Analysis of the Rates of Ion–Molecule Association Reactions. Proton-Bound Dimers of NH_3, CH_3NH_2, and $(CH_3)_2NH$

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Abstract: A method is presented for predicting rates of three-body ion-molecule association reactions of the form $A^+ + B + M \rightarrow AB^+ + M$. A critical postulate of the method is that the internal energy is randomized in the newly formed collision complex of A^+ and B. The unimolecular decomposition of this ionic collision complex back to the reactants is treated by application of RRKM theory. The method is shown to predict accurately both the pressure dependence and temperature dependence of the rate of formation of the proton-bound dimers $H_3N\text{-}H\cdots NH_3^+$, $CH_3NH_2\text{-}H\cdots NH_2CH_3^+$, and $(CH_3)_2NH\text{-}H\cdots NH(CH_3)_2^+$.

An understanding of the chemical interactions that take place during an ion–molecule reaction can lead not only to more knowledge about this class of reactions, but also a better understanding about reaction dynamics in general. The ease of detecting and identifying charged particles by mass spectrometric techniques and the excellent methods of measuring rate constants and controlling and measuring the kinetic energy of the ions have led to a great number of experimental results on the dynamics of ion–molecule reactions.[2]

A large number of these reactions proceed at the capture or hard sphere collision rate, because the long-range attractive force between the two particles is enough to overcome any barrier that might exist. An understanding of the long-range attractive potential has led to the successful prediction of collision rates (and therefore reaction rates for many processes) between ions and neutral nonpolar molecules.[3] More recently, this theory has been adapted to the much more complicated case of collisions between ions and neutral molecules which have permanent dipoles.[4]

The short-range chemical interactions which take place during ion-molecule reactions are much less well known. They must be important in reactions which proceed at significantly less than the collision rate, they affect the lifetimes of collision complexes, and they influence the overall energy distribution in the products. They remain relatively obscure, however, because they are often masked by the long-range force. Nevertheless, some attempt to uncover them can be made by modeling the reaction and then comparing the theoretical and experimental results.

In general, reactions which proceed through "direct" mechanisms (no long-lived complex) are best treated by quantum mechanical methods or a series of trajectory calculations.[5] For reactions which proceed via intermediate complexes, these methods become time consuming and costly, even for relatively small polyatomics. In systems of significant size (more than a few atoms) the problems are formidable and thus far have proved insurmountable.

Reactions which take place through intermediate complexes, however, may be treated with a simplifying assumption which appears to be true in many cases—randomization of the internal energy in the complex. If this energy is statistically distributed in the various internal modes, the reaction can be treated by one of the statistical methods, which by avoiding the problems of molecular dynamics are much easier to apply than either quantum mechanical or classical trajectory methods. For intermediate complexes formed in neutral–neutral reactions, there has been some controversy over whether the internal energy is randomized before the complexes decompose.[6,7] In an ion-molecule intermediate complex, randomization is very likely because of the long-range coupling. Classical trajectory calculations on ion–polar molecule collisions have shown that multiple reflections usually occur during a single encounter.[8] This greatly enhances the chances for energy randomization within the collision complex. Klots has recently shown that even translational energy release can be accommodated by a statistical model in an ion-molecule reaction.[9]

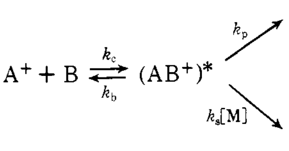
Light has developed and applied a phase-space theoretical treatment of bimolecular ion-molecule reactions.[10] This theory, although applied to small systems where statistical methods are least applicable, agrees well with experimental observables such as cross sections and deuterium isotope effects in some cases, although poorly in others. A limited form of transition-state theory has been used to explain the temperature dependence of some ion-molecule reaction rates.[11] However, as Field has pointed out,[12] the particular form used treats only entropy effects, ignoring enthalpy, and thus fails where the latter is important.

Statistical theory using a complete transition state formulation can include effects of both enthalpy and entropy. When applied to neutral molecules, this is called RRKM (Rice-Ramsperger-Kassel-Marcus) theory;[13,14] when applied to ionic fragmentations, it is called QET (quasi-equilibrium theory of mass spectra).[13a,15] QET has been applied to a few ion-molecule reactions in order to predict product ratios.[16,17]

In this paper, we apply RRKM theory to several three-body association reactions. These reactions are assumed to proceed through an intermediate collision complex which can decompose back to reactants, go on to products (proton transfer), or be collisionally stabilized by a third body. Thus, these systems are a good test case for a statistical theory. Meot-Ner and Field have recently attempted to treat these reactions in a similar manner.[12] Their theoretical treatment, however, was a single oscillator, quantum RRK theory with an adjustable oscillator frequency. In order to fit the experimental data, they needed one oscillator frequency, 1750 cm^{-1}, for the absolute value of the rate constants and another, 650–850 cm^{-1}, for the temperature dependence. In our more complete, many oscillator method, we choose the frequencies to fit measured thermodynamic quantities and leave no parameters adjustable in order to fit the experimental kinetic results. One problem of any transition state theory is the lack of a unique choice for the transition state and its parameters (frequencies and moments of inertia). In the cases to be discussed here, there is one logical choice for the transition state model, a major advantage in testing the applicability of RRKM theory.

