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Dissociative photoionisation of acetylene-ethane van der Waals clusters

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Abstract

Intracluster ion–molecule reactions have been studied by dissociative photoionization of mixed acetylene–ethane van der Waals clusters in a supersonic molecular beam. The studies were carried out by recording threshold photoelectron–photoion coincidence mass spectra of the clusters at different photon energies between 10.8 and 11.3 eV. Intracluster reactions have been observed in mixed dimer, trimer, pentamer, and hexamer clusters. In the case of the mixed dimer ion $[(C_2H_2)(C_2H_6)]^+$, two fragment ions result from intramolecular reactions: $C_3H_5^+$ (CH_3 loss), and $C_2H_4^+$ (C_2H_4 loss). This indicates that the dimer ion isomerizes into the 2-butene ion prior to dissociation, as is the case for ethylene dimer ions. Mixed trimer ions also dissociate by CH_3 loss. No intracluster hydride transfer prior to dissociation is observed, although this reaction channel is important in bimolecular $C_2H_2^+ + C_2H_6$ collisions. Two very specific intracluster reactions leading to C_2H_4 loss were observed for pentamer and hexamer mixed cluster ions. A model involving evaporation and intracluster reactions leading to CH_3 and C_2H_4 loss is proposed to explain this surprising result. (Int J Mass Spectrom 199 (2000) 201–209) © 2000 Elsevier Science B.V.

Keywords: Acetylene-ethene; van der Waals clusters; Photoionisation

1. Introduction

To understand the mechanisms of simple gas phase chemical reactions, it is often very informative to compare bimolecular and unimolecular reactions involving the same supramolecular system. Another way of probing the reaction potential energy hypersurface is to photoionize van der Waals molecules formed by aggregation of the two neutral reactants and compare the fragmentation pattern with the bimolecular reaction products.

The $C_4H_8^+$ system has been used as a model system for these studies by several groups over the past 20 years. Experimental studies on this system have probed dissociation dynamics of state-selected $C_4H_8^+$ ions [1–3], bimolecular $C_2H_4^+ + C_2H_4$ ion–molecule reactions involving a long-lived $C_4H_8^+$ intermediate complex [4–6,1], as well as unimolecular decomposition of $(C_2H_4)_2^+$ ethylene dimers [7–9]. Theoretical studies that use phase space theory have been carried out by a number of groups [10–15], and *ab initio* calculations of the $C_4H_8^+$ potential energy surface

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Dedicated to Henri Edouard Audier on the occasion of his 60th birthday.

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have been done [16,17]. All these studies indicate that the two main ionic products, i.e. $C_3H_5^+$ and $C_4H_7^+$, are formed through a $C_4H_8^+$ long-lived intermediate complex dissociation. For both unimolecular and bimolecular reactions, this complex rearranges into the most stable 2-butene ion prior to dissociation.

In this study, we have investigated the same $C_4H_8^+$ supramolecular system by photoionization of mixed acetylene–ethane van der Waals clusters. This method initiates the reaction from a different part of the potential energy hypersurface, which implies that we are probing a higher internal energy domain, for which a new reaction channel is open: $C_2H_5^+ + C_2H_3$. This reaction channel is a nominal H^- transfer. The main goal is to compare the fragment ions produced by the dissociative photoionization of the acetylene–ethane clusters with the bimolecular reaction products of the $C_2H_2^+ + C_2H_6$ ion–molecule reaction, i.e.

