formation, H-bonding appears to be an important factor in determining the conformation in the isolated molecule in the gas phase. However, even if N—H···O is a strong kind of hydrogen bond, it appears to be not as strong as O—H···N (see ref 2 and 5–8 and the Introduction). The experimental evidence that the conformer of GLY with a bifurcated hydrogen bond (double N—H···O hydrogen bond) is about 0.5 kcal/mol more stable than the conformer with the O—H···N internal hydrogen bond[2] suggests that the bond energy of N—H···O is slightly more than half that of the O—H···N bond, at least in molecular systems where the hydrogen bond belongs to a five-membered ring including a sp^2 carbon.

The C═O group appears to be in the middle of the amine group, because otherwise it could there be (i) a double minimum with tunnelling, which would originate two O$^+$ and O$^-$ levels close in energy, or (ii) a deeper double minimum which would cause two different NHD species, but we did not observe either of the two effects.

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Supplementary Material Available: A listing of the experimental transitions frequencies is available (3 pages). Ordering information is given on any current masthead page.

A Study of the Unimolecular Decomposition of the $(C_2H_2)_3^+$ Complex

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Abstract: The $C_6H_5^+$, $C_6H_4^+$, $C_4H_4^+$, $C_4H_3^+$, $C_4H_2^+$, and $C_3H_3^+$ ions were identified as the primary fragment ions from the unimolecular decomposition of $(C_2H_2)_3^+$ in the total energy range 17.10–26.10 eV (neutral $(C_2H_3)_3$ heat of formation plus excitation energy). The appearance energies (AE) for $C_6H_5^+$, $C_6H_4^+$, $C_4H_4^+$, and $C_3H_3^+$ were found to be identical and have the value of 10.10 ± 0.04 eV (1228 ± 5 Å). The ionization energy (IE) of $(C_2H_2)_3$ was determined to be 9.83 ± 0.04 eV (1261 ± 5 Å). The measured AE's for the formation of $C_4H_3^+$ and $C_4H_2^+$ from $(C_2H_2)_3$ in the total energy scale were found to be in agreement with those determined for $C_4H_3^+$ and $C_4H_2^+$ from 2,4-hexadiyne, 1,5-hexadiyne, and benzene. This, together with the favorable comparison observed between the relative intensities of the $C_6H_5^+$, $C_6H_4^+$, and $C_3H_3^+$ ions from $(C_2H_2)_3$ measured in this work and those reported previously from the benzene, 2,4-hexadiyne, and 1,3-hexadiyne molecular ions in the total energy range 16.87–17.37 eV, strongly supports the conclusion that the $(C_2H_2)_3^+$ ions rearrange to some common precursors as do other stable $C_6H_6^+$ isomers prior to dissociation. The difference (0.26 ± 0.06 eV) of the AE's for $C_6H_5^+$, $C_6H_4^+$, $C_4H_4^+$, and $C_3H_3^+$ and the IE of $(C_2H_2)_3$ is interpreted as the potential energy barrier for the rearrangement of $(C_2H_2)_3^+$ to other stable $C_6H_6^+$ isomers.

The mechanism for the unimolecular decomposition of the benzene ion has been the subject of many experimental[1–9] and theoretical[7,10,11] investigations during the last decade. The major fragment ions resulting from the unimolecular decomposition of the excited benzene molecular ions with excitation energies below 20 eV are $C_6H_5^+$, $C_6H_4^+$, $C_4H_4^+$, and $C_3H_3^+$. The same product ions are observed from $C_6H_6^+$ formed by photoionization of some stable isomers of C_6H_6 such as 1,5-hexadiyne,[8,12] 2,4-hexadiyne,[8,12–14] and 1,3-hexadiyne.[12,14] The fact that, within experimental errors, the benzene, 1,5-hexadiyne, and 2,4-hexadiyne molecular ions dissociate to the four product ions with identical branching ratios in the total energy range ~15.0–15.5 eV (neutral C_6H_6 heat of formation plus excitation energy) indicates that all these isomers of $C_6H_6^+$ rearrange to a common precursor ion prior to fragmentation. The experimental and calculated unimolecular fragmentation rates for $C_6H_6^+$ are consistent with the interpretation that this common precursor has the benzene molecular ion structure.[8] Above this energy range, there is evidence that newly accessible processes involve some intermediate complexes other than the common precursor ions.[8,13,14] The kinetic energy release data of Keough et al.[15] suggest that the reactive form of the benzene molecular ion at higher excitation energies has an acyclic structure.

In this paper, we report the results of a study of the unimolecular decomposition of acetylene trimer ions which are synthesized by the direct photoionization of van der Waals trimers of acetylene.

$$(C_2H_2)_3 + h\nu \rightarrow (C_2H_2)_3^+ + e^- \tag{1}$$

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(1) B. Andlauer and Ch. Ottinger, *J. Chem. Phys.*, **55**, 1471 (1971); B. Andlauer and Ch. Ottinger, *Z. Naturforsch., A*, **27A**, 293 (1972).

(2) J. H. D. Eland and H. Schulte, *J. Chem. Phys.*, **62**, 3835 (1975).

(3) J. H. D. Eland, R. Frey, H. Schulte, and B. Brehm, *Int. J. Mass Spectrom. Ion Phys.*, **21** 209 (1976).

(4) J. H. Beynon, R. M. Caprioli, W. O. Perry, and W. E. Baitinger, *J. Am. Chem. Soc.*, **94**, 6828 (1972).

(5) W. A. Chupka in "Chemical Spectroscopy and Photochemistry in the Vacuum-Ultraviolet", C. Sandorfy, P. J. Ausloos, and M. B. Robin, Eds., Reidel, Dordrecht, 1974, p 433.

(6) W. A. Chupka, J. Berkowitz, and S. I. Miller, paper presented at American Society for Mass Spectrometry, 20th Annual Conference on Mass Spectrometry and Allied Topics, Dallas, Texas, June 1972.

(7) H. M. Rosenstock, J. T. Larkins, and J. A. Walker, *Int. J. Mass Spectrom. Ion Phys.*, **11**, 309 (1973).

(8) T. Baer, G. D. Willett, D. Smith, and J. S. Phillips, *J. Chem. Phys.*, **70**, 4076 (1979).

(9) B. O. Jonsson and E. Lindholm, *Ark. Fys.*, **39**, 65 (1969).

(10) C. E. Klots, *Z. Naturforsch., A*, **27A**, 553 (1972).

(11) M. L. Vestal in "Fundamental Processes in Radiation Chemistry", P. Ausloos, Ed., Wiley, New York, 1968, p 59.

(12) H. M. Rosenstock, K. E. McCulloh, and F. P. Lossing, *Int. J. Mass Spectrom. Ion Phys.*, **25**, 327 (1977).

(13) J. Dannacher, *Chem. Phys.* **29**, 339 (1978).

(14) J. Dannacher, *Adv. Mass Spectrom.*, **8A**, 37 (1979).

(15) T. Keough, T. Ast, J. H. Beynon, and R. G. Cooks, *Org. Mass Spectrom.*, **7**, 245 (1973).

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Due to the weak interactions between the acetylene molecules in $(C_2H_2)_3$, the ionization reaction, eq 1, to a first approximation, involves the ionization of only one of the acetylene molecules. The resulting $(C_2H_2)_3^+$ ion, consisting of an acetylene molecular ion and two neutral acetylene molecules held together by polarization forces, can be considered to be a collisional complex formed in a trimolecular collision of $C_2H_2^+ + 2C_2H_2$. An interesting question concerning these loose trimer ions is whether they isomerize to some stable $C_6H_6^+$ ions before fragmenting. By identifying the fragment ions of $(C_2H_2)_3^+$ and comparing the branching ratios of the fragments from $(C_2H_2)_3^+$ with those observed from other stable $C_6H_6^+$ isomers at the same total energy, we have obtained significant insight into the unimolecular decomposition of $(C_2H_2)_3^+$.

