergodic and nonergodic behavior has been distinguished even for a collisionally prepared ensemble of reacting molecules. Ideas that apply to Slater's extreme "normal mode" form of theory can also extend, *ceteris paribus*, to other variants¹⁰¹⁻¹⁰³ of orthogonal-mode theories which "make" small molecules out of big ones.

It has been suggested⁴ that the random distribution may not only be prepared by collision but may also be maintained by (elastic) collisional perturbations having cross sections 100-fold larger than conventional kinetic values. This could occur on a time scale short with respect to reaction so that intramolecular energy

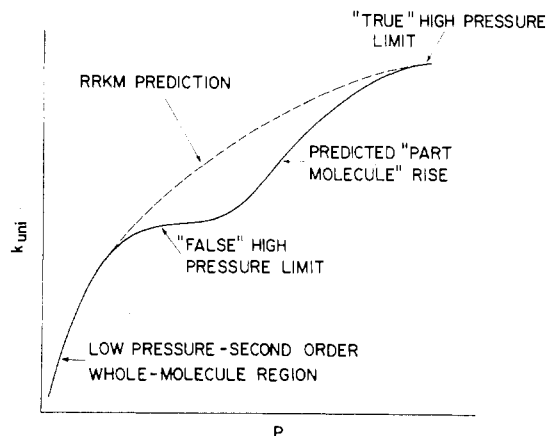


Figure 2. Unimolecular rate coefficient vs. pressure (after ref 16). Falloff behavior for an "intrinsic" non-RRKM molecule having an internal bottleneck.

randomization is simulated even for intrinsically non-RRKM molecules. This is one of several arguments that have been offered in the past few years as an alternative to the generality of the central assumption of statistical theory; it will be considered in the next section.

Recently, trajectory calculations on the methyl isocyanide molecule (with an assumed molecular potential) have led Bunker and co-workers^{3,16} to conclude that methyl isocyanide is an "intrinsic" non-RRKM molecule with an internal bottleneck to redistribution of energy. The segmentation of the phase space of the molecule into two parts (Figure 1) leads to the prediction¹⁶ of a false, premature high-pressure limit (represented by point c) followed by a subsequent rise of a "part molecule" to the conventional limit at higher pressures (Figure 2). The data on methyl isocyanide²¹ were considered by these authors to correspond to the false limit, and early high-pressure experimental work by Harris^{3,22} indicated the occurrence of the predicted "part molecule" (Figure 2) rise. (Of course, a bottleneck would not exist and such rise would not occur in the collisional perturbation model; trajectory calculations^{16b} on methyl isocyanide suggest, however, that internal energy is *not* randomized by collisions.) More recent work²³ on CH_3NC at pressures up to 350 atm has revealed errors in the earlier report^{3,22} and confirms the high-pressure limit of Schneider and Rabinovitch.²¹ As a matter of fact, RRKM theory gives good agreement with both the position and shape of the falloff for CH_3NC and for a series of isocyanides (CH_2DNC , CD_3NC , $\text{C}_2\text{H}_5\text{NC}$, $\text{C}_2\text{D}_5\text{NC}$). It is evident that a "part-molecule" bottleneck model is necessarily based on "happenstance" features of molecular potential (mode frequency, anharmonicities, and couplings). It cannot explain the behavior for CH_3NC or the rest of the series.

Several other thermal unimolecular systems have been examined experimentally at supra-high pressures to test for any alteration in k_∞ measured at lower pressures. The study of ethylcyclobutane up to ~ 200 atm showed a small decrease in rate which was simply

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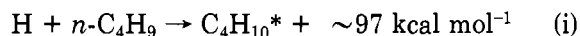
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attributed to a volume of activation, i.e., a many-body effect.²⁵ Nitryl chloride²⁶ showed no deviation from RRKM behavior up to ~ 300 atm. At pressures up to ~ 300 atm, nitrogen pentoxide²⁶ showed a small change in k_{∞} which the present writers believe represents only experimental complications.

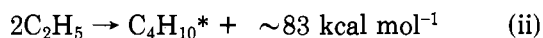
In conclusion, RRKM behavior in thermal systems has been tested up to very high pressures. The results indicate overwhelmingly that no verified deviations from RRKM behavior have been seen, and the theory continues on this basis as a working model and when suitably modified applies to reaction types involving low reverse barriers.²⁷

Chemical Activation Systems

Chemical activation involves production of internally excited species by chemical reactions.²⁸ Most unequivocal with respect to the energy level of the product molecules are bimolecular association reactions such as

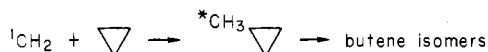


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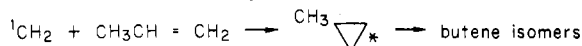


Different activation reactions can excite the same molecule in characteristically different ways, i.e., molecules may be injected into different regions of the space that describes the initial internal states of the nascent molecules (Figure 1). Thus, for reaction i, the initial state of excitation involves deposition of a high proportion of the excitation energy in C-H stretching motion. For reaction ii, the initial state heavily involves C-C stretching and skeletal motion. For nonergodic behavior of excited butane, C-H and C-C rupture would be facilitated in i and ii, respectively.