$$[C_2H_2—C_2H_6] + h\nu \rightarrow [C_2H_2—C_2H_6]^+ + e$$

$$\rightarrow \text{products}$$

$$C_2H_2^+ + C_2H_6 \rightarrow \text{products}$$

2. Experimental

The experimental setup, called SAPHIRS (acronym for “Spectroscopie d’Agrégats Photoionisés par le Rayonnement Synchrotron”), has already been described in detail [18]. Briefly, a supersonic molecular beam is intersected at right angles by monochromatized synchrotron radiation from a normal incidence 3 m monochromator equipped with a Jobin-Yvon 2200 lines/mm holographic grating, blazed around 100 nm. Photoelectrons and photoions are both analysed in coincidence in a time-of-flight (TOF) spectrometer. Threshold photoelectrons are extracted by a small 1 V/cm electrical field and selected with about 20 meV resolution, by using both a geometrical and a temporal discrimination against energetic electrons. When a threshold electron is detected, photoions are extracted by a pulsed 80 V/cm electrical field, high enough to avoid angular discrimination of energetic fragment ions up to 1 eV kinetic energy. Both parent and fragment ions are mass analysed by their TOF and detected by microchannelplates. Coincidence mass spectra are recorded with threshold electrons as starts and ions as stops of a multichannel analyser. They are then corrected for false coincidences, which are measured by using identical experimental conditions, except random starts are used in place of the threshold electron starts [19]. These false coincidence spectra are subtracted from the real coincidence spectra, after normalization to the same total start number.

Mixed acetylene–ethane clusters are formed in the expansion of a supersonic molecular beam, using a 50 μm nozzle and argon as buffer gas. Pure ethane and argon are used without any further purification, but acetylene is introduced through a dry ice bath in order to remove acetone traces.

3. Results

We found that argon as buffer gas is much more efficient than helium for forming clusters in the expansion. Pure acetylene clusters and pure ethane clusters were easily formed up to pentamers. Mixed acetylene–ethane clusters were much more difficult to make. Fig. 1 shows coincidence TOF mass spectra recorded for different pressure conditions of the molecular beam of argon seeded with acetylene and ethane. We looked for pressure conditions which favor both small clusters and the mixed ones. In Fig. 1(a) the ethane proportion is 5 times that of acetylene, whereas it is only two times higher in Fig. 1(b). This enhances the formation of pure ethane clusters up to tetramers, but does not favor the mixed clusters. In Fig. 1(c) the proportions of the different gases are the same as for Fig. 1(b), but the total stagnation pressure is raised to 2.9 bar instead of 1.9 bar. This increases the number of mixed clusters formed in the expansion, without enhancing too much the higher order cluster formation. So we chose the conditions of the spectrum in Fig. 1(c), i.e. a total pressure of 2.9 bar with 9% C_2H_2, 18% C_2H_6, and 73% Ar.

Ion TOF spectra were recorded in coincidence with threshold electrons. No temporal selection of thresh-

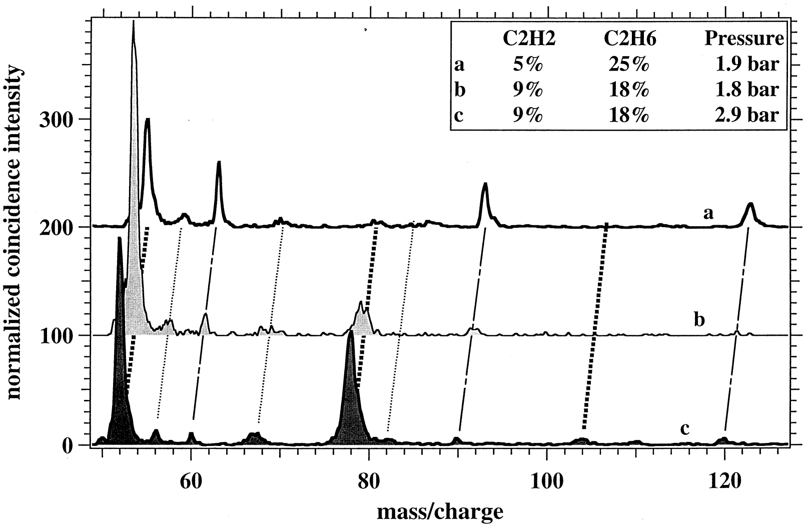

Fig. 1. Coincidence mass spectra recorded for different pressure conditions. Heavy-dotted lines, dot-dashed lines and light-dotted lines indicate pure acetylene clusters, pure ethane clusters and mixed acetylene–ethane clusters peaks, respectively.

old electrons was used in these experiments, which decreased the electron resolution slightly as energetic electrons were not discriminated against completely. This should not effect the conclusions of this study. All coincidence spectra were corrected for false coincidences by using the method described previously. A slow accumulation rate was used, so the rate of false coincidences was never more than 15% of the total coincidence rate. The photon energy range used in these experiments, 10.8–11.3 eV, was below both the acetylene ionization energy (11.4 eV) and the ethane ionization energy (11.54 eV). If the photon energy was raised to 11.4 eV, the percentage of false coincidences caused by the photoionization of monomers was unacceptably high.