Experimental Section

The experimental arrangement and procedures were essentially the same as those described previously.[16,17] Briefly, the apparatus consists of a 3 m near normal incidence vacuum ultraviolet (VUV) monochromator (McPherson 2253M), a supersonic molecular beam production system, a capillary discharge lamp, a VUV light detector, and a quadrupole mass spectrometer for ion detection. The gratings employed in this study are Bausch and Lomb 1200 lines/mm MgF_2 or Os coated aluminum gratings blazed at 1360 Å. Either the hydrogen many-lined peudocontinuum or the helium Hopfield continuum was used as the light source, depending on the wavelength region desired.

The acetylene was obtained from Matheson with a quoted purity of ≥99.6%. The $(C_2H_2)_3$ was produced by supersonic expansion through a 120-μm-diameter nozzle at a nozzle temperature (T_0) of approximately 230 K and a stagnation pressure (P_0) of 1000 torr. Under these expansion conditions, ions containing more than six carbon atoms cannot be detected, indicating that the concentrations of higher acetylene clusters $(C_2H_2)_n$, $n > 3$, are negligible and C_2H_2, $(C_2H_2)_2$, and $(C_2H_2)_3$ are the major constituents of the molecular beam. Since the acetylene beam was sampled in a collisionless environment, the observed fragment ions represent the primary fragments of $C_2H_2^+$, $(C_2H_2)_2^+$, and $(C_2H_2)_3^+$.

All the data were obtained with an optical resolution of 1.4 Å (fwhm). Data points were taken typically at either 0.5- or 1-Å intervals. Due to the low signal intensity of the $C_6H_4^+$ ion, data were taken at 25 Å intervals beyond the threshold region. The standard deviations obtained are ≤10% for $C_6H_6^+$ (or $(C_2H_2)_3^+$), $C_6H_5^+$, and $C_4H_4^+$ and ≤20% for $C_6H_4^+$ and $C_3H_3^+$. Each photoionization efficiency (PIE) curve was based on at least two scans, and the prominent structures in the curves were found to be reproducible. Wavelength calibrations were achieved with known atomic resonance lines, or H_2 emission lines[18] when the H_2 pseudocontinuum was used.

Results and Discussion

The ions observed in the region 600–1260 Å are C_2H^+, $C_2H_2^+$, $C_3H_3^+$, $C_4H_2^+$, $C_4H_3^+$, $C_4H_4^+$ (and/or $(C_2H_2)_2^+$), $C_6H_4^+$, $C_6H_5^+$, and $(C_2H_2)_3^+$ (and/or $C_6H_6^+$). The analyses of the PIE curves for C_2H^+ [19] and $C_2H_2^+$ [20] near the thresholds have been reported elsewhere. The profiles of the PIE curves for $C_3H_3^+$, $C_4H_2^+$, $C_4H_3^+$, $C_4H_4^+$, (and/or $(C_2H_2)_2^+$), $C_6H_4^+$, $C_6H_5^+$, and $(C_2H_2)_3^+$ (and/or $C_6H_6^+$) are similar.

Figure 1a–e shows the PIE curves for $(C_2H_2)_3^+$ (and/or $C_6H_6^+$), $C_6H_5^+$, $C_6H_4^+$, $C_4H_4^+$ (and/or $(C_2H_2)_2^+$), and $C_3H_3^+$, respectively, in the region ~650–1275 Å obtained at $P_0 \approx 1000$ torr and with a wavelength resolution of 1.4 Å (fwhm). The peak observed in the PIE curves at ~800–850 Å arises from autoionizing states of C_2H_2. A similar structure was evident in the PIE curve for $C_2H_2^+$.[21] At energies higher than approximately 12.56 eV (987 Å), which is the thermochemical threshold for the reaction

$$(C_2H_2)_2 + h\nu \rightarrow C_3H_3^+ + CH + e^- \quad (2)$$

$C_3H_3^+$ might also arise from the fragmentation of $(C_2H_2)_2$. The ionization energy (IE) of $(C_2H_2)_3$ was determined to be 9.83 ± 0.04 eV (1261 ± 5 Å). Within experimental uncertainties, the appearance energies (AE) for $C_3H_3^+$, $C_4H_4^+$, $C_6H_4^+$, and $C_6H_5^+$ from $(C_2H_2)_3$ were all found to be 10.10 ± 0.04 eV (1228 ± 5 Å).

A logical question to ask at this point is whether the mass 52 ions observed near the onset as shown in Figure 1d have the tight $C_4H_4^+$ or the loose $(C_2H_2)_2^+$ structure. Interestingly, the AE of the mass 52 ion determined at $P_0 \approx 1000$ torr was found to be approximately 0.36 eV lower than that obtained at a lower stagnation pressure ($P_0 \approx 350$ torr), where the concentrations of $(C_2H_2)_3$ and heavier clusters are negligible. The PIE curves near the thresholds for the mass 52 ion obtained at $P_0 \approx 1000$ and 350 torr are plotted at the same sensitivity scale and shown in Figure 2, parts a and b, respectively. At $P_0 \lesssim 350$ torr, the mass 52 ions should have the structure of $(C_2H_2)_2^+$ and are mainly produced by the photoionization reaction

$$(C_2H_2)_2 + h\nu \rightarrow (C_2H_2)_2^+ + e^- \quad (3)$$

Therefore, the IE of $(C_2H_2)_2$ was determined to be 10.44 ± 0.04 eV (1188 ± 5 Å). At $P_0 \approx 1000$ torr, the mass 52 ions can be formed by reaction 3 and the photodissociative ionization reactions

$$(C_2H_2)_3 + h\nu \rightarrow (C_2H_2)_2^+ + C_2H_2 + e^- \quad (4)$$

$$(C_2H_2)_3 + h\nu \rightarrow C_4H_4^+ + C_2H_2 + e^- \quad (5)$$

Since the AE of reaction 4 is expected to be higher than the IE of $(C_2H_2)_2$, the mass 52 ions observed in Figure 1d below the IE of $(C_2H_2)_2$ must have a structure corresponding to some stable isomers of $C_4H_4^+$ instead of a loose $(C_2H_2)_2^+$ structure.

The observation that the AE for the mass 52 ion from $(C_2H_2)_3$ is lower than the IE of $(C_2H_2)_2$ is contrary to the expectation of previous findings concerning the threshold measurements of the clusters of some simple inorganic molecules such as $(O_2)_{n=2-5}$,[22,23] $(N_2)_{n=2,3}$, $(CO)_{n=2,3}$,[24] $(CO_2)_{n=2-4}$,[25] and $(CS_2)_{n=2-5}$.[26] In all the latter cases, AE's of the dimer ion fragments from the trimers and heavier clusters were all found to be higher than the IE's of the corresponding dimers. A reasonable explanation for the difference observed in systems involving hydrocarbons[27] and simple inorganic molecules is that, for hydrocarbon cluster ions, there exists a tight structure such as $C_4H_4^+$ which is much more stable than the loose $(C_2H_2)_2^+$ complex, whereas the cluster ions of these simple inorganic molecules can only exist as loose complexes. The lower AE of reaction 5 in comparison with reaction 4 is simply the result that $\Delta H_f^\circ((C_2H_2)_2^+)$ is greater than $\Delta H_f^\circ(C_4H_4^+)$.

