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RRKM and Non-RRKM Behavior in Chemical Activation and Related Studies

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An expression is derived for the pressure dependence of a chemical activation unimolecular rate constant at a fixed total energy and angular momentum in terms of the distribution of unimolecular lifetimes. This rate constant is shown to have a certain insensitivity at low pressures to the form of the lifetime distribution. A kinetic model is then introduced based on a finite rate of intramolecular vibrational energy redistribution. The model provides an analytical explanation of a recent finding in a trajectory calculation for a particular chemical activation system, that the chemical activation unimolecular rate constant at low pressures equals the $\tau = 0$ microcanonical value even though the unimolecular lifetime distribution is highly non-RRKM. A similar result is predicted for a class of such systems. Implications are described.

1. Introduction

Many different unimolecular reaction rates have been interpreted with RRKM theory, e.g., ref 1–4. Rapid intramolecular vibrational energy redistribution is tactily assumed in the theory, the dissociation probability thus becoming random. Thereby, the "lifetime distribution"[2,5-9] (defined later by eq 3) for a fixed total energy and angular momentum has the form of an exponential

$$P(\tau) = k \exp(-k\tau) \qquad (1)$$

where k is the RRKM rate constant. Information on initial states prepared nonrandomly has been determined from chemical activation experiments at high pressures.[10] For a few reactions the unimolecular decay of a molecule of given energy has been observed in real time in a collision-free environment.[11-13] Nonexponential decay or implications thereof are commonly referred to as non-RRKM behavior.[14]

Recently the unimolecular dynamics of a model alkyl reaction H—C—C → H + C=C was studied by quasiclassical trajectories.[15] Excitation was by a chemical activation step, H + C=C → H—C—C, and unimolecular lifetimes were calculated for the resulting vibrationally excited H—C—C species. This lifetime distribution was found to be strongly nonexponential and hence non-RRKM; most noticeably, it showed a long-time exponential tail. Nevertheless and perhaps surprisingly, the pressure dependence of the collision-averaged chemical activation rate constant, derived with the simplest assumptions (strong and random collisions), was found to be relatively insensitive to the non-RRKM features of the trajectory lifetime distribution. In particular, the calculated chemical activation unimolecular rate constant, defined later in eq 2 for an ensemble of systems of *fixed total energy*, changed by only a factor of 4 over 4 orders of magnitude change in pressure (from the low- to high-pressure limit). Moreover, the trajectory-calculated chemical activation unimolecular rate constant in the low-pressure limit agreed very closely with that of the trajectory-calculated "$\tau = 0$" value[16] of the microcanonical (equilibrium) rate constant, $k_{MIC}(0)$.

In the present paper we (1) derive an expression for the pressure dependence of a chemical activation unimolecular rate constant in terms of the distribution of lifetimes (section 2), obtain simple results for this rate constant in the high- and low-pressure limits, and use them (section 3) to extract kinetic properties from the trajectory data, (2) introduce a kinetic model for intramolecular energy transfer based on a decomposition of the intramolecular phase space into two or three regions (section 4) (a "two-state" type of model has been used previously to interpret experimental data for some chemical activation reactions[10]), (3) show that a three-state kinetic model agrees with the trajectory-calculated distribution and show that the equality cited above, namely, of $k_{MIC}(0)$ with the low-pressure limit of the chemical activation unimolecular rate constant, which occurs in spite of a highly non-RRKM behavior, is not an accident but rather a property obeyed by certain kinetic models (section 4), and (4) consider the molecular aspects of the subdivided phase space, and suggest a tentative molecular assignment of the phase space as a basis for a more detailed physical analysis of future trajectory studies (section 4). The results are discussed and summarized in section 5.

2. Rate Constant Expressions for Collision-Averaged Unimolecular Rate Constant

The phenomenological collision-averaged chemical activation rate constant is defined as[17]

$$k = \omega D/S \qquad (2)$$

where ω is the collision frequency per molecule, D is the probability of forming decomposition products, and S is the probability of forming collisionally stabilized reactant. To study the pressure

† Contribution no. 7056.

