

Effect of Fluctuations in State-Specific Unimolecular Rate Constants on the Pressure Dependence of the Average Unimolecular Reaction Rate

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The standard (i.e., Lindemann mechanism, strong-collision assumption, etc.) treatment of thermal unimolecular reactions expresses the effective, pressure-dependent unimolecular rate constant (usually called k_{uni}) in terms of the average unimolecular rate constant for a given total energy, $k(E)$ (and, more rigorously, for a given total angular momentum). Several experimental and theoretical studies have shown, however, that unimolecular rate constants for individual quantum states (all of essentially the same total energy and angular momentum) can have significant variations about the average rate, i.e., a significant degree of state specificity. This paper examines the effect that these fluctuations have on the effective, pressure-dependent rate, k_{uni} . The general result is that fluctuations reduce the rate, most prominently at high pressures.

The remarkable determinations by several research groups¹⁻⁴ of unimolecular decay rates for molecules in *individual quantum states* has shown a high degree of state specificity. That is, the rate constant for states of essentially the same total energy (and total angular momentum) can differ substantially. A similar degree of state specificity has also been seen in theoretical calculations for the formaldehyde decomposition and for other model problems.⁵⁻⁸ One expects to see more experimental and theoretical determinations of state-specific unimolecular rates in the future.

The theoretical framework for discussing the distribution of individual rate constants about their average value has been borrowed from the field of nuclear physics, the most popular such distribution being the family of Porter-Thomas distributions:⁹

$$P(k) = \left(\frac{\nu}{2\bar{k}}\right) \left(\frac{\nu k}{2\bar{k}}\right)^{(\nu/2)-1} \exp\left[-\frac{\nu}{2}(k/\bar{k})\right] / \Gamma\left(\frac{\nu}{2}\right) \quad (1)$$

Here $P(k)$ is the probability distribution of unimolecular rate constants; i.e., $P(k) dk$ is the probability of the rate constant having a value between k and $k + dk$, where \bar{k} is the average rate constant

$$\bar{k} = \int_0^\infty dk P(k)k \quad (2)$$

and ν is the "effective number of decay channels" which characterizes the distribution. Levine¹⁰ has recently reviewed this subject quite extensively. See also the work by Polik et al.¹¹ which derives a more general class of distribution functions which includes the Porter-Thomas family as a special case.

The purpose of this letter is to consider the effect that these fluctuations in unimolecular rate constants have on the thermal unimolecular reaction rate of "classical" unimolecular theory.

Thus the standard textbook treatment of the Lindemann mechanism (with the strong-collision assumption) gives the effective unimolecular rate constant as¹²

$$k_{\text{uni}}(\omega, T) = \sum_i e^{-\beta E_i} \frac{k_i \omega}{k_i + \omega} / \sum_i e^{-\beta E_i} \quad (3)$$

where $\beta = (kT)^{-1}$, ω is the collision frequency of buffer gas, and k_i is the unimolecular rate constant for state i . The standard procedure¹² is now to assume that k_i depends only on the energy of state i (or, more rigorously, also on the total angular momentum), i.e.,

$$k_i = \bar{k}(E_i) \quad (4)$$

where $\bar{k}(E)$ is the average rate constant for energy E (which is usually approximated by RRK, or RRKM models). It is precisely this assumption, (4), that we wish to supersede in the present treatment.

To rewrite (3), first insert the identity

$$1 = \int_0^\infty dE \delta(E - E_i) \quad (5)$$

(δ = Dirac delta function) into the summand of the denominator and interchange the order of the sum and integral:

$$\begin{aligned} D &\equiv \sum_i e^{-\beta E_i} = \int_0^\infty dE e^{-\beta E} \sum_i \delta(E - E_i) \\ &= \int_0^\infty dE \rho(E) e^{-\beta E} \end{aligned} \quad (6)$$

where ρ

$$\rho(E) = \sum_i \delta(E - E_i) \quad (7)$$

is the usual density of states. D , of course, is the partition function of the reactant molecule. In the numerator one inserts into the summand the identity (5) and also the identity factor

$$1 = \int_0^\infty dk \delta(k - k_i) \quad (8)$$

so that it becomes

$$\sum_i e^{-\beta E_i} \frac{k_i \omega}{k_i + \omega} = \int_0^\infty dE e^{-\beta E} \int_0^\infty dk \frac{k \omega}{k + \omega} \sum_i \delta(E - E_i) \delta(k - k_i) \quad (9)$$

