Statistical Phase Space Theory of Polyatomic Systems. Application to the Unimolecular Reactions $C_6H_5CN\cdot^+ \rightarrow C_6H_4\cdot^+ + HCN$ and $C_4H_6\cdot^+ \rightarrow C_3H_3^+ + \cdot CH_3$

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Abstract: The formalism necessary for applying statistical phase space theory to unimolecular reactions of polyatomic species is developed. This theory is applied in conjunction with RRKM theory to the reactions 1 and 2: $C_6H_5CN\cdot^+ \rightarrow C_6H_4\cdot^+ + HCN$ (1); $C_4H_6\cdot^+ \rightarrow C_3H_3^+ + \cdot CH_3$ (2). Both the energy dependence of the rate constant and the product kinetic energy distributions are calculated and compared with experiment. Phase space theory establishes upper limits on the fragmentation rate constants as a function of energy. The magnitude of these rate constants is quantitatively fit to experiment using RRKM theory and reasonable values of the parameters involved. Reaction 2 is interesting in that it appears an isomerization reaction is rate determining in the fragmentation, rather than the fragmentation step itself. The experimental product kinetic energy distribution of both reactions is well fit by statistical phase space theory. Reasons are given why RRKM theory should not be used to calculate these distributions. Our results are in conflict with previously reported work. Cooks et al. conclude from RRKM calculations that the experimental product kinetic energy distribution of reaction 1 is not statistical. Werner and Baer conclude the energy dependence of the rate constant for a number of C_4H_6 isomers reacting via (2) cannot be fit using statistical theory. A thorough discussion of each system is given in the text.

I. Introduction

The area of unimolecular reactions has been one of the richest sources of kinetic information on reactions of excited systems for over 40 years. Up until the last few years collisional or chemical activation (in neutral systems) had been the principal means of creating activated molecules and comparisons of the pressure dependence of deactivation and reaction rate constants with theoretical calculations the usual way of testing our understanding of the kinetics of these reactions.[1] In ionic systems mass spectral fragmentation patterns or charge transfer breakdown graphs have been the principal data for comparison with theory.[2] In both neutral and ionic systems these relative rate types of comparisons have been very useful in developing our chemical intuition but the amount of information obtained by these studies had leveled off by the late 1960's and interest in unimolecular reactions dwindled.

In recent years, however, significant experimental and theoretical advances have been made that have rekindled interest in unimolecular chemical reactions. Perhaps most significant are the experimental data on the energy dependence of the unimolecular rate constant as a function of the internal energy in the fragmenting species. All of these data are on ionic systems and may be portentous of the expanding role ion-molecule reactions may play in increasing our understanding of the fundamental aspects of chemical kinetics. The first such data were obtained by Andlauer and Ottinger[3] using charge transfer spectroscopy to generate excited ions above the fragmentation threshold. By varying the reagent ion, differing amounts of energy can be deposited in the substrate species. The technique had been successfully used for years to generate breakdown graphs as a function of energy[2] (i.e., relative rate constants) but Andlauer and Ottinger first obtained absolute rate data.

Very recently a second technique has become available, photoion-photoelectron coincidence spectroscopy. This technique, pioneered by Eland and co-workers[4] and Baer and co-workers,[5] uses time of flight analysis to detect ionic products that correspond to electrons of a selected energy; i.e., both the ion and the conjugate electron result from the same photoionization event. By invoking conservation of energy it is possible to extract the fragmentation rate constant of an excited ion as a function of energy (when the experiments are performed at energies above the fragmentation threshold).

Beynon, Cooks, and co-workers[6] have recently reported the first measurements of the kinetic energy distribution of the products of a unimolecular fragmentation. The information is obtained from the measurement and subsequent deconvolution of ion kinetic energy peak shapes in a mass spectrometer. The technique has the disadvantage that the fragmenting parent ions have a distribution of internal energies due to their generation via electron impact. Reasonable estimates of the internal energy distribution can be made from electron energy deposition function and rate constant vs. energy data, however, so the information is still very useful. In any case, it appears hopeful that product kinetic energy distributions will soon be available from photoionization studies,[7] eliminating the energetic uncertainties of the electron impact ionization process.

Theoretical work on unimolecular reactions goes back as far as Lindemann and Hinshelwood,[1a,b] but most modern theory has as a basis the RRKM formulation,[1a,b,8] or the quasiequilibrium theory (QET) formulation.[1b,2a,9] The critical step in the fragmentation of an energized molecule according to these theories is the formation of a suitable "transition" state, located at the highest point on the potential energy surface on the most favorable reaction path to products. The rate of the reaction is then determined statistically by comparing the state densities of the transition state with those of the reactant in its normal configuration at a given energy in excess of threshold. Hence, the nature of the transition state dominates the magnitude of the rate constant in a given reaction channel, particularly at energies near threshold.

Recently, Klots[10] has reformulated QET (or RRKM theory) by invoking the principle of detailed balance and by recasting the theory in the statistical phase space formalism. By allowing the long-range charge-induced dipole interaction to dominate the potential, Klots effectively moved the transition state into the product region of configuration space. As a result, the rate constants predicted by this theory correspond to the very loose transition state and hence represent maximum or near maximum values. Further, since angular momentum

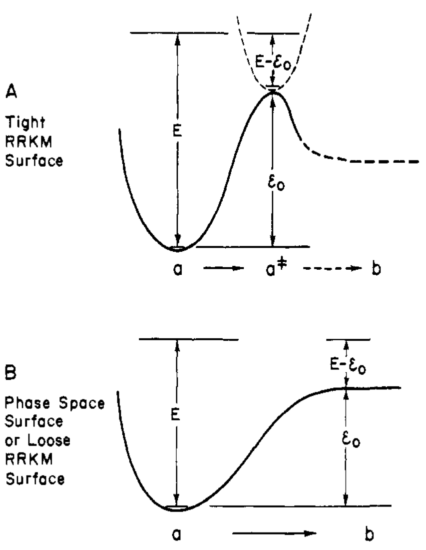
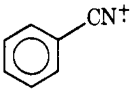