Method and Results

The general mechanism for an ion-molecule reaction which involves formation of an intermediate complex is given by eq 1. In the reactions to be discussed here, $k_p = 0$. The experimental observables for these reactions are the disappearance of A^+ and the appearance of AB^+, which follow the kinetic expression



$$A^+ + B \underset{k_b}{\overset{k_c}{\rightleftarrows}} (AB^+)^* \begin{cases} \xrightarrow{k_p} C^+ + D \\ \xrightarrow{k_s[M]} AB^+ \end{cases} \qquad (1)$$

$$-d[A^+]/dt = d[AB^+]/dt = k_f[A^+][B] \qquad (2)$$

Applying the steady-state approximation to $[(AB^+)^*]$ in eq 1, with $k_p = 0$, the rate constant k_f is given by:

$$k_f = k_c k_s[M]/(k_b + k_s[M]) \qquad (3)$$

Because the energy distribution of activated AB^+ ions is pressure dependent, k_b is also pressure dependent. However, this dependence is very weak, so k_b can be calculated from eq 3 and either the experimental or calculated k_f if k_c and k_s are known. The collision rate constant, k_c, can be calculated by either the Langevin[3] or the ADO method,[4] depending on whether B is nonpolar or polar, respectively. In addition, k_s can be calculated if the assumption is made that the stabilizing collisions are strong, i.e., every time an intermediate complex has a collision, it is stabilized. If this is true, and a strong case for its truth will be made later, k_s can be calculated by the same methods as k_c. In this way the unimolecular rate constant, k_b, for the decomposition of the activated $(AB^+)^*$ can be derived from the three-body association rate constant, k_f.

The experimentally observable k_f can be calculated directly by using the framework of RRKM theory, as will be shown below. This system is an example of chemical activation, where the $(AB^+)^*$ formed on collision of an ion and a neutral is vibrationally excited and can either decompose back to the reactants or be stabilized by collision with another molecule. The analogy between chemical activation and thermal systems is discussed in detail by Forst,[18] and from his derivations it can be shown that the overall rate for the appearance of the stabilized AB^+ is given by:

$$\frac{d[AB^+]}{dt} = \frac{d[(AB)^+]^*}{dt} \int_0^\infty \frac{k_s[M]}{k(E) + k_s[M]} F(E)\, dE \qquad (4)$$

where $k(E)$ is the microscopic rate constant defined later in eq 7. The rate of appearance of the activated ionic complex is given by the mechanism in eq 1, i.e., $d[(AB)^+]^*/dt = k_c[A^+]\cdot[B]$. The integral in eq 4 is merely k_{uni}/k_∞.[18] Adding to that a substitution for $d[AB^+]/dt$ from eq 2 results in

$$k_f = k_c(k_{uni}/k_\infty) \qquad (5)$$

Here, k_{uni} and k_∞ are the thermal decomposition rates of AB^+ at the pressure of interest and at the high pressure limit, respectively. The energy distribution function $F(E)$ of activated ions produced by bimolecular reaction is identical in this class of chemical activation systems with the distribution function of reacting molecules in the thermal reverse reaction, due to microscopic reversibility.[18] The RRKM calculations have been done in a fairly conservative way where the integral is approximated by a closely spaced converging sum,[13b]

$$k_{uni} = \frac{Q_1^\dagger}{hQ_1Q_2} \exp(-E_0/RT)\Delta E^\dagger \times \sum_{i=1}^{i_{max}} \frac{G(E^\dagger)\exp(-E^\dagger/RT)}{1 + (k(E^*)/fk_s[M])} \qquad (6)$$

where $Q_1^\dagger/Q_1$ = ratio of adiabatic partition functions, Q_2 = partition function for the ionic complex, E_0 = critical energy for the reaction, $\Delta E^\dagger$ = energy increment in the summation, $k(E^*)$ = microscopic rate constant, and f = centrifugal correction factor. The sum of quantum states for the transition state, $G(E^\dagger)$, and the density of states for the ionic complex, $N(E^*)$, have been evaluated accurately using an efficient algorithm developed by Stein and Rabinovitch,[19a] which is based on a computational technique reported by Beyer and Swinehart.[19b] The following relations have been used in the computation:

$$k(E^*) = G(E^\dagger)/hN(E^*) \qquad (7)$$

$$E^\dagger = (i - \tfrac{1}{2})\Delta E^\dagger \qquad i = 1 \ldots i_{max} \qquad (8a)$$

$$E^* = E_0 + E^\dagger + \langle \Delta E_J \rangle \qquad (8b)$$

The change in the average rotational energy, $\langle \Delta E_J \rangle$, arises from the conservation of angular momentum J when going through the configuration changes necessary for the transition state. Those configuration changes relate to the ratio of the respective moments of inertia $I^\dagger/I$ and the contribution of the rotational energy is given by:

$$\langle \Delta E_J \rangle = (1 - I^\dagger/I)RT$$

For the same purpose the centrifugal correction factor is introduced to account for changes in internal energy which are necessary in order to conserve angular momentum as the moment inertia changes (the centrifugal correction factor, F_W, is given by Waage and Rabinovitch[20]):

$$f = F_W(Q_1^\dagger/Q_1) \qquad (9)$$

In order to calculate the density and sum of states, the oscillator frequencies and internal free rotor moments of inertia for both the ionic complex and the transition state must be known. The models for these and the rationale for choosing them will be given in detail for the ammonia system and summarized for the two amine systems.

