In analogy to C_{60} and C_{70}, all even-numbered clusters C_{70+2n} ($n \geq 1$) are believed to correspond to polyhedral, spheroidal carbon cages.[9,10,20,21] The fullerene hexagon + pentagon structures are especially suitable for large C_{70+2n} clusters because they have the minimal 12 pentagons needed for geometric closure but retain most of the graphite stabilization energy because of their hexagonal rings.[20] Very recent theoretical studies[22,23] on the stability of fullerenes indicate that at least one fullerene-type (12 pentagons and $n-1$ hexagons cage) structure exists for all even C_{2n} ($2n \geq 20$). The present observation of even-numbered large carbon molecules strongly suggests the presence of a series of such fullerenes in laboratory-produced carbon soot. It should be noted in passing that one of the predicted large-sized magic number fullerenes C_{240}[9,10] does not show particularly enhanced intensity in the present FAB-MS observation.

As described already, large carbon molecules (possibly fullerenes) as large as C_{300} are detected in the current FAB-MS detection of quinoline extracts of carbon soot. However, because of the limited sensitivity of the FAB mass spectrometer for the large carbon molecules having large m/z values, the fullerenes larger than C_{300} are not detected even if they might actually be present in the quinoline extracts or in carbon soot per se. We are currently trying to observe such giant fullerenes ($>C_{300}$).

(20) Fowler, P. W. *Chem. Phys. Lett.* **1986**, *131*, 444.
(21) Fowler, P. W. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 2073.
(22) Bakowies, D.; Thiel, W. *Chem. Phys.* **1991**, *151*, 309.
(23) Bakowies, D.; Thiel, W. *J. Am. Chem. Soc.* **1991**, *113*, 3704.

Conclusion

Large carbon molecules, possibly fullerenes, are observed by fast atom bombardment mass spectrometry of quinoline extracts from carbon soot produced by the contact arc method. The mass spectra reveal the presence of a remarkably wide distribution of a series of large even-numbered fullerenes C_{70+2n} ($n \geq 1$) up to around C_{300}. No distinct peaks are observed in the corresponding mass region. Giant fullerenes ($>C_{300}$) might also be present in the present quinoline extracts.

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Injection of Helium Atoms into Doubly and Triply Charged C_{60} Cations

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Results are reported for high-energy beam experiments with C_{60}^{2+} and C_{60}^{3+} conducted with a four-sector mass spectrometer. Collision-induced dissociation spectra were recorded with helium as the collision gas at kinetic energies of 6, 8, 10, and 16 keV for C_{60}^{2+} and 9 keV for C_{60}^{3+}. The spectra show the loss of C_{2n} fragments and reveal accompanying signals corresponding to the retention of He. Their interpretation indicates that a helium atom has been incorporated into the multiply charged C_{60} cations in the course of the collisions and so provides additional evidence for the formation of endohedral fullerene compounds.

The strongly exponential growth[2,3] in knowledge of the properties and behavior of the fascinating fullerene molecules[3] is providing increasing evidence for the possibility of generating endohedral fullerene compounds and so is giving birth to a new field of endohedral chemistry.[4] For example, metal-containing cluster ions of the type $C_{60}M^+$ (with M = La, Ni, Na, K, Rb, and Cs) have been observed in the mass spectra produced in laser vaporization experiments on graphite doped with metal salts.[5,6] However, opinions differ on the location of the metal atom: Smalley et al.[5] indicate that these experimental results point to the formation of a spherical C_{60} cluster with the metal atom inside; on the other hand, Cox et al.[6] are of the opinion that $C_{60}La$, for example, is an empty C_{60} cluster which has "custody" of the metal on its outside surface, and Freiser et al.[7] recently presented evidence for the formation of *exohedral* $C_{60}M^+$ complexes (M = Fe, Co, Ni, Cu, Rh, La, and VO). In our laboratory[8,9c] we recently were able to demonstrate that the noble gases He and Ne can be injected into $C_{60}^{\bullet+}$ and $C_{70}^{\bullet+}$ at a laboratory energy of 8 keV and so provided the first evidence for the formation of endohedral carbon cluster compounds by high-energy bimolecular reactions.[8,9c] This work was later confirmed and extended by related studies in the laboratories of Ross et al.[9a] and Gross et al.[9b]

The success with the experiments revealing the injection of He into $C_{60}^{\bullet+}$ prompted us to extend the investigations to more highly charged cations, C_{60}^{n+} ($n = 2, 3$), with the suspicion that the inert nature of this noble gas would facilitate the inclusion of an atom

