positive ion electron impact. The combination of generating ions with structures both unstable toward fragmentation and close to the structure of the original compound and using a technique which favors simple cleavages seems of special interest: it may provide more useful structural information about many compounds than conventional positive ion mass spectrometry in its several forms. The example at hand certainly supports this hypothesis, and we intend to explore it further.

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Consequences of Charge Reversal of Gaseous Formate and Acetate Ions. Acyloxy Ions

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Abstract: Positive-ion collision-induced decomposition (CID) mass-analyzed ion kinetic energy (MIKE) spectra of formate and acetate anions were compared with the CID MIKE spectra of $COOH^+$, CH_2COOH^+, and $COOCH_3^+$, the likely simple rearrangement products of the formyloxy and acetyloxy cations. The spectra of the charge-reversed ions formed from the carboxylate anions differed from the spectra of the models, and gave fragment ions consistent with no structural rearrangement. The initially formed ion was found to rearrange with no energy barrier to $COOR^+$ using MINDO/3; for $HCOO^+$ this was duplicated by STO-3G and 4-31G calculations.

The acyloxy or acyloxoniumylidene cations $RCOO^+$ are examples of electron-deficient species which have not previously been detected or isolated. They are a subset of the class of oxenium ions of which alkoxy ions RO^+ form another subset. There has been much interest recently in alkoxy ions, both from an experimental[1-3] and theoretical[4,5] viewpoint. On the other hand, not so much has appeared on acyloxy ions.

Evidence for the simplest member of the series, the formyloxy cation $HCOO^+$, does not appear to have been clearly established experimentally. Long ago it was noted that, in the mass spectrometer, formic acid molecules specifically labeled with deuterium attached to either carbon or oxygen may lose either hydrogen on electron impact:[6]

$$DCOOH^{+\cdot} \rightarrow D + COOH^+ \qquad 37\% \qquad (1)$$

$$HCOOD^{+\cdot} \rightarrow H + COOD^+ \qquad 61\% \qquad (2)$$

$$DCOOH^{+\cdot} \rightarrow H + DCOO^+ \qquad 40\% \qquad (3)$$

$$HCOOD^{+\cdot} \rightarrow D + HCOO^+ \qquad 18\% \qquad (4)$$

The percentage values given in eq 1–4 refer to the percent intensities of these ions in the electron-impact mass spectra of the labeled formic acids. The further reactivity of these molecules has been studied by analysis of the ion–molecule reactions in formic-*d* acid.[7] The two ions react with neutral formic-*d* acid at different rates:

$$DCOO^+ + DCOOH \rightarrow DCOOHD^+ + CO_2$$
$$K = 1.7_2 \times 10^{-9}\ \mathrm{cm^3/molecules \cdot s} \qquad (5)$$

$$COOH^+ + DCOOH \rightarrow DCOOH_2^+ + CO_2$$
$$k = 1.9_3 \times 10^{-9}\ \mathrm{cm^3/molecule \cdot s} \qquad (6)$$

but the difference in reactivity is not large. If $DCOO^+$ has time to rearrange to $COOD^+$ before reactive collision occurs

$$DCOO^+ \rightarrow COOD^+ \qquad (7)$$

then the difference in reactivity could be explained as an isotope effect upon the reactivities of $COOH^+$ and $COOD^+$ as well as by the difference in structure between $DCOO^+$ and

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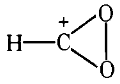
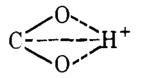
$COOH^+$. The appearance potentials for $DCOO^+$ and $COOH^+$ from DCOOH were found to be slightly different, 12.4 ± 0.1 and 12.8 ± 0.1 eV, respectively.[7] The heat of formation of the $DCOO^+$ ion is thus 143 kcal/mol at most.[8] Other measurements suggest that the heat of formation of $COOH^+$ is nearly the same: after consideration of excess energy effects, the value of $\Delta H_f(COOH^+)$ from acetic acid is 145 kcal/mol;[8] data from equilibrium studies in flowing afterglow[9] and ion cyclotron resonance[10] experiments for the equation

$$CH_5^+ + CO_2 \rightleftarrows CH_4 + CO_2H^+ \quad (8)$$

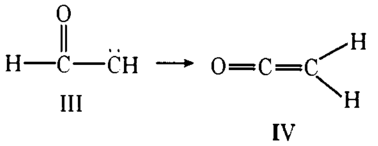
combined with standard thermochemical data yield a value of 141.6 kcal/mol for the heat of formation of protonated carbon dioxide. The slight difference in the appearance potentials cited for $DCOO^+$ and $COOH^+$ may be thus the result of an excess energy in the formation of $COOH^+$ and the ions may be of similar structure. That is, one or the other may form by rearrangement at threshold.