Early chemical activation experiments were designed to show that rapid intramolecular relaxation occurs after the initial excitation event; that the initial subset of highly excited vibrational modes of motion of the nascent molecule relaxes rapidly into the full set of internal motions. Butler and Kistiakowsky²⁹ demonstrated that the quantitative proportions of the olefin products that arise from methylcyclopropane are independent of the activating reaction, whether centered on the side chain, as by the insertion reaction



or centered on the ring via the addition reaction



Many such examples have ramified over the years.

A variety of chemical activation experiments at differing energy levels, size, and complexity of substrate

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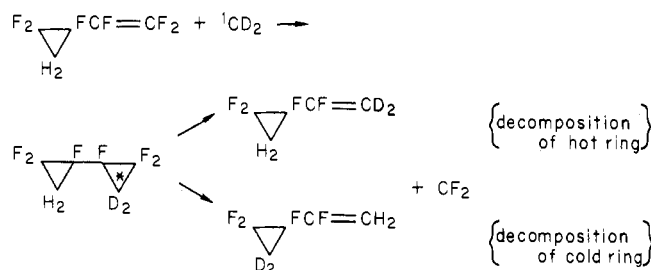
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structure have revealed good adherence between statistical theory and the microscopic specific rates, $k(E)$. Examples are the series of 2-alkyl radicals³¹ from C_4 to C_{16} at pressures up to 200 atm,^{14c} with microscopic rate constants that vary from 10^7 to 10^3 s^{-1} ; a series of alkylcyclopropanes,³² along with the analogous perfluoroalkyl members, having specific rates that vary over the range 10^{10} to 10^5 s^{-1} ; and a truly multitudinous and impressive series of haloalkane molecules C_2 , C_3 , and C_4 , studied by Setser and co-workers,³³ having various combinations and numbers of halogen substituents whose rates range from $\sim 10^5$ to $\sim 10^{11} \text{ s}^{-1}$.

It is possible that not *all* large polyatomic molecules obey statistical theory, although reliable exceptions are difficult to find.³⁴ The vinyl³⁵ and the ethyl³⁸ radical decompositions are so mentioned, although as noted by the investigators further work is necessary and complete theoretical treatment requires careful consideration of conservation of angular momentum in these cases.³⁶

The studies described above say nothing about the time scale of the intramolecular energy relaxation other than that it must be substantially faster than the decomposition process so that RRKM behavior is manifested. In recent years, a number of chemical activation experiments have been designed to measure the internal energy relaxation constants. The first such study involved the simultaneous activation and symmetrization of a molecule:¹¹



The H and D substituents label the hot (*) "nascent" and cold "old" rings and have no other isotopic purpose. Excitation corresponds to injection of the molecule into its phase space (point b in Figure 1) in a position proximate to the bounding plane for rupture of the nascent ring (line Y in Figure 1). Internal energy randomization (diffusion of the system into the body of the phase space) competes with decomposition of the nonrandomized molecule (diffusion across the critical bounding plane, y). Decomposition of the nascent ring predominates at high pressure since molecules can diffuse only in very small numbers through the phase space to the critical hyperplane for rupture of the old ring (internal randomization) before being deactivated by collisions. Theoretical analyses of the proportions of nonrandom decomposition of the nascent ring, stabilization, and decomposition of randomized mol-

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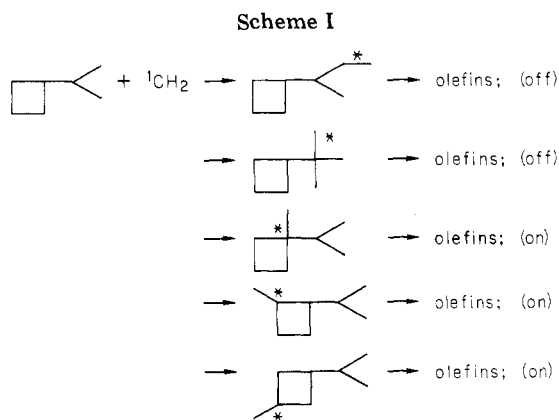
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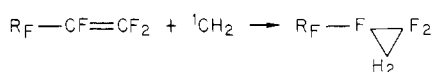
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ecules lead to the value for the intramolecular relaxation constant, $\lambda \approx 10^{12} \text{ s}^{-1}$.

