J. Am. Chem. Soc. 1993, 115, 4363–4364 4363

Annealing of Carbon Cluster Cations: Rings to Rings and Rings to Fullerenes

Gert von Helden, Nigel G. Gotts, and Michael T. Bowers*

Department of Chemistry, University of California
in Santa Barbara, Santa Barbara, California 93106

Received February 11, 1993

Carbon clusters have long been the focus of an intense research effort. An excellent review article on research conducted up to 1988 has been given by Weltner and van Zee.[1] We recently applied the new gas-phase ion chromatography technique[2] to carbon cluster cations[3] and anions.[4] Valuable information on cluster structure and the abundance of different isomeric forms as a function of cluster size were obtained. These results indicate that most clusters in the size range C_7–C_{80} exist in a distribution of isomeric structures.[5] Computer simulations of mobilities allowed unambiguous structural assignment for most of these isomeric forms.[5] Among the different structures found for the cations are monocyclic rings, first appearing at C_7^+, bicyclic rings, first present at C_{21}^+, tricyclic rings starting at C_{30}^+, "3-D rings" first observed at C_{29}^+, and fullerenes from C_{30}^+ on. Interestingly, no "graphitic" or "cup"-type species were observed at any cluster size for either positive or negative ions. This paper will be concerned primarily with the size range from C_{30}^+ to C_{40}^+ where mono-, bi-, and tricyclic rings dominate the isomer distribution but fullerenes begin to efficiently compete. Above C_{40}^+, fullerenes rapidly become dominant, especially for even-sized clusters.

Little is known about the relative stability of these structures. For neutral clusters, ab initio calculations predict the fullerenes to be lower in energy than the monocyclic ring starting at about C_{30},[6] although other calculations indicate that the crossover might be as early as C_{20} and/or C_{24}.[7] However, fullerenes are not observed for cluster sizes below C_{30} for either positive or negative ions.[4,5,7d] Calculations also indicate that bi- and tricyclic ring structures are higher in energy than the monocyclic ring.[7d] In this paper, we present results from annealing experiments, similar to those first done by Jarrold and Hanoea on silicon clusters,[8] and obtain information on the energetics and dynamics of carbon cluster cations with between 30 and 40 atoms. We will also try to answer the puzzling question of why fullerenes mysteriously appear at C_{30} when no structurally similar "building blocks" are present for smaller sizes[7d] and whether planar monocyclic or planar polycyclic ring systems are more stable.

The ion chromatography experiment[3–5] has been described previously and will not be repeated here. Figure 1 shows a mass spectrum obtained by scanning the quadrupole following the chromatography cell when injecting C_{37}^+ at 150 eV. Extensive fragmentation is apparent. The main fragments are from the loss of a neutral carbon atom, the loss of C_3, and the loss of C_{14}, C_{18}, and C_{22}. ATDs for the parent C_{37}^+ injected at 50 and 150 eV and for the fragments C_{36}^+, C_{34}^+, and C_{23}^+, obtained at 150-eV injection, are shown in Figure 2. The ATD for C_{37}^+ at 50 eV (Figure 2a) shows the same features as previously reported.[3] At the shortest time, a small amount of fullerene (the shaded peak) is observed, followed at substantially longer times by the 3-D ring isomer (B), tricyclic ring (C), bicyclic ring (D), and finally the monocyclic ring (E). The ATD for C_{37}^+ ions that survive injection at 150 eV, however, looks quite different (Figure 2b), with the bicyclic and tricyclic rings almost completely absent and the monocyclic ring now the dominant feature. The ATD for the C_{36}^+ fragment, Figure 2c (resulting from the loss of a neutral carbon atom), consists of only a single peak, and therefore only a single isomer is present. The mobility of this fragment is identical to the C_{36}^+ fullerene mobility, and consequently we can conclude unambiguously that this fragment is indeed C_{36}^+ fullerene. The same analysis can be performed for the ATD of the C_{34}^+ fragment (Figure 2d). In this case the dominant peak (93%) is C_{34}^+ fullerene (the two minor features are C_{34}^+ 3-D ring and monocyclic ring). On the other hand, analysis of the ATDs for the C_{15}^+, C_{19}^+, and C_{23}^+ fragments indicate that all of them have exclusively monocyclic ring structures (only the C_{23}^+ ATD is shown in Figure 2e).

