stant 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

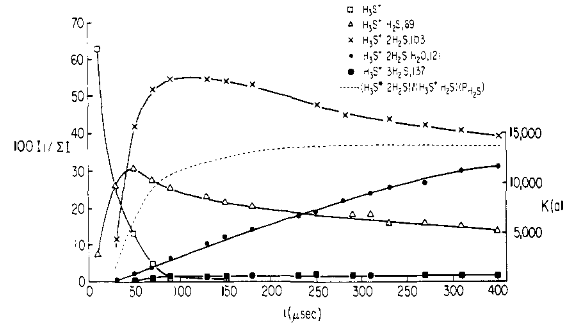

Figure 1. Normalized ion intensities as a function of reaction time in a reaction system of 14.8% H_2S in N_2 at 220 K and a total source pressure of 1.1 Torr. The value of the measured equilibrium constant for the formation of $H_3S^+{\cdot}2H_2S$, i.e., $(I_{103^+})/(I_{69^+})(P_{H_2S})$, is indicated by the broken line and the right-hand side ordinate.

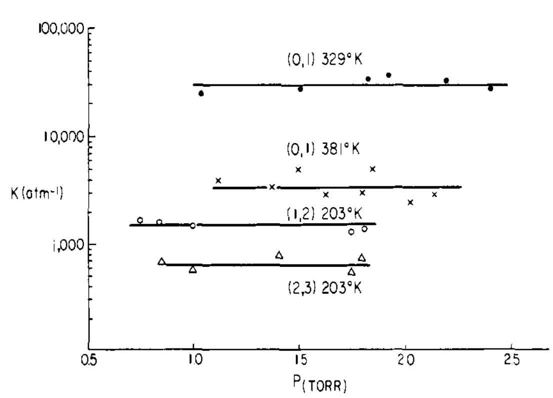

Figure 2. Observed equilibrium constants vs. total source pressure for the equilibria $H_3S^+{\cdot}\ (n-1)H_2S + H_2S \rightleftharpoons H_3S^+{\cdot}nH_2S{\cdot}\ (n-1, n)$ and the temperature are given on the plot. The (0, 1) equilibrium at 329 K was obtained in a mixture of 10% H_2S in CH_4; other pressure studies shown were in a mixture of 14.8% H_2S in N_2.

on this system were performed in this laboratory by continuous ionization techniques[1,2] and by Kebarle et al.[3,4] by the pulsed ionization technique which allows the observation of ion intensities as a function of reaction time. Results for the stabilities of higher water clusters ($n \geq 3$) obtained by the two methods were in good agreement, but results for the formation of lower order clusters (n = 1 and 2) were significantly different. One objective of the present study was to reexamine the stability of protonated water clusters by the pulsed technique in order to resolve this disagreement. In addition, we also measured the stabilities of the cluster ions $H_3S^+{\cdot}nH_2S$ and $H_3S^+{\cdot}H_2O$ to obtain information on the effect of hydrogen bonding on ion-molecule clustering. Furthermore, we investigated the kinetics for cluster formation and for the dissociation of excited and of stabilized ion-molecule complexes in the strongly bound $H_3O^+{\cdot}H_2O$ and the more weakly bound $H_3S^+{\cdot}H_2S$ species.

Experimental Section

The measurements reported in this study were performed on The Rockefeller University chemical physics mass spectrometer. Ionic reactions were initiated by the bombardment of the reaction mixture by a 40-μs pulse of 600 V electrons. The intensities of the ions of interest as function of reaction time were recorded on a multichannel analyzer with channels of 10 μs width. The clusters $H_3O^+{\cdot}nH_2O$ were studied in a mixture of 1% H_2O in methane. The mass spectrum of the methane-water system (using continuous ionization) was similar to that found previously.[1] Formation of the $H_3S^+{\cdot}nH_2S$ clusters was studied in mixtures of 10–20% H_2S in CH_4 or N_2 and in a mixture consisting of 5% H_2S, 10% H_2, and 85% N_2. All the mixtures containing H_2S flowed into the ion source through a trap filled with Linde 3A molecular sieve cooled to −40 °C to remove water impurity. Materials used in this study were H_2S, CP grade, CH_4 Ultra-High Purity grade, and N_2, Prepurified grade, all from Matheson Gas Products.