Fig. 2 shows an example of a coincidence TOF mass spectrum recorded at 11.3 eV photon energy. Pure acetylene ionic clusters are observed up to pentamers (*m/z* 26, 52, 78, 104, 130) and pure ethane clusters up to tetramers (*m/z* 30, 60, 90, 120). Only mixed $[C_2H_2—C_2H_6]^+$ dimers (*m/z* 56) and mixed $([C_2H_2)_2—C_2H_6]^+$ trimers (*m/z* 82) are observed, the latter one appearing as a very weak peak in the spectrum. The acetylene dimer and trimer ion TOF peaks, which are the dominant peaks in the spectra, are broad compared, for example, to the $C_2H_2^+$ monomer peak. The weak $C_2H_2^+$ peak, which is observed below the acetylene ionization potential, can be explained in several ways: the presence of a weak tail in the photon energy distribution, due to the wide photon bandwidth used in this experiment or some collision induced ionization of acetylene Rydberg states. The width of acetylene dimer and trimer ions is due to kinetic energy release, which indicates that they come from the dissociation of higher order clusters. According to Booze and Baer [20,21], no stable acetylene dimer ions can be obtained by direct photoionization, all dimer ions come from the dissociation of trimer ions. Pure ethane clusters appear as narrow peaks, as narrow as the acetylene monomer ion. This is clearly true for dimer and trimer ions, but less obvious for tetramer ions because of the low signal to noise ratio. It can be concluded that dimer and trimer ions are directly formed from photoionization of the neutral clusters of the same size. This result is unusual for molecular clusters and indicates that there is an overlap between the Franck-Condon regions of the neutral and ionic clusters, i.e. similar equilibrium geometries. The peak for the mixed acetylene–ethane dimer ion are broadened, as can be seen by comparing the *m/z* peak with that of the ethane dimer ion in Fig. 2. This indicates that they are formed by dissociation

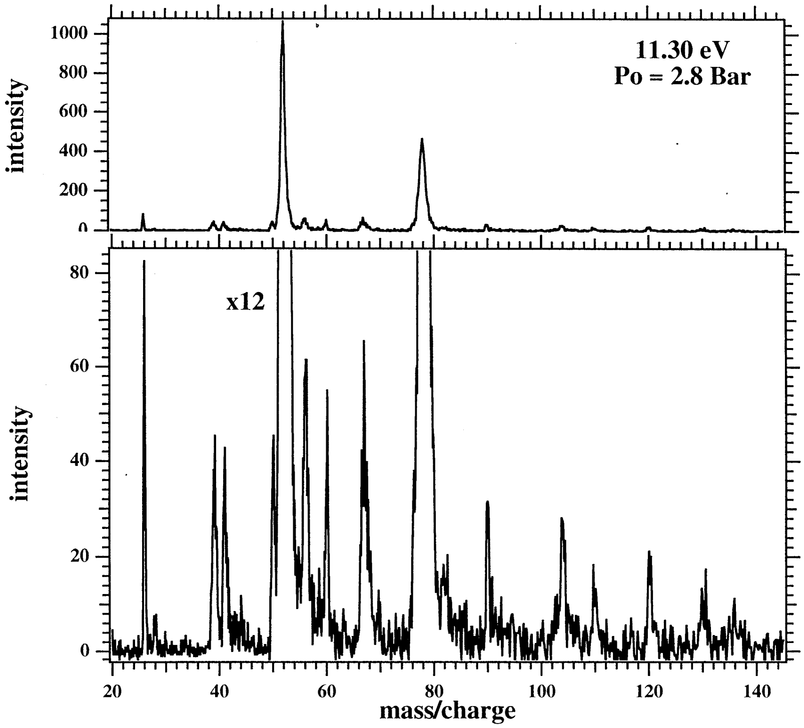

Fig. 2. Example of a coincidence mass spectrum recorded at 11.3 eV photon energy in a mixture of 9% C_2H_2, 18% C_2H_6 in argon with a total pressure of 2.8 bar. The bottom panel is an enlargement of the top spectrum.

of bigger clusters as for acetylene dimer and trimer ions. The other peaks are due to fragments of cluster ions and will be described in the following.