Theoretical approaches to this problem have been few. One analysis of the π system of the formyloxy cation, radical, and formate anion used fixed geometries for the ions and radical.[11] Variation of these parameters was allowed in a MINDO/2 study,[12] in which the most stable form of formyloxy cation was found to be I. Structure II was found as a second, higher minimum. It is known that MINDO/2 overestimates stabilities of small-ring compounds.

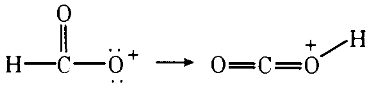

I


II

The isoelectronic carbene III readily isomerizes (eq 9) to ketene IV with passage of 13-16% of the molecules through the oxirene V.[13] This is isoelectronic with structure I, and may be offered as an experimental analogy for it.


III IV

(9)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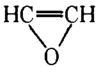

V

As an approach to the experimental observation of these ions, we have used collision-induced charge stripping of stable negative ions to produce positive ions:

$$M^- + N \rightarrow M^+ + N + 2e \quad (11)$$

The procedure has been reported before and applied to large negative ions. Work on positive ions suggests that the technique is useful for structural analysis of such ions.[14-17] The same seems to be true for negative ions as well.[18-20] In general, simple cleavages dominate the spectrum of positive fragment ions produced by collision-induced charge stripping (eq 12), although in some aromatic compounds rearrangements which can be described as ortho effects were observed.[20]

$$A\text{-}B\text{-}C^- + N \rightarrow A\text{-}B^+ + C + 2e + N \quad (12)$$

This study was restricted to the experimental detection of products from the charge reversal of formate and acetate ions:

$$HCOO^- + N \rightarrow 2e + N + HCOO^+ \rightarrow \text{fragments} \quad (13)$$

$$CH_3COO^- + N \rightarrow 2e + N + CH_3COO^+ \rightarrow \text{fragments} \quad (14)$$

Table I. CID MIKE Spectra of CHO_2^+ According to Method of Formation

		% of induced dissociations[a]		
m/z	$HCOO^+$	$COOH^+$ (from HCOOH)	$COOH^+$ (from CF_3COOH)	$COOH^+$ (from CO_2 and CH_5^+)
12		6	2	2
16	5	6	2	2
17	4	6	2	3
28	15	27	29	29
29	43	17	11	14
44	33	38	54	50

[a] As percent of total ion current, corrected for contributions from unimolecular decompositions and for multiplier response.

The hydrogen lost from formic acid to produce the $(M - 1)^-$ anion has been shown by labeling experiments to be that originally attached to oxygen (eq 15-18), so that there is no ambiguity concerning the structure of the negative ion produced from this species in the mass spectrometer.[6]

$$e + DCOOH \rightarrow DCOO^- + H\cdot \quad 100\% \quad (15)$$

$$e + DCOOH \rightarrow COOH^- + D\cdot \quad 1\% \quad (16)$$

$$e + HCOOD \rightarrow HCOO^- + D\cdot \quad 100\% \quad (17)$$

$$e + HCOOD \rightarrow COOD^- + H\cdot \quad 0\% \quad (18)$$

Experimental Section

Formic acid and acetic acid were obtained in highest available purity from commercial sources. The compounds used to generate model ions for comparison of collision-induced dissociation spectra, viz., trifluoroacetic acid, iodoacetic acid, and methyl trifluoroacetate, were obtained in purities exceeding 99% from commercial sources. Conventional mass spectra of the samples were obtained to ensure the absence of significant amounts of impurities, and then the collision-induced spectra were immediately obtained on pertinent ions.

