

Oxygenated Species in the Products of Fluorination of [60]- and [70]-Fullerene by Fluorine Gas

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Fluorination of pure [60]fullerene and [70]fullerene by fluorine gas shows batch variation, and is accompanied by colour changes as fluorine slowly penetrates the fullerene lattice. Attempted partial fluorination produces a mixture of highly and unfluorinated material due to this slow penetration. [60]Fullerene undergoes fluorination more slowly than [70]fullerene, due to better packing of the crystal lattice in the former, and this explains why [60]fullerene contaminated with [70]fullerene is fluorinated faster than pure [60]fullerene. The NMR spectrum of fluorinated [70]fullerene shows a number of singlets between δ -151.2 and -153.65, indicating the formation of a mixture of derivatives each possessing high symmetry. The IR of fluorinated [70]fullerene shows a broad band at 1112 cm⁻¹. The mass spectra of fluorinated [60]- and [70]-fullerenes reveals species containing up to eleven and sixteen oxygen atoms, respectively (DCI probe, deposition from dichloromethane), or up to eighteen oxygen atoms in each case (deposition from methanol). The maximum site occupancies of species detected (assuming that oxygen is present as the epoxide) are 68 and 70, respectively. Methylene- and (after reaction with methanol) trifluoromethyl-containing species are also evident in the mass spectrum of fluorinated [60]fullerene; corresponding species are not found in fluorinated [70]fullerene. The high level of epoxide formation with the fluorofullerenes indicates that the tendency for fullerenes generally to form epoxides derives from the strong electron withdrawal by the cages.

Fluorinated [60]fullerene has been the subject of considerable interest in the fullerene field,¹⁻¹³ initially because of the assumed value of the products as lubricants. This application became unrealisable when we showed that, although these hydrophobic materials are reasonably stable in air, they are immediately hydrolysed in the presence of a cosolvent for fluorinated fullerene and water, *e.g.*, acetone, tetrahydrofuran (THF) and alcohols.⁴ Since solvent traces are generally present in the atmosphere, particularly in industrial and mechanical environments, gradual breakdown of the fluorinated fullerene by moisture can be expected. This reactivity, which we have attributed to nucleophilic substitution,³ suggests that the fluorinated fullerenes will be valuable synthons, especially as they are very soluble in polar solvents, unlike many other fullerene derivatives. The limiting factor at present is the ability to carry out selective fluorination of these carbon molecules, and some progress has recently been made with the isolation of C₆₀F₄₈.¹³

Previously, we reported spectroscopic data for fluorination of [60]fullerene by fluorine gas, and noted that the ¹⁹F NMR spectrum exhibited a sharp singlet at δ -150.5 and/or -153 superimposed upon a broad double-humped background, the hump centres being at *ca.* δ -144.4 and -158.0, the former being slightly more intense.¹ (This spectrum has now been confirmed by Kniaz *et al.*¹¹) We suggested that this singlet might be due to C₆₀F₆₀, and noted that other symmetrical species, *e.g.*, C₆₀F₆, C₆₀F₁₂ and C₆₀F₂₀ would also produce similar singlets.¹ We reported subsequently that the mass

spectrum showed the presence of species containing many oxygen atoms per fluorinated fullerene, and up to eighteen oxygens on reaction with *aq.* methanol.⁹ We now report further details, together with spectroscopic data for the fluorination of pure [70]fullerene by fluorine gas, and for the reaction of the product with *aq.* methanol.

Experimental

[60]- and [70]-fullerene, each purified by the chromatographic procedure,¹⁴ were heated at 180 °C at 0.1 mmHg to remove all traces of solvent. The mass spectrum of purified [60]fullerene† showed the presence of only traces of [60]fullerene epoxide. Each fullerene (*ca.* 10–20 mg samples) contained in fluoro-carbon tubes were then heated at *ca.* 70 °C under fluorine (*ca.* 2 atm) for periods of up to 6 weeks, with occasional agitation.

The ampoules were then pumped free of fluorine gas, sealed and transferred to a nitrogen dry box and stored to await processing. After intervals of up to three weeks (this depended upon the availability of instrumentation), samples were removed for mass spectrometry studies and were exposed to air; no significant difference in the spectra with regard to oxygen content were obtained whether this exposure was for a few minutes or for many days. The mass spectrometer was operated under EI conditions, using a temperature-ramped DCI 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 u, and exponential scanning over 2000–20 u at 10 s per decade.

Results and Discussion

Colour Changes Accompanying Fluorination and the Effect of the Crystalline State on Fluorination Rate.—Fluorination of [60]fullerene is accompanied initially only by an increase in

† Copies of the mass spectra of F₂-fluorinated [60]fullerene and [70]fullerene, and of the product of the latter reaction after treatment with methanol (Figs. S1–S3, respectively) have been deposited with the British Library [Supp. Pub. No. 57053 (4 pp.)]. For details of the Supplementary Publications Scheme, see 'Instructions for Authors (1995)', *J. Chem. Soc., Perkin Trans. 2*, 1995, issue 1.