Fig. 3 shows coincidence spectra recorded at seven different photon energies from 10.8 to 11.3 eV. Acetylene cluster ions (*m/z* 52, 78, 104, 130) are already all present at 10.8 eV photon energy, as expected from the previous study of Booze and Baer [20,21]. Pure ethane cluster ions (*m/z* 60, 90, 120) appear at 11.2 eV, which indicates a binding energy for these ionic clusters of 0.34 ± 0.05 eV (11.54–11.2 eV). Mixed acetylene–ethane dimer and trimer ions are already weakly present at 10.8 eV, which indicates a binding energy for these clusters of at least 0.6 eV (11.4–10.8 eV).

Besides parent cluster ion peaks, there are some fragment ions which come from intracluster ion reaction and dissociation. Two peaks, *m/z* 39 ($C_3H_3^+$) and *m/z* 50 ($C_4H_2^+$) come from the dissociation of acetylene dimer ions, corresponding to CH_3 loss and H_2 loss, respectively. These processes have already been studied by Booze and Baer [20,21] and are not the subject of the present study. Pure ethane cluster ions do not dissociate in this photon energy range. Several other fragment peaks are present in the spectra which are all due to the dissociation of mixed acetylene–ethane cluster ions: *m/z* 28, *m/z* 41, *m/z* 67, *m/z* 110 and *m/z* 136. Their assignment to mixed cluster ion dissociation is made by the fact that those peaks are absent in expansions of pure acetylene or pure ethane in argon. The identification of the dissociation processes is more difficult and is made from possible mass combination with stable neutrals. However this assignment is not always unique, as discussed below.

The *m/z* 41 and *m/z* 28 peaks are unambiguously $C_3H_5^+$ and $C_2H_4^+$ fragment ions, coming from the dissociation of $[C_2H_2—C_2H_6]^+$ dimer ions giving CH_3 loss and C_2H_4 loss, respectively. Fig. 4 shows the intensity of these three ions as a function of photon energy, calculated from the integrated peaks of the

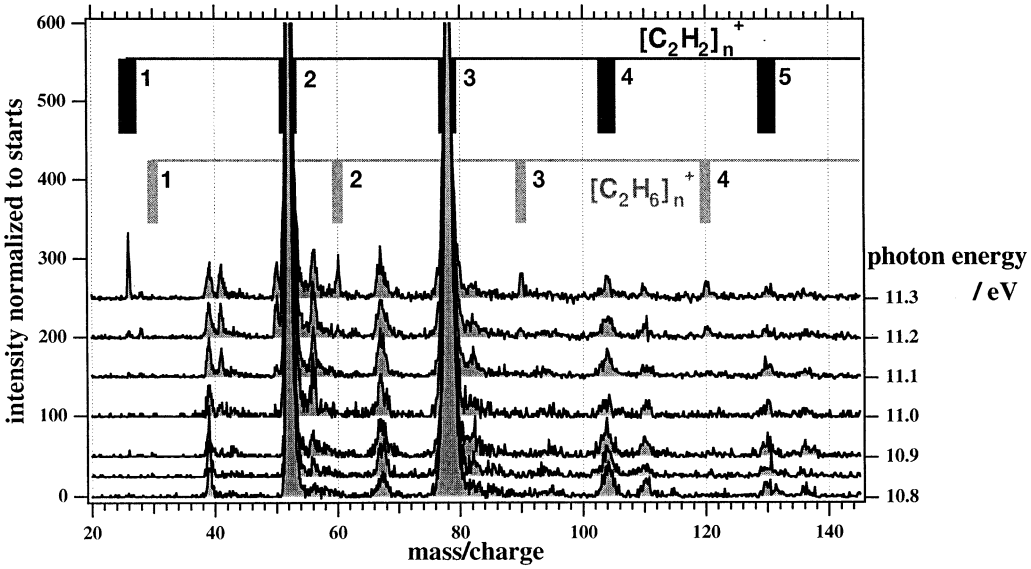

Fig. 3. Coincidence mass spectra recorded at different photon energies in a mixture of 9% C_2H_2, 18% C_2H_6 in argon with a total pressure of 2.9 bar.