Criteria for the Achievement of Reaction Equilibria. Ionization of our reaction mixtures by electron bombardment yields primary ions such as CH_4^+, CH_3^+, N_2^+, H_2O^+, H_2S^+, etc. Under our high-pressure chemical-ionization conditions these ions react completely in 10–40 μs to form the ions H_3O^+ and H_3S^+, which undergo further reactions only in clustering processes. In order that the measured intensities of the ions participating in the clustering reactions represent equilibrium concentrations, all the reactions in which these ions participate must reach equilibrium before the ion signal becomes undetectable because of ion depletion processes. The establishment of equilibrium may not occur if the approach to equilibrium is too slow or if components of the equilibrium system undergo irreversible reactions. The latter type of difficulty arose under some conditions in the measurement of the hydrogen sulfide cluster stabilities because of the formation of $H_3O^+{\cdot}nH_2O$ and $H_3S^+{\cdot}nH_2S{\cdot}mH_2O$ clusters from trace water impurities in the source. This difficulty was surmounted by conducting the equilibrium studies for the formation of $H_3S^+{\cdot}H_2S$ at temperatures greater than 350 K where water cluster formation from impurities was negligibly slow and for the higher clusters at temperatures less than 250 K where most of the water impurity is frozen out. For similar reasons, formation of the $H_3S^+{\cdot}H_2O$ cluster was studied only between 450 and 550 K, at $P_{H_2O} \leq 0.01$ Torr, where the irreversible formation of $H_3O^+{\cdot}H_2O$ was negligibly slow. As shown in the following discussion, the slow formation of some mixed $H_3S^+{\cdot}nH_2S{\cdot}H_2O$ clusters under these conditions did not interfere with our equilibrium measurements.

Equilibrium Criteria. In pulsed high-pressure mass spectrometry the establishment of equilibrium is deduced from the nature of the variations of ion intensities as a function of reaction time. As an example, intensities for the major ions in the N_2–H_2S system at 220 K are shown in Figure 1. The major reactions can be summarized as

$$H_3S^+ \xrightarrow[k_{\rm I}]{H_2S} H_3S^+\cdot H_2S \underset{k_{-\rm II}}{\overset{H_2S,\ k_{\rm II}}{\rightleftharpoons}} H_3S^+\cdot 2H_2S$$

$$\xrightarrow[k_{\rm III}]{H_2O} H_3S^+\cdot 2H_2S\cdot H_2O$$

Computer simulation of the reaction system gives pseudo-first-order rate constants $k_{\rm I} = 4.9 \times 10^4$, $k_{\rm II} = 4.0 \times 10^4$, $k_{\rm III} = 0.16 \times 10^4\ s^{-1}$, and the value $k_{-\rm II} = 1.4 \times 10^4\ s^{-1}$. Using these values the simulation gives the steady state ion ratio $((H_3S^+{\cdot}2H_2S)/(H_3S^+{\cdot}H_2S))_{\text{steady state}} = 2.56$ at reaction times of 200–500 μs. This value can be compared with the true equilibrium ion ratio calculated as $k_{\rm II}/k_{-\rm II} = 2.63$. The presence of the slow irreversible reaction leading to $H_3S^+{\cdot}2H_2S{\cdot}H_2O$ leads only to an error of 2.5% in the measurement of the equilibrium constant.

As another example of the time dependence of normalized ion intensities, we observed the intensities of the major ions in the CH_4–H_2S system at 370 K. We noted the diminution of H_3S^+ and the formation of $H_3S^+{\cdot}H_2S$ until an equilibrium ratio of $H_3S^+{\cdot}H_2S/H_3S^+ = 0.88$ is established at ca. 200 μs after the initial ionization event. The very slow formation of $H_3S^+{\cdot}H_2O$ which constituted only ca. 5% of the total ion intensity after 250 μs caused again negligible interference with the measurement of equilibrium in the formation of $H_3S^+{\cdot}H_2S$. Apart from the ions related to H_3S^+, i.e., the group of ions H_3S^+, $H_3S^+{\cdot}H_2S$, and $H_3S^+{\cdot}H_2O$, the ion CH_3S^+ (m/e 47), presumably formed by fast reactions after the electron bombardment, and its clustered product, $CH_3S^+{\cdot}H_2S$ (m/e 81), are also observed in this system. We noted that the two groups of ions constitute each a "closed" reaction group. This is shown by the fact that the sum of the intensities $I_{H_3S^+} + I_{H_3S^+{\cdot}H_2S} + I_{H_3S^+{\cdot}H_2O}$ constitutes a constant fraction, 82%, and the sum $I_{CH_3S^+} + I_{CH_3S^+{\cdot}H_2S}$ constitutes a constant fraction, 14%, of the total ion intensity at all reaction times. In other words, the ions within each group can interconvert by chemical reactions, but ions from one group cannot be converted to ions in the other groups. Consequently, the presence of the "extraneous" ions CH_3S^+ and $CH_3S^+{\cdot}H_2S$ also does not interfere with the equilibrium $H_3S^+ + H_2S + CH_4 \rightleftharpoons H_3S^+{\cdot}H_2S + CH_4$.

