Photochemical Processes on $Ar_n{\cdot}C_4H_6^+$ Cluster Ions for *n* in the Range 1–40

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It is well established now that, following electron impact ionization, molecular ions can undergo quite extensive fragmentation when in association with inert gas clusters, i.e., Ar_n.[1] Approximately 40 examples of such behavior have now been identified, ranging from diatomics, such as I_2, through to complex polyatomics, such as the methyl formate ion, $CH_3OC(H)O^+$.[2] In the latter example, $Ar_n{\cdot}CH_3OC(H)O^+$ clusters have been observed to undergo two- and three-step sequential chemical processes where, in each case, the fragment ion remains attached to the inert gas component.[2] To date, a serious drawback to the development of a quantitative understanding of these experiments has been the lack of correlation between a given parent ion signal and those recorded for any of the fragments; for the same value of *n* there is no clear relationship between the two sets of observations.

It is evident that a more systematic approach is needed to the study of reactivity in (or on) clusters in order to establish the influence such an environment may have on the chemistry. In this communication the preliminary results are reported of a new series of experiments in which we use existing information on the laser chemistry of single gas-phase ions, to evaluate their behavior within the environment of a cluster. These first results are concerned with reactions promoted in a mass-selected system consisting of the 1,3-butadiene ion in association with argon clusters, $Ar_n{\cdot}C_4H_6^+$. Photochemical processes in isolated, gas-phase $C_4H_6^+$ have been the subject of numerous experimental studies,[3] and two principal reaction paths have been identified:

$$C_4H_6^+ + h\nu \rightarrow C_4H_5^+ + H \qquad (1)$$

$$\rightarrow C_3H_3^+ + CH_3 \qquad (2)$$

Kinetic energy release measurements have also been performed on each of these reactions, the most accurate being those of Bunn and Bowers,[3] who established that, for a photon energy of 2.41 eV, only the products from reaction 1 emerge with an appreciable kinetic energy, ≈0.35 eV. The kinetic energy release distributions could be reproduced using phase space theory, and form this information, together with a study of ion peak shapes as a function of laser polarization angle, it has been concluded that each of reactions 1 and 2 follows a statistical decay pattern.[3] Appearance energy measurements give the barriers to reactions 1 and 2 as 2.31 and 2.48 eV, respectively.[3]

For the experiments discussed here, mixed neutral clusters of argon with butadiene were prepared using a "pickup" technique. The adiabatic expansion of pure argon through a pulsed supersonic nozzle resulted in the formation of clusters with a size range extending out to several hundred atoms. After passing through a skimmer, the cluster beam entered a flight tube approximately 70 cm long, in which the background pressure had been increased to 10^{-5} mbar through the introduction of butadiene gas via a needle valve. During their passage through this region, some of the clusters form collision complexes with butadiene molecules; the latter then remain attached because any excess energy appears to be dissipated through the evaporation of argon atoms from the clusters. On leaving the flight tube, the beam entered the ion source of a high-resolution, reverse geometry, double-focusing mass spectrometer (VG ZAB-E) where the clusters were ionized by electron impact.[4] The "pickup" technique resulted in the formation of a comparatively stable and intense ion beam of mixed clusters of the form $Ar_n{\cdot}C_4H_6^+$; there was no evidence of more than one butadiene molecule becoming attached to an argon cluster.

Ions of a single size were mass-selected using a magnetic sector and then passed into a field-free region, where the butadiene component was photoexcited using a 10-ns pulse from a frequency-doubled (532 nm) Nd:YAG laser, which is aligned coaxially with the ion beam. The overlap between the cluster ion beam and the laser covers a distance of approximately 150 cm. At the point of entry into the mass spectrometer, the laser energy was approximately 10 mJ/pulse. The use of a short laser pulse avoids some of the multiple photon (but not multiphoton, see below) events that have hampered previous attempts to study reactions on clusters using CW lasers. These events are characterized by two or more sequential steps involving photon absorption followed by a response, usually in the form of photofragmentation, and they occur throughout the period ions spend traveling along the 150-cm laser interaction region. During a 10-ns laser pulse, the ions are, more or less, stationary, and our results lead us to believe that the observed reactions are a consequence of the clusters absorbing up to two photons simultaneously. Fragment ion masses were identified using an electrostatic analyzer, and their intensities were measured with a scintillation (Daly) detector in association with gated photon counting.