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(2) In the first 5 months of 1991, over 130 papers dealing with the chemical and physical properties of fullerenes were submitted for publication; this corresponds to the incredible rate of nearly one report per day: Squires, R. R. 39th Annual Conference on Mass Spectrometry, Allied Top. (ASMS), Nashville, TN, 21 May 1991.
(3) (a) Kroto, H. W. *Science* **1988**, *242*, 1139. (b) Weltner, W., Jr.; Van Zee, R. J. *Chem. Rev.* **1989**, *89*, 1713. (c) Smalley, R. E. In Bernstein, E. R., Ed. *Atomic and Molecular Clusters*; Elsevier: Amsterdam; 1990; Chapter 1. (d) Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 70. (e) Miller, J. S. *Adv. Mater.* **1991**, *3*, 262. (f) Diederich, F.; Whetten, R. L. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 678. (g) Smalley, R. E. *Sciences (N.Y.)* **1991**, *31* (2), 22. (h) Baggott, J. *New Scientist* **1991**, 33.
(4) For theoretical studies on endohedral fullerene complexes, see: (a) Rosen, A.; Wästberg, B. *J. Am. Chem. Soc.* **1988**, *110*, 8701. (b) Cioslowski, J. *Ibid.* **1991**, *113*, 4139. (c) Cioslowski, J.; Fleischmann, E. D. *J. Chem. Phys.* **1991**, *94*, 3730. (d) Chang, A. H. H.; Ermler, W. C.; Pitzer, R. M. *Ibid.* **1991**, *94*, 5004. (e) Bakowies, D.; Thiel, W. *J. Am. Chem. Soc.* **1991**, *113*, 3704. (f) Wästberg, B.; Rosen, A. *Phys. Scr.*, in press.
(5) (a) Heath, J. R.; O'Brien, S. C.; Zhang, Q.; Lin, Y.; Curl, R. F.; Kroto, H. W.; Tittel, F. K.; Smalley, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 7779. (b) Weiss, F. D.; Elkind, J. L.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Ibid.* **1988**, *110*, 4464.
(6) Cox, D. M.; Trevor, D. J.; Rechmann, K. C.; Kaldor, A. *J. Am. Chem. Soc.* **1986**, *108*, 2457.
(7) (a) Roth, L. M.; Huang, Y.; Schwedler, J. T.; Cassady, C. J.; Ben-Amotz, D.; Kahr, B.; Freiser, B. S. *J. Am. Chem. Soc.* **1991**, *113*, 6298. (b) Huang, Y.; Freiser, B. S. *J. Am. Chem. Soc.*, in press.
(8) Weiske, T.; Böhme, D. K.; Hrušák, J.; Krätschmer, W.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 884.
(9) Experiments aimed at the generation of $C_{60}He^{\bullet+}$ and other clusters are described by: (a) Ross, M. M.; Callahan, J. H. *J. Phys. Chem.* **1991**, *95*, 5720. (b) Caldwell, K. A.; Giblin, D. E.; Hsu, C. S.; Cox, D.; Gross, M. L. *J. Am. Chem. Soc.*, submitted for publication. (c) Weiske, T.; Hrušák, J.; Böhme, D. K.; Schwarz, H. *J. Am. Chem. Soc.*, submitted for publication.

0022-3654/91/2095-8451$02.50/0

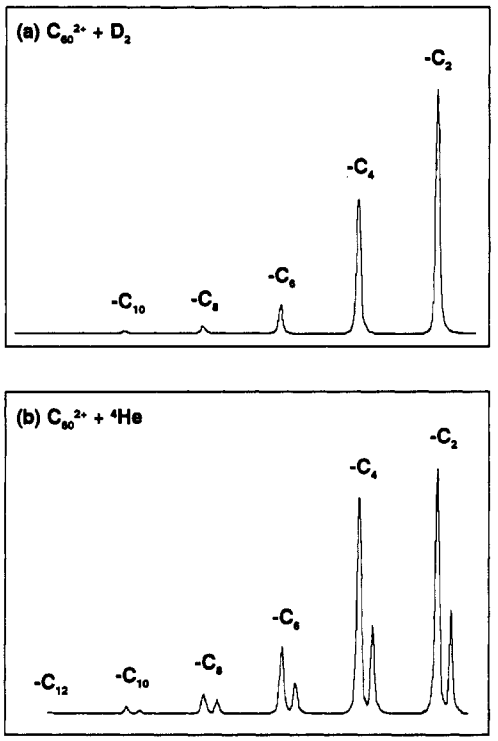

Figure 1. CA mass spectrum for (a) C_{60}^{2+} and D_2 and (b) C_{60}^{2+} and ^4He at a laboratory kinetic energy of 6 keV. (Primary ions were accelerated through a potential of 3 kV.)

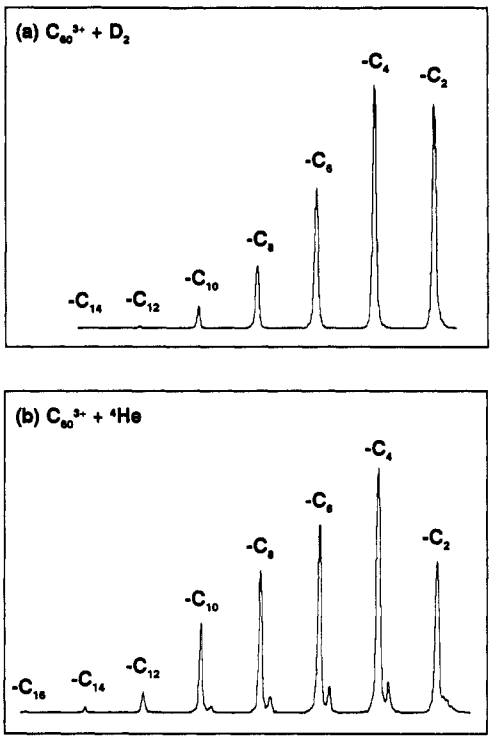

Figure 2. CA spectrum for (a) C_{60}^{3+} and D_2 and (b) C_{60}^{3+} and ^4He at a laboratory kinetic energy of 9 keV. (Primary ions were accelerated through a potential of 3 kV.)