Figure 1. Schematic reaction potential surfaces for (a) RRKM theory with a tight transition state and (b) statistical phase space theory for RRKM theory with a loose transition state.

is conserved (although only for zero total angular momentum in the Klots[10] formulation) the theory is very useful for predicting product state distributions, particularly kinetic energy distributions. Very recently, Chesnavich and Bowers[11] have developed a rigorous classical method for determining phase space volumes of pairs of polyatomic molecules under the constraints of the conservation of energy and angular momentum. These results have been applied to low-energy bimolecular ion-molecule reactions[12] and to unimolecular reactions of rotationally excited ions formed via low-energy ion-molecule reaction.[13]

In this paper the two reactions 1 and 2 are considered.



$\longrightarrow C_6H_4^{+} + HCN$ (1)

$\longrightarrow C_3H_3^{+} + \cdot CH_3$ (2)

The dependence of the rate constant of these reactions on internal energy in the fragmenting ion has been reported by charge transfer spectroscopy[3] ($C_6H_5CN\cdot^{+}$) and by photoion-photoelectron coincidence spectroscopy ($C_6H_5CN\cdot^{+}$,[4c] $C_4H_6\cdot^{+}$ [5a]). Kinetic energy distributions are also available for both reactions measured by ion kinetic energy spectroscopy ($C_6H_5CN\cdot^{+}$,[6a] $C_4H_6\cdot^{+}$ [14]). Klots[10] has reported a theoretical calculation of $k_1(E)$ using a statistical phase space theory similar to that presented here and Werner and Baer[5a] have reported a QET calculation on $k_2(E)$. In the following sections we briefly summarize the statistical phase space theory and apply it in conjunction with RRKM theory to the reactions in question. From the comparison of theory with experiment conclusions will be drawn regarding the reaction mechanism, the structures of the ionic products, and the implications of the data for the ergodic hypothesis central to RRKM and statistical phase space theory.

II. Theory

Hinshelwood[15] first suggested that the probability a molecule will be collisionally excited to an internal energy between E and $E + dE$ is proportional to the density of states of the molecule in that energy regime. Shortly afterwards, Rice and Ramsberger[16] and Kassel[17] (RRK) independently suggested that the density of states of a molecule in the energy regime of interest also governs the rate at which it will decompose. For molecules composed of degenerate quantum oscillators, the logical conclusion of this assumption yields eq 3 for the rate constant

$$k(E) = A(1 - \mathcal{E}_0/E)^{l-1} \qquad (3)$$

where $\mathcal{E}_0$ is the threshold energy of the reaction, A is a constant in units of frequency, and l is (ideally) the number of vibrational modes in the molecule. While it has turned out that l must be treated as a variable parameter, and the degenerate quantum oscillation model is not realistic, eq 3 was a real beginning toward a detailed unimolecular rate theory.

In the early 50's, Marcus and Rice[8] (RRKM) and Rosenstock et al.[9] (QET) incorporated the RRK concepts with the transition state theory of Eyring.[18] Such a step formally recognized the importance of the potential energy surface in determining the rate of unimolecular reactions. A schematic potential surface is given in Figure 1A. The resulting rate constant is given in eq 4

$$k(E) = \frac{\sigma}{h}\int_0^{E-\mathcal{E}_0} \frac{\rho^{\ddagger}(E - \mathcal{E}_0 - \mathcal{E}_{rc})\,d\mathcal{E}_{rc}}{\rho(E)} \qquad (4)$$

where $\mathcal{E}_{rc}$ is the energy in the reaction coordinate, $\rho(E)$ is the density of vibrational states at energy E in the molecule in its normal configuration, $\rho^{\ddagger}(E - \mathcal{E}_0 - \mathcal{E}_{rc})$ is the density of states in the transition state configuration of the molecule at energy $E - \mathcal{E}_0 - \mathcal{E}_{rc}$, and σ is a factor that accounts for reaction path degeneracy.[20] The constant h arises from the usual transition state model for the rate of passage of molecules through the critical region of the potential surface.

Up to this point, the theoretical models have all been cast from the perspective of the fragmenting molecule. There is, of course , a second perspective, that of the products that are being formed. Klots[10] was the first to develop this perspective for unimolecular chemical reactions. Central to this development is the principle of detailed balance

$$R_{\mathcal{J}}(a \rightarrow b) = R_{\mathcal{J}}(b \rightarrow a) \qquad (5)$$

where $R_{\mathcal{J}}(a \rightarrow b)$ is the total rate of passage of reactants, "a", with total angular momentum $\mathcal{J}$, to products "b", also with total angular momentum $\mathcal{J}$. The forward rate is simply

$$R_{\mathcal{J}}(a \rightarrow b) = k_{\mathcal{J}}(E)_a \rho_a(E - \mathcal{E}_r{}^a) S_r \qquad (6)$$

where $k_{\mathcal{J}}(E)_a$ is the unimolecular rate constant of a → b at total energy E and angular momentum $\mathcal{J}$, $\rho_a(E - \mathcal{E}_r{}^a)$ is the vibrational density of states of molecule "a" with total energy E and rotational energy $\mathcal{E}_r{}^a$, and S_r is the degeneracy associated with a given rotational energy in the molecule "a". For example, in the classical limit, for a spherical molecule $\mathcal{E}_r{}^a = B_a\mathcal{J}^2$ and $S_r = (2J)^2$, i.e., a$(2J)$ spatial degeneracy and a$(2J)$ internal projection degeneracy.

