Formation of endohedral carbon-cluster noble-gas compounds with high-energy bimolecular reactions: $C_{60}He^{n+}$ ($n=1, 2$)

Thomas Weiske, Jan Hrusak [1], Diethard K. Böhme [2] and Helmut Schwarz [3]

Institut für Organische Chemie der Technischen Universität Berlin, Strasse des 17. Juni 135, W-1000 Berlin 12, Germany

Received 15 August 1991

Results are reported for high-energy beam studies of the formation of adduct ions in the reactions of $C_{60}^{+\cdot}$ and C_{60}^{2+} with He and D_2 in a four-sector mass spectrometer. Studies of the addition of He to $C_{60}^{+\cdot}$ at translational energies of 2, 3, 4, 5, 6 and 8 keV showed optimal adduct formation from 5 to 6 keV. The $C_{60}He^{2+}$ adduct was observed in collions between C_{60}^{2+} and He at 6 keV translational energy. No adduct formation was observed between D_2 and $C_{60}^{+\cdot}$ or C_{60}^{2+} at 6 keV translational energy.

1. Introduction

The impact that the production and availability of fullerene molecules has had on chemistry is common knowledge [1]. One new field of chemistry which has been spawned is that of endohedral chemistry – chemistry proceeding inside a cage of (carbon) atoms [2]. A case has been made by Smalley et al., although opinions differ [3], that the metal-containing cluster ions $C_{60}M^+$ (with M=La, Ni, Na, K, Rb, and Cs) which have been observed in the mass spectra of the laser-induced vapors of graphite doped with metal salts are spherical C_{60} molecular ions with the metal atom located inside. Mass-spectrometric experiments in our laboratory have shown that He may be injected into singly [4], doubly [5], and triply [5] charged C_{60} cations, but only the observed fragmentations have been reported [#1]. Shortly thereafter Ross and Callahan [6] were able to identify $C_{60}He^{+\cdot}$ unambiguously and to show that the helium adduct formation in the high-energy collision of $C_{60}^{+\cdot}$ with He is not necessarily accompanied by expulsion of a neutral fragment [#2]. In the meantime, we have learned from extensive $C_{60}^{+\cdot}$ collision experiments at various kinetic energies and with several different scan modes that the cross section for He attachment is strongly dependent on energy and that the linked-scan mode used in our initial experiments for fundamental reasons was not ideal for the unambiguous detection of $C_{60}He^{+\cdot}$. We report here a confirmation of the direct formation of $C_{60}He^{+\cdot}$ from the collision of $C_{60}^{+\cdot}$ with He reported by Ross and Callahan, the dependence of the efficiency of the formation of this adduct on kinetic energy, the failure of D_2 to add with a measurable efficiency to $C_{60}^{+\cdot}$ and C_{60}^{2+}, and the first observation of the direct formation of the adduct ion $C_{60}He^{2+}$ from the collision of C_{60}^{2+} with He.

2. Experimental

The experiments were performed with a four-sec-

[1] Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Heyrovsky Square 2, 16202 Prague, Czechoslovakia.

[2] Department of Chemistry and Centre for Research in Earth and Space Science, York University, North York, Ontario, Canada M3J 1P3.

[3] To whom correspondence should be addressed.

[#1] The incorporation of Ne was also observed, but only for singly-charged $C_{60}^{+\cdot}$ cations, and with a much smaller efficiency [4]. Furthermore, $C_{60}He^{+\cdot}$ was observed in the fragmentation spectrum produced by the collisions of 8 keV $C_{70}^{+\cdot}$ ions with He [4].

[#2] Although we also saw signals in our mass-spectrometer experiments performed at 8 keV kinetic energy that could explain the formation of $C_{60}He^{+\cdot}$, we did not report these in our initial communication [4].

