Evidence for the Formation of Transient $CH_4C_{60}^{+\cdot}$ following High-energy Collisions between $C_{60}^{+\cdot}$ Radical Cations and Methane

Helen J. Cooper,[a] Richard T. Gallagher,[a] Paul F. Greenwood,[a] Tore Vulpius[b] and Peter J. Derrick*[a]

[a] *Institute of Mass Spectrometry and Department of Chemistry, University of Warwick, Coventry, UK CV4 7AL*
[b] *Department of General and Organic Chemistry, University of Copenhagen, HC Ørsted Institute, DK-2100, Copenhagen, Denmark*

High-energy collisions of the $C_{60}^{+\cdot}$ radical cation with methane produce $CH_2C_{60}^{+\cdot}$ and CHC_{60}^{+}, characterised by deficits in translational energy consistent with their formation from $CH_4C_{60}^{+\cdot}$.

We report evidence for the capture of the target gas CH_4 by $C_{60}^{+\cdot}$ radical cations in high-energy collisions. Target capture is the phenomenon whereby an ion in a beam and a target gas do not separate following collision and was predicted by Neumann *et al.*[1] The cage-like structure of [60]fullerene (C_{60})[2] around a 'perfect vacuum' has inspired experiments to probe this phenomenon.[3,4,5] The inclusion of helium within the fragments of the $C_{60}^{+\cdot}$ incident ion was first observed by Schwarz *et al.*[3] Ross and Callahan later confirmed the existence of $He@C_{60}^{+\cdot}$[4] (The notation $M@C_{60}^{+}$ describes an endohedral fullerene complex[6]). The study of target capture has been extended to capture of ammonia and methane by the peptide renin substrate[7].

Experiments were performed on a Kratos Analytical Concept IIHH four-sector (EBEB) mass spectrometer; a Jeol HX110A/HX110A four-sector mass spectrometer was also used. The $C_{60}^{+\cdot}$ ions were produced by electron impact ionisation, accelerated through a potential of 7.9 kV and selected by the first half of the mass spectrometer (*i.e.* the first two sectors). The ions were focused into the collison cell, which was floated at 6.9, 7.2, 7.4 or 7.6 kV and contained methane at a pressure sufficient to reduce the ion beam to 80% of its original intensity. The second electric sector was set at a chosen potential and the final magnet was scanned to identify the products.

Fig. 1 shows the spectrum obtained with $C_{60}^{+\cdot}$ ions and methane when the laboratory-frame collision energy was 500 eV. Peaks corresponding to $[M + 14]^{+\cdot}$, $[M + 13]^{+}$ and $[M + 1]^{+}$ can be seen, along with the smaller $[M + 12]^{+\cdot}$ and $[M + 15]^{+}$. At this collision energy the $[M + 14]^{+\cdot}$ ions are at their most abundant. It would be wrong to conclude from this spectrum, however, that the $[M + 14]^{+\cdot}$ adduct ion was of greater abundance than the parent ion. In order to observe adduct ions, it was necessary to reduce the second electric sector potential below that appropriate for $C_{60}^{+\cdot}$ ions in the absence of collisions. Results at 700 eV collision energy were very similar to those at 500 eV. At a laboratory-frame energy of 1000 eV, the peak corresponding to $[M + 13]^{+}$ was the most intense adduct.

Results obtained at 300 eV laboratory-frame energy are shown in Fig. 2 for the target gases CH_4, $^{13}CH_4$ and CD_4. The necessary reduction in the electric sector potential was lower at 300 eV collision energy, so the parent ions were less defocused and the $C_{60}^{+\cdot}$ peaks appear relatively more intense in Fig. 2 (*cf.* Fig. 1). The peaks $[M + 14]^{+}$, $[M + 15]^{+\cdot}$ and $[M + 16]^{+}$ for $^{13}CH_4$ and $[M + 14]^{+}$, $[M + 16]^{+\cdot}$ and $[M + 18]^{+}$ for CD_4 confirm that the adduct peaks with CH_4 are due to CHC_{60}^{+}, $CH_2C_{60}^{+\cdot}$ and $CH_3C_{60}^{+}$. At lower collision energies (100–300 eV) no adduct peaks were observed.