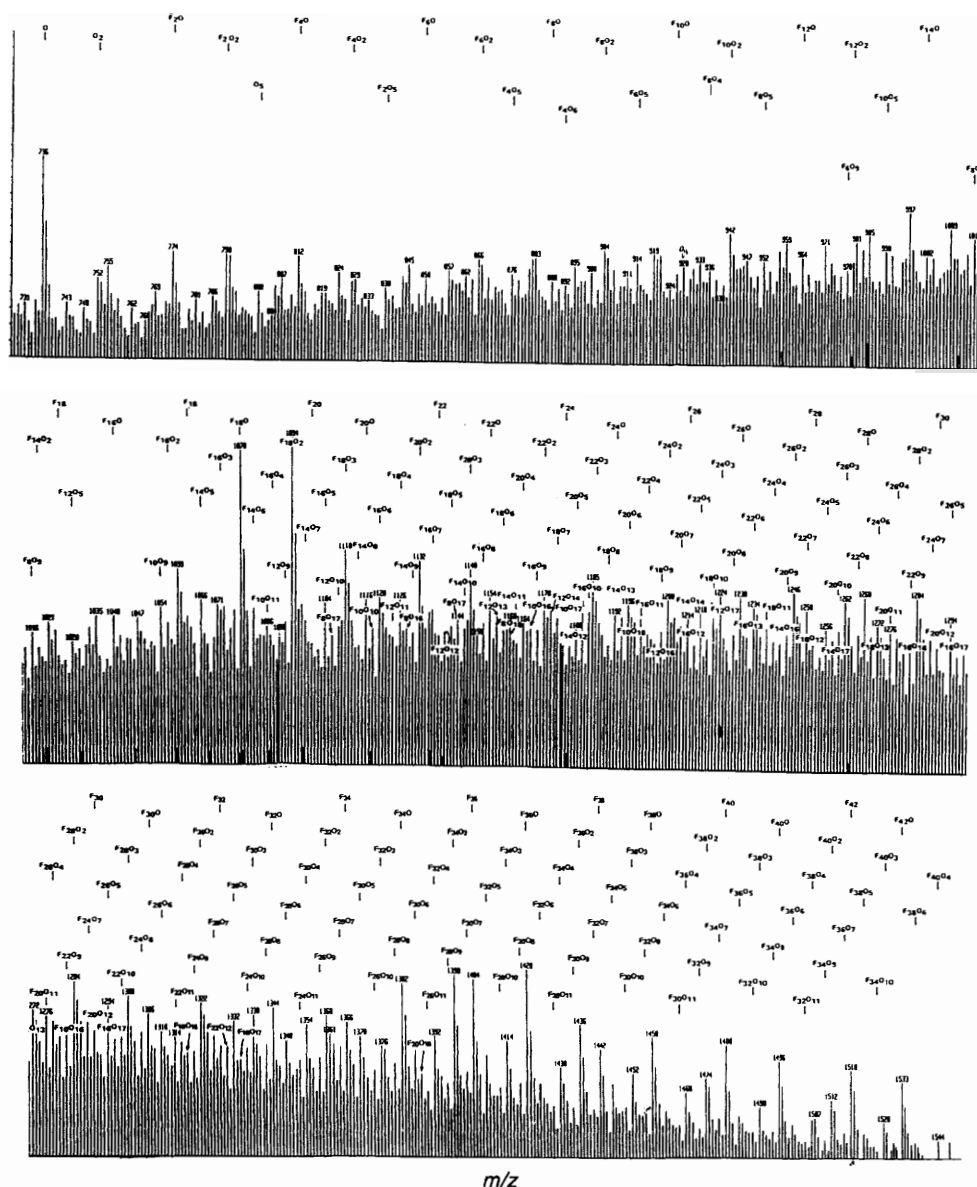


Fig. 1 Mass spectrum (EI conditions) of the sample giving the spectrum in Fig. S1,† after reaction with methanol (C_{60} is deleted from all peak labels)

volume. After *ca.* 4 days the colour changes to dark brown, then after a further *ca.* 4–6 days to light brown and finally after an extended period, to off-white; the final colour for fluorinated [70]fullerene is pink. We attributed provisionally, the colour changes of [60]fullerene to the formation of stable partly fluorinated derivatives.¹ Further experiments showed that the brown material consists of a mixture of highly fluorinated material (which can be separated using a polar solvent), and completely unchanged [60]fullerene. These colour changes are thus associated with gradual penetration of the fullerene lattice. It will thus be extremely difficult to produce partially fluorinated material of low fluorine content by heterogeneous fluorination with fluorine gas because of this penetration aspect. Moreover, once fluorine has added across one of the double bonds in a hexagonal ring of the fullerene, localisation of electrons on the remaining double bonds will be increased, thereby facilitating further addition on the same molecule.