Decomposition of the members of a homologous series



was also studied;¹² $\text{R}_F \equiv \text{CF}_3$, C_3F_7 , and C_5F_{11} . Again the values $\lambda = 1 (\pm 0.4) \times 10^{12} \text{ s}^{-1}$ were found.

More recently, alkylcyclobutane¹³ hydrocarbons have been investigated. This provides a gross selection of the initial nonrandom state of excitation of the chemically activated molecules, as illustrated for isopropylcyclobutane substrate^{13b} (see Scheme I, where "off" indicates excitation off, and "on" indicates excitation on the ring). The reaction in each case is ring rupture to form olefins whose structure is diagnostic of the particular source (a) to (e). It is evident that reaction a represents excitation at a site farthest from the ring, corresponding to injection of the "methyl" isopropylcyclobutane molecules into regions of their phase space remote from the critical plane for decomposition of the ring (point a in Figure 1). The excited species cannot decompose until energy randomization occurs, i.e., the subset of initially excited vibrational motions must expand to include ring motions. In reaction c, excitation takes place on the ring which will break; i.e., the molecule is injected into a part of the phase space proximate to the dividing reaction plane (point b in Figure 1). The initial subset of excited vibrations includes ring motions, and the nonrandomized molecule may decompose in competition with internal relaxation. The study of methylcyclobutane substrate^{13a} leads to the estimation of the internal relaxation constant, $\lambda > 5 \times 10^{12} \text{ s}^{-1}$. The isopropylcyclobutane system^{13b} provides values of $\lambda \approx 2.9 (\pm 0.5) \times 10^{12} \text{ s}^{-1}$. Latest work on neopentylcyclobutane system^{13c} also gives values of $\lambda \approx 2.1 (\pm 0.5) \times 10^{12} \text{ s}^{-1}$. Within the uncertainty of the experiments, these values are several-fold larger than those for fluorocarbons.

Work in progress on the bicyclobutyl substrate^{13d} reveals similar behavior.

It has been suggested³⁷ that, unlike photoactivation, chemical activation cannot illustrate substantial non-random effects. The rationale for this idea is that the reaction event, unlike light absorption, causes a profound perturbation of the nascent molecule that effectively couples the whole molecule. (By contrast, some proponents of the view that internal relaxation in reacting systems is not invariably fast cite chemical activation such as the vinyl and ethyl radical systems, mentioned earlier,^{35,38} as examples of their model.) This

proposal is designed to support the proposition that RRKM theory only *appears* to give a quantitative account of the data. However, if a nascent molecule is profoundly perturbed, such also must be the case for a highly extended or decomposing molecule (with avoidance of the case of a pathological extreme of excitation), and randomness should apply. As N. B. Slater has shown, reacting molecules repeatedly explore the limiting regions of their phase space before a favorable excursion occurs. The cyclopropane and cyclobutane systems just described demonstrate that energy randomization does *not* occur upon formation of the hot species by chemical reaction but is a process that follows excitation with a characteristic smallest relaxation constant of $\approx 10^{12} \text{ s}^{-1}$. In any case, it is not a sufficient condition for obedience to RRKM behavior that an ensemble of molecules is formed initially with microscopic energy distributions that follow random statistics. Indeed, this postulate was used in the classical Slater theory. It is also requisite that a statistical redistribution of energy be maintained on a time scale that is short compared to the chemical degradative process so that the energy above E_0 is available in the reaction coordinate. The redistribution can be obtained via the intramolecular mechanism or by the intermolecular collisional perturbation process proposed by S. A. Rice and co-workers.⁴ However, the collisional perturbation mechanism is contrary to a variety of experimental evidence that we summarize.

First, chemical activation studies of the butyl radical system were shown some time ago⁴⁰ to yield rate coefficients that are independent of pressure effects down to pressures below 10^{-2} torr, i.e., at nominal collision rates $\leq 10^5 \text{ s}^{-1}$, relative to decomposition rate constants $\geq 10^7 \text{ s}^{-1}$, so that collisional redistribution would be inadequate. A number of such low-pressure cases are known.

Second, in some of the intramolecular relaxation studies cited in ref 11 and 36 the effects of the internal relaxation become observable at pressures of 0.2–20 torr, where the nominal collision rate is only 10^6 – 10^8 s^{-1} and even elastic phenomena occur only with a frequency of $\sim 10^8$ – 10^{10} s^{-1} . By contrast, the internal relaxation occurs on a time scale of 10^{-12} s , i.e., much less than collision intervals.

