

Highly Oxygenated Derivatives of Fluorinated C₆₀, and the Mode of Fragmentation of the Fluorinated Cage under Electron Impact Ionization Conditions

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Reaction of fluorinated C₆₀ (C₆₀F_n, values of *n* all even and up to at least 54) with water produces numerous species C₆₀F_xO_y (*x* all even) with up to eighteen oxygen atoms attached to the cage, the maximum values of *x* + 2*y* being 52–58.

Reaction between C₆₀ and either one or two oxygen atoms was first detected by mass spectrometry,¹ and the mono-epoxide was subsequently isolated.² Mass spectroscopic evidence for the formation of C₆₀O and C₇₀O together with methylene adducts has also been reported.³ In that work UV irradiation of ether washings of soot extract yielded traces of C₆₀O_{*n*} (*n* = 2–5) and C₇₀O₂. Electrochemical oxidation of C₆₀ also yields C₆₀O_{*n*} (*n* = 1–4),⁴ and C₇₀O has been separated from higher

fullerenes by HPLC.⁵ Mass spectrometry of the product of phenylation of C₆₀ by a mixture of benzene, bromine, and iron(III) chloride showed the presence of additional derivatives containing one and two oxygen atoms.⁶ Mass spectrometry of the product of reaction of benzyne with C₆₀ also shows the presence of derivatives containing one and two oxygen atoms.⁷ Formation of oxygenated derivatives of C₆₀ and C₇₀ is thus well established, with the addition of one, and

to a lesser extent two, oxygen atoms being common. The presence of species containing either one or two oxygen atoms in the mass spectrum of a mixture of fluorinated C_{60} - C_{70} has been described very recently, the origin of the oxygen (believed to be present as epoxide) being unclear.⁸ This prompts us to report that fluorinated C_{60} appears to give derivatives containing up to an astonishing *eighteen* oxygen atoms, and to suggest a mechanism for their incorporation.

Previously we showed that fluorinated C_{60} is extremely reactive towards nucleophiles. The reaction with water (in a solvent common for both reagents) is exothermic and produces HF; we followed the progress of reaction by ^{19}F NMR

spectroscopy.⁹ We have now analysed the reaction products by mass spectrometry under electron impact (EI) conditions (heated probe). (Spectra were recorded as 70 eV EI data on a normal geometry double focusing VG Analytical instrument, using 6 kV accelerating voltage, 400 °C source temperature, 500 mA DCI current, calibration at 2000 resolution up to m/z 1979, and exponential scanning over m/z 2000–20 at 10 s per decade.) The results show that the reaction with water is so facile that maintaining fluorinated material entirely free of oxygenated derivatives is likely to be very difficult.

The mass spectra taken before, and immediately after, addition of aqueous methanol to a sample of fluorinated C_{60}