in the multiply charged fullerene as well. In earlier experiments no evidence for the retention of collision gases was reported.[10]

Both C_{60}^{2+} and C_{60}^{3+} were readily generated by electron impact ionization (100 eV) of the vapor of C_{60} (the temperature of the solid probe tip was 550 °C) at a low pressure of 10^{-6} mbar and a source-block temperature of 270 °C. The C_{60}^{n+} (n = 1, 2) ions were accelerated up to 8 keV, mass-selected by means of the magnetic and electric sectors of our BEBE four-sector machine,[11] and then reacted in the region between $E(1)$ and $B(2)$. Product ions were searched with a combined momentum and energy analysis ("linked scan") of $B(2)/E(2)$ = constant.[12]

The injection of helium into C_{60}^{2+} was investigated at kinetic energies of 6, 8, 10, and 16 keV. The results obtained at 6 keV are shown in Figure 1 where they are compared with results obtained with D_2 with which there was no evidence for retention at the sensitivity of the experiments. However, helium retention was observed at all four kinetic energies, decreasing in efficiency with increasing energy. Although the ratio of C_xHe^{2+}/C_x^{2+} fragment ion intensities ($46 < x < 60$) depends on the $B(2)/E(2)$ = constant law scan, the kinetic energy effect is obvious as indicated by the following data: 6 keV (30%), 8 keV (34%), 10 keV (14%), and 16 keV (<1%). The accompanying fragmentation which occurs by loss of even-numbered carbon units is in agreement with results obtained in collision-induced dissociation experiments conducted elsewhere[10b,c] in which O_2 was used as the collision gas. In our experiments up to 16 carbons were lost from C_{60}^{2+} at 6 keV and 20 carbon atoms at 16 keV.

The retention of helium by C_{60}^{3+} was monitored at a kinetic energy of 9 keV.[13] The experiments were more difficult due to the lower signal intensities, but Figure 2 clearly shows the fragmentation with loss of 16 carbon atoms in even-numbered carbon units which has previously been reported.[10b,c] The detailed mechanism of carbon loss in the collision-induced dissociation experiments with both C_{60}^{2+} and C_{60}^{3+} is unknown. For example, carbon may be lost as intact C_{2n} units or by sequential elimination of C_2 units.[14] In any event, because of its inertness, *He is expected to be retained only if it has been physically trapped inside the cage*. Therefore, while earlier experiments[10] did not provide evidence for the retention of the collision gas, the present study for the first time demonstrates the incorporation of a helium atom in multiply charged fullerenes.[15]

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(10) (a) Luffer, D. R.; Schram, K. M. *Rapid Commun. Mass Spectrom.* **1990**, *4*, 552. (b) Young, A. B.; Cousins, L. M.; Harrison, A. G. *Ibid.* **1991**, *5*, 226. (c) Doyle, R. J., Jr.; Ross, M. M. *J. Phys. Chem.* **1991**, *95*, 4954. (d) Lifshitz, C.; Iraqi, M.; Peres, T.; Fischer, J. E. *Rapid Commun. Mass Spectrom.* **1991**, *5*, 238. (e) Ben-Amotz, D.; Cooks, R. G.; Dejarme, L.; Gunderson, J. C.; Hoke, S. H., II; Kahr, B.; Payne, G. L.; Wood, J. M. *J. Am. Chem. Soc.*, submitted for publication. (f) Drewello, T.; Asmus, K.-D.; Stach, J.; Herzschuh, R.; Foote, C. S. *J. Phys. Chem.*, in press.

(11) For a detailed description of the machine, see: (a) Srinivas, R.; Sülzle, D.; Weiske, T.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1991**, *107*, 369. (b) Srinivas, R.; Sülzle, D.; Koch, W.; DePuy, C. H.; Schwarz, H. *J. Am. Chem. Soc.* **1991**, *113*, 5970.

(12) Chapman, J. R. *Practical Organic Mass Spectrometry*; Wiley: Chichester, 1985; Chapter 6.

(13) At 24 keV kinetic energy helium-containing C_xHe^{3+} fragments were below detection limit.

(14) (a) Reference 3c. (b) O'Brien, S. C.; Heath, J. R.; Curl, R. F.; Smalley, R. E. *J. Chem. Phys.* **1988**, *88*, 220.

(15) We recently succeeded in the formation of the *adduct* ion $C_{60}He^{2+}$ in the reaction of C_{60}^{2+} with He at a laboratory energy of 6 keV. No adduct formation with D_2 is observed: Weiske, T.; Hrušák, J.; Bohme, D. K.; Schwarz, H. *Chem. Phys. Lett.*, in press.