A VG Micromass ZAB/2F mass spectrometer equipped with a collision cell and MIKES scan unit was used to obtain unimolecular and collision-induced MIKE spectra of model ions in the normal MIKE scan mode and to obtain collision-induced charge reversal MIKE spectra of formate and acetate ions with appropriate reversals of the draw out and accelerating potentials and magnetic field, but not the electric analyzer. The source was operated at 200 °C with 200-μA trap current and 70-eV electron energy (sample pressure in the source, 10^{-6} Torr on gage) for negative ions. The accelerating voltage was variously 6 or 8 kV in different experiments; Table I gives data for only 8-kV ions. Samples were introduced through an all-glass heated inlet system. The collision gas was N_2. For collision-induced fragmentation the collision cell was operated at a gage pressure of 8×10^{-7} Torr. The true pressure in the cell was then ca. 10^{-3} Torr, and a positive main beam intensity was reduced to roughly half its initial value. Negative main beams were not detected in the experimental setup, and the intensity of the $HCOO^+$ main beam from charge reversal of $HCOO^-$ was small; for CH_3COO^+ from CH_3COO^- it was zero.

Full MIKE spectra were scanned at 100 ms/eV, where eV refers to the kinetic energy of the energy- and mass-analyzed ion. The tabular data include corrections for contributions due to metastable ions undergoing unimolecular decompositions and for multiplier discrimination due to ion kinetic energy differences.[14] The reproducibility of data corresponds to an error of ±2 in the tabular data.

Results and Discussion

Table I presents the collision-induced decomposition spectra of CHO_2^+ isomers formed by the routes given in the equations

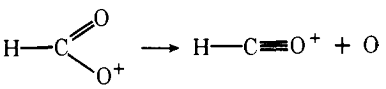
$$HCOO^- \rightarrow HCOO^+ + 2e \quad (19)$$

$$HCOOH^{+\cdot} \rightarrow H + CHO_2^+ \quad (20)$$

$$CF_3COOH^{+\cdot} \rightarrow CF_3 + COOH^+ \quad (21)$$

and eq 8. The first of these is charge reversal of formate ion; the second is by loss of H from the positive molecular ion of formic acid; the third is by loss of CF_3 from the molecular ion of trifluoroacetic acid; the fourth is by protonation of carbon dioxide. In the third case CHO_2^+ is the base peak in the spectrum[21] and no other combination of elements can produce an m/z 45 ion. As noted above, the structure of the M − 1 ion in formic acid is not clear because either hydrogen may be lost, and rearrangement to the more stable form can follow.

From the results in Table I, the ion generated by charge reversal is different from the other two. The principal, and characteristic, difference between its spectrum and the others is that loss of O forms its major decomposition channel. During collisional activation and subsequent rapid fragmentation of ions, it is expected that structures do not change. The loss of O by simple fragmentation is expected to be characteristic of only the $HCOO^+$ structure (eq 22 and 23): the product of eq



(22)

$$O{=}C{=}\overset{+}{O}H \longrightarrow {:}C{=}\overset{+}{O}{-}H + O \quad (23)$$

22 is about 20 kcal/mol more stable than its isomer,[22,23] the latter does not interconvert easily to formyl ion,[23] and $HCOO^+$ is expected to be significantly less stable than $COOH^+$ (vide infra). The loss of an oxygen atom to form a stable ion is reminiscent of the behavior of the alkoxy ions:[3]

$$CH_3O^+ \rightarrow CH_3^+ + O \quad (24)$$

Comparison of the other columns of Table I shows the resemblance of the CHO_2^+ ion from the molecular ion of formic acid to the $COOH^+$ ion generated from trifluoroacetic acid and to carbon dioxide protonated on oxygen. The experimental evidence shows that the structure cannot be $HCOO^+$ and it is not easy to propose other stable structures. Therefore, the ions generated from $HCOOH^{+\cdot}$ by loss of hydrogenation are mostly $COOH^+$ after a few microseconds, irrespective of whether they were formed by loss of hydroxy H or formyl H. Rearrangement of the ions which have lost hydroxyl H to $COOH^+$ must occur on a time scale rapid with respect to 1 μs. This result, of course, is in agreement with suggestions made earlier.[8] Since the spectra of the $COOH^+$ ions from different sources do not exactly coincide in a number of respects, one must consider that some other structure is also attained by the $(M - 1)^+$ ions from formic acid. The differences between the spectra of $COOH^+$ ions from different sources cannot be explained by contributions from the ions assigned the $HCOO^+$ structure. Therefore, only an insignificant fraction of these ions can remain after a few microseconds.