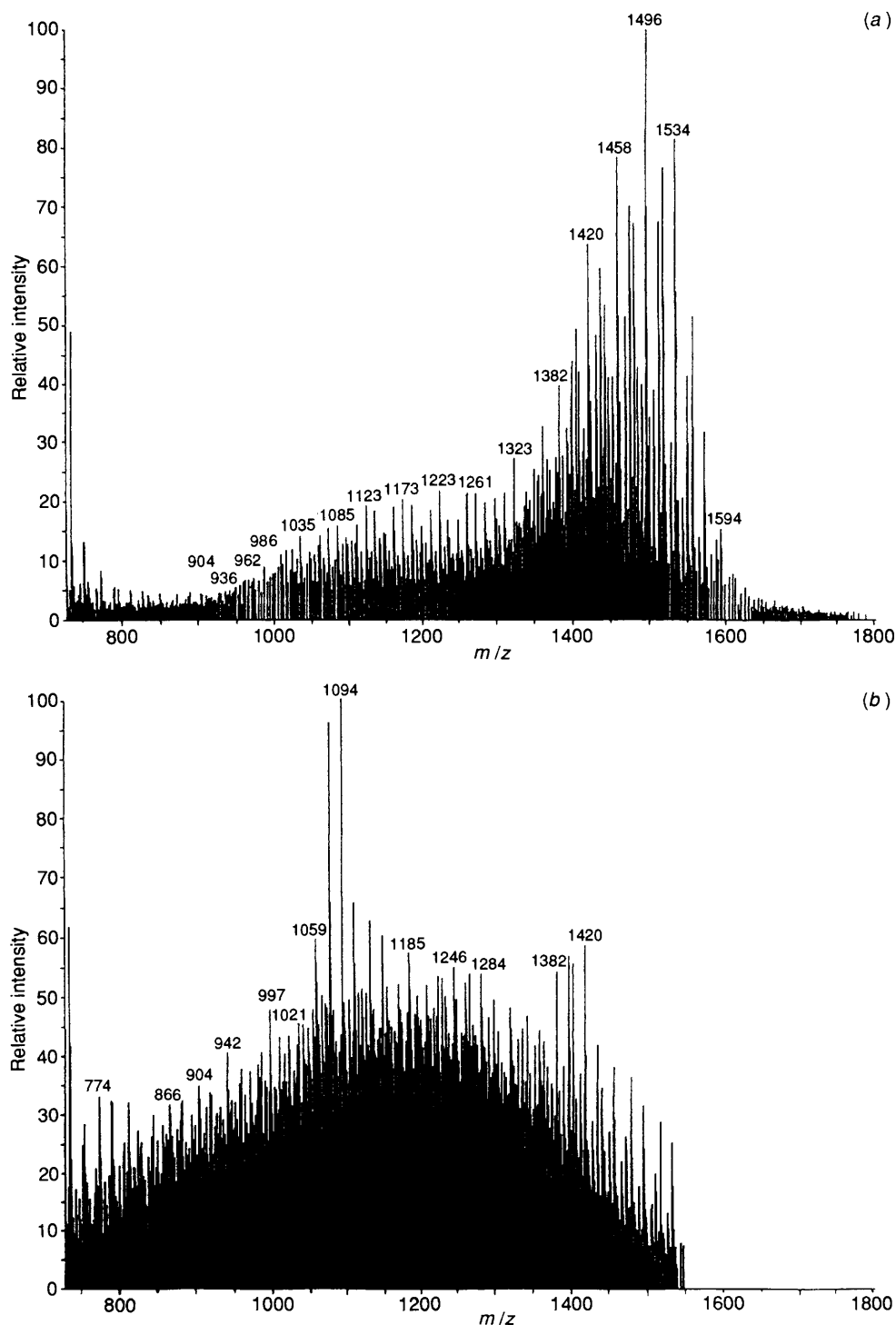


Fig. 1 (a) Electron impact mass spectrum of fluorinated C_{60} (heated probe); (b) electron impact mass spectrum of fluorinated C_{60} (same batch of material used for the spectrum in a), obtained immediately after the addition of aqueous methanol

are shown in Figs. 1(a) and 1(b), from which it is evident that a major change has occurred. More information is contained in these spectra than can be described in this preliminary communication, and only the main features are discussed here. It is convenient to consider the spectra under three mass ranges.

The Sample Before Reaction [Fig. 1(a)].—(i) $m/z > 1340$. This part of the spectrum consists almost exclusively of even mass peaks up to $m/z = 1790$. The highest C-F species detected is $C_{60}F_{54}$ but the products of reaction suggest that more sites are occupied in the sample used. (We note here that both $C_{60}F_{50}$ and $C_{60}F_{52}$ were reported earlier,¹⁰ cf. a recent view that $C_{60}F_{48}$ is the highest fluorinated species so far detected by mass spectrometry.⁸) Since fluorinated C_{60} decomposes fairly rapidly on heating under vacuum at 80 °C, use of elevated temperatures to increase fluorine incorporation is counter-productive. The extent of fluorination of C_{60} also varies with sample, but the reason for this is not yet clear.

The more intense ions correspond to a wide range of species $C_{60}F_{2n}O_m$, where n varies from 13 to 24 and m varies from 0 to 11. The highest site occupancies (oxygen must occupy two sites; see below) are 52 (1664, $C_{60}F_{48}O_2$), 54 (1504, $C_{60}F_{32}O_{11}$; 1570, $C_{60}F_{38}O_8$), 56 (1696, $C_{60}F_{48}O_4$) and 58 (1712, trace, $C_{60}F_{48}O_5$). The most intense peaks are consistent with species containing a single oxygen, with $C_{60}F_{40}O$ the most prominent. The oxygen could be derived from water chemisorbed on the C_{60} , a possibility supported by recent investigations of C_{60} purity.¹¹ Alternatively it could be acquired as a result of diffusion through the fluoroplastic reaction vessel/container (delays are inevitable between production and mass spectrometry), or it could originate from traces of moisture acquired during evaporation of the trace of dichloromethane used as solvent for deposition of the sample onto the mass spectrometer heated probe. We confirmed that the C_{60} sample used for the fluorination contained only traces of $C_{60}O$. The results are reproduced with different batches of fluorinated material.