When the IE's of C_2H_2 (11.396 ± 0.003 eV)[20,28,29] and $(C_2H_2)_2$ and the estimated dissociation energy of $C_2H_2{\cdot}C_2H_2$ are used, the dissociation energy ($D_0((C_2H_2)_2^+)$) can be calculated from the relation

$$D_0((C_2H_2)_2^+) = IE(C_2H_2) + D_0((C_2H_2)_2) - IE((C_2H_2)_2) \quad (6)$$

The calculated dissociation energy for $C_2H_2^+{\cdot}C_2H_2$ is 22.5 ± 1 kcal/mol. It is interesting to note that, within error estimates of the experiments, this value is equal to the dissociation energies

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[16] Y. Ono, S. H. Linn, H. F. Prest, M. E. Gress, and C. Y. Ng, *J. Chem. Phys.*, **73**, 2523 (1980).

[17] Y. Ono, S. H. Linn, H. F. Prest, C. Y. Ng, and E. Meischer, *J. Chem. Phys.*, **73**, 4855 (1980).

[18] K. E. Schubert and R. D. Hudson, "A Photoelectric Atlas of the Intense lines of the Hydrogen Molecular Emission Spectrum from 1025 to 1650 Å at a Resolution of 0.1 Å", Report No. ATN-64(9233)-2, Aerospace Corp., Los Angeles, 1963.

[19] Y. Ono and C. Y. Ng, *J. Chem. Phys.*, **74**, 6985 (1981).

[20] Y. Ono, E. A. Osuch, and C. Y. Ng, *J. Chem. Phys.*, **76**, 3905 (1982).

[21] R. Botter, V. H. Dibeler, J. A. Walker, and H. M. Rosenstock, *J. Chem. Phys.*, **44**, 1271 (1966).

[22] S. L. Anderson, T. Hirooka, P. W. Tiedemann, B. H. Mahan, and Y. T. Lee, *J. Chem. Phys.*, **73**, 4779 (1980).

[23] S. H. Linn, Y. Ono, and C. Y. Ng, *J. Chem. Phys.*, **74**, 3348 (1981).

[24] S. H. Linn, Y. Ono, and C. Y. Ng, *J. Chem. Phys.*, **74**, 3342 (1981).

[25] S. H. Linn and C. Y. Ng, *J. Chem. Phys.*, **75**, 4921 (1981).

[26] Y. Ono, S. H. Linn, H. F. Prest, M. E. Gress, and C. Y. Ng, *J. Chem. Phys.*, **73**, 2523 (1980).

[27] A Similar observation was found in the photoionization study of $(C_2H_4)_2$ and $(C_2H_4)_3$. Y. Ono and C. Y. Ng, to be submitted for publication.

[28] V. H. Dibeler and J. A. Walker, *Int. J. Mass Spectrom. Ion Phys.*, **11**, 49 (1973).

[29] V. H. Dibeler, J. A. Walker, and K. E. McCulloh, *J. Chem. Phys.*, **59**, 2264 (1973).

[30] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids", Wiley, New York, 1964, p 1213.

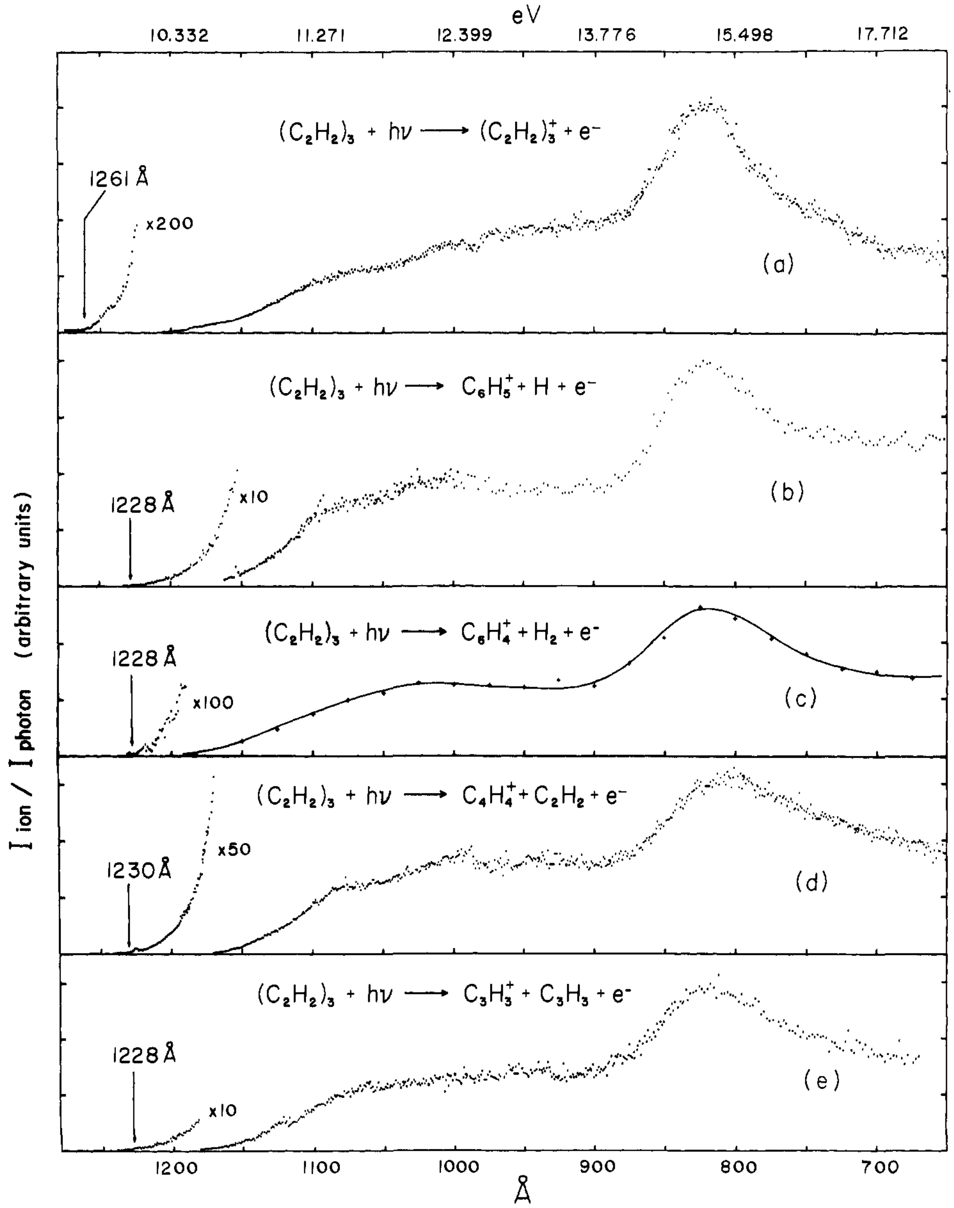

Figure 1. (a) PIE curve for $(C_2H_2)_3^+$ in the region 650–1275 Å. (b) PIE curve for $C_6H_5^+$ in the region 650–1235 Å. (c) PIE curve for $C_6H_4^+$ in the region 650–1240 Å. (d) PIE curve for $C_4H_4^+$ in the region 650–1240 Å. (e) PIE curve for $C_3H_3^+$ in the region 650–1240 Å. Experimental conditions: $P_0 \approx 1000$ torr, $T_0 \approx 230$ K, wavelength resolution = 1.4 Å (fwhm).