coincidence spectra shown in Fig. 3. Parent mixed dimer ions are still present and even more intense than the fragments. This incomplete dissociation is most probably due to the broad internal energy distribution of these dimers coming from higher order cluster dissociation. Dissociation increases as a function of photon energy, i.e. as a function of the internal energy content in dimer ions. The *m/z* 67 fragment peak can

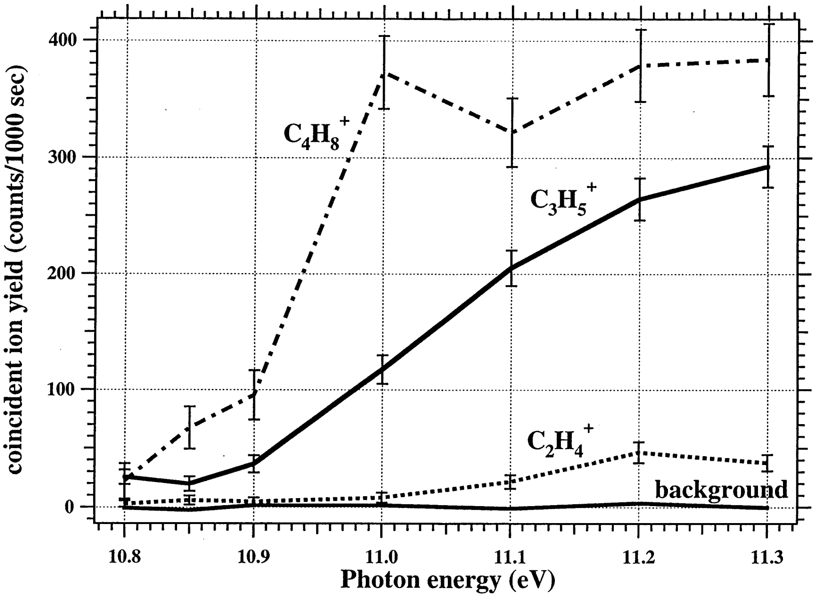

Fig. 4. Coincident ion yields as a function of photon energy.

also be unambiguously assigned to CH_3 loss from the $[(C_2H_2)_2—C_2H_6]^+$ trimer ions. It is the most intense fragment peak of the coincidence spectra, the mixed trimer parent ion being much weaker. The two other fragments, *m/z* 110 and *m/z* 136 can result from two different dissociation processes: H_2 loss from mixed $[(C_2H_2)_2(C_2H_6)_2]^+$ tetramer ions and $[(C_2H_2)_3(C_2H_6)_2]^+$ pentamer ions or C_2H_4 loss from mixed $[(C_2H_2)_3(C_2H_6)_2]^+$ pentamer ions and $[(C_2H_2)_4(C_2H_6)_2]^+$ hexamer ions, respectively. No other fragment ions are produced significantly in this photon energy range. In particular, no $C_2H_5^+$ fragment peak (*m/z* 29) or any C_2H_3 loss from higher order ionic clusters, corresponding to intracluster H^- transfer, are observed within our experimental detection sensitivity.

4. Discussion

Previous studies on molecular clusters [22] have demonstrated the difficulty of forming ionic dimers from direct photoionization of neutral dimers. This is due to the fact that the equilibrium intermolecular distance is usually very different in the neutral and the ionic species. Therefore only the dissociative part of the ionic dimer potential energy surface can be reached in the Franck-Condon region. Further, a supersonic molecular beam usually produces a population of clusters with different sizes and the determination of pressure conditions which favor smaller clusters is somewhat empirical. In order to favor the formation of mixed acetylene–ethane clusters, the best proportion between the two hydrocarbon molecules seems to be twice as much ethane as acetylene. The weak intensity of the mixed ionic clusters underlines the difficulty to produce them compared to pure acetylene ionic clusters. In the pressure conditions used for this study, the mixed cluster distribution seems to be centered around dimers and trimers.