(ii) $m/z = 995-1339$. Before reaction, most peaks discernible have odd-numbered masses, attributable to five sets of fragmentation ions: $C_{58}F_{31-37}$, $C_{57}F_{25-37}$, $C_{56}F_{23-35}$, $C_{55}F_{21-31}$ and $C_{53}F_{37-41}$. Moreover, in the higher mass range described under (i) above, peaks due to $C_{59}F_{37-41}$ are evident at m/z 1411, 1449 and 1487. Previous reports have referred only to $C_{59}F_{33}$,¹⁰ and to species containing 57–59 carbons.⁸ Thus, in contrast to the parent fullerene which is generally observed to lose C_2 fragments, the fluorinated derivative loses C fragments. This is consistent with the presence of the weaker single C-C bonds in the fluorinated material. Our observation of peaks for CF_3 (m/z 69, intense), C_2F_5 (m/z 119) and C_3F_7 (m/z 169) supports the view⁸ that fragmentation begins with loss of these fragments; we also observe peaks for C_3F_5 (m/z 131) and C_4F_7 (m/z 181). Subsequent fragmentation involves loss of either F_2 or CF_2 , the latter resulting in loss of 50 mass units, a prominent feature of the spectrum. Thus peaks at m/z 1123, 1073, 1023, 973 and 873 are due to C_54F_{25} , C_53F_{23} , C_52F_{21} , C_51F_{19} and C_49F_{15} . It is not yet possible to determine whether a 56C species (say) is produced by initial loss of C_2F_5 followed by two CF_2 fragments, or by one-step loss of C_4F_7 . The fragmentation shows that the fluorinated material is not stable under mass spectrometric conditions. Both chlorinated¹² and brominated¹³ C_{60} are degraded to C_{60} during mass spectrometry, but accompanying degradation of the cage has not been reported, probably because of the rapidity of the loss of the halogen.

Some even mass peaks at m/z 1054 ($C_{60}F_{10}O_9$), 1104 ($C_{60}F_{16}O_5$), 1142 ($C_{60}F_{18}O_5$) and 1192 ($C_{60}F_{24}O$) are also prominent in this mass range.

(iii) $m/z = 720-994$. Most of the principle peaks here are of even mass, and are consistent with the C_{60} derivatives, $C_{60}F_{2n}O_m$, where $n = 0-10$, and $m = 0, 1, 2, 3, 4, 8, 10$ and 12. Intensities, and the number of species identified, decrease with increasing oxygen content.

*The Sample After Reaction [Fig. 1(b)].—*The highest even mass peak is now at only m/z 1544 ($C_{60}F_{40}O_4$), and even-