A further criterion of equilibrium is the independence of the equilibrium constant on pressure. We performed pressure studies on each equilibrium reported here and observed no systematic changes in the measured equilibrium constant with pressure (Figure 2). We interpret these results as indicating that collision-induced dissociation of cluster

Table I. Thermodynamic Values for Clustering Reactions of H_3O^+ and H_3S^+

Reaction	$-\Delta H°$, kcal/mol				$-\Delta S°$, eu				$-\Delta G°_{300}$, kcal/mol			
	a	*b*	*c*	*d*	*a*	*b*	*c*	*d*	*a*	*b*	*c*	*d*
1. $H_3O^+ + H_2O \rightleftharpoons H_3O^+ \cdot H_2O$	33.0	36.0	31.6	16.3	33.6	33.3	24.3	17.2	22.9	25.0	24.3	11.2
2. $H_3O^+ \cdot H_2O + H_2O \rightleftharpoons H_3O^+ \cdot 2H_2O$	21.0	22.3	19.5	14.8	19.8	29.0	21.6	16.9	15.1	13.6	13.0	9.7
3. $H_3O^+ \cdot 2H_2O + H_2O \rightleftharpoons H_3O^+ \cdot 3H_2O$	16.0	17.0	17.5	17.6	20.3	28.3	27.3	20.0	9.9	8.5	9.3	8.6
4. $H_3S^+ + H_2O \rightleftharpoons H_3S^+ \cdot H_2O$	17.0				17.8				11.7			
5. $H_3S^+ + H_2S \rightleftharpoons H_3S^+ \cdot H_2S$	12.8				18.7				7.2			
6. $H_3S^+ \cdot H_2S + H_2S \rightleftharpoons H_3S^+ \cdot 2H_2S$	7.2				17.3				2.0			
7. $H_3S^+ \cdot 2H_2S + H_2S \rightleftharpoons H_3S^+ \cdot 3H_2S$	5.4				(10-20)[e]				1.2			
8. $H_3S^+ \cdot 3H_2S + H_2S \rightleftharpoons H_3S^+ \cdot 4H_2S$	3.3				(10-20)[e]				0.5			

[a] Present work. [b] Reference 3. [c] Reference 4. [d] Reference 2. [e] Error estimates based on standard error in least-squares calculation on van't Hoff plots are ±1.5 kcal/mol and ±4 eu. Because of the large error and small absolute values of $\Delta H°$ and $\Delta G°_{300}$ for reactions 7 and 8, the value of $\Delta S° = (\Delta H° - \Delta G°_{300})K$ for these reactions is highly uncertain.

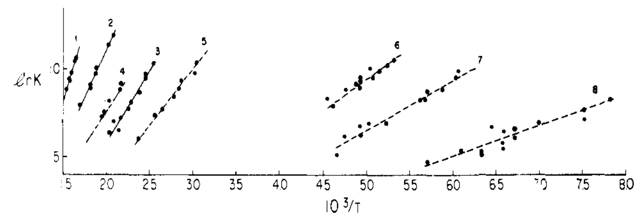

Figure 3. van't Hoff plots for clustering equilibria of H_3O^+ and H_3S^+. Numbers correspond to reactions as listed in Table I.

ions outside the ion exit slit are not a significant source of error in our apparatus in the pressure range used. This possibility has been suggested by Kebarle et al.[4] for some of their experiments. The constancy of K_{eq} with pressure was checked for each equilibrium reported in this study. Each equilibrium study reported here was replicated two to six times.

Results and Discussion

(1) The Stability of the Cluster Ions $H_3O^+ \cdot nH_2O$ (n = 1–3). van't Hoff plots for the formation of the water cluster ions are shown in Figure 3. The thermodynamic results are summarized in Table I. We observed that our present results are in fair agreement with the results of Kebarle et al.,[4] while they are at variance with the results obtained previously by the continuous ionization technique.[1] We concur with the conclusion of Kebarle that in the continuous ionization mode studies equilibrium was not established in the formation of the $H_3O \cdot H_2O^+$ and $H_3O \cdot 2H_2O^+$ ions.

