Activation of Unimolecular Reactions by Ambient Blackbody Radiation

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The historical "radiation hypothesis" as a mechanism for activating unimolecular thermal dissociation of gas-phase molecules, long discredited on the authority of Langmuir, has been revitalized by the discovery and characterization of the process of thermal dissociation of trapped gas-phase ions by the ambient blackbody radiation field surrounding the ions. This development was made possible by improvements in Fourier transform ion cyclotron instrumentation that allowed long-time trapping of weakly bound cluster ions at extremely low pressures. Binding energies can be derived from measurements of these dissociation rate constants both by detailed kinetic modeling and by simpler Arrhenius temperature-dependence approaches, although the latter require special considerations for small molecules. These approaches have been applied to thermal dissociations of molecules, including cluster ions and large biomolecule ions.

Unimolecular reactions progress from a single reactant molecule, A, to product molecules (or atoms) B and C in a manner apparently independent of the composition of the surroundings according to

$$A \rightarrow B + C \qquad (1)$$

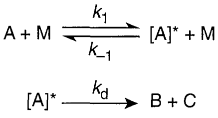
A classical unimolecular process is then one in which the rate of the unimolecular decomposition appears to depend only on the amount of the reactant molecule present [A]. The disappearance of this reactant with time t exhibits an exponential decay according to

$$[A] = [A]_o e^{-k_u t} \qquad (2)$$

where k_u is the reaction rate constant and $[A]_o$ is the amount of A present at time t = 0. In a very early attempt to explain the observed unimolecular behavior, Perrin hypothesized that blackbody radiation from the hot reaction vessel was responsible for the activation of the reactant molecules toward dissociation (*1*). This radiation hypothesis initially acquired some credence because, with increasing temperature, the reaction rate constant increases in parallel with the intensity of radiation $\rho(\nu)$ at a given frequency ν, which in turn is governed by the Planck or Wien radiation law

$$\rho(\nu) = \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{e^{-h\nu/kT} - 1} \qquad (3)$$

where h is the Planck constant, c is the speed of light, k is the Boltzmann constant, and T is temperature. Langmuir posed two conditions that he deemed must be met for Perrin's hypothesis to be valid. First, the reacting substance would have to absorb radiation at the frequency required to produce the activation, and, second, the radiation density must be sufficient at this frequency to supply the energy of activation. Langmuir rejected the radiation hypothesis on the grounds that the activation energies observed for the reactions being considered were sufficiently high to imply frequencies well into the ultraviolet and the molecules in question were known not to absorb light at these frequencies (*2*). In addition, even at the highest experimental temperatures considered, the radiation density was too low. Shortly thereafter, Lindemann (*3*) and Christiansen (*4*) independently proposed that bimolecular collisions with molecules, M, were the means by which molecules became energized (Scheme 1). Application of the steady-state approximation (where k_d is the unimolecular dissociation rate constant and k_1 and k_{-1} are the collisional activation and deactivation rate constants, respectively) to the activated molecule A^*, which assumes that the rate of energy exchange from collisions is fast compared with the rate of dissociation of energized molecules, gives the apparent rate constant k_u for unimolecular decomposition (Eq. 4). In the high-pressure limit, corresponding to the conditions of these early experiments, competition between activation and deactivation processes leads to an overall pseudo–first-order kinetic process, whereas in the low-pressure limit the reaction will be second order, with the apparent unimolecular rate constant dependent on the concentration of molecules in the reaction medium [M]. When data became available to test this possibility, the Lindemann-Christiansen hypothesis explained thermal unimolecular reactions successfully. Thus, the radiation hypothesis came to be considered little more than a historical curiosity.