The probability distribution of reaction rates for total energy E is defined by

(12) See, for example, Johnston, H. S. *Gas Phase Reaction Rate Theory*; Ronald Press: New York, 1966; p 263 *et seq.*

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$$P_E(k) \equiv \frac{\sum_i \delta(E-E_i) \delta(k-k_i)}{\sum_i \delta(E-E_i)} \equiv \langle \delta(k-k_i) \rangle_E \quad (10)$$

so that with this definition and (7), (9) becomes

$$\sum_i e^{-\beta E_i} \frac{k_i \omega}{k_i + \omega} = \int_0^\infty dE \rho(E) e^{-\beta E} \int_0^\infty dk P_E(k) \frac{k \omega}{k + \omega} \quad (11)$$

The final expression for k_{uni} is thus

$$k_{\text{uni}}(\omega, T) = \int_0^\infty dE \rho(E) e^{-\beta E} k_{\text{uni}}(\omega, E) / \int_0^\infty dE \rho(E) e^{-\beta E} \equiv \langle k_{\text{uni}}(\omega, E) \rangle_T \quad (12a)$$

where the *microcanonical pressure-dependent rate constant* is

$$k_{\text{uni}}(\omega, E) = \int_0^\infty dk P_E(k) \frac{k \omega}{k + \omega} \quad (12b)$$

Equation 12 is the more general expression that is the focus of this letter. In the limit that $P_E(k)$ is strongly peaked about the average rate for energy E , i.e.,

$$P_E(k) \rightarrow \delta(k - \bar{k}(E)) \quad (13a)$$

(12b) becomes

$$k_{\text{uni}}(\omega, E) \rightarrow \frac{\bar{k}(E) \omega}{\bar{k}(E) + \omega} \quad (13b)$$

and in this limit one recognizes (12) to be the standard textbook expression.¹² The present interest is to see how (13b) is changed when the distribution $P_E(k)$ is not a δ delta function about the average rate.

To this end we consider the Porter–Thomas distribution, which has the form

$$P_E(k) = p(k/\bar{k}(E)) / \bar{k}(E) \quad (14)$$

where $p(z)$ is a function only of the dimensionless rate $z = k/\bar{k}(E)$. The microcanonical pressure-dependent rate of (12b) then becomes

$$k_{\text{uni}}(\omega, E) = \bar{k}(E) \int_0^\infty dz p(z) z \lambda / (z + \lambda) \quad (15a)$$

where λ is the collision frequency in units of $\bar{k}(E)$:

$$\lambda = \omega / \bar{k}(E) \quad (15b)$$

With the Porter–Thomas form of $p(z)$, the explicit expression for the microcanonical pressure-dependent rate is

$$k_{\text{uni}}(\omega, E) / \bar{k}(E) = \Gamma\left(\frac{\nu}{2}\right)^{-1} \int_0^\infty dz \left(\frac{z\nu}{2}\right)^{\nu/2} \exp\left(-\frac{\nu z}{2}\right) \lambda / (\lambda + z) \quad (16)$$

In the limit $\nu \rightarrow \infty$ the Porter–Thomas distribution actually approaches a delta function about the average rate, i.e., (13a), so in this limit the more general expression, (16), reverts to the usual result

$$k_{\text{uni}}(\omega, E) / \bar{k}(E) \rightarrow \lambda / (\lambda + 1) \quad (17)$$

in terms of λ . The Porter–Thomas distribution is broadest for $\nu = 1$, so this is the case for which (16) should show the largest deviation from the standard result. The limiting expressions for the general case are

$$k_{\text{uni}}(\omega, E) / \bar{k}(E) \sim \lambda \quad \text{as } \lambda \rightarrow 0$$

$$\sim 1 - \left(1 + \frac{2}{\nu}\right) / \lambda \quad \text{as } \lambda \rightarrow \infty \quad (18)$$