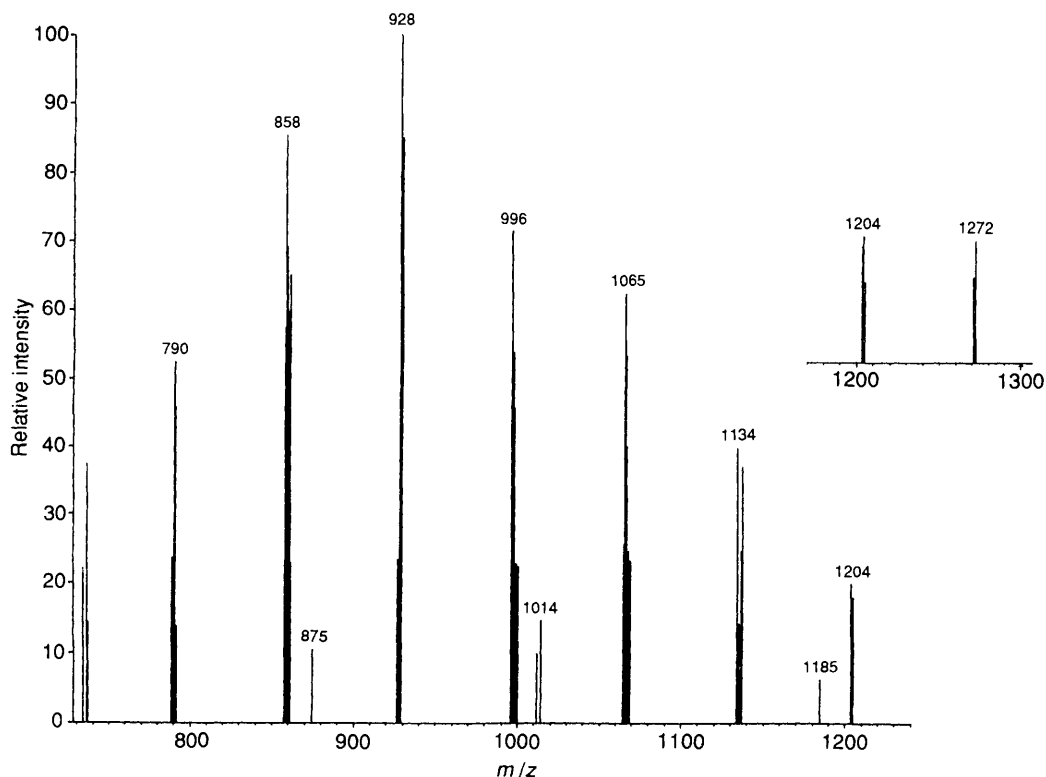


Fig. 2 Electron impact mass spectrum of sample shown in Fig. 1(b), after heating to remove volatile components. Inset shows the high mass region of a second sample.

Table 1 Range of fluorinated derivatives of C₆₀ containing between 0 and 18 oxygen atoms

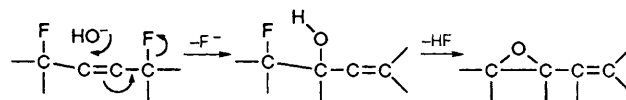
No. of oxygens	No. of fluorines	No. of oxygens	No. of fluorines
None	2, 16–42	10	10–34
1	2–42	11	10–32
2	2–40	12	12–22
3	16–40	13	12–18
4	8, 16–40	14	14–22
5	2–38	15	None detected
6	4, 14–38	16	2–18
7	14–36	17	6–18
8	14–34	18	8, 10
9	6–34		

numbered mass peaks dominate throughout the mass range (Table 1), with those containing two oxygen atoms being the most abundant. The most intense ions appear at $m/z = 1094$ (C₆₀F₁₈O₂) and 1078 (C₆₀F₁₈O), whilst C₆₀F₃₆O and C₆₀F₃₆O₂ are also prominent, suggesting that these are more stable than some other species initially present. Both C₆₀H₁₈ and C₆₀H₃₆ have been reported in reduction of C₆₀,¹⁴ and this suggests that a common stabilising factor underlies these site occupancies. Other features (as yet unexplained) are the abundance of what we believe to be O₅ and O₉ species (this tendency was evident in the material before reaction), and the absence of O₁₅ species; C₆₀O₅ (m/z 800) and C₆₀O₉ (m/z 864) are also prominent in the spectrum. Both C₆₀F₃₄O₁₀ and C₆₀F₃₂O₁₁ indicate derivation from C₆₀F₅₄.

Fragmentation ions are again seen as species with odd mass numbers. Lower mass fragments are now more evident, the most prominent ones being as follows: C₅₈F_{7–15}, C₅₆F_{13–27}, C₅₅F_{5–25}, C₅₄F_{5–21}, C₅₃F_{5–21} and C₅₂F_{11–21}.

We suspect that the epoxides are produced by nucleophilic substitution of F by OH (probably involving addition–elimination),⁹ followed by elimination of HF from adjacent OH and F groups; the mechanism of this latter step is presently unclear. One oxygen will become attached to the cage for every two fluorine atoms removed (Scheme 1). Although CO and COF appear in the low mass region, we see no other evidence for fragmentation of the epoxides, which may be more stable owing to reduced steric interactions.¹⁵ The fact that the more nucleophilic OMe groups from the aqueous methanol do not substitute suggests that the inability to gain stabilisation by forming the epoxide is disadvantageous. With the much more nucleophilic sodium methoxide, fluorine is replaced by methoxy.⁹

On progressively raising the temperature of the heated probe, the more volatile components are removed and the spectrum changes to that shown in Fig. 2. These results are consistent with the presence of either a series of F, O, and OH containing compounds (involatile owing to hydrogen bonding), or a series of CF₃-containing compounds. The latter seemed less probable because (i) these compounds, prepared by an unambiguous route, are comparatively volatile,¹⁶ (ii) no aliphatic fluorine is evident in the ¹⁹F NMR spectrum of the starting material, and (iii) the peak at m/z 790 would indicate addition of HCF₃. However, the mass spectrum of purified compounds C₆₀(CF₃)_n has now been obtained, and is identical to that in Fig. 2.¹⁶ These compounds may be produced by a pyrolytic route as the temperature is raised, and replacement by displaced fluorine of hydrogen in the methyl groups of methanol may be involved; this is under further investigation.

