phase transitions without some other check on the phase structure of the materials in question; this caveat obviously applies to biological and food scientists also.

REFERENCES AND NOTES

1. T. P. Russell and J. T. Koberstein, *J. Polym. Sci.* **23**, 1109 (1985).
2. W. Bras *et al.*, *J. Phys. IV* (*Paris*) **3** (no. 8), 447 (1993).
3. M. Bark, C. Schulze, H. Zachmann, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Sci.* **31** (no. 2), 106 (1990).
4. J. L. Koenig, *Spectroscopy of Polymers* (ACS Reference Book, American Chemical Society, Washington, DC, 1992).
5. C. W. Macosko, *RIM: Fundamentals of Reaction Injection Molding* (Hanser, Munich, 1988).
6. H. S. Lee and S. L. Hsu, *Macromolecules* **22**, 1100 (1989).
7. R. D. Priester Jr. *et al.*, *J. Cell. Plast.* **26** 346, (1990).
8. W. P. Yang and C. W. Macosko, *Makromol. Chem. Macromol. Symp.* **25**, 23 (1989).
9. H. S. Lee, Y. K. Wang, W. J. MacKnight, S. L. Hsu, *Macromolecules* **21**, 270 (1988).
10. M. J. E. Elwell, thesis, University of Manchester (1993).
11. A. J. Ryan, M. J. E. Elwell, G. E. Derbyshire, D. Bogg, W. Bras, in preparation.
12. The FTIR and SAXS data acquisition systems were controlled by separate computers. The 1-min time resolution allowed a manual start of both systems without the introduction of a significant error.
13. M. J. E. Elwell, A. J. Ryan, H. J. M. Grünbauer, H. C. van Lieshout, J. A. Thoen, *Prog. Rubber Plast. Technol.* **9**, 120 (1993).
14. A. J. Ryan *et al.*, *Macromolecules* **24**, 2883 (1991).
15. F. S. Bates and G. H. Fredrickson, *Annu. Rev. Phys. Chem.* **41**, 525 (1990).
16. The SAXS relative invariant is

$$Q' = \int_{0\ 01}^{0\ 20} I(q,t)q^2dq$$

where I is the intensity of the signal, q is the scattering vector, and t is time.

17. The Engineering and Physical Sciences Research Council (EPSRC) is acknowledged for x-ray beam time. D. Bouch and P. Hindley provided valuable technical support. Reagents were supplied by and M.J.E. was supported by Dow Chemicals. J.C. and S.N. were supported by EPSRC studentships.

11 August 1994; accepted 6 December 1994

Evidence from Ion Chromatography Experiments That Met-Cars Are Hollow Cage Clusters

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Ion chromatography studies were performed to assess various models proposed for the structure of M_8C_{12} species, the met-cars. A laser desorption source was used to make a sequence of titanium-carbon clusters centered around $Ti_8C_{12}^+$. The $Ti_8C_{12}^+$ was determined to be a hollow cage cluster, with the dodecahedron structure originally proposed giving the best fit to experiment; cubic structures could be excluded. Collisional breakup of $Ti_8C_{12}^+$ yielded only $Ti_7C_{12}^+$ under the experimental conditions described herein, and modeling indicated that the cage structure was retained. Both $Ti_8C_{11}^+$ and $Ti_8C_{13}^+$ were made by the cluster source, and again, dodecahedral-type cage structures were consistent with experiment. The extra carbon atom in $Ti_8C_{13}^+$ was attached exohedrally to a single titanium atom. No evidence for an endohedral species was found.

The discovery (*1*) and bulk synthesis (*2*) of fullerenes has allowed the structure of these hollow cage carbon clusters to be determined by traditional spectroscopic means (*3*). However, for all other larger ($n \geq 10$) carbon clusters, the most reliable and nearly exclusive structural evidence comes from ion chromatography (IC) studies (*4*, *5*). The IC studies showed that large, planar ring systems competed with fullerenes in the size range $n = 30$ to 60 (*4–8*) and in fact are the primary precursors of fullerenes formed in laser desorption sources (*8–10*).

