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Kinetics and Thermodynamics of Ion–Molecule Association Reactions of Water, Hydrogen Sulfide, and Benzene. Comments on Intermolecular Entropy Effects

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Abstract: Rates of three-body ion-molecule association reactions of the type $A^+ + B + M \rightarrow AB^+ + M$ have been calculated. A critical assumption in the analysis is that the internal energy of the collision complex formed from A^+ and B is randomized; RRKM theory is used to model the decomposition of the collision complex back to reactants. The formation of the proton-bound dimers of H_2O and H_2S is examined, as is the formation of the benzene dimer radical cation, $(C_6H_6)_2{}^{+\cdot}$. Agreement with experimental kinetic data is good. Applications of this analysis to obtaining thermodynamic data for ion-molecule reactions from experimental kinetic data are considered. Finally, the suggestion that nonideal contributions to ΔS for ion-molecule reactions may be significant is discussed critically.

Introduction

We have previously reported[2a] the successful application of a statistical model to the analysis of the rates of some three-body ion-molecule association reactions of the general type illustrated in the equation

$$A^+ + B \underset{k_b}{\overset{k_c}{\rightleftharpoons}} (AB^+)^* \xrightarrow{k_s[M]} AB^+ \tag{1}$$

In order to understand this type of process, it is necessary to model both the long-range and the short-range interactions between the ion and the neutral. The long-range forces determine the rate of collision between ions and molecules and, therefore, govern the rate of formation of $(AB^+)^*$ and its rate of collisional stabilization to AB^+. The short-range interactions determine the lifetime of the complex, $(AB^+)^*$, with respect to dissociation.

The long-range forces governing ion-molecule collisions are fairly well understood, and rate constants for such processes can be calculated quite accurately using either Langevin theory,[3] in the case of ion-nonpolar molecule collisions, or average dipole orientation (ADO) theory,[4] in the case of ion-polar molecule collisions. In order to model the short-range interactions, which determine the fate of the collision complex before stabilization, we assumed that the internal energy was randomized and applied Rice-Ramsperger-Kassel-Marcus (RRKM) theory[5] to model the unimolecular decomposition of the complex. This analysis allowed us to reproduce accurately the experimental pressure and temperature dependences of the kinetics for the association reactions leading to the formation of proton-bound dimers of ammonia, methylamine, and dimethylamine without using any adjustable parameters to force agreement.[2a,b] The benefits from this model are twofold. First, it allows us to understand and predict rate constants for gas-phase ion-molecule association reactions. Second, it gives us a general quantitative model for the unimolecular decomposition of long-lived ion-molecule collision complexes. Such a model may then be incorporated into kinetic schemes for more complicated ion-molecule reactions, such as nucleophilic displacement[2c] and carbonyl displacement reactions.[2d]

In this paper we elaborate on some of the details of the model and extend its application to several other systems. In the process of examining these systems, we have tested the sensitivity of the model to changes in geometry and size of the complex and to the thermodynamic parameters used in the RRKM analyses. We have applied our method to the analysis of the rates of formation of the proton-bound dimers of H_2O and H_2S, recently determined by Meot-Ner and Field.[6] These systems represent the smallest complexes we have yet modeled. We find good agreement between our calculations and the experimental data in both cases. We have also analyzed the kinetics of the formation of a much larger molecular complex, the benzene dimer radical cation, $(C_6H_6)_2{}^{+\cdot}$. While there is as yet very little experimental kinetic data for this system, our results are reasonable and agree well with the available experimental data.[7] Inherent in our analysis is the assumption that the systems under study behave as ideal gases and that their thermodynamics are therefore adequately described by normal statistical mechanical considerations. Some recent work by Lias and Ausloos[8] on nonideal contributions to ΔS for ion-molecule reactions has caused us to consider this assumption carefully. We have found that the assumption remains valid and discuss at length our reasons for questioning Lias and Ausloos's results.

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Method and Results

The reaction illustrated in eq 1, when treated in the steady-state approximation, yields

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

where k_f, the experimentally observable rate constant, is given by

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

The rate constants k_c and k_s are the collision and stabilization rate constants, respectively, and k_b is the rate constant for the unimolecular decomposition of $(AB^+)^*$.

It is readily shown[2a,9] that in terms of RRKM theory

$$k_f = k_c(k_{uni}/k_\infty) \qquad (4)$$

$$k_{uni}/k_\infty = \int_0^\infty \frac{k_s[M]}{k(E) + k_s[M]} F(E) dE \qquad (5)$$

where k_{uni}/k_∞ is the ratio of the thermal unimolecular rate constant to its value in the high-pressure limit, $k(E)$ is the microscopic unimolecular rate constant at energy E, and $F(E)$ is the energy distribution function for $(AB^+)^*$ produced by collision of A^+ and B. The rate constant k_c is simply an ion-molecule collision rate constant and can be calculated from Langevin or ADO theory. The rate constant k_s can be taken as an ion-molecule collision rate constant if we assume strong collisions; that is, every collision of $(AB^+)^*$ deactivates it sufficiently so that it no longer has enough energy to decompose. With this assumption, k_s is also readily calculated from Langevin or ADO theory. With this value for k_s, we can use RRKM theory to obtain an expression for the integrand in eq 5 and evaluate the integral numerically as previously described.[2a] In order to do this, however, it is necessary to know the oscillator frequencies and moments of inertia for the ionic complex and for the transition state leading to its decomposition. We will discuss how these were obtained for $H_5O_2^+$ in some detail and more briefly for $H_5S_2^+$ and $C_{12}H_{12}^+$ in the following sections.

