Isolation of oxides and hydroxides derived from fluoro[60]fullerenes

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Oxygen-containing fluoro[60]fullerenes have been isolated from HPLC purification of $C_{60}F_{36}$ (obtained by fluorination of [60]fullerene with MnF_3) and partly characterised by mass, IR, and ^{19}F NMR spectroscopy. They include $C_{60}F_{35}OH$ (1402 amu), arising from nucleophilic substitution of F in $C_{60}F_{36}$ by OH, and $C_{60}F_{34}O$ (1382 amu) due to subsequent elimination of HF. Both $C_{60}F_{33}O{\cdot}OH$ (1380 amu) and $C_{60}F_{32}O_2$ (1360 amu), obtained by repetition of these steps, are also formed. The EI mass spectra show the presence of $C_{59}F_{34}$ (1354 amu), $C_{59}F_{32}O$ (1332 amu) and $C_{58}F_{32}$ (1304 amu), due to CO loss from the oxide precursors. The corresponding hydroxides and epoxides, derived from the presence of traces of $C_{60}F_{34/38/40}$, are also observed. The slow conversion of $C_{60}F_{36}$ to $C_{60}F_{34}O$ in $CDCl_3$, arising from reaction with traces of water in the solvent, was monitored by ^{19}F NMR spectroscopy. On a Cosmosil Buckyprep column, compounds containing more fluorines elute faster than those with correspondingly less, oxides elute slower than the precursor fluorides, and hydroxides elute faster than the corresponding fluorides. The oxides are more soluble in hexane than $C_{60}F_{36}$, which aids preliminary purification. Some fluorofullerene epoxides show strong IR bands in the carbonyl region but this probably does not reflect alternative ketonic structures (derivable in principle by six-centre eliminations from fluorohydroxyfullerenes) since they would be cage-opened.

Previously, we described the formation of a large number of oxygenated derivatives of both [60]- and [70]-fullerenes, from the reaction of a mixture of fluorofullerenes with water or aqueous methanol.[1] In this way it appeared possible to add a very large number of oxygens to the cages, with one oxygen added for every two fluorines replaced. We conjectured a mechanism whereby a fluorine atom is first replaced by hydroxy, possibly by addition–elimination since the normal S_N2 mechanism is impossible and the S_N1 mechanism improbable, and that subsequent elimination of HF from the adjacent OH and F groups yielded the epoxides. The mechanism requires that formation of the epoxide here is a *cis* process rather than the normal *trans* one; the HF eliminated could be readily detected by ^{19}F NMR spectroscopy. Further investigation into the process has been hampered by the unavailability of specifically fluorinated fullerenes.

More recently, the preparation, separation by HPLC, and characterisation of two isomers of $C_{60}F_{36}$ was described.[2,3] In this work, which was complicated by the ease with which the fluorofullerenes undergo nucleophilic substitution,[1] a number of oxygenated species were separated. We report here their partial spectroscopic analysis, which has yielded detailed information on the substitution and subsequent elimination processes that occur. The separation characteristics thus provided should aid large-scale isolation of these species, thereby allowing their full structural characterisation, and chemical derivatisation.

Experimental

^{19}F NMR spectra were obtained at 338.87 MHz ($CFCl_3$ reference) using $CDCl_3$ as solvent. IR spectra were obtained using either solutions of the products in toluene or chloroform (solvent blank, 0.1 mm cell) or as KBr discs. Mass spectra were obtained under EI conditions (70 eV, VG Autospec).

$