for each of the carbons are determined. Because of the puckering displacements, the origin of the coordinate system of the $\bar{C}_i$ vectors will not in general coincide with the Cremer–Pople coordinate system or even that of the molecular center of gravity. Therefore to proceed in the calculations of the D_{ij}'s we resort to the procedure described in Appendix A, i.e., first transform the origin to the new center of gravity and then to the Cremer–Pople coordinate system.

Registry No. Bis(4-hexyloxy)azoxybenzene, 2857-42-0; phase V, 37268-47-6; cyclopentane, 287-92-3; 1,2,2,5,5-pentadeuteriocyclopentane, 82544-88-5; cyclopentanone, 120-92-3; 2,2,5,5-cyclopentanone-d_4, 3997-89-5; 2,2,5,5-cyclopentanol-d_4, 35447-71-3; 2,2,5,5-cyclopentyl-d_4 bromide, 75621-29-3.

Preferential Solvation of Hydrogen Ions in Mixed Clusters of Water, Methanol, and Ethanol

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Received January 11, 1982

Abstract: The electron-impact ionization of neutral mixed clusters composed of water and alcohol molecules results in the formation of $\{(ROH)_n{\cdot}(H_2O)_m\}H^+$ ion clusters. With use of a combined molecular beam–mass spectrometer apparatus, clusters of the above type have been formed for $n + m < 25$ and for ROH = CH_3OH and C_2H_5OH. By monitoring the competitive decomposition processes via the metastable peak intensities, it has been possible to determine which of the species present in the ion cluster is preferentially bound to the proton. The results show that in $\{(ROH)_n{\cdot}H_2O\}H^+$ clusters the alcohol molecules are preferentially attached to the proton up to $n = 9$ for methanol and $n = 10$ for ethanol; thereafter the water molecule is the most strongly bound species. These results can be rationalized in terms of the ion–dipole and ion–induced dipole interactions present in the cluster.

A study of the reactions of ionic clusters can provide information at a microscopic level on the interations that exist between an ion and one or more solvent molecules.[1-4] In particular, the use of techniques to study cluster complexes in the gas phase has the advantage that ions at varying stages in the solvation process can be examined without interference from either the bulk solvent or ions of the opposite sign.

Two main techniques have been used to produce and study ion clusters. Kebarle and co-workers have used high-pressure mass spectrometry with considerable success to determine equilibrium data for both metallic and nonmetallic ions in a variety of solvents.[1,2] The alternative technique of using free-jet expansion[5] to produce clusters can take two forms. Either neutral clusters can be ionized by electron or photon impact following the expansion process[6-8] or ions can be expanded along with the solvent of interest.[9] For those examples where there is an overlap, results show that all three techniques can yield similar information even if the comparison can only be made at a qualitative level.[8-11] However, producing ion clusters by electron or photon impact following the adiabatic expansion of neutral molecules results in a nonequilibrium distribution of cluster sizes, and this places a severe limitation on the amount of qualitative thermodynamic information such studies can yield. Also the lack of data on ionization efficiencies means that there is no direct relationship between the distributions of neutral and ionic clusters.

In this paper the results of a series of experiments in which we have used ion clusters to study the competitive solvation of hydrogen ions in solvent mixtures are presented. Although the clusters are initially formed as the neutral species by adiabatic expansion, information on the competitive aspect of the solvation process has been obtained by considering the relative intensities of reaction products from the unimolecular decomposition of ion clusters at varying stages of solvation.

