teractions in the disubstituted alkyl β-aminovinyl ketones. All these parameters used in the semiempirical calculations have been determined by following the least-square deviation method and are summarized in Table II. Semiempirical diamagnetic susceptibilities have been calculated by the values of parameters and are included in Table I along with the parametric representation of diamagnetic susceptibilities.

It is obvious from the semiempirical calculations that the semiempirically calculated values of diamagnetic susceptibility agree excellently with their corresponding experimental values, as the divergency between semiempirical and experimental diamagnetic susceptibilities is less than 1%. Such an excellent agreement is due to the fact that, in addition to the other structural factors, the effect of the conjugation and the effect of change of hybridization of the orbital of unshared electrons, which have not been duly accounted for in the Pascal, Pacault, and Hoarau method as well as in the wave–mechanical approach, have been duly considered in the form of parameters in the semiempirical calculation, since the parameters, in view of their diamagnetic susceptibility contributions, depend on the nature of the structural environments present in the molecules.

Since the semiempirical approach has provided interesting and encouraging results of diamagnetic susceptibility for the alkyl β-aminovinyl ketones because it considers almost all the structural factors persisting in these molecules and contributing considerably to the molecular diamagnetism, it can be concluded that the semiempirical approach can be applied not only to the simple organic and organometallic compounds but also to the compounds of polyfunctional groups with sufficient accuracy for calculating diamagnetic susceptibilities. Therefore, the semiempirical approach, no doubt, will prove its importance in resolving various existing structural controversies and will add new dimensions to structural chemistry.

Registry No. $CH_3C(O)CH{=}CHNH_2$, 2976-86-5; $CH_3CH_2C(O)CH{=}CHNH_2$, 6140-26-7; $CH_3(CH_2)_2C(O)CH{=}CHNH_2$, 27485-74-1; $i\text{-}C_3H_7C(O)CH{=}CHNH_2$, 27485-75-2; $i\text{-}C_4H_9C(O)CH{=}CHNH_2$, 27526-43-8; $CH_3C(O)CH{=}CHNHEt$, 27485-76-3; $CH_3(CH_2)_2C(O)CH{=}CHNHEt$, 20965-00-8; $CH_3(CH_2)_3C(O)CH{=}CHNHEt$, 27485-78-5; $CH_3C(O)CH{=}CHNMe_2$, 1190-91-6; $CH_3CH_2C(O)CH{=}CHNMe_2$, 6137-82-2; $CH_3(CH_2)_2C(O)CH{=}CHNMe_2$, 6135-08-6; $i\text{-}C_4H_9C(O)CH{=}CHNMe_2$, 18927-45-2; $CH_3C(O)CH{=}CHNEt_2$, 1809-59-2.

Chemical Reactions on Clusters. 3. Gas-Phase Unimolecular Decomposition of $(CH_3)_2O^+$ in Association with Argon Clusters

A. J. Stace*

Contribution from the Department of Chemistry, The University, Southhampton, Hants SO9 5NH, U.K.

Received November 2, 1983

Abstract: Ion clusters of the type $Ar_n{\cdot}(CH_3)_2O^+$ for n in the range 1–21 have been formed by electron impact following the adiabatic expansion of an argon/dimethyl ether mixture. Despite the apparent fragile nature of these species it is observed that the dimethyl ether ion undergoes extensive unimolecular decomposition without significantly disrupting the argon component of the cluster. The observed product ions are $Ar_n{\cdot}CH_3OCH_2^+$ and $Ar_n{\cdot}CHO^+$. From a detailed experimental study of the factors governing these processes the following conclusions have been drawn: (1) in large clusters excitation of the ether appears to proceed via a charge-transfer mechanism; (2) the excited ether ion decomposes because of the comparatively slow rate of intermolecular energy transfer between it and the argon component; (3) the molecular ion appears to "sit on" the cluster. The results suggest that the ions $Ar_{12}{\cdot}CHO^+$ and $Ar_{18}{\cdot}CHO^+$ are particularly stable; from this observation an analogy has been made between the formation of "magic" numbers of argon atoms and the predicted behavior of small metal clusters.

In two recent publications[1,2] we have presented preliminary results from a series of experiments concerning the unimolecular decomposition of organic ions in association with argon clusters. The general experimental procedure involves the formation of neutral clusters of the form $Ar_n{\cdot}X$. Following electron impact ionization, product ions arising from the unimolecular decomposition of X^+ combined with all or part of the argon component of the cluster are observed. So far approximately 18 examples of this type of behavior have been recorded,[3] ranging from X = I_2 to $(CH_3CH_2)_2CO$.

The purpose of this paper is to present the results of a detailed study of the unimolecular decomposition of the dimethyl ether ion in clusters of the type $Ar_n{\cdot}(CH_3)_2O^+$. A mechanism for excitation of the dimethyl ether ion will be proposed, and we also believe that the results presented will substantiate our previous conclusions regarding the position and behavior of the organic ion with respect to the main body of the cluster.[1,2] Briefly these conclusions were (1) the ion "sites on" rather than "within" the cluster,[1] (2) the excited ion decomposes because of the relatively slow rate of intermolecular energy transfer between it and the argon component of the cluster,[1,2] and (3) individual clusters appear to exhibit a phase transition, with the total product ion intensity being dependent upon whether the argon component is in a liquidlike or a solidlike state.[2]

From the nature of the experiment and the provisional conclusions drawn from the results it is possible to identify several related research areas; the results from which may be useful in the interpretation of the present data. The fact that the ion appears to reside on the surface could provide an interesting analogy with small metal clusters and some of their predicted properties.[4,5] Recent IR photodissociation experiments by Gough et al. suggest that CH_3F occupies a surface site in neutral argon clusters.[6] With regard to the competition between intramolecular and intermo-

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* Present address: School of Molecular Sciences, University of Sussex, Falmer, Brighton, Sussex BN1 9QJ, U.K.

