($E^{0'}$ contains the ln [H$^+$] term) if and only if

$$\frac{[QH_2]}{[Q]} = \exp(E^{0'} - E)\frac{2F}{RT} = B(E) \tag{A-2}$$

It is also assumed that

$$\begin{aligned}\Gamma_0 &= [QH_2]_0 + [Q]_0;\ t = 0\\ \Gamma &= [QH_2] + [Q];\ t > 0\end{aligned} \tag{A-3}$$

"Eliminating" [QH$_2$] from eq A-1 using eq A-2 implies

$$-d\Gamma/dt = k_a[Q]^2B(E) + k_b[Q]^2 \tag{A-4}$$

if and only if

$$-d\Gamma/dt = (k_aB(E) + k_b)[Q]^2 \tag{A-5}$$

From eq A-2 and A-3 it follows

$$\Gamma = (1 + B(E))[Q] \Leftrightarrow [Q] = \Gamma/(1 + B(E))$$

"Eliminating" [Q]^2 from eq A-5 implies

$$-\frac{d\Gamma}{dt} = (k_aB(E) + k_b)\frac{\Gamma^2}{(1 + B(E))^2} \tag{A-6}$$

if and only if

$$-\frac{d\Gamma}{\Gamma^2} = \frac{(k_aB(E) + k_b)}{(1 + B(E))^2}\,dt \tag{A-7}$$

Integration yields

$$\text{(left side)} - \int_{\Gamma_0}^{\Gamma}\frac{d\Gamma}{\Gamma^2} = -\left[-\frac{1}{\Gamma}\right]_{\Gamma_0}^{\Gamma} = \frac{1}{\Gamma} - \frac{1}{\Gamma_0} \tag{A-8}$$

$$\text{(right side)}\ \frac{(k_aB(E) + k_b)}{(1 + B(E))^2}\int_0^t dt = \frac{(k_aB(E) + k_b)}{(1 + B(E))^2}t \tag{A-9}$$

implying

$$\left(\frac{1}{\Gamma} - \frac{1}{\Gamma_0}\right) = \frac{(k_aB(E) + k_b)}{(1 + B(E))^2}t \tag{A-10}$$

which is eq 3.

Registry No. PSCH2, 84432-98-4; PECH2, 84432-99-5; NADH, 58-68-4; graphite, 7782-42-5; 3,4-methylenedioxybenzyl chloride, 20850-43-5; triphenylphosphine, 603-35-0; 3,4-methylenedioxybenzyltriphenylphosphonium chloride, 63368-35-4; 1-pyrenecarboxaldehyde, 3029-19-4; (*E*)-3,4-[2-(1-pyranyl)vinyl]methylenedioxybenzene, 84433-00-1; 3,4-[2-(1-pyrenyl)ethano]methylenedioxybenzene, 84433-01-2; 3,4-methylenedioxybenzyl alcohol, 495-76-1; oxidized PSCH2, 84433-02-3; oxidized PECH2, 84433-03-4.

Solvation of Hydrogen Ions in Mixed Water–Alcohol Ion Clusters

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Abstract: From a study of the competitive decomposition processes of mixed ion clusters of the type $\{(ROH)_n{\cdot}(H_2O)_m\}H^+$ for $n + m < 20$, it has been possible to determine which of the species present in the cluster preferentially solvates the proton. The experiments have been performed on the following alcohols: propan-1-ol, propan-2-ol, butan-1-ol, 2-fluoroethanol, and 2-chloroethanol. In each case the occurrence of either alcohol or water loss from the ion clusters has been monitored as a function of *n* and *m*. Results for $\{(ROH)_n{\cdot}H_2O\}H^+$ show that in small clusters the alcohol molecules preferentially solvate the proton, but as the size of the cluster increases so the preference changes in favor of water. The value of *n* for which this transition occurs appears to depend upon the nature of the alcohol concerned. RRKM calculations have been used to investigate those features of the ion clusters which might be responsible for the observed transition in solvent preference. In particular, it is found that at least one of the reaction critical energies has to decrease as *n* increases, and that at some stage there has to be a transition in the relative magnitudes of the two critical energies. Two models are proposed to account for the experimental observations, and for each it is assumed that the solvent molecules are attached to a central stable nucleus of the form $(ROH)_3H^+$.