In a previous study of the water–methanol system using a high-pressure mass spectrometer, Kebarle et al. formed ion clusters of the type $\{(CH_3OH)_n{\cdot}(H_2O)_m\}H^+$ for $m + n \leq 6$.[12] Their results showed that in small ion clusters the proton is preferentially solvated by the methanol molecules. By extrapolation they concluded that there is no preference when $m + n = 9$ and that when $m + n > 9$ the interaction with water will be stronger than that with methanol. In the present study we have been able to form mixed ion clusters of the type $\{(CH_3OH)_n{\cdot}(H_2O)_m\}H^+$, $\{(C_2H_5OH)_n{\cdot}(H_2O)_m\}H^+$, and $\{(C_2H_5OH)_n{\cdot}(CH_3OH)_m\}H^+$ for $m + n \leq 25$, and we have been able to monitor the reactions of those

Table I

molecule	μ,[a] D	α_p,[b] Å^3	PA,[c] kJ mol^{-1}
H_2O	1.85	1.48	727
CH_3OH	1.70	3.23	777
C_2H_5OH	1.69	5.62	799

[a] Dipole moment, taken from ref 13. [b] Polarizability, taken from ref 13. [c] Proton affinity, taken from ref 14.

[†] Present address: Department of Chemistry, University of Warwick, Coventry CV4 7AL, U.K.

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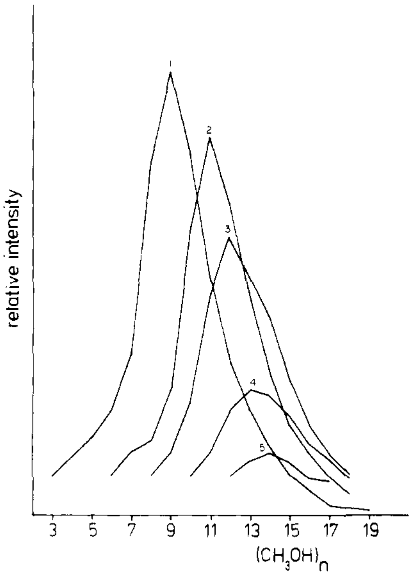

Figure 1. Distribution of ion cluster intensities resulting from the adiabatic expansion of a water–methanol mixture containing 50% methanol. For $\{(CH_3OH)_n{\cdot}(H_2)_m\}H^+$ clusters the values of m are given on each curve.

for which $m + n \leq 15$. With this range of data it is expected that the experiments will probe the behavior of protons surrounded by at least two and quite possibly three shells of solvent molecules.

Table I lists some of the factors which need to be taken into consideration when discussing the interaction of individual solvent molecules with an ion. The ion–dipole interaction decreases as the square of the intermolecular distance while the ion–induced dipole or polarizability decreases as the fourth power. Thus the considerably higher polarizabilities of methanol and ethanol will favor their preferential solvation of the proton in small mixed ion clusters of water and alcohol. However, the higher dipole moment of water will provide a stronger interaction at the increased intermolecular distances found in the larger ion clusters. Certainly the results of Kebarle et al.[12] on water–methanol mixed clusters can be explained on this basis. An indication of the short-range behavior of the ion–solvent interaction can be obtained from the proton affinity data, also given in Table I. As might be expected from the discussion given above, these values closely follow the trend given by the polarizabilities. If the solvation process is influenced by size or steric factors then obviously water presents the smallest molecular volume.

Experimental Section

Neutral clusters[15,16] are generated by expanding vapor from the liquid sample together with argon through a 0.005-cm orifice into a chamber maintained at a pressure of 1×10^{-5} torr. After passing through a skimmer the cluster beam is modulated at 110 Hz by an electrically driven tuning fork. The clusters are then ionized by electron impact and mass analyzed on a modified A.E.I. MS 12 mass spectrometer. After preamplification the modulated ion current is fed into a lock-in amplifier which is synchronized with a reference signal from the beam chopper.

The beam is maintained by passing argon at a pressure of approximately 3000 torr through a small reservoir filled with the liquid sample heated to approximately 80 °C. The saturated carrier gas is then expanded through the nozzle which is held at a temperature of 100 °C. This technique provides a stable beam of clusters and avoids the use of large gas reservoirs or the excessive heating of liquid samples.