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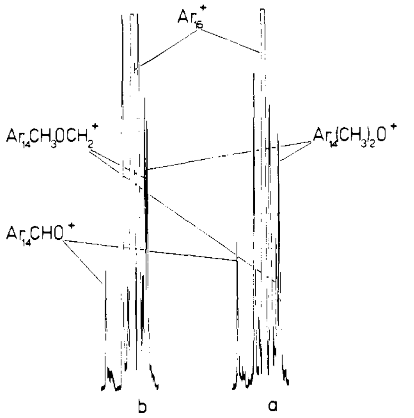

Figure 1. Typical example of the recorded mass spectrum at two different nozzle stagnation pressures for a 100-μm-diameter nozzle: (a) 28 psi; (b) 34 psi. Also present in the spectrum are the Ar^{36} and Ar^{38} isotope peaks and a metastable peak due to the reaction $Ar_{17}^+ \rightarrow Ar_{16}^+ + Ar$.

lecular energy transfer, there is probably some common ground between our experiments and the study of nonradiative processes in liquids and low-temperature matrices.[7-10] Perhaps, however, the most relevant comparison is with vibrational energy transfer and predissociation in van der Waals molecules.[11-18]

Experimental Section

Neutral clusters are generated by the adiabatic expansion of a gas mixture through a pulsed nozzle operating at approximately 20 Hz. Following collimation through a 0.5-mm skimmer positioned 2 cm from the nozzle, the modulated cluster beam is ionized by electron impact and mass analyzed on a modified A. E. I. MS 12 mass spectrometer. In order to form clusters of the type $Ar_n{\cdot}(CH_3)_2O$ it was found necessary to maintain the ether concentration below 100 ppm; any higher than this and the mass spectrum becomes dominated by ether clusters. Under certain conditions it was possible to form $Ar_n{\cdot}\{(CH_3)_2O\}_2^+$. The presence of this ion was found to influence the measured relative intensities of the product ions. We believe this to be due to the reaction

$$Ar_n{\cdot}\{(CH_3)_2O\}_2^+ \rightarrow Ar_n{\cdot}(CH_3)_2O^+ + (CH_3)_2O \qquad (1)$$

Typically, the mixed-cluster intensities were between 10^2 and 10^3 lower than those of the accompanying pure argon clusters. Because of these comparatively low intensities, both the source and collector slits on the mass spectrometer were set to their maximum values. This resulted in some loss of resolution and meant that peaks lying above 800 amu and separated by 1 amu were difficult to resolve completely. Similarly, the peak for $Ar_5{\cdot}CH_3OCH_2^+$ could not be resolved from the metastable peak for the reaction $Ar_8^+ \rightarrow Ar_7^+ + Ar$. The experiments were performed with a nozzle diameter of 100 μm and a range of nozzle stagnation pressures between 20 and 70 psi. Unless otherwise stated, an electron impact energy of 70 eV has been used. Figure 1 shows a typical example of the recorded mass spectrum. Apart from the reaction product peaks there are also present isotope peaks due to Ar^{36} and Ar^{38} and a metastable peak due to the reaction $Ar_{17}^+ \rightarrow Ar_{16}^+ + Ar$. Because of the permanent presence of these peaks, care has to exercised in the selection of reactant ions. The very low intensities involved means that product ion peaks can quite easily be lost through coincidences in mass. Each data point plotted in the subsequent diagrams represents an average taken from at least six spectra of the above type.

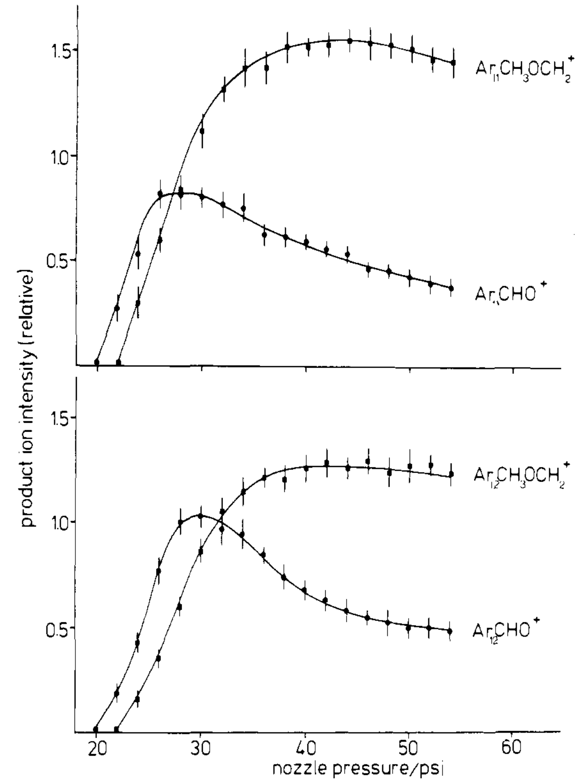

Figure 2. Relative product ion intensities as a function of nozzle stagnation pressure. In each case the intensities of the $Ar_n{\cdot}CH_3OCH_2^+$ and $Ar_n{\cdot}CHO^+$ peaks have been divided by the intensity of the $Ar_n{\cdot}(CH_3)_2O^+$ peak. The error bars represent ±1 standard deviation.