1. $(H_5O_2)^+$. The proton-bound dimer of water can be observed in a high-pressure mass spectrometer at pressures high enough (ca. 1 Torr) that collisional stabilization can occur at a reasonable rate. The rate of formation of $H_5O_2^+$ has been measured as a function of temperature and pressure by Meot-Ner and Field.[6] In order to obtain the oscillator frequencies and rotational constants for $H_5O_2^+$, which have not been determined spectroscopically in the gas phase, it is necessary to establish a geometry for the complex and to know its entropy. The entropy is readily available from $\Delta S°$ for reaction 6 and the known entropies of H_2O and H_3O^+. Since both Field[6] and Kebarle[10] have measured the thermochemical parameters in equilibrium studies, and since the values differ considerably, both sets of values were considered.[11]

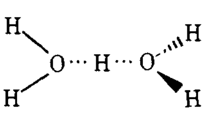
$$H_2O + H_3O^+ \rightleftarrows H_5O_2^+ \qquad (6)$$

$$\text{Field:}^6\ \Delta H° = -33.0\ \text{kcal/mol}$$

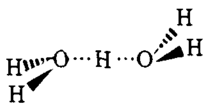
$$\Delta S° = -33.6\ \text{eu}$$

$$\text{Kebarle:}^{10}\ \Delta H° = -31.6\ \text{kcal/mol}$$

$$\Delta S° = -24.3\ \text{eu}$$



1a



1b

Several theoretical studies[12-14] have suggested that the optimal geometry for $H_5O_2^+$ is of D_{2d} symmetry with a symmetrical hydrogen bond, **1a.** While a symmetrical hydrogen bond in such species is somewhat unusual, it has also been suggested by several spectroscopic studies of $H_5O_2^+$ in inorganic crystals.[15,16] In these crystal studies, the ion has a geometry with approximately C_{2h} symmetry, **1b,** presumably due to hydrogen bonding of the four terminal protons to other atoms in the crystal lattice. As discussed below, the choice of D_{2d} symmetry instead of C_{2h} does not have a significant effect on our results. We chose to use the geometry optimized by Newton and Ehrenson[13] with r_{OH} = 0.95 Å for the terminal protons, r_{OO} = 2.36 Å, and an angle of 115° between each terminal O-H bond and the O-H-O axis. Using this geometry, all of the contributions to the entropy of $H_5O_2^+$ except the vibrational entropy, $S°_{vib}$, can be calculated from the usual statistical thermodynamic formulas.[17] The total entropy of $H_5O_2^+$ is available from the experimentally determined $\Delta S°$ for the reaction and the known entropies of H_2O and H_3O^+. $S°_{vib}$ is then calculated as the difference between the total entropy of $H_5O_2^+$ and the rotational and vibrational contributions. This analysis leads us to question Meot-Ner and Field's thermochemical data,[6] since slightly *negative* values of $S°_{vib}$ were required for D_{2d} symmetry and any other reasonable geometry such as C_{2h} or C_s. Thus, we were only able to carry out calculations based on Kebarle's thermochemical data.[10]

Four O-H stretching motions and six bending motions were estimated from the frequencies of H_2O and H_3O^+. The symmetric and antisymmetric O-H-O stretching frequencies have been assigned for $H_5O_2^+$ in the perchlorate salt.[18] The remaining internal degrees of freedom are a free internal rotation and two O-H-O bending motions. The reduced moment of inertia for the free rotation was calculated for the chosen geometry, and the two bending frequencies were adjusted to fit the required vibrational entropy.

There is one more pertinent degree of freedom, the external rotation about the O-H-O axis. As discussed by Forst[19] and Troe,[20] this rotation is not adiabatic and may couple with the vibrational degrees of freedom. Although the rotations associated with the quantum numbers J and K cannot be separated rigorously for a nonlinear symmetric top, Troe has suggested that it is useful to treat the external rotation associated with K as fully active and has discussed the errors introduced by this approximation.[20] The effect of making this rotor active is not large, but it does improve agreement between the calculated and experimental rate constants for all the systems we have tested.[21] The critical energy (E_0) was adjusted so that the calculated high-pressure activation energy for decomposition of the complex at 300 K was equal to ΔE for the reaction (i.e., $E_a = -\Delta H° - RT$).

