

## Polymerization of Ionized Acetylene Clusters into Covalent Bonded Ions: Evidence for the Formation of Benzene Radical Cation

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The chemistry of acetylene has received considerable attention and continues to be an active area of research.<sup>1,2</sup> This is due not only to the acetylene polymerization to produce a variety of industrially and technologically important conducting polymers<sup>1</sup> but also to the important roles of acetylene in flames and combustion processes, particularly for the mechanism of soot formation, and in interstellar clouds particularly for the origin of larger hydrocarbon and other complicated molecular species observed in interstellar medium.<sup>2</sup>

Since the discovery of acetylene and benzene in protoplanetary nebulae under powerful ultraviolet ionizing radiation, efforts have been made to investigate the polymerization of ionized acetylene.<sup>2,3</sup> It has been postulated that benzene is the “missing link” between simple carbon molecules and the complex molecules made of hundreds of carbon atoms that could be responsible for the unidentified infrared bands.<sup>2,3</sup> Here we report the efficient formation of benzene ions within gas-phase ionized acetylene clusters  $(C_2H_2)_n^+$  with  $n = 3-60$ .

The search for benzene ions has been attempted within ionized small acetylene clusters.<sup>4</sup> Early experiments found the fragment ions observed from the photoionization of acetylene trimers to be identical to those obtained from other stable  $C_6H_6^+$  isomers such as benzene, 2,4-hexadiyne, 1,3-hexadiyne and 1,5-hexadiyne.<sup>4a</sup> However, photoelectron-photoion coincidence experiments and ab initio calculations showed that ionized acetylene trimers and tetramers rearrange to produce stable covalent core ions ( $C_4H_4^+$  and  $C_6H_6^+$ , respectively), and the  $C_6H_6^+$  ion was suggested to be the benzvalene ion.<sup>4c</sup> Electron impact (EI) ionization of acetylene clusters  $(C_2H_2)_n^+$  showed magic numbers at  $n = 3$  and 14 which were speculated to be the benzene ( $C_6H_6^+$ ) and  $C_{28}H_{28}^+$  molecular ions, respectively.<sup>4d</sup> However, none of the speculated structures in all the previous experiments on ionized acetylene clusters have been verified.<sup>4</sup> Here we use a combination of mass-selected ion mobility, collisional induced dissociation (CID), and theoretical calculations to provide the most conclusive evidence for the formation of benzene ions from the largest ever reported, ionized acetylene clusters.

Figure 1 displays a typical mass spectrum obtained by 50 eV EI ionization of neutral acetylene clusters formed by supersonic beam expansion. The distribution of the cluster ions formed reveals some striking features corresponding to the enhanced intensities (magic numbers) for the  $(C_2H_2)_n^+$  ions with  $n = 3, 6, 14, 33, 36,$  and  $54-56$ . The strong magic number at  $n = 3$  is consistent with previous work and suggests the formation of a stable  $C_6H_6^+$  ion in an exothermic process that can lead to extensive evaporation of neutral acetylene molecules from the cluster.<sup>4</sup> Following EI ionization, energy transfer to the low-frequency cluster modes leading to evaporation can dissipate the excess energy resulting from the covalent addition reactions. The depletion of the ion intensity for the  $n = 4$  and 5 clusters is a direct manifestation of the exothermic isomerization process coupled with evaporative cooling to produce the  $C_6H_6^+$  covalent ion.<sup>4c</sup> The other magic numbers such as  $n = 14, 33,$  etc. reflect the solvation of the  $C_6H_6^+$  core ion with neutral acetylene molecules where solvent shells are formed with specific numbers of the acetylene molecules.

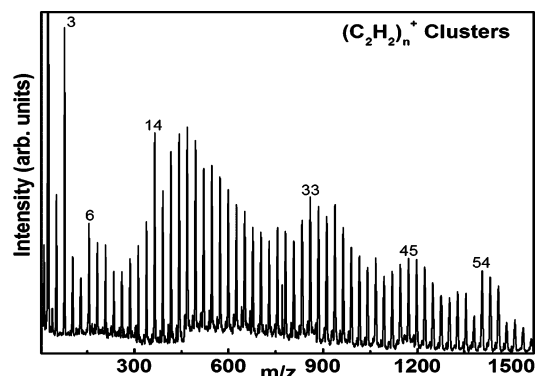


Figure 1. EI mass spectrum of acetylene clusters.