The heterogeneous nature of the fluorination and possible differences in the crystalline condition of the fullerene, causes significant variations between runs. This was evident in both the time taken for the reaction apparently to complete, and in the extent of fluorination detected by mass spectrometry. Our

results (and presumably of others) should be taken only as a guide to what is achievable. We find that [70]fullerene is fluorinated more rapidly than is [60]fullerene and have attributed this to the better molecular packing in the latter.¹⁵ It follows also that impure [60]fullerene will fluorinate faster than the pure material, which explains the differences in rates between the two initial reports of fluorination.^{1,2} Hamwi *et al.*, have recently reached similar conclusions from their fluorination studies.¹⁰

The Extent of Fluorination.—Previously we reported the marked difference in profile of the mass spectrum of fluorinated [60]fullerene when deposited on a heated probe from methanol as opposed to dichloromethane;¹¹ fluorinated [70]fullerene shows parallel behaviour (compare Figs. S2 and S3[†]); Fig. 1 shows the expanded spectrum of the product of reaction of fluorinated [60]fullerene with methanol. For these particular (dichloromethane-deposited) batches the most highly fluorinated species detected in significant as opposed to trace quantities are $C_{60}F_{48}$ and $C_{70}F_{48}$, which may be compared with other reports *viz.*, $C_{60}F_{52}$, $C_{70}F_{46}$;² $C_{60}F_{48}$, $C_{70}F_{54}$;⁵ $C_{60}F_{44}$, $C_{70}F_{44}$;¹⁰ $C_{60}F_{54}$;⁹ $C_{60}F_{60}$;¹² $C_{60}F_{76}$.⁸ We find the

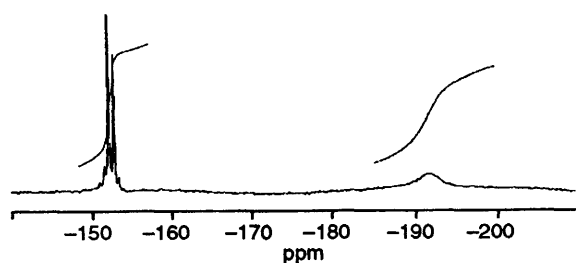


Fig. 2 ^{19}F NMR spectrum of the product of F_2 -fluorination of [70]fullerene

Table 1 Species that could correspond to the fluorinated [60]fullerene molecular ions of 16 amu increments in the range $m/z = 1328$ –1504 (Fig. 5)^a

| m/z | Species | | |
|-------|---|------------------------------|------------------------------|
| 1328 | $\text{C}_{60}\text{F}_{32}$ | $\text{C}_{60}\text{F}_{32}$ | $\text{C}_{79}\text{F}_{20}$ |
| 1344 | $\text{C}_{60}\text{F}_{32}\text{O}$ | $\text{C}_{55}\text{F}_{36}$ | $\text{C}_{74}\text{F}_{24}$ |
| 1360 | $\text{C}_{60}\text{F}_{32}\text{O}_2$ | $\text{C}_{50}\text{F}_{40}$ | $\text{C}_{69}\text{F}_{28}$ |
| 1376 | $\text{C}_{60}\text{F}_{32}\text{O}_3$ | $\text{C}_{45}\text{F}_{44}$ | $\text{C}_{64}\text{F}_{32}$ |
| 1392 | $\text{C}_{60}\text{F}_{32}\text{O}_4$ | $\text{C}_{40}\text{F}_{48}$ | $\text{C}_{59}\text{F}_{36}$ |
| 1408 | $\text{C}_{60}\text{F}_{32}\text{O}_5$ | $\text{C}_{35}\text{F}_{52}$ | $\text{C}_{54}\text{F}_{40}$ |
| 1424 | $\text{C}_{60}\text{F}_{32}\text{O}_6$ | $\text{C}_{30}\text{F}_{56}$ | $\text{C}_{49}\text{F}_{44}$ |
| 1440 | $\text{C}_{60}\text{F}_{32}\text{O}_7$ | $\text{C}_{25}\text{F}_{60}$ | $\text{C}_{44}\text{F}_{48}$ |
| 1456 | $\text{C}_{60}\text{F}_{32}\text{O}_8$ | $\text{C}_{20}\text{F}_{64}$ | $\text{C}_{39}\text{F}_{52}$ |
| 1472 | $\text{C}_{60}\text{F}_{32}\text{O}_9$ | $\text{C}_{15}\text{F}_{68}$ | $\text{C}_{34}\text{F}_{56}$ |
| 1488 | $\text{C}_{60}\text{F}_{32}\text{O}_{10}$ | $\text{C}_{10}\text{F}_{72}$ | $\text{C}_{29}\text{F}_{60}$ |
| 1504 | $\text{C}_{60}\text{F}_{32}\text{O}_{11}$ | C_5F_{76} | $\text{C}_{24}\text{F}_{64}$ |