The transition state was taken as the point where the sum of the potential and centrifugal energies is at a maximum.[22] Such a choice of transition state is reasonable in the absence of more detailed information about the reaction coordinate and has been discussed and justified previously.[2a,23] At this point along the reaction coordinate, the interfragment distance (ca. 6 Å) is sufficiently large that we may take the oscillator frequencies to be those of isolated H_2O and H_3O^+. The remaining degrees of freedom are the one-dimensional internal and external rotations also present in the complex and two new two-dimensional internal rotations corresponding to the tumbling of the fragments about the axes not included in the one-dimensional rotor. The parameters used in the calculation are summarized in Table I.

The calculated and experimental values of k_b are plotted vs. temperature in Figure 1. The calculations are based on a calculated collision frequency, $k_s[M]$, of 3×10^7 s^{-1}, which corresponds to the number density at which the experimental data was obtained. We also calculated the pressure dependence

Table I. Parameters Used in the Calculation of the $H_5O_2^+$ Decomposition[a]

	complex	transition state
ν_i	3100 (4)	3870 (2)
	1800 (1)	3760 (1)
	1600 (2)	3757 (1)
	500 (4)	3756 (1)
	410 (1)	1595 (1)
	142 (2)	1550 (2)
		1050 (1)
B_i (external)	5.96 (1)	5.17 (1)
B_i (internal)	22.7 (1)	20.7 (1)
		11.1 (1)
		7.36 (1)
		27.7 (1)
		12.1 (1)
σ	8	1
$I^\dagger/I$	6.12	
E_0	30.8	

[a] Degeneracies are in parentheses. Frequencies (ν_i) and rotational constants (B_i) are in cm^{-1}. 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 the ionic complex. E_0 is in kcal/mol.

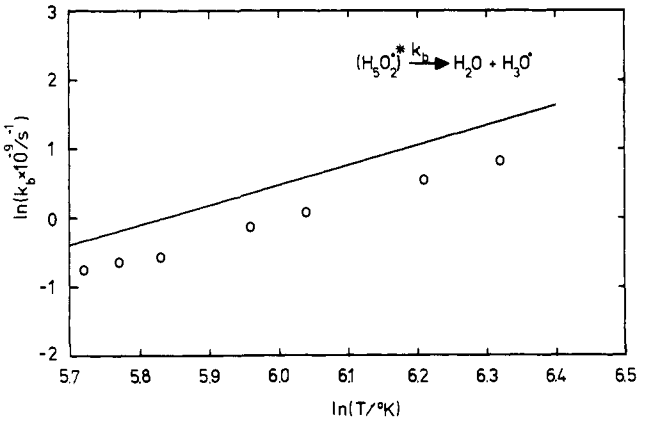


Figure 1. Temperature dependence of the experimental (○) and calculated rate constants k_b for the reaction $(H_5O_2^+)^* \rightarrow H_2O + H_3O^+$.

of k_f for the small pressure range (0.5–1.0 Torr) over which the experimental data was measured and found agreement to be within a factor of 2. The bath gas was methane in all cases.

In order to ensure that our choice of D_{2d} symmetry for the complex was not a critical factor, we also carried out the calculations for $H_5O_2^+$ with C_{2h} symmetry. The temperature and pressure dependences were not significantly affected, with the calculated curves moving slightly farther away from the experimental values. The change was well within the estimated uncertainty of our calculations.

Table II. Parameters Used in the Calculation of the $H_5S_2^+$ Decomposition[a]

	complex A	complex B	transition state
ν_i	2600 (4)	2600 (4)	2627 (1)
	1500 (1)	1500 (1)	2614 (1)
	1000 (2)	600 (2)	2333 (1)
	500 (4)	400 (4)	2328 (2)
	208 (1)	208 (1)	1183 (1)
	131 (2)	52 (2)	1122 (1)
			992 (1)
B_i (external)	3.00 (1)	3.00 (1)	2.50 (1)
B_i (internal)	12.1 (1)	12.1 (1)	9.55 (1)
			5.26 (1)
			4.69 (1)
			11.1 (1)
			8.91 (1)
σ	4	4	1
$I^\dagger/I$	6.23	6.23	
E_0	14.8	12.7	

[a] See Table I for explanation and units.

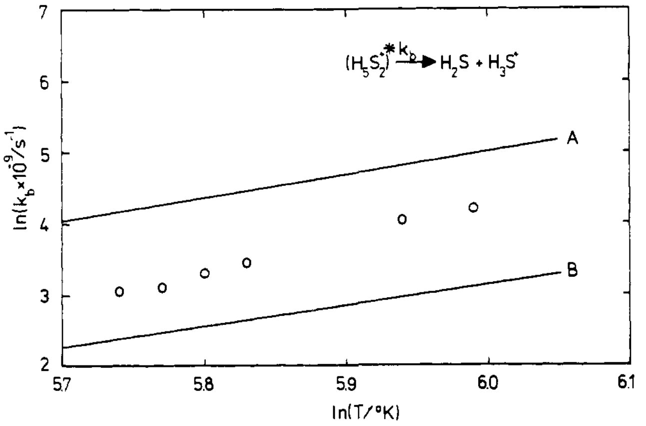
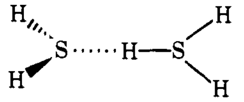


Figure 2. Temperature dependence of the experimental (○) and calculated rate constants k_b for the reaction $(H_5S_2^+)^* \rightarrow H_2S + H_3S^+$. A and B refer to the two models discussed in the text.