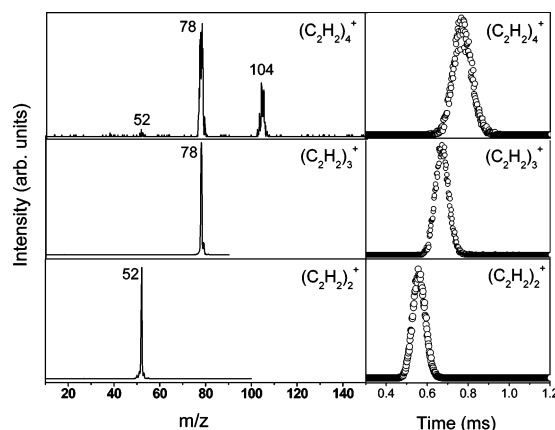
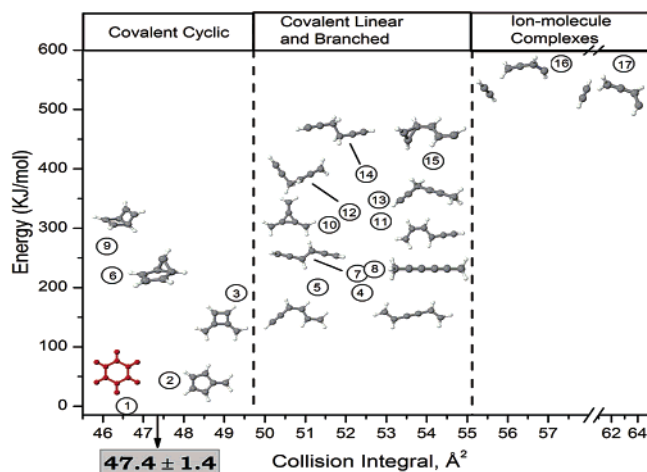


Figure 2. Mass spectra and ATDs of the acetylene dimer, trimer, and tetramer ions.

To obtain information on the relative stability, dissociation products, and structures of the ionized acetylene clusters, we used the established drift-tube techniques.<sup>5</sup> Our mass-selected drift-tube apparatus has previously been described in detail.<sup>6</sup> Mobility is measured by injecting a 20–50  $\mu$ s pulse of the mass-selected ions into the drift tube and recording the arrival time distribution (ATD) at the detector.

Figure 2 displays the mass spectra and ATDs of the mass-selected  $(C_2H_2)_2^+$ ,  $(C_2H_2)_3^+$  and  $(C_2H_2)_4^+$  ions injected into a drift tube containing 1.5 Torr of He at 300 K using an injection energy of 12 eV. Under these conditions, typical cluster ions show extensive fragmentation upon the ion injection process. For example, a benzene dimer cation with a significant binding energy of 18 kcal/mol shows 72% fragmentation to the benzene cation with the 12 eV injection energy into the drift tube.<sup>6a,b</sup> In contrast, the  $(C_2H_2)_2^+$  and  $(C_2H_2)_3^+$  ions show no fragmentations upon their injections using the 12 eV injection energy consistent with the formation of stable  $C_4H_4^+$  and  $C_6H_6^+$  covalent ions, respectively. However, the  $(C_2H_2)_4^+$  cluster shows extensive fragmentation mainly to the  $(C_2H_2)_3^+$  ion. No multiple peaks were observed in the ATDs, indicating that only one structure is present for each species as

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**Figure 3.** Relative energies and collision integrals of  $C_6H_6^+$  isomers.

suggested by the excellent fits of the measured ATDs to the calculated ones obtained from transport theory (Supporting Information).

Given the indications that the  $(C_2H_2)_3^+$  ions are most likely benzene ions, we investigated their fragmentation using high injection energy (IE) and CID experiments (Supporting Information). Using an IE of 62 eV, the observed fragments from the  $(C_2H_2)_3^+$  ion are  $C_6H_5^+$ ,  $C_6H_4^+$ ,  $C_4H_4^+$ ,  $C_4H_3^+$ ,  $C_4H_2^+$ , and  $C_3H_3^+$  corresponding to  $m/z$  of 77, 76, 52, 51, 50, and 39, respectively. The origin of the  $C_3H_3^+$  fragment is interesting since, unlike the  $C_4H_3^+$  and  $C_4H_2^+$  fragments, the  $C_3H_3^+$  ion is not produced by any of the known ion–molecule reactions of acetylene.<sup>4a,7</sup> All the observed fragment ions from  $(C_2H_2)_3^+$  are identical to the major fragment ions resulting from the unimolecular decomposition of the benzene ion.<sup>4a</sup> However, this result does not provide conclusive evidence for the formation of a benzene cation since identical CID spectra do not necessarily mean identical ion structures. In fact, it is well-known that the CID spectra of the benzene cation and its acyclic isomers such as 1,5-hexadiyne, 2,4-hexadiyne, and 1,3-hexadiyne ions are essentially identical.<sup>8</sup>