Table II provides a comparison of the collision-induced fragments formed by $C_2H_3O_2^+$ ions of different structures. The first, CH_3COO^+, is formed from acetate ions by charge reversal (eq 14). The second, CH_2COOH^+, is formed from a simple cleavage of the molecular ion of iodoacetic acid

$$ICH_2COOH^{+\cdot} \rightarrow CH_2COOH^+ + I \quad (25)$$

and is the most intense peak in the conventional electron-impact spectrum of that compound.[22,24] The third, $COOCH_3^+$, is the most important fragment ion in the spectrum of methyl trifluoroacetate:[24]

$$CF_3COOCH_3^{+\cdot} \rightarrow COOCH_3^+ + CF_3 \quad (26)$$

These two products are the simplest possible rearrangement products of CH_3COO^+, for CH_2COOH^+ is the product of H migration and $COOCH_3^+$ is the product of CH_3 migration. We did not examine further isomers of $C_2H_3O_2^+$ because they are unlikely: these ions fragment on an extremely fast time scale because of the large amount of internal energy in them, and a complex rearrangement should not occur to any great extent in highly excited ions before they fragment. As will be evident below, even the simpler rearrangements do not occur, and more complex rearrangements are even less likely than these on this fast time scale.

Table II. CID MIKE Spectra of $C_2H_3O_2^+$ Ions According to Method of Formation

	% of induced dissociations[a]		
m/z	CH_3COO^+	CH_2COOH^+	$COOCH_3^+$
12		3	3
13	3	5	5
14	10	14	15
15	(23)[b]	(49)[b]	(677)[b]
16	2		
17		2	2
28	2	5	23
29	6	26	27
30	1	12	
40		1	
41	4	3	
42	11	6	
43	36		
44	21	6	17
45	5	16	2
58		1	7

[a] As percent of total ion current, correct for contributions from unimolecular decompositions and for multiplier response. [b] Product of low-energy process, excluded from the sum of ion currents.

The major collision-induced decompositions of CH_3COO^+ are easily rationalized on the basis of simple cleavages. The four most intense peaks are formed as in eq 27–30. The identity of the ion as CH_3COO^+ is supported by the major fragmentation to CH_3CO^+, which is reminiscent of the loss of O from $HCOO^+$ and from alkoxy cations. This ion does not occur in the spectra of the most likely rearrangement products, CH_2COOH^+ and $COOCH_3^+$. Thus, CH_3COO^+ formed by charge reversal does not rearrange to either of these within microseconds.

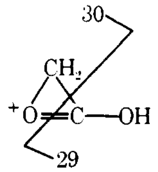
$$CH_3COO^+ \rightarrow CH_3CO^+ + O \quad (27)$$

$$CH_3COO^+ \rightarrow CH_3^+ + CO_2 \quad (28)$$

$$CH_3COO^+ \rightarrow CO_2^{+\cdot} + CH_3 \quad (29)$$

$$CH_3COO^+ \rightarrow CH_2CO^{+\cdot} + O + H \quad (30)$$

Two of the major decompositions of CH_2COOH^+ to ions of m/z 29 and 30 are most simply accounted for in terms of the product VI of the simple ring closure. The other major products



VI

at m/z 14 and 45 are explained in terms of simple cleavage:

$$CH_2^{+\cdot} + COOH \leftarrow CH_2COOH^+ \rightarrow COOH^+ + CH_2 \quad (31)$$

The formation of CH_3^+ requires a 1,3 shift. Though this has a high energy barrier, that would be easily overcome by ions near the higher end of the energy distribution, which by analogy is in excess of 14 eV.[3]

The final ion, $COOCH_3^+$, is methylated carbon dioxide, and it forms methyl ion in a low-energy process:

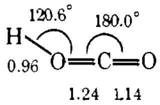
$$^+O{\equiv}COCH_3 \rightarrow O{=}C{=}O + CH_3^+ \qquad (32)$$

The dominance of m/z 28 in this spectrum alone is also to be expected from the structure

$$^+O{\equiv}COCH_3 \rightarrow O{=}C^+ + OCH_3 \qquad (33)$$

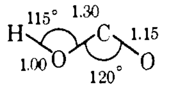
as is the m/z 44 ion. It is not obvious whether the large amount of m/z 15 is related to the m/z 14 detected, but in any case the formation of HCO^+ must be a rearrangement.