determined for $N_2^+{\cdot}N_2$ (20.8 ± 1.2 kcal/mol) and $CO^+{\cdot}CO$ (22.4 ± 1 kcal/mol).[24] This observation leads one to speculate that the interaction of the electrons in the carbon–carbon triple bonds of C_2H_2 and $C_2H_2^+$ is mainly responsible for the stability of $(C_2H_2)_2^+$. The good agreement found between the dissociation energies for $(C_2H_2)_2^+$, $(N_2)_2^+$, and $(CO)_2^+$ can also be taken as a support for the validity of the IE of $(C_2H_2)_2$ determined here. When it was assumed that the binding energy for $(C_2H_2)_2 + C_2H_2$ was the same as that for $C_2H_2 + C_2H_2$ and when the IE's of $(C_2H_2)_2$ and $(C_2H_2)_3$ were used, a value of 14.4 ± 1 kcal/mol was deduced from a relation similar to eq 6. This value, however, was found to be substantially greater than the lower bounds for the dissociation energies for $(CO)_2^+{\cdot}CO$ (3.7 kcal/mol) and $(N_2)_2^+{\cdot}N_2$ (1.4 kcal/mol) reported by Linn et al.[24]

The $C_4H_2^+$ and $C_4H_3^+$ ions are the major fragment ions from $(C_2H_2)_2$. The analysis of the PIE curves for $C_4H_2^+$ and $C_4H_3^+$ will be published in a separate paper.[31] However, the pressure-dependence measurements of the intensities for $C_4H_3^+$ and $C_4H_2^+$ strongly suggest that the $C_4H_3^+$ and $C_4H_2^+$ ions are among the primary fragments from $(C_2H_2)_3$ in the region ~650–1142 Å. Figure 3, parts a and b, shows the PIE curves for $C_4H_2^+$ and $C_4H_3^+$ near the thresholds obtained at $P_0 \approx 1000$ torr. The AE's of these two ions were also found to be identical and have the value of 10.86 ± 0.05 eV (1142 ± 5 Å). The neutral products for the $C_4H_3^+$ and $C_4H_2^+$ channels are not known. On the basis of the known thermodynamic data[30,32–35] (see Table I), the thermochemical thresholds for reactions 7–10 are calculated to be 9.10,

$$(C_2H_2)_3 + h\nu \rightarrow C_4H_3^+ + C_2H_3 + e^- \quad (7)$$

$$\rightarrow C_4H_3^+ + C_2H_2 + H + e^- \quad (8)$$

$$\rightarrow C_4H_2^+ + C_2H_4 + e^- \quad (9)$$

$$\rightarrow C_4H_2^+ + C_2H_2 + H_2 + e^- \quad (10)$$

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[31] Y. Ono and C. Y. Ng, *J. Chem. Phys.*, in press.

[32] H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data*, **6**, Suppl. 1 (1977).

[33] F. H. Field, J. L. Franklin, and F. W. Lampe, *J. Am. Chem. Soc.*, **79**, 2665 (1957).

[34] W. L. Smith, *Proc. R. Soc. London, Ser. A*, **300**, 519 (1967); C. Baker and D. W. Turner, *Chem. Commun.*, 797 (1967); *Proc. R. Soc. London, Ser. A*, **308**, 19 (1968).

[35] A. G. Harrison and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 519 (1960).

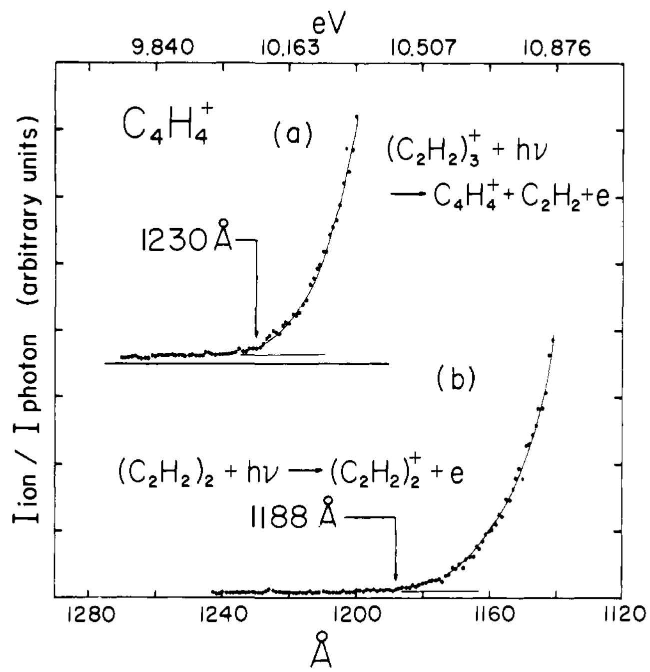

Figure 2. (a) PIE curve for $C_4H_4^+$ near the threshold. Experimental conditions: $P_0 \approx 1000$ torr, $T_0 \approx 230$ K, wavelength resolution = 1.4 Å (fwhm). (b) PIE curve for $(C_2H_2)_2^+$ near the threshold. Experimental conditions: $P_0 \approx 350$ torr, $T_0 \approx 230$ K, wavelength resolution = 1.4 Å (fwhm).

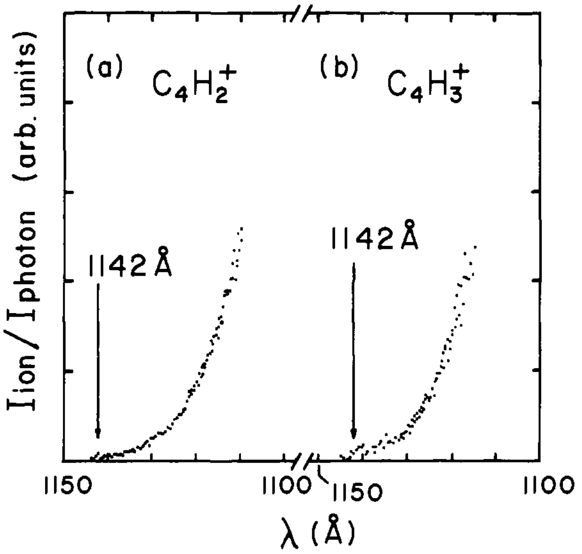

Figure 3. (a) PIE curve for $C_4H_2^+$ near the threshold. (b) PIE curve for $C_4H_3^+$ near the threshold. Experimental conditions: $P_0 \approx 1000$ torr, $T_0 \approx 230$ K, wavelength resolution = 1.4 Å (fwhm).

10.89, 8.60, and 10.40 eV, respectively. Since these values are lower than or equal to that observed AE's of $C_4H_3^+$ and $C_4H_2^+$, reactions 7–10 must be considered to be possible reactions near the experimental onsets. From the metastable transitions,[36] it is known that the $C_6H_5^+$ and $C_6H_4^+$ ions from benzene fragment further to form $C_4H_3^+$ and $C_4H_2^+$, respectively. Hence, this finding also suggests that $C_2H_2 + H$ and $C_2H_2 + H_2$ should be included as likely neutral products for the $C_4H_3^+$ and $C_4H_2^+$ channels, respectively.

According to previous photoionization studies on benzene,[7,8,12] the $C_6H_5^+$, $C_6H_4^+$, $C_4H_4^+$, and $C_3H_3^+$ ions formed at the fragmentation thresholds are believed to have the structure of the phenyl, benzyne, methylenecyclopropene, and cyclopropenyl ions, respectively. In order to visualize the observation of this study, a pseudo-reaction-coordinate diagram (Figure 4) is constructed with use of the thermochemical data reported in the literature[8,12,30,32–35,37–49] and those obtained in this study (Table I). The