Introduction

In a recent publication,[1] results were presented in which the competitive solvation of hydrogen ions in mixed clusters of the type $\{(ROH)_n{\cdot}(H_2O)_m\}H^+$, had been studied as a function of cluster size for ROH equal to either methanol or ethanol. Although the results could be interpreted in terms of ion–dipole and ion–induced dipole interactions, it was only possible to produce a qualitative picture of intermolecular bonding within the ion clusters. The purposes of this paper are to present new experimental data which have been obtained by using alcohols with different molecular properties to those considered previously and to present the results of a series of calculations with which an attempt has been made to develop a more quantitative understanding of the bonding processes within mixed clusters of the above type. As before,[1] our objective in this work is to contribute toward a microscopic understanding of those interactions that exist between an ion and one or more solvent molecules. The study of ion clusters in the gas phase provides us with an opportunity to examine ions at varying stages of the solvation process without interference from the bulk solvent.[2-5]

The interpretation of our previous work[1] took into account those ion–dipole and ion–induced dipole interactions that it might be assumed are present in an ion cluster. It is obvious that this represents an oversimplification and that a detailed description of ion solvation is very much more complicated.[6] In addition to

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those interactions already mentioned, one might also expect the following to be present:[6] (1) lateral interactions between the orientated dipoles surrounding the ion; (2) because the positive charge provides a field gradient, ion–quadrupole interactions, particularly for water molecules, will be important. Also, many of these interactions will not be pairwise-additive; a multipole moment induced in one component will act to modify the charge distribution which generated it.[7]

In the case of water–alcohol ion clusters, the picture is further complicated by proton mobility.[1,8] Unlike metal cations,[2-5] the presence of the proton makes it difficult to identify structures associated, for example, with the formation of a primary solvation shell. It is, however, possible to recognize small stable units, i.e., $(H_2O)_4H^+$ and $(CH_3OH)_3H^+$,[9] which may serve to act as solvation nuclei. Within such a unit the bonding will be strongly electrostatic and a detailed description of the various ion–solvent interactions is obviously necessary in order to provide an accurate picture of the ion cluster's structure.[10,11] Outside these nuclei a more simplified description based, for example, on relative hydrogen bond strengths[12] may be sufficient for the purposes of accounting for the behavior of molecules situated in subsequent solvation shells. However, if in this region the positive charge is still capable of influencing the behavior of solvent molecules, then any hydrogen bond description must include to some extent interactions of the type mentioned above.

Experimental Section

Details of the experimental procedure have been published elsewhere.[1,13] Briefly, neutral clusters are generated by the adiabatic expansion of a mixture of water and alcohol through a 0.005-cm orifice using argon as a carrier gas. Following collimation the modulated cluster beam is ionized by electron impact and mass analyzed on a modified A.E.I. MS 12 mass spectrometer. For all the results presented here an electron impact energy of 70 eV has been used. In addition to providing relative ion intensities, the mass spectrometer has also been used to monitor the intensities of metastable peaks. If an ion has a lifetime in the range 10^{-5} to 10^{-6} 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 instrument and is recorded as a diffuse peak at a noninteger position on the mass scale. Such peaks are normally referred to as metastable peaks.[14] It is this feature of the experiment which provides all the information on the decomposition routes of the ion clusters.

The relative metastable peak intensities have been measured for a number of decomposition processes involving mixed ion clusters composed of water in combination with the following alcohols: propan-1-ol; propan-2-ol; butan-1-ol; 2-fluoroethanol, and 2-chloroethanol. Both propan-1-ol and butan-1-ol produce very clean cluster mass spectra with little or no evidence of monomer unit fragmentation.[15] As a result, there are only a few instances of interference between the normal ion peaks and the metastable peaks. The remaining alcohols do exhibit fragmentation of their respective monomer units within the ion clusters[15-17] and this results in many more cases of overlap between normal and metastable ion peaks with a subsequent loss of information. A number of experiments were also performed on mixed ion clusters of water in conjunction with pentan-1-ol and hexan-1-ol. For the pentan-1-ol system there was extensive overlap between the normal ion peaks and those metastable peaks of interest, with the result that very little useful information could be extracted. Hexan-1-ol forms both protonated and unprotonated ion clusters in conjunction with water, and this led to many instances of interference between metastable peaks formed by the decomposition of parent ions separated by only one mass unit. Because of these problems the results for pentan-1-ol and hexan-1-ol have not been included in this report.

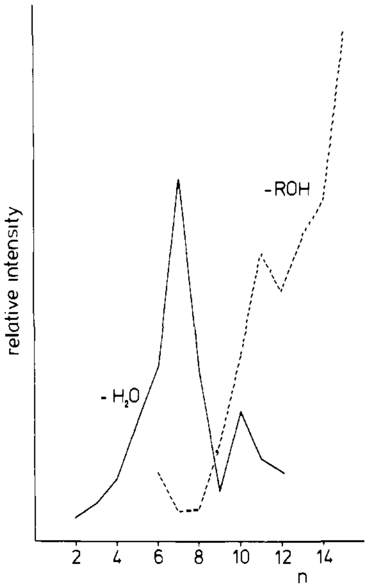

Figure 1. Relative metastable peak intensities for the unimolecular decomposition of $\{(C_3H_7OH)_n{\cdot}H_2O\}H^+$ clusters as a function of *n*. For each value of *n* the metastable peak intensity has been divided by the intensity of the respective parent peak. The solid line is for the reaction involving loss of the water molecule, and the dashed line is for the reaction involving the loss of an alcohol molecule.