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2. $(H_5S_2)^+$. Meot-Ner and Field have also measured the kinetics of the formation of $H_5S_2^+$ as a function of temperature and pressure.[6] Once again two sets of thermodynamic values are available, and once again they are significantly different. Since there is no theoretical or experimental data available on the geometry of $H_5S_2^+$, we have taken the terminal S–H bond length to be 1.3 Å, as in H_2S, and the S–S distance to be 3.0 Å, the distance calculated for the S···H–S bond in the dimer of dithioformic acid.[25] The angles were taken to be the same as in $H_5O_2^+$. There is no evidence for (or against) a symmetric hydrogen bond in this case, so we chose C_{2v} symmetry, **2**, for the molecule instead of D_{2d} symmetry. The entropy of H_3S^+, which is also unknown, was estimated from the entropy of structurally similar PH_3. Both sets of experimental thermochemical data can accommodate the entropy analysis. We, therefore, carried out calculations using both Kebarle's[24] (complex A) and Field's[6] (complex B) thermochemical values. The parameters are summarized in Table II.

$$H_2S + H_3S^+ \rightleftarrows H_5S_2^+ \qquad (7)$$

$$\text{Field:}^{6}\ \Delta H° = -13.8\ \text{kcal/mol}$$

$$\Delta S° = -18.7\ \text{eu}$$

$$\text{Kebarle:}^{24}\ \Delta H° = -15.7\ \text{kcal/mol}$$

$$\Delta S° = -24.4\ \text{eu}$$

The results are shown in Figure 2. The temperature dependence of k_b was calculated with a collision frequency of 5.6 × 10^7 s^{-1} in order to duplicate the experimental conditions. The pressure dependence of k_f was also calculated and was found to agree with experiment to within a factor of 3 for both complex A and complex B over the pressure range 1.0–2.5 torr.

Table III. Parameters Used in Calculation of the $(C_6H_6)_2^+$ Decomposition[a]

	complex	transition state
ν_i	3082 (6)	3082 (6)
	3080 (2)	3080 (2)
	3062 (1)	3062 (1)
	3060 (1)	3060 (1)
	3047 (2)	3047 (2)
	1597 (6)	1597 (6)
	1596 (2)	1596 (2)
	1485 (2)	1485 (2)
	1326 (1)	1326 (1)
	1310 (1)	1310 (1)
	1178 (2)	1178 (2)
	1146 (1)	1146 (1)
	1089 (10)	1089 (10)
	1037 (2)	1037 (2)
	1010 (1)	1010 (1)
	992 (1)	992 (1)
	985 (1)	985 (1)
	970 (2)	970 (2)
	847 (3)	849 (2)
	800 (2)	847 (3)
	703 (1)	703 (1)
	600 (1)	671 (1)
	400 (7)	606 (2)
	300 (2)	508 (5)
	70 (5)	405 (2)
B_i	0.189 (1)	0.189 (1)
		0.189 (2)
		0.189 (2)
σ	6	24
$I^\dagger/I$	3.88	
E_0	14.50	

[a] See Table I for explanation and units.

To ensure that the assumption of an asymmetric hydrogen bond was not critical to the results, we also carried out the calculations for $H_5S_2^+$ with D_{2d} symmetry. Again, the changes in k_f and k_b were insignificant.

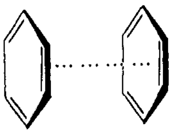
3. $(C_6H_6)_2^+$. The dimerization reaction

$$C_6H_6 + C_6H_6^+ \rightleftarrows (C_6H_6)_2^+ \qquad (8)$$

$$\Delta H° = -15.06 \text{ kcal/mol}$$

$$\Delta S° = -23.18 \text{ eu}$$

has been observed at both high[26] and low[7] pressures, and the relevant thermodynamic parameters have been determined.[26] There is little experimental data available regarding the geometry of dimeric complexes such as $(C_6H_6)_2^+$. ESR studies of polycyclic aromatic species suggest dimers with a "face to face" geometry.[27] We have, therefore, assumed the geometry 3 with an inter-ring separation of 3.1 Å, comparable to the inter-ring distance found in benzene excimers.[28] The entropy of the benzene radical cation was estimated by assuming the same translational and rotational entropy as benzene and using the vibrational frequencies assigned by Klots[29] to obtain the vibrational entropy. The parameters for the dimer and the transition state are summarized in Table III. The calculated temperature dependence of k_b is shown in Figure 3. Little experimental data is available for comparison. We note that at a temperature of 300 K and a pressure of ca. 10^{-3} Torr our calculated k_f (1.48×10^{-12} cm^3 molecule^{-1} s^{-1}) is in reasonable agreement with the observed value[7] of 4.07×10^{-12} cm^3 molecule^{-1} s^{-1}. The bath gas is benzene itself.