(1) $[H_3N\text{-}H\cdots NH_3]^+$. The ammonia solvate of ammonium ion (proton-bound dimer) can be observed in the reaction of NH_4^+ and NH_3 at high enough pressures or long enough times so that a third molecule can stabilize the excited collision complex.

$$NH_4^+ + NH_3 \underset{k_b}{\overset{k_c}{\rightleftarrows}} [N_2H_7^+]^* \xrightarrow{k_s[CH_4]} N_2H_7^+ \qquad (10)$$

The rate of formation of this complex has been measured experimentally by Meot-Ner and Field over a wide temperature range.[12]

There are no spectroscopic measurements of the oscillator frequencies of $N_2H_7^+$, so they must be estimated. The RRKM calculation is fairly insensitive to variations in these estimated frequencies as long as the entropy of the complex is constant. This entropy is known from the entropy change which has been measured experimentally for the equilibrium in the equation

$$NH_4^+ + NH_3 \rightleftarrows (H_3N\text{-}H \cdots NH_3)^+ \qquad (11)$$

Kebarle:[21] $\Delta H^\circ = -24.8$ kcal/mol;
$\Delta S^\circ = -26.0$ cal/deg mol

Futrell:[22] $\Delta H^\circ = -21.5$ kcal/mol;
$\Delta S^\circ = -20.0$ cal/deg mol

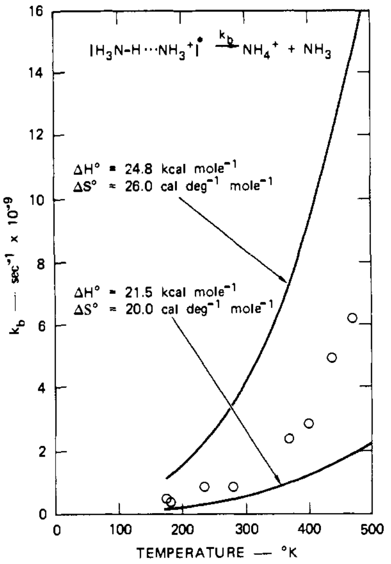


Figure 1. Temperature dependence of the experimental (O) and calculated rate constants k_b for the reaction $[N_2H_7^+]^* \rightarrow NH_4^+ + NH_3$. The experimental data are from ref 12. The upper curve was calculated from model A in Table I and the lower curve from model B.

Table I. Parameters Used in the Calculation of the Ammonia Proton-Bound Dimer Decomposition[a]

	Ionic complex A $H_3N\text{-}H\cdots NH_3^+$	Ionic complex B $H_3N\text{-}H\cdots NH_3^+$	Transition state $NH_4^+\cdots\cdots NH_3$
ν_i	3100 (6)	3100 (6)	3444 (2)
	1676 (1)	1676 (1)	3337 (1)
	1450 (6)	1200 (6)	3134 (3)
	1200 (4)	668 (1)	3033 (1)
	668 (1)	500 (4)	1685 (2)
	150 (2)	160 (2)	1627 (2)
			1397 (3)
			950 (1)
B_i	11.54 (1)	11.54 (1)	13.77 (1)
			8.52 (2)
			5.25 (2)
σ	9	9	36
$\Delta S°_{600K}$	−26.0	−20.0	
E_0	23.1	21.8	
$I^\dagger/I$	5.42	5.42	

[a] Degeneracies are in parentheses. Frequencies (ν_i) and rotational constants (B_i) are in cm^{-1}, calculated entropy change ($\Delta S°_{600K}$) is for reaction 11, critical energy (E_0) is in kcal/mol. The value of σ is the product of the symmetry numbers for the external and internal rotations. $I^\dagger/I$ is the ratio of the moments of inertia for the transition state and ionic complex used in calculating the centrifugal correction factor.

and the known entropies of NH_4^+ and NH_3. The six NH_3 stretching motions and ten NH_3 bending motions can be estimated from methyl group frequencies in neutral compounds. The symmetric and antisymmetric N-H-N stretches have been calculated in an ab initio study of the $N_2H_7^+$ potential energy surface.[23] The remaining internal degrees of freedom are a free rotation of the NH_3 groups and two N-H-N bending motions. The reduced moment of inertia for the former can be calculated from the moment of inertia of ammonia about one axis. The frequencies of the latter have been adjusted to fit the experimental overall entropy change.[24] Because the two experimental equilibrium studies disagree about $\Delta S°$, we have carried out RRKM calculations using $N_2H_7^+$ models which fit each of these studies. The critical energies (E_0) for the reaction were adjusted so that the calculated high pressure activation energies[13a] at 600 K were equal to the two energies of reaction ($E_a = -\Delta H° - RT$). This approach assumes that the activation energy for the forward reaction is zero.