During the course of an experiment the pressure in the expansion chamber is approximately 1×10^{-4} torr, in the collimation chamber it is 1×10^{-6} torr, and in the ion source of the mass spectrometer the pressure remains below 1×10^{-6} torr. The latter low value allows us to disregard the possibility that ion–molecule reactions are responsible for the effects we observe.

Results and Discussion

In the normal mass spectrum of dimethyl ether the following ions are the most intense:[19] $(CH_3)_2O^+$ (46^+), $CH_3OCH_2^+$ (45^+), CH_3O^+ (31^+), CHO^+ (29^+), and CH_3^+ (15^+). The following mechanism has been proposed[20,21] to account for the formation of these ions

$$\mathit{(CH_3)_2O^+} \rightarrow \mathit{CH_3OCH_2^+} + H \rightarrow CH_3^+ + HCHO \qquad (2)$$

$$\rightarrow CH_3O^+ + CH_3 \rightarrow \mathit{CHO^+} + H_2 \qquad (3)$$

The route given for the formation of CH_3^+ is based on heat of formation data; however, Haney and Franklin[22] have suggested that it is formed directly from the parent ion. Bowen and Williams[21] have presented results which indicate that 31^+ is probably CH_3O^+ rather than CH_2OH^+; the second step in (3) above can then proceed via a symmetry-allowed 1,1-elimination reaction.

When dimethyl ether is clustered with argon the following peaks are observed: $Ar_n{\cdot}(CH_3)_2O^+$ ($Ar_n + 46^+$), $Ar_n{\cdot}CH_3OCH_2^+$ ($Ar_n + 45^+$), and $Ar_n{\cdot}CHO^+$ ($Ar_n + 29^+$) for n in the range 1–21. These ions are italic in the mechanism given above. For certain values of n there is evidence of very weak peaks at $Ar_n + 30^+$ and

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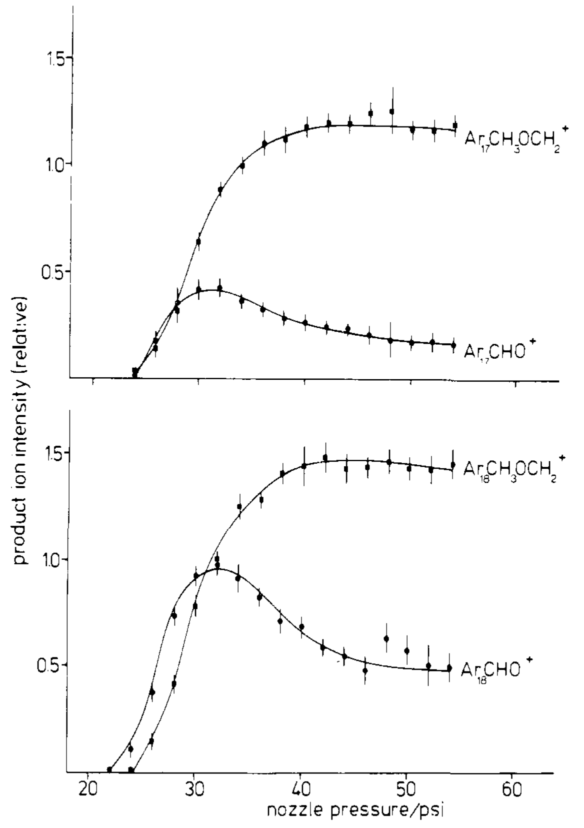

Figure 3. As for Figure 2.

Ar_n + 31^+. By analogy with the normal mass spectrum of dimethyl ether it has been assumed that the peak at Ar_n + 29^+ is $Ar_n{\cdot}CHO^+$ rather than $Ar_n{\cdot}C_2H_5^+$. In a discussion of similar results for the diethyl ether–argon system[1] it was suggested, again from a comparison with the mass spectrum for the isolated ion, that the peak at Ar_n + 29^+ observed in that case was $Ar_n{\cdot}C_2H_5^+$. However, the interpretation of the present results together with other observations[3] may lead us to modify that conclusion. The decomposition route leading to the formation of CH_3^+ does not appear to be present in any of the cluster mass spectra.

For the isolated ether molecule the appearance potentials of the three principal ions observed in the cluster mass spectra are[20,23] $(CH_3)_2O^+$ (10.01 eV), $CH_3OCH_2^+$ (11.04 eV); and CHO^+ (13.96 eV). In view of the fragile nature of the argon component of the cluster, the observation of fragmentation products requiring upward of 1 eV for their formation is somewhat surprising. The energy necessary to remove a single argon atom is going to be of the order of 0.01 eV. Therefore, on the time scale of the experiment ($\simeq 10^{-6}$ s) it should be expected that most of the argon atoms would be lost from the cluster rather than the dimethyl ether undergo fragmentation.