^a Those species that are unrealistic through having either too many carbons or fluorines, are italicised.

most abundant species to be $\text{C}_{60}\text{F}_{42}$ and $\text{C}_{70}\text{F}_{38}$, *cf.*, $\text{C}_{60}\text{F}_{36}$, $\text{C}_{70}\text{F}_{40}$;² $\text{C}_{60}\text{F}_{46}$, $\text{C}_{70}\text{F}_{52}$;⁵ $\text{C}_{60}\text{F}_{40}$;¹² $\text{C}_{60}\text{F}_{48}$.⁸ The only reasonable conclusion from these results at present is that the components of highest yield and maximum stability under mass spectrometry conditions average around $\text{C}_{60}\text{F}_{42}$ and $\text{C}_{70}\text{F}_{46}$.

Given however the fact that chloro- and bromo-fullerenes are completely degraded to the parent fullerene under identical conditions, it would be surprising indeed if no degradation of the fluorofullerenes occurred during mass spectrometry. Moreover, the mass spectra show the presence of fragmentation ions, and the parent fullerenes. These latter probably derive from fluorofullerene degradation, because the parent molecules are relatively insoluble in the dichloromethane used for preparing samples for mass spectrometry. Other workers also have evidence that fluorine is readily lost from more highly fluorinated fullerenes.¹¹ A considerable amount of fluorine is also lost in processing (see below) and we suggest that the number of fluorines per fullerene cage indicated in the mass spectra does not reflect the number initially attached. Differences in the amount of fluorine added to the cages will also depend on the temperature of fluorination. Other workers⁵ have used temperatures up to 275 °C and it is unclear as to how this may affect the uptake of fluorine.

The ^{19}F NMR spectrum for the products of fluorination of [70]fullerene (Fig. 2) shows singlets at δ -152.36 and -153.03 (intensity ratio 2:1), three other small singlets at δ -151.2, -151.79 and -153.65, and virtually no background hump (the latter being a characteristic of the spectrum of fluorinated [60]fullerene). The singlets indicate the formation of one or more highly symmetrical products. The IR spectrum for this material deposited on a KBr plate from a THF solution (Fig. 3),

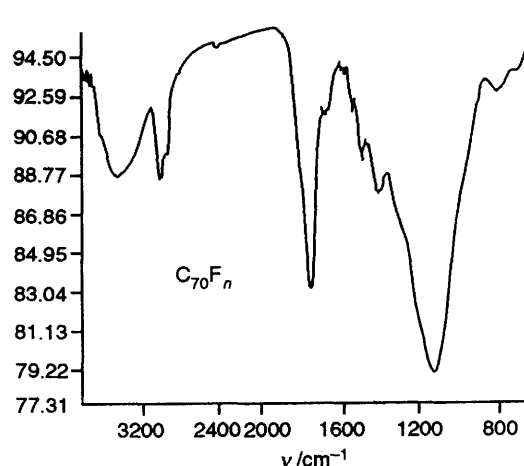


Fig. 3 IR spectrum of the product of F_2 -fluorination of [70]fullerene

shows the presence of C=O, OH and C=H bands which may be due to occluded solvent, but attempts to remove this by heating at 80 °C *in vacuo* were unsuccessful.

Validity of the Mass Spectra Analyses.—The number of species identified in the mass spectra is probably unique and it is first necessary to establish that the analysis is valid. A pronounced feature of the spectra is the repetitiveness of the peak pattern. This is evident in Fig. 1 (there is less interference from fragmentation ions in the spectra obtained after addition of methanol), in which there is an 11-fold repeat pattern of 38 amu (F_2) between 1094 and 1512 amu. This pattern (more clearly seen in the higher mass regions) is shown for greater clarity as a simplified representation in Fig. 4 (peak heights are not to scale though the six most intense ions are shown as such). For these peaks, the four isotope peaks are apparent, but for the less intense peaks, the third and fourth isotope peaks are underneath the parent ion of another species. Notable features are: (i) Left to right in Fig. 4 the peaks correspond to the species $\text{C}_{60}\text{F}_n\text{O}_m$, for values of $m = 2, 7, 0, 5, 10, 3, 8, 1, 6, 18, 11, 4$ and 9. (ii) The most intense ions present have values of $m = 0$ –5, which is both expected, and further justifies the interpretation. (iii) At certain points throughout the mass range, peaks corresponding to $m = 12$ –17 are also evident. (iv) A corresponding pattern exists for the mass spectrum of fluorinated [70]fullerene (Fig. S3[†]), but differs slightly from that shown in Fig. 4, because whereas the intensities of the ions for $\text{C}_{60}\text{F}_n\text{O}_m$ decrease for values of $m = 2 > 1, 3 > 4 > 0, 5 >$ others, those for $\text{C}_{70}\text{F}_n\text{O}_m$ decrease regularly for increasing values of m . This may reflect either differences in mass spectroscopy conditions, or conceivably, a difference in reactivity of these fullerenes towards nucleophilic substitution.