Results and Discussion

Information on the preferential solvation of protons in mixed ion clusters can be obtained from our experiment by using the fact that for two competing unimolecular processes, the respective metastable peak intensities will reflect any difference between the critical energies for the two reactions. A semiquantitative justification for this approach has been given previously,[1] and a more detailed disuccion will be presented later in this section. The two competing reactions found to be most suitable for studying the solvation process were[1]

$$\{(ROH)_n{\cdot}H_2O\}H^+ \rightarrow (ROH)_nH^+ + H_2O \qquad (1)$$

$$\{(ROH)_n{\cdot}H_2O\}H^+ \rightarrow \{(ROH)_{n-1}{\cdot}H_2O\}H^+ + ROH \qquad (2)$$

The most facile of these reactions will produce a metastable peak, while the decomposition step involving the loss of that species which is most strongly bound to the ion cluster will not produce a metastable peak of significant intensity. In a sense the single water molecule acts as a probe as to the nature of the dominant interaction present in the ion cluster as its size varies. All the alcohols considered in this and a previous publication have dipole moments which are less than that of water, whereas their polarizabilities are larger than that of water. It is to be expected, therefore, that the shorter ranged ion–induced dipole interaction will favor solvation of the proton by alcohol molecules in small ion clusters. However, the higher dipole moment of water would be expected to provide a stronger interaction with the proton at the increased internuclear distances found in the larger ion clusters. Based on this rather simple analysis, reaction 1 should dominate in small ion clusters, but as the cluster size increases, reaction 2 should become more important. Such behavior has already been observed in mixed ion clusters of water with methanol and ethanol.[1]

Figures 1–5 show plots of the relative metastable peak intensities arising from reactions 1 and 2 as a function of *n* for mixed ion clusters of water with the following alcohols: Figure 1, propan-1-ol; Figure 2, propan-2-ol; Figure 3, butan-1-ol; Figure 4, 2-fluoroethanol; Figure 5, 2-chloroethanol. In the case of butan-1-ol it has also been possible to follow the reaction

$$\{(ROH)_n{\cdot}(H_2O)_2\}H^+ \rightarrow \{(ROH)_{n-1}{\cdot}(H_2O)_2\}H^+ + ROH \qquad (3)$$

over a limited range of *n*. For each of the examples studied the

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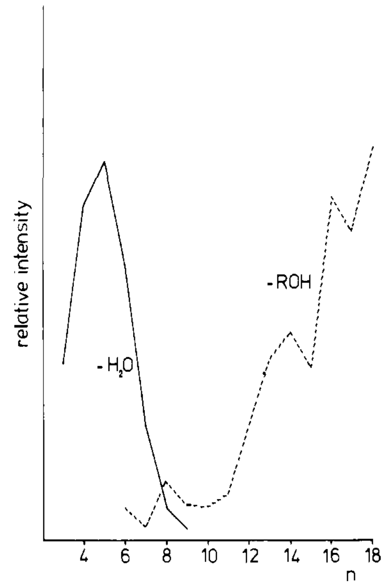

Figure 2. As for Figure 1, but for the unimolecular decomposition of $\{(CH_3CH(OH)CH_3)_n{\cdot}H_2O\}H^+$ clusters.

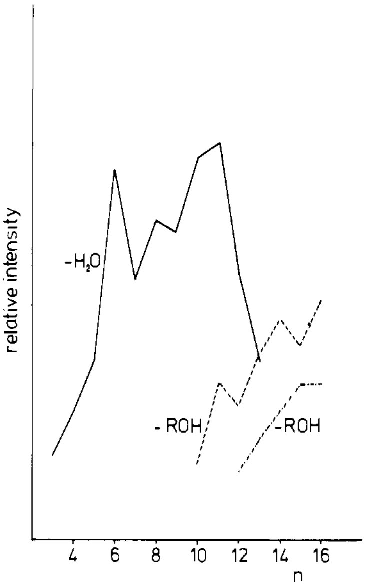

Figure 3. As for Figure 1, but for the unimolecular decomposition of $\{(C_4H_9OH)_n{\cdot}H_2O\}H^+$ clusters. Also shown as a dot-dashed line are the metastable peak intensities resulting from the loss of an alcohol molecule from $\{(C_4H_9OH)_n{\cdot}(H_2O)_2\}H^+$.

basic trend is the same; reaction 1 dominates when *n* is small, but as the size of the cluster increases, reaction 2 becomes the more probable decomposition route. There are, however, difference in the value for *n* at which this transition occurs.