(1) Robinson, P. J.; Holbrook, K. A. "Unimolecular Reactions"; Wiley: New York, 1972.
(2) Forst, W. "Theory of Unimolecular Reactions"; Academic Press: New York, 1973.
(3) Hase, W. L. In "Dynamics of Molecular Collisions"; Miller, W. H., Ed.; Plenum Press: New York, 1976; Part B, p 121.
(4) Oref, I.; Rabinovitch, B. S. *Acc. Chem. Res.* **1979**, *12*, 166.
(5) The terminology "lifetime distribution" was first introduced by Bunker[6,7] and follows indirectly from the related gap distribution of Slater theory.[8] It might be more precise to call $P(\tau)$ the lifetime distribution frequency. See also ref 9 for a detailed analysis.
(6) Bunker, D. L. *J. Chem. Phys.* **1964**, *40*, 1946.
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(15) Hase, W. L.; Duchovic, R. J.; Swamy, K. N.; Wolf, R. J. *J. Chem. Phys.* **1984**, *80*, 714.
(16) The microcanonical rate constant at $\tau = 0$ was evaluated by using classical trajectories to calculate the initial decay rate for a microcanonical ensemble of HCC molecules. Hase, W. L.; Wolf, R. J. *J. Chem. Phys.* **1981**, *75*, 3809.
(17) Rabinovitch, B. S.; Setser, D. W. *Adv. Photochem.* **1964**, *3*, 1.

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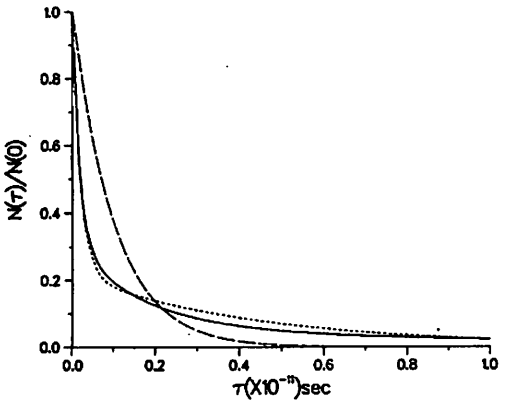

Figure 1. Plot of the relative number of molecules vs. time for a model H–C–C Hamiltonian. The line with long dashes is the prediction based on eq 1 with $k = k_{MIC}(0)$. The solid line is the fit of the three-state model (three exponentials).[15] The line with short dashes is the fit of the two-state model two exponentials).

dependence of the chemical activation unimolecular rate constant, it is useful to relate D and S to the "lifetime distribution" function $P(\tau)$, defined in the literature as[3]

$$P(\tau) = -\frac{1}{N(0)}\frac{dN(\tau)}{d\tau} \tag{3}$$

In the simplest analysis one assumes that collisions between bath molecules and the energized reactant are uncorrelated and that each collision results in stabilization. (One can modify the latter assumption for the case of "weak" collisions.[1,2]) The probability that the reactant avoids a collision for time τ is $W(\tau)$:[18]

$$W(\tau) = \exp(-\omega\tau) \tag{4}$$

Since $P(\tau)\,d\tau$ is the probability that a reactant molecule dissociates in the time interval τ, $\tau + d\tau$, the total probability of dissociation is

$$D = \int_0^\infty W(\tau)\,P(\tau)\,d\tau \tag{5}$$

The probability of stabilization S equals $1 - D$, i.e.

$$S = 1 - \int_0^\infty W(\tau)\,P(\tau)\,d\tau \tag{6}$$

The above equations yield the chemical activation unimolecular rate constant k as a function of ω, i.e., of pressure.

