Benzene Cation from Acetylene Clusters – Precursor of PAHs in Space

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Abstract. The explanation of formation of Polycyclic Aromatic Hydrocarbons in space is one of the biggest challenges of modern astrochemistry. Neutral gas phase pathways are complicated and have extremely low cross sections. Here we present the experimental evidence for the effective formation of benzene cation in small acetylene clusters, after electron irradiation. This can be important heterogeneous chemistry step of PAH formation occurring on interstellar ices.

Introduction

Clusters are aggregates of several to several thousands of molecules, allowing us to study the processes on the border between the gas phase and bulk. Additionally clusters are naturally occurring species of high importance, since they can provide specific environment for chemical reactions. For example water ice nanoparticles play crucial role in ozone depletion process, as known from famous work of Molina [see Molina 1995].

In the interstellar space, nanoparticles are found in dark molecular clouds, where they can play significant role in the formation of complex molecules [Tielens 2005]. In the gas phase, formation of complex molecules is rather complicated multistep process with low cross section. By the way of example we can imagine the simplest reaction of two hydrogen atoms forming H₂. After the H-atom association the energy of the system still exceeds the dissociation limit and the H₂ molecule has to be stabilized in collision with a third partner, which can carry away the excess energy in the form of its kinetic energy. The dissociation proceeds on a time scale significantly faster compared to the collision rate in interstellar medium leading to the conclusion that the reaction is nearly impossible.

On the other hand, the clusters can significantly enhance the reaction probability by essentially two effects: first, they serve as reservoir for the reactants; and second, they act as an efficient energy bath for the reaction product stabilization. The cross section for adsorption of the atom on the cluster surface is relatively high, usually significantly higher than geometrical cross section, as shown in our recent publication [Lengyel et al. 2012]. After the adsorption, H atom can remain on the cluster surface for long periods – cluster acts as a reservoir of reactants. After adsorption of next H atom, the probability of meeting of the two species is stochastic process inversely proportional only to the cluster surface. Therefore, the probability for the two reactants to meet is higher on smaller clusters as studied in present work, in comparison to large nanoparticles or grains, usually modelled by bulk surfaces. After the reaction occurs, the product H₂ can be stabilized through energy dissipation into the cluster, e.g. the cluster vibrational modes are excited and eventually some of the cluster constituents are evaporated. This behaviour is crucial for heterogeneous associative reactions and will be of the main interest in the present work.

When moving to larger systems like Polycyclic Aromatic Hydrocarbons (PAHs) situation is more complicated. The example can be napthalene formation at low temperatures recently studied in Kaisers group [Parker et al. 2012]. The first experimentally confirmed step to formation of PAHs in space is result of interaction of vinylacetylene and phenyl radical. Both precursors are formed in complex photochemical reactions proposed previously [Kaiser et al. 2011, Mebel et al. 2008]. On the other side in clusters complex reactions can occur even after absorption of one electron by the cluster/reactant complex [e.g., El Shall 2008].

Here we focus on the formation of benzene cation after irradiation of acetylene clusters by electrons. This is important precursor of PAHs in ion-molecule reactions [e.g. Bohme et al. 1991]. Additionally, it is well known [e.g., Miyazaki et al. 2004] that on water clusters, benzene cation undergoes proton transfer to form H₂O⁺ – phenyl radical pair which is of high importance in the neutral – neutral chemistry, as explained before.
The benzene cation formation after electron irradiation of acetylene clusters was first proposed in Garvey group [Gumina et al. 1992, Coolbaugh et al. 1992]. In their works the formation of stable benzene cation was deduced from the electron ionization mass spectra exhibiting strong m/z 78 “magic” peak. Extensive studies were performed in the group of El Shall [Momoh et al. 2006, 2007] to illuminate the structure and formation of the ion. The combined experimental and theoretical works were based on the IMS-MS approach and, in principle, confirmed the conclusions of the previous works that benzene ion is formed. On the other side, several conformers of (C\textsubscript{2}H\textsubscript{2})\textsuperscript{3+} ion are reported in the recent work of Relph et al. [2009]. In present work we provide a possible explanation for the differences by measuring the mass spectra of acetylene clusters produced under different expansion conditions. Additionally, electron impact ion yields are reported for acetylene clusters providing further experimental proof of the covalently bound (C\textsubscript{2}H\textsubscript{2})\textsuperscript{3+} ion formation after electron irradiation of the acetylene clusters.