A search was also made for evidence of metastable peaks resulting from reactions involving ion clusters containing predominantly water molecules, i.e.

$$\{ROH{\cdot}(H_2O)_m\}H^+ \rightarrow \{ROH{\cdot}(H_2O)_{m-1}\}H^+ + H_2O \qquad (4)$$

$$ROH{\cdot}(H_2O_m\}H^+ \rightarrow (H_2O)_mH^+ + ROH \qquad (5)$$

For all accessible values of *m* only peaks arising from reaction 4 were observed. Figures 6a and b show plots of the relative intensities of metastable peaks from reaction 4 for propan-1-ol and butan-1-ol.

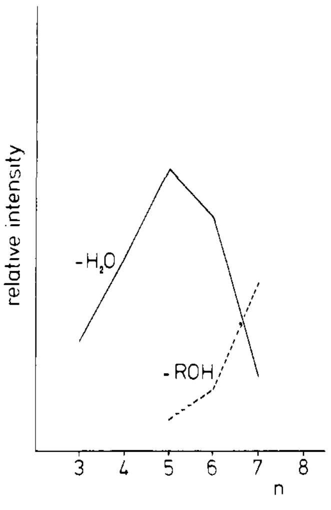

Figure 4. As for Figure 1, but for the unimolecular decomposition of $\{(CH_2FCH_2OH)_n{\cdot}H_2O\}H^+$ clusters.

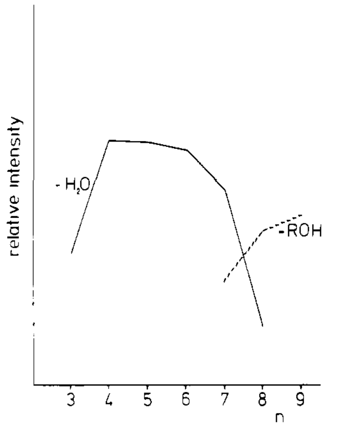

Figure 5. As for Figure 1, but for the unimolecular decomposition of $\{(CH_2ClCH_2OH)_n{\cdot}H_2O\}H^+$ clusters.

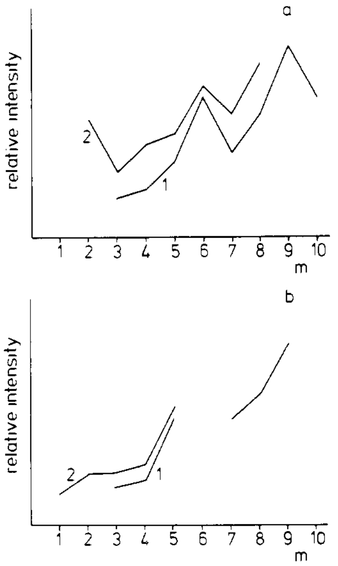

Figure 6. Relative metastable peak intensities for the unimolecular decomposition of $\{(ROH)_n{\cdot}(H_2O)_m\}H^+$ clusters via reaction 4 as a function of *m*. The value for *n* is given beside each curve: (a) propan-1-ol; (b) butan-1-ol.

So far we have only rationalized our results in qualitative terms. The nonequilibrium nature of the experiment means that it is not possible to relate ion intensities directly to thermodynamic quantitites of interest. It is, however, this nonequilibrium aspect which provides the capability for generating the large ion clusters observed. To produce a quantitative interpretation it is, therefore, necessary to make a detailed examination of those aspects of the experiment which led to the observation of metastable peaks and to analyze what relationship, if any, they have to the properties of the ion clusters.

For two competing decompositions ($A^+ \rightarrow B^+$ or $A^+ \rightarrow C^+$) it is possible to show that the respective metastable peak intensities are given by the equations

$$m_B^* = \alpha \int_{\epsilon_1}^{E_{max}} f(E) \frac{k_1(E)}{k_1(E) + k_2(E)} \times \{\exp(-\{k_1(E) + k_2(E)\}t_1) - \exp(-\{k_1(E) + k_2(E)\}t_2)\} \, dE \quad (6)$$

$$m_C^* = \alpha \int_{\epsilon_2}^{E_{max}} f(E) \frac{k_2(E)}{k_1(E) + k_2(E)} \times \{\exp(-\{k_1(E) + k_2(E)\}t_1) - \exp(-\{k_1(E) + k_2(E)\}t_2)\} \, dE \quad (7)$$