(2) The Stability of the Clusters $H_3S^+ \cdot nH_2S$ (n = 1–4) and of $H_3S^+ \cdot H_2O$. The stabilities of protonated ion clusters are affected significantly by the polarities, hydrogen bonding properties, and proton affinities of the constituent molecules. The understanding of the roles of these physical factors can be enhanced by comparative studies on clustering reactions in systems with varying physical properties. For example, Long and Franklin[5] found that the stabilities of $PH_4^+ \cdot nPH_4$ clusters are much smaller than those of the analogous clusters $NH_4^+ \cdot nNH_4$. This was related to the decreased polarity and hydrogen bonding of PH_3 vs. NH_3. In the present study we compare the stability of bonding in $H_3S^+ \cdot nH_2S$ clusters, $H_3O^+ \cdot nH_2O$ clusters, and the mixed cluster $H_3S^+ \cdot H_2O$. van't Hoff plots for the formation of the clustered ions are shown in Figure 3. The thermodynamic values are summarized in Table I.

Comparing the enthalpy changes for association in reactions 1 and 5 in Table I, we observe that the exothermicity of dimer formation in protonated water is more exothermic by 20.2 kcal/mol than the analogous reaction in hydrogen sulfide. It is reasonable to assign the difference mostly to the difference in the hydrogen bonding capacities of H_2O and H_2S. This difference could result from the larger fractional charge on the hydrogens of H_3O^+ as compared with H_3S^+ and/or from the greater facility of lone-pair electrons of H_2O to enter into hydrogen bonding. To clarify this point, we measured the stability of $H_3S^+ \cdot H_2O$. The dissociation enthalpy in the formation of this species is −17 kcal/mol, much closer to −12.8, ΔH for the formation of $H_3S^+ \cdot H_2S$, than to −33, ΔH for the formation of $H_3O^+ \cdot H_2O$. The data thus seem to indicate that partial charge on the hydrogen of the clustered ion is the quantity determining the strength of hydrogen bonding. This result, which is not unexpected, is further amplified by comparing the enthalpy of clustering for the formation of $H_3O^+ \cdot H_2O$, $NH_4^+ \cdot NH_3$,[6] $H_3S^+ \cdot H_2S$, and $PH_4^+ \cdot PH_3$,[5] with the partial charge on the hydrogens in the protonated species. The exothermicities for cluster formation are 33.0, 24.8, 12.8, and 11.5 kcal/mol, respectively. The values of partial charge on the hydrogens in H_3O^+, NH_4^+, H_3S^+, and PH_4^+, as calculated by the methods of Pauling,[7] are 0.26, 0.18, 0.04, and 0.0. The two sets of values can be approximately related by the linear relationship

$$-\Delta H_{\text{assoc}} = 100 \times (\text{partial charge}) + 9 \text{ kcal/mol}$$

Physically this relationship can be interpreted to indicate that about 9 kcal/mol of the binding energy between the protonated ions and the neutrals results from forces not directly related to hydrogen bonding (e.g., ion–dipole forces), while binding energy above this value results from the operation of hydrogen bonding interactions which are proportional to the partial charge of the hydrogen.

Reactions producing higher order cluster ions in hydrogen sulfide show the usual decrease in exothermicity with increasing cluster size. No significant discontinuity is observed between the formation of the $H_3S^+ \cdot 3H_2S$ and $H_3S^+ \cdot 4H_2S$ clusters.

(3) Association Kinetics and the Lifetimes of the Excited Complexes $H_3O^+ \cdot H_2O^+$ and $H_3S^+ \cdot H_2S^*$. In a previous kinetic study[8] we found that strong bonding in the radical ion complexes $N_2^+ \cdot N_2$ and $CO^+ \cdot CO$ led to faster rates of association but lesser temperature dependence of the rate than in the case of the more weakly bound complexes $N_2H^+ \cdot N_2$ and $HCO^+ \cdot CO$. It is of interest to extend the investigation of the effect of association enthalpy on reaction kinetics to the present reaction system. In theoretical treatments of reaction kinetics such as the RRKM theory the rate of decomposition of a molecular entity is determined in part by the vibrations and rotations of the entity. The number and nature of the vibrational and internal rotational degrees of freedom in the $H_3O^+ \cdot H_2O$ and $H_3S^+ \cdot H_2S$ complexes are presumably similar (except the vibrations associated with the ion–neutral bond), and conse-

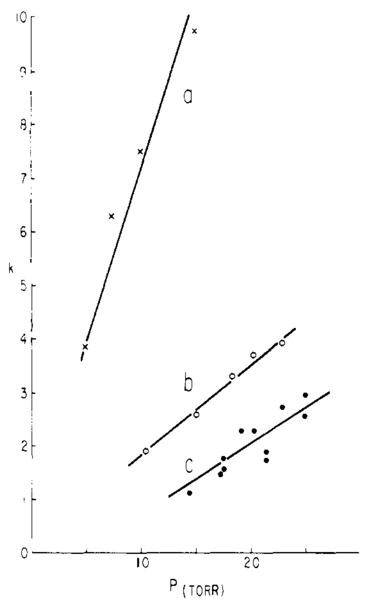

Figure 4. Dependence of rate constants on total source pressure: (a) k_1 (10^{-11} cm^3/(mol s)) for $H_3O^+ + H_2O + CH_4 \rightarrow H_3O^+{\cdot}H_2O + CH_4$ at 359 K; (b) k_1 (10^{-12} cm^3/(mol s)) for $H_3S^+ + H_2S + CH_4 \rightarrow H_3S^+{\cdot}H_2S + CH_4$ at 329 K; (c) k_{-1} (10^3 s^{-1}) for $H_3S^+{\cdot}H_2S + CH_4 \rightarrow H_3S^+ + H_2S + CH_4$ at 329 K.