$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [A]^* + M$$

$$[A]^* \xrightarrow{k_d} B + C$$

Scheme 1.

$$k_u = \frac{k_1 k_d[M]}{k_{-1}[M] + k_d} \qquad (4)$$

Steinfeld *et al.* (*5*) have commented on the fact that the rejection of Perrin's hypothesis may have been overly hasty. They noted that, particularly in the case of large molecules, absorption in the infrared (IR) region of the electromagnetic spectrum is strong and, furthermore, the radiation density at IR wavelengths is more than sufficient to promote unimolecular dissociation. A multiphoton IR absorption mechanism can thus avoid Langmuir's objections. However, they ultimately rejected the radiation hypothesis because no evidence for a truly pressure-independent "unimolecular" rate constant in the low-pressure regime had been described at the time. However, the lack of such observations does not imply that such reactions could not exist in an appropriate regime. The low pressures and long trapping times of the Fourier transform ion cyclotron resonance (FT-ICR) ion trap provides exactly the experimental conditions needed to observe blackbody radiation–induced dissociation.

Experimental Methodology

Fourier transform ion cyclotron resonance spectrometry is an excellent technique for the study of gas-phase ion-molecule reactions at very low pressure (*6, 7*). The technique is based on the principles of ion motion in combined weak electric and strong magnetic fields. This combination creates an effective electromagnetic bottle in which ions can be trapped for controlled, nearly unlimited periods of time.

In 1990 (*8*), a high-pressure, molecular cluster ion source was mated to the FT-ICR

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spectrometer at the University of Waterloo. Although this apparatus was developed to study the effects of solvation on the bimolecular reactivity of gaseous cluster ions, the conditions were also ideal for observing (over very long periods of time) the behavior of weakly bound cluster ions in a virtually collision-free environment. This condition was exactly that required for the first observations of blackbody radiation–driven unimolecular decompositions.

Initial Observations

One of the first studies undertaken with this new apparatus (*9*) investigated the system of F^- associated with alcohol molecules, $F^-(ROH)_n$ ($n = 1$ to 3). The F^- ion solvated by three methanol molecules exhibited an unexpected spontaneous dissociation:

$$F^-(CH_3OH)_3 \rightarrow F^-(CH_3OH)_2 + CH_3OH \qquad (5)$$

despite the fact that, under the conditions used, virtually no collisions of the parent cluster ions with the background gas were occurring. The apparent unimolecular rate constant of $6 \times 10^{-3}\ s^{-1}$ was unaffected by the presence of either argon or methanol added to the FT-ICR cell up to pressures as high as 1×10^{-7} mbar. This result and other early investigations gave strong indications of unimolecular reactions not readily explicable by conventional mechanisms.

The Blackbody Radiation Mechanism

The radiation hypothesis appeared to be the only possible explanation for a pressure-independent means of activation. Although this idea was qualitatively palatable, the precise means by which such a low-intensity IR source could quantitatively explain the dissociation of bonds in the 10 to 20 kcal mol^{-1} range remained elusive until the analogy with previous low-intensity continuous-wave CO_2 laser dissociation experiments was recognized. These experiments had shown that a low-intensity laser driving a reaction by IR multiphoton absorption could be considered as effectively equivalent to a blackbody source (*10–13*). The quantitative understanding of such CO_2 laser experiments could be transferred quite directly to the thermal blackbody radiation situation. A study of a number of small H^+ and Cl^- clusters having water and dimethyl ether ligands marked the first clear understanding of the role of the radiation mechanism in dissociation chemistry in the FT-ICR ion trap (*14*).

Three lines of reasoning have led to the confident conclusion that the blackbody radiation mechanism is the correct explanation for these observations. First, the pressure-dependence behavior of the low-pressure dissociation rates is incompatible with a purely collisional activation mechanism of the Lindemann-Christiansen type. Typical results supporting this argument are shown in Fig. 1 for the dissociation of $H_3O^+[(CH_3)_2O][H_2O]_2$ clusters at two temperatures. A combination of blackbody radiation–induced and collisional activation mechanisms is expected to give an overall rate constant having a low-pressure unimolecular component,

$$k_u = k_{abs}[h\nu] + k_f[M] \qquad (6)$$

where k_{abs} is the rate constant for blackbody radiation–induced dissociation and k_f is the collisionally activated rate constant (from Eq. 4 in the low-pressure regime). At each temperature, there is both a nonzero slope and a substantial nonzero intercept, showing that both the radiation mechanism and the collisional activation mechanism contribute substantially under the experimental conditions used (Fig. 1). As expected, both the slope and the intercept increase with increasing temperature. The zero-pressure intercepts are independent of the bath gas used, thus confirming a contribution that is independent of the nature of the collisions; the slopes increase strongly with increasing molecular complexity of the bath gas, indicating an additional contribution driven by collisional energy transfer. Because most unimolecular reactions studied in the past would have been carried out at pressures several orders of magnitude higher than those here, the zero-pressure intercept would have been not readily distinguishable from zero.