We also applied molecular orbital methods to the structural problem. The formyloxy ion was studied by the semiempirical MINDO/3[25] and the ab initio STO-3G[26,27] methods. According to MINDO/3 the formyloxy ion (with initial coordinates equal to those of the formate ion,[28] as if the double ionization is rapid relative to nuclear motion) is not an energy minimum; instead, the hydrogen migrates from C to O without an energy barrier. The final geometry for the singlet ion is as in VII. Thus, the heavy atoms of protonated carbon dioxide form a linear molecule with a C-O-H angle of 120.6°. The energy is −756.2304 eV and the heat of formation is 108.8383 kcal/mol. Attempts to study the triplet state by MINDO/3 were unsuccessful because of convergence problems.

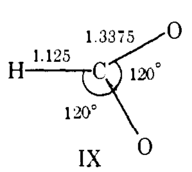


VII

According to STO-3G calculations in which the internuclear distances were varied in increments of 0.025 Å and the angles by 5°, the $HCOO^+$ form does not represent a stable singlet. No evidence was found for an energy minimum in the vicinity of the formate coordinates, and the stable singlet was again protonated carbon dioxide (VIII), which by this method was planar. The energy is −185.373 11 au. The structure was confirmed with slight variations by rough 4-31G calculations[29,30] (to the nearest 5° and 0.05 Å). According to the STO-3G method, the lowest triplet of the formyloxy cation is in fact an energy minimum (−185.357 31 au), more stable than the isomeric triplet $COOH^+$ structure. To the nearest 5°, the geometry is planar as in IX. The singlet energy is much higher in this configuration; note that the level of calculation is Hartree-Fock. The MINDO/3 method failed in this geometry because of convergence problems. Thus, the stable forms of the singlet and triplet ions formed by charge reversal appear to be substantially different.

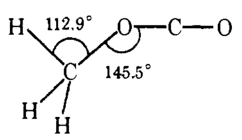


VIII



IX

We also examined the singlet acetyloxy cation by the MINDO/3 method as well. Briefly, this method indicates that there is again no minimum in the vicinity of the geometry of acetate anion for the acetyloxy cation; instead, there is no energy barrier to rearrangement to a final form in which the methyl group has migrated from C to O. This form is methylated carbon dioxide, $COOCH_3^+$, which would be generated from methyl trifluoroacetate by eq 26. The O-C-O portion of the ion (X) is linear with C-O-C angle of 145.5°.



X

While one must be properly suspicious of the total absence of a barrier to H and CH_3 migration as a MINDO/3 result for the formyloxy and acetyloxy cations, it is probably safe to say that any barrier to migration is probably quite low and, therefore, only a few ions at most out of the population of charge-reversed singlet ions generated by collision of formate and acetate ions with the neutral gas could be so low in energy content as to be stable to rearrangement. The experimental observation of a substantial difference in reactivity between $HCOO^+$ from formate and $COOH^+$ from trifluoroacetic acid or protonated CO_2 (and between CH_3COO^+ from acetate and $COOCH_3^+$ from methyl trifluoroacetate) can be interpreted in either of two ways, or as a combination of the two ways. (1) There is little correlation between the electrons lost when two are removed during a collision, so that the triplet state is also accessible as a product. Reaction from states of differing multiplicities has been noted for charge reversal of positive halogen ion[31] producing singlet halide anions; reversibility of this process indicates that the formation of positive ions of different multiplicities from ground-state anions is allowed. (2) The geometrical constraints on the migration of H or CH_3 from C to O suggest that the rate constant for this process will rise more slowly with increasing internal energy than the rate constants for simple cleavage. If the rearrangement must compete with simple cleavages in ions so excited that fragmentation occurs in less than 1 ns, then it may not compete successfully. Hence, for the highly excited ions examined here, fragments may still reflect the initial structure. The relative importance of these two explanations has not yet been assessed.

To summarize, those characteristics which distinguish these spectra from one another are exactly the ones which identify their structures. They show that the ions generated by charge reversal retain the structure of the carboxylate anion for at least the time required for most fragmentation to occur. The results can be explained by fragmentation before rearrangement to a more stable form, or by the formation of triplet ions, whose most stable form is the one first generated.