**Scheme 1** Suggested route to epoxide formation, involving replacement of F by OH (addition–elimination) followed by loss of HF. A novel mechanism may be involved in the last step.

Methylene-containing species [C₆₀F_n(CH₂)₂] are also evident at m/z 824, 862, 900 ($n = 4, 6$ and 8 , respectively), and at other points in the spectrum, but discussion of this is deferred.

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References

- 1 A. W. Allaf, S. P. Balm, R. A. Hallett, K. G. McKay and H. W. Kroto, *Proc. Indian Acad. Sci. (Chem. Sci.)*, 1991, **103**, 517; J. M. Wood, B. Kahr, S. H. Hoke, L. Dejarne, R. G. Cooks and D. Ben-Amotz, *J. Am. Chem. Soc.*, 1991, **113**, 5907.
- 2 K. M. Creegan, J. L. Robbins, W. K. Robbins, J. M. Millar, R. D. Sherwood, P. J. Tindall and D. M. Cox, *J. Am. Chem. Soc.*, 1992, **114**, 1103.
- 3 J. M. Wood, B. Kahr, S. H. Hoke, L. Dejarne, R. G. Cooks and D. Ben-Amotz, *J. Am. Chem. Soc.*, 1991, **113**, 5907.
- 4 W. A. Kalsbeck and H. W. Thorp, *J. Electroanal. Chem.*, 1991, **314**, 363.
- 5 F. Diederich, R. Ettl, Y. Rubin, R. L. Whetten, R. Beck, M. Alvarez, D. Sensharma, F. Wudl, K. C. Khemani and A. Koch, *Science*, 1991, **252**, 548.
- 6 R. Taylor, G. J. Langley, M. F. Meidine, J. P. Parsons, A. K. Abdul-Sada, T. J. Dennis, J. P. Hare, H. W. Kroto and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1992, 667.
- 7 S. H. Hoke, J. Molstad, D. Dilettato, M. J. Jay, D. Carlson, B. Kahr and R. G. Cooks, *J. Org. Chem.*, 1992, **57**, 5069.
- 8 A. A. Tuinman, P. Mukherjee, J. L. Adcock, R. L. Hettich and R. N. Compton, *J. Phys. Chem.*, 1992, **96**, 7584.
- 9 R. Taylor, J. H. Holloway, E. G. Hope, A. G. Avent, G. J. Langley, T. J. Dennis, J. P. Hare, H. W. Kroto and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1992, 665; *Nature*, 1992, **355**, 27.
- 10 H. Selig, C. Lifshitz, T. Peres, J. E. Fischer, A. R. McGhie, W. J. Romanow, J. P. McCauley and A. B. Smith, *J. Am. Chem. Soc.*, 1991, **113**, 5475.
- 11 H. Werner, D. Bublak, U. Göbel, B. Henschke, W. Bensch and R. Schlögl, *Angew. Chem., Int. Edn. Engl.*, 1992, **31**, 868.
- 12 F. N. Tebbe, J. Y. Becker, D. B. Chase, L. E. Firment, E. R. Holler, B. S. Malone, P. J. Krusic and E. Wasserman, *J. Am. Chem. Soc.*, 1991, **113**, 9900; G. A. Olah, I. Bucsi, C. Lambert, R. Aniszfeld, N. J. Trivedi, D. K. Sensharma and G. K. S. Prakash, *J. Am. Chem. Soc.*, 1991, **113**, 9385.
- 13 P. R. Birkett, P. B. Hitchcock, H. W. Kroto, R. Taylor and D. R. M. Walton, *Nature*, 1992, **357**, 479; F. N. Tebbe, R. L. Harlow, D. B. Chase, D. L. Thorn, G. C. Campbell, J. C. Calabrese, N. Herron, R. J. Young and E. Wasserman, *Science*, 1992, **256**, 822.
- 14 R. E. Haufler, J. Conceicao, L. P. F. Chibante, Y. Chai, N. E. Byrne, S. Flanagan, M. M. Haley, S. C. O'Brien, C. Pan, Z. Xiao, M. A. Ciufolini, R. H. Hauge, J. L. Margrave, L. J. Wilson, R. F. Curl and R. E. Smalley, *J. Phys. Chem.*, 1990, **94**, 8634.
- 15 R. Taylor, *Philos. Trans. R. Soc. London, A.*, 1993, **343**, 87.
- 16 J. D. Crane, A. D. Darwish, G. J. Langley, S. Firth, H. W. Kroto, R. Taylor and D. R. M. Walton, unpublished work.