0009-2614/91/$ 03.50

tor $B(1)$ $E(1)$ $B(2)$ $E(2)$ mass spectrometer [7]. $C_{60}^{+\cdot}$ and C_{60}^{2+} were generated by electron impact ionization at 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 ions were accelerated up to 8 keV maximum, mass selected with the magnetic and electric sectors $B(1)$ $E(1)$, and then allowed to collide with ^4He or D_2 in a collision chamber located in the field-free region between $E(1)$ and $B(2)$. The resulting two-dimensional ion-current surface was explored either with a $B(2)^2/E(2)$ = constant linked scan (collecting all ions with the same m/z, but different kinetic energies) or with a $B(2)/E(2)$ = constant linked scan (sampling all fragment ions arising from the same precursor ion) [8].

3. Results and discussion

Measurements of the efficiency of the addition of He and $C_{60}^{+\cdot}$ were performed at laboratory energies of 2, 3, 4, 5, 6, and 8 keV. They indicate the occurrence of translational energy loss of the $C_{60}^{+\cdot}$ ion in collisions with He as is evident from the spectrum shown in fig. 1. The translational energy loss was found to be approximately linearly proportional to the kinetic energy of the $C_{60}^{+\cdot}$ beam in the range from 2 to 8 keV. Our measurements indicate that retention of He by $C_{60}^{+\cdot}$ is easily visible at 4, 5 and 6 keV,

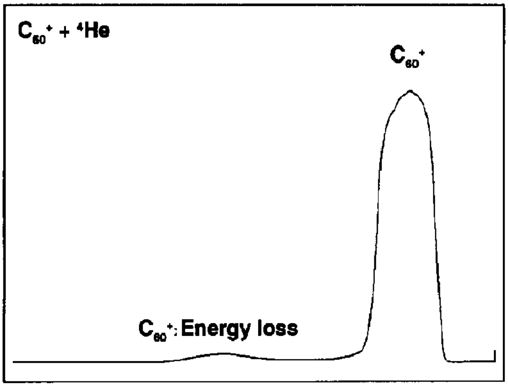

Fig. 1. $B(2)^2/E(2)$ = const. linked scan in the vicinity of the centre of the parent ion $C_{60}^{+\cdot}$ with an initial translational energy of 6 keV. The peak on the right represents the original parent ion and the smaller peak on the left the energy-loss distribution resulting from impact with ^4He atoms.

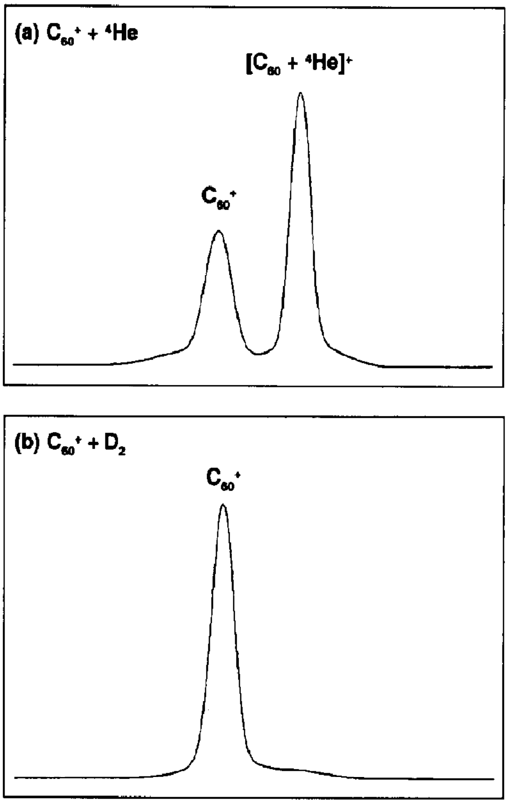

Fig. 2. (a) $B(2)/E(2)$ = const. linked scan in the vicinity of the centre of the $C_{60}{}^4He^{+\cdot}$ adduct ion with an initial translational kinetic energy of 6 keV with ^4He as a target gas. The large peak on the right represents the $C_{60}{}^4He^{+\cdot}$ adduct ion and the peak on the left arises from cutting the energy-loss tail of $C_{60}^{+\cdot}$ in the $B(2)$, $E(2)$ two-dimensional surface. (b) Similar experiments with D_2 as a target gas. There is no real evidence for a $C_{60}D_2^{+\cdot}$ adduct ion on the right.