A sometimes legitimate complaint about RRKM theory is that there is a considerable freedom of choice of parameters for the transition state. This is not true for the present system or the other systems to be discussed. There is a strong long-range interaction between the ion and molecule (∼0.5 kcal/mol at 8-Å separation). As a result, the transition state, which is taken to be where the sum of the inherent potential energy and the centrifugal energy reach a maximum,[20] is at a large separation of the two species (∼7-12 Å, depending on the rotational energy of the complex). At this distance, the oscillator frequencies are essentially equal to those of the separated NH_4^+ and NH_3, of which the frequencies are known.[25] The remaining internal degrees of freedom are the reaction coordinate, the one-dimensional free rotor which also exists in the ionic complex, and two two-dimensional free rotors. The latter correspond to the free tumbling of the two fragments about the axes other than the one covered by the one-dimensional rotor. This model for the transition state has been referred to as the Gorin model[26] for neutral molecule decompositions. Although there has been some controversy over whether it is accurate for neutrals, it ought to be good for ions because of the much longer range of the interaction between the fragments. The parameters used in the calculations are summarized in Table I.

The experimental and calculated values of k_b are plotted against the temperature in Figure 1. This rate constant is slightly pressure dependent. For instance, the calculated rate constants at 350 °C increase by 4 and 15% for models A and B, respectively, in the pressure range 0.3–1.8 Torr ($k_s[M] = 1 \times 10^7$ to 6×10^7 s^{-1}). In Figure 1 the values which are plotted were calculated at a collision frequency of 3×10^7 s^{-1}, which is intermediate in the range at which the experiments were performed.

(2) $[CH_3NH_2\text{-}H\cdots NH_2CH_3]^+$. Essentially the same experiment as for $N_2H_7^+$ has been carried out for methylamine by Meot-Ner and Field.[12] In addition to the temperature dependence of this third-body stabilization, they have studied the pressure dependence. The procedure for doing the RRKM calculations on this ionic complex is similar to that of $N_2H_7^+$. The enthalpy of the reaction and the entropy change were taken from the equilibrium constant for the reaction

$$CH_3NH_3^+ + CH_3NH_2 \rightleftarrows CH_3NH_2\text{-}H\cdots NH_2CH_3^+ \quad (12)$$

$$\Delta H° = -21.7 \text{ kcal/mol};\ \Delta S° = -23.6 \text{ cal/deg mol}$$

as measured by Yamdagni and Kebarle.[27] The fundamental frequencies of ethane were used for the methylammonium ion, except for the N-H stretches, which were taken to be 3300 cm^{-1}. The parameters for the calculation are summarized in Table II.

The calculated and experimental pressure dependence and temperature dependence of this reaction are compared in Figures 2 and 3. As in the case of ammonia, the rate constants in Figure 3 were calculated at a collision frequency of 3×10^7 s^{-1}.

(3) $[(CH_3)_2NH\text{-}H\cdots NH(CH_3)_2]^+$. The experiments and method of calculation for the dimethylamine proton-bound dimer are very similar to those for methylamine. The equilibrium study for this reaction resulted in the following thermodynamic quantities.[27]

$$(CH_3)_2NH_2^+ + (CH_3)_2NH \rightleftarrows (CH_3)_2NH\text{-}H\cdots NH(CH_3)_2^+ \quad (13)$$

$$\Delta H° = -20.8 \text{ kcal/mol};\ \Delta S° = -25.7 \text{ cal/deg mol}$$

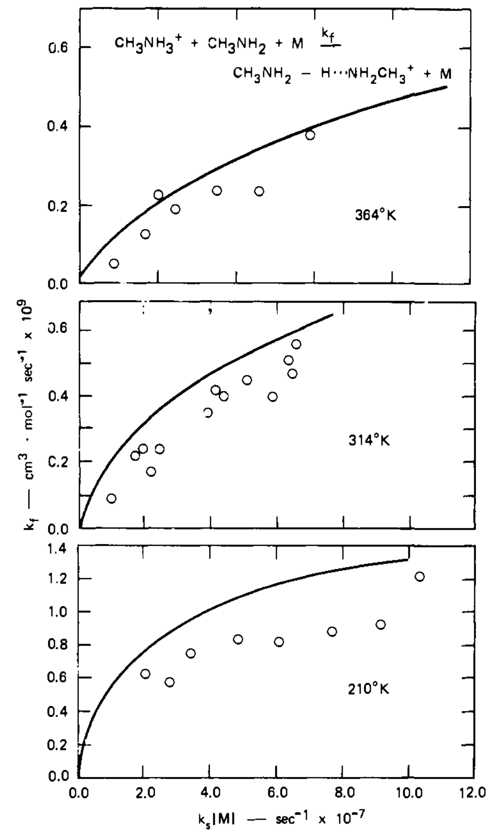


Figure 2. Pressure dependence of the experimental (○) and calculated rate constants k_f for the appearance of $CH_3NH_2\text{-}H \cdots NH_2CH_3^+$ at three temperatures. The experimental data are from ref 12.