Figures 2 and 3 show the relative intensities of the two principal decomposition products for several different sized clusters plotted as a function of nozzle stagnation pressure. The marked pressure dependence is again an unexpected result. Normally, it is assumed that electron impact ionization is sufficiently violent that the resultant ion retains little or no memory of its neutral state. Adiabatic expansion methods are now routinely used to generate cold molecules,[13,24] and because of the low momentum of the electron, rotational cooling often remains following electron impact ionization.[25] However, depending on the ionization cross section the average internal energy of the resultant ion can be as high as 10 eV when high energy electrons are used. It is this internal energy which determines the fate of an ion with respect to fragmentation, and in most cases it is going to be very much larger than any residual thermal energy. Figure 4 shows the relative intensities of the decomposition products from the isolated ion following adiabatic expansion of the neutral molecule in helium over a range of nozzle stagnation pressures. The absence of any significant pressure effect would suggest that there is no temperature or thermal energy dependence associated with the fragmentation of the isolated ion. There was no evidence of either ether–helium or pure ether ion clusters in the mass spectrum. Also shown in Figure 4 is the pressure dependence of a typical ion cluster resulting from the adiabatic expansion of pure argon. An important feature of Figures 2 and 3 is that at sufficiently low nozzle pressures it is possible to generate $Ar_n{\cdot}(CH_3)_2O^+$ clusters with no evidence of the corresponding fragment ions. A discussion of this pressure dependence has been given in ref 2. It was suggested that such behavior could be due to a phase transition, with the argon component moving from a liquidlike to a solidlike state as the nozzle pressure is increased. The relative product ion intensities are also sensitive to the temperature of the expansion nozzle.[3]

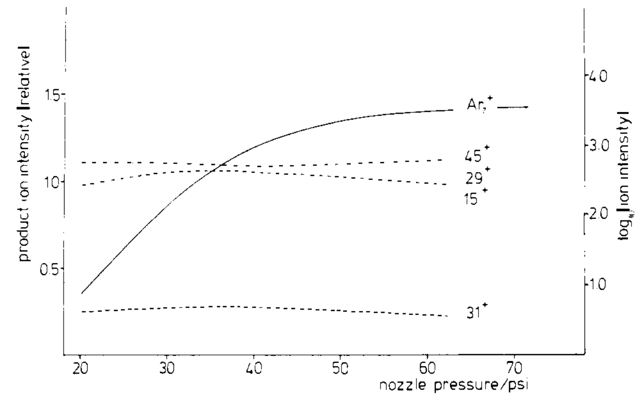

Figure 4. Relative intensities of the decomposition products from the isolated dimethyl ether ion following adiabatic expansion of the molecule in helium over a range of nozzle pressures. Also shown is the absolute intensity variation of an argon ion cluster following the adiabatic expansion of pure argon at various nozzle pressures.

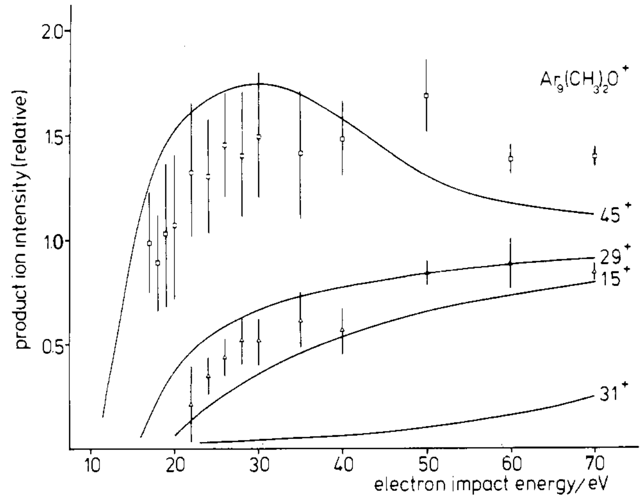

Figure 5. Electron impact energy dependence of the ion decomposition process: (solid lines) dimethyl ether ion; (open squares) $Ar_9{\cdot}CH_3OCH_2^+$; (open triangles) $Ar_9{\cdot}CHO^+$. The error bars represent ±1 standard deviation.

Because the dimethyl ether molecule has a lower ionization potential than that of argon (15.75 eV), the former probably carries the majority of the positive charge. The molecule can acquire this charge in two ways, either by direct electron impact or by charge transfer following ionization of the argon component. In an attempt to establish which of these mechanisms is appropriate the product ion intensities for two values of n were monitored as a function of electron impact energy. Figure 5 shows the relative

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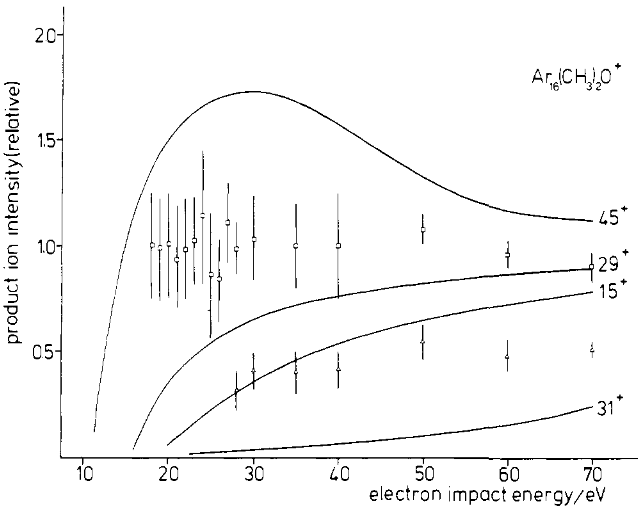