It is necessary to consider whether the peaks attributed to oxygenated fluorofullerenes could be due to some other species. Accurate mass measurements are difficult to obtain due to the plethora of peaks, and even when it is possible it may not help much because both fluorine and oxygen have near-integer atomic masses. For example the peak at 1094 amu (the most intense one) in the spectrum of F_2 -fluorinated [60]fullerene (Fig. 1) and attributed to $\text{C}_{60}\text{F}_{18}\text{O}_2$ could conceivably be $\text{C}_{50}\text{F}_{26}$. Accurate mass measurement gives 1093.9962 amu, *cf.* 1093.9610 and 1093.9584 for these species, respectively. The differences from theory are 5 and 8 ppm, respectively, so both are within the normally acceptable range of agreement.

Mathematical arguments are more compelling. Consider the series of peaks from 1328 to 1504 amu (Fig. 1), which we attribute to $\text{C}_{60}\text{F}_{32}\text{O}_m$, where m varies from 0 to 11. Table 1 shows the possible alternative species, but those italicised are

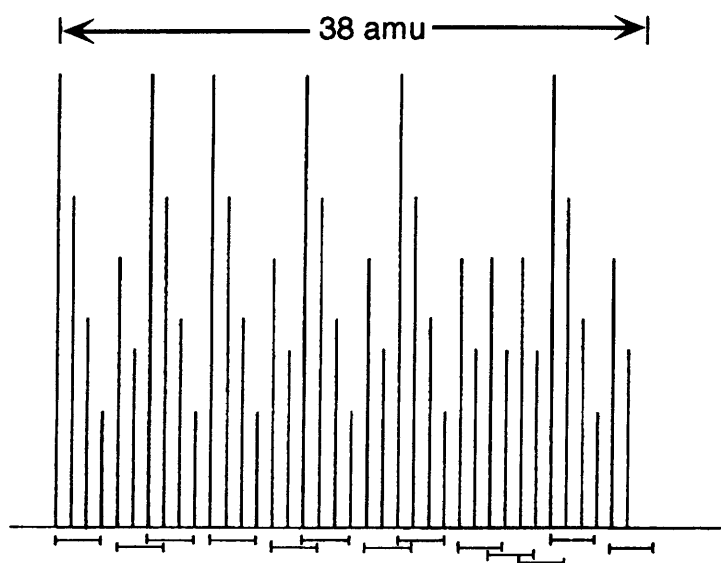


Fig. 4 Simplified representation of the repetitive peak pattern observed between 1094 and 1512 amu in the mass spectrum of fluorinated [60]fullerene

not meaningful, because either they contain too many fluorines relative to carbon, or they have too many carbons overall. Similar constraints apply to all the other series of oxygenated species, and to those derived from [70]fullerene as well. Moreover, the intensities of the ions tend to decrease as the number of oxygens attached increases. This is entirely reasonable for such a series of compounds, but would be most unreasonable for the alternative sets of ions, even supposing feasible structures could exist throughout a series of them. Lastly it should be noted that species with more than eighteen oxygen atoms attached to the cages may be present, but since the mass of nineteen oxygens is nominally the same as sixteen fluorines, a species having say $m/z = 1366$ could also be either $C_{60}F_{34}$ or $C_{60}F_{18}O_{19}$.

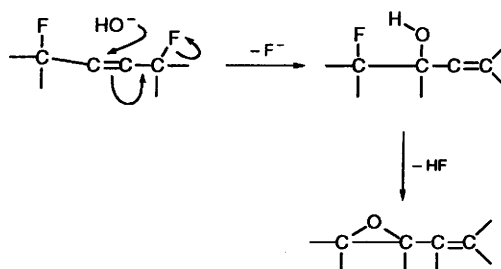
The Oxygenated Species.—Thus a notable feature of the spectra is the large numbers of oxygen atoms attached to each fluorinated fullerene cage. Oxygen attachment to fullerenes, is becoming a dominant aspect first noted in the mass spectrum for $C_{60}O$.¹⁶ Further mass spectroscopic evidence for both this species and $C_{60}O_2$ was obtained subsequently,^{17,18} and the mono-epoxide isolated.¹⁹ Mass spectroscopic evidence for the formation of $C_{60}O$ and $C_{70}O$ together with methylene adducts, and traces of $C_{60}O_n$ ($n = 2-5$) and $C_{70}O_2$ has also been reported.¹⁸ Electrochemical oxidation of [60]fullerene yields $C_{60}O_n$ ($n = 1-4$),²⁰ and [70]fullerene epoxide has been separated from higher fullerenes by HPLC.²¹ Phenylation of [60]fullerene by a mixture of benzene, bromine and iron(III) chloride produces derivatives containing one and two oxygen atoms,²² as does the product of reaction of benzyne with [60]fullerene.²³

As well as our preliminary report of the presence of up to eighteen oxygen atoms in fluorinated [60]fullerene,⁹ other reports refer to species containing either one or two^{8,10} or five¹² oxygen atoms in the mass spectra of fluorinated [60,70]fullerenes, and it is reasonably certain that the oxygen is present as epoxide.^{8,9,12} We suggest that a significant factor that favours epoxide formation in general is the strong electron-withdrawing property of the fullerene cage. This being so, the large number of epoxides present on the fluorinated fullerene cage becomes readily understandable.