where $f(E)$ is the internal energy distribution for A^+, α is a normalization constant, $k_1(E)$ is the rate constant for the reaction $A^+ \rightarrow B^+$ with a critical energy ϵ_1, and $k_2(E)$ is the rate constant for the reaction $A^+ \rightarrow C^+$ with a critical energy of ϵ_2. E_{max} is the maximum internal energy an ion can possess and is approximately equal to the electron beam energy minus the ionization potential of A; t_1 and t_2 are the times at which the ions enter and leave the field-free region, respectively. From RRKM theory the rate constant for the unimolecular decomposition of an ion with internal energy E is given by[18]

$$k(E) = \frac{\beta \sum P(E - \epsilon)}{hN(E)} \quad (8)$$

where β is the reaction path degeneracy, h is Planck's constant, $\sum P(E - \epsilon)$ is the sum of energy states for the reaction transition state, and $N(E)$ is the density of energy states in the activated ion.

Equations 6, 7, and 8 have been used to calculate relative metastable peak intensities for the two competing unimolecular decompositions represented by reactions 1 and 2. In order to normalize the results for each value of n the total parent ion intensity has been calculated from the following expressions

$$P_E = \alpha \int_{\epsilon_1}^{E_{max}} f(E) \exp(-\{k_1(E) + k_2(E)\}t_3) \, dE \quad (9)$$

$$P_0 = \alpha \int_0^{\epsilon_1} f(E) \, dE \quad (10)$$

where ϵ_1 is assumed to be the lowest of the two critical energies, P_E is the fraction of ions with internal energy in excess of ϵ_1 which fail to decompose, P_0 is the fraction of ions with insufficient energy to decompose, and t_3 is the time taken by the ions to travel from the ion source to the collector. The times t_1, t_2, and t_3 were calculated from a knowledge of instrument geometry, accelerating voltage and ion mass.[19] Unfortunately, the shape of the internal energy distribution, $f(E)$, for ion clusters is unknown, but the general form is common to many species[20] and can be represented by the equation

$$f(E) = E^{1/4}(E_{max} - E) \exp\{-(E/E_{max})^2\} \quad (11)$$

Distributions of this form have been used in a number of successful calculations on ion fragmentation processes.[21-23]

For the purposes of evaluating eq 8 all the intramolecular vibrational degrees of freedom were assigned typical frequency values,[24] and each intermolecular vibrational mode was assigned a frequency value of 50 cm^{-1}. One of the latter degrees of freedom was taken to be the reaction coordinate; apart from that all the other vibrational modes were assumed to be unaffected by the formation of the transition state. As it is our intention in these preliminary calculations to minimize the number of parameters, the adoption of a more elaborate transition state would serve no useful purpose. The four integrals were evaluated numerically using Simpson's rule, and the sums and densities of energy states were calculated using the approximation of Whitten and Rabinovitch.[25]

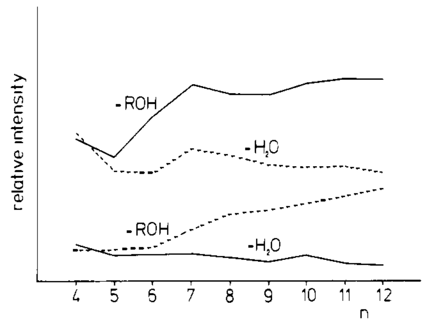

Figure 7. Calculated metastable peak intensities for the unimolecular decomposition of $\{(C_2H_5OH)_n{\cdot}H_2O\}H^+$ clusters as a function of n. The decomposition route is given beside each curve. The solid line corresponds to the case where $\epsilon_1 = \epsilon_2 = 9.0$ kcal mol^{-1} and the reaction path degeneracy, β, is equal to n. The dashed line is for the case where $\epsilon_1 = 8.0$ kcal mol^{-1}, $\epsilon_2 = 9.0$ kcal mol^{-1}, and $\beta = n$. The subscripts 1 and 2 refer to reactions 1 and 2 in the text.

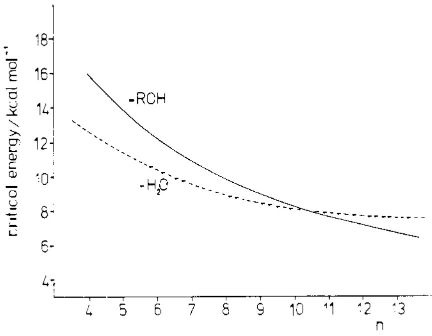

Figure 8. Critical energies used to calculate the metastable peak intensities for the unimolecular decomposition of $\{(ROH)_n{\cdot}H_2O\}H^+$ clusters as a function of n. The dashed line gives ϵ_1 and the solid line ϵ_2.