Table II. Parameters Used in the Calculation of the Methylamine Proton-Bound Dimer Formation and Decomposition[a]

	Ionic complex $CH_3NH_2\text{-}H \cdots NH_2CH_3^+$	Transition state $CH_3NH_3^+ \cdots CH_3NH_2$
ν_i	3300(4)	3300 (5)
	2970 (6)	2970 (6)
	1600 (1)	1520 (2)
	1450 (6)	1450 (9)
	1175 (4)	1175 (4)
	1000 (3)	1000 (2)
	900 (2)	820 (2)
	820 (2)	780 (1)
	740 (2)	270 (2)
	600 (1)	
	400 (1)	
	300 (2)	
	200 (2)	
	175 (2)	
B_i	0.766 (1)	2.28 (1)
		1.03 (2)
		1.22 (2)
σ	1	3
ΔS°_{575K}	−23.6	
E_0	22.6	
$I^\dagger/I$	5.6	

[a] See Table I for explanation and units.

The fundamental frequencies of propane were used for the dimethylammonium ion, except for the N-H stretches, which were taken to be 3300 cm^{-1}. The parameters for the calculation are summarized in Table III.

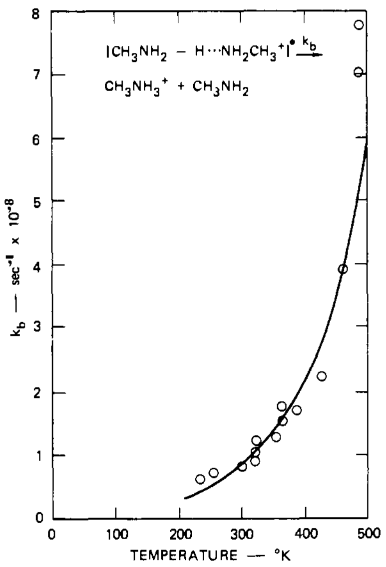


Figure 3. Temperature dependence of the experimental (○) and calculated rate constants k_b for the reaction $[CH_3NH_2\text{-}N \cdots NH_2CH_3^+]^* \rightarrow CH_3NH_3^+ + CH_3NH_2$. The experimental data are from ref 12.

Table III. Parameters Used in the Calculation of the Dimethylamine Proton-Bound Dimer Formation and Decomposition[a]

	Ionic complex $(CH_3)_2NH_2\text{-}H \cdots NH(CH_3)_2^+$	Transition state $(CH_3)_2NH_2^+ \cdots (CH_3)_2NH$
ν_i	3300 (2)	3300 (3)
	2970 (12)	2970 (12)
	1600 (1)	1485 (1)
	1450 (12)	1450 (12)
	1150 (6)	1350 (3)
	930 (2)	1150v1 (6)
	900 (4)	980 (4)
	800 (3)	930 (2)
	600 (2)	740 (2)
	350 (2)	375 (2)
	310 (2)	225 (4)
	275 (2)	
	200 (2)	
	175 (4)	
B_i	0.387 (1)	0.527 (1)
		0.594 (2)
		0.524 (2)
σ	1	2
ΔS°_{575K}	−25.7	
E_0	22.4	
$I^\dagger/I$	4.9	

[a] See Table I for explanation and units.

The calculated and experimental pressure dependence and temperature dependence of this reaction are compared in Figures 4 and 5. The rate constants in Figure 5 were calculated at a collision frequency of $3 \times 10^7\ s^{-1}$.

Discussion

The agreement between the RRKM calculations and the experimental studies of Meot-Ner and Field is good. In the case of ammonia (Figure 1) there are calculations for two models of $N_2H_7^+$ based on the two differing equilibrium measurements on this system. The experimental points for the unimolecular decomposition rate constant fall between these two extremes, suggesting that the correct values for the thermo-

Table IV. Comparison of Representative Calculated and Experimental Rate Constants[a]

Reaction	$k_sM \times 10^{-7}$, s^{-1}	$k_c \times 10^9$, $cm^3/mol\ s$ 250 °C	350 °C	k_{uni}/k_∞ 250 °C	350 °C	$k_f \times 10^9$ (250 °C), $cm^3/mol\ s$ Calcd	Exptl	$k_f \times 10^9$ (350 °C), $cm^3/mol\ s$ Calcd	Exptl
10 (complex A)	2.8	2.3	2.1	0.011	0.0047	0.025	0.093	0.0099	0.030
10 (complex B)	2.8	2.3	2.1	0.064	0.031	0.15	0.093	0.065	0.030
12	2.2	1.8	1.7	0.32	0.15	0.57	0.40	0.25	0.23
13	1.8		1.4		0.31			0.44	0.32

[a] Rate constant designations are explained in the text. The calculations were carried out using the parameters in Tables I-III. Experimental rate constants are from ref 12.