On a single-focusing mass spectrometer, such as the MS 12, it is not possible to determine if the intensity of a particular cluster ion peak is due entirely to the ionization of a cluster of that mass or if it's intensity is due in part to the unimolecular decompositon of higher ion clusters within the ion source. However, if an ion has a lifetime in the range 10^{-6}–10^{-5} s, there is a high probability that it will decompose in the field-free region between the ion source and the magnet. Under such circumstances the product ion is not properly focused by the magnet but is recorded as a diffuse peak at a noninteger position on the mass scale. Such peak are normally referred to as metastable peaks.[17] For the decompositon processes discussed in this paper each metastable peak for a particular reaction occurs at a unique position, and it is this feature of the experiment that allows us to monitor the unimolecular decompositions. However, because of either accidental overlap with other peaks or low intensity some data points are missing.

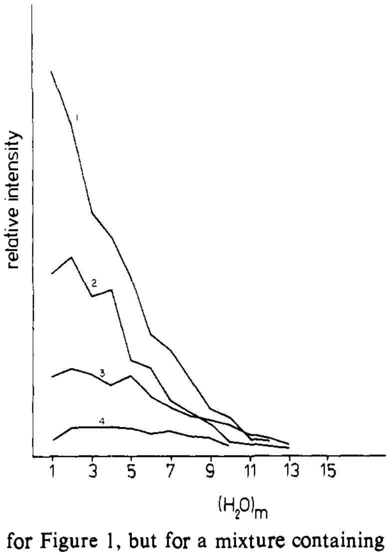

Figure 2. As for Figure 1, but for a mixture containing 1% methanol. In this case the values of n are given on each curve.

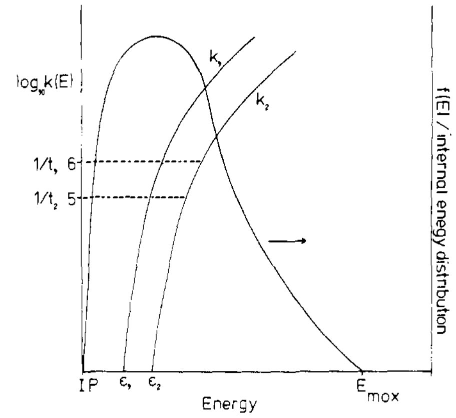

Figure 3. A plot of the rate constants for the two competitive decomposition processes for the ion A^+ as a function of internal energy. For the reaction $A^+ \rightarrow B^+$ the rate constant is k_1 and the critical energy is ϵ_1, and k_2 and ϵ_2 are the rate constant and critical energy, respectively, for the reaction $A^+ \rightarrow C^+$. t_1 and t_2 are the times at which the ion A^+ enters and leaves the field-free region of the mass spectrometer, respectively. IP is the ionization potential of A and E_{max} is the electron-impact energy. Also given is a shape often assumed for $f(E)$, the internal energy distribution for A^+.[18,19]

Results and Discussion

Upon ionization the neutral clusters of both water and the alcohols[15] form protonated ion clusters. Hence when a mixture of water and an alcohol is expanded through the nozzle and ionized the resulting ions have the general formula $\{(ROH)_n{\cdot}(H_2O)_m\}H^+$. The range of m and n depends upon the alcohol content of the mixture prior to expansion. If this is above 5% then $n > m$, particularly in the small ion clusters; but as in the ion cluster size increases the addition of two or more water molecules becomes more probable. Figure 1 shows the ion cluster distribution that arises when the mixture contains 50% methanol. In order to produce ion clusters that are predominantly water, i.e., $m > n$, it is necessary to reduce the alcohol content of the initial mixture to <1%. Figure 2 shows the type of ion cluster distribution

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obtained under such circumstances. Despite the differences in experimental technique the above observations are consistent with those of Kebarle et al.[12]