**Methods**

The experiments were carried out by means of a CLUster Beam (CLUB) apparatus that has already been described in detail elsewhere [Farnik, 2011].

The sketch of the system is in Figure 1. It is molecular beam experimental setup built to study electron and photon induced chemistry in clusters. In the present study clusters were formed by expansion of acetylene (Prixair 99.6%) in argon (Messer 99.996) buffer through divergent nozzle into vacuum. Expansion mixture of 10% acetylene in argon was prepared in stainless steel cylinder connected to nozzle. Nozzle diameter was 55 µm and temperature was kept at 243K.

Recently the CLUB apparatus has been extended with a new beam analysing technique – Bipolar Erasable Energy Reflectron Time of Flight mass spectrometer (BEER-TOF) mounted orthogonally to the beam axis. It was custom built on the basis of our specifications by Stefan Kaesdorf, Geräte für Forschung und Industrie, Munich. The system is able to detect ions in the mass range above 10 kDa with resolution approaching \( m/\Delta m = 10000 \) in both positive and negative ion mode. Ionization can be induced by external laser or by built-in electron source with pulsed (12 kHz) electron gun with variable energy in (5–90) eV range and resolution \( \approx 0.7 \) eV, which is the typical energy spread of the used thermionic tungsten cathode. This is sufficient for relative cross section measurements in positive

![Figure 1. Scheme of CLUB experimental setup. The parts used in present experiment are signed red = cluster beam source and reflectron TOF mass spectrometer (BEER – TOF).](image)
ion mode. Ions are detected on microchannel plate detector in chevron configuration and collected using time to digital conversion (TDC) method. In the present experiments the ion signal was detected as the function of two parameters m/z ratio and electron energy. Both mass spectra and electron energy dependent ion yields could be then extracted from the obtained data. Appearance energies of particular ions were derived from Wannier fits of the measured energy dependent ion yields near threshold \cite{Wannier1953}.

Results & Discussion

The mass spectra of acetylene clusters are shown in Figure 2 measured at electron energy of 70eV for two different stagnation pressures: 2bar and 4bar corresponding to smaller and larger clusters, respectively.

Only pure acetylene ion fragment clusters are observed, no species mixed with Ar despite the 10 times higher Ar content in the expansion. This is caused by high difference between C$_2$H$_2$ cluster binding energy of $\approx$120meV and much lower Ar cluster binding energy of $\approx$12meV: although the collisions with Ar are much more frequent, the Ar atoms evaporate from the cluster when C$_2$H$_2$ coagulation occurs. On the other hand, due to low acetylene concentration in the argon buffer the expansion conditions are expected to be similar to that of pure argon. The mean cluster sizes in the pure Ar expansion at the conditions specified would be 59 and 184 for 2 bar and 4 bar stagnation pressure, respectively (shown by light and dark lines, respectively, in Figure 2) \cite{Hagena1992}. Assuming that the energy released by the acetylene coagulation should evaporate all the Ar atoms from the clusters to yield the pure acetylene clusters, we can obtain an estimate for the lower limits of the observed acetylene cluster mean sizes to be $\approx$6 and $\approx$18 molecules. This is a rough estimate, however, based on this we can assume that the neutral cluster sizes of clusters generated in our experiments were in the range tens of acetylene molecules. The estimation of the cluster size from the known expansion conditions is discussed in more detail in our previous publication \cite{Farnik2009}. It is also worth mention at this point that the ionization threshold measurements below provide further evidence that pure acetylene clusters were the neutral precursors of the observed ion fragments, and not Ar-acetylene mixed clusters from which the Ar atoms would have evaporated upon ionization.