The second argument confirming the radiation mechanism in these systems is that known molecular constants and the application of straightforward kinetic theory not only rationalize the observations but actually make it unavoidable that radiative thermal dissociation would occur as observed (*15*, *16*). This mechanism has been demonstrated (*16*) in a detailed study of the $Cl^-(H_2O)_n$ cluster ions ($n = 2$ and 3). With the use of density functional calculations for the IR spectral parameters, combined with high-pressure mass spectrometry values of the bond strengths and the known characteristics of the blackbody radiation field, no adjustable quantities remained for assignment. Kinetic modeling of $Cl^-(H_2O)_n$ reproduced the absolute experimental dissociation rates for both ions, as well as the $Cl^-(H_2O)_3$ temperature dependence.

The third piece of evidence for the radiation mechanism is the effect of deuterium substitution in the cluster molecules on the unimolecular dissociation rate constant (*17*). For most organic molecules, C-H stretches have high IR oscillator strengths, but they occur in the region of 3000 cm^{-1}, where the room temperature blackbody radiation intensity is minimal. However, C-D stretches occur in the vicinity of 2200 cm^{-1}, where the light intensity is considerably higher. Thus, substitution of C-H by C-D bonds should be efficient in enhancing the rate of blackbody-induced unimolecular dissociation. This hypothesis was confirmed in the dissociations of H_3O^+-DME_3, H_3O^+-DME_2, Cl^--acetone, and Cl^--benzene clusters relative to their completely deuterated analogs, with observed enhancements ranging from 20% to as much as 120%.

Kinetic Modeling and the Determination of Bond Strengths

Apart from their intellectual interest, these processes may have practical importance because they can give bond strengths of molecules. The link between

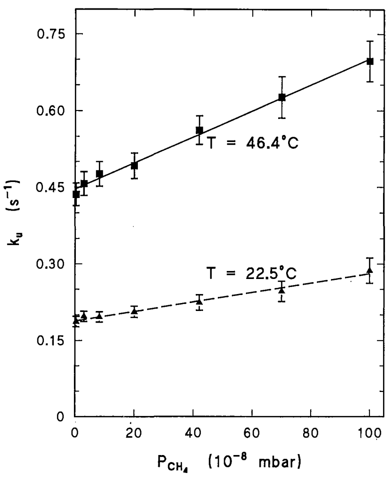

Fig. 1. Dependence of the $H_3O^+[(CH_3)_2O][H_2O]_2$ ion dissociation rate k_u on pressure P, showing the nonzero intercept at zero pressure of methane bath gas.

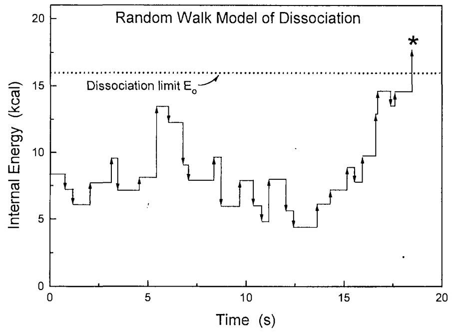

Fig. 2. Schematic illustration of the random walk on the energy axis executed by a molecule absorbing and emitting IR photons and ultimately dissociating (asterisk).

barrierless dissociation kinetics and bond strengths can be made by kinetic modeling based on a statistical picture, in which a population of molecules is described according to their location along the axis of internal energy E_{int} (Fig. 2). Any given molecule is constantly gaining and losing increments of internal energy as it exchanges energy with its surroundings by IR-radiative (and possibly collisional) processes. This process can be considered as a random walk along the E_{int} axis, where the step size is the photon energy (or collisional energy transfer increment). Dissociation occurs when a molecule rises sufficiently far above the true activation energy E_o.