The origin of the oxygen is unclear. The amount present in

the original [60]fullerene (Fig. 1) is too small to account for the observed results. The anhydrous conditions under which fluorine was introduced onto the samples in perfluorinated tubes is unlikely to result in oxygen being introduced. The oxygen is unlikely to come from the mass spectrometer because the source is at *ca.* 10^{-7} mB, 10^{-10} atm, so the amount of oxygen present is infinitesimally small. Moreover, if the sample could react that quickly with oxygen, then it should do so in air. By contrast, a sample left open in the laboratory for 8 weeks showed only a minor alteration in the spectrum, Hamwi *et al.*¹⁰ have arrived at the same conclusion. Conceivably, oxygen (as water) may be bound to the surface of the reaction vessel, since Tuinman *et al.*, found the amount of oxygenated species to vary according to the reaction vessel used, being 25–35% in Pyrex, 10–20% in quartz and 5–10% in stainless steel.⁸ Water may also be chemisorbed onto the fullerene,²⁴ or trapped within the fullerene lattice given that solvents are tenaciously retained in this way.²⁵ The possibility that the oxygen comes from water introduced during evaporation of the dichloromethane used to deposit the fluorofullerene on the DCI probe is discounted by our finding that the use of a solid sample (capillary tube) probe produces similar spectra.

We suggest that the epoxides arise from nucleophilic substitution of F by OH (probably involving addition–elimination)^{3,4} followed by elimination of HF from adjacent OH and F groups, the mechanism of this latter step being presently unclear.⁹ One epoxide would then be formed for every two fluorines that are replaced (Scheme 1).



Scheme 1 Proposed route for epoxide formation from fluorinated fullerenes. The initial addition–elimination is followed by loss of HF, which may involve a novel mechanism.

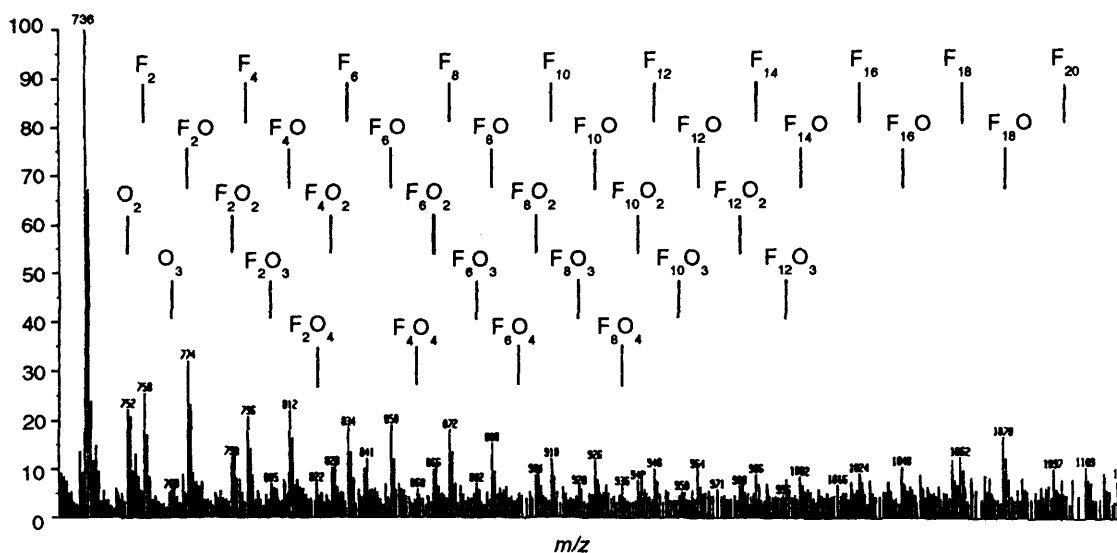


Fig. 5 Mass spectrum (low mass region) of a second sample of fluorinated [60]fullerene

Comparison of the Mass Spectra Before and After Addition of Methanol.—First we emphasize that the results are batch-dependent. For the samples that we investigated in detail, the following features were evident:

Fluorinated [60]fullerene. (a) Before addition. Species up to 1790 amu are evident, the highest fluorinated species detectable initially being $C_{60}F_{54}$ (1746 amu), and the highest site occupancies (epoxide oxygen must occupy two sites) are 52 ($C_{60}F_{48}O_2$, 1664 amu), 54 ($C_{60}F_{32}O_{11}$, 1504 amu; $C_{60}F_{38}O_8$, 1570 amu), 56 ($C_{60}F_{48}O_4$, 1696 amu) and 58 ($C_{60}F_{48}O_5$, 1712 amu). Peaks at 1774 and 1790 amu, may be due to the species $C_{60}F_{54}(CH_2)_2$ and $C_{60}F_{54}(CH_2)_2O$ (58 and 60 site occupancies, respectively). Evidence for methylene-containing species appears at other points in the spectrum, e.g. $C_{60}(CH_2)_2$, $C_{60}F_2(CH_2)_2$ and $C_{60}F_4(CH_2)_2$ at 748, 786 and 824 amu, respectively. The origin of these species (others appear after methanol addition) is unclear, but they are a recurring feature of fullerene chemistry. These species were not evident in the low mass end of a further sample of fluorinated [60]fullerene (Fig. 5).

Below ca. 1377 amu peaks of odd mass dominate and these are attributed to fragmentation ions. Clearly identifiable are $C_{59}F_{37-41}$, $C_{58}F_{31-37}$, $C_{57}F_{25-37}$, $C_{56}F_{25-35}$, $C_{55}F_{21-31}$, $C_{54}F_{19-29}$, $C_{53}F_{23,37-41}$, as well as $C_{52}F_{21}$ (1073 amu), $C_{51}F_{19}$ (973 amu) and $C_{49}F_{15}$ (873 amu). Other workers have observed only $C_{59}F_{33}$ ² and species containing 57–59 carbons.⁵ The notable difference in fragmentation between the parent fullerene and these derivatives is that the former lose C_2 fragments (due to the presence of the stronger double bonds), whereas the fluoro derivatives lose single carbon fragments.

(b) After addition. There is a marked difference in the spectrum here (Fig. 1) with the species of highest mass being at 1544 amu. The loss of mass arises from the replacement of a pair of fluorines by oxygen, which must be present as an epoxide. Peaks of even mass now dominate throughout the range, because there is a general shift to lower mass of the more stable (even mass) species present. The most highly oxygenated species present are now O_{18} ones, cf. O_{11} species before methanol addition. The most fluorinated of these is $C_{60}F_{20}O_{18}$, which corresponds to 56 site occupancies, almost identical with that found before methanol addition. This thus provides good confirmation of the number of fluorines initially present, and provides a useful method for overcoming the difficulty associated with obtaining meaningful mass spectra for highly fluorinated fullerenes (at least with the techniques more generally available), due to their tendency to

degrade during analysis. Epoxides are more stable due, probably, to reduced steric interactions.

The most intense ions are $C_{60}F_{18}O$ (1078 amu) and $C_{60}F_{18}O_2$ (1094 amu), and both $C_{60}F_{36}O$ and $C_{60}F_{36}O_2$ are also strong. Since both $C_{60}H_{18}$ and $C_{60}H_{36}$ have been reported on reduction of C_{60} ,²⁶ this suggests that there is a common stabilising feature that underlies these site occupancies. Methylene-containing species, $C_{60}F_n(CH_2)_2$, are now seen at 748, 824, 862 and 900 amu ($n = 0, 4, 6, 8$).

A most surprising result was obtained on progressively raising the temperature of the heated probe during mass spectrometry of the material that had been treated with methanol. The more volatile components giving the spectrum in Fig. 1 were removed, the residue giving the spectrum shown in Fig. 6. This appears to correspond to the species $C_{60}(CF_3)_n$, $n = 1-8$, which is anomalous since these compounds are known to be very volatile.²⁷ However, a series of less volatile compounds containing both trifluoromethyl and hydroxy groups also give the same mass spectrum, due to the lability of the hydroxy groups.²⁷ We therefore believe that the compounds giving rise to the spectrum in Fig. 6 also contain some hydroxy groups. How these molecules are formed is not known, but it is noteworthy that fluorinated [70]fullerene does not behave in the same way, and this may reflect the greater electrophilicity of [60]fullerene compared with [70]fullerene.

Fluorinated [70]fullerene. (a) Before addition. Species up to 1862 amu are evident in trace amounts (Fig. S2[†]). Species with the highest site occupancies are $C_{70}F_{42}O_{14}$ (1862 amu, 70 occupancies), $C_{70}F_{38}O_{14}$ (1786 amu, 66 occupancies), $C_{70}F_{34}O_{16}$ (1742 amu, 66 occupancies), $C_{70}F_{46}O_9$ (1858 amu, 64 occupancies) and $C_{70}F_{42}O_9$ (1782 amu, 60 occupancies). The highest fluorinated non-oxygenated species is $C_{70}F_{48}$ and the most intense ion is that for $C_{60}F_{38}$. Oxygenated species have mainly up to 11 oxygens, though species with 12, 13, 14 and 16 oxygens are evident in small amounts. Many odd-mass fragmentation ions are present, especially $C_{68}F_{37-27}$, $C_{67}F_{33-27}$, $C_{66}F_{31-29}$ and some, e.g., $C_{68}F_{37-33}O_2$ contain oxygen. No C_{69} fragment ions are evident suggesting that the initial step in fragmentation of fluorinated [70]fullerene involves C_2 loss.