The situation is a bit more complex for the reverse rate $R_{\mathcal{J}}(b \rightarrow a)$. If the reaction a → b is a fragmentation then the products "b" have not only rotational and vibrational degrees of freedom but relative translational degrees of freedom as well. Hence a collision must occur in going from b → a and the total rate will be

$$R_{\mathcal{J}}(b \rightarrow a) = \frac{\sigma_a}{\sigma_b} S_r{}'$$
$$\times \int\int \bar{k}_{\mathcal{J}}(\mathcal{E}_r{}^b,\mathcal{E}_t)\rho_t(\mathcal{E}_t)\,d\mathcal{E}_t\,\rho_b(E - \mathcal{E}_0 - \mathcal{E}_{tr}{}^b)\,d\mathcal{E}_{tr}{}^b \qquad (7)$$

where $\bar{k}_{\mathcal{J}}(\mathcal{E}_r{}^b,\mathcal{E}_t)$ is the capture collision rate constant for the collision of species "b" at relative translational energy $\mathcal{E}_t$ and rotational energy $\mathcal{E}_r{}^b$, $\rho_t(\mathcal{E}_t)$ is the translational density of states per unit volume of "b", $\rho_b(E - \mathcal{E}_0 - \mathcal{E}_{tr}{}^b)$ is the vibrational density of states of "b" at energy $E - \mathcal{E}_0 - \mathcal{E}_{tr}{}^b$ where $\mathcal{E}_{tr} = \mathcal{E}_r{}^b + \mathcal{E}_t$ is the rotation/translation energy sum, and $S_r{}'$ is the spatial degeneracy factor. The integrals are over all available energy consistent with angular momentum conservation. The ratio of symmetry numbers, σ_a/σ_b, accounts for the fact of reaction path degeneracy.[19] Hence, from eq 5–7 we have for the forward rate constant

$$k_{\mathscr{J}}(E)_a = \frac{S_r'\sigma_a}{\sigma_b S_r \rho_a(E - \mathscr{E}_r{}^a)} \times \int\int \bar{k}_{\mathscr{J}}(\mathscr{E}_r{}^b,\mathscr{E}_t)\rho_b(\mathscr{E}_t)\,d\mathscr{E}_t\,\rho_b(E - \mathscr{E}_0 - \mathscr{E}_{tr}{}^b)\,d\mathscr{E}_{tr}{}^b \quad (8)$$

It is usual in ion–molecule reactions to use the Langevin theory[20] for estimating the capture rate constant. The partial capture rate constant associated with formation of a collision complex with angular momentum $\mathscr{J}$, from reactants with translational energy $\mathscr{E}_t$ and rotational energy $\mathscr{E}_r{}^b$, from Langevin theory, is

$$\bar{k}_{\mathscr{J}}(\mathscr{E}_r{}^b,\mathscr{E}_t) = \frac{v\pi\hbar^2}{2\mu\mathscr{E}_t}\mathscr{P}_b(\mathscr{E}_t,\mathscr{E}_r{}^b,\mathscr{J}) \quad (9a)$$

where $\mathscr{P}_b(\mathscr{E}_t,\mathscr{E}_r{}^b,\mathscr{J})$ is the density of angular momentum states in b for the conditions discussed above, v is the relative velocity of the colliding species, and μ is their reduced mass. The density of translational states per unit volume is given by (9b).[1a]

$$\rho_b(\mathscr{E}_t)\,d\mathscr{E}_t = \frac{\mu^2 v}{2\pi^2\hbar^3}\,d\mathscr{E}_t \quad (9b)$$

If one recalls the sum of angular momentum states at a given $\mathscr{E}_{tr}$ and $\mathscr{J}$ is defined by (9c)[11,12]

$$\Gamma_b(\mathscr{E}_{tr},\mathscr{J}) = \int \mathscr{P}_b(\mathscr{E}_t,\mathscr{E}_r,\mathscr{J})\,d\mathscr{E}_t \quad (9c)$$

then substitution of eq 9 into eq 8 yields the result

$$k_{\mathscr{J}}(E)_a = \frac{S_r'\sigma_a}{\sigma_b S_r h\rho(E - \mathscr{E}_r{}^a)} \times \int_{\mathscr{E}_{tr}{}^{\ddagger}}^{E-\mathscr{E}_0} \rho_b(E - \mathscr{E}_0 - \mathscr{E}_{tr})\Gamma_b(\mathscr{E}_{tr},\mathscr{J})\,d\mathscr{E}_{tr} \quad (10a)$$

The lower limit on the integral, $\mathscr{E}_{tr}{}^{\ddagger}$, occurs at the minimum value of $\mathscr{E}_{tr}$ for which $\Gamma_b(\mathscr{E}_{tr},\mathscr{J}) > 0$. In order to obtain rate constants that can be compared to experiment, $k_{\mathscr{J}}(E)_a$ must be convoluted with the distribution of rotational energies of species a. For the reactions reported in this work, it is assumed this distribution is thermal. For the unimolecular reaction of a complex formed by ion–molecule reaction a $\mathscr{J}$ distribution calculated by phase space techniques must be used.[13] Hence, the final result is given in eq 10b:

$$k(E)_a = \int_0^{\infty} k_{\mathscr{J}}(E)_a g_{\mathscr{J}} e^{-\mathscr{E}_r{}^a/kT}\,d\mathscr{J} \quad (10b)$$

where $g_{\mathscr{J}}$ is the degeneracy of the rotational level.