Third, crossed molecular-laser beam studies on a wide variety of complex molecules, in experiments which are intrinsically designed to be collision free, have been shown by Lee and co-workers⁴¹ (see later) to be in reasonable accord with various aspects of statistical RRKM theory.

Finally, very recently the ultraviolet excited decomposition of internally converted cycloheptatrienes under very low pressure collision-free conditions have been shown to accord well with statistical theory.⁴²

Single and Multiphoton Vibrational Excitation

Laser-induced unimolecular decomposition is of great current interest.^{43–72} (Extensive references are cited

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in these papers; the mechanism of multiphoton absorption^{54,57,58} need not be discussed here.) Multiphoton infrared laser excitation brings about activation of the molecule by irradiation at a particular frequency corresponding to one of the modes of vibration. The average energy of a photon from a CO₂ TEA laser is ~3 kcal mol⁻¹ and the number absorbed is above 30 in some cases. A cardinal question has been—does a molecule decompose in a mode-specific manner or does it explore its potential surface prior to decomposition?

There is mounting evidence that the multiphoton decomposition of excited molecules follows ergodic behavior.^{41,47,48,60–62,66b} However, it is important to realize that the term “collisionless region”, so often used, usually refers to conventional kinetic cross sections. A test of the elastic collisional perturbation model for intramolecular energy redistribution requires pressures that are a 100-fold smaller. Many experiments that were performed in the “kinetic” collisionless region were not at low enough pressure to provide a clear test.

The clearest support from laser studies of the statistical approach is provided by the work of Lee and co-workers.^{41,46–48} Several crossed molecular beam–CO₂ laser experiments on the dissociation of SF₆, halo-

methanes, etc., give spatial distributions of products and lifetime estimates in accord with RRKM theory.

Other laser work has been carried out at higher pressures and does not provide as unequivocal test of the behavior. In some cases, at least part of the data are definitely in the “kinetic” multicollision pressure regime, i.e., $k_{-1}[M] > k(\epsilon)$ (eq 2). In other cases, the specific rate constants are not known or not given, and it is impossible to say clearly whether $k_{-1}[M] \ll k(\epsilon)$, a necessary condition for “elastic” collisionless behavior. Nevertheless, important information is provided by this work. They correspond very well to the predictions of the statistical model; they show little evidence⁶⁶ for mode-specific decomposition. Setser and co-workers⁶² irradiated CH₂FCH₂Br at the C–F stretching frequency under kinetic collisionless conditions. This should favor HF elimination if nonergodic behavior occurred. The product ratio was HBr:HF = 10:1, which is predicted by statistical theory since HBr is eliminated with lower threshold energy than HF. In another study,⁴⁶ CCl₂F₂ was excited in the multicollision region, first at the CCl₂ stretching frequency and then via the CF₂ stretching mode. The reaction products were identical in both cases, revealing no temporal or molecular spatial memory prior to decomposition. Dissociation of ethyl acetate⁶¹ under the conditions of low pressures and high laser intensity gave a rate coefficient consistent with RRKM theory. “Collision-free” dissociation of CF₂Cl₂ and CF₂Br₂ produces⁶⁰ vibrationally excited CF₂ in which the energy is distributed statistically and can be expressed by a single Boltzmann distribution characterized by a single parameter which is the vibrational temperature T_v . The decomposition of CH₂F₂⁶⁹ follows the thermodynamically predicted route of fission of the C–H bond.

Laser isotope separation in large polyatomic molecules has been the subject of a large number of investigations.^{54,71,72} No novel theories need yet be invoked for the interpretation of the decomposition process.

Some confusion with regard to internal relaxation of energy has arisen in conclusions derived from laser studies by use of inappropriate models for collisional energy transfer in the high-energy region concerned.^{70a} It should be noted that collisional activation/deactivation by cold bath molecules is principally V–T,R (i.e., the internal modes of the cold bath molecule do *not* participate) and takes place on every collision.^{5,70a} However, the efficiency of V–T,R transfer may decline dramatically at higher bath temperatures,⁵ and the correct models to be used in partially, or completely collisionally equilibrated, high fluence laser systems are not known. There can be V–V transfer in collision between highly excited molecules in the neat gas^{63,64} in systems where the average absorbed energy per molecule is high,^{45,50,62} as occurs at high energy density. This process is different from vibrational energy transfer at low levels of excitation,⁶⁵ as shown in energy mapping on methyl halides.^{66–68}

The above systems involve multiphoton excitation. With higher energy photons, only one^{59a} or a few photons^{59b} are absorbed prior to decomposition. The decomposition of formic acid to give CO + H₂O was studied as a function of pressure using an HF laser.^{59b} Only three photons of 10 kcal mol⁻¹ were needed to

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effect decomposition. The authors propose that intramolecular energy relaxation takes place following the photoexcitation.