is optimal at kinetic energies in the range from 5 to 6 keV, and that it falls at higher and lower energies. When the $B(2)/E(2)$ = constant linked scan is chosen optimally with full recognition of possible complications due to the presence of an energy loss peak, the $C_{60}He^{+\cdot}$ is easily visible and separated from the energy-loss peak for $C_{60}^{+\cdot}$ as shown for a laboratory energy of 6 keV in fig. 2a. Similar experiments with D_2 point toward a negative result with this molecule. As seen in fig. 2b, no significant addition of D_2 and $C_{60}^{+\cdot}$ is apparent at 6 keV nor was it observed at 3, 4 and 8 keV.

Collision experiments with C_{60}^{2+} and He revealed the formation of the $C_{60}He^{2+}$ adduct ion at a laboratory kinetic energy of 6 keV as shown in fig. 3a.

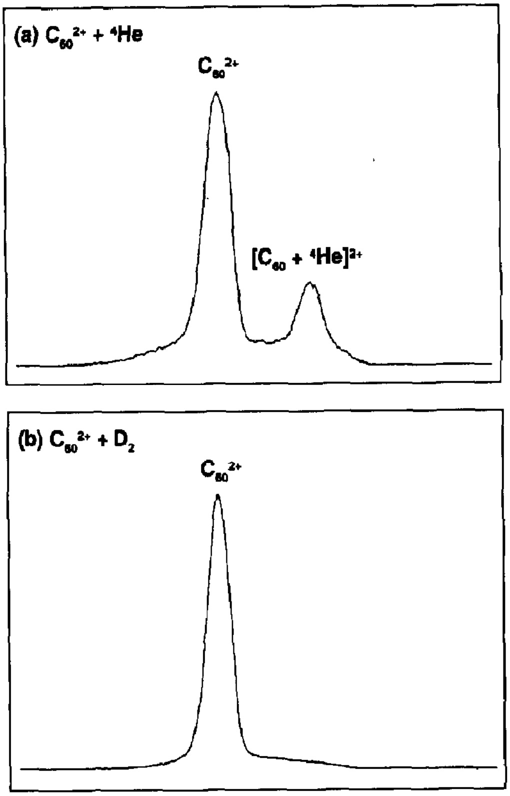

Fig. 3. (a) $B(2)/E(2)$=const. linked scan in the vicinity of the center of the $C_{60}{}^4He^{2+}$ adduct ion with an initial translational kinetic energy of 6 keV with ^4He as a target gas. The small peak on the right represents the $C_{60}{}^4He^{2+}$ adduct ion and the large peak on the left arises from cutting the energy-loss tail of C_{60}^{2+} in the $B(2)$, $E(2)$ two-dimensional surface. (b) Similar experiments with D_2 as a target gas. There is no real evidence for a $C_{60}D_2^{2+}$ adduct ion on the right.

Again, however, similar experiments with D_2 did not show adduct formation as is evident in fig. 3b.

4. Conclusions

(1) Collision experiments with a four-sector *BEBE* mass spectrometer have shown the formation of the adduct ion $C_{60}He^{+\cdot}$ in the kinetic energy range 2–8 keV with a peak in efficiency at 5–6 keV. These observations confirm the earlier results reported by Ross and Callahan [6]. There is no doubt that $C_{60}He^{+\cdot}$ is an endohedral complex. Previous model ab initio MO calculations for the addition of He to $C_6H_6^{+\cdot}$ indicate a binding energy of less than 0.2 eV [4]. Taken together with the observation [4] of unimolecular loss from mass-selected $[C_xHe]^{+\cdot}$ ions of C_2 rather than He and the observation [6] of loss of C_2 units with retention of He in the Xe collision-induced dissociation of $C_{60}He^{+\cdot}$, these results provide the necessary evidence for endohedral-complex formation. The upper limit of 10 eV calculated for the energy required to force He through a C_6H_6 or $C_6H_6^{+\cdot}$ plane [4] suggests that the penetration of $C_{60}^{+\cdot}$ by He is possible at all of the kinetic energies investigated in this study.