In order to obtain the translational energy distribution it is useful to first fix the translational energy at a specific value and then calculate the partial rate constant for that value of $\mathscr{E}_t$;

$$k_{\mathscr{J}}(E,\mathscr{E}_t)_a = \frac{S_r'\sigma_a}{\sigma_b S_r h\rho_a(E - \mathscr{E}_r{}^a)} \times \int_{\mathscr{E}_r{}^{\ddagger}}^{E-\mathscr{E}_0} \rho_b(E - \mathscr{E}_0 - \mathscr{E}_t - \mathscr{E}_r{}^b)\mathscr{P}(\mathscr{E}_t,\mathscr{E}_r{}^b,\mathscr{J})\,d\mathscr{E}_r{}^b \quad (11)$$

where $\mathscr{E}_r{}^{\ddagger}$ is the minimum value of $\mathscr{E}_r{}^b$ for which $\mathscr{P}(\mathscr{E}_t,\mathscr{E}_r{}^b,\mathscr{J}) > 0$ at the fixed value of $\mathscr{E}_t$. The probability the products have a translational energy $\mathscr{E}_t$ for a given energy E and angular momentum $\mathscr{J}$ in the fragmenting molecule is, then

$$P_{\mathscr{J}}(E,\mathscr{E}_t) = k_{\mathscr{J}}(E,\mathscr{E}_t)_a / \int k_{\mathscr{J}}(E,\mathscr{E}_t)_a\,d\mathscr{E}_t = k_{\mathscr{J}}(E,\mathscr{E}_t)_a / k_{\mathscr{J}}(E)_a \quad (12)$$

What must be done before comparison with experiment can be made is to stipulate the $\mathscr{J}$ distribution and the distribution of internal energies of the fragmenting molecule. For the unimolecular reactions considered in this work a Boltzmann distribution of $\mathscr{J}$ values is appropriate. The internal energy distribution of the fragmenting ion is generated in the following way. From the random lifetime assumption,[1a] the probability that a fragmenting ion of energy E will have lifetime τ is given by (13):

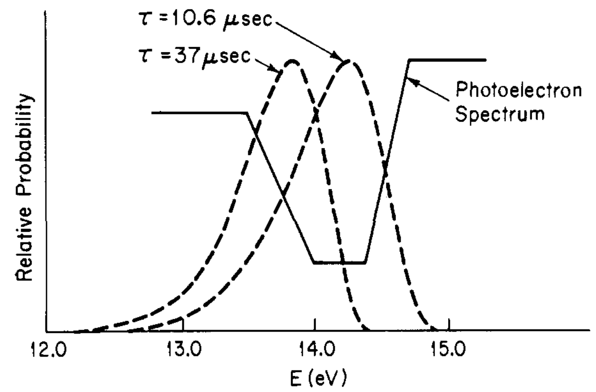


Figure 2. The dashed curves represent the lifetime distribution of ions as a function of their internal energy for two reaction times, τ = 37 and 10.6 μs. These curves were calculated from eq 13 in the text using the values of $k(E)$ given in Figure 3. The solid line is a good approximation of the photoelectron spectrum of C_6H_5CN in the energy range of interest [D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, London, 1970].

$$P_\tau(E) = k(E)e^{-k(E)\tau} \quad (13)$$

For our purposes, τ is picked to correspond to the observation time of the experiment. For metastable ions in a mass spectrometer the range of values is $0 < \tau < 40$ μs. The values of $k(E)$ are taken from experiment, where possible, or if necessary are approximated by calculations. In the systems considered here, $k(E)$ has been experimentally determined for most of the energy range of interest (C_6H_5CN,[3,4c] C_4H_6[5a]). Hence, $P_\tau(E)$ can be generated by inserting $k(E)$ in (13) for a specifically chosen τ. Two curves for $P_\tau(E)$ vs. E for the benzonitrile reaction 1, done at τ 10.6 and 37 μs, are given in Figure 2.

The probability that an ion will have a particular internal energy E when formed via electron impact at electron energy V is termed the electron energy deposition function, $P(E,V)$. For complex molecules these distributions are difficult to obtain experimentally[21] but they can be estimated from photoelectron spectra to a good first approximation.[22] A good approximation to the photoelectron spectrum of C_6H_5CN is given by the straight lines in Figure 2. Hence, convolution of $P(E,V)$ with $P_\tau(E)$ gives the probability that a fragmenting ion will have internal energy E for an experiment of total reaction time τ. The theoretical distribution of kinetic energies suitable for comparison with experiment is then

$$P(\mathscr{E}_t) = \int_{\mathscr{E}_0}^{\infty}\int_0^{\infty} P_{\mathscr{J}}(E,\mathscr{E}_t)P_\tau(E)P(E,V)g_{\mathscr{J}} \times e^{-\mathscr{E}_r{}^a/kT}\,dE\,d\mathscr{J} \quad (14)$$

Calculations using this formula on reactions 1 and 2 will be discussed in the following section.

III. Results and Discussion

(A) $C_6H_5CN^{\cdot +} \rightarrow C_6H_4{}^{\cdot +} + HCN$ ($k_1(E)$). The experimental values of $k_1(E)$ for reaction 1 obtained by Andlauer and Ottinger[3] with corrected energy scale of Eland and Schulte[4c] are given as the open circles in Figure 3. Also given in Figure 3 are two phase space calculations, curves A and B, and one RRKM calculation, curve C. The phase space calculations are for two different $C_6H_4{}^{\cdot +}$ ion structures: curve A corresponds to an

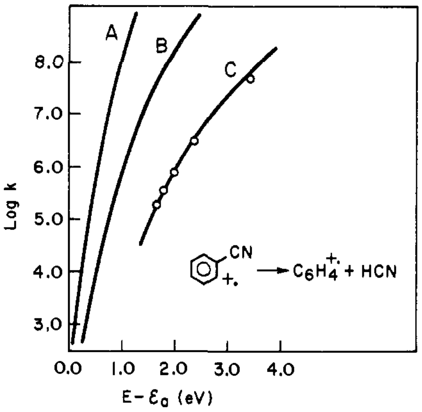
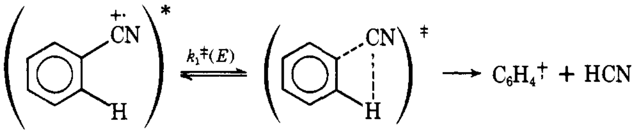