An interesting experiment is the dye laser ($\sim 7300 \text{ \AA}$) single photon isomerization,^{59a} $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{NC}$. Excitation took place to internal levels, of the ground electronic state, above the threshold for decomposition E_0 . Good agreement was obtained with RRKM calculations. However, the authors invoked a more elaborate mechanism to explain the experimental results. The molecule was assumed to be nonergodic, with intramolecular energy redistribution assisted by collisions. This mechanism has been criticized in an earlier section. So far, molecular ergodicity provides a simple, consistent explanation of the observed results.

Molecular Beam Systems

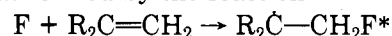
A reaction in crossed molecular beams takes place under truly collision-free conditions, thereby providing an elegant way of monitoring the primary decomposition process of the chemically activated molecule. Many ingenious experiments have been executed. Information is obtained on the spatial and velocity distributions of the products. A long-lived ($\geq 10^{-12} \text{ s}$) collision complex which undergoes many rotations prior to decomposition gives a symmetric product distribution relative to the center-of-mass vector due to the fact that detailed memory of complex orientation is lost. This has been found to be the case for some reactions of an atom with an alkali halide molecule,⁷³ Cs, K + RbCl and⁷⁴ Ca + NaCl, which form a three-center complex; for bimolecular reactions of CsCl with KCl and KI, which form a four-center complex;⁷⁵ and for atom + polyatomic molecule, Cs + SF_6 ;⁷⁶ K, Rb, and Cs with SnCl_4 and SF_6 ;⁷⁷ Cl + olefin⁷⁸ and F + olefin.^{13,79} Thus, many nominally bimolecular reactions are examples of fast unimolecular processes.

When a long-lived reaction complex is formed, the question is whether the available internal vibrational-rotational energy of the complex is randomized throughout the complex. The interpretation of the data is subject to physical and sometimes computational constraints imposed by the model. One model which has been widely used to explain the product translational energy distribution is derived from RRKM theory.⁸⁰ A potential which takes into consideration the long-range (r^{-6}) interactions and centrifugal energy of the complex is employed. The translational energy in the reaction coordinate plus the potential energy of the centrifugal barrier are assumed to convert to translational energy of the products. The product translational energy distribution calculated in this way

was found to agree with the experimental distribution obtained in the reactions $\text{CsCl} + \text{KCl}$, KI ;⁷⁵ $\text{Cs} + \text{SnCl}_4$, SF_6 ;⁷⁶ and K , $\text{Cs} + \text{RbCl}$.⁷⁴

Vibrational energy transfer involves the extent of intramolecular relaxation in a collision complex. In many cases, the behavior is nonergodic, and the internal degrees of freedom of the cold bath molecule do not relax.⁵ The models of ref 5 and 80 have been used to interpret the results of inelastic scattering of vibrationally excited KBr by polar molecules.⁸¹ In these cases, V-T, and for the very polar bath gas (CH_3NO_2) V-V, transfers are observed and large amounts of energy are removed ($10\text{--}30 \text{ kcal mol}^{-1}$). The interpretation of the results has been questioned⁸² since conservation of probability was not observed. An expression which provides obedience to the conservation rules and detailed balance has been given in ref 7.

A system which has been studied very carefully under velocity-selected conditions is the decomposition^{13,79} of $\text{C}_2\text{H}_4\text{F}^*$ and alkyl-substituted fluoroethyl. The excited radical was formed by the reaction



The angular distribution of the decomposition products indicates that the radical has a lifetime which is much longer than the period of rotation. The average lifetimes of excited fluoroethyl radicals measured in chemical activation systems⁸⁵ accord well with RRKM theory. A major finding of Y. T. Lee and co-workers was that the translational energy distribution of the products seemed to be at variance with statistical theory. As the reactant energy increases, the fraction of the product energy that appears as translation remains constant; it was expected that the fraction would go down since the excess energy should be distributed among the internal modes. Assumption of only a limited number of effective vibrational degrees of freedom to explain the translational distributions results in unreasonably short lifetimes.