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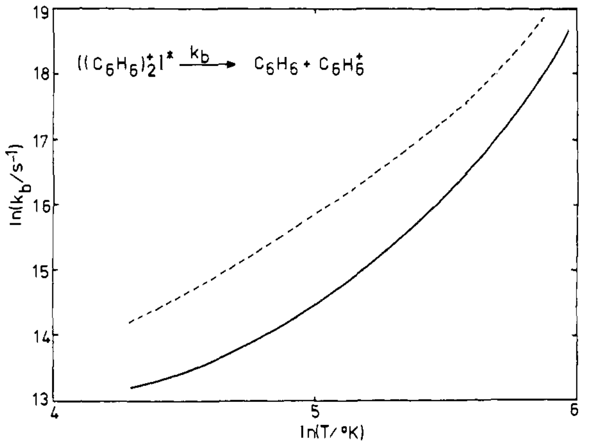

Figure 3. Calculated temperature dependence of the rate constant k_b for the reaction $(C_6H_6)_2^+ \rightarrow C_6H_6^+ + C_6H_6$ at 1 (---) and 10^{-4} Torr (—).

Discussion

Considering the uncertainties inherent in the determination of thermochemical data by equilibrium studies in high-pressure mass spectrometers and the fact that the estimated collision rate constants may be off by as much as 30%,[30] the agreement between experiment and our calculated rate constants is quite good. Based on our entropic considerations, we favor Kebarle's[10] thermodynamic parameters for reaction 6. Neither entropic considerations nor the calculated pressure and temperature dependences of the rate constants allow us to differentiate between the available thermodynamic parameters for reaction 7 in the experimental range studied. The results for reaction 8 are in good agreement with the one experimental point available. It will be interesting to see if the agreement is good when more experimental data becomes available. Our model works as well for these systems as it does for the amine proton-bound dimers. The results further support the assumptions regarding the mechanism of the reaction, the randomization of internal energy in the complex, and the transition-state model which went into the analysis. We have also shown that our results are not very sensitive to the exact geometry of the ionic complex as long as the entropy is kept constant. This result is not surprising given that the results of RRKM calculations on neutral species are quite insensitive to the choice of transition-state parameters provided that the entropy of activation is held constant.[31] In the case of neutrals the parameters for the molecule are usually well-known, while the parameters for the transition state are chosen to satisfy the entropy requirement. In our case it is the transition state for which the parameters are reasonably well-known and the complex for which the parameters are chosen to accommodate the entropy. This is important since it is, at present, impossible to obtain experimental bond lengths and angles for large gas-phase ions. We have thus shown that, given equilibrium thermochemical data for a three-body association reaction, it is possible to calculate the association rate constant rather accurately. In fact, the association rate constant in the true low-pressure regime depends only on the thermodynamic values and not directly on k_b. Figure 4 shows the calculated value of k_f as a function of pressure in all regimes. The fall-off for the H_2O and H_2S systems occurs at significantly higher pressure than that for the amine proton-bound dimers and $(C_6H_6)_2^+$. This reflects the fact that $H_5O_2^+$ and $H_5S_2^+$ have fewer internal degrees of freedom than the other systems.

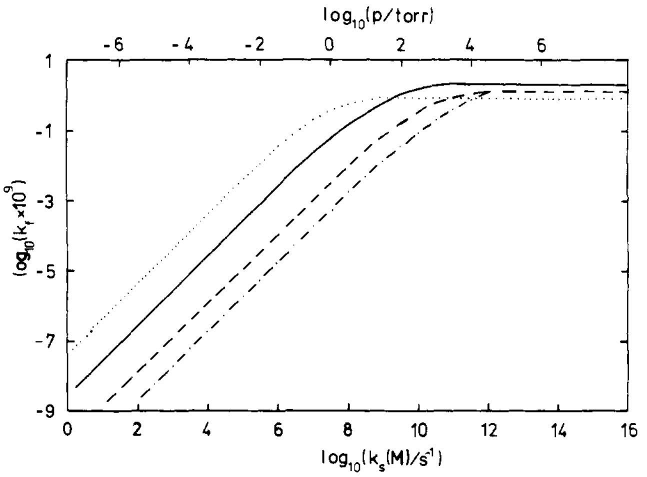

Figure 4. Calculated pressure dependence of k_f in units of cm^3 molecule^{-1} s^{-1}: $(C_6H_6)_2^+$ at 300 K (• • •); $H_5O_2^+$ at 359 K (—); $H_5S_2^+$ model A at 329 K (- - -); $H_5S_2^+$ model B at 329 K (–·–). The pressure scale is for $H_5O_2^+$. Values of k_s for $H_5O_2^+$, $H_5S_2^+$, and $(C_6H_6)_2^+$ are 1.13×10^{-9}, 1.04×10^{-9}, and 1.06×10^{-9} cm^3 molecule^{-1} s^{-1}, respectively.