In all pressure conditions which were tested, no narrow TOF peak has been observed for the mixed acetylene–ethane ionic dimers (*m/z* 56), even at low photon energies near threshold. These dimers are thus formed by dissociation of bigger clusters, most probably trimers with a second acetylene molecule, as acetylene makes clusters more easily than ethane. The fact that mixed dimer ions are already observed at 10.8 eV photon energy leads us to conclude that their binding energy is larger than 0.6 eV. However further work with a detailed analysis of the peak shape (width, asymmetry due to possible metastability) would be necessary in order to specify more precisely the origin of these mixed ionic dimers.

The fragmentation of mixed $[C_2H_2—C_2H_6]^+$ dimer ions gives $C_3H_5^+$ and $C_2H_4^+$ fragments. Fig. 4 plots their coincident ion yields as a function of photon energy. The ratio between the three ions does not vary with photon energy within experimental errors. The relative yields of the $C_3H_5^+$ and $C_2H_4^+$ fragments is about 85 ± 5%:15 ± 5% at all photon energies, which is very close to the ratio found by Van der Meij *et al*. [2] for the dissociation of the $C_4H_8^+$ butene ion above the threshold for forming these fragments.

The $C_4H_7^+$ (*m/z* 55) and $C_3H_4^+$ (*m/z* 40) which are known products of the butene ion dissociation could not be extracted from our spectra, due to the presence of intense nearby peaks leading to mass overlaps in these two regions. However the similarity in the fragmentation pattern leads us to think that the acetylene–ethane dimer ion quickly isomerizes to the butene ion prior to dissociation with the following mechanism:

$$[(C_2H_2)_x—(C_2H_6)_y] + h\nu \rightarrow [C_2H_2—C_2H_6]^+ + (x-1)C_2H_2 + (y-1)C_2H_6 + e$$

$$[C_2H_2—C_2H_6]^+ \rightarrow C_4H_8^+ \qquad \text{isomerization into 2-butene ion}$$

$$\begin{aligned} C_4H_8^+ &\rightarrow C_3H_5^+ + CH_3 \qquad \text{dissociation} \\ &\rightarrow C_2H_4^+ + C_2H_4 \\ &\rightarrow C_4H_7^+ + H \\ &\rightarrow C_3H_4^+ + CH_4 \end{aligned}$$

So even though the total available internal energy is much higher than in the case of the ethylene dimer ions [9], the system ends up in the same potential

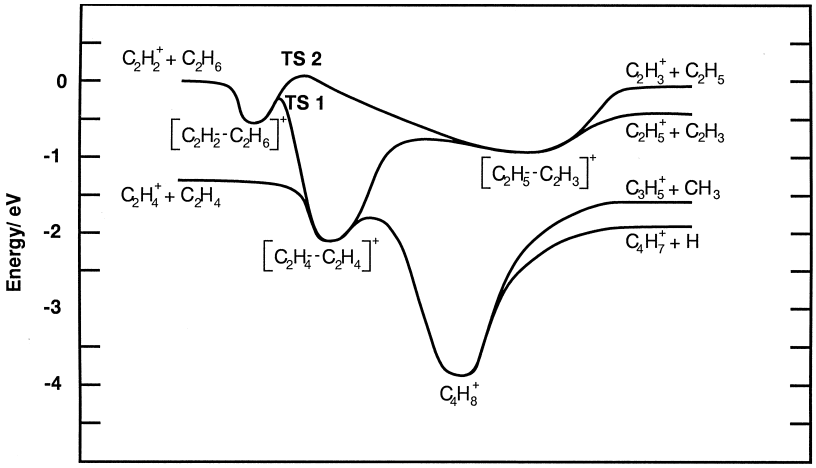

Fig. 5. Schematic potential energy diagram for acetylene–ethane ionic clusters.

energy surface region as when ionizing $[C_2H_4—C_2H_4]$, which finally leads to the most stable 2-butene ion $C_4H_8^+$ isomer.