Figure 1 shows the microcanonical pressure-dependent rate, (16), as a function of the dimensionless collision frequency λ for the cases $\nu = 1, 2$, and ∞ . The general effect is that fluctuations about the average rate *decrease* the average, pressure-dependent rate from the standard result ($\nu = \infty$). These effects, most prominent in the *falloff region* and as the high-pressure limit is approached, will thus add to the difficulty of extrapolating ex-

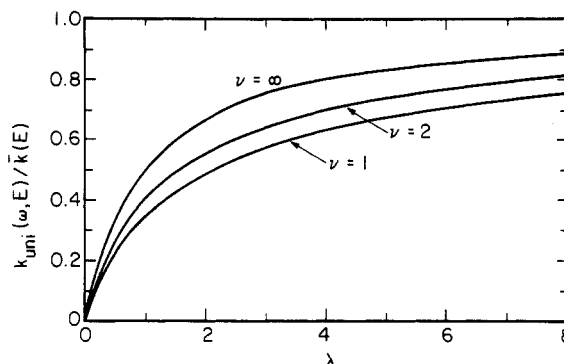


Figure 1. Microcanonical pressure-dependent rate constant (normalized to the average microcanonical rate $\bar{k}(E)$), as a function of the reduced collision frequency $\lambda \equiv \omega/\bar{k}(E)$, as given by (16) of the text. ν is the “number of channels” which characterizes the Porter–Thomas distribution; $\nu = \infty$ is the function $\lambda/(\lambda + 1)$, the standard textbook result.

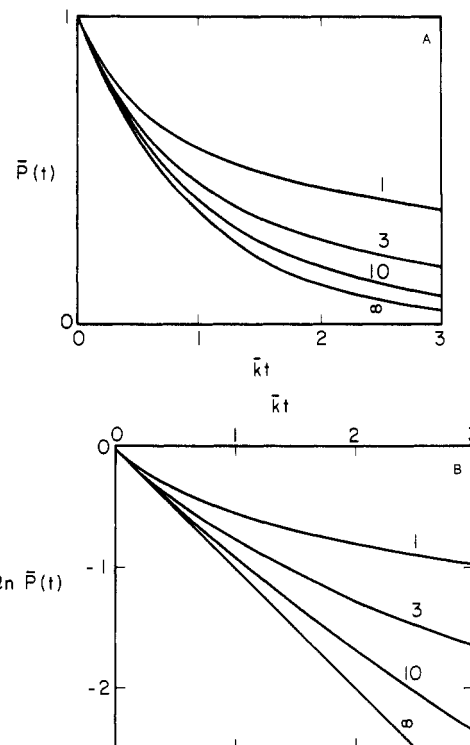


Figure 2. (A) Average survival probability, given by (21), for various values of ν , the effective number of decay channels. (B) Same as (A), but a semilogarithmic plot to emphasize deviation from exponential behavior for $\nu < \infty$.

perimental measurements to obtain the “true” high-pressure limit of the rate.

Finally, it is interesting to note the effect that a distribution of rate constants has on the *time dependence* of the unimolecular decay process. The survival probability $P(t)$ for a molecule in an individual quantum state with unimolecular rate constant k is simple exponential decay:

$$P(t) = e^{-kt} \quad (19)$$

Thus if there is a distribution of rate constants $P(k)$, the average survival probability $\bar{P}(t)$ is

$$\bar{P}(t) \equiv \int_0^\infty dk P(k) e^{-kt} \quad (20)$$

With the distribution of (1) this is easily found to be

$$\bar{P}(t) = \left(1 + \frac{2}{\nu} \bar{k} t\right)^{-\nu/2} \quad (21)$$

\bar{k} being the average rate constant. (For the more general distribution function noted in ref 11, $\bar{P}(t) = D(t)^{-1/2}$, where $D(t)$ is

given by (4.18b) of ref 11.) In the limit of a large number of effective decay channels, $\nu \rightarrow \infty$, (21) reverts to simple exponential decay (as expected from (13a)),

$$\lim_{\nu \rightarrow \infty} \bar{P}(t) = e^{-kt} \quad (22)$$

but deviations from exponential behavior are prominent for small ν ; see Figure 2. Nonexponential decay resulting from a distribution of rate constants has been seen by Crim et al.,¹³ the distribution of rates coming from a distribution of total energies. The point of the present discussion is that a distribution of rate constants, and thus nonexponential decay, may also exist even if all molecules have the same total energy (and angular momentum).