Of particular interest are the low-pressure ($\omega \to 0$) and high-pressure ($\omega \to \infty$) limits of the unimolecular rate constant. From eq 3–5 one obtains

$$D = 1 - \omega\int_0^\infty [N(\tau)/N(0)]e^{-\omega\tau}\,d\tau \tag{7}$$

The expression for k in the low-pressure limit k^0 is found by writing k equal to $\omega D/(1 - D)$: Recognizing that $D \to 1$ as $\omega \to 0$, we see that k^0 equals $\lim \omega/(1 - D)$ as $\omega \to 0$. After setting the $\omega = 0$ in $\exp(-\omega\tau)$ in eq 7, one obtains

$$k^0 = N(0)/\int_0^\infty N(\tau)\,d\tau \quad (\omega \to 0) \tag{8}$$

In the high-pressure limit $S \to 1$ as $\omega \to \infty$, so that the k in eq 2, denoted by k^∞, equals ωD. Only the extremely small τ's contribute to the integrand in eq 5 when $\omega \to \infty$, as one sees from eq 4. Thus, it is found that k^∞ equals $\omega P(0)\int_0^\infty e^{-\omega\tau}\,d\tau$, i.e.

$$k^\infty = P(0) \quad (\omega \to \infty) \tag{9}$$

From eq 9 it is seen that k^∞ is equal to the "lifetime distribution function" $P(\tau)$ evaluated in the limit $\tau \to 0$. In contrast, eq 8 shows that k^0 does not provide direct information about $P(\tau)$ at $\tau \to \infty$. A feature of eq 8 is that it does not require an exponential $N(\tau)$ for k^0 to approximately equal the $\tau = 0$ microcanonical unimolecular rate constant, $k_{MIC}(0)$.

(18) Reference 8, p 19.

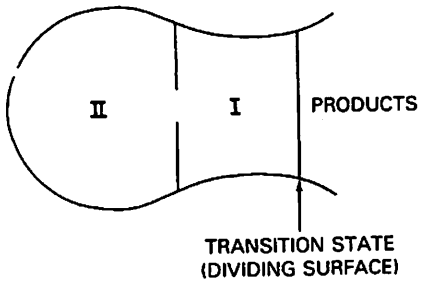

Figure 2. Depiction of the classical phase space for the two-state model. Either region I (eq 10a) or II (eq 18) is excited in the chemical activation step.

3. Comparison with an HCC Trajectory Study

The distribution of lifetimes in ref 15 $N(\tau)/N(0)$ is plotted in Figure 1 (solid line) for the trajectory-calculated unimolecular dissociation H—C—C → H + C≡C, the latter being initiated by the step H + C≡C → H—C—C. The chemical activation unimolecular rate constant in the low-pressure limit k^0 calculated from trajectories by using eq 8 is found to be 0.91 ps^{-1}.[15] This value may be compared with a $k_{MIC}(0)$[16] of 1.0 ps^{-1}. (This difference between the rate constants is within the statistical errors of the trajectory calculations.) The curve predicted by assuming an exponential lifetime distribution [eq 1 with $k = k_{MIC}(0)$] is also given in Figure 1. Figure 1 clearly shows that the near equivalence of these two rate constants results not from an exponential trajectory lifetime distribution of eq 1, but rather from similar areas under the trajectory-calculated and exponential-calculated curves of $N(\tau)/N(0)$ vs. τ.

We note in passing that, because the chemical activation rate constant at $\tau = 0$ was substantially greater than the microcanonical value at $\tau = 0$ (4 vs. 1 ps^{-1}), there must have been an initial nonrandom excitation of the H–C–C phase space in the chemical activation. This phenomenon has been considered in detail in previous work.[3,14,19]

A kinetic model for treating the nonrandom distribution is described next.

4. Kinetic Models for Nonexponential Decay

A model in which the intramolecular phase space of the reacting molecule is treated as containing two or three regions, each with its own kinetic behavior, will be referred to as a two- or three-state model. Two-state and three-state models, both including steps for intramolecular energy transfer, are described below for interpreting the nonexponential distribution of lifetimes. Indeed, it has been shown in ref 15 that a model with three time exponentials is needed to represent the trajectory data. However, the two-state model is instructive and qualitatively applicable and is considered first.