It would be valuable if we were able to use our analysis to obtain thermochemical data from kinetic data. In principle, this could be done by choosing the value of E_0 so that the calculated rate constants agree with the experimental values, and from this obtain a value of $\Delta H°$ for the reaction. In order to assess this possibility, it is necessary to ascertain the sensitivity of the calculated rate constants to E_0. We tested this by varying E_0 for reaction 6 by 1, 5, and 10 kcal/mol from 30.8 kcal/mol, the value obtained from the experimental $\Delta H°$ as discussed above. Table IV shows the change in k_b at 300 K. These results show that, while it is possible to decide whether E_0 is 30 or 40 kcal/mol, the sensitivity of k_b to E_0 is not great enough to obtain a more accurate value, since our calculated rate constants are only reliable to within approximately a factor of 2. Thus, we really cannot differentiate between E_0 = 30.8 kcal/mol and E_0 = 35.8 kcal/mol.

The above considerations suggest that the most useful experimental value to have for a three-body ion-molecule association reaction is the equilibrium constant or $\Delta G°$. Using a statistical thermodynamic analysis of the entropy similar to that outlined above, it should be possible to estimate $\Delta S°$ quite accurately. It would then be possible to obtain $\Delta H°$ and calculate the association rate constant as a function of temperature and pressure.

Intermolecular Entropy Effects

Some recent work by Lias and Ausloos[8,32,33] deserves comment in this regard. They have proposed that there can be significant contributions (up to 3 eu) to ΔS for ion-molecule reactions arising from nonideality due to the long-range interactions of the ion and the neutral. Such a contribution does not appear in a value of $\Delta S°$ computed solely from ideal gas partition functions. Lias and Ausloos propose that this nonideal term can be readily estimated from ion-molecule collision theory considerations. This result may be important if we wish to obtain $\Delta H°$ and the rate constants for an ion-molecule reaction from a single value of $\Delta G°$ as outlined above. Such nonideality may also be important to the results we have already obtained, since it was not considered when we calculated third-law entropies by difference from experimentally determined values of ΔS. If such a nonideal contribution is significant, it would show up entirely in our calculated $S°_{\text{vib}}$ for the ionic complex and could lead to significant errors in our assignment of vibrational frequencies. For these reasons and because of the fundamental importance of a claim that measurable deviations from ideal behavior occur in a gaseous mixture of ions and neutrals in the pressure range where ion-molecule equilibria are studied (typically 10^{-6}–1 Torr), we have given serious consideration to this matter. We believe that there are, in fact, no significant nonideal contributions in this regime and we show that the expression derived by Lias and Ausloos is associated with a violation of microscopic reversibility.

Table IV. Dependence of the Calculated Values of k_b on the Critical Energy for the Decomposition of $H_5O_2^+$ [a]

E_0	$k_b \times 10^{-9}$	E_0	$k_b \times 10^{-9}$
30.8	0.69	40.8	0.10
31.8	0.56		0.47[b]
35.8	0.25		

[a] E_0 is in kcal/mol. The rate constant k_b is in s^{-1} and was calculated at 300 K and a collision frequency of 3×10^7 s^{-1}. [b] Experimental value of k_b from ref 6.

Their derivation[8] is based on the description of the phenomenological rate constants for some charge transfer reactions, k_f and k_r, in terms of simple collision theory as the product of a collision rate constant Z, a steric factor P, and an exponential energy term in the endothermic direction, eq 9–13, where ΔH is the enthalpy change for the exothermic forward reaction.

$$A^+ + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} A + B^+ \tag{9}$$

$$k_f = Z_f P_f \tag{10}$$

$$k_r = Z_r P_r e^{\Delta H/RT} \tag{11}$$

$$K_{eq} = \frac{k_f}{k_r} = \frac{Z_f P_f}{Z_r P_r} e^{-\Delta H/RT} = e^{\Delta S/R} e^{-\Delta H/RT} \tag{12}$$

therefore

$$\Delta S = R[\ln (Z_f/Z_r) + \ln (P_f/P_r)] \tag{13}$$

Lias and Ausloos provide several examples of reactions for which the ideal entropy change should be close to zero and for which k_f is found experimentally to be close to Z_f and k_r to $Z_r e^{\Delta H/RT}$, where Z_f and Z_r are Langevin[3] or ADO[4] rate constants. Thus, for these reactions, if P_f/P_r is close to unity, this implies that ΔS is given by

$$\Delta S = R \ln (Z_f/Z_r) \tag{14}$$

The authors claim that eq 14 represents an approximation to the configuration integral which would arise from a proper statistical mechanical treatment of the ion-neutral interaction potential, since Z_f and Z_r take into account such interactions.