Table II. Rate Constants for the Third-Order Reactions $H_3X^+ + H_2X + CH_4 \rightarrow H_3X^+{\cdot}H_2X + CH_4$ and for the Decomposition of the Excited Complexes $(H_3X^+{\cdot}H_2X)^* \rightarrow H_3X^+ + H_2X$[a]

T, K	b	c	d	e	f
293		1.86	0.27		
305	42				0.47
310		0.87	1.18	21.5	
320	37	0.81	0.92	22.9	0.52
329		0.66	2.19	27.8	
341	34	0.57	2.87	32.0	0.56
380		0.31	10.7	57.5	
387	21				0.87
401		0.26	19.9	67.7	
420	17				1.09
498	9.5				1.77
556	6.8				2.34

[a] Temperature studies were carried out in reaction mixtures of 1.05% H_2O in CH_4, at total source density of 2.7×10^{16} mol/cm^3 and in mixtures of 10.1% H_2S in CH_4 at a total source density of 5.4×10^{16} mol/cm^3. [b] $H_3O^+ + H_2O + CH_4 \rightarrow H_3O^+{\cdot}H_2O + CH_4$: k_3 (10^{-28} cm^6/(mol^2 s)). [c] $H_3S^+ + H_2S + CH_4 \rightarrow H_3S^+{\cdot}H_2S + CH_4$: k_3 (10^{-28} cm^6/(mol^2 s)). [d] $H_3S^+{\cdot}H_2S \rightarrow H_3S^+ + H_2S$: k_{-1} (10^3 s^{-1}). [e] $(H_3S^+{\cdot}H_2S)^* \rightarrow H_3S^+ + H_2S$: k_d (10^9 s^{-1}). [f] $(H_3O^+{\cdot}H_2O)^* \rightarrow H_3O^+ + H_2O$: k_d (10^9 s^{-1}).

quently differences in the reaction kinetics between the two systems will reflect mostly the effect of enthalpy on the reaction rate.

Association reactions of the type investigated here are generally assumed to proceed by the energy-transfer mechanism

$$AH^+ + A \underset{k_d}{\overset{k_a}{\rightleftharpoons}} (AH^+ \cdot A)^* \tag{1}$$

$$(AH^+ \cdot A)^* + M \xrightarrow{k_s} AH^+ \cdot A + M \tag{2}$$

This mechanism was recently demonstrated experimentally for clustering reactions of NH_4^+, $CH_3NH_3^+$, and $(CH_3)_2NH_2^+$.[9] In the case of a reversible reaction the overall process may be written as

$$AH^+ + A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AH^+ \cdot A + M \tag{3}$$

with

$$k_1 = \frac{k_a k_s(M)}{k_d + k_s(M)} \tag{4}$$

which, if $k_d \gg k_s(M)$, reduces to

$$k_1 = k_a k_s(M)/k_d \tag{5}$$

i.e., the reaction follows third-order kinetics with the third-order constant $k_3 = k_a k_s/k_d$.

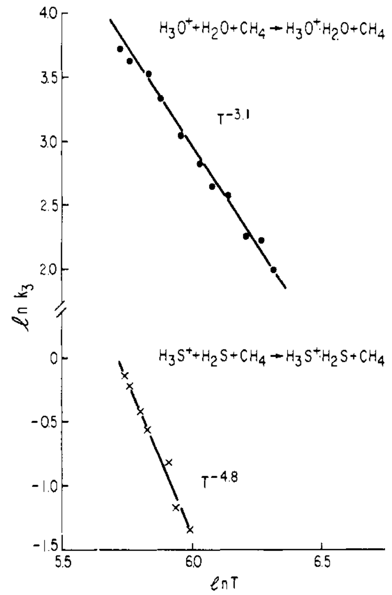

Figure 5. Temperature dependences of the third-order association rate constants. Slopes give the temperature dependence in $k_3 = AT^{-n}$ (k_3 in units of 10^{-28} cm^6/(mol^2 s)).