Figure 3. Plot of $k_1(E)$ vs. E. The points are those of Andlauer and Ottinger, ref 3, on a corrected energy scale according to the data of Eland and Schulte, ref 4c. Curves A and B are phase space curves assuming a linear and cyclic structure respectively for $C_6H_4{\cdot}^+$. Curve C is an RRKM calculation assuming a loose four-centered transition state. The frequencies are given in Table I.

acyclic diyne structure and curve B to a cyclic benzyne structure. The benzyne structure leads to a predicted $k_1(E)$ curve much closer to experiment than the acyclic structure although the theoretical rate remains ca. 10^2 larger than experiment over most of the energy range. The curves in Figure 3 correspond to our "most reasonable" estimate of vibrational frequencies (see Table I) in the $C_6H_4{\cdot}^+$ ion. Variation of these frequencies could improve the fit (by ca. one order of magnitude) but it was felt the resulting frequencies were not as reasonable as those given in Table I. Hence, we conclude phase space calculations overestimate the rate constant by a substantial margin.

Curve C corresponds to a RRKM calculation that assumes a "loose" four-centered transition state. Clearly the fit is very good. The phase space calculations assume a "totally loose" transition state which in this case does not appear to correspond to the real world. It is, in fact, reasonable that some form of transition state is involved in this reaction since at least two bonds must be broken and one formed for the reaction to proceed. Schematically the reaction proceeds as shown.



The RRKM rate constant corresponds to $k_1^{\ddagger}(E)$, which in this case is rate determining. The phase space calculations ignore the transition state and hence provide an upper limit to the rate constant (schematically shown in Figure 1).

The experimental product kinetic energy distribution of reaction 1 has been reported by Terwilliger et al.[6a] and discussed by Cooks et al.[23] It is given in Figure 4 as the bar graph. Cooks et al.[23] indicate both the distribution function and the average energy of the products are independent of ion flight time in the range $4 \leq \tau \leq 37$ μs. Phase space results for flight times of 10.6 and 37 μs are given as the dashed curves A and B in Figure 4. It is apparent the theoretical curves accurately reproduce the experimental data including the independence of the distribution function on reaction flight time in the mass spectrometer.

We interpret these comparisons of theory and experiment as indicative of a statistical partitioning of the energy in the fragmentation process. Hence, both the rate constant and kinetic energy distribution appear to proceed statistically in reaction 1.

Cooks et al. come to a different conclusion than ours regarding the details of the fragmentation process. These authors suggest the independence of the kinetic energy release on flight time (i.e., internal energy in the fragmenting ion) necessitates a strong dependence of $k_1(E)$ on E, in fact a much stronger dependence than that observed experimentally by Andlauer and Ottinger[3] (and reproduced in our Figure 3). In contrast, our analysis indicates the independence of the kinetic energy release results from the convolution of $P_\tau(E)$ with $P(E,V)$ as indicated in eq 14 and shown schematically in Figure 2. The 10.6 μs data samples ions with higher internal energies than the 37 μs data but this fact does not strongly affect the product kinetic energy distribution. There are a number of reasons for this. First, a window in the energy deposition function occurs in the energy region that corresponds to the change in reaction times from 37 to 10 μs (see Figure 2). Hence, the higher energy ions have lower probability. Second, the reactant ion energy at both 37 and 10.6 μs is well above threshold, due to the kinetic shift,[24] and hence changes in this energy have a reduced effect relative to energy changes near threshold. Finally, the product vibrational states act as a buffer of sorts, because any excess energy must be partitioned between both vibrational and translational degrees of freedom. Cooks et al.[23] had assumed that all ion internal energies which can contribute to the metastable peak under given instrumental conditions are equally probable. This assumption is a poor one for benzonitrile in the energy region of interest of these studies and led to their

Table I. Parameters Used in the Phase Space and RRKM Calculations on Reaction 1 ($C_6H_5CN{\cdot}^+ \rightarrow C_6H_4{\cdot}^+ + HCN$)

Species	Rotational constant, cm^{-1}	$\alpha \times 10^{24}$ cm^3 [a]	$\Delta H_f°_{298}$,[b] kcal/mol
$C_6H_5CN{\cdot}^+$	0.0934[d]		277
$C_6H_4{\cdot}^+$	0.144[d]		316[c]
HCN	1.46	2.6	32.3

$C_6H_5CN{\cdot}^+$ [e]	$C_6H_4{\cdot}^+$ (A)[f]	$C_6H_4{\cdot}^+$ (B)[g]	HCN
	Vibrational frequencies, cm^{-1}		
3100 (3)	3300 (2)	3100 (4)	3300
3000 (2)	3000 (2)	1900	2100
2200	2000 (2)	1600 (2)	700 (2)
1600 (2)	1500	1500 (3)	
1500	1300	1200 (3)	
1400	1200	1100 (3)	
1300 (2)	900 (3)	1000 (2)	
1200 (3)	800	800	
1100	600 (5)	600 (2)	
1000 (4)	300 (6)	500	
900		400 (2)	
800 (3)			
700			
600			
500 (2)			
400 (2)			
300 (2)			
200			

[a] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids", Wiley, New York, N.Y., 1954. [b] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Heron, K. Draxl, and F. H. Field, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 26** (1969). [c] Reference 24. [d] In the phase space calculations $C_6H_5CN{\cdot}^+$ and $C_6H_4{\cdot}^+$ are treated as spherical top molecules. The geometric means of the rotational constants are given. It has been shown that this approximation leads to maximum errors of a few percent in the results (ref 11). [e] The symmetry factor for the phase space calculations is 1 and for the RRKM calculations 2. In the RRKM calculation the following changes were made in going to the activated complex: 3100 → 1500; 400 → 150; 800 → RC. [f] Frequencies used for phase space curve A in Figure 3, corresponding to a linear $C_6H_4{\cdot}^+$ structure. [g] Frequencies used for phase space curve B in Figure 3, corresponding to a cyclic benzyne $C_6H_4{\cdot}^+$ structure.