Table I. 298 K Heats of Formation in (kcal/mol) of Neutrals and Ions[a]

compound	neutrals	ions
$(C_2H_2)_3$	162.2 ± 0.4[b] (30, 32)	388.9 ± 1.0[c]
benzene	19.82 ± 0.12 (32)	233 (32)
2,4-hexadiyne	86 ± 1 (8)	291 ± 1 (8)
	90 ± 2 (12)	295 ± 5 (12)
1,3-hexadiyne	95 ± 2 (12)	301 ± 5 (12)
1,4-hexadiyne	98 ± 2 (12)	316 ± 5 (12)
1,5-hexadiyne	99.5 (12)	328 ± 1 (8)
		329 ± 2 (12)
$C_6H_5^+$		264 ± 1 (8)
		266 ± 2 (38, 39)
		270 ± 4 (40)
		270 (47)
$C_6H_4^+$		~318 (7)
		315 ± 3 (48)
$(C_2H_2)_2$	108 ± 0.2[b] (30, 32)	348.9 ± 1[c]
C_4H_4		276 ± 2 (8)
		280 ± 2 (41)
		285 ± 3 (49)
C_4H_3		307 (33)
C_4H_2		348 (34)
C_3H_3	80 (8)	255 (8)
	80.7 (42)	256 ± 2 (43)
		255.5 (44)
		257 (12)
C_2H_4	12.49 (32)	
C_2H_3	65 (35)	
C_2H_2	54.34 (32)	317.2 (32)
	54.19[b] (32)	
H	52.10 (32)	

[a] The numbers in the parentheses are the references. [b] Heats of formation at 0 K. [c] This work. Because of the high degree of rotational and low frequency vibrational relaxation in the supersonic expansion, these values, which are deduced from the measured IE's for $(C_2H_2)_2$ and $(C_2H_2)_2$, can be considered to be the heats of formation at 0 K.

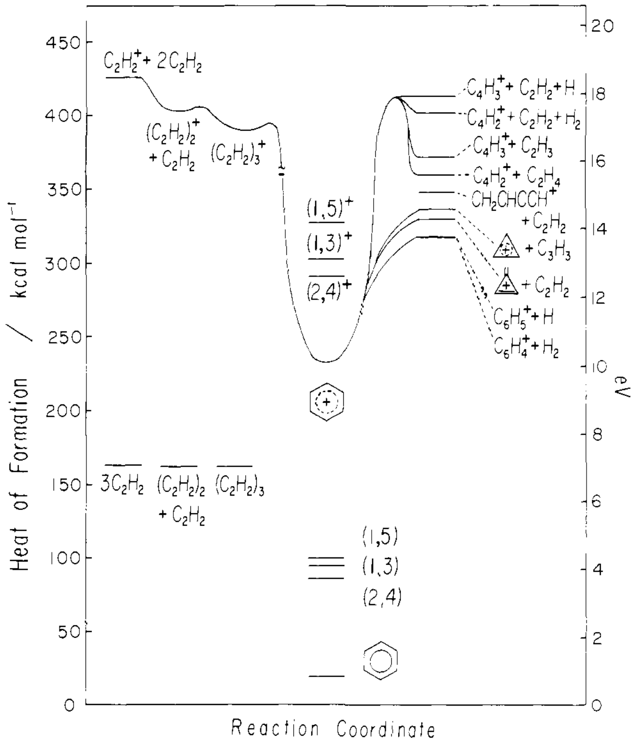

Figure 4. Pseudo-reaction-coordinate diagram for the decomposition of $(C_2H_2)_3^+$. Here (1,3), (1,5), (2,4), $(1,3)^+$, $(1,5)^+$, and $(2,4)^+$ represent 1,3-hexadiyne, 1,5-hexadiyne, and 2,4-hexadiyne and their ions, respectively.

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(36) Ch. Ottinger, *Z. Naturforsch., A*, **20A**, 1229 (1965).

Table II. Selected Experimental Appearance Energies (AE) of $C_6H_5^+$, $C_6H_4^+$, $C_4H_4^+$, $C_4H_3^+$, $C_4H_2^+$, and $C_3H_3^+$ from $(C_2H_2)_3^+$ and Some Stable $C_6H_6^+$ Isomers

reaction	AE, eV	TE,[a] eV	ref
$(C_2H_2)_3 + h\nu \rightarrow C_6H_5^+ + H + e^-$	10.10 ± 0.04	17.13 ± 0.04	this work
$HC\equiv C-CH_2-CH_2-C\equiv CH + h\nu \rightarrow C_6H_5^+ + H + e^-$	10.16 ± 0.08	14.47 ± 0.11	12
$HC\equiv C-CH_2-C\equiv C-CH_3 + e^- \rightarrow C_6H_5^+ + H + 2e^-$	10.21 ± 0.1	14.46 ± 0.13	12
$H_3C-C\equiv C-C\equiv C-CH_3 + h\nu \rightarrow C_6H_5^+ + H + e^-$	10.55 ± 0.09	14.28 ± 0.10[b] 14.45 ± 0.12[c]	12
C_6H_6 (benzene) $+ h\nu \rightarrow C_6H_5^+ + H + e^-$	13.78 ± 0.08	14.64 ± 0.08	12
	~13.95		7
C_6H_6 (benzene) $+ h\nu \rightarrow C_6H_5^+ + H + e^-$	13.74 ± 0.1	14.60 ± 0.1	12
$(C_2H_2)_3 + h\nu \rightarrow C_6H_4^+ + H_2 + e^-$	10.10 ± 0.04	17.13 ± 0.04	this work
C_6H_6 (benzene) $+ h\nu \rightarrow C_6H_4^+ + H_2 + e^-$	~13.90	~14.76	7
$(C_2H_2)_3 + h\nu \rightarrow C_4H_4^+ + C_2H_2 + e^-$	10.10 ± 0.04	17.13 ± 0.04	this work
$HC\equiv C-CH_2CH_2-C\equiv CH + h\nu \rightarrow C_4H_4^+ + C_2H_2 + e^-$	10.42 ± 0.08	14.73 ± 0.11	12
$H_3C-C\equiv C-C\equiv C-CH_3 + h\nu \rightarrow C_4H_4^+ + C_2H_2 + e^-$	11.27 ± 0.2	15.00 ± 0.2	12
C_6H_6 (benzene) $+ h\nu \rightarrow C_4H_4^+ + C_2H_2 + e^-$	14.17 ± 0.08	15.03 ± 0.08	12
	~14.30		7
$(C_2H_2)_3 + h\nu \rightarrow C_4H_3^+ + C_2H_3$ (or $C_2H_2 + H$) $+ e^-$	10.86 ± 0.05	17.89 ± 0.08	this work
$H_3C-C\equiv C-C\equiv C-CH_3 + h\nu \rightarrow C_4H_3^+ + C_2H_3$ (or $C_2H_2 + H$) $+ e^-$	14.6 ± 0.1	18.33 ± 0.11[b] 18.50 ± 0.13[c]	13
$HC\equiv C-CH_2-CH_2-C\equiv CH + h\nu \rightarrow C_4H_3^+ + C_2H_3$ (or $C_2H_2 + H$) $+ e^-$	13.05–13.78	17.36–18.10	12
C_6H_6 (benzene) $+ e^- \rightarrow C_4H_3^+ + C_2H_3$ (or $C_2H_2 + H$) $+ 2e^-$	17.6 ± 0.1	18.46 ± 0.1	45
$(C_2H_2)_3 + h\nu \rightarrow C_4H_2^+ + C_2H_4$ (or $C_2H_2 + H_2$) $+ e^-$	10.86 ± 0.05	17.89 ± 0.08	this work
$H_3C-C\equiv C-C\equiv C-CH_3 + h\nu \rightarrow C_4H_2^+ + C_2H_4$ (or $C_2H_2 + H_2$) $+ e^-$	14.1 ± 0.05	17.83 ± 0.07[b] 18.00 ± 0.10[c]	46
	14.05 ± 0.1	17.78 ± 0.11[b] 17.95 ± 0.13[c]	13
$HC\equiv C-CH_2-CH_2-C\equiv CH + h\nu \rightarrow C_4H_2^+ + C_2H_4$ (or $C_2H_2 + H_2$) $+ e^-$	13.05–13.78	17.38–18.10	12
C_6H_6 (benzene) $+ e^- \rightarrow C_4H_2^+ + C_2H_4$ (or $C_2H_2 + H_2$) $+ 2e^-$	17.05 ± 0.3	18.36 ± 0.3	45
$(C_2H_2)_3 + h\nu \rightarrow C_3H_3^+ + C_3H_3 + e^-$	10.10 ± 0.04	17.13 ± 0.04	this work
C_6H_6 (benzene) $+ h\nu \rightarrow C_3H_3^+ + C_3H_3 + e^-$	~14.25	~15.11	7

[a] Total energy = AE plus the heat of formation of the neutral isomer. [b] Calculated values with $\Delta H_f{}^\circ{}_{298}$(2,4-hexadiyne) = 86 ± 1 kcal/mol. See ref 8. [c] Calculated values with $\Delta H_f{}^\circ{}_{298}$(2,4-hexadiyne) = 90 ± 2 kcal/mol. See ref 12.