Figure 6. As for figure 5, but (open squares) $Ar_{16}{\cdot}CH_3OCH_2^+$ and (open triangles) $Ar_{16}{\cdot}CHO^+$.

intensities of $Ar_9{\cdot}CH_3OCH_2^+$ (Ar_9 + 45$^+$) and $Ar_9{\cdot}CHO^+$ (Ar_9 + 29$^+$), and Figure 6 those of $Ar_{16}{\cdot}CH_3OCH_2^+$ and $Ar_{16}{\cdot}CHO^+$. Also plotted are the electron impact energy dependences of the products from fragmentation of the isolated ion. In both experiments the nozzle pressure was held at 34 psi. From Figure 5 it can be seen that the product ion intensities from the clusters approximately reproduce the trends observed for the same products from the isolated ion. In Figure 6 this is not the case; within experimental error the intensities of the clustered products are almost independent of electron impact energy. Such behavior could be associated with the ion receiving a fixed amount of internal energy as the result of charge transfer. As further support for this mechanism we find no evidence of fragmentation in those systems for which the following relationship holds: $IP(Ar)-IP(X)-\epsilon_0 < 0$, where ϵ_0 is the critical energy of reaction. From these results we conclude that formation of an excited ion in small clusters probably results from direct electron impact ionization. However, as the size of the cluster increases so charge transfer becomes the dominant mechanism for excited-ion formation. This conclusion would imply that ionization occurs at a localized site on the argon component, which is not an unrealistic assumption. The de Broglie wavelength of an electron at 70 eV is 1.5 Å, which is less than half the diameter of an argon atom. It is anticipated that the use of a different inert gas will help to substantiate the above conclusion.

If it is assumed that none of the argon atoms remain in excited states, then one of the consequences of charge transfer is that excited ether ions are generated with a fixed amount of internal energy, i.e., $IP(Ar) - IP((CH_3)_2O) \simeq 5.7$ eV. This value can be used to place an upper limit on the rate constant for unimolecular decomposition of the ion with respect to each of the available reaction channels, which in turn will provide an estimate of the lifetime of the ion. Rate constants have been calculated from the equation[26]

$$k(E) = \frac{\alpha \sum P(E - \epsilon_0)}{hN(E)} = 1/\tau \qquad (4)$$

where $\sum P(E - \epsilon_0)$ is the sum of energy states in the transition state, $N(E)$ is the density of energy states in the activated ion, E is the internal energy, h is Planck's constant, α is the reaction path degeneracy, and τ is the lifetime of the ion. The sums and densities of energy states were calculated by using the approximation due to Whitten and Rabinovitch.[27] Because of the presence of competitive and kinetic shifts,[28,29] appearance potential data do not provide reliable estimates of reaction critical energies. Therefore, values of ϵ_0 have been calculated from available heat of formation data for the isolated ion and reaction products.[20,30] For the reaction

$$Ar_n{\cdot}(CH_3)_2O^+ \rightarrow Ar_n{\cdot}CH_3OCH_2^+ + H \qquad (5)$$

this gives $\epsilon_0 = 1.01$ eV. When the initial assumption that the reaction proceeds independent of the argon component is made and vibrational frequencies for the ether ion are selected from standard tables,[30] eq 4 gives $k_5 \simeq 1 \times 10^{13}$ s^{-1} with $E = 5.7$ eV. For the purposes of calculating the rate constant for the formation of $Ar_n{\cdot}CHO^+$ it has been assumed that the reaction proceeds via a single step, i.e.

$$Ar_n{\cdot}(CH_3)_2O^+ \rightarrow Ar_n{\cdot}CHO^+ + H_2 + CH_3 \qquad (6)$$

Because the second step in reaction 3 is believed to have a very low critical energy,[21] the rate constant can be calculated on the assumption that it is the first step which is rate determining. The same reasoning also allows us to neglect the possibility of energy partitioning in the first reaction step. Heat of formation data give ϵ_0 as 2.2 eV and the calculated rate constant is $k_6 \simeq 1 \times 10^{12}$ s^{-1}. Alternatively, k_6 can be estimated by using the value for k_5 which is probably the more reliable of the calculated rate constants. Individual product ion intensities in the ion source at a single excitation energy are given by

$$P_i = (k_i/\sum_{j=1}^{m} k_j)\{1 - \exp(-\sum_{j=1}^{m} k_j t_1)\} \qquad (7)$$

for m competing reactions, where t_1 is the time spent in the ion source. The ratio of any two intensities is, therefore, $P_i/P_j = k_i/k_j$. From the calculated value for k_5 and the intensity data presented in Figures 2 and 3 this gives $k_6 \simeq 3 \times 10^{12}$ s^{-1}. If it is also assumed that CH_3^+ could be formed in a single step, i.e.

$$Ar_n{\cdot}(CH_3)_2O^+ \rightarrow Ar_n{\cdot}CH_3^+ + CH_3O \qquad (8)$$

then the calculated critical energy is 3.6 eV and $k_8 \simeq 1 \times 10^9$ s^{-1}. This comparatively low value may be one of the reasons why ions of the type $Ar_n{\cdot}CH_3^+$ are not observed. It may also be that energy partitioning in the first step of reaction 2 reduces the actual value of the rate constant still further. Other possible reasons for the absence of $Ar_n{\cdot}CH_3^+$ will be presented later.