In parallel development, Castleman and co-workers (*11*) discovered a class of stable metallo-carbon composites with the stoichiometry M_8C_{12}, where M was one of several transition metals. These species were identified by their "magic" character in mass spectra where, under certain source conditions, the mass-to-charge (m/z) peak corresponding to M_8C_{12} completely dominated neighboring species. Castleman proposed a dodecahedral cage structure of T_h symmetry composed of a cube of M atoms with C_2 units raised off each cube face and coined the term met-cars for these putative metallocarbohedrene species.

This proposition prompted a rapid response from the theoretical community, which rather quickly confirmed that M_8C_{12} cages were particularly stable species (*12*), although a somewhat lower energy was predicted for a distorted M_8 cube of T_d symmetry with the C_2 units rotated along the cube diagonals. This structure is composed of two tetrahedral pairs of four metal atoms rather than the eight equivalent atoms of the dodecahedral structure. Castleman and coworkers provided indirect evidence for a cage structure by showing that $Ti_8C_{12}^+$ would attach a maximum of eight polar ligands (H_2O, ND_3, and CH_3OH), indicating that all Ti centers were available for bonding (*13*). Only four π-type ligands could be attached (C_2H_4, C_6H_6), which could indicate that either steric hindrance is involved or four of the Ti atoms are more accessible than the remaining four. Subtle changes in the structure of the Ti_8C_{12} backbone could occur as a result of the attachment reactions.

We applied the IC technique (*14*, *15*) to both carbon cluster ions (*4–6*, *8*, *9*) and to small carbon-metal composite clusters (*16*). In conjunction with computer modeling, IC allows us to probe the shape of cluster ions by measuring their mobilities. We have shown that isomeric species that differ substantially in structure can be readily identified and many salient features about their structures unambiguously determined. The experimental setup has been described (*15*, *17*). Cluster cations were generated in a standard laser vaporization supersonic expansion source (*18*). Once inside the IC cell, the mass-selected pulse of ions was subjected to a small uniform electric field that gently drifted the ions through a bath of He gas, usually present at 3 to 5 torr (at 300 K). The ion packet eventually exited the cell, was mildly accelerated, and was passed through a quadrapole mass filter, and an arrival time distribution (ATD) was obtained at the detector. For a single geometric isomer of a single cluster ion, the ATD could be readily converted to an ionic mobility. If multiple isomeric structures were present, then the IC device would spatially and temporally separate them if they differed significantly in shape. In this case, the ATD would have several peaks. The detailed shape (that is, the width) of each individual peak could, if necessary, be accurately reproduced by using the transport characteristics of that ion through He gas.

A mass spectrum obtained under typical operating conditions is shown in Fig. 1A. The series of peaks are separated by 12 atomic mass units (amu), and the strong peak at 528 amu corresponds to the correct mass of a singly charged Ti_8C_{12} cluster. However, the 528-amu peak could possibly be C_{44}^+. A high-resolution spectrum (Fig. 1B) shows that the underlying isotopic distribution agrees within 1% of that expected for $Ti_8C_{12}^+$ and bears no resemblance to that expected for C_{44}^+. Similarly, the peaks centered near 516 and 540 amu can be shown to be $Ti_8C_{11}^+$ and $Ti_8C_{13}^+$, respectively.

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An IC spectrum of $Ti_8C_{12}^+$ is given in Fig. 2, along with a predicted spectrum for a species with a mobility of 5.78 $cm^2\ V^{-1}\ s^{-1}$. The agreement between the two curves indicates that the IC peak is due primarily to a single species, although the presence of a small amount (<10%) of a second species with a similar mobility cannot be ruled out. The structure of the species giving rise to the IC peak can be determined as follows. First, trial structures must be obtained by some process. For carbon clusters (*5*), we used either ab initio or semiempirical methods to calculate stable structural candidates. In the case of Ti_8C_{12}, a number of theoretical structures have already been proposed, so we chose to use these to see if a fit is obtained. Once a structure is chosen, Monte Carlo methods are used to obtain its rotationally averaged cross section for collision with helium, and from this cross section it is straight forward to calculate the corresponding mobility (*5*, *19*). The theoretically predicted structures we have chosen to model are the dodecahedral structure first suggested by Castleman (*11*), the distorted dodecahedron found to be slightly lower in energy by several groups (*12*), a "cubic" structure suggested by Pauling (*20*) where the Ti atoms occupy the apices of the cube and C_2 units the faces, and a "cubic" structure proposed by Khan (*21*) where again the Ti atoms form a cube but this time the 12 carbon atoms form a hollow ball inside the cube. The predicted mobilities of each of these models and their agreement with experiment is given in Table 1.