In the present work we investigated the kinetics of the formation of $H_3O^+{\cdot}H_2O$ between 305 and 570 K and of $H_3S^+{\cdot}H_2S$ between 310 and 400 K. The formation of $H_3O^+{\cdot}H_2O^+$ (leading also to the consecutive formation of $H_3O^+{\cdot}2H_2O$ and $H_3O^+{\cdot}3H_2O$ at low temperatures) was irreversible over the temperature range quoted. The formation of $H_3S^+{\cdot}H_2S$ was reversible in the temperature range studied. The rate constant measurements and calculations were performed according to procedures published previously.[8,9] The rate measurements yield pseudo-first-order rate constants from which k_3 is obtained by dividing by the concentrations of A and M. The linear dependence of the experimental value of k_1 on (M) (Figure 4) shows that the reactions are indeed third order.

Values of the rate constants k_3 for the formation of $H_3O^+{\cdot}H_2O$ and $H_3S^+{\cdot}H_2S$ are given in Table II. The temperature dependence of the rate constants is illustrated in plots of ln k_3 vs. ln T in Figure 5. We observe that the rate constants for protonated water dimer formation are about 50 times larger than those of hydrogen sulfide. The temperature dependences can be expressed as $k_3(H_2O) = A_1T^{-3.1}$ and $k_3(H_2S) = A_2T^{-4.8}$. Both the increased absolute value of k_3 in the case of the strongly bound $H_3O^+{\cdot}H_2O$ and the larger negative temperature dependence of k_3 in the more loosely bound $H_3S^+{\cdot}H_2S$ are similar to the relation between ion clustering kinetics and bonding strength that we found in CO and N_2.[8] Measurements of k_3 for the formation of $H_3O^+{\cdot}H_2O$ at several temperatures have been made by Kebarle et al.[4] Two of their measured values fall within the temperature range used in our measurements, and they are lower than our values by about 35% and a factor of 3, respectively. The temperature depen-

Table III. Kinetic Parameters for the Thermal Decomposition $AH^+ \cdot A + M \rightarrow AH^+ + A + M$ (k_{-1}) of Cluster Ions in the Low-Pressure (0.5–3 Torr) Bimolecular Range

$AH^+ \cdot A$	M	$k_{-1}/(M)$,[a] $cm^3/(mol\ s)$	E_a, kcal/mol	ΔH,[b] kcal/mol	log A[c]
1. $H_3S^+ \cdot H_2S$	CH_4	3.6×10^{-10}	10.2	12.6	−3.9
2. $H_3O^+ \cdot H_2O$	CH_4	8.2×10^{-23}	29.8	33.0	−1.7
3. $NH_4^+ \cdot NH_3$	CH_4	3.1×10^{-15}	19.8	24.8	−3.7
4. $CH_3NH_2^+ \cdot CH_3NH_2$	i-C_4H_{10}	1.7×10^{-14}	18.3	21.7	−3.8
5. $(CH_3)_2NH_2^+ \cdot (CH_3)_2NH$	i-C_4H_{10}	1.1×10^{-11}	17.5	20.8	−1.4
6. $H_3^+ \cdot H_2$	H_2	2.3×10^{-10}	8.4	9.7	−5.1

[a] At 400 K. For reaction 1, $k_{-1}/(M)$ was obtained from the kinetics of approach to equilibrium. For reactions 2–5, values of $k_{-1}/(M)$ were obtained from $k_{-1}/(M) = K_{calcd}/k_1(M)$, where K_{calcd} is the equilibrium constant calculated from thermodynamic data (see footnote b) and k_1 is the forward rate constant for the formation of $AH^+ \cdot A$ from ref 9. Data for reaction 6 are from ref 11. [b] Thermodynamic values for reactions 1 and 2 from present work; those for reactions 3–5 are from R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **95**, 3504 (1973); those for reaction 6 are from ref 12. [c] A in units of $cm^3/(mol\ s)$.

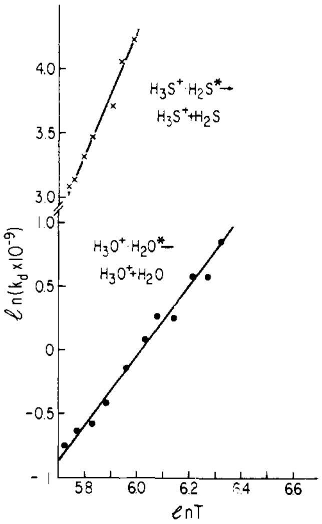

Figure 6. Temperature dependences of the decomposition rate constants (k_d in units of s^{-1}) of the excited association complexes $H_3S^+ \cdot H_2S^*$ and $H_3O^+ \cdot H_2O^*$.