In contrast with the case of the ethylene dimer ion [9], it is more difficult to imagine a possible chemical path for the isomerization of $[C_2H_2—C_2H_6]^+$ into the 2-butene ion. A possible potential energy diagram is shown in Fig. 5, involving either a double H transfer in one step, or a H transfer followed by a proton transfer to give $[C_2H_4—C_2H_4]^+$ dimer ion prior to isomerization into butene ion. Theoretical calculations would be necessary to further support one of these two hypotheses. A similar mechanism could explain the dissociation of mixed $[(C_2H_2)_2–C_2H_6]^+$ trimer ions leading to the *m/z* 67 fragment corresponding to CH_3 loss (i.e. $[C_3H_5^+—C_2H_2] + CH_3$). The other fragments of the trimer ions, in particular the C_2H_4 loss (*m/z* 54), could not be identified because of overlaps with nearby mass peaks.

No H^- transfer in mixed dimer ions (no $C_2H_5^+$ fragments) is observed, even though the thermochemical onset of this process is expected to be around 11 eV. This is in contrast with the case of the $C_2H_2^+ + C_2H_6$ bimolecular reaction, for which this channel is significant [23]. It supports the hypothesis of a potential energy barrier in this channel and the fact that there is not enough internal energy left in the parent cluster ion. As dimer ions were shown to be produced by dissociation of bigger clusters, some energy is released into kinetic energy, leaving the dimer ions with a lower internal energy content. In order to check whether an H^- transfer is possible in the $[C_2H_2—C_2H_6]^+$ dimer ion before isomerization into the butene ion structure, it would be necessary to increase the internal energy content of the dimer ions. Two possible experimental approaches can be considered: either a two photon photoionization process to produce directly dimer ions from the neutral mixed dimers or using higher photon energies in the single photon photoionization process if the false coincidence problem due to acetylene and ethane monomers can be properly solved. Let us note that this H^- transfer channel prior to dissociation is also not observed in higher order clusters.

For larger clusters, two fragments are observed, *m/z* 110 and *m/z* 136, which are the result of very specific dissociation processes, involving particular tetramers, pentamers or hexamers. These mass peaks can be assigned either to H_2 loss of mixed tetramers and pentamers or C_2H_4 loss from mixed pentamers and hexamers. One possible explanation is that there is a competition between evaporation and intracluster reaction followed by dissociation. If there is a rapid isomerization of $[(C_2H_2)(C_2H_6)]^+$ into $C_4H_8^+$ butene ion inside the cluster, it could be followed by dissociation with CH_3 loss and C_2H_4 loss. The exothermicity of the CH_3 loss process (1.58 eV) could then be used for the evaporation of acetylene and ethane molecules, whereas this evaporation process could not occur associated to the less exothermic C_2H_4 loss process (1.30 eV). This 0.28 eV energy difference could be sufficient to evaporate several molecules if they are weakly bound. This model would explain why only the C_2H_4 loss is observed for mixed pentamer and hexamer ions, whereas mainly the CH_3 loss is observed for mixed dimer and trimer ions. The proposed mechanism for pentamer mixed ions can be summarized as follows:

$$\underset{m/z\ 136}{[(C_2H_2)_3(C_2H_6)_2]^+} \rightarrow \underset{m/z\ 136}{[(C_4H_8)^+(C_2H_2)_2(C_2H_6)]} \qquad \text{isomerization}$$

$$\rightarrow \underset{m/z\ 123}{[(C_3H_5)^+(C_2H_2)_2(C_2H_6)]} + CH_3 \qquad \text{dissociation}$$

$$\rightarrow \underset{m/z\ 67}{[(C_3H_5)^+(C_2H_2)]} + CH_3 + C_2H_2 + C_2H_6 \qquad \text{evaporation}$$

$$\underset{m/z\ 136}{[(C_2H_2)_3(C_2H_6)_2]^+} \rightarrow \underset{m/z\ 136}{[(C_4H_8)^+(C_2H_2)_2(C_2H_6)]} \qquad \text{isomerization}$$

$$\rightarrow \underset{m/z\ 110}{[(C_2H_4)^+(C_2H_2)_2(C_2H_6)]} + C_2H_4 \qquad \text{dissociation}$$

Only the final *m/z* 67 and *m/z* 110 fragment ions are observed.