Figure 7 shows the results of two sets of calculations in which ROH was taken to be C_2H_5OH. In the first calculation it was assumed that $\epsilon_1 = \epsilon_2 = 9.0$ kcal mol^{-1}, and the reaction path degeneracy, β, for reaction 2 was put equal to n. For the second calculation ϵ_1 was set at 8.0 kcal mol^{-1} and ϵ_2 at 9.0 kcal mol^{-1} (the subscripts 1 and 2 now refer to reaction 1 and 2 in the text). Neither set of calculated results displays the behavior found for any of the mixed ion cluster reactions, although it is evident that reaction path degeneracy would ultimately cause the relative metastable peak intensities to crossover at large values of n. Experimental evidence showing that reaction path degeneracy is not the only determining factor has been presented previously.[1] In a further series of calculations the two critical energies were assigned values which were dependent upon n. These energies are plotted in Figure 8 and the two important features are that both critical energies decrease as n increases, and they cross between $n = 10$ and $n = 11$. There is no experimental foundation to the exact energy values presented in Figure 8, but the general trend is characteristic of many ion cluster systems.[2-5] The type of crossover behavior suggested has been observed in experimental measurements of relative bond energies for the attachment of either H_2O or NH_3 to metal ions.[24-26] The relative metastable peak intensities calculated using these energies are given in Figure 9a, and in this case the intensity profiles do reproduce the general

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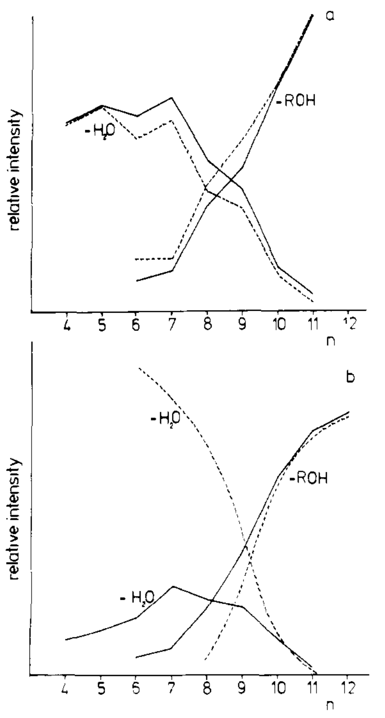

Figure 9. (a) Calculated metastable peak intensities for the unimolecular decomposition of $\{(C_2H_5OH)_n{\cdot}H_2O\}H^+$ as a function of n. The critical energies given in Figure 8 have been used. For the solid line $\beta = n$ has been used for the reaction path degeneracy of reaction 2 and for the dashed line $\beta = n - 3$ has been used. (b) Solid line: as above, but for the unimolecular decomposition of $\{(C_4H_9OH)_n{\cdot}H_2O\}H^+$ clusters as a function n and with $\beta = n - 3$; dashed line: as above but with $\epsilon_1 = 8.0$ kcal mol^{-1} and with ϵ_2 retaining the dependence it has on n as given in Figure 8.

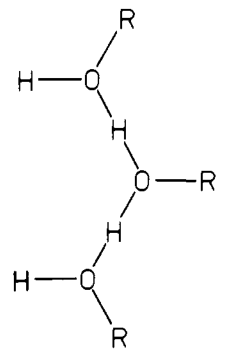

Figure 10. Structure assumed for the stable unit within the alcohol ion clusters.[9,11]

pattern found in the experimental results. It has been suggested[9,11] that the protonated alcohol clusters, and in particular those of methanol, form stable units composed of two alcohol molecules hydrogen bonded to a third protonated species. Such a structure is shown in Figure 10. Additional molecules would then occupy sites that are situated further from the proton, which in turn means that they would be less strongly bound to the cluster. The formation of such a unit could mean that the three central alcohol molecules are effectively eliminated from participation in reaction 2. As a result, the reaction path degeneracy would be reduced by 3. The effect using $\beta = n - 3$ has on the calculated intensities is also shown in Figure 9a. The shape of the profiles is retained, but the crossover point is shifted by approximately 1.

The formation of a metastable peak relies on the decomposition of ions whose lifetimes lie within a well-defined range. Hence a change in the size of the alcohol, or more specifically the number of degrees of freedom, could have an influence on the value for n at which the transition in solvent preference is observed. To examine this possibility, the previous calculations were repeated using vibrational frequencies more appropriate to C_4H_9OH rather than C_2H_5OH. As before, the critical energy dependences given in Figure 8 were used with $\beta = n - 3$. The results of these calculations are given in Figure 9b; as can be seen, the intensities are affected but there is no appreciable shift in the crossover position. From additional calculations it was also found that the value assigned to $E_{\max}$ in eq 6, 7, 9, and 11 had no effect on the position of the crossover. However, it was assumed in each calculation that $E_{\max}$ remained constant and independent of n, and this may not be the case. To summarize, it would appear that the position of the crossover primarily depends upon the relative critical energies of the two competing processes, but that there is a contribution from reaction path degeneracy.