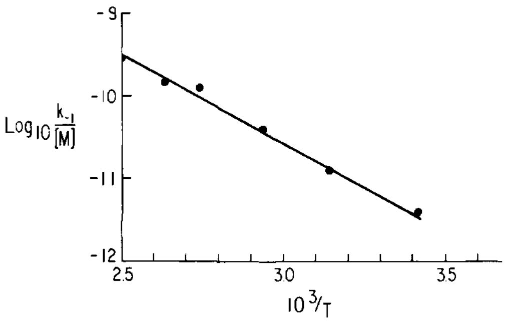

Figure 7. Arrhenius plot for the decomposition of the thermalized cluster ion $H_3S^+ \cdot H_2S$ ($k_{-1}/(M)$ in units of $cm^3/(mol\ s)$).

dence that they define is approximately $T^{-4.7}$, which is larger than our dependence.

k_a and k_s are rate constants for processes involving ion-molecule collisions. For the present purposes we take k_a and k_s as being equal to the collision rate as calculated from the average dipole orientation theory.[10] With the use of the relation $k_3 = k_a k_s / k_d$ we calculated k_d, the dissociation rate of the excited complexes $H_3S^+ \cdot H_2S^*$ and $H_2O^+ \cdot H_2O^*$ (Table II). Plots of ln k_d vs. ln T are shown in Figure 6. The collision rate constants k_a and k_s are similar in the H_2O and H_2S systems and are only very slightly dependent on temperature. Consequently, the differences in the absolute value of k_3 and its temperature dependence originate from the difference in k_d for the two systems.

(4) Kinetics of the Thermal Decomposition of the Stabilized Cluster Ions $H_3S^+ \cdot H_2S$ and $H_3O^+ \cdot H_2O$. Activation Energies. Since k_1, the forward rate constant, and K, the equilibrium constant, for our reactions are known, we can calculate k_{-1}, the rate of the thermal decomposition of the stabilized cluster ions. Under our conditions the association reactions exhibit third-order kinetics, i.e., the stabilization of the excited complexes, $AH^+ \cdot A^* + M \rightarrow AH^+ \cdot A + M$, is the rate-determining step. By the principle of microscopic reversibility, the opposite of the stabilization step, i.e., the activation of the thermalized species, $AH^+ \cdot A + M \rightarrow AH^+ \cdot A^* + M$, must be the rate-determining step for the decomposition process. Correspondingly, we expect and, indeed, find experimentally that the decomposition reactions display second-order kinetics, i.e., k_{-1} is proportional to (M) (Figure 4). In other words, the dissociation of $AH^+ \cdot A$ is a unimolecular process in the bimolecular, low-pressure fall-off region, with the bimolecular rate constant $k_{-1}/(M)$. From the plots of $k_{-1}/(M)$ vs. $10^3/T$ (Figure 7) we find the activation energies for the dissociations of $H_3S^+ \cdot H_2S$ and $H_3O^+ \cdot H_2O$ (Table III). We observe that the activation energy for the dissociation of $H_3S^+ \cdot H_2O$ is 10.2 kcal/mol, which is lower by 2.4 kcal/mol than the endothermicity of the process. We also calculated E_a for the dissociation of $H_3O^+ \cdot H_2O$, $NH_4^+ \cdot NH_3$, $CH_3NH_3^+ \cdot CH_3NH_2$, and $(CH_3)_2NH_2^+ \cdot (CH_3)_2NH$, using for the amines kinetic data obtained in the course of a previous study.[9] In all cases, we find that the activation energy is smaller by 0.5–4 kcal/mol than the endothermicity for the dissociation. This result can, in fact, be rationalized on the basis of the experimentally observed negative temperature dependence of $k_1(T)$, and, of course, it can be explained by conventional unimolecular dissociation theory, as follows. The thermodynamic constraint

$$k_1(T)/k_{-1}(T) = K_{eq} = \exp(-\Delta H/RT + \Delta S/R) \qquad (6)$$

leads to the relation between the functional forms of $k_1(T)$ and $k_{-1}(T)$:

$$k_{-1}(T) = Ck_1(T)e^{\Delta H/RT} \qquad (7)$$

where C is independent of temperature. For ion-molecule clustering reactions exhibiting third-order kinetics, often $k_1 = AT^{-n}$ (see ref 8 and Figure 6) and therefore $k_{-1} = CT^{-n}e^{\Delta H/RT}$. Consequently, the activation energy for the decomposition of the complex will be smaller than ΔH for the process, i.e.,

$$E_{a(-1)} \equiv -R\frac{d \ln k_{-1}}{d(1/T)} = -\Delta H - nRT \qquad (8)$$

In this equation n is the exponent of the temperature dependence of the forward reaction ($k_1 \propto T^{-n}$), which for our systems is in the range 3–5. Thus we expect the observed activation energies to be approximately 3–5 kcal/mol less than the endothermicities of the dissociation reactions, and this is in agreement with our measured values.