For information on the preferential solvation of protons to be obtained, use has been made of the fact that for two competing unimolecular decomposition processes the respective metastable peak intensities will reflect any difference between the critical energies for the two reactions. This point is best illustrated through the use of the example presented in Figure 3, where typical rate constants are plotted for the unimolecular decomposition of an ion A^+ via two competing processes, each with a different critical energy. For the process $A^+ \rightarrow B^+$ the intensity of the metastable peak can be calculated from the expression[18,19]

$$m_B^* = \alpha \int_{\epsilon_1}^{E_{\max}} f(E) \frac{k_1(E)}{k_1(E) + k_2(E)} \times \{\exp(-\{k_1(E) + k_2(E)\}t_1) - \exp(-\{k_1(E) + k_2(E)\}t_2)\}\, dE \quad (1)$$

and for the process $A^+ \rightarrow C^+$ the intensity can be calculated from

$$m_C^* = \alpha \int_{\epsilon_2}^{E_{\max}} f(E) \frac{k_2(E)}{k_1(E) + k_2(E)} \times \{\exp(-\{k_1(E) + k_2(E)\}t_1) - \exp(-\{k_1(E) + k_2(E)\}t_2)\}\, dE \quad (2)$$

Most of the terms in these two equations are defined in Figure 3; $k_1(E)$ is the rate constant for the reaction $A^+ \rightarrow B^+$, $k_2(E)$ is the rate constant for the reaction $A^+ \rightarrow C^+$, α is a normalization constant, t_1 and t_2 are the times the ion enters and leaves the field-free region, respectively, and $f(E)$ is the internal energy distribution for A^+ (a commonly assumed form for this is given in Figure 3,[18,19] however, in the present analysis a knowledge of the exact shape of $f(E)$ is not essential). If the process $A^+ \rightarrow B^+$ is to yield a metastable peak then it is necessary that $k_1(E) \simeq 1/t_1$; therefore as $k_1(E) \gg k_2(E)$ and $t_1 < t_2$ the metastable peak intensity at a particular energy is given by the approximate expression

$$m_B^*(E)\, dE \simeq \alpha f(E)\, dE \quad (3)$$

Applying the same criteria to the process $A^+ \rightarrow C^+$ under those conditions where $k_2(E) \simeq 1/t_1$ gives

$$m_C^*(E)\, dE \simeq \alpha f(E) \frac{k_2(E)}{k_1(E)} \exp(-k_1(E)t_1)\, dE \quad (4)$$

but as $k_2(E) << k_1(E)$ when $k_2(E) \simeq 1/t_1$ (see Figure 3) then $m_C^*(E)\, dE \simeq 0$ over the appropriate energy range. This ability the lowest energy process has to influence the metastable peak intensities for competing processes is often referred to as the competitive shift.[19,20] A similar argument to that given above has been used to rationalize the determination of proton affinities from relative metastable peak intensities.[21]

For the mixed water–alcohol ion clusters two such competing processes could be:

$$\{(ROH)_n \cdot (H_2O)_m\}H^+ \rightarrow \{(ROH)_{n-1} \cdot (H_2O)_m\}H^+ + ROH \quad (5)$$

$$\{(ROH)_n \cdot (H_2O)_m\}H^+ \rightarrow \{(ROH)_n \cdot (H_2O)_{m-1}\}H^+ + H_2O \quad (6)$$

Applying the above analysis means that the most facile of these two reactions will yield a metastable peak, whilst the decomposition process involving the loss of that species which is most tightly bound to the ion cluster will not produce a metastable peak.