(2) Collision experiments with D_2 have shown that D_2 does not form measurable amounts of adduct ions with $C_{60}^{+\cdot}$ at kinetic energies of 3, 4, 6 and 8 keV or with C_{60}^{2+} at a kinetic energy of 6 keV.

(3) Collision experiments with C_{60}^{2+} and He indicate formation of the $C_{60}He^{2+}$ adduct at kinetic energies of 6 keV.

Acknowledgement

Generous financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. DKB is grateful to the Alexander von Humboldt Foundation for a Senior Scientist Award. We are indebted to Dr. W. Krätschmer and K. Fostiropoulos for the generous supply of C_{60} samples. Enlightening discussions with Dr. M.M. Ross and Dr. J.H. Callahan are appreciated, and we are grateful for having received a preprint of their paper [6].

References

[1] H.W. Kroto, Science 242 (1988) 1139;
W. Weltner Jr. and R.J. van Zee, Chem. Rev. 89 (1989) 1713;
R.E. Smalley, in: Atomic and molecular clusters, ed. E.R. Bernstein (Elsevier, Amsterdam, 1990) ch. 1;
J.F. Stoddart, Angew. Chem. Intern. Ed. Eng. (1991) 70;
J.S. Miller, Advan. Mater. 3 (1991) 262;
F. Diederich and R.L. Whetten, Angew. Chem. Intern. Ed. Engl. 30 (1991) 678;
R.E. Smalley, Sciences (NY) 31 (1991) 22;
J. Baggot, New Scientist (1991) 33.
[2] A. Rosen and A. Wästberg, J. Am. Chem. Soc. 110 (1988) 8701;
J. Cioslowski, J. Am. Chem. Soc. 113 (1991) 4139;

J. Cioslowski and E.D. Fleischmann, J. Chem. Phys. 94 (1991) 3730;
A.H.H. Chang, W.C. Ermler and R.M. Pitzer, J. Chem. Phys. 94 (1991) 5004;
D. Bakowies and W. Thiel, J. Am. Chem. Soc. 113 (1991) 3704;
B. Wästberg and A. Rosen, Phys. Scripta, in press.

[3] J.R. Heath, S.C. O'Brien, Q. Zang, Y. Lin, R.F. Curl, H.W. Kroto, F.K. Tittel and R.E. Smalley, J. Am. Chem. Soc. 107 (1985) 7779;
D.M. Cox, D.J. Trevor, K.C. Rechmann and A. Kaldor, J. Am. Chem. Soc. 108 (1986) 2457;
F.D. Weiss, J.L. Elkind, S.C. O'Brien, R.F. Curl and R.E. Smalley, J. Am. Chem. Soc. 110 (1988) 4464.

[4] T. Weiske, D.K. Böhme, J. Hrusak, W. Krätschmer and H. Schwarz, Angew. Chem. Intern. Ed. Engl. 30 (1991) 884.

[5] T. Weiske, D.K. Böhme and H. Schwarz, J. Phys. Chem., submitted for publication.

[6] M.M. Ross and J.H. Callahan, J. Phys. Chem., in press.

[7] R. Srinivas, D. Sülzle, T. Weiske and H. Schwarz, Intern. J. Mass Spectrom. Ion Processes 107 (1990) 369;
R. Srinivas, D. Sülzle, W. Koch, C.H. DePuy and H. Schwarz, J. Am. Chem. Soc. 113 (1991) 5970.

[8] C.G. Macdonald and M.J. Lacey, Org. Mass Spectrom. 19 (1984) 55;
J.R. Chapman, Practical organic mass spectrometry (Wiley, New York, 1985) ch. 6.