In interpreting the results in Table 1, several things should be considered. First, the modeled mobilities have an inherent uncertainty of ~1%, primarily from the finite sampling in the Monte Carlo process. For pure carbon clusters, the mobilities could be determined with only one adjustable parameter, the sum of the He and C van der Waals radii. From fitting a very large amount of data, the best number for this sum was chosen to be 2.70 Å (*5*). However, when a cluster is composed of more than one kind of atom, individual van der Waals radii are needed. The He van der Waals radius was determined from He–He interaction potential calculations (*22*, *23*) yielding 1.09 Å. Consequently, carbon has a van der Waals radius of 2.70 – 1.09 = 1.61 Å. We estimated the Ti van der Waals radius to be 2.10 Å by calculating Ti^+–He interaction potentials (*24*), a procedure that worked very well in obtaining the van der Waals radius of the Cl atom (*22*) and the van der Waals radii of other metal atoms (*23*). These three van der Waals radii were used in all model mobility calculations reported here, yielding a probable uncertainty of ~2% in these quantities.

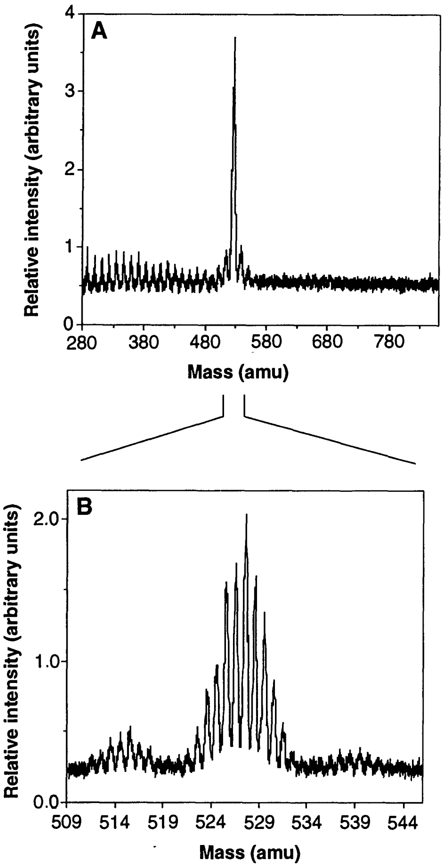

Fig. 1. (**A**) A low-resolution mass spectrum of clusters formed by laser desorption of a titanium rod with 1% CH_4 present in the He expansion gas. The peaks are separated by 12 amu. (**B**) The peaks centered at *m/z* = 516, 528, and 540 are recorded under higher mass resolution.

The dodecahedral structure first proposed by Castleman gives the best agreement with experiment. The 1.4% difference between the model mobility and experiment is typical of variances observed for carbon clusters. For reasons outlined above, however, a somewhat larger uncertainty is present for the Ti-C clusters and hence the more compact structures predicted theoretically, and listed as a distorted dodecahedron in the table, cannot be excluded. However, the cubic structures of Pauling, and especially of Khan, are far outside the acceptable uncertainty range and can be excluded. The important result is that the Ti_8C_{12} met-car definitely has a hollow cage–type structure not dissimilar to the one initially proposed by Castleman and co-workers.

Our interest includes determining the growth mechanism of these species. In this regard, several additional experiments were carried out on systems related to $Ti_8C_{12}^+$. The first of these involved injecting $Ti_8C_{12}^+$ into the IC cell at high energy to see if any fragments were formed and to determine their structure (Fig. 3) (*25*). Only one fragment was observed, loss of Ti to form $Ti_7C_{12}^+$. Neither a C_2 unit nor a Ti–C_2 unit was ejected. A similar result was obtained by Pilgrim and Duncan upon photodissociation of $Ti_8C_{12}^+$, where the primary process was loss of a single Ti atom along with smaller losses of two and three Ti atoms (*26*). The IC spectrum of $Ti_7C_{12}^+$ consisted of a single peak, and its mobility was determined. There are no theoretical structures of $Ti_7C_{12}^+$ reported, and calculations on this species was deemed beyond the scope of this work. We did, however, model $Ti_7C_{12}^+$ formed by simply removing a Ti atom from the dodecahedron cage. The results are given in Table 1. Good agreement with experiment was found, confirming that the cage structure is retained. Some relaxation will occur around the defect site making the actual structure slightly more compact, which would probably improve the comparison with experiment.