RRKM theory makes no statement about the disposal of reverse barrier potential energy. Its relative distribution between translation and internal modes depends on the shape of the surface. Dynamical constraints are not considered in the calculation of the rate coefficient for the decomposition of the excited molecule. For cases where system angular momentum is of the same order of magnitude as molecular angular momentum, calculation of exit channel translational energy can prove extremely complicated.^{7,83} Recently, Worry and Marcus⁸⁶ developed a statistical adiabatic extension of RRKM theory. A distinction between loose and tight complexes is made. For a loose complex in the exit channel, no coupling of radial and internal coordinates exists and the final product distribution reflects the internal distribution of the complex. This is a restatement of the model of ref 80 discussed above. In the case of a tight complex, coupling between radial and internal coordinates affects the final product energy distribution. Bending vibrations in the complex become free rotations of the product. Because of the wider spacing of the vibrational compared with the rotational

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levels, the adiabatic transformation of the former into the latter causes a shift to higher product translational energies. This occurs when coupling between various modes of the complex and the products is introduced. This model was applied to $(\text{CH}_3)_2\dot{\text{C}}-\text{CH}_2\text{F}^*$ and reasonable agreement was obtained between experimental and calculated⁸⁶ energy distributions. There is better agreement between experiment and statistical theory than with loose⁸⁷ transition-state theory.

In a series of elegant experiments which complement molecular beam studies, McDonald and co-workers⁸⁸ studied the internal energy of products by the arrested relaxation of infrared chemiluminescence. In this method the emission from the vibrational modes of the product molecule is recorded and the observed energy of each mode compared with the prediction of statistical theory. Fluorine and chlorine substitution reactions $\text{F} + \text{C}_2\text{H}_3\text{Y}$, $\text{F} + \text{C}_6\text{H}_5\text{Y}$, $\text{Cl} + \text{C}_2\text{H}_3\text{Br}$, $\text{Cl} + \text{C}_6\text{H}_5\text{Br}$, and $\text{Cl} + \text{C}_3\text{H}_5\text{Br}$, where Y is H, CH_3 , Cl or Br, were investigated. Nonrandom distribution of vibrational energy was observed for product molecules with density of states of less than 10^4 states/cm⁻¹. Of course, statistical behavior is expected only when the density of states is high. In a trajectory study⁸⁹ on the internal energy distribution following chemical activation of methane-*d*₃ and chloromethane-*d*₃, it was shown that the energy becomes randomized in less than 5×10^{-12} s. The distribution in the final product is statistical if no exit channel interactions exist in the system.

Charged particle reactions are not discussed here for lack of space. Statistical theory has been applied in mass spectrometry under the name of quasi-equilibrium theory (QET). The experimental results have been summarized recently.⁹² It has been found that for polyatomic ions with lifetimes from 10^{-3} to 10^{-11} s randomization of energy takes place prior to decomposition. The early work of Wolfgang⁹⁰ and Henglein⁹¹ on ion-molecule crossed beams showed that intramolecular energy redistribution in the collision complex occurred on the time scale of 10^{-12} s. Where exit channel interactions exist, it is necessary to modify statistical QET to obtain good agreement between calculated and experimental translational energy distributions. Cases involving isolated electronic states are excluded.

Photochemistry. Vibronic Excitation

There are common features of internal energy disposal between photochemical reactions and gas-phase emission spectroscopy. The molecules can be in an excited electronic state, such as S_1 or T_1 , or in the ground state S_0 following internal conversion. Multi-channel decomposition from various excited levels can occur. Only a few selected topics are considered here.

The reactant molecule produced in photoexcitation may be identified with A^* of reactions R1 and R2 presented earlier. The rate constant is calculable via

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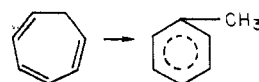
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an expression similar to eq 2. The assumption is made that internal energy is statistically distributed among all the modes of the electronically excited molecule.^{15,93-95} The value of $k(E)$ can be calculated from eq 1 provided that the vibration frequencies of the excited molecule and activated complex are known, not a very certain situation in many cases.

There are cases where it cannot be assumed a priori that energy will be statistically distributed among all the modes of the molecule. Consider, for example, the photodecomposition of azoalkane,¹⁵ $\text{RN}=\text{NR} \rightarrow 2\text{R} + \text{N}_2$. The excitation is via the $n \rightarrow \pi^*$ transition on the nitrogens. The decomposing bonds are the two R-N adjacent to the initially excited bond. The intramolecular energy relaxation of the energy into all the available modes is fast with rate coefficient^{11-15,81-84} $> 10^{11} \text{ s}^{-1}$. If the system can be intercepted in a short time, it is possible to observe decomposition exclusively from an initially excited moiety in which most of the excitation energy resides. One way to intercept the molecules before the energy randomizes is to observe the decomposition at extremely high pressures, i.e., high collisional frequency. The expected behavior is a curved Stern-Volmer plot, and indeed such curvature has been observed.¹⁵ Now $k(E)$ for randomized $\text{C}_2\text{H}_5\text{N}=\text{NC}_2\text{H}_5$ is expected, and found to be larger than that for $\text{C}_3\text{H}_7\text{N}=\text{NC}_3\text{H}_7$, which in turn is larger than that for $\text{C}_4\text{H}_9\text{N}=\text{NC}_4\text{H}_9$. By contrast, the value of $k(E)$ for decomposition from the (identical) excited moiety in each molecule is not expected to change much throughout the series and was found to be relatively constant.