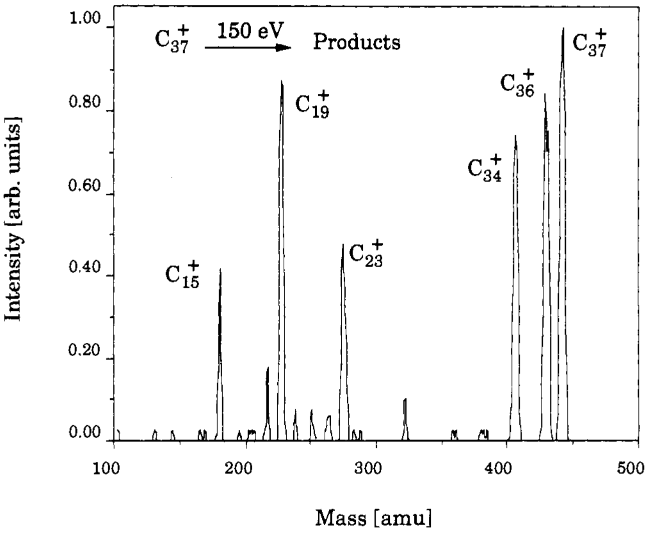


Figure 1. Mass spectrum obtained by scanning the quadropole following the chromatography cell when injecting C_{37}^+ at 150 eV into the drift cell. The main fragments are formed by loss of neutral C_1, C_3, C_{14}, C_{18}, and C_{22}.

We performed annealing experiments with all C_n^+ clusters with $30 \leq n \leq 40$ at 150-eV injection energy (Figure 3). The probability of collision-induced dissociation (CID) increases dramatically as cluster size increases (Figure 3a). Also, the dissociation channels change as cluster size increases (Figure 3b). The first fullerene observed is C_{30}^+, resulting from C_3 loss in the annealing of C_{33}^+. This process is fairly inefficient for C_{33}^+, with only 13% of all clusters undergoing CID and only 17% of the CID products being fullerenes; the remaining 83% are monocyclic rings. For precursors with an even number of atoms, the first fullerene fragment observed is C_{34}^+, resulting from the loss of C_2 from C_{36}^+. It appears that isomerization of the ring species occurs before neutral loss so that the more stable even fullerene species can be formed by ejecting C_1, C_2, or C_3 from the nascent product. If C_{10}, C_{14}, C_{18}, or C_{22} is lost, products are always monocyclic rings. The very specific loss of these neutrals strongly suggests they are primary building blocks in the bi- and tricyclic planar ring systems. Similar preferred losses of C_{10} and C_{14} have been reported[9] in the metastable ion spectra of energized carbon clusters in the parent ion range C_{24}^+–C_{29}^+.

---

(1) Weltner, W., Jr.; van Zee, R. J. *Chem. Rev.* **1989**, *89*, 1713.

(2) Kemper, P. R.; Bowers, M. T. *J. Am. Chem. Soc.* **1990**, *112*, 3231; *J. Phys. Chem.* **1991**, *95*, 5134.

(3) von Helden, G.; Hsu, M.-T.; Kemper, P. R.; Bowers, M. T. *J. Chem. Phys.* **1991**, *95*, 3835.

(4) von Helden, G.; Kemper, P. R.; Gotts, N. G.; Bowers, M. T. *Science* **1993**, *259*, 1300. Gotts, N. G.; von Helden, G.; Kemper, P. R.; Bowers, M. T., to be published.

(5) von Helden, G.; Gotts, N. G.; Hsu, M. T.; Kemper, P. R.; Bowers, M. T., to be published. See also 7d.

(6) Feyereisen, M.; Gutowski, M.; Simons, J.; Almlöf, J. *J. Chem. Phys.* **1992**, *96*, 2926.