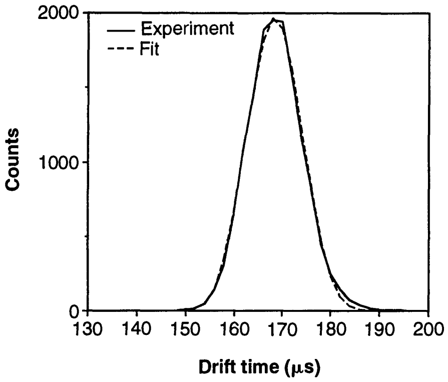

Fig. 2. Arrival time distribution of $Ti_8C_{12}^+$ after it has passed through the ion chromatography cell (solid line). The dotted line is a predicted peak shape of a single component with a mobility of 5.71 $cm^2\ V^{-1}\ s^{-1}$ obtained by solving the transport equations under the conditions of the experiment.

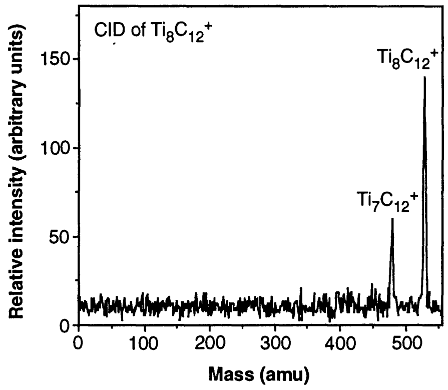

Fig. 3. A mass spectrum obtained by scanning the quadrapole mass filter following the IC cell under conditions where pure $Ti_8C_{12}^+$ is injected into the cell at 150 eV. CID, collision-induced dissociation.

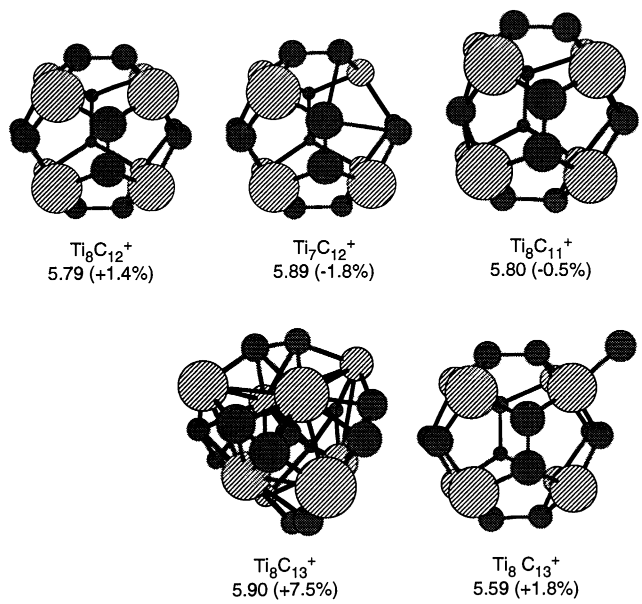

Fig. 4. Cartoons of several of the species used as model structures for $Ti_8C_{12}^+$, $Ti_7C_{12}^+$, $Ti_8C_{11}^+$, and $Ti_8C_{13}^+$. The predicted mobilities are given along with the percent deviation from experiment. The Ti atoms are shown as the lighter shaded species, and the C atoms are the darker cross-hatched species.

Table 1. Comparison of experimental and model mobilities for various $Ti_xC_y^+$ clusters; the deviation is (model − experiment)/(experiment).