Internal conversion of S_1 to S_0 produces a vibrationally hot molecule. The value of E_0 should be identical with that for thermally initiated decomposition of the same species. An example is the photoirradiated ground-state isomerizations of cycloheptatriene to toluene:^{42,97}



It is found that E_0 for the isomerization is the same for the thermal and photoisomerization processes.

The radiationless, reactive, and radiative processes and products ratios are, naturally, a function of the level of excitation. Provided that the vibrational manifold is dense enough and the level of excitation high enough, ergodicity is observed⁹⁹ in the decomposing molecules; otherwise, single vibronic level chemistry can be observed.¹⁰⁰⁻¹⁰⁵

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Photosensitization

Photosensitization is a useful method for exciting an acceptor via electronic energy transfer from a donor molecule.¹⁰⁶⁻¹⁰⁹ Unlike sensitization in condensed media where low vibrational states prevail, gas-phase processes can take place from an excited internal state in the higher electronic manifold.

A model has been proposed^{15,110} which assumes statistical partitioning of excess internal energy between the departing pair. The following serves as an example. It is found¹¹² that the Cd(⁵P₁)-sensitized decomposition of C₂H₃F has a higher quantum yield than the benzene(³B₁)-sensitized decomposition. Both have almost the same triplet energy, and therefore the total energy available for partitioning, E_T , is similar for both cases. The reason for the higher yield of the Cd-C₂H₃F pair, according to the model, is that the donor has no internal modes and therefore can carry away only translational energy. Benzene, on the other hand, has many internal modes which provide a sink for the internal energy available for distribution. The acceptor acquires less of the available energy so that $k(E)$ is smaller and the quantum yield is reduced.

The partition of E_T between donor and acceptor molecules is also exemplified by the singlet transfer in benzene-aniline gas mixtures.¹¹¹ The quenching of benzene fluorescence by aniline was investigated. It was found that the available internal energy is distributed between acceptor and donor in a statistical manner.

Photophysics

Photophysical experiments are another potential source of information on the internal energy distribution in excited electronic states of polyatomic molecules. The available models vary from those that postulate that the excited molecule is ergodic prior to electronic relaxation^{99,100} to those that predict local mode behavior wherein the bond excitation is uncoupled from the rest of the molecular modes.¹⁰¹⁻¹⁰³ The rules that govern photophysical processes are similar to those discussed for reacting systems: at low levels of excitations, i.e., low density of states, the radiative decay process has the specific traits of the excited mode;^{100,104} it is possible to follow the behavior of a single vibronic level;¹⁰⁵ for moderate and large polyatomic molecules at high levels of excitation, the internal energy is relaxed through the vibrational manifold of the excited electronic state.¹⁰⁰ Examples of single level behavior at low levels of excitation are benzene¹⁰⁴ and cyclobutane.¹⁰⁵ CHCl, CHCBr,¹⁰¹ and H₂CO¹⁰⁵ are examples of small molecules where similar behavior is observed. In large molecules like tetracene and pentacene¹⁰⁰ at high levels of excitation, it was found that intramolecular energy redistribution

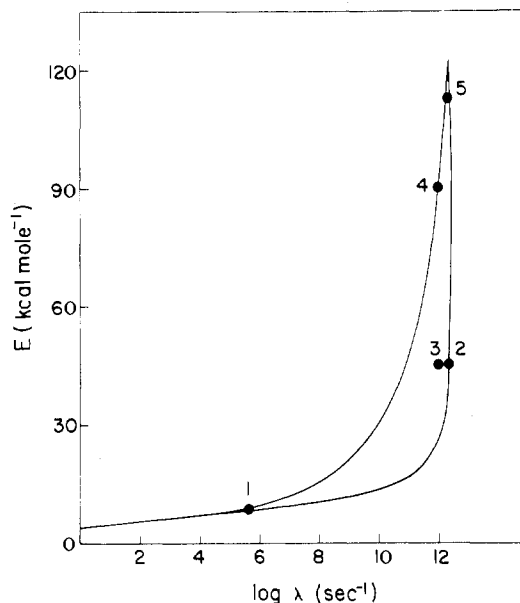


Figure 3. Internal energy vs. $\log \lambda$. General behavior of intramolecular rate coefficient λ as a function of the internal energy. The area between the lines A is the region of uncertainty (see discussion). Points: (1) ref 106; (2, 3) ref 14; (4) ref 41; (5) ref 11, 12.

occurs on a time scale shorter than electronic energy relaxation. But naphthalene has been reported to be a contrary case.^{100b} The above findings cohere with the results of McDonald^{88,89} and agree with the major features of reactive systems.