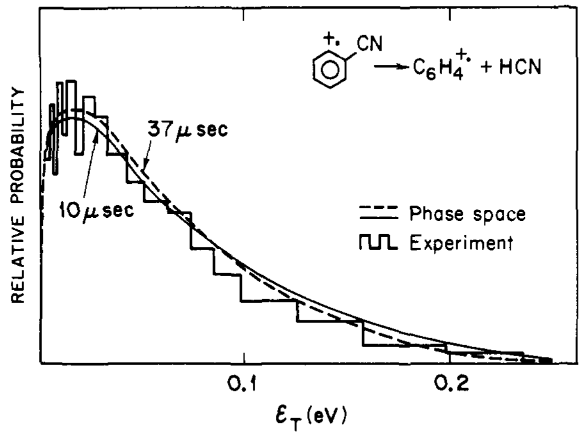


Figure 4. The experimental product kinetic energy distribution, ref 6a, for reaction 1 is plotted as the solid bar graph. Theoretical phase space curves for reaction times $\tau = 37$ and 10.6 μs are plotted as the dashed and solid lines. See text for discussion.

erroneous conclusions regarding the energy dependence of $k_1(E)$.

Cooks et al.[23] made a further point based on comparison of the experimental kinetic energy release with predictions of RRKM theory. They calculated fom RRKM theory the nonfixed energy, $E - \mathcal{E}_0$, in the benzonitrile parent ion necessary to give the observed kinetic energy release. When this value was added to $\mathcal{E}_0$ (also estimated from RRKM consideration) a value of E was obtained that differed from the experimental AP − IP value by between 1 and 2 eV. Cooks et al. suggest such a discrepancy is irreconcilable with fragmentation of ground state $C_6H_5CN\cdot^+$ ions and conclude the reaction proceeds from an isolated electronic state 1-2 eV above the ground state. The phase space analysis presented here indicates statistical reaction of ground state ions in contrast to the analysis of Cooks et al.

A caution is appropriate at this point regarding the proper use of RRKM calculations. These calculations compare only the properties of the transition state of the fragmenting molecule with those of the excited normal configuration of the molecule. Hence RRKM theory is only appropriate for calculating rates or distributions in the region of the transition state on the potential energy surface. RRKM theory is not appropriate for calculation of the properties of the system in the products region of the energy surface. There are, for example, $3n - 12$ vibrational degrees of freedom in the products compared to $3n - 6$ in the normal configuration of the fragmenting molecule and $3n - 7$ in the transition state, a fact not included in an RRKM analysis. Further, RRKM theory does not conserve angular momentum nor does it account for the long-range potential of the system. Both factors can strongly affect product energy distributions. Similar cautions have recently been voiced by Marcus[25] regarding the application of RRKM theory to product kinetic energy distributions in neutral systems.

(B) $C_4H_6\cdot^+ \rightarrow C_3H_3^+ + CH_3$ ($k_2(E)$). The reactions of a number of isomeric $C_4H_6\cdot^+$ ions have been studied by Werner and Baer[5a] using photoion-photoelectron coincidence spectroscopy. Their data for $k_2(E)$ for various energies and various isomers are shown in Figure 5 as the points. Also shown in Figure 5 are a phase space calculation and two RRKM calculations. The vibrational frequencies and molecular parameters used in the calculations are given in Table II.

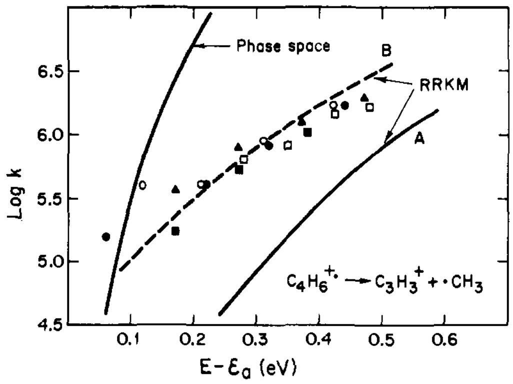


Figure 5. Plot of $k_2(E)$ vs. E. The experimental data, ref 5a, are given as the points: (●) 1,3-butadiene, (□) 1,2-butadiene, (○) cyclobutene, (■) 2-butyne, and (▲) 1-butyne. The results of a phase space calculation are given as the solid line. RRKM curve A is that given in ref 5a assuming 1,3-butadiene ion is the normal configuration of the $C_4H_6\cdot^+$ ion and 2-methylcyclopropene is the transition state in the fragmentation. RRKM curve B was derived from the potential surface in Figure 6 assuming the mechanism of reactions 15. See discussion in the text. Parameters are given in Table II.