Figure 4 shows a plot of the relative metastable peak intensities for the following competitive decomposition processes as a function of n

$$\{(CH_3OH)_n \cdot H_2O\}H^+ \rightarrow (CH_3OH)_nH^+ + H_2O \quad (7)$$

$$\{(CH_3OH)_n \cdot H_2O\}H^+ \rightarrow \{(CH_3OH)_{n-1} \cdot H_2O\}H^+ + CH_3OH \quad (8)$$

For one set of results presented in Figure 4 it has been assumed that all the methanol molecules are equivalent and the intensities have been divided by n. However, even without that assumption, it can clearly be seen that there is a distinction between values of n for which one reaction dominates over the other. Figure 5 shows the corresponding graph for metastable peaks arising from the decomposition of mixed ion clusters of ethanol and water. Again there is a clear transition between the region where n is small and loss of water is the most facile process and where n is large and the ion clusters prefer to lose an alcohol molecule.

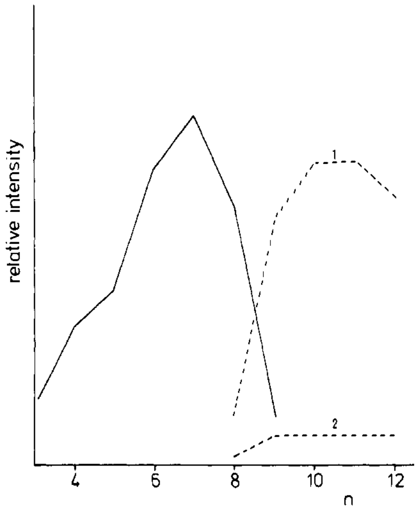

Figure 4. Relative metastable peak intensities for the unimolecular decomposition of $\{(CH_3OH)_n \cdot H_2O\}H^+$ clusters as a function of n. The solid line is for the reaction involving the loss of H_2O and the dashed line is for the reaction involving the loss of CH_3OH. For each value of n the metastable peak intensity has been divided by the intensity of the respective parent peak. For curve 2 the results for the reaction involving loss of CH_3OH have been divided by n.

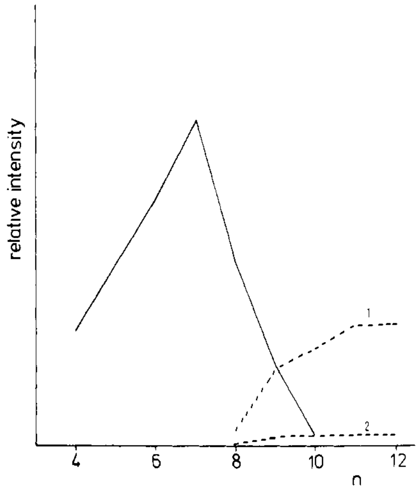

Figure 5. Relative metastable peak intensities for the unimolecular decomposition of $\{(C_2H_5OH)_n \cdot H_2O\}H^+$ clusters as a function of n. The solid line is for the reaction involving loss of H_2O and the dashed line is for the reaction involving loss of C_2H_5OH. For curve 2 the results for the latter reaction have been divided by n.

In the case of ion clusters which predominantly contain water molecules, i.e., $m > n$, a search was made for metastable peaks arising from the following reactions

$$\{ROH \cdot (H_2O)_m\}H^+ \rightarrow \{ROH \cdot (H_2O)_{m-1}\}H^+ + H_2O \quad (9)$$

$$\{ROH \cdot (H_2O)_m\}H^+ \rightarrow (H_2O)_mH^+ + ROH \quad (10)$$

for both alcohols and for all accessible values of m the only peaks observed were those resulting from reaction 9.

The above results are consistent with the type of behavior one would expect given the molecular properties presented in Table I. For small values of n the ion clusters prefer to lose water molecules; thus the larger polarizabilities of both alcohols provide the strongest interaction with the proton. As the size of the cluster increases this effect is reduced until at a certain critical size the