The nature of our experiment is such that measurements are made on peaks that have relatively low intensities, often <2% that of the precursor ion. The correspondingly low signal to noise ratio means that it is difficult to make precise intensity measurements, which in turn means that the crossover positions given in Figures 1–5 are probably only accurate to $n \pm 1$. Hence, our analysis of the experimental data will consider only the trends exhibited by the alcohols rather than a detailed interpretation of individual examples.

If the experimental results are considered in relation to the model calculations, then it can be concluded that in small ion clusters the proton prefers to be solvated by alcohol molecules rather than water molecules. However, at some critical size a transition takes place and the ion clusters begin to display a distinct preference for water molecules in any subsequent solvation. Given that the profiles presented in Figures 1–5 are all similar, it could be assumed that the above statement is true for all the alcohols studied so far.[1] However, the critical size at which the transition takes place does appear to depend upon the nature of the alcohol concerned. This initial preference of protons for alcohol molecules has also been concluded from measurements of ionic transfer free energies in mixed solvents.[29,30] It is most probable that these liquid phase experiments[29] are not sufficiently sensitive to detect subtle changes in free energy brought about by changes in preference beyond the first solvation shell, particularly as the lifetimes of species such as those considered above will be extremely short in the bulk liquid. Thermodynamic data on hydrogen bond strengths in proton-bound mixed dimers of water and alcohol molecules also show that the proton prefers to be bonded to the alcohol rather than the water molecule.[31]

In our previous analysis of the experimental data we considered in some detail the possibility of proton transfer.[1,8] It was suggested[1] that a stable unit, similar to that give in Figure 10, would restrict mobility by virture of the fact that such a structure would have a relatively low potential energy. Although the position of the proton may fluctuate, the time scale of such events will be short in comparison to the experimental time scale, with the result that the distribution of proton positions will appear highly averaged and maximized at the position of lowest potential energy, i.e., within a structure of the type shown in Figure 10. This view is supported by the data presented in Figure 6. If on the reaction time scale the proton moved a significant distance from the alcohol molecule in clusters of the type $\{ROH{\cdot}(H_2O)_m\}H^+$, the decrease in strength of the electrostatic interaction between the proton and the alcohol molecule may be sufficient for loss of ROH to occur, but this is not observed. Our interpretation of the experimental data will assume that the proton resides within a small stable unit of the form $(ROH)_3H^+$. How the remaining alcohol and water molecules interact with this unit can, as we shall show, be viewed in two slightly different ways.

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Table I

molecule	μ, D[a]	α_p, Å^3 [b]	PA, kJ mol^{-1} [c]
C_3H_7OH	1.66	7.43	804
$CH_3CH(OH)CH_3$	1.68	7.48	816
C_4H_9OH	1.66	9.38	
CH_2FCH_2OH		5.50	
CH_2ClCH_2OH		7.48	
H_2O	1.85	1.48	727

[a] Dipole moment. [b] Polarizability, calculated from eq 12. [c] Proton affinity, C_3H_7OH taken from ref 33; $CH_3CH(OH)CH_3$ taken from ref 31.

From molecular orbital calculation[11] on $(CH_3OH)_3H^+$ it has been found that the bonding is essentially electrostatic but that a significant degree of charge transfer also takes place. Additional alcohol molecules are then attached via hydrogen bonds to the terminal H atoms on each free hydroxyl group. The participation of an alcohol molecule in hydrogen bonding results in its terminal H atom becoming more cationic, this enhances further bonding and can lead to the formation of a cluster chain.[11] Such a chain could serve to transmit the proton's influence throughout the ion cluster. Obviously, the addition of alcohol molecules does not continue indefinitely because at some stage the ion cluster displays a preference for a water molecule. If the general features of the molecular orbital calculations on methanol ion clusters are common to clusters composed of other alcohols, then there is a possibility that our experimental results could correlate directly with either the polarizabilities of the alcohols concerned or their proton affinities. This assumes that the dominant contribution to hydrogen bonding is a localized electrostatic interaction between a cationic terminal H atom and a single alcohol molecule, and it involves little or no charge transfer. Table I presents a summary of the available data on dipole moments, polarizabilities, and proton affinities for the alcohols considered in the text. The polarizabilities were calculated from the equation[32]