This interpretation cannot be correct. Any reasonable approximation for a nonideal contribution to a thermodynamic state function must go to zero in the limit of zero pressure; eq 14 is completely independent of pressure. Further, it is difficult to believe that significant deviations from ideality can be observed in a gaseous ion-molecule mixture at pressures of 10^{-6}–1 Torr. Any such deviations should be reflected in the second virial coefficient of the mixture, $B(T)$, which is given[34] by

$$B(T) = \sum_{\alpha}\sum_{\beta} \chi_\alpha \chi_\beta B_{\alpha\beta}(T) \tag{15}$$

where χ_α is the mole fraction of species α, χ_β is the mole fraction of a species β, and $B_{\alpha\beta}(T)$ is the second virial coefficient for a pair of interacting species α and β. For neutral gases at moderate temperature B is on the order of 10–100 cm^3 mol^{-1}. Typical ion densities in ion-molecule mixtures used in equilibrium studies are on the order of 10^5 cm^{-3}. At a pressure of 1 Torr at 300 K, this corresponds to a mole fraction of 10^{-11}. Therefore, even an ion-neutral interaction for which $B_{\alpha\beta}(T)$ was as large as 10^{13} cm^3 mol^{-1} would only contribute terms of the order of the neutral-neutral interactions to eq 15. A second virial coefficient of 10^{13} cm^3 mol^{-1} is unreasonable under any realistic circumstances. For example, an estimate of $B_{\alpha\beta}(T)$ for the interaction of Xe atoms with He$^+$ ions at 300 K gave $B_{\alpha\beta} = 10^7$ cm^3 mol^{-1}. In making this estimate, we used a Sutherland potential[35] with a Langevin attractive interaction,[3] and took the turning point to be the sum of the van der Waals radii of Xe and He (2.8 Å). The correct turning point to use is probably somewhat larger, since the Langevin impact parameter is close to 8 Å in this case. Therefore our estimate should be regarded as an upper limit. Even so, $B_{\alpha\beta}$ is still six orders of magnitude too small to make a contribution to eq 15 which is of the same order of magnitude as the neutral-neutral terms. Even at low pressure ($\sim 10^{-6}$ Torr) with ion densities at $\sim 10^5$/cm^3, the ion-molecule interaction terms are only becoming comparable to the neutral-neutral terms which are, of course, very small at this pressure.

Given that eq 14 does not appear reasonable as an approximation to a nonideal entropy term, we must consider what the term $R \ln (Z_f/Z_r)$ does represent and whether or not it is a real contribution to the entropy change. In fact, this term is not a real contribution to ΔS, and arises as an artifact of the kinetic mechanism used in the derivation. In order to see this, it is useful to recast the derivation of eq 14 in terms of transition-state theory. For simplicity, we will take A and B in eq 9 to be atoms. It is well-known that the bimolecular collision rate constant can be written in terms of the translational partition functions of the reactants and the translational and rotational partition functions of the transition state.[36] The transition state appropriate to the collision process will then be equivalent to a diatomic molecule with some internuclear distance r. The collision rate constant for the forward process is given by

$$Z_f = \frac{kT}{h}\left(\frac{q^\ddagger}{q_{A^+}q_B}\right)_{\text{trans}} q_{\text{rot}}^\ddagger \tag{16}$$

Upon substitution of the appropriate partition functions, this reduces to

$$Z_f = \left(\frac{8\pi kT}{\mu}\right)^{1/2} r^2 \tag{17}$$

where μ is the reduced mass. In order for this to reduce to the Langevin[3] expression for Z_f, r must be taken as the separation at which the sum of the potential and centrifugal energies is at a maximum. This distance is given[3,22] by

$$r^2 = \left(\frac{\pi\alpha e^2}{2kT}\right)^{1/2} \tag{18}$$

where α is the polarizability of the neutral and e is the charge on the ion. Thus, r serves to define the transition state for the collision process.

Now, consider the mechanism which led Lias and Ausloos to eq 14, that is, $k_f = Z_f$ and $k_r = Z_r e^{\Delta H/RT}$. Unless the polarizability of A is exactly equal to that of B, the internuclear separation in the transition state for the forward process is different from that for the reverse process; i.e., the transition states for the forward and reverse reactions are different. Equations 11 and 12 assume that the system of reactants and products is thermal (Boltzmann). Under these conditions the principle of detailed balance requires that the transition states for the forward and reverse reactions be identical. Thus microscopic reversibility has been violated in writing eq 12. This does not mean that k_f and k_r cannot be given by eq 10 and 11. If they are, however, the system cannot be thermal. The experimentally determined forward and reverse rate constants for the reactions reported by Lias and Ausloos[8] do appear to be given empirically by eq 10 and 11. This suggests that the systems studied may involve nonthermal energy distributions and may not be at true thermodynamic equilibrium.

The correct treatment of a reaction whose collision dynamics are controlled by Langevin forces must include the effects of two centrifugal barriers and model the behavior of the system as it passes through the region between these local maxima. In the limit of a statistical treatment, this would involve adding a reaction channel to the model described previously,[2a,c] allowing a chemical reaction to compete with dissociation to reactants. If there is a single intermediate

$$A^+ + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X^+ \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} C^+ + D \tag{19}$$

$$k_f = k_1k_{-2}/(k_{-1} + k_{-2}) \text{ and } k_r = k_2k_{-1}/(k_{-1} + k_{-2}) \tag{20}$$