If a collision between C_{60} and CH_4 results in a transient $CH_4C_{60}^{+\cdot}$ complex, this complex would acquire additional internal energy equal to the centre-of-mass collision energy. Translational energy of the complex would be reduced below that of the $C_{60}^{+\cdot}$ precursor by this same amount. Subsequent unimolecular decomposition to an ion (mass m_A) would result in

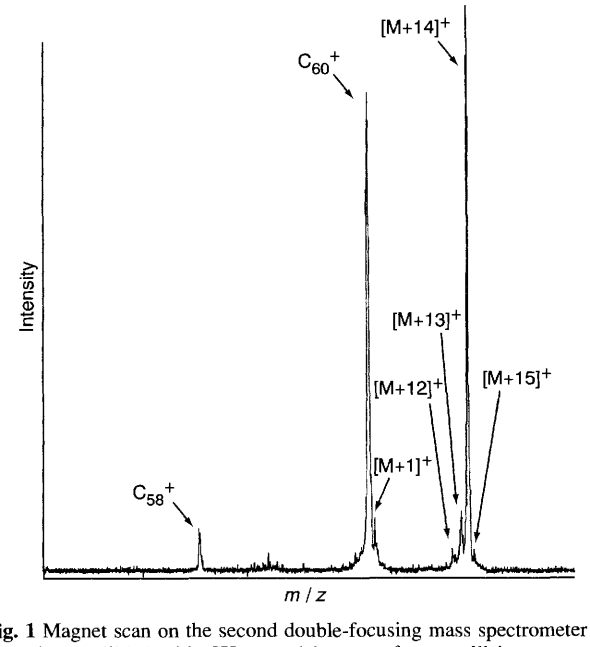

Fig. 1 Magnet scan on the second double-focusing mass spectrometer for $C_{60}^{+\cdot}$ ions collided with CH_4 at a laboratory-frame collision energy of 500 eV

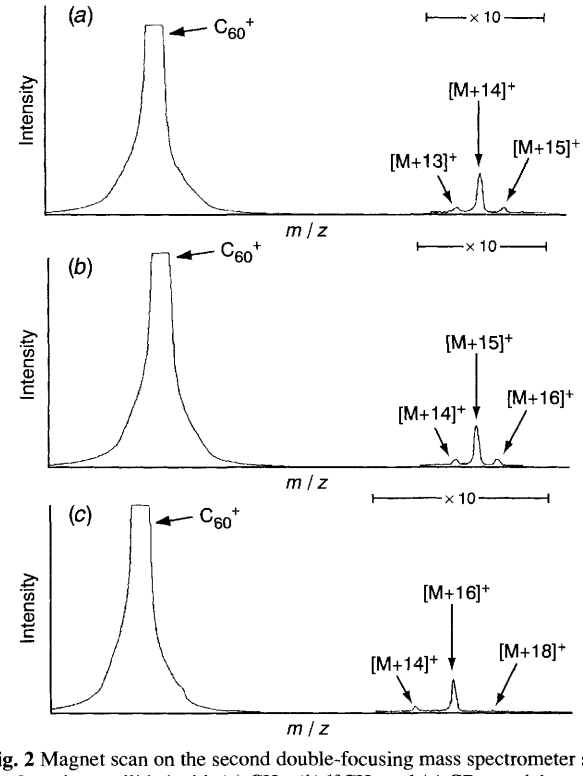

Fig. 2 Magnet scan on the second double-focusing mass spectrometer scan for $C_{60}^{+\cdot}$ ions collided with (*a*) CH_4, (*b*) $^{13}CH_4$ and (*c*) CD_4 at a laboratory-frame collison energy of 300 eV

this ion exhibiting a deficiency in translational energy, E_{def}, relative to that of the $C_{60}^{+\cdot}$ ion prior to collision, given by eqn. (1).

$$E_{def} = E - \frac{m_A}{m_G + m_P}\left(E - \frac{m_G}{m_G + m_P}E\right) \quad (1)$$

where m_P = mass of the parent (= 720); m_G = mass of the target gas (= 16); E = laboratory-frame collision energy.

We have found that the observed adducts are characterised by energy deficits, as predicted on the basis of the mechanism above. The energy deficits measured for $CH_2C_{60}^{+\cdot}$ and CHC_{60}^{+} at various laboratory-frame collision energies are shown in Table 1 together with the values predicted [from eqn. (1)] on the basis that these adducts are formed by unimolecular decomposition of an intermediate $CH_4C_{60}^{+\cdot}$ complex. Values predicted on the basis of a 'stripping' mechanism (in which the unattached neutrals remain stationary) are also shown. The agreement between the measured values and those calculated from eqn. (1) is consistent with the adduct ions being the result of fragmentation of a $CH_4C_6^{+\cdot}$ ion.