The Dependence of the Intramolecular Relaxation Constant on E

It is of interest to speculate on the dependence of the observed (smallest) intramolecular relaxation constant λ on the energy content of the molecule. A pragmatic hybrid curve for large fluoromolecules such as SF₆ and CF₃-c-C₃F₄D₂ may be constructed. In an elegant experiment, Deutsch and Brueck¹⁰⁶ excited the ν_3 mode of SF₆ to the $\nu = 3$ level (~ 9 kcal mol⁻¹). They interpreted their results to mean that ν_3 came into equilibrium with other degrees of freedom with a time constant of ~ 3 μ s, i.e., $\lambda \approx 3 \times 10^5$ s⁻¹. Obviously, $\lambda \rightarrow 0$ for relaxation of the $\nu = 1$ level, for which small vibration theory works well, so that a curve of λ vs. E is asymptotically horizontal at low energies. For fluorocyclopropanes, at a total energy of ~ 115 kcal mol⁻¹, it has been shown above^{11,12} that $\lambda \sim 10^{12}$ s⁻¹. Since classical dynamical considerations do not allow for increase in λ beyond $\sim 10^{13}$ s⁻¹ with increasing energy, the curve of λ vs. E is asymptotically vertical at higher energies. Figure 3 represents the combined behavior. The area between the curves, A, is an arbitrary representation of the region of uncertainty and cannot be probed for these molecules by reaction dynamical studies since they decompose at energies above 45 kcal mol⁻¹ ($E_0 = 45$ kcal, CF₃-c-C₃D₂F₄; $E_0 \approx 86$ kcal SF₆). On the other hand, utilization of related molecules such as N₂F₄ for which E_0 is only 19 kcal mol⁻¹ might be counterproductive for the reason described below. Obviously, the shape and behavior of curves such as those in Figure 3 depend on specific features of the internal potential function for each molecular species. Exactly how universal such curves are, for smaller hydrocarbons, for example (with low re-

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duced-mass H motions), remains to be seen. Step features may occur. We know that internal randomization must fail for all species at low energies.

The region A is a potentially fruitful subject for theoretical delineation. Various theoretical treatments of the temporal and amplitude evolution of a set of anharmonic oscillators^{4,113} have been given. In general, some degree of stochastic behavior seems assured if the anharmonicity and coupling of the members of the set are sufficiently great as the total energy of the set becomes large. The often postulated "bottleneck" to internal relaxation of energy is a consequence of the occurrence of nonoverlapping resonances which can "trap" the energy of the set for a number of vibrational cycles of the motion (nonergodicity). The overlap of resonances can lead to stochastic behavior.^{113h}

Several recent treatments^{113f-h} suggest that overlap behavior may result if the energy in a particular mode is greater than 0.7–0.9 of the bond dissociation energy D or if the total energy E exceeds some critical criterion value E_c , which depends on the nonharmonic terms of the potential function and may be less than or greater than D . But the degree of stochastic behavior required to rigorously satisfy statistical theory may be much greater than that which satisfies pragmatic experimental tests.^{113h} This difference can explain why it is

that conventional statistical theories do have such broad practical applicability.

In conclusion, it seems that the answer to the title question is "yes", so far, for large reactive systems, on a time scale $>10^{12}$ s. The high hope of earlier laser experimentation—that allegedly mode-specific excitation could be carried out and be shown to reveal nonstatistical unimolecular behavior—has failed to reveal any substantiated example of such. Most unimolecular studies have been made at moderate to high levels of excitation (40–100 kcal mol⁻¹); the possibility exists that such behavior could be detected at lower energy levels. Several molecules, such as N₂O₄, the dioxetanes, and N₂F₄, have critical threshold for decomposition E_0 close to 15–25 kcal and suggest themselves as possible candidates. However, such systems may prove to be a vain hope because even though E_0 decreases, the existence of severe anharmonicities attendant upon bond rupture and the occurrence of a shallow col(s) near the configuration of critical extension of the molecule could lead to a concomitant decrease in the critical criterion value E_c . Conventional experimentation of adequate refinement is needed. One study in progress on *t*-C₄H₉O decomposition ($E_0 \sim 15$ kcal mol⁻¹) by Batt is a hopeful possibility.¹¹⁴

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