(7) (a) Brabec, C. J.; Anderson, E. B.; Davidson, B. N.; Kajihara, S. A.; Zhang, Q.-M.; Bernholc, J.; Tomanek, D. *Phys. Rev. B Rapid Commun.* **1992**, *46*, 7326, (b) Jensen, F.; Toftlund, H. *Chem. Phys. Lett.* **1993**, *201*, 89, (c) Parasuk, V.; Almlöf, J. *Chem. Phys. Lett.* **1991**, *184*, 187. (d) von Helden, G.; Hsu, M. T.; Gotts, N. G.; Kemper, P. R.; Bowers, M. T. *Chem. Phys. Lett.* **1993**, *204*, 15.

(8) Jarrold, M. F.; Honea, E. C. *J. Am. Chem. Soc.* **1992**, *114*, 459.

(9) Radi, P. P.; Bunn, T. L.; Kemper, P. R.; Molchan, M. E.; Bowers, M. T. *J. Chem. Phys.* **1988**, *88*, 2809.

0002-7863/93/1515-4363$04.00/0

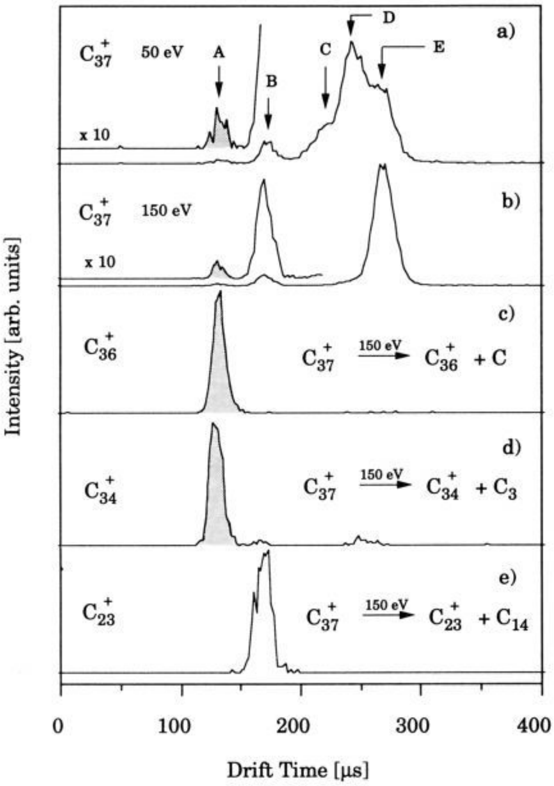


Figure 2. Arrival time distributions (ATDs), or chromatograms, for C_{37}^+ and its main fragmentation products. The top trace (labeled a) is an ATD for C_{37}^+ injected at low energies. No fragmentation or isomerization occurs at these energies. Peak A is a fullerene, B a 3-D ring, C a tricyclic planar ring, D a bicyclic planar ring, and E a monocyclic planar ring isomer. Justification for these assignments is given elsewhere.[3-5,7d] The trace labeled b is an ATD for C_{37}^+ injected at high energies (150 eV). Note that peak C and D are completely absent. The traces labeled c, d, and e are ATDs for the fragments C_{36}^+, C_{34}^+, and C_{23}^+ when C_{37}^+ is injected at 150 eV. The dominant peaks in the C_{36}^+ and C_{34}^+ ATDs correspond to 100% fullerene, while the single peak for C_{23}^+ is a monocyclic ring. In parts a, b, c, and d fullerene peaks are shaded.