A decrease in the activation energy of thermal unimolecular reactions at the low-pressure limit is predicted by the RRK theory as:[11]

$$E_a^0 = E_a^\infty - (s - 1)RT \qquad (9)$$

where E_a^0 and E_a^∞ are the activation energy at the low- and high-pressure limits, correspondingly, and s is the number of active oscillators in the sense of the Kassel theory. The absence of an activation energy for the association process indicates that the energy barriers for the dissociation are equal to ΔH; therefore $E_a^\infty \approx \Delta H_{\text{dissoc}}$. Making reasonable guesses for the magnitudes of s ($s \approx \frac{1}{2}(3N - 6)$) one calculates from eq 9 that E_a^0 will again be less than E_a^∞ by several kilocalories per mole. It is also of interest to note that eq 8 and 9 yield the result that $n = s - 1$.

(5) Kinetics of the Thermal Decomposition of Cluster Ions. Preexponential Factors. Inspection of the preexponential factors for k_{-1} in Table III reveals that some of these values are larger by up to seven orders of magnitude than the collision rate between $AH^+{\cdot}A$ and (M) which corresponds to $\log A \approx -9$, for A in units of $cm^3/(mol\ s)$. Preexponential factors higher by up to two orders of magnitude than the rate for activating collisions are common in decomposition reactions of neutral molecules. The effect is often attributed to activation involving internal degrees of freedom. In recent work on $H_3^+{\cdot}H_2$ Hiraoka and Kebarle[12] found a preexponential factor of $\log A = -5.1$, which is four orders of magnitude larger than the collision rate between $H_3^+{\cdot}H_2$ and H_2. We find preexponential factors for the decomposition of cluster ions which are larger by five to nine orders of magnitude than the calculated rate of activating collision, i.e., of $k_{\text{collision}}e^{-E_a/RT}$, even when the already low activation energies given in Table III are used. It appears that unusually large preexponential factors are common in the thermal decomposition of gaseous ions, and we can offer no explanation for this interesting phenomenon.

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Generalized Valence Bond Studies of the Electronic Structure of SF_2, SF_4, and SF_6

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Abstract: The electronic structure of SF_2, SF_4, and SF_6 is investigated from the standpoint of ab initio generalized valence bond (GVB) calculations. Analysis of the GVB orbitals in these molecules and in the model reaction $SF_4 \rightarrow SF_2 + 2F$ leads to the conclusion that the stability of the hypervalent SF_4 and SF_6 systems is largely due to the incorporation of charge-transfer configurations, with 3d functions on the sulfur playing a lesser role. Molecular properties for SF_2 and SF_4 are reported.

The ability of elements in groups 5–8 to form more bonds than the classical octet rule permits has provided an intriguing topic in the modern development of the theory of electronic structure. The discovery of the xenon fluorides[1] in 1962 stimulated further activity in the area of "hypervalent" molecules.

In valence bond (VB) theory[2] the concept of the "expanded valence shell" was introduced whereby atoms could make use of d orbitals to form additional bonds. This notion has led to controversy over whether the promotion energies and spatial extent of d orbitals are consistent with the observed molecular properties.[3-6] The importance of ionic "resonance structures" has also been acknowledged in VB treatments.[2]

Molecular orbital (MO) theory provides a conceptual framework to treat nonclassical multicenter bonds without resorting to the expanded valence shell. After the discovery of the xenon fluorides it was demonstrated how MO treatments could describe these systems using s and p orbitals.[7-9]

Although examination of MO's can be particularly valuable in understanding charge distributions and geometrical preferences of molecules, the problem of determining chemical stability depends on evaluation of the matrix elements of the total energy of a molecule. Calculations at the Hartree–Fock level can lead to poor predictions of molecular binding energies when the two species have different numbers of bonds.[10]

Simpler schemes have been proposed by Coulson[11] and Pitzer[12] to explain the stability of hypervalent molecules which focus on the incorporation of charge-transfer configurations in the wave function.

In this paper we examine the electronic structure of SF_2, SF_4, and SF_6 using ab initio generalized valence bond (GVB) wave functions.[13,14] The GVB method can be viewed as a synthesis of valence bond (VB) and molecular orbital (MO) theories. It retains the VB form of the wave function but can still be analyzed in terms of a multiconfiguration wave function, where the configurations are comprised of (localized) molecular orbitals.

The GVB wave function is particularly well-suited for in-