The accepted view is that the noble gas adducts, including that of krypton,[8] formed in such experiments with $C_{60}^{+\cdot}$ ions are endohedral. Given the methane and krypton are similar in size (34.88 and 32.13 Å^3, respectively), an endohedral methane complex would be plausible. On the other hand, the neutral exohedral methanofullerene (H_2C_{61}) is a well-characterised species.[9,10,11,12]

Table 1 Experimental energy deficits of the adducts CHC_{60}^{+} and $CH_2C_{60}^{+}$ at collision energies 300, 500, 700 and 1000 eV, compared with theoretical values predicted on the basis of eqn. (1) Values shown in brackets are predicted on the basis of direct formation of the adducts *via* a 'stripping' mechanism (in which the unattached neutrals remain stationary)

Adduct species (collison energy/eV)	Predicted energy deficit/eV	Experimental energy deficit/eV
$CH_2C_{60}^{+}$ (318)	7.8 (6.1)	7.1 ± 1
CHC_{60}^{+} (318)	8.2 (5.6)	8.5 ± 1
$CH_2C_{60}^{+}$ (512)	12.5 (9.8)	14.4 ± 2
CHC_{60}^{+} (512)	13.2 (9.1)	15.3 ± 2
$CH_2C_{60}^{+}$ (719)	17.5 (13.7)	17.2 ± 1
CHC_{60}^{+} (719)	18.5 (12.8)	19.1 ± 2
$CH_2C_{60}^{+}$ (1020)	24.9 (19.5)	25.5 ± 2
CHC_{60}^{+} (1020)	26.3 (18.1)	26.3 ± 1

In conclusion, the energy deficits observed for the adducts CHC_{60}^{+} and $CH_2C_{60}^{+\cdot}$ constitute strong evidence that the full complex $CH_4C_{60}^{+\cdot}$ is formed as a transient species as a result of collisions between $C_{60}^{+\cdot}$ ions and methane.

We would like to acknowledge the assistance of Dr Steen Hammerum and Mr Michael Vaughan. Dr M. Wilson (CSIRO, Australia) provided samples of crude fullerenes. H. J. C. acknowledges the EPSRC, Kratos Analytical and the EC Network for Gas-Phase Ion Chemistry and Mass Spectrometry for financial support. P. F. G. acknowledges CSIRO for a CSIRO Postdoctoral Award.

Received, 12th April 1995; Com. 5/02354H

References

1 G. M. Neumann, M. M. Sheil and P. J. Derrick, *Z. Naturforsch Teil A*, 1984, **39**, 584.
2 H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, *Nature*, 1985, **318**, 612.
3 T. Weiske, D. K. Böhme, J. Hrusak, W. Kratschmer and H. Schwarz, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 884.
4 M. M. Ross and J. H. Callahan, *J. Phys. Chem.*, 1991, **95**, 5720.
5 K. A. Caldwell, D. E. Giblin and M. L. Gross, *J. Am. Chem. Soc.*, 1992, **114**, 3743.
6 Y. Chai, T. Guo, C. Jin, R. E. Haufler, L. P. F. Chibante, J. Fure, L. Wang, J. M. Alford and R. E. Smalley, *J. Phys. Chem.*, 1991, **95**, 7564.
7 X. Cheng and C. Fenselau, *J. Am. Chem. Soc.*, 1993, **115**, 10327.
8 T. Weiske, H. Schwarz, D. E. Giblin and M. L. Gross, *Chem. Phys. Lett.*, 1994, **227**, 87.
9 F. Wudl, *Acc. Chem. Res.*, 1992, **25**, 157.
10 T. Suzuki, Q. Li, K. C. Khemani, F. Wudl and O. Almarsson, *Science*, 1991, **254**, 1186.
11 K. Raghavachari and C. Sosa, *Chem. Phys. Lett.*, 1993, **209**, 223.
12 T. Suzuki, Q. Li, K. C. Khemani and F. Wudl, *J. Am. Chem. Soc.*, 1992, **114**, 7301.