Figure 2. Measured Mass spectra for (a and b) C$_2$H$_2$/Ar coexpansion and c) pure Ar expansion.
The mass spectra show also the doubly charged ions of type ($\text{C}_2\text{H}_2)_n^{2+}$ in addition to the singly charged ($\text{C}_2\text{H}_2)_n^+$ and ($\text{C}_2\text{H}_2)_n\text{CH}^+$ progressions. These are formed for $n > 54$ since the smaller clusters cannot accommodate two charges due to their coulomb repulsion (see e.g. [Mahr et. al, 2007]). Besides, these doubly charged ion fragments also show that clusters up to the sizes of $\approx 100$ molecules are present in the neutral beam.

Focusing just on dimer and trimer we can see the decrease of the signal with the increase in the cluster size, Figure 2b. This can be caused by the mechanism of the trimer ion formation which can be different from small and from larger clusters. Additionally, the dimer/trimer ratio stays nearly constant. This points to a strong correlation of these fragments which was already studied in the work of [Booze et al., 1993].

Appearance energies for several cluster ions were evaluated from the fits of electron energy dependent ion yields, as depicted in Figure 3. The values for particular ions are summarized in Table 1. $\text{H}_2\text{O}$ background signal (beam off) was used for energy calibration according to NIST value 12.621 eV [Lias 2011]. Two different cluster progressions observed in mass spectra ($\text{C}_2\text{H}_2)_n^+$ and ($\text{C}_2\text{H}_2)_n\text{CH}^+$ have two different appearance energies $\approx 11.7$ and $\approx 21.5$eV. These are in good agreement with the ionization energy of acetylene 11.4eV ($\text{(C}_2\text{H}_2)_n^+$ progression) and appearance potential of CH$^+$ ion from acetylene molecule $\approx 21$ eV ($\text{(C}_2\text{H}_2)_n\text{CH}^+$ progression) [Plessis & Mamet, 1986]. The cluster ion formation can be then clearly attributed to direct ionization of acetylene in the first case and dissociative ionization of acetylene into CH$^+$ in the latter one. However, there is a clear exception in the case of ($\text{C}_2\text{H}_2)_2\text{CH}^+$ cluster ion which is formed at $\approx 13.7$ eV far below the threshold for mentioned dissociative ionization channel of acetylene. At such a low energy there is only one rational explanation for its formation – dissociation of covalently bound ion formed after electron ionization: most probably the benzene cation.

**Conclusion**

Mass spectra of acetylene cluster ions are presented in so far unreported range. The values of appearance energies for several cluster ions were measured in the present experiment. $\text{C}_3\text{H}_3^+$ ion appearance energy could be rationalized by considering the dissociation of covalently bound cation within the clusters. Such ions are formed after electron irradiation, in process usually referred to as cluster ion polymerization. Further experiments with acetylene clusters formed on the surface of ice nanoparticles are in progress to model the conditions in interstellar medium.

**Table 1.** Values of Appearance Energies (AE) of selected ionic fragments. Background $\text{H}_2\text{O}$ value for calibrations and $\text{N}_2$ for further test of the approach.

<table>
<thead>
<tr>
<th>Assigned Ion</th>
<th>$\text{H}_2\text{O}^+$ (18)</th>
<th>$\text{N}_2^+$ (28)</th>
<th>CH$^+$ (13)</th>
<th>C$_2$H$_2^+$ (26)</th>
<th>C$_3$H$_3^+$ (39)</th>
<th>(C$_2$H$_2$)$_2^+$ (52)</th>
<th>(C$_2$H$_2$)$_3$CH$^+$ (65)</th>
<th>(C$_2$H$_2$)$_3^+$ (78)</th>
<th>(C$_2$H$_2$)$_4^+$ (91)</th>
<th>(C$_2$H$_2$)$_5^+$ (104)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AE $^+/-0.5$ eV</td>
<td>12.621</td>
<td>15.6</td>
<td>23.6</td>
<td>11.8</td>
<td>13.7</td>
<td>11.7</td>
<td>21</td>
<td>11.6</td>
<td>21.5</td>
<td>11.7</td>
</tr>
</tbody>
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References