Two-State Statistical Model. We assume here that the phase space of the excited molecule can be divided into two parts, as depicted in Figure 2. The intramolecular relaxation and unimolecular dissociation processes are then written as

$$\text{initiation} \rightarrow N_1 \tag{10a}$$

$$N_1 \underset{k_3}{\overset{k_2}{\rightleftharpoons}} N_2 \tag{10b}$$

$$N_1 \xrightarrow{k_1} \text{products} \tag{10c}$$

where k_2 and k_3 are intramolecular energy-transfer rate constants.

(19) Hase, W. L.; Wolf, R. J. In "Potential Energy Surfaces and Dynamics Calculations"; Truhlar, D. G., Ed.; Plenum Press: New York, 1981; p 37.

In the context of the present study region I is the one initially excited by the chemical activation process and may include, as a minimum, extensive excitation of the newly formed C–H bond. Region II would then consist of the remaining phase space.

Solving the system of first-order kinetic equations for the system of eq 10b and 10c, with the initial conditions $N_1 = N(0)$ and $N_2 = 0$, $N(0)$ being the initial number of HCC molecules, one obtains the number of surviving HCC molecules at time τ:

$$N(\tau)/N(0) = [(k_1 - \lambda_2)e^{-\lambda_1\tau} - (k_1 - \lambda_1)e^{-\lambda_2\tau}]/(\lambda_1 - \lambda_2) \quad (11)$$

where λ_1 and λ_2 are the eigenvalues of the linear system in eq 10b and 10c and satisfy

$$\lambda_1 + \lambda_2 = k_1 + k_2 + k_3 \qquad \lambda_1\lambda_2 = k_1k_3 \quad (12)$$

Using eq 9 and evaluating $P(\tau)$ in the limit $\tau \to 0$ from eq 3 and 11 one obtains the high-pressure chemical activation rate constant

$$k^\infty = k_1 \quad (13)$$

The chemical activation unimolecular rate constant in the low-pressure limit is found from eq 8 and 11 to be

$$k^0 = k_1k_3/(k_2 + k_3) \quad (14)$$

There are three rate constants k_1–k_3 in eq 11–14 and two quantities (k^∞ and k^0) known from trajectory data. The remaining independent constant k_2 (or k_3) is then chosen to provide the best two-state fit of the calculated $N(\tau)/N(0)$ to the trajectory data.

We next deduce an expression for $k_{MIC}(0)$, the microcanonical rate constant at $\tau = 0$. In terms of the kinetic scheme of eq 10b and 10c $k_{MIC}(0)$ is obtained by assuming a microcanonical equilibrium of N_1 and N_2 at $\tau = 0$, N_1^e and N_2^e; namely one assumes $k_2N_1^e = k_3N_2^e$. Since the rate at $\tau = 0$ for this system is $k_1N_1^e$, $k_{MIC}(0)$ equals $k_1N_1^e/(N_1^e + N_2^e)$. One thus finds that

$$k_{MIC}(0) = k_1k_3/(k_2 + k_3) \quad (15)$$

Comparison of eq 14 and 15 shows that for the mechanism given by eq 10 the expression for the low-pressure chemical activation rate constant k^0 is identical with that for the microcanonical rate constant at $\tau = 0$.

$N(\tau)/N(0)$ determined with the two-state model is compared in Figure 1 with the HCC trajectory results and with the prediction based on eq 1 where k now equals $k_{MIC}(0)$. The parameters in eq 11 chosen as described earlier, are $k_1 = 3.97$, $k_2 = 1.17$, and $k_3 = 0.295$, all in ps^{-1}. Overall, the fit is far superior to the prediction based on eq 1. It does not, however, account for the long-time tail of the $N(\tau)/N(0)$ distribution in Figure 3. For this, a three-state model, given in the next section, is needed.