Formula	Structure	Model mobility (cm^2 V^{-1} s^{-1})	Deviation (%)
$Ti_8C_{12}^+$	Dodecahedron (*11*)	5.79	+1.4
	Distorted dodecahedron (*12*)	5.89	+3.2
	Cubic (*19*)	5.24	−8.2
	Cubic (*20*)	4.73	−17.2
$Ti_7C_{12}^+$	Dodecahedron (less Ti atom)	5.89	−1.8
$Ti_8C_{11}^+$	See Fig. 4	5.80	−0.5
$Ti_8C_{13}^+$	Endohedral (*27*)	5.90	+7.5
$Ti_8C_{13}^+$	Exohedral (Fig. 4)	5.59	+1.8

We could not dislodge a C atom from $Ti_8C_{12}^+$, but we could observe $Ti_8C_{11}^+$ coming from the cluster source (see Fig. 1). This species yielded an IC spectrum with a single peak from which a mobility was determined. To model this cluster, we removed one of the C atoms from dodecahedral $Ti_8C_{12}^+$ and shifted the remaining C atom to the cube face (see Fig. 4). The results are given in Table 1. Again, excellent agreement with experiment was obtained.

Pilgrim and Duncan (*27*) have observed a large "magic" peak in the mass spectrum at an *m/z* value corresponding to $Ti_{14}C_{13}^+$. They suggested that this species had a cubic structure and was a 3 × 3 × 3 face-centered-cubic lattice fragment. Of interest here is the fact that photodissociation of $Ti_{14}C_{13}^+$ loses six Ti atoms and forms $Ti_8C_{13}^+$ as the dominant fragment, not $Ti_8C_{12}^+$ (*27*). Pilgrim and Duncan suggest that the central carbon in the 3 × 3 × 3 $Ti_{14}C_{13}^+$ lattice fragment may become trapped endohedrally inside a met-car $Ti_8C_{12}^+$ cage. In our experiment, $Ti_8C_{13}^+$ is made in the cluster source (Fig. 1). This species gives a single-peak IC spectrum from which a mobility is obtained. We modeled $Ti_8C_{13}^+$ using an endohedral structure and an exohedral structure where the C atom was attached to a single Ti atom (see Fig. 4 and Table 1). The endohedral species does not agree with experiment within allowed error limits, whereas the exohedrally bonded carbon model is in excellent agreement with experiment. Hence, growth of Ti-C composites immediately beyond the $Ti_8C_{12}^+$ met-car occurs by first attaching carbon to the outside of the met-car cage. Somewhere between the formation of $Ti_8C_{13}^+$ and $Ti_{14}C_{13}^+$ a major structural transformation must occur. Neither our experiment nor that of Pilgrim and Duncan yielded equilibrium structures (that is, they are kinetically controlled); hence, it is very possible that $Ti_8C_{13}^+$ made from photodissociation of $T_{14}C_{13}^+$ does have the extra C atom trapped inside a $Ti_8C_{12}^+$ cage.