The above rate constants have been calculated on the assumption that the argon component does not participate in the energy randomization process. Obviously this is not the case; if there were no mechanism for dissipating the excess energy resulting from charge transfer, we would not expect to observe any parent ions $Ar_n{\cdot}(CH_3)_2O^+$. However, at all values of n these ions are quite intense. Assuming the argon component behaves classically then for each atom participating in the energy randomization process, individual rate constants will be reduced by a factor $(1 - \epsilon_0/E)^3$. In the case of k_5 this is $\simeq$0.56. In order, therefore, to generate a lifetime which might compete with a typical predissociation time ($\simeq 10^{-9}$ s)[17,18,31] approximately 15 argon atoms would have to participate. To bring the rate constant down to a value where the lifetime of the ion is comparable with the experimental time scale would require the involvement of approximately 26 argon atoms. However, this is obviously an unrealistic proposal. Once a significant fraction of the argon component begins to participate in energy randomization it is most probable that the far more facile predissociation step will become the dominant decomposition route. In effect the ion clusters at that stage will begin to dissipate excess energy through the evaporation of argon atoms. Once such a process has precipitated it will be difficult for the ion clusters to revert to a state where unimolecular decomposition of the ether ion can proceed. This is because loss of energy from the molecular ion will increase its

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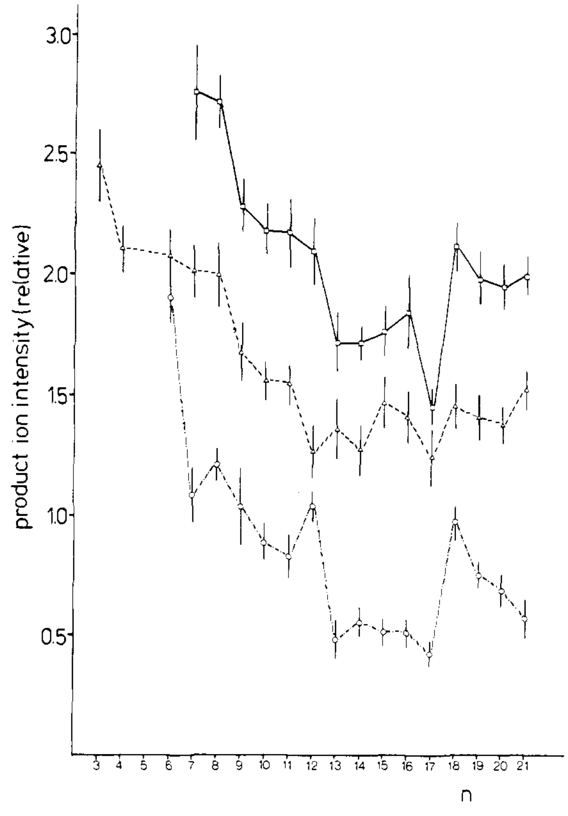

Figure 7. Maximum intensities of each of the two decomposition products as a function of cluster size: (open circles) $Ar_n{\cdot}CHO^+$; (open triangles) $Ar_n{\cdot}CH_3OCH_2^+$; (open squares) $Ar_n{\cdot}CH_3OCH_2^+ + Ar_n{\cdot}CHO^+$.

lifetime which in turn will increase the probability of further energy loss through argon atom evaporation. Thus it is very unlikely that the observed parent ions, $Ar_n{\cdot}(CH_3)_2O^+$, are long-lived excited species. They are more likely to be either ions stabilized through the loss of argon atoms or low-energy ions resulting from the direct ionization of ether molecules on clusters. This latter option becomes less probable as the cluster size increases.