The evolution of the population of ions resulting from all of these processes can be modeled directly with a biased random walk simulation (*12*, *18*) or (as in most recent work) by the master-equation approach (*11*, *16*). A weakly coupled harmonic oscillator picture of the molecule is usually assumed. Modeling then requires the normal mode frequencies and IR intensities of the vibrational modes, as well as the unimolecular dissociation rate as a function of E_{int}. None of these parameters are commonly available from experiments for gas-phase ions, so they must normally be calculated, although a semiquantitative approach to estimating the parameters (the "standard hydrocarbon" scheme) has been useful (*19–21*).

Some IR spectral parameters may be available from experiments (*22*), but for these parameters one usually resorts to ab initio calculations. The most uncertain aspect of modeling is likely to be the unimolecular dissociation rates. For small, loosely bound complexes, transition-state theory [Rice-Ramsperger-Kassel-Marcus theory, phase space theory, or variational transition-state theory (*23*)] with a very loose transition state is probably appropriate. Detailed modeling in this spirit has been done for a number of systems (*24*).

The Temperature Dependence and Arrhenius Analysis

For data at a single temperature, the modeling approaches discussed above provide the most useful route from measured rates to bond energies. However, measurement of a temperature dependence offers a shortcut around this intensive analysis, making use of the slope and intercept of an Arrhenius plot (Fig. 3). The barrierless Arrhenius activation energy E_a can provide a good approximation to the actual bond strength if appropriate conditions are met.

In an Arrhenius-type analysis, it is important to consider the size of the molecule (that is, the number of internal degrees of freedom among which internal energy flows). For very large molecules, the Arrhenius activation energy E_a, defined by $E_a = -d\ln(k_u)/[d(1/RT)]$ (where R is the ideal gas constant) and determined from the slope of the temperature dependence, corresponds closely to the true activation energy E_o. The corresponding Arrhenius factor A then gives the entropy of activation of the dissociation process, $A = (ekT/h)\exp(\Delta S^{\ddagger}/R)$, where e is the base of natural logarithms and $\Delta S^{\ddagger}$ is the standard entropy of activation. For small molecules, the apparent E_a value does not correspond directly to E_o, but it can be corrected as outlined below, with the truncated Boltzmann picture and the modified Tolman theorem (*10*). The greatest difficulties in interpretation are posed by the intermediate-size regime, where the apparent activation energy E_a is lower than the true E_o by a substantial amount that can only be assessed accurately by detailed kinetic modeling. The model master-equation calculations displayed in Table 1 illustrate the transition from small-molecule to large-molecule behavior.

In the large-molecule case (often called the rapid energy exchange limit), the typical unimolecular dissociation rate of the activated molecules is slow compared with the rate of energy equilibration of a molecule with the surroundings by photon exchange. In contrast, in the small-molecule case, a molecule activated above E_o dissociates rapidly compared with the rate of energy equilibration by photon exchange. This situation is closely analogous to conventional Lindemann-Christiansen collision-mediated dissociation kinetics. Just as in the low-pressure "fall-off region" of conventional unimolecular kinetics, the small-molecule regime of radiatively induced thermal dissociation shows greatly depressed rate constants, apparent E_a values substantially below E_o, and apparent frequency factors A much smaller than the large-molecule limiting values.

In the small-molecule case, the equilibrium distribution of internal energies is distorted by the steady removal of the most energy-rich component of the population through dissociation (Fig. 4). In this small-molecule situation, a simple kinetic analysis known as the truncated (or depleted) Boltzmann analysis avoids the complexity of a full master-equation treatment (*15*, *16*). In this approach, the dissociation rate is given by

$$k_u = P(E_{n-1} \rightarrow E_o)k_{abs} \qquad (7)$$

where $P(E_{n-1} \rightarrow E_o)$ is the probability that a given molecule will lie in the internal energy interval between E_o and $E_o - h\nu_{av}$ and k_{abs} is the rate at which molecules absorb IR photons. Here, ν_{av} is the average energy of the IR photons being absorbed. The true activation energy E_o can be estimated from E_a by applying the modified Tolman theorem (*10*, *15*)