$$\alpha_p = \frac{(n_D^2 - 1)M3}{(n_D^2 + 2)\rho 4\pi N_A} \tag{12}$$

where n_D is the refractive index measured using the sodium D line, M is the mass, ρ is the density, and N_A is Avogadro's number. Comparing these data with Figures 1–5 shows that the alcohol with the highest polarizability, butan-1-ol, has the crossover situated at a relatively high value of n ($\simeq 13$), while the alcohol with the lowest polarizability, 2-fluoroethanol, has the crossover situated at approximately $n = 7$. Similarly, for methanol which has a low polarizability the transition in solvent preference occurs at $n \simeq 8$.[1] Although the correlation with polarizability may account for trends within the alcohols, it does not explain why the transition in solvent preference occurs because water has a much lower polarizability than any of the alcohols considered in the text (see Table I). On a purely electrostatic basis, therefore, it would seem unlikely that a water molecule could compete effectively with an alcohol molecule in terms of forming a strong hydrogen bond with any of the cationic H atoms.[31] However, it would be possible to accommodate a water molecule if it were assumed that it occupied a nonhydrogen bonded position close to the central $(ROH)_3H^+$. The molecule could be held in position by an electrostatic force dominated by the ion–permanent dipole interaction which would favor the high dipole moment of the water molecule. If, as we have already discussed, the proton remains within the $(ROH)_3H^+$ unit, then the strength of the water molecule's interaction would be almost independent of cluster size. Our experimental observations could then be explained on the basis that in small ion clusters the water–cluster interaction will be weaker than the charge-enhanced hydrogen bonds formed between the alcohol molecules. However, because the influence of the positive charge will decrease as the size of the ion cluster increases, it is possible that at some critical size the hydrogen bond strength could drop below that of the water–cluster interaction, at which point the loss of an alcohol molecule would become the dominant unimolecular reaction. The trend in going from 2-fluoroethanol to butan-1-ol could then be explained in terms of a variation in molecular polarizability and the effect it has on hydrogen bond strengths.

To examine the implications of the above discussion in terms of metastable peak intensities, the calculations on $\{(C_4H_9OH)_n{\cdot}H_2O\}H^+$ were repeated using $\epsilon_1 = 8$ kcal mol^{-1}, i.e., the value it has at the crossover point in Figure 8, while ϵ_2 retained the dependence it has on n as given in Figure 8. The results of these calculations are presented in Figure 9b. Perhaps the most significant feature is that the transition from one decomposition route to the other is more abrupt than in any of the previous calculations. Although such a feature is also present in a number of the experimental results, this alone is not sufficient evidence for us to assume that the above structure is the correct one.

An alternative picture of the ion cluster can be generated by assuming that beyond the central $(ROH)_3H^+$ core, the remaining solvent molecules are held in position by through-space electrostatic interactions. With no formal hydrogen bond network the outer shells of solvent molecules would then be far less structured than in the cluster chain arrangement discussed above. However, it is to be expected that the alcohols would be aligned with their hydroxyl groups pointing toward the central unit. Once again the high polarizabilities of the alcohol molecules would ensure that they are the more strongly bound species in small clusters. But as the size increases, the longer ranged ion–permanent dipole interaction would begin to dominate, and this would favor retention of the water molecule in any subsequent unimolecular decomposition of the ion cluster. This picture of the ion cluster would also account for our experimental observations. However, one cannot be sure that the behavior we equate with a positive charge and a single molecule remains the same when the positive charge is shielded by one or more shells of solvent molecules.[30]

It is most likely that the true cluster structure lies somewhere between the two alternatives discussed above. The positive charge will ensure that the cluster has short range order, but because of the presence of internal energy the solvent molecules, and in particular those at the perimeter, will be in a state of motion and will, therefore, be unable to maintain the optimum conformation necessary for efficient hydrogen bond formation. Thus, it is to be expected that the degree of disorder will increase the further molecules are sited from the central $(ROH)_3H^+$ nucleus. This is much the same behavior that one would expect in a liquid. Indeed, the observed change in decomposition route may mark the onset of disorder within the ion clusters.

Conclusion

The experimental results presented in this paper have extended our previous study[1] of hydrogen ion solvation in mixed water–alcohol clusters. These together with the calculations support the view that there is a change in solvent preference from alcohol to water as the size of the ion cluster increases. The critical size at which this transition occurs appears to depend upon the nature of the alcohol concerned. From neither the experimental nor the calculated results is it possible to identify structures associated with the formation of distinct solvation shells about some central nucleus. However, our results can be interpreted by assuming the formation of a stable $(ROH)_3H^+$ unit at the center of the ion cluster. Results from similar experiments on mixed ion clusters of water and ammonia do exhibit behavior associated with the formation of 2 or more shells of solvent molecules.[34]

Registry No. Propan-1-ol, 71-23-8; propan-2-ol, 67-63-0; butan-1-ol, 71-36-3; 2-fluoroethanol, 371-62-0; 2-chloroethanol, 107-07-3; proton, 12586-59-3.

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