The two-state model in eq 10 serves to approximate one aspect of a variety of chemical activation reactions and ensuing unimolecular dissociations.[4] However, other reaction schemes are possible, for example where the decomposition occurs not to redissociate the newly formed bond, as in eq 10c, but rather to dissociate another bond. In this case the region initially excited is not the one which leads directly to the decomposition. An alternative scheme to eq 10a–10c then is one in which eq 10a is replaced by a reaction in which region II is initially excited

$$\text{initiation} \rightarrow N_2 \quad (16)$$

but in region I continues to be the exit channel. One then finds

$$1/k^0 = 1/k_{MIC}(0) + 1/k_3 \qquad k^\infty = 0 \quad (17)$$

The results in eq 17 clearly do not apply to the trajectory results of ref 15, both because according to eq 17 $k^\infty = 0$ and $k^0 \neq k_{MIC}(0)$. Because of the nature of the initial excitation and the dissociation in ref 15, this alternative model should indeed be inappropriate for those data.

The kinetic model which has been used in the interpretation of some experimental chemical activation studies[10] is a variant of the above: a phase space region I is initially excited, and two different products are obtained, one arising from region I and the other from region II.

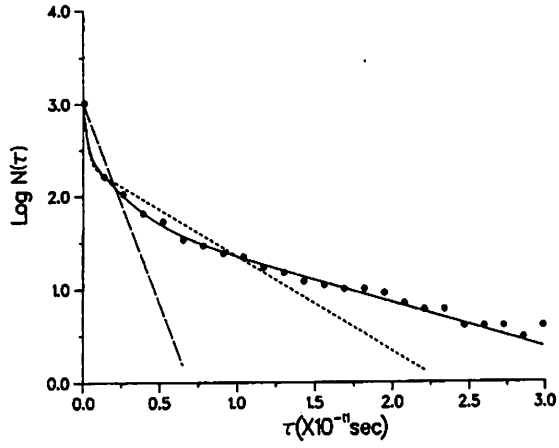

Figure 3. Plots of log $N(\tau)/N(0)$ vs. time for a quasiclassical simulation of HCC dissociation following chemical activation. The solid circles denote the trajectory results.[15] The line with long dashes is the prediction based on eq 1 with $k = k_{MIC}(0)$. The line with short dashes is the fit of the two-state model, eq 11. The solid line is the fit of the three-state model, eq 21.

Three-State Statistical Model. In the potential energy surface used in ref 15 there is at high CH excitations a near 2:1 resonance of the CH and CC stretching vibrations in HCC. (A more realistic surface is expected to have, instead, at high excitations, a near 2:1 resonance of the CH stretching and HCC bending.) Thus, it is possible that the relevant phase space is divided from a kinetic point of view into three regions, involving, respectively, excitation of the CH stretch, excitation of the CC stretch, and excitation of the HCC bend. More generally, the several regions might be the bond stretch of the newly formed or initially excited bond, some subsystem with which it is in a near resonance, and the remaining coordinates. To this end, and to interpret the trajectory results in ref 15, a particular "three-state" model is considered, in which one merely supplements the scheme in eq 10b and 10c with the step

$$N_1 \underset{k_5}{\overset{k_4}{\rightleftharpoons}} N_3 \quad (18)$$

The value of $k_{MIC}(0)$ is now readily shown to be

$$k_{MIC}(0) = k_1/[1 + k_2/k_3 + k_4/k_5] \quad (19)$$

instead of eq 15.

The set of linear equations for N_1, N_2, and N_3, plus initial conditions, contains in the solution five constants: the three eigenvalues in the time-dependent exponentials, λ_1, λ_2, λ_3, and two preexponential factors. Solution of the linear equations yields

$$\lambda_1\lambda_2\lambda_3 = k_1k_3k_5$$

$$\lambda_1 + \lambda_2 + \lambda_3 = \sum_{i=1}^{5} k_i$$

$$\lambda_1^{-1} + \lambda_2^{-1} + \lambda_3^{-1} = k_3^{-1} + k_5^{-1} + [k_{MIC}(0)]^{-1} \quad (20)$$

and, for $N(\tau)$

$$\frac{N(\tau)}{N(0)} = \sum_{i=1,2,3} \frac{[k_2k_5 + k_3k_5 + k_3k_4 + \lambda_i^2 - \lambda_i \sum_{j\neq i} k_j]e^{-\lambda_i\tau}}{\prod_{j\neq i} (\lambda_i - \lambda_j)} \quad (21)$$