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Gas-Phase Ion-Molecule Association Reactions. A Statistical Phase Space Theory Approach

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Abstract: A theoretical treatment of gas-phase ion-molecule association reactions is presented. The treatment is developed for the energy-transfer model $AH^+ + A \rightleftarrows (A_2H^+)^*$; $(A_2H^+)^* + A \rightarrow A_2H^+ + A$. Explicit distribution functions for the activating reaction and for the steady-state distribution of $(A_2H^+)^*$ are presented. The phase space theory technique utilized rigorously conserves energy and angular momentum. Unimolecular reaction of $(A_2H^+)^*$ is shown to depend strongly on angular momentum. Detailed comparison between theory and experiment is made for A = NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$ over a wide range of temperature and pressure. The phase space theory results give semiquantitative agreement with experiment for all systems except possibly NH_3. The mechanism of the reaction is discussed in detail.

I. Introduction

Statistical approaches to reaction rate theory are well established as useful tools in understanding rates and mechanisms of chemical reactions. Useful summaries of the development of the theory as applied to unimolecular reactions have been presented by Robinson and Holbrook[1a] and by Forst.[1b] The central focus of the theory is the calculation of the microscopic rate constant for unimolecular fragmentation from a given reactant state. To obtain macroscopic rates for comparison with experiments the microscopic rates are incorporated into the details of the particular reaction mechanism being studied. For example, the application of statistical theory to the association reaction

$$AH^+ + A \xrightarrow{k_2} A_2H^+ \tag{1}$$

may be accomplished by use of the chemical activation mechanism

$$AH^+ + A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} (A_2H^+)^* \xrightarrow{k_s[A]} A_2H^+ \tag{2}$$

This mechanism has recently been invoked by Meot-Ner and Field[2] and Neilson et al.[3] to characterize the dimerization kinetics of ammonium ions in ammonia and the methylamines. With the assumption that $(A_2H^+)^*$ is in a steady state the kinetics yield

$$k_2 = \frac{k_f\omega}{\bar{k}_b + \omega} \tag{3a}$$

or

$$\frac{1}{k_2} = \frac{1}{k_f} + \frac{\bar{k}_b}{k_f\omega} \tag{3b}$$

where the substitution $k_s[A] = \omega$ has been made. Equation 3 may be used to obtain values of $\bar{k}_b$ from measured values of k_2 and estimated values of k_f and k_s. For the amine systems in reaction 2 the following assumptions are commonly used to estimate k_f and k_s: (1) All AH^+/A collisions result in the formation of $(A_2H^+)^*$ complexes. (2) All $(A_2H^+)^*/A$ collisions result in stabilized A_2H^+, i.e., the "strong collision" assumption. (3) The ion-molecule collision rates in (1) and (2) are governed by the long-range term in the potential and are therefore given by Langevin[4] or ADO[5] theory. These three assumptions also lay the groundwork for the calculation of theoretical k_2 values from[1]

$$k_2 = \iint \left[\frac{k_f\omega}{k_b(E,\mathcal{J}) + \omega}\right] F(E,\mathcal{J})\,\mathrm{d}E\,\mathrm{d}\mathcal{J} \tag{4}$$

where $F(E,\mathcal{J})$ is the distribution function for the activating reaction that forms $(A_2H^+)^*$ and $k_b(E,\mathcal{J})$ is the microscopic rate constant for dissociation of $(A_2H^+)^*$ at energy E and angular momentum $\mathcal{J}$. According to statistical theory the basis for the calculation of $k_b(E,\mathcal{J})$ is embodied in the following two assumptions: (1) The rate of reaction is governed by passage through a transition state located along the reaction coordinate at the point of minimum flux on the system potential energy hypersurface. (2) The decomposing molecule reaches a state of quasi-equilibrium before decomposing; i.e., all energy accessible states in the system phase space have equal probabilities of being populated. Within this framework the microscopic decomposition rate constant for a molecule with available internal energy E above the threshold for reaction and with angular momentum $\mathcal{J}$ is

$$k(E,\mathcal{J}) = \frac{\mathrm{flux}(E,\mathcal{J})}{\rho(E,\mathcal{J})} \tag{5}$$

That is, the rate constant is the ratio of the flux at the transition state to the density of states of the reacting molecule.

In the most extensively used formulation of statistical theory, called RRKM[6] when applied to neutral systems and QET[7] when applied to ionic systems, eq 5 is written more explicitly as

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