From the examples given in Figures 2 and 3 it can be seen that each product ion intensity reaches a maximum which varies as a function of argon cluster size. This is most evident when $Ar_{17}{\cdot}CHO^+$ and $Ar_{18}{\cdot}CHO^+$ are compared in Figure 3. Figure 7 presents a plot of the maximum intensities reached by each of the two product ions as a function of cluster size. Also plotted are the maxima in $Ar_n{\cdot}CH_3OCH_2^+ + Ar_n{\cdot}CHO^+$, i.e., the total product ion intensity. Because the two product ions reach maxima at different nozzle pressures, the above sum does not necessarily correspond to the addition of the individual quantities plotted in the figure. The results display a number of interesting features and we believe these to be closely related to the structure and chemistry of the ether–argon ion clusters. The high product ion intensities at small n we would suggest are due to argon atom loss from higher order ion clusters. It seems reasonable to assume that excited product as well as parent ions will undergo predissociation, and this will increase the intensities of the small clusters at the expense of the larger ones. Therefore, below $n = 9$–10 it is unlikely that the intensities reflect the properties of individual ion clusters. The ions $Ar_{12}{\cdot}CHO^+$ and $Ar_{18}{\cdot}CHO^+$ appear to have comparatively high intensities; this is also evident from Figures 2 and 3 especially in the case of $Ar_{18}{\cdot}CHO^+$. Fragment ions in the range $Ar_{13}{\cdot}CHO^+$–$Ar_{17}{\cdot}CHO^+$ have relatively low intensities and the total product ion intensity $Ar_{17}{\cdot}CH_3OCH_3^+ + Ar_{17}{\cdot}CHO^+$ is particularly low. Within experimental error there appear to be no distinctive intensity variations in the $Ar_n{\cdot}CH_3OCH_2^+$ ions. Intensity fluctuations of the above type were also observed in product ions from the fragmentation of $Ar_n{\cdot}(CH_3CH_2)_2O^+$ clusters.[1] It was suggested in ref 1 that the molecular ion "sits on" the cluster and that those associated with "magic" numbers of argon atoms, i.e., Ar_{13}, Ar_{19}, etc.,[32] might behave differently from other combinations. The improved resolution of the present data has led to a slight modification of that suggestion. It is clear from Figures 2, 3, and 7 that Ar_{12} and Ar_{18} are the critical sizes; we therefore propose that the oxygen atom provides the additional atom necessary to produce the "magic" number icosahedral configuration. The remaining hydrocarbon part of the ion then protrudes out from the body of the cluster. There are a number of structural and chemical features of the present study and other ion cluster systems[1,3] which support this slight departure from our initial conclusion regarding the position of the molecular ion. It has already been proposed that the ether molecule carries the positive charge. From a consideration of its molecular orbitals[33] it can be seen that the lowest ionization potential of the molecule involves the removal of an electron from a nonbonding orbital on the oxygen atom. Providing there is no significant electron rearrangement, such a charge site would provide a natural center around which argon atoms could cluster. The moderately high polarizability of the argon atom would help to maintain the stability of these structures through ion–induced dipole interactions. Previous work[34] has shown that in the absence of alternative information[35] ion cluster intensities can provide evidence of the presence of stable[34] and unstable[35] ion cluster structures. In a number of mass spectrometric studies the "magic" numbers 13 and 19 have featured promonently[35-37] in the form of ion clusters with relatively high intensities, and recent experiments[35] have demonstrated that Ar_{19}^+ is a stable ion cluster. It is not unreasonable, therefore, to propose that ions in the present system might also adopt such configurations. For this reason we suggest that the relatively high intensities of $Ar_{12}{\cdot}CHO^+$ and $Ar_{18}{\cdot}CHO^+$ are due to the formation of stable icosahedrallike structures with the oxygen providing the necessary additional atom. Because CHO^+ is linear, there would be little or no distortion of the structures through steric interference. Structural similarities between $Ar_n{\cdot}(CH_3)_2O^+$ and $Ar_n{\cdot}CH_3OCH_2^+$ may be one of the reasons why the latter ion does not appear to exhibit intensity fluctuations; this would be exaggerated by the fact that it is the ratio of these two which is plotted. If the above picture of the ion cluster does extend to $Ar_n{\cdot}(CH_3)_2O^+$ and $Ar_n{\cdot}CH_3OCH_2^+$, there could well be steric interference between the argon component and the methyl and methylene groups and this could destabilize any "magic" number configurations. This could also be the reason why the total product ion intensity $Ar_{17}{\cdot}CH_3OCH_2^+ + Ar_{17}{\cdot}CHO^+$ is relatively low.

The proposal that the oxygen atom forms an active part of the structure of the cluster is also supported by the types of chemical reactions observed. In the present system both unimolecular reactions involve retention of the oxygen atom in the product ion. In the mass spectrum of the isolated ether ion CH_3^+ is quite abundant, but the $Ar_n{\cdot}CH_3^+$ ion is not observed as a product from ion cluster fragmentation. If our assumption regarding cluster structure is correct, then, apart from the kinetic analysis presented earlier, the formation of $Ar_n{\cdot}CH_3^+$ would involve displacement of the oxygen atom from its favored position. Similarly, in our preliminary analysis of the $Ar_n{\cdot}(CH_3CH_2)_2O^+$ data it was found that the oxygen atom was retained in the two principal decomposition products. If, in light of the present results, we now suggest that the ion $Ar_n + 29^+$ in the diethyl ether–argon system is $Ar_n{\cdot}CHO^+$ rather than $Ar_n{\cdot}C_2H_5^+$, then the oxygen atom is retained in all the product ions. The original suggestion that $Ar_n{\cdot}C_2H_5^+$ may be present was based on evidence from the mass spectrum of the isolated diethyl ether ion.[20,38] However, of the product ions from $(C_2H_5)_2O^+$ the appearance potential of $C_2H_5^+$ is the highest at 12.5 eV,[20] which could result in the rate constant

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for its formation being quite low. There is also not evidence of product ions from $Ar_n \cdot (CH_3CH_2)_2O^+$, where the oxygen atom is involved in a rearrangement reaction (this is still the case if $Ar_n \cdot CHO^+$ is one of the fragmentation products). For example, 45^+, $CH_3CH{=}OH^+$, is present in the mass spectrum of the isolated ion,[20] and 31^+, CH_2OH^+, is the most intense ion at 70 eV, but neither of these are present in the cluster mass spectra. If the oxygen atom occupies the position suggested, then steric interference from the argon component could be responsible for their absence. The most pronounced intensity fluctuations in the diethyl ether–argon system were found for the ion $Ar_n \cdot CH_3CH_2O{=}CH_2^+$.[1] Like $Ar_n \cdot CHO^+$ in the present study there were intensity maxima in the regions Ar_{12}–Ar_{13} and Ar_{18}–Ar_{19} and an intensity minimum in the region Ar_{15}–Ar_{16}. In view of the obvious size difference between CHO^+ and $CH_3CH_2O{=}CH_2^+$ it would seem unlikely that the same specific numbers of argon atoms could adopt regular structures when partially or completely surrounding these ions. It should be stated that the results reported for the diethyl ether–argon system are very preliminary, in particular a detailed pressure-dependent study has yet to be performed.