To more conclusively determine the structure of the  $(C_2H_2)_3^+$  ions, we measured the reduced mobility of the mass-selected  $(C_2H_2)_3^+$  ion. Mobility can provide direct structural characterizations of the ions on the basis of their collision integrals ( $\Omega$ ) which depend on the geometric shapes of the ions.<sup>5,6</sup> This is, of course, a better criterion for judging the structures of ions that have similar CID spectra. Our results indicate that reduced mobility of the  $(C_2H_2)_3^+$  ions is  $11.54 \pm 0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , in excellent agreement with the value measured for the benzene cation ( $11.43 \pm 0.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ).<sup>6b</sup> The corresponding collision integrals at 300 K for the  $(C_2H_2)_3^+$  and the benzene ions are  $47.4 \pm 1.4 \text{ \AA}^2$  and  $47.9 \pm 1.4 \text{ \AA}^2$ , respectively. For comparison with the linear isomers and other possible structures of the  $C_6H_6^+$  ions, collision integrals for candidate geometries of 17  $C_6H_6^+$  isomers were calculated using the trajectory method.<sup>9</sup> The geometries of the  $C_6H_6^+$  isomers were determined from ab initio calculations using unrestricted DFT with the PBE (Perdew, Burke, and Ernzerhoff) correlation and exchange functionals and the aug-cc-pVDZ basis set.<sup>10</sup>

Figure 3 displays the collision integrals ( $\Omega$ ) calculated for the  $C_6H_6^+$  isomers and their relative total energies (with the energy of the benzene ion, the most stable  $C_6H_6^+$  isomer, taken as zero). The  $C_6H_6^+$  isomers can be grouped into three distinct categories based on similarities in their collision integrals (Supporting Information). These groups are identified as covalent cyclic, covalent linear and branched, and noncovalent ion–molecule isomers. The ions in the

second and third groups, including all the acyclic isomers, have collision integrals substantially larger than the measured values for the  $(C_2H_2)_3^+$  and benzene cations. In the first group, other cyclic isomers such as fulvene, 3,4-dimethylenecyclobutene, and benzvalene have collision integrals similar to those measured for the  $(C_2H_2)_3^+$  and benzene cations within experimental uncertainty. Previous studies have found major differences in the CID spectra of the benzene cation and these cyclic isomers.<sup>11</sup> Specifically, the diminished intensity of the  $C_3H_3^+$  fragment ion in the CID spectra of the cyclic isomers benzvalene, 3,4-dimethylenecyclobutene, and fulvene provides a distinction from the CID spectrum of the benzene cation.<sup>11b</sup> Therefore, among the cyclic isomers which have collision integrals similar to those measured for the  $(C_2H_2)_3^+$  (Figure 3), only the benzene cation exhibits a fragmentation pattern (including the characteristic  $C_3H_3^+$  fragment) similar to that measured for the  $(C_2H_2)_3^+$  ion. Clearly, the combination of ion mobility and fragmentation data provides conclusive evidence that the  $(C_2H_2)_3^+$  ion formed from the ionization of large neutral acetylene clusters has indeed the structure of the benzene cation.

In conclusion, the  $(C_2H_2)_3^+$  ion formed from the ionization of large neutral acetylene clusters has unusual stability similar to that of the benzene cation, its primary fragment ions are similar to those reported from the benzene cation, and it has a collision cross section of  $47.4 \text{ \AA}^2$  in helium at 300 K, similar to the value of  $47.9 \text{ \AA}^2$  reported for the benzene cation. In other words,  $(C_2H_2)_3^+$  structurally looks like benzene, it has stability similar to that of benzene, it fragments like benzene, therefore, it must be benzene!

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**Supporting Information Available:** Calculated low-energy structures of  $C_6H_6$  radical cations and their total energies, CID data, comparison of ATD with transport theory, and complete ref 10. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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