(b) After addition. Here also there is a marked change in the spectrum, with a general lowering of the amu of the products (Fig. S3[†]). The species of highest mass is now $C_{70}F_{48}O_2$ (trace, 1784 amu) and the species of highest site occupancies are $C_{70}F_{28}O_{18}$, $C_{70}F_{30}O_{17}$ and $C_{70}F_{32}O_{16}$ (each with 64 occupancies). The most fluorinated non-oxygenated species is

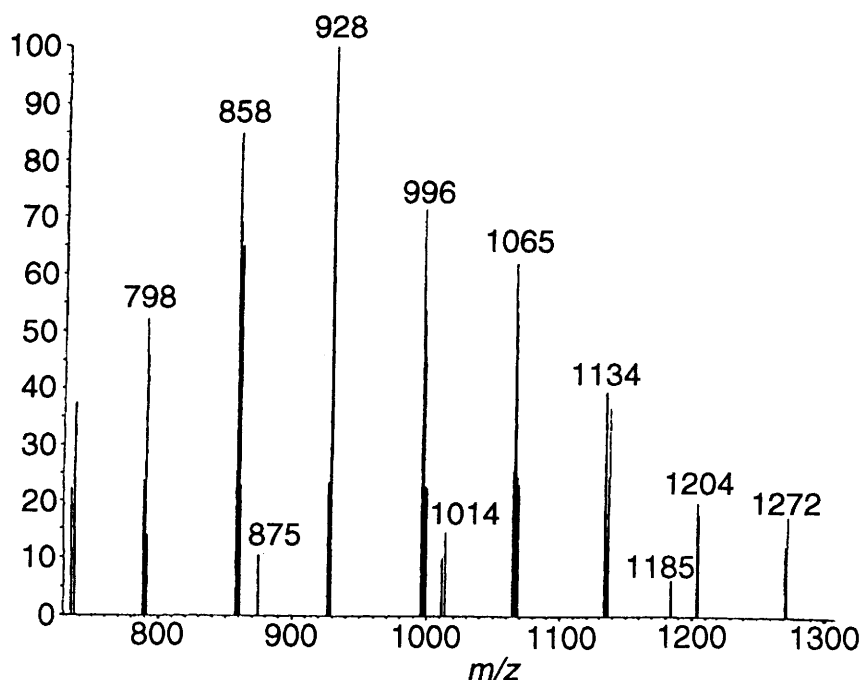


Fig. 6 Mass spectrum of sample shown in Fig. 1, after heating to remove volatiles

$C_{70}F_{46}$, and the most intense ion is that for $C_{70}F_{26}O_3$. There are now many examples of species containing up to 18 oxygen atoms.

In the lower mass range, there are a number of intense odd-mass peaks due to fragmentation ions. Examples are $C_{63}F_{17-5}$, $C_{61}F_{19-15,9}$, and a particularly intense ion at 1139 amu appears to be due to $C_{68}F_{17}$, and the series of even mass ions between 972 and 1124 amu appear to be due to $C_{67}F_{8-16}O$ species.

On raising the temperature of the heated probe there was no evidence of the presence of CF_3 derivatives in contrast with the result obtained with fluorinated [60]fullerene, and also there was no evidence in either spectrum for fluorinated [70]fullerene of the presence of methylene-containing species. The failure to observe either species may be attributable to a reactivity difference between [60]fullerene and [70]fullerene.

Extensive further investigations will be necessary to understand the significance of the features we have observed here.

Use of Fluorinated Fullerenes as Lubricants.—The potential for fluorinated fullerenes (and $C_{60}F_{60}$ in particular) was based, reasonably, on a presumed analogy with Teflon. However, this overlooked an important feature, evident on inspection of models, in that the eclipsing interactions between adjacent fluorines cannot be substantially relieved by twisting of the carbon backbone,²⁸ as is the case for Teflon (which has a spiral backbone as a result). This spiralling, and the close packing of the fluorines that results, makes it impossible for reagents to approach the carbon backbone. The only alternative is for the C–F bonds to be stretched and thus weakened; reaction with nucleophiles is thus enhanced in the case of fluorinated fullerenes. Although the hydrophobic fluorofullerenes are reasonably stable in air, there will inevitably be a slow breakdown particularly where there is likely to be solvent contamination, as for example in industrial environments.

Acknowledgements

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