$$E_O \cong E_a + E' - 0.9 \text{ kcal mol}^{-1} \qquad (8)$$

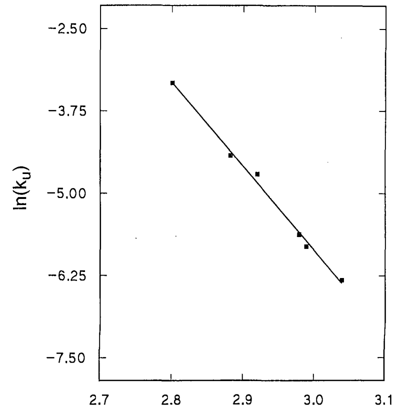

Fig. 3. Arrhenius plot for the dissociation kinetics of a pentanone proton-bound dimer ion.

Table 1. The progression from small-molecule to large-molecule kinetics, illustrated with master-equation modeling of IR blackbody thermal dissociation (T = 357 K). Tabulated are the dissociation rate constant k_u, apparent activation energy $E_a = -d\ln k/[d(1/RT)]$, and Arrhenius frequency factor A for molecules having a true dissociation energy E_o of 25 kJ mol^{-1} and a moderately loose transition state. N is the number of vibrational degrees of freedom.

N	k_u (10^{-3} s^{-1})	E_a (kcal mol^{-1})	$\log_{10}(A)$
60	0.05	20.0	7.9
200	3.0	19.8	9.4
1500	8.5	23.6	12.3
$N = \infty$	10	25.1	13.3

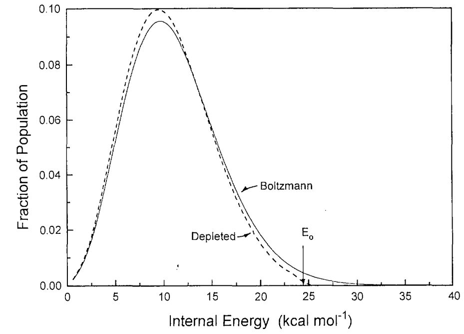

Fig. 4. The normal (solid line) and depleted (dashed line) Boltzmann distributions at 500 K for a population of molecules with 60 degrees of freedom undergoing dissociation with a dissociation energy E_o of 24.5 kcal mol^{-1} (small-molecule case).

Here, E' is the average energy of the perturbed distribution (like the dashed curve in Fig. 4), which can be estimated by simple arguments within the truncated Boltzmann picture.

How Large Is Large?

Given the great simplification of interpretation in the large-molecule canonical limit, it is of interest how big a molecule must be for this limit to be valid. We addressed this question through master-equation modeling based on typical properties of hydrocarbon-type ions. A size of ~500 degrees of freedom is a rough lower limit for "large" molecules. However, this limit depends strongly on several features of the specific dissociation process, notably (i) tight or loose transition state, (ii) fast or slow dissociation at the given temperature, and (iii) high or low activation energy. A somewhat better idea of the range of sizes (gauged by N, the number of degrees of freedom) corresponding to the large-molecule boundary for a range of situations is given in Fig. 5. It can be seen that in the most favorable situations (tight transition state, low temperature, and slow rate), large-molecule kinetic behavior can be approached for molecules as small as $N = 100$; whereas, at the other extreme, substantial deviations from the large-molecule kinetic limit might be encountered for systems as large as $N = 5000$ (*25*).

A quantitative activation energy analysis in a clear small-molecule situation has been described for the $Cl^-(H_2O)_n$ ($n = 2$ and 3) clusters (*16*). For $Cl^-(H_2O)_2$ ($N = 15$), a 0-K E_o value of 10.1 kcal mol^{-1} was derived in excellent agreement with a high-pressure mass spectrometry measurement. Similarly, analysis of tetramethylsilane ion ($N = 33$, $E_a = 13.0$ kcal) gave an E_o value of 15.4 kcal mol^{-1} in excellent agreement with a concurrent threshold collision-induced dissociation measurement (*26*), and tetraethylsilane ion ($N = 83$, $E_a = 9.9$ kcal) gave $E_o = 16.3$ kcal (*27*).