REFERENCES AND NOTES

1. H. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **318**, 1662 (1985).
2. W. Krätschmer, K. Fostiropolis, D. R. Hoffman, *Chem. Phys. Lett.* **170**, 167 (1990); R. E. Haufler *et al.*, *J. Phys. Chem.* **94**, 8634 (1990); R. Taylor, J. P. Hare, A. K. Abdulsada, H. W. Kroto, *J. Chem. Soc. Chem. Commun.* **N20**, 1423 (1990).
3. Special issue, "Buckminster Fullerenes," *Acct. Chem. Res.* **95**, 3 (March 1992).
4. G. von Helden, M.-T. Hsu, P. R. Kemper, M. T. Bowers, *J. Chem. Phys.* **95**, 3835 (1991).
5. G. von Helden, M.-T. Hsu, N. Gotts, M. T. Bowers, *J. Phys. Chem.* **97**, 8182 (1993).
6. Negative carbon clusters exhibit the same families of structures as the cationic clusters, although the relative abundances are different [N. Gotts, G. von Helden, M. T. Bowers, unpublished results; see also G. von Helden, P. R. Kemper, N. G. Gotts, M. T. Bowers, *Science* **259**, 1300 (1993)].
7. J. M. Hunter, J. L. Fye, M. F. Jarrold, *J. Chem. Phys.* **99**, 1785 (1993).
8. G. von Helden, N. G. Gotts, M. T. Bowers, *J. Am. Chem. Soc.* **115**, 4363 (1993).
9. ______, *Nature* **363**, 60 (1993).
10. J. Hunter, J. Fye, M. F. Jarrold, *Science* **260**, 784 (1993).
11. B. C. Guo, K. P. Kerns, A. W. Castleman Jr., *ibid.* **255**, 1411 (1992); S. Wei, B. C. Guo, J. Purnell, S. Buzza, A. W. Castleman, *J. Phys. Chem.* **96**, 4166 (1992); B. C. Guo, S. Wei, J. Purnell, S. Buzza, A. W. Castleman Jr., *Science* **256**, 515 (1992).
12. I. G. Dance, *J. Chem. Soc. Chem. Commun.* (no. 24) (1992), p. 1779; M.-M. Rohmer, M. Bénard, C. Henriet, C. Bo, J.-M. Poblet, *ibid.* (no. 15) (1993), p. 1182; Z. Lin and M. B. Hall, *J. Am. Chem. Soc.* **115**, 11165 (1993).
13. B. C. Guo, K. P. Kerns, A. W. Castleman, *J. Am. Chem. Soc.* **115**, 7415 (1993).
14. P. R. Kemper and M. T. Bowers, *J. Phys. Chem.* **95**, 5134 (1991).
15. M. T. Bowers, P. R. Kemper, G. von Helden, P. A. M. van Koppen, *Science* **260**, 1446 (1993).
16. G. von Helden, N. G. Gotts, P. Maitre, M. T. Bowers, *Chem. Phys. Lett.* **227**, 601 (1994).
17. P. P. Radi, G. von Helden, M.-T. Hsu, P. R. Kemper, M. T. Bowers, *Int. J. Mass Spectrom. Ion Processes* **109**, 49 (1991).
18. For the work reported here, a pure Ti rod was exposed to pulses of photons from an excimer laser operating at 308 nm. The rod was continuously translated and rotated to provide fresh metal for each laser pulse. The expansion gas was He seeded with 1% CH_4 at a backing pressure of 80 psi behind a Newport pulsed valve. A timing circuit allowed variable delays between triggering the pulse valve and the laser. Cluster ions exiting the source were mass selected with a double-focusing reverse geometry sector mass spectrometer. At this point either a mass spectrum could be taken or a specific cluster ion mass selected and pulse injected into the IC cell through a small entrance hole. A 5-μs pulse was typical.
19. E. A. Mason and E. W. McDaniel, *Transport Properties of Ions in Gases* (Wiley, New York, 1988).
20. L. Pauling, *Proc. Natl. Acad. Sci. U.S.A.* **89**, 8125 (1992).
21. A. Khan, *J. Phys. Chem.* **97**, 10937 (1993).
22. G. von Helden, E. Porter, N. G. Gotts, M. T. Bowers, *ibid.*, in press.
23. A thorough discussion of the procedures used in estimating van der Waals radii is given in G. von Helden, thesis, University of California at Santa Barbara (1994).
24. In the case of titanium, calculations on met-car–type structures indicate that the Ti atoms have a formal charge of about +1 and the C_2 units a formal charge of about −0.67. Consequently, we modeled Ti^+ interacting with He. Because the exact electronic configuration of the Ti species in Ti_8C_{12} is unknown, we averaged the interaction over a variety of possible electronic states. Modeling also showed that if a Ti van der Waals radius of 2.20 was used (+5%) the mobility of $Ti_8C_{12}^+$ decreased by 2.8%. These values would represent the maximum uncertainties in these quantities. Only two quantities are needed for the modeling: the sum of the He and C van der Waals radii and the sum of the He and Ti van der Waals radii. We used 2.7 and 3.19 Å for these quantities, respectively.
25. M. F. Jarrold and E. C. Honea, *J. Am. Chem. Soc.* **114**, 459 (1992).
26. J. S. Pilgrim and M. A. Duncan, *ibid.* **115**, 4395 (1993).
27. ______, *ibid.*, p. 9724.
28. The support of the Air Force Office of Scientific Research under grants FA9620-93-1-0134 and FA9620-93-1-0305 and the NSF under grant CHE 91-19752 is gratefully acknowledged. We thank I. Dance for providing results before publication.

27 September 1994; accepted 21 November 1994