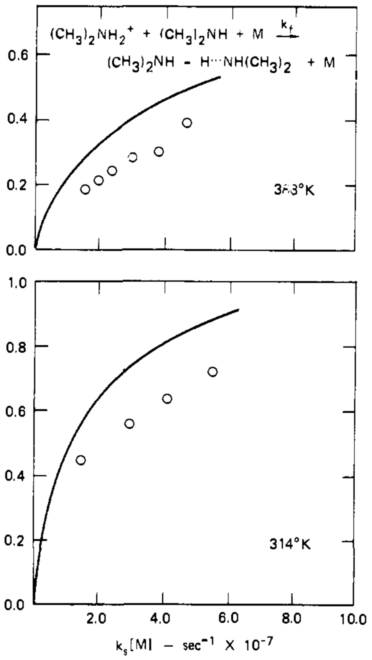


Figure 4. Pressure dependence of the experimental (○) and calculated rate constants k_f for the appearance of $(CH_3)_2NH$-$H\cdots NH(CH_3)_2^+$ at two temperatures. The experimental data are from ref 12.

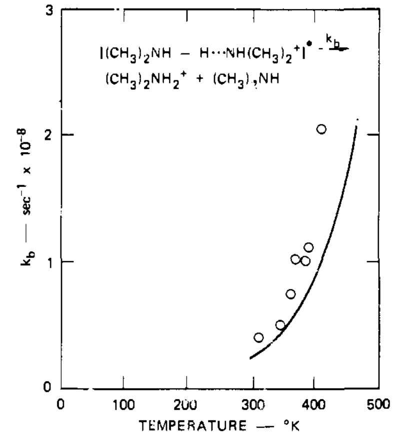


Figure 5. Temperature dependence of the experimental (○) and calculated rate constants k_b for the reaction $[(CH_3)_2NH$-$H\cdots NH(CH_3)_2^+]^* \rightarrow (CH_3)_2NH_2^+ + (CH_3)_2NH$. The experimental data are from ref 12.

dynamic quantities $\Delta H°$ and $\Delta S°$ fall between the two pairs of values reported. The functional form of the temperature dependence is very similar for both of the models and the experiment.

For the methylamine and dimethylamine proton-bound dimers, both the pressure dependence of k_f and the temperature dependence of k_b are matched closely by the calculations. This result increases the confidence in the experimental values for $\Delta H°$ and $\Delta S°$, as well as demonstrating the applicability of RRKM theory to the systems.

The pressure dependence of k_f does not follow the simple Lindemann mechanism, eq 3, but is more complex. This arises because k_b is not independent of pressure—a phenomenon well known in unimolecular reaction theory.[28] Thus, k_b increases with increasing pressure because the energy distribution of decomposing dimers is shifted to higher energies. At very low pressures none of the activated dimers is stabilized, so they all decompose. At high pressures a large proportion of the activated dimers is stabilized by collision. The ones that are lower in energy are preferentially stabilized because they are longer lived. Therefore the *decomposing* dimers have a higher average energy and a shorter lifetime than those at low pressures. Thus, although the microscopic rate constant $k(E)$ is not dependent on pressure, the phenomenological rate constant k_b is pressure dependent. Over the small pressure range which is covered in Meot-Ner and Field's experiments this dependence is small, but it becomes quite substantial over a wider pressure range. For example, methylamine at 300 °C has $k_b = 2.9 \times 10^7\ s^{-1}$ (stabilization frequency = $0\ s^{-1}$); $k_b = 5.1 \times 10^7$ (stabilization frequency = $3 \times 10^6\ s^{-1}$); $k_b = 28 \times 10^7$ (stabilization frequency = $3 \times 10^{10}\ s^{-1}$). The overall result of this effect is that k_f is less dependent on [M] than predicted by eq 3, which assumes that k_b is pressure independent, and plots of $1/k_f$ vs. $1/[M]$ are quite nonlinear over wide ranges of pressure.[29] The functional form of $k_f([M])$ is shown in eq 5 and 6 and is shown graphically in Figure 6. The importance of experiments in the low pressure regime is evident from this figure. Such experiments are now in progress.[30]

An important part of these results is the use of the ADO and Langevin theories to calculate k_c and k_s, respectively. Recent comparisons of the ADO collision rate constant with experimental rate constants for reaction, which are expected to proceed on every collision,[31] have shown that the theoretical rate constant might be off by as much as 30%. Rate constants predicted by Langevin theory, which is applicable only to nonpolar molecules, are usually better. However, the proton-bound dimers studied here have very large dimensions, approaching the Langevin cross section in the case of methylamine and dimethylamine. Therefore, the calculated values of k_s may be in error also. The errors introduced by these uncertainties are the same order of magnitude as the differences between the calculated and experimental results in Figures 2 through 5. Considering this and the fact that any error in the experimental values of $\Delta H°$ and $\Delta S°$ is reflected in our calculation, the agreement is excellent.