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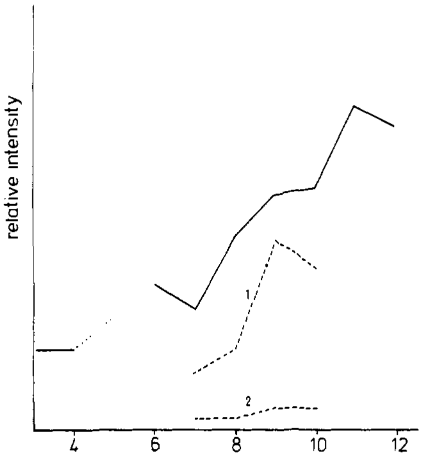

Figure 6. Relative metastable peak intensities for the unimolecular decomposition of $\{(C_2H_5OH)_n{\cdot}CH_3OH\}H^+$ clusters as a function of n. The solid line is for the reaction involving loss of CH_3OH and the dashed line is for the reaction involving loss of C_2H_5OH. For curve 2 the results for the latter reaction have been divided by n.

ion–dipole interaction becomes relatively more important. At this point the water molecule becomes the more strongly bound species and the loss of alcohol molecules is the dominate process. In methanol–water ion clusters the critical size occurs at the point predicted by Kebarle et al.,[12] i.e., when $m + n > 9$; in ethanol–water it would appear to be when $m + n > 10$. However, in neither case is the transition point well defined and it obviously depends upon whether or not the alcohol molecules are considered to be equivalent. The picture presented by the results for reactions 9 and 10 suggests that the single alcohol molecules is more strongly bound to the proton than any of the water molecules and that in the large ion clusters, at least, it must lie close to the center. These results do not necessarily mean that reaction 10 does not take place. However, we do know from the results for reactions 7 and 8 that if the alcohol molecule is positioned to far from the proton then its loss will become the most facile process and an appropriate metastable peak will be observed. The type of crossover behavior exhibited in Figures 4 and 5 has also been observed in experimental measurements of the relative bond energies for the attachment of individual solvent molecules, either H_2O or NH_3, to metal ions.[22-24]

To complete the picture we have also studied competing processes in mixed ion clusters of methanol and ethanol. From the data given in Table I it can be seen that these two molecules have approximately equal dipole moments, but quite different polarizabilities. It should be expected, therefore, that in small ion clusters the methanol molecules will be the less strongly bound of the two species, and hence their loss will produce the most intense metastable peaks. At no stage, however, should the dominant process change dramatically from loss of methanol to loss of ethanol, because for both molecules the long-range interaction with the proton will be approximately equal. Figure 6 presents the relative metastable peak intensities for the two competing processes

$$\{(C_2H_5OH)_n{\cdot}CH_3OH\}H^+ \rightarrow (C_2H_5OH)_nH^+ + CH_3OH \quad (11)$$

$$\{(C_2H_5OH)_n{\cdot}CH_3OH\}H^+ \rightarrow \{(C_2H_5OH)_{n-1}{\cdot}CH_3OH)\}H^+ + C_2H_5OH \quad (12)$$

As can be seen, loss of methanol is the dominant process and only in the larger ion clusters does the alternative reaction compete effectively. This behavior further substantiates the type of semiquantitative approach we have used to discuss features of the proton–molecule interaction. The fact that there is a difference between the results presented in Figures 4 and 5 and those given in Figure 6 rules out the possibility that the crossover behavior exhibited by the water–alcohol ion clusters results entirely from statistical factors.

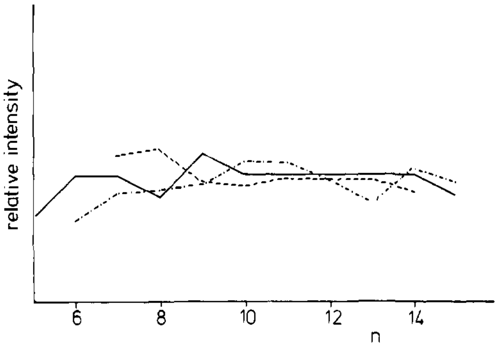

Figure 7. Relative metastable peak intensities for the unimolecular decomposition of $\{(C_2H_5OH)_n{\cdot}(CH_3OH)_m\}H^+$ clusters as a function of m and n in the range 0–2: (–·–) $n = 0$; (—) $n = 1$; (– –) $n = 2$.