The equations yield

$$k^0 = k_{MIC}(0) \qquad k^\infty = k_1 \quad (22)$$

The rate constants k_1–k_5 for the three-state model can be determined from the values of k^0, k^∞, and the three λ_i's, by using the above equations. Values of k^0, k^∞, λ_1, λ_2, and λ_3 for the HCC trajectory study have been reported previously.[15] The resulting values for the k_i's are, in units of ps^{-1}, $k_1 = 3.97$, $k_2 = 1.14$, $k_3 = 0.796$, $k_4 = 0.226$, and $k_5 = 0.117$. The fit of the three-state

model to the trajectory data for $N(\tau)$ is compared with those of the two-state model and the $k_{MIC}(0)$-based curve in Figures 1 and 3. The smallness of the k_4 and k_5 values is responsible for the long-time tail in these plots.

When a model which is the three-state analogue of eq 17 is considered, one finds

$$1/k^0 = 1/k_{MIC}(0) + 1/k_3 \qquad k^\infty = 0 \tag{23}$$

instead of eq 22.

The three-state model in eq 10 and 18 could also be applied to the lifetime studies of an ensemble that was initially microcanonical rather than being produced by chemical activation. One could also test it to see whether the k_i's so obtained in a numerical fit to the trajectory data agree with those obtained above from a fit to the chemical activation study. However, an accurate lifetime distribution curve for the former was not given in ref 16.

5. Discussion and Summary

We have seen in ref 15 that a highly nonexponential lifetime distribution in a quasiclassical simulation of HCC unimolecular decomposition gave, nevertheless, chemical activation rate constants at low and high pressure which agreed with (k^0) or were not too different from (k^∞, factor of 4) the value of $k_{MIC}(0)$, the microcanonical rate constant at $\tau = 0$. Two- and three-state statistical models are described in the present paper, for which a slow energy transfer occurs between regions of phase space. They have a highly nonexponential lifetime distribution for both the microcanonical and chemical activation ensembles but, nevertheless, give a chemical activation rate constant in the low-pressure regime which agress analytically with the microcanonical $\tau = 0$ value. The three-state model was used to fit accurately the temporal behavior, including the long-time tail.[15] The model may also apply to other forms of excitation, such as high CH overtome excitation after a time interval for quantum-mechanical "dephasing" of the initial excitation.

Although such kinetic models may have a correct physical basis for some systems, in other cases it may be necessary to formulate a model which allows nonstatistical transitions in the phase space that are not simply described by kinetic schemes. This situation could arise when the intramolecular motion is so highly correlated that a trajectory undergoes infrequent (and hence nonstatistical) transitions between different types of motion which may themselves be nearly quasiperiodic or chaotic.[20]

The individual trajectories in ref 15 were not studied in sufficient detail to see whether one can identify three regions in phase space (if they indeed exist), for example, in terms of the various excitations of the coordinates mentioned earlier. In such a study one could use the spectral trajectory method,[21] applied to each of the relevant coordinates, to determine from the spectral intensities in the neighborhood of various frequencies the temporal behavior for occupation of the various parts of phase space.

Some caution is needed in the use of classical trajectory studies. The long-time tail in Figures 1 and 3 was due to "nearly trapped" trajectories. Quantum mechanically the system could also escape from such a trapping by tunneling to other parts of phase space. Again, another quantum-mechanical effect, one which could occur particularly at short rather than at long times, is a dephasing of a time evolving wave packet. The relation between the quantum-mechanical treatment and a kinetic model has been discussed in ref 22 for radiationless transitions.

We have not commented on the relation between $k_{MIC}(0)$ and the RRKM-calculated value of k appearing in eq 1, since this has been done in ref 19. The two values agree, within the error of the harmonic count in the calculation of k_{RRKM} in that reference. (A more accurate phase space count could be used to see the precise relation.) This result is not unexpected, since there was no recrossing[23] of the transition state in those trajectories. The microcanonical distribution of lifetimes in ref 16 was highly non-RRKM, a result consistent with the kinetic models used here and consistent with an equality of $k_{MIC}(0)$ and k_{RRKM}.

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