Table II. Parameters Used in the Phase Space and RRKM Calculations on Reaction 2 ($C_4H_6\cdot^+ \rightarrow C_3H_3^+ + \cdot CH_3$)

Species	Rotational constant, cm^{-1}	$\alpha \times 10^{24}$ cm^3	$\Delta H_f{}^\circ{}_{298}$, kcal/mol
$C_4H_6\cdot^+$	0.295[a]		236[c]
$C_3H_3^+$	0.722[a]		255[d]
$\cdot CH_3$	7.644[a]	2.2[b]	34.5

Vibrational frequencies, cm^{-1} $C_4H_6\cdot^+$ [e]	$C_3H_3^+$	$\cdot CH_3$
3100 (3)	3100 (3)	3100 (2)
3000 (3)	1200 (4)	300
1600 (2)	1100 (3)	1400 (2)
1400 (2)	900 (2)	800
1300 (2)		
1200		
1000 (3)		
900 (3)		
800		
500 (2)		
300		
200		

[a] In the phase space calculations, all species are treated as spherical top molecules. The geometric means of the rotational constants are given. This approximation leads to maximum errors of a few percent (ref 11). [b] Calculated from atomic polarizabilities. [c] For the 1,3-butadiene structure; J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Heron, K. Draxl, and F. H. Field, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 26** (1969). [d] Reference 5a. [e] The symmetry factor for the phase space calculation is 1/18. In the RRKM calculation of curve B in Figure 5 the following changes were made in going to the transition state: 3100 → 1500; 500 → 150; 800 → RC.

The phase space calculation assumed the 1,3-butadiene structure for the $C_4H_6\cdot^+$ ion. It predicts rate constants greater than those experimentally observed over most of the energy range. This result is consistent with the notion that the phase space rate constants are generally considered upper limits in the statistical approximation. However, it appears near threshold the experimental results might become larger than the phase space predictions if extrapolation from higher energy experimental values is performed. Such a turnover would result from the fact that the phase space rate constants decrease at a much faster rate than the experimental rate constants as energy decreases.

The RRKM curve A is that reported by Werner and Baer[5a] and is uniformly one to two orders of magnitude lower than the experimental results over the entire energy range. This calculation assumed the 1,3-butadiene structure for the $C_4H_6\cdot^+$ ion in its stable configuration and a methylcyclopropene

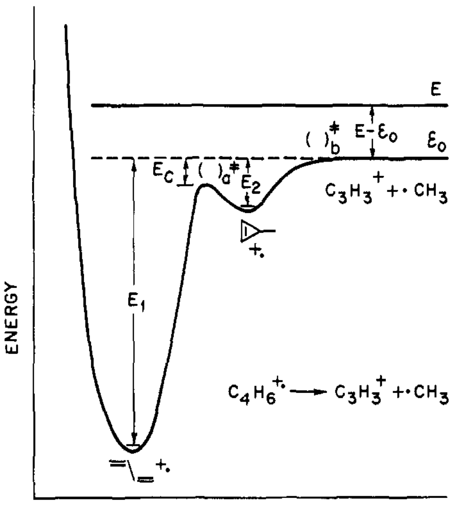


Figure 6. Schematic reaction coordinate vs, energy curve for reaction 2 used to generate RRKM curve B in Figure 5. See text for discussion.

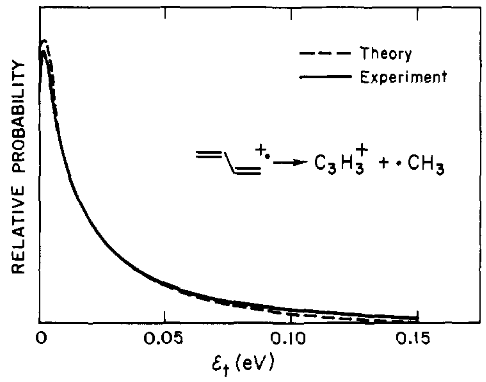
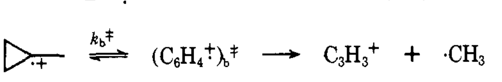


Figure 7. The experimental product kinetic energy distribution, ref 14, for reaction 2 is plotted as the solid line. A phase space curve for a reaction time of 8.5 μs is shown as the dashed line.

transition state. Similar results were obtained using a linear transition state.[5a] Since all the isomers yielded the same threshold energy for $C_3H_3^+$ formation and all have very similar $k(E)$ vs. E dependence, Werner and Baer felt a common surface was sampled by all of the ions regardless of their isomeric origin. Hence the single calculation was felt to be representative of all of the fragmenting $C_4H_6\cdot^+$ systems. Werner and Baer further argue that the fact this calculation grossly disagrees with experiment indicates that the fragmentations of the various isomers are not statistical. They suggest that the ergodic hypothesis central to statistical theory may be violated for this reaction.

Such a suggestion must be evaluated in light of RRKM curve B. We have generated this curve from the schematic potential surface given in Figure 6. For convenience we will discuss the mechanism only in terms of the 1,3-butadiene ion and the 2-methylcyclopropene ion. We assume this part of the surface is common to the reactions of all the C_4H_6 isomers reported by Werner and Baer.[5a] While this assumption need not necessarily be true, it is very reasonable in light of the similarities of the $k(E)$ vs. E data and the identical C_3H_3' threshold for all of the isomers. As suggested in Figure 6, we assume the reaction proceeds in two steps: isomerization of the butadiene ion to 2-methylcyclopropenium ion followed by fragmentation of the cyclopropenium ion to products. That is


$\xrightleftharpoons{k_a^{\ddagger}} (C_6H_4{}^{\dot{+}})_a{}^{\ddagger} \rightleftharpoons$ (15a)

$\xrightleftharpoons{k_b^{\ddagger}} (C_6H_4{}^{\dot{+}})_b{}^{\ddagger} \longrightarrow C_3H_3^+ + \cdot CH_3$ (15b)

where $k_a{}^{\ddagger}$ and $k_b{}^{\ddagger}$ are the rate constants of interest here. The transition state of the fragmentation reaction 15b, $(C_4H_6\cdot^+)_b{}^{\ddagger}$, is assumed to be essentially a 2-methylcyclopropenium ion with an elongated bond between the methyl carbon and the ring carbon. The consequence of having this "loose" transition state and the shallow well depth of the 2-methylcyclopropenium ion (ca. 0.35 eV)[26] is that the rate constant $k_b{}^{\ddagger}$ rises very rapidly immediately above threshold. Hence the rate constant $k_a{}^{\ddagger}$ becomes rate determining essentially at the threshold for the appearance of $C_3H_3\cdot^+$.