Finally, Figure 7 presents the results obtained from an examination of the behavior of ion clusters at the other extreme to those considered for reactions 11 and 12; these are

$$\{(C_2H_5OH)_n{\cdot}(CH_3OH)_m\}H^+ \rightarrow \{(C_2H_5OH)_n{\cdot}(CH_3OH)_{m-1}\}H^+ + CH_3OH \quad (13)$$

for n equal to either 0, 1, or 2. No metastable peaks corresponding to the loss of an ethanol molecule are observed. Within the range of data available there appears to be no significant difference in behavior between the three ion cluster series. Together they suggest that the ethanol molecules lie close to the cluster center and that their presence has no real influence on the reactive process.

Conclusion

In this paper the results have been presented of a study in which the competitive aspect of the unimolecular decomposition of ions in a mass spectrometer has been utilized to provide details of bonding in ion clusters. Although the experiments at this stage do not yield detailed thermodynamic information, they do provide semiquantitative results concerning the bonding characteristics of molecules in quite large ion clusters. In particular, we have been able to probe the behavior of solvent molecules situated in the second and third solvation shells.

To summarize the results it is necessary to consider one aspect of the bonding problem which has not previously been mentioned, proton mobility. In those studies where the central cation is metallic,[22-24] there is no question about where the positive charge resides because the ionization potential of the metal atom is nearly always significantly lower than that of the solvent molecules. However, in those systems where a proton is the charge carrier and the solvent molecules contain disposable hydrogen atoms, there exists the possibility that proton movement can lead to the formation of a large number of nearly degenerate configurations.[25] For protonated clusters of the type studied in the present experiments the number of such configurations could be severely limited for two reasons. First, the presence of alkyl groups CH_3 and C_2H_5 will serve to block the formation of an extensive hydrogen bond network, and this will reduce the physical range over which proton transfer can occur. Second, the introduction of a solvent molecule like C_2H_5OH into an ion cluster of the type $(H_2O)_mH^+$, i.e., the species considered in reaction 9 above, will by virtue of it's high polarizability reduce the potential energy in the immediate environment of the proton. Theoretical[26,27] and experimental[28,29] studies indicate that proton transfer takes place

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on a time scale of $<2 \times 10^{-12}$ s. This means that although the position of the proton may fluctuate, the time scale for such events will be short in comparison to the average lifetime of an ion cluster. Hence, on the reaction time scale of approximately 1×10^{-6} s the distribution of proton positions will appear highly averaged and maximized at the configuration of lowest potential energy. The experimental results support this view. If on the reaction time scale the proton moved a significant distance from either the methanol or ethanol molecules in $\{ROH \cdot (H_2O)_m\}H^+$ clusters, the decrease in the strength of the ion–induced dipole interaction would be sufficient for loss of ROH to occur, and this is not observed.

The picture in $\{(ROH)_n \cdot H_2O\}H^+$ clusters will be slightly different. If proton transfer throughout the entire ROH network were significant then it might be expected that the alcohol molecules, with their high polarizabilities, would always be preferentially bound to the cluster irrespective of it's size. However, the fact that this type of ion cluster does reach a size where long-range interactions between the proton and the alcohol molecules become important must mean that in the configuration of lowest potential energy some alcohol molecules reside a relatively long distance from the proton site. This introduces the possibility that a subset of alcohol molecules within ion clusters of this type form a stable structure containing the proton, with the remaining ROH molecules situated at the perimeter. Unfortunately, the results in Figures 4 and 5 do not indicate whether such a structure is present and if so how many ROH molecules it contains. It may be possible to investigate this problem further by studying reaction 13 for larger values of n than those given in Figure 7. The reactions involving loss of CH_3OH may then act as a probe as to features of the cluster core. If the size of this central structure can be determined then it will be possible to assign a symmetry number to processes like reaction 7 in the text.