Similarly for hexamer mixed ions:

$$\underset{m/z\ 164}{[(C_2H_2)_4(C_2H_6)_2]^+} \rightarrow \underset{m/z\ 164}{[(C_4H_8)^+(C_2H_2)_2(C_2H_6)_2]} \qquad \text{isomerization}$$

$$\rightarrow \underset{m/z\ 151}{[(C_3H_5)^+(C_2H_2)_2(C_2H_6)_2]} + CH_3 \qquad \text{dissociation}$$

$$\rightarrow \underset{m/z\ 93}{[(C_3H_5)^+(C_2H_2)_2} + C_2H_2 + C_2H_6 + CH_3 \qquad \text{evaporation}$$

$$\rightarrow \underset{m/z\ 67}{[(C_3H_5)^+(C_2H_2)} + 2\ C_2H_2 + C_2H_6 + CH_3 \qquad \text{evaporation}$$

$$\underset{m/z\ 164}{[(C_2H_2)_4(C_2H_6)_2]^+} \rightarrow \underset{m/z\ 164}{[(C_4H_8)^+(C_4H_8)(C_2H_2)_2]} \qquad \text{isomerization}$$

$$\rightarrow \underset{m/z\ 138}{[(C_2H_4)^+(C_4H_8)(C_2H_2)_2]} + C_2H_4 \qquad \text{dissociation}$$

As only the final *m/z* 67 and *m/z* 138 fragment ions are observed, it implies an evaporation of three molecules following the CH_3 loss process. The intense *m/z* 67 peak could thus be well explained with this model, as it could result from different mixed cluster ions.

As a consequence of this possible interpretation, we favor the hypothesis of the assignment of the *m/z* 110 and *m/z* 138 peaks to C_2H_4 loss from mixed $[(C_2H_2)_3(C_2H_6)_2]^+$ pentamer ions and $[(C_2H_2)_4(C_2H_6)_2]^+$ hexamer ions, respectively. Ab initio binding energy calculations in this type of clusters would be necessary to further support this model.

Further studies, both experimental and theoretical, are necessary to better understand those surprising specific intracluster reactions. One could, for example, vary in a wider range the relative proportions of acetylene and ethane in the expansion. The much higher intensity delivered by the new undulator beamline of the Super-ACO Storage Ring should allow us to continue this study in better conditions.

5. Conclusion

Mixed acetylene–ethane cluster ions can be produced in a molecular beam containing about 20% acetylene, 10% ethane and 70% argon at a total stagnation pressure of 2.9 bar. They are shown to come from the dissociative photoionization of higher order neutral clusters, because they carry some kinetic energy.

In the threshold photoelectron–photoion coincidence mass spectra recorded between 10.8 and 11.3 eV photon energy range, two fragment ions, namely $C_3H_5^+$ (CH_3 loss) and $C_2H_4^+$ (C_2H_4 loss), are dissociation products resulting from intracluster reactions in $[(C_2H_2)(C_2H_6)]^+$ mixed dimer ions. This leads us to propose that the dimer ion isomerizes into the 2-butene ion prior to dissociation, as is the case with ethylene dimer ions. Mixed trimer ions also dissociate giving CH_3 loss. No intracluster H^- transfer reaction prior to dissociation is observed, whereas this reaction channel is an important one in bimolecular $C_2H_2^+ + C_2H_6$ collisions.

Two very specific intracluster reactions prior to dissociation are observed for pentamer and hexamer mixed cluster ions. They might be due to an intracluster isomerization of $[(C_2H_2)(C_2H_6)]^+$ into $C_4H_8^+$ butene ion followed by C_2H_4 loss, whereas the CH_3 loss leads to *m/z* 67 $[(C_3H_5)^+(C_2H_2)]$ fragment ion after evaporation of the excess acetylene and ethane molecules. This model will require further experimental and theoretical work for verification.

Acknowledgements

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