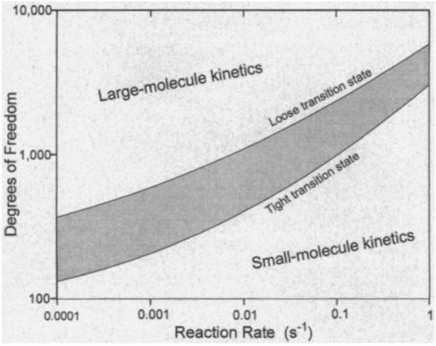

Fig. 5. The range of sizes that correspond to the lower limits of "large-molecule" kinetics. For a reaction observed to have a given k_u value, large-molecule Arrhenius analysis will be appropriate if the number of degrees of freedom puts the system above the shaded region and may be appropriate within the shaded region, depending on the nature of the transition state. Systems below the shaded region will not approach the large-molecule limit. In these model calculations, temperatures were chosen in the range 300 to 440 K to give k_u values ranging from fast (1 s^{-1}) to quite slow (10^{-4} s^{-1}). (E_o = 24 kcal mol^{-1}, with a range of transition-state types from tight to loose, corresponding to log A ranging from 11.9 to 15.5.)

Somewhat larger systems, illustrating probable intermediate-size behavior, are the proton-bound dimers of 3-pentanone, 4-heptanone, and 5-nonanone ($N = 93$ to 165). The E_a values (25.4, 27.6, and 28.4 kcal mol^{-1}, respectively) are significantly lower than the E_o values (28.1, 30.5, and 31.0 kcal mol^{-1}, respectively, from high-pressure mass spectrometry).

Moving into the large-molecule regime, E. R. Williams' group has used thermal dissociation to determine kinetic parameters for a variety of dissociations of oligopeptides and large polypeptides. With bond strengths typically around 37 kcal mol^{-1}, these molecules give easily observable thermal unimolecular dissociation lifetimes of seconds to minutes (*28*, *29*) at temperatures on the order of 200°C, with no pressure dependence (*29*). Their work has encompassed molecules in the large-molecule limit such as bradykinin (*28*) and ubiquitin (*29*), where the measured E_a is a good measure of the dissociation energy, and also smaller ions (dipeptides) that lie in the intermediate-size regime and had to be analyzed carefully with master-equation modeling (*30*).

The frequency factors found in some of these examples suggest the progression from small- to large-molecule behavior. For small cluster ions such as $Cl^-(H_2O)_3$ and $(H_2O)_4H^+$ ($N \sim 30$), A factors of 10^{13} s^{-1} are derived. For the proton-bound ketone dimers (N in the range 90 to 160), the A factors range from 10^{14} s^{-1} to the mid-10^{16} s^{-1} area. [Values on the order of 10^{16} s^{-1} are normal for the high-pressure limit for simple bond cleavages (*31*).] For large polypeptide ions (N typically 1000) where there is substantial loosening of the molecular geometry during dissociation, Williams and co-workers have measured A factors as large as ~10^{18} s^{-1}.

Conclusion

The experimental data and theoretical interpretation presented above demonstrate that, despite nearly eight decades of rejection, Perrin's original "radiation hypothesis" is a viable mechanism for the activation of unimolecular reactions. Observations of this phenomenon became possible because of the ability to trap weakly bound ionic species for very long times in the nearly collision-free environment of an FT-ICR cell. Theoretical modeling of this phenomenon revealed that, given accurate vibrational frequencies and intensities, the dissociation process can be quantitatively reproduced. Thus, given experimental measurements of the unimolecular rate constants, preferably as a function of temperature, accurate bond energies may be derived from barrierless dissociation reaction kinetics. Overall, the ambient blackbody radiation activation mechanism represents a major addition to the field of chemical kinetics, with particularly promising applications to cluster ions and large biomolecule ions (*28*–*30*).

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