In clusters where the nucleus is an alkali metal ion the thermodynamic data indicate the presence of a well-defined coordination shell for the attachement of species like NH_3.[22-24] Behavior similar to that found in the present work is observed when the enthalpies of clustering for H_2O and NH_3 (μ = 1.48 D, α_P = 2.26 Å^3) are compared. The bond energy for the attachment of a single NH_3 is greater than that for H_2O; but beyond the fourth cluster molecule H_2O is more strongly bound. However, the results in Figures 4 and 5 suggest that at least 9 and quite possibly 10 alcohol molecules are preferentially bound to a proton. That such relatively large numbers are involved could be the result of two factors: (1) the alcohols both have larger polarizabilities than NH_3; and (2) if a fixed number of alcohol molecules form a stable core in association with the proton, then by virtue of the large surface area it could present to the solvent molecules the core would have a high coordination number for the first and subsequent solvation shells. In order to provide a detailed analysis of the behavior of these large ion clusters it may be necessary to take into account not only ion–molecule interactions but also solvent molecule–solvent molecule interactions for those species sited a relatively long distance from the central ion.

Registry No. Proton, 12586-59-3; methanol, 67-56-1; ethanol, 64-17-5.

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Heat of Formation for Acetyl Cation in the Gas Phase

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Abstract: The ionization energies and CH_3CO^+ appearance energies have been measured by photoionization mass spectrometry for a series of substituted methyl ketones. When the *stationary* electron convention for cationic heats of formation is used, a value of 657.0 ± 1.5 kJ mol^{-1} is obtained for $\Delta H_f°_{298}(CH_3CO^+)$ which leads to an absolute proton affinity for ketene of 825.4 ± 3.2 kJ mol^{-1}. Previous acetyl cation heats of formation obtained from photoionization data are shown to be in error because of an incorrect method of calculation. From the results for acetic anhydride an upper limit of ≤ -227 kJ mol^{-1} can be placed on the heat of formation for the acetoxy radical. With few exceptions there is little evidence to suggest any significant excess energy at the decomposition threshold. It is shown that translational energy measurements made at energies greater than threshold cannot be applied in a straightforward manner as thermochemical corrections for the experimental CH_3CO^+ appearance energies.

One of the predominant fragment ions observed in the mass spectra of oxygenated organic compounds is the acetyl ion. Despite the wealth of information available for this gas-phase cation there is still considerable uncertainty surrounding its 298 K enthalpy of formation. The recommended value of Rosenstock et al.[1] is 630 kJ mol^{-1}, which is based on a photoionization value for the appearance energy (AE) of CH_3CO^+ from acetone,[2] corrected for 10.5 kJ mol^{-1} translational energy of decomposition.[3] Other cited photoionization values vary between 648 and 667 kJ mol^{-1}.[1]

In a recent paper[4] we discussed the relationship between photoionization AE measurements and absolute gas-phase heats of formation. It was shown that for the general process

$$AB + h\nu \rightarrow A^+ + B + e^-$$

the standard cationic heat of formation at temperature T could be given by

$$\Delta H_f°_T(A^+) = AE_T - \Delta H_f°_T(B) + \Delta H_f°_T(AB) + \Delta H_{corr} \quad (1)$$

where AE_T is the experimental appearance energy based on a threshold linear extrapolation of the photoion yield curve and ΔH_{corr} is given by

$$\Delta H_{corr} = \int_0^T Cp(A^+)\,dT + \int_0^T Cp(B)\,dT - \tfrac{5}{2}RT \quad (2)$$

The ΔH_{corr} term in eq 1 was not included in the calculated 298 K heats of formation obtained by Rosenstock et al,[1] which will result in a range of underestimated values. It should be noted

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