The possibility that "magic" numbers of argon and reactant/product atoms can coexist provides an opportunity for making an interesting analogy with the proposed catalytic action of small metal clusters. While we do not wish to present argon clusters as potential catalysts or even as realistic models for metals, a limited comparison is possible. There has been growing interest in the properties of metal clusters because of the possibility these small systems might adopt very different structures from those found in the bulk material.[4,5] This is certainly true for argon. Small clusters adopt icosahedrallike structures[39] whereas large clusters and solid argon have face-centered cubic symmetry.[40] Calculations on small metal clusters,[41–43] such as Cu_{13} and Ni_{13}, show the presence of a well-developed electronic band structure similar to that observed in the bulk metal. However, it is also found that the spatial orientations of some of the electronic orbitals give rise to active sites at the edges and corners of the clusters, and these appear ideally suited for the preferential chemisorption of gas molecules. What the present results would suggest is that it may not be necessary for the metal alone to adopt a stable structure, i.e., Cu_{13} or Cu_{19}, but that one or more of the atoms belonging to the chemisorbed species could contribute to the formation of the structure. Active sites would then consist of "holes" on the surface of the metal cluster. Under such circumstances compatibility of atom size would be an important consideration and could lead to metal clusters being atom-specific catalysts.

Conclusion

In this paper we have presented the results of a detailed experimental study of the unimolecular decomposition of the dimethyl ether ion in association with argon clusters. From a consideration of these and previous experimental data[1] and in conjunction with some approximate calculations, the following conclusions have been drawn: (1) in large clusters excited ether ions appear to be generated by a charge-transfer mechanism. In small clusters direct ionization and charge transfer probably operate in competition; (2) the excited ether ion decomposes because of the comparatively slow rate of intermolecular energy transfer between it and the argon component of the cluster; (3) the structural and chemical information contained within the results would suggest that the product ions, and possibly the parent ion, "sit on" the cluster, with the oxygen atom acting as an active component of the configuration of the cluster. Figure 8 presents a pictorial summary of some of these conclusions. In addition to those given above, the pressure-dependent behavior appears to support an earlier conclusion[2] that the clusters exhibit a phase transition.

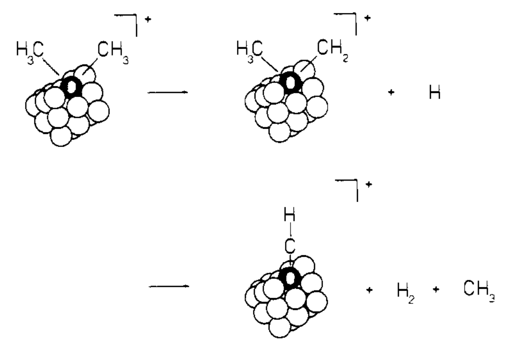

Figure 8. Diagramatic summary of some of the conclusions reached in the present paper regarding the position and reactions of the ion clusters.

It is obvious that many questions remain unanswered. The structure of the neutral cluster is perhaps the biggest uncertainty; although, given the calculated reaction times scales it could be assumed that the neutral cluster has a structure similar to that suggested for the ion. It is unlikely that the system would have time to undergo extensive rearrangement before reaction, and if the neutral molecule were surrounded by argon atoms, it is difficult to see how the resultant ion from such a structure could lose H_2 and CH_3 without incurring the loss of most or all of the argon. It is encouraging to note that recent IR photodissociation experiments support the view that molecules can reside on the surface of clusters.[6] Such behavior could result from an anisotropy in the dipole–induced dipole interaction between the ether molecule and the argon atoms.

The possibility that the reactant ions initially contain very large numbers of argon atoms and that many of these are lost during decomposition cannot be completely ruled out. In this case there would not be a direct relationship between the observed products and those ions we have assumed are the parents. To minimize the possibility of disruptive decomposition we are in the process of studying the system $Ar_n \cdot CH_2O^+$. These ion clusters lose H· only. If, therefore, our assumption regarding the position of the molecular ion is not quite correct, it should be possible for the hydrogen atom to tunnel out from within the cluster without significantly disturbing the argon atoms. However, the same line of reasoning could also be applied to the principal product ion, $Ar_n \cdot CH_3OCH_2^+$, in the present study.

Much of the interpretation of our results has relied on the proposal that the molecular ion receives a fixed amount of internal energy as the result of charge transfer from the argon component. On the basis that the ion contains approximately 5.7 eV of internal energy, the calculated lifetime with respect to each of the two principal decomposition routes is less than the expected vibrational predissociation lifetime. Only through coupling effectively with the cluster can the molecular ion dissipate sufficient internal energy to suppress decomposition. However, there is the possibility that the parent and product ions have different origins, with $Ar_n \cdot (CH_3)_2O^+$ clusters arising from direct ionization of the molecule accompanied by almost no internal excitation, i.e., E is less than the lowest ϵ_0 value. This is essentially the same mechanism that leads to the appearance of parent ions in a normal mass spectrum. The product ions on the other hand could all be formed as a result of the charge-transfer mechanism. If this were the case, however, the ratios plotted in Figure 6 would be expected to decrease with electron impact energy in much the same way as they do in Figure 5. Also, because of the increased probability of the electron hitting the argon component, one would expect to observe a gradual decline in the intensity of the parent ion as the cluster size increases. However, even in ions as large as $Ar_{30}I_2^+$ or $Ar_{40} \cdot (CD_3)_2CO^+$ such behavior is not observed.[44]

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