The isomerization reaction 15a is similar to the reaction Werner and Baer used to characterize the fragmentation with one very important difference. The threshold of the isomerization reaction occurs at a lower energy than the fragmentation threshold, as denoted by the energy E_c in Figure 6. Hence, for an energy $E - \mathcal{E}_0$ above the fragmentation onset the system is at energy $E - \mathcal{E}_0 + E_c$ above the isomerization threshold. This condition leads to a relatively large value of $k_a{}^{\ddagger}$ at the fragmentation threshold. The value of $k_a{}^{\ddagger}$ rises relatively slowly with energy, however, due to the moderating effect of the deep butadiene well. To get the fit shown in Figure 5 as RRKM curve B, the energy E_c was treated as a variable parameter under the constraint $0 \leq E_c \leq 0.35$ eV, where 0.35 eV is the well depth of the 2-methylcyclopropenium ion. A value of $E_c = 0.20$ eV gave the curve B in Figure 5 which fits the data very well. No attempt was made to vary the vibration frequencies to improve the fit. As a consequence of this analysis we suggest that the $C_4H_6\cdot^+$ ion does fragment at a rate in agreement with statistical theory predictions but an isomerization reaction is the rate-determining step rather than the fragmentation reaction.

The product kinetic energy distribution of reaction 2 has been recently measured by Cooks[14] using electron impact ionization of 1,3-butadiene and a mass spectrometric technique for detection.

$$C_4H_6\cdot^+ \rightarrow C_3H_3^+ + \cdot CH_3 \qquad (2)$$

The data are given as the solid curve in Figure 7. The phase space curve is given by the dashed line in Figure 7. The phase space result was derived for an ion flight time of 8.5 μs which approximately corresponds to the stated experimental conditions.[14] This distribution agrees very well with experiment over the entire energy range. Hence, the reaction appears to yield a statistical distribution of product kinetic energies.

The kinetic energy distribution and, subsequently, the average kinetic energy release should be fairly strong functions of the flight time of the ions in reaction 2. This result contrasts with the HCN elimination from benzonitrile where no change was observed experimentally or predicted by theory. A set of experimental kinetic energy distributions for reaction 2 as a function of flight time $1\ \mu s \leq \tau \leq 10\ \mu s$ would be very useful diagnostic data for further study of the mechanism of this interesting reaction.

IV. Summary and Conclusions

In this paper we have applied both statistical phase space theory and RRKM (or QET) theory to reactions 1 and 2. For both reactions, product kinetic energy distributions and the dependence of the fragmentation rate constant on energy have been experimentally reported. Statistical phase space calculations gave upper limits to the rate constants of both reactions, a consequence of the "totally loose" nature of the transition state assumed in this theory. RRKM theory was then utilized to predict rate constants by including a transition state(s) in the potential surface. The energy dependence of the rate constant of both reactions 1 and 2 was shown to be adequately characterized by RRKM theory using reasonable assumptions regarding the transition states and the mechanism of the reaction. These results demonstrate the utility of using both phase space theory and RRKM theory to characterize the reaction mechanism.

Statistical phase space theory was utilized to calculate product kinetic energy distributions of reactions 1 and 2. In both cases the fragmentations appear to give statistical kinetic energy distributions. The necessity of using the phase space formulation of statistical theory for these calculations was emphasized. RRKM theory is useful for predicting properties only in the region of the transition state not in the products region of the potential surface. Further it was pointed out that care must be taken to carefully reproduce the experimental conditions in the theoretical calculation if the comparison of theory with experiment is to be meaningful. Failure to do this, or failure to use theory as an aid in discussing the reaction mechanism, can lead to erroneous conclusions being drawn from the experimental data.

Previous publications on both the $C_6H_5CN^{10,23}$ and $C_4H_6{}^{5a}$ systems have suggested that these reactions did not proceed according to the predictions of statistical theory. We feel the results presented here indicate that both reactions proceed statistically, using either the absolute rate constant or the product kinetic energy distribution as diagnostic indicators. The important experiments that are analyzed here, as well as those that are continuing to be produced by similar or complimentary methods, will go far toward furthering our insight into the detailed mechanism of chemical reactions. However, this paper makes it clear that every effort must be made to use theory as rigorously as possible if valid mechanistic information is to be extracted from the data. Statistical theory plays too central a role in chemical kinetics for less than rigorous tests to be used to define the boundaries of its applicability.

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(26) The heat of formation of 2-methylcyclopropenium ion was obtained as follows. The ionization potential of cyclopropene has been reported as 9.86 eV [M. B. Robin, C. R. Brundle, N. A. Kuebler, G. B. Ellison, and K. B. Wiberg, *J. Chem. Phys.*, **57**, 1758 (1972)] and that of 2,2-dimethylcyclopropene measured in our laboratories as 9.38 eV. Assuming a linear methyl additivity effect, the IP of 2-methylcyclopropene is 9.62 eV. The heat of formation of cyclopropene is known to be 2.87 eV [J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970]. By using methyl-substituted cyclopropanes as a model, a methyl group should stabilize the cyclopropene ring by ca. 7 kcal/mol. Hence, the heat of formation of 2-methylcyclopropene is ca. 2.59 eV. Using these data, and the threshold for $C_3H_3^+$ formation given by Werner and Baer in ref 5a, a well depth of 0.35 ± 0.1 eV is obtained for the 2-methylcyclopropenium ion.