The most important result that comes from this agreement is an understanding of the details of these ion-molecule interactions, and strong evidence in favor of the assumptions that went into the treatment. The mechanism for the reactions is indeed as shown in eq 1. The intermediate excited $(AB^+)^*$ is successfully described as having the same structure as ground state AB^+, with the excess energy randomized among all its internal vibrations and rotations. The fact that this energy is randomized allows the application of a statistical reaction rate theory, such as phase space or RRKM, and, conversely, the successful application of a statistical theory implies that the energy is indeed randomized. A similar conclusion has been reported recently by Hase,[32] stating that rate constants using the RRKM and activated complex theories are the same, within the uncertainties in the computational procedure.

In the three cases studied here, it would be very surprising if the energy were not randomized. The lifetimes of the intermediate excited complexes fall in the range of 10^{-10} to 10^{-8} s. This is very long compared to a typical vibration of 10^{-13} s. In the case of addition of methylene to a vinylcyclopropane, it takes about 10^{-12} s for the energy to randomize.[33] Thus, a molecule does not need very many vibrational periods to randomize the energy put in any specific mode or modes. For the proton-bound dimers of amines, the internal energy starts out in the NHN antisymmetric stretch. It is then randomized among the internal modes. The small percentage of excited complexes that have enough energy in the NHN antisymmetric stretch, which is the reaction coordinate, dissociate. Because the internal energy of the complex starts off in the same mode where it is needed to dissociate, it would not have been too surprising to find that the complex was very short-lived. But the experimental fact that it is long-lived enough to be stabilized by collision with a third body at relatively low pressures (1 Torr) is fairly good evidence that the energy is randomized.

There are now many examples of collision-stabilized ion-molecule complexes.[34] These include very simple systems such as rare gas clustering reactions as well as complicated organic molecules. It seems to be a general trait of ion-molecule collisions that they lead to long-lived complexes. This is especially true of systems which contain more than a few atoms. Thus a statistical approach, such as RRKM theory, can be a very powerful predictive tool. The only prerequisites are some knowledge about the structure of the transition state and the ionic complex, as well as the potential energy difference between them. The structures of the transition states for most complex decompositions are similar to the ones for the cases treated here. Thus, if the moments of inertia and fundamental frequencies of the separated ion and molecule are known, that is all the information needed about the transition state. This transition-state model is the same as the one used in the very successful theories which predict ion-molecule collision cross sections.

The other prerequisite is knowledge of the structure and fundamental frequencies of the ionic complex. As we have shown here, it is sufficient to know the entropy of the complex, as calculated from the temperature dependence of the equilibrium constant for the overall reaction. Then the frequencies can be adjusted to fit this experimental entropy. This is analogous to the variation of transition state frequencies to fit high pressure *A* factors, a common practice in applying unimolecular transition-state theories.

Another assumption we have made in addition to the basic randomization of energy in the intermediate complex is that every collision between the complex and a bath gas molecule leads to deactivation. This strong collision assumption is very common in thermal systems, where none of the activated molecules is more than a few kilocalories above the barrier to reaction. However, in many chemical activation systems where the activated molecule is far above the barrier, it breaks down. In these cases, a model which assumes that a constant increment of energy is removed on every collision works well. In several studies of this stepladder model, it has been found that several kilocalories per mole is a typical increment size for polyatomic bath gas molecules.[35] The systems analyzed here are, formally, examples of chemical activation, but the vibrationally-excited ionic complexes do not have much excess energy above the barrier. Because of this, and because the bath gases are efficient deactivators, methane (in the case of ammonia) and isobutane (in the case of the amines), the strong collision assumption is justified.

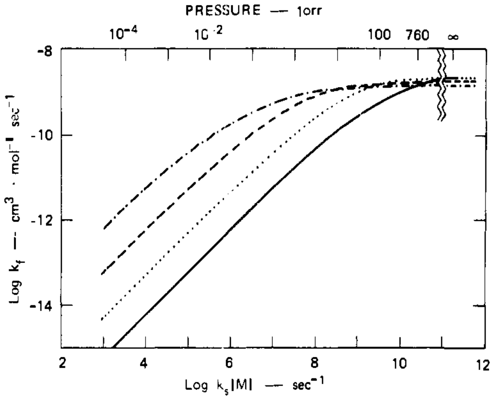


Figure 6. Calculated pressure dependence of the rate constant for formation of proton-bound dimers of nitrogen bases at 300 K: NH_3 model A (—); NH_3 model B (·····); CH_3NH_2 (- - - -); $(CH_3)_2NH$ (-·-·). The pressure scale in Torr is for $k_s = 1.1 \times 10^{-9}$ cm^3 mol^{-1} s^{-1}, which is the Langevin stabilization frequency of the ammonia and dimethylamine proton-bound dimers in methane and isobutane, respectively. For methylamine in isobutane the stabilization frequency is 1.2×10^{-9} cm^3 mol^{-1} s^{-1}. All four systems are at their low pressure limits at $k_s[M] = 10^3$ s^{-1} so they will decrease linearly at lower pressures. The high pressure limits are also shown.