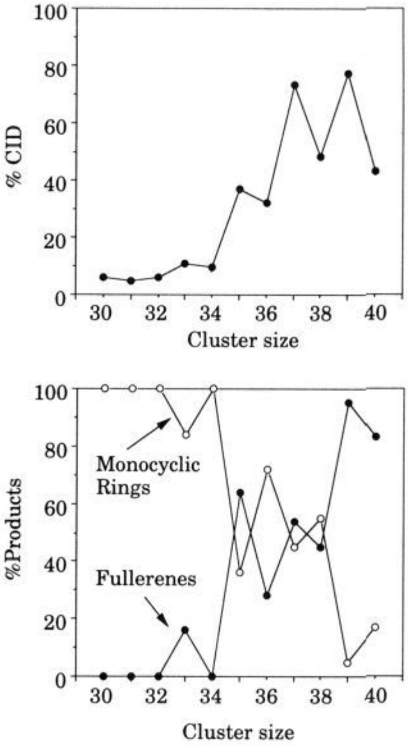
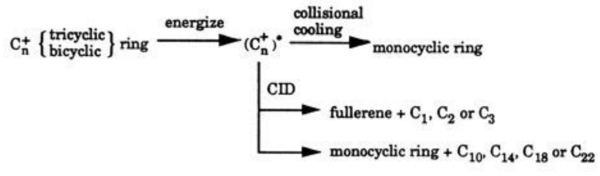


Figure 3. (a) Total amount of CID occurring when injecting C_n^+ ($30 \leq n \leq 40$) clusters with 150 eV in the chromatography cell as a function of cluster size. The percent CID observed varies with source conditions. (b) Percentage of the fragments that are fullerenes or monocyclic rings under the same conditions as above.

The data presented here indicate that the monocyclic rings and fullerenes are the most stable isomers for a given cluster size, with monocyclic rings most likely being more stable below C_{30} and fullerenes being more stable above C_{36}. The fact that we see monocyclic rings and fullerenes competing as isomeric products between C_{30}^+ and C_{36}^+ indicates that these species must have similar energies in this size range. Given these observations, our qualitative view of the annealing process is given in the following reaction sequence.



In our experiments, fullerene formation is always accompanied by loss of C_1, C_2, or C_3, presumably to evaporatively cool the nascent fullerene product. As a consequence, the isomerisation reaction rings → fullerenes must be highly exothermic for parent ions where these processes dominate. The above discussed reaction sequence is consistent with ab initio calculations[6] that suggest that fullerenes become much more stable than monocyclic rings for clusters larger than C_{36}.

The data presented here also indicate that the rearrangement barrier for transformation from planar ring systems to fullerenes must be relatively low in energy, despite the high degree of structural transformation that must be occurring, and it must significantly decrease as cluster size increases. This is the only reasonable explanation for the observation that the fractions of fullerene formation and parent CID both increase with cluster size even though the amount of internal energy per carbon atom (obtained from 150-eV injection of the parent ion into the drift cell) decreases. Most previous concepts of fullerene formation[10] have involved graphitic cup-shaped fullerene precursors where growth was presumed to occur by addition of small carbon fragments. The fact that these potential precursors are not observed for the cations[3,5,7d] or the anions[4,7d] from laser vaporization sources indicate that they are probably not important in fullerene formation. Since large amounts of multicyclic rings systems are observed and since these ring systems can be efficiently converted to fullerenes, they most likely play an important role in the fullerene formation process both in laser vaporization sources and in carbon arc reactors. Some support for the mechanism presented here comes from the work of Rubín et al.[11] and McElvany et al.[12] where large, positively charged ring systems (C_{18}^+, C_{24}^+, C_{30}^+) are reported to react with their neutral precursors to form C_{60}^+ and C_{70}^+, whose structures appear to be fullerene. The details of the fullerene formation mechanism will be discussed in more detail in a separate publication.[13]

Acknowledgment. Support of the Air Force Office of Scientific Research under grant AFOSR 92-J-0021 and from National Science Foundation under grant CHE91-19752 is gratefully acknowledged.

---

[10] For a review, see: Curl, R. F. *Phil. Trans. R. Soc. London, A*, in press.

[11] Rubin, Y.; Kahr, M.; Knobler, C. B.; Diederich, F.; Wilkins, C. L. *J. Am. Chem. Soc.* **1991**, *113*, 495.

[12] McElvany, S. W.; Ross, M. M.; Goroff, N. S.; Diederich, F. *Science* **1993**, *259*, 1594.

[13] von Helden, G.; Gotts, N. G.; Bowers, M. T. *Nature*, in press.