Now, if $k_1 = Z_f$ and $k_2 = Z_r$

$$\frac{k_f}{k_r} = \frac{Z_f}{Z_r}\frac{k_{-2}}{k_{-1}} \tag{21}$$

In general, $k_{-2} \neq k_{-1}e^{-\Delta H/RT}$ since the preexponential factors are different. For the simple case of two *atomic* reactants, only the rotational partition functions need be considered, and if the system is Boltzmann we can write

$$\frac{k_{-2}}{k_{-1}} = \frac{8\pi^2kT\mu r_2^2/h^2}{8\pi^2kT\mu r_1^2/h^2}e^{-\Delta H/RT} = \frac{r_2^2}{r_1^2}e^{-\Delta H/RT} \tag{22}$$

where r_1 and r_2 are the internuclear separations for transition states 1 and 2 respectively. Thus

$$K = \frac{k_f}{k_r} = \frac{Z_f r_2^2}{Z_r r_1^2}e^{-\Delta H/RT} = e^{-\Delta H/RT} \tag{23}$$

and the collisional terms vanish. For more complex systems, one needs to consider the vibrational partition functions as well. When done correctly this will give the correct $\Delta S°$, but the same basic considerations regarding collision cross sections will still be valid. For some reactions the dynamics may not be statistical and/or the Langevin collision description may also be incorrect. The analysis given here is not appropriate under such circumstances.

Conclusion

We have demonstrated that our model gives good agreement with the experimental results for two more ion-molecule association reactions, and we have predicted values for a third. Our results strongly support the idea that these three-body ion-molecule association reactions proceed via long-lived intermediate complexes in which the internal energy may be taken to be randomized. We have also shown that the term $R \ln (Z_f/Z_r)$, proposed as a nonideal contribution to ΔS, is in no way an approximation to the configuration integral as claimed by Lias and Ausloos. At present, there is no reason to believe that the thermodynamic functions for ion-molecule equilibria cannot be adequately determined by assuming ideal-gas behavior.

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

and eq 8b should read

$$E^* = E_0 + E^{\dagger} \tag{8b}$$

The above corrections apply only to the equations stated in the paper. The correct equations were used in the actual calculations. (b) For additional discussion of the amine association reactions, see P. V. Neilson, M. T. Bowers, M. Chau, W. R. Davidson, and D. H. Aue, *J. Am. Chem. Soc.*, **100,** 3649 (1978). (c) W. N. Olmstead and J. I. Brauman, *ibid.*, **99,** 4219 (1977). (d) O. I. Asubiojo and J. I. Brauman, *ibid.*, in press.

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Mechanism of Base-Promoted Phosphonium Salt Hydrolyses. Kinetics and Multiple Substituent Effects for a Nucleophilic Attack at Phosphorus

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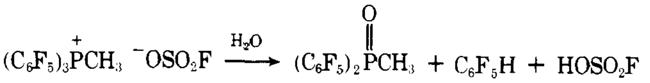
Abstract: Hammett analysis of substituent effects on the kinetics of the hydroxide-promoted conversion of phosphonium salts ($R_4P^+X^-$) into phosphine oxides (R_3PO) and hydrocarbons (RH) supports a mechanism with a transition state that varies along the path for each class of R groups studied. An intermediate hydroxyphosphorus adduct (R_4P-OH) that was originally proposed by Ingold is supported by kinetic and pH measurements. A kinetic analysis is offered to clarify previous mechanistic proposals. The hydrolytic lability of a new, reactive methyltris(perfluorophenyl)phosphonium salt is described.

Introduction

Reported herein are mechanistic interpretations of results from analysis of multiple substituent effects on the kinetics of hydrolysis of quaternary phosphonium salts in aqueous methanolic solutions. Studies concerning the effects of substituents on phosphorus ylides in Wittig reactions have led us to the observation that methyltris(pentafluorophenyl)phosphonium fluorosulfonate is hydrolytically extremely labile. Cleavage of this quaternary phosphonium salt to methylbis(pentafluorophenyl)phosphine oxide and pentafluorobenzene occurs at room temperature with the addition of just 1 equiv of water. In comparison, alkyltriphenylphosphonium salts are stable in aqueous solutions, as exemplified by benzyltriphenylphosphonium bromide, which may in fact be recrystallized from water.[2] The conditions normally required for the hydrolysis of these salts are added base and/or elevated temperatures.[3]



$$(C_6F_5)_3\overset{+}{P}CH_3\ {}^{-}OSO_2F \xrightarrow{H_2O} (C_6F_5)_2\overset{\overset{\displaystyle O}{\|}}{P}CH_3 + C_6F_5H + HOSO_2F$$

In 1929, Marvel and Ingold[2] separately published the first mechanistic suggestions for the formation of phosphine oxides and hydrocarbons from phosphorus ylides and water, or quaternary phosphonium salts and aqueous base, respectively. Ingold's detailed mechanism, in which initial hydroxide attack at the phosphorus was originally purported to be rate limiting (step 1), is given in Scheme I. Since this original mechanism was proposed, several other related mechanisms have been suggested and reviewed.[3-7] Results largely from the work of McEwen and VanderWerf,[6] Allen,[7] and Hoffmann[4a] have led to the current belief that the mechanism for alkaline hydrolysis

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