AE's for the formation of $C_6H_5^+ + H$, $C_6H_4^+ + H_2$, $C_4H_4^+ + C_2H_2$, $C_4H_3^+ + C_2H_3$ (or $C_2H_2 + H$), $C_4H_2^+ + C_2H_4$ (or $C_2H_2 + H_2$), and $C_3H_3^+ + C_3H_3$ from benzene, 1,5-hexadiyne, 2,4-hexadiyne, and 1,4-hexadiyne have been measured previously by photoionization[7,12,13,46] and electron impact[12,45] mass spectrometry. Some selected measurements on the AE's of these fragments are listed in Table II and compared with the results obtained here in the total energy scale. We note that the $C_6H_5^+$ as well as the $C_4H_4^+$ fragment onsets from benzene are very close in the total energy scale to values obtained from the linear C_6H_6 isomers. The differences between the AE's and the corresponding thermochemical thresholds of these processes were attributed to the kinetic shift effects.[50-52] These effects have been demonstrated by studying the effect of the ion residence time on the AE of $C_6H_5^+$ in benzene.[53-55] Gordon and Reid[55] found that the AE decreased from 14.2 ± 0.1 to 12.7 ± 0.1 eV as the ion residence time increased from ca. 5 to 1200 μs. The kinetic energy release studies of Cooks et al.[56] and Jones et al.[57] reveal only small kinetic energy releases for the $C_4H_4^+ + C_2H_2$ and $C_6H_5^+ + H$ channels, indicating that there are no significant barriers to the reverse reactions. The total energies corresponding to the AE's for $C_6H_5^+$, $C_6H_4^+$, $C_4H_4^+$, and $C_3H_3^+$ from $(C_2H_2)_3^+$ are much higher than those deduced from the AE's of these fragment ions from other stable $C_6H_6^+$ precursors. This is partly due to the higher heat of formation of $(C_2H_2)_3^+$ in comparison to the stabilities of the product fragments $C_6H_5^+ + H$, $C_6H_4^+ + H_2$, $C_4H_4^+ + C_2H_2$, and $C_3H_3^+ + C_3H_3$. We have interpreted the difference of 0.26 ± 0.06 eV between the AE's for $C_6H_5^+$, $C_6H_4^+$, $C_4H_4^+$, and $C_3H_3^+$ from $(C_2H_2)_3$ and the IE of $(C_2H_2)_3$ to be the potential-energy barrier for the rearrangement of $(C_2H_2)_3^+$ to other stable $C_6H_6^+$ ions. One of the most interesting results of this study is that the total energies (412 kcal/mol) corresponding to the AE's for $C_4H_3^+$ and $C_4H_2^+$ determined here are in fair agreement with those derived from the AE's of these two ions from stable $C_6H_6^+$ isomers (see Table II). Assuming the formations of $C_4H_3^+$ and $C_4H_2^+$ to be mainly due to reactions 7–10, this observation is consistent with the conclusion that the $(C_2H_2)_3^+$ ions rearrange to some stable $C_6H_6^+$ precursor ions before fragmenting.

The relative intensities for $(C_2H_2)_3^+$ (and/or $C_6H_6^+$), $C_6H_5^+$, $C_6H_4^+$, $C_4H_4^+$, and $C_3H_3^+$ measured at 1200 Å (10.33 eV) were 24, 1.0, 0.29, 6.5, and 0.37, respectively. At this excitation energy, there should be no contribution to the $C_3H_3^+$ and $C_4H_4^+$ ions from the acetylene dimers. The uncertainty in internal energy of the $(C_2H_2)_3^+$ ions formed is expected to be equal to $h\nu - \mathrm{IE}((C_2H_2)_3) = 10.33 - 9.83 = 0.5$ eV. Assuming a uniform distribution of internal energies for $(C_2H_2)_3^+$ in the total energy range 16.87–17.37 eV, the observed branching ratios for $(C_2H_2)_3^+$

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(37) S. W. Benson, "Thermochemical Kinetics", John Wiley and Sons, New York, 1968.

(38) Y. Sergeev, M. E. Akopyan, and G. I. Vilesov, *Opt. Spektrosk.*, **32**, 230 (1972).

(39) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969).

(40) J. L. Beauchamp. *Adv. Mass Spectrom.*, **6**, 717 (1974).

(41) J. H. D. Eland, J. Berkowitz, H. Schulte, and R. Frey, *Int. J. Mass Spectrom. Ion Phys.*, **28**, 297 (1978).

(42) W. Tsang, *Int. J. Chem. Kinet.*, **2**, 23 (1970).

(43) F. P. Lossing, *Can. J. Chem.*, **50**, 3973 (1972).

(44) A. C. Parr and F. A. Elder, *J. Chem. Phys.*, **49**, 2659 (1968).

(45) C. Lifshitz and B. G. Reuben, *J. Chem. Phys.*, **50**, 951 (1969).

(46) Reference 13 of ref 12.

(47) H. M. Rosenstock, R. Stockbauer, and A. C. Parr, *J. Chem. Phys.*, **73**, 773 (1980).

(48) H. M. Rosenstock, R. Stockbauer, and A. C. Parr, *J. Chim. Phys. Phys.-Chim. Biol.*, **77**, 745 (1980).

(49) H. M. Rosenstock, R. Stockbauer, and A. C. Parr, *Int. J. Mass Spectrom. Ion Phys.*, **38**, 323 (1981).

(50) L. Friedman, F. A. Long, and M. Wolfsberg, *J. Chem. Phys.*, **26**, 714 (1957).

(51) L. Friedman, F. A. Long, and M. Wolfsberg, *J. Chem. Phys.*, **27**, 613 (1957).

(52) W. A. Chupka, *J. Chem. Phys.*, **30**, 191 (1959).

(53) M. L. Gross, *Org. Mass Spectrom.*, **6**, 827 (1972).

(54) C. Lifshitz, A. M. Peers, M. Weiss, and M. J. Weiss, *Adv. Mass Spectrom.*, **6**, 871 (1974).

(55) S. M. Gordon and N. W. Reid, *Int. J. Mass Spectrom. Ion Phys.*, **18**, 379 (1975).

(56) R. G. Cooks, K. C. Kim, T. Keough, and J. H. Beynon, *Int. J. Mass Spectrom. Ion Phys.*, **15**, 271 (1974).

(57) E. G. Jones, L. Bauman, J. H. Beynon, and R. G. Cooks, *Org. Mass Spectrom.*, **7**, 185 (1973).