Since the exact choice of oscillator frequencies for the ionic complexes is somewhat arbitrary, we have tested the sensitivity of the RRKM calculation to them. If all the frequencies for the methylamine proton-bound dimer are taken to be the same as those in the transition state and the four new oscillator (the two two-dimensional rotors in the transition state) frequencies are adjusted to keep the same entropy, the predicted k_b would be lowered by 20% at 350 K. Thus the model is fairly insensitive to the exact choice of frequencies as long as the entropy is kept constant. If the very low frequencies (175 and 200 cm^{-1}) are raised to 250 cm^{-1}, the calculated k_b will be 125% higher at 350 K. This corresponds to an entropy change of 2.25 eu at 575 °C, which is greater than the experimental uncertainty in the entropy.

What would happen to the intermediate complex in reaction 1 if another channel to decomposition were open ($k_p \neq 0$)? If the energy is randomized, the competition between competing channels would be predictable by RRKM theory, assuming the necessary parameters are known. This type of application of a statistical theory, chemical activation, is common for neutral molecules.[36] If there is only one product channel and the rates for the two decomposition channels can be calculated, the overall bimolecular rate constant can be calculated from

$$k_{bi} = k_c k_p / (k_b + k_s[M] + k_p) \qquad (14)$$

Many proton-transfer reactions can be treated in this way. If the reactions are exothermic the dissociation of the complex to products is favored ($k_p > k_b$). Thus many proton-transfer reactions occur on well over half the collisions.[37] In the case of symmetric reactions ($k_p = k_b$) the overall rate is predicted by eq 14 to be one-half of the collision rate at low enough pressures so clustering is not important (small $k_s[M]$). This has been found to be true for the symmetric proton transfers in ammonia, methylamine, dimethylamine, and other bases.[28]

There is a growing body of thermoneutral and exothermic ion-molecule reactions which are slow.[38-40] Presumably these reactions involve more than one complex, and the overall rate is governed by the competition between k_b and the rate constant for complex interconversion.[40] We are presently trying to model such reactions by the RRKM method.

Conclusion

These results strongly suggest that the internal energy is randomized in the collision complex of ammonium ions and their conjugate bases. The absolute lifetimes of these complexes and their temperature dependence can be predicted accurately using RRKM theory. This treatment should be general to other ionic complexes if their stability and entropy relative to the separated ion and molecule are known. In addition to absolute lifetimes, which are useful in predicting stabilization rate constants, the relative branching into various decomposition channels should be predictable. These could be used to calculate overall bimolecular rate constants and product ratios.

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Stability, Association, and Dissociation in the Cluster Ions $H_3S^+{\cdot}nH_2S$, $H_3O^+{\cdot}nH_2O$, and $H_2S^+{\cdot}H_2O$

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Abstract: Cluster ion stabilities were measured by pulsed, high-pressure mass spectrometry. Enthalpies for the reactions $H_3O^+{\cdot}(n-1)H_2O + H_2O + M \rightarrow H_3O^+{\cdot}nH_2O + M$ were measured as −33.0, −21.0, and −16.0 kcal/mol for $n = 1, 2$, and 3, respectively, in good agreement with values obtained by Kebarle and co-workers. Enthalpies for analogous reactions involving H_2S were −12.8, −7.2, −5.4, and −3.3 kcal/mol for $n = 1, 2, 3$, and 4. The enthalpy for the association of H_3S^+ with H_2O was −17.0 kcal/mol. The results reflect the contribution of the partial charge on the hydrogens of the protonated ion to the stabilities of the cluster ions, which can be expressed quantitatively as $-\Delta H_{\mathrm{assoc}} = 100 \times (\text{partial charge}) + 9$ kcal/mol. Kinetic measurements on the association reactions yielded third-order rate constants $k_3 = 37 \times 10^{-28}$ and 0.81×10^{-28} cm^6/(mol^2 s) for the formation of $H_3S^+{\cdot}H_2O$ and $H_3S^+{\cdot}H_2S$ at 320 K. k_3 exhibits negative temperature dependences of $T^{-3.1}$ and $T^{-4.8}$ for the two reactions. These are related to the positive temperature dependences of the decomposition rates of the excited complexes $H_3O^+{\cdot}H_2O^*$ and $H_3S^+{\cdot}H_2S^*$, which are found to be $k_d = 0.52 \times 10^9$ and 22.9×10^9 s^{-1} at 320 K. Decomposition rates of the thermalized association ions $H_3O^+{\cdot}H_2O$ and $H_3S^+{\cdot}H_2S$, which exhibit second-order kinetics at our pressures, are $k_{-1}/(M) = 8.2 \times 10^{-23}$ and 3.6×10^{-10} cm^3/(mol s) for the two ions in methane at 400 K. The thermal decomposition reactions have Arrhenius activation energies lower by ~3 kcal/mol than the endothermicities of the reactions, with preexponential factors larger by factors of 10^5–10^7 than collision rates for the activating collisions with methane molecules.

The stabilities of cluster ions formed by the solvation of protonated molecules in the gas phase have been investigated by the observation of ion equilibria in high-pressure mass spectrometers in this laboratory and by other workers. Because of its importance in nature, the water cluster system $H_3O^+{\cdot}nH_2O$ was the subject of much early interest. Measurements