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The consequences of this nonexponential time dependence are being explored more fully by Hase et al.,¹⁴ including other distribution functions and the effect of collisions on the result.

Acknowledgment. This letter resulted from my reading of Dr. W. F. Polik's Ph.D. thesis, where questions about the effects of these fluctuations were raised. I also acknowledge a stimulating discussion with Prof. W. L. Hase concerning the time dependence resulting from a distribution of rate constants that led to the last paragraph of this paper. This research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract No. DE-ACO3-76SF00098.

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Rotationally Resolved Electronic Spectrum of Jet-Cooled Cyclopentadienyl Radical

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A completely rotationally resolved laser-induced fluorescence spectrum of the $\tilde{A}^2A_2'' - \tilde{X}^2E_1''$, 0_0^0 electronic transition of the cyclopentadienyl radical has been obtained in a supersonic free jet expansion. Over 150 individual rotational transitions have been combined in a least-squares fit to determine the molecular parameters of both electronic states. Clear evidence is obtained for Jahn-Teller distortion of the ground state.

Introduction

The cyclic aromatic hydrocarbon radicals, C_nH_n ($n = \text{odd}$), are extremely fascinating species for chemists with interests ranging from organic synthetic to theoretical. Of these radicals, perhaps the most accessible to physical observation and measurement is the cyclopentadienyl radical, C_5H_5 . It has been the subject of numerous theoretical calculations,¹⁻⁵ many emphasizing the Jahn-Teller distortion of the radical and estimating its stabilization energy. There appears to be very little consensus with estimates ranging from $\approx 500 \text{ cm}^{-1}$ to over 5000 cm^{-1} for the barrier to D_{5h} symmetry. The barriers for pseudorotation around the ring have been estimated from essentially zero to 1225 cm^{-1} .

Experiments have yielded only slightly more definitive information about the distortion of C_5H_5 . Early flash photolysis experiments observed the electronic spectrum of C_5H_5 in the gas phase.^{6,7} Engleman and Ramsay⁸ established from optical spectra that upon deuteration there are only eight distinct species, i.e., consistent with five equivalent carbon atoms. Liebling and McConnell⁹ observed the EPR spectra of C_5H_5 prepared in a single crystal of C_5H_6 . They reported that the unpaired spin densities on the carbon atoms were equivalent above $\sim 120 \text{ K}$ but inequivalent below 70 K . They argued that this inequivalence must be due to an intramolecular Jahn-Teller distortion because the radical was rotating in the crystal. They believed that these observations imply barriers to pseudorotation of at least 50 cm^{-1} . However, Hedaya¹⁰ estimated a barrier only one-fifth as large, based upon EPR measurements on C_5H_5 in a Ne matrix.

Recently there have been reports¹¹⁻¹³ of laser-induced fluorescence detection of C_5H_5 . Nelson et al.¹¹ report extensive and extremely complicated ground-state vibrational structure for the radical, but there has as of yet been no successful analysis

of this structure in terms of the understanding of the Jahn-Teller effect.

Ultimately one can expect that high-resolution gas-phase data on the vibrational, rotational, and perhaps even the hyperfine structure of this radical will be required for a complete understanding of its structure and energy levels. In this letter we report a significant advance in this quest. We have observed completely resolved rotational structure for the $\tilde{A}^2A_2'' - \tilde{X}^2E_1''$ electronic transition of C_5H_5 in a supersonic free jet expansion at rotational temperatures ranging from 0.6 to 10 K . We have analyzed over 150 individual rotational transitions and have obtained the first quantitatively precise parameters directly dependent upon the Jahn-Teller distortion.

Experimental Section

The cyclopentadienyl radical was probed in a supersonic free jet expansion via laser-induced fluorescence. The experimental technique has been well described previously,¹⁴ but the essential

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