Table III. The Average Values for Relative Fragment-Ion Intensities from the Dissociation of Various Isomers of $C_6H_6^+$ and $(C_2H_2)_3^+$ in the Total Energy (Ionization Energy + Neutral C_6H_6 (or $(C_2H_2)_3$) Heat of Formation) Range of 16.87–17.37 eV (Normalized for the Intensity of $C_6H_5^+$)

	fragments[a]				
isomer	$C_6H_6^+$ (or $(C_2H_2)_3^+$)	$C_6H_5^+$	$C_6H_4^+$	$C_4H_4^+$	$C_3H_3^+$
$(C_2H_2)_3$[b]	24 ± 1.8	1.00 ± 0.10	0.29 ± 0.06	6.5 ± 0.7	0.37 ± 0.07
benzene[c]	~0	1.00 ± 0.37	0.23 ± 0.14	1.66 ± 0.46	0.44 ± 0.26
benzene[d]	~0.08	1.00	0.20	2.73	0.72
2,4-hexadiyne[e]	~0	1.00 ± 0.08	0.28 ± 0.03	2.00 ± 0.14	0.56 ± 0.05 (0.40 ± 0.05)[g]
1,3-hexadiyne[f]	~0	1.00 ± 0.14	0.12 ± 0.04	1.92 ± 0.14	0.52 ± 0.07

[a] The average values for the fragment-ion intensities in the total energy range 16.87–17.37 eV from various isomers of $C_6H_6^+$ are obtained by scaling breakdown diagrams shown in refs 3, 9, 13, and 14. [b] This work. [c] Reference 3. The total energy range 16.87–17.37 eV corresponds to the excitation energy in the range 16.0–16.5 eV. [d] Reference 9. [e] Reference 13. The total energy range 16.87–17.37 eV corresponds to the excitation energy in the range 13.14–13.64 eV. Since the data in the excitation energy range ~13.14–13.4 are not available, the values listed in the table represent the average values in the excitation energy range ~13.4–13.64 eV. [f] Reference 14. The total energy range 16.87–17.37 eV corresponds to the excitation energy in the range ~12.75–13.25 eV. [g] The value of 0.4 for the relative intensity of $C_3H_3^+$ is deduced from the ratio of the $C_3H_3^+$ and $C_4H_4^+$ intensities obtained in ref 8 and the average relative intensity for $C_4H_4^+$ reported in ref 13.

(and/or $C_6H_6^+$), $C_6H_5^+$, $C_6H_4^+$, $C_4H_4^+$, and $C_3H_3^+$ from $(C_2H_2)_3$ can be viewed as state-selected data with an energy spread of ~0.5 eV. The relative fragment-ion intensities from state-selected benzene,[3,9] 2,4-hexadiyne,[13] and 1,3-hexadiyne[14] molecular ions have been determined previously by photoion–photoelectron coincidence and charge-transfer methods. The energy resolutions used in ref 3, 13, and 14 are estimated to be 0.2, 0.3, and 0.3 eV, respectively. In order to make a meaningful comparison of the results of these studies and those observed here, we have obtained the relative intensities[58] of $C_6H_5^+$, $C_6H_4^+$, $C_4H_4^+$, and $C_3H_3^+$ by averaging the values scaled from the breakdown diagrams reported in ref 3, 9, 13, and 14 at intervals of ~0.1 eV in the total energy range ~16.87–17.37 eV. These average values, together with the results of the present study, are listed in Table III. The intensity of $C_6H_5^+$ has been normalized to 1.0. The branching ratios for $C_6H_5^+$, $C_6H_4^+$, and $C_3H_3^+$ from $(C_2H_2)_3$ are in reasonable agreement with those from benzene, 2,4-hexadiyne, and 1,3-hexadiyne. However, the relative intensity of $C_4H_4^+$ from $(C_2H_2)_3$ is approximately a factor of three greater than those observed from other stable C_6H_6 isomers. The higher intensity for $C_4H_4^+$ observed here might be partly due to the finite collisional dissociation reaction

$$(C_2H_2)_3^+ + M \rightarrow (C_2H_2)_2^+ + C_2H_2 + M \qquad (11)$$

Because of the relatively low dissociation energy for $(C_2H_2)_2^+\cdot C_2H_2$, the cross section for reaction 11 is expected to be large. The assumption that the distribution of internal energies for $(C_2H_2)_3^+$ is uniform in the total energy range 16.87–17.37 eV might also give rise to some discrepancies in this comparison. According to the study of Baer et al.,[8] at total energies above ~16.5 eV, there is evidence that the precursors involved in the fragmentation of the 1,5-hexadiyne ion are different from those involved in the dissociation of the benzene and 2,4-hexadiyne ions. Thus, it is possible that $(C_2H_3)_3^+$ might also react by a different, direct mechanism at these energies without sampling a common $C_6H_6^+$ phase space. In any case, the good agreement observed between the relative intensities of $C_6H_5^+$, $C_6H_4^+$, and $C_3H_3^+$ from $(C_2H_2)_3$ and those of ref 3, 9, 13, and 14 supports the interpretation that the dominate route for the decomposition of the $(C_2H_2)_3^+$ ions is the complex mechanism which involves the rearrangement of $(C_2H_2)_3^+$ to some precursors prior to dissociation as do other stable $C_6H_6^+$ isomers. Thus

$$(C_2H_2)_3^+ \rightarrow (C_6H_6^+)^* \rightarrow C_6H_5^+ + H \qquad (12)$$

$$\rightarrow C_6H_4^+ + H_2 \qquad (13)$$

$$\rightarrow C_4H_4^+ + C_2H_2 \qquad (14)$$

$$\rightarrow C_3H_3^+ + C_3H_3 \qquad (15)$$

Table IV. Photoionization Mass Spectra of $(C_2H_2)_3^+$[a, b]

λ, Å	$C_6H_6^+$ or $(C_2H_2)_3^+$	$C_6H_5^+$	$C_6H_4^+$	$C_4H_4^+$	$C_3H_3^+$
1200	24.0	1.00	0.29	6.5	0.37
1175	8.7	1.00	0.20	6.8	0.34
1100	3.2	1.00	0.19	14.3	0.43
1000	3.2	1.00	0.19	15.0	0.53
900	3.0	1.00	0.19	15.2	0.65
800	3.1	1.00	0.20	15.4	0.71
700	2.9	1.00	0.19	15.2	1.02
650	2.8	1.00	0.20	14.3	1.10

[a] These measurements have not been corrected for the transmission factors of various ions. [b] The error estimates for the relative intensities of $C_6H_6^+$ (or $(C_2H_2)_3^+$), $C_6H_5^+$, and $C_4H_4^+$ (or $(C_2H_2)_2^+$) are approximately 10%. For the relative intensities of $C_6H_4^+$ and $C_3H_3^+$, the uncertainties are estimated to be better than 20%.

The longest reaction time sampled in this experiment is $\sim 10^{-5}$ s, which is defined by the flight time of an ion from the ionization region to the entrance of the quadrupole mass spectrometer. Since the potential-energy barrier for the rearrangement of $(C_2H_2)_3^+$ to other stable $C_6H_6^+$ isomers is only ~0.26 eV, the lifetimes of the $(C_2H_2)_3^+$ complexes having internal excitations slightly above the barrier are expected to be shorter than 10^{-5} s. As shown in Table III, the intensity for $(C_2H_2)_3^+$ (and/or $C_6H_6^+$) is found to be much higher than those for the stable $C_6H_6^+$ ions observed in ref 3, 9, 13, and 14, implying that only a fraction of the $(C_2H_2)_3^+$ ions formed by reaction 1 at 1200 Å (10.33 eV) have high enough internal energies to overcome this barrier and dissociate according to reactions 12–15. As the excitation energy increases, the internal energy distribution will favor the dissociation processes and the intensity of the parent ion should decrease. Table IV lists the relative intensities of $(C_2H_2)_3^+$ (and/or $C_6H_6^+$), $C_6H_4^+$, $C_4H_4^+$ (and/or $(C_2H_2)_2^+$), and $C_3H_3^+$ obtained at several photon energies. The rapid decrease of the intensity of $(C_2H_2)_3^+$ (and/or $C_6H_6^+$) relative to other species is in accordance with this expectation. It is interesting to find that the relative intensities of $C_6H_5^+$ and $C_6H_4^+$ remain constant in the energy range 10.33–19.10 eV. The increases in intensities for $C_4H_4^+$ and $C_3H_3^+$ with respect to those of $C_6H_5^+$ and $C_6H_4^+$ at higher energies probably have the contributions from reactions 2 and 3.

Summary and Conclusions

Using the molecular beam photoionization method, we have determined the stabilities of the $(C_2H_2)_2^+$ and $(C_2H_2)_3^+$ complexes. By sampling the fragment ions in collision-free environments, we have also been able to identify the primary fragments from $(C_2H_2)_3^+$ and obtain the AE's of these fragments. The potential energy barrier for the rearrangement of $(C_2H_2)_3^+$ to other stable $C_6H_6^+$ isomers was measured to be 0.26 ± 0.06 eV.

In summary, the experimental observations which support the conclusion that the $(C_2H_2)_3^+$ ions rearrange to some common precursors as do other stable $C_6H_6^+$ isomers are as follows:

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[58] The relative intensities for $C_6H_5^+$, $C_6H_4^+$, $C_4H_4^+$, and $C_3H_3^+$ as shown by the breakdown diagrams in ref 3, 9, 13, and 14 only vary slightly in the total energy range 16.87–17.37 eV.

(1) The fragment ions observed from $(C_2H_2)_3^+$ are identical with those from other stable $C_6H_6^+$ isomers.

(2) The AE of $C_4H_4^+$ from $(C_2H_2)_3$ was found to be lower in energy than the IE of $(C_2H_2)_2$.

(3) The measured AE's for the formation of $C_4H_3^+$ and $C_4H_2^+$ from the $(C_2H_2)_3$ in the total energy scale are in agreement with the AE's of these two ions from 2,4-hexadiyne, 1,5-hexadiyne, and benzene.

(4) The relative intensities of the $C_6H_5^+$, $C_6H_4^+$, and $C_3H_3^+$ ions from $(C_2H_2)_3$ and those reported previously from benzene, 2,4-hexadiyne, and 1,3-hexadiyne in the total energy range 16.87–17.17 eV were found to be in fair agreement.

Acknowledgment. We would like to thank Mr. J. Erickson and Mr. S. H. Linn for their assistance in obtaining part of the data for this experiment. The authors also wish to thank the referees for their comments which have led us to perform a more thorough analysis of our experimental data.

Registry No. $C_6H_6^+$, 34504-50-2; $C_6H_5^+$, 17333-73-2; CH_2CHCCH^+, 59699-48-8; $C_3H_3^+$, 26810-74-2; $C_4H_4^+$, 79105-72-9; $C_6H_4^+$, 70220-84-7; 2,4-hexadiyne, 2809-69-0; 1,5-hexadiyne, 628-16-0; benzene, 71-43-2; 1,3-hexadiyne, 4447-21-6.

Electronic Structure of Bridged Dialuminum Compounds

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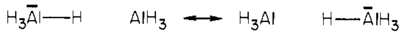
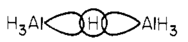
Abstract: Geometry-optimized 3-21G ab initio calculations were performed on the $[R_3Al\cdots H\cdots AlR_3]^-$ ion with R = H or R = CH_3. The lowest energy was obtained with a linear Al···H···Al structure. Small rotational barriers and bending energies are also reported. In addition, the structure of $[H_3Al\cdots Cl\cdots AlH_3]^-$ was calculated for comparison and found to be bent.

Atwood[2] et al. have reported an X-ray diffraction study of several electron-deficient species that possess a linear, singly hydrogen-bridged $[(CH_3)_3Al\cdots H\cdots Al(CH_3)_3]^-$ structure. This is particularly important, since it has been widely recognized that direct metal-to-metal bonding, resulting in a nonlinear structure (such as in the $[Cl_3AlClAlCl_3]^-$ ion) may be significant.[3] The bonding present in such electron-deficient compounds has been widely discussed in the literature.[4]

We wish to report ab initio geometry-optimized calculations on the $[R_3Al\cdots H\cdots AlR_3]^-$ ion, where R = H and R = CH_3, and, for comparison, $[H_3AlClAlH_3]^-$. The calculations were performed with the GAUSSIAN-80 program with a 3-21G basis set. The optimized geometry parameters are given in Table I. The linear Al···H···Al bond is of importance and reproduces the experimental data. That the bridging Al···H is longer than the terminal Al–H bond is expected by considering either the resonance structures in **1** or on the basis of the bonding molecular orbital fragment shown in **2**, which makes up the electron-deficient bond.


1


2

On examination of the nature of the Al···H···Al central bond, it is found to exhibit a similarity to a hydrogen bond where the electron-donating atom would be the hydrogen while the formally vacant aluminum sp^3 hybrid would be functioning as an acceptor orbital constituting what we would call an "aluminum bond". Similar bonding has been found in organolithium compounds to exist between oligomers.[5]

Table I. Geometry-Optimized Parameters and Energies for $[R_3Al\cdots H\cdots AlR_3]^-$ Species

	R = H, 3-21G	R = CH_3[a], 3-21G[a]	R = CH_3, exptl[2]
Al···H, Å	1.720	1.731	1.665
R–Al, Å	1.632	2.030	
Al···H···Al, deg	180.0	180.0	
R–Al···H, deg	104.4	104.0	
energy, au	−485.226	−718.2540	

[a] The H–C length and H–C–Al angle optimized to 1.091 Å and 111.4°, respectively.

Table II. Geometry-Optimized Parameters and Energy for $[R_3Al\cdots Cl\cdots AlR_3]^-$ Species

	R = H, 3-21G	R = Cl, exptl[3]
Al···Cl, Å	2.467	2.24
R–Al, Å	1.621	2.10
Al···Cl···Al, deg	132.6	110.0
R–Al···Cl, deg	103.0	
energy, au	−942.0464	

The rotational barriers, calculated as being less than 1 kcal/mol, are predictably small. This might be interpreted as being due to negligible direct interaction between the AlH_3 units. The Al–Al distance is in excess of 3.4 Å. An additional cause may be that the central hydrogen bears only an s-type orbital. We have also performed optimized 3-21G calculations on ethane-like Al_2H_6 in D_{3h} and D_{3d} geometries and again obtained a barrier of <1 kcal/mol even though the Al–Al distance now optimizes to approximately 2.76 Å. Another point concerning interaction is that

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[1] (a) Brooklyn College. (b) John Jay College. (c) Queensborough College.

[2] (a) Atwood, J. L.; Rogers, M. J.; Zaworotko, M. Y.; Hunter, W. E.; Hrncir, D. C., presented at the Tenth International Conference on Organometallic Chemistry, Toronto, August, 1981. (b) Atwood, J. L.; Hrncir, D. C.; Rogers, M. J.; Howard, J. A. K.; *J. Am. Chem. Soc.*, in press.

[3] Loken, D. A.; Couch, T. W.; Corbett, J. D., "Abstracts of Papers", 160th National Meeting of the American Chemical Society, Chicago, September 1970; American Chemical Society: Washington, D.C., 1970.

[4] (a) Oliver, J. P., *Adv. Organomet. Chem.* **1977**, *15*, 239–250. (b) Cocco, L.; Eyman, D. P., *J. Organomet. Chem.*, **1979**, *179*, 1. (c) Pelissier, M.; Malrieu, J. P., *Theor. Chim. Acta*, **1980**, *56*, 175.

[5] (a) Sapse, A. M.; Howell, J. M., presented at the Tenth International Conference on Organometallic Chemistry, Toronto, August, 1981. (b) Submitted for publication.