Following mass selection and photoexcitation, all cluster ions for *n* in the range 1–40 were observed to undergo the following reactions:

$$Ar_n{\cdot}C_4H_6^+ + h\nu \rightarrow C_4H_6^+ + nAr \qquad (3)$$

$$Ar_n{\cdot}C_4H_6^+ + h\nu \rightarrow C_3H_3^+ + CH_3 + nAr \qquad (4)$$

Some loss of hydrogen to form $C_4H_5^+ + H + nAr$ was also observed for small cluster ions, but could not be resolved for the larger species. Clearly, the nature of the neutral reaction products is open to question (see below), and in particular, it is very doubtful if the system would contain sufficient residual energy to shatter the cluster completely. Figure 1a shows a plot of the relative intensities of the parent $Ar_n{\cdot}C_4H_6^+$ ions as a function of size; the only pronounced fluctuation is at $n = 18$, which suggests that $Ar_{18}{\cdot}C_4H_6^+$ may correspond to a "magic number" or stable structure. Stable configurations of molecular and fragment ions in association with 18 argon atoms have been observed previously,[1,5] the structures being rationalized in terms of a single atom or group, such as CH_2 or CH_3, from the molecule combining with the argon cluster to give a stable 19-atom icosahedral arrangement. Such a configuration would imply that a major fraction of the molecule extends out from the surface of the inert gas cluster (see below). Figure 1b shows a plot of the reaction product ratio, $C_3H_3^+/C_4H_6^+$, as a function of cluster size.

A number of earlier studies on the reactivity of molecular ions in association with argon clusters were interpreted in terms of the molecular ion being on or very close to the surface.[1] This view was adopted not only to explain the degree of reactivity exhibited by ions, but also to account for the range of stable (magic number) structures found to be associated with fixed numbers of argon

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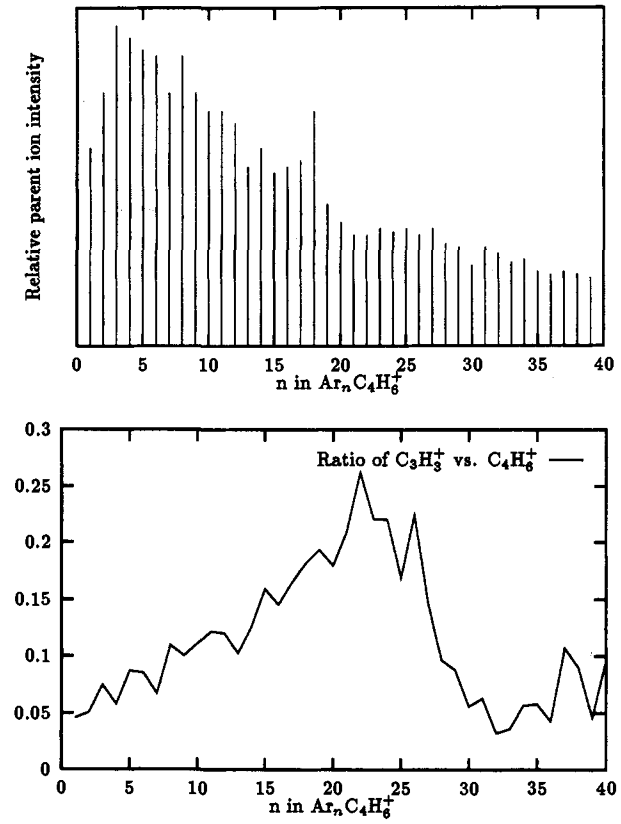

Figure 1. (a) Relative intensities of the Ar$_n$·C$_4$H$_6^+$ cluster ions plotted as a function of *n*. (b) The photofragment ratio, C$_3$H$_3^+$/C$_4$H$_6^+$, plotted as a function of *n*, recorded following the excitation of mass-selected Ar$_n$·C$_4$H$_6^+$ at 532 nm.

atoms, i.e., Ar$_{18}$ and Ar$_{54}$, and fragment ions of very different sizes, i.e., I$^+$ and CH$_2$OH$^+$.[1] The data shown in Figure 1 would appear to support the notion of a surface-bound molecular ion. Previous experiments on the photoexcitation of pure argon clusters ions[6] have found that, for a photon energy of 2.33 eV, approximately 25 atoms are removed. When these experiments are repeated on molecular ions clustered with argon atoms, then slightly different behavior is observed.[7] If the ion is (assumed to be) solvated, then argon atoms are still lost; but far fewer and mixed molecule/argon cluster ions are also observed as fragments. For example, in the case of Ar$_n$·CO$_2^+$ cluster ions, excitation of Ar$_8$·CO$_2^+$ at 514 nm gives Ar·CO$_2^+$ and Ar$_2$·CO$_2^+$ as the most intense fragments.[7] Similar behavior has been seen by Lineberger and co-workers[8] following the photoexcitation of Br$_2^-$·(CO$_2$)$_n$ and I$_2^-$·(CO$_2$)$_n$ clusters where Br$^-$·(CO$_2$)$_m$ and I$^-$·(CO$_2$)$_m$ ($n \leq m$) are seen as fragments. However, that is not the case for the butadiene/argon system; no mixed cluster ions are observed as photofragments.

It is clear from Figure 1 that the butadiene ion is fragmenting and that the product ion intensity exhibits a dependence on the size of the initial cluster (there is almost a 5-fold increase in the relative intensity of the fragment ion on going from Ar to Ar$_{22}$). There are several possible scenarios which could account for some or all of these observations. First, photon absorption could lead to an initial (rapid) separation of the argon cluster from the butadiene ion, and the latter would then undergo unimolecular decomposition on a longer time scale. This being the case, then one of two responses from the argon clusters might have been expected; either the cluster acts as a spectator, in which case there should be almost no size dependence, or the cluster is seen as a heat sink which is gradually increasing in size and, as a result, removes energy and reduces the degree of reactivity, accordingly. A second possibility is that the absorption of one photon removes the molecular ion from the cluster and an additional photon then promotes reactivity. For reasons similar to those given above, we would not expect this sequence of events to result in the type of size dependence seen in Figure 1. The final proposal is that fragmentation of the butadiene ion and the departure of C$_3$H$_3^+$ from the cluster are, more or less, simultaneous events. For this mechanism to operate effectively, the parent ion would have to reside close to the surface of the cluster (as discussed above), and the size dependency would then arise according to the ease with which the cluster allows the ion to rearrange before fragmentation. The neutral photofragment could then (possibly) take the form CH$_3$·Ar$_m$ with $m \leq n$. Since the parent ions must be cold (any residual vibrational energy from electron impact would lead to predissociation of the argon atoms long before reaching the laser interaction region), dissociation is likely to be a two-photon process, one photon increasing the internal energy (either vibrational or electronic) and a second photon then promoting rapid fragmentation. The assumption of a two-photon mechanism would be consistent with the measurements of Bunn and Baer[9] on the fragmentation of C$_4$H$_6^+$ at photon energies similar to those used here. Although the exact nature of the electronic transition(s) concerned has yet to be identified, the chemical reactions exhibited by C$_4$H$_6^+$ are interpreted in terms of a rapid radiationless transition which converts the electronic energy into vibrational energy of the ground state.[9]

Thus, for systems containing up to 25 argon atoms, the presence of the cluster facilitates the two-photon fragmentation of C$_4$H$_6^+$; beyond this point, the degree of reactivity appears to decline quite rapidly, which could be due to two factors. It is possible that some form of cage effect begins to operate; although the sequential evaporation of argon atoms would then leave an isolated C$_4$H$_6^+$, such behavior does not match the existing observations on mixed molecular ion/rare gas clusters discussed above; i.e., photoexcitation removes just a small fraction of the atoms when the clusters are large. A cage process would imply solvation, which does not equate with the continued observation of isolated C$_4$H$_6^+$ as a photofragment. A second possibility is that the presence of a large argon component suppresses an initial butadiene–butyne rearrangement process that may precede the loss of CH$_3$,[9] in which case the ion may be unable to react *before* being ejected from the cluster.

It has been demonstrated that photochemical processes can be promoted on mass-selected clusters consisting of a molecular ion in association with varying numbers of argon atoms. As a consequence of the selection process, a clearer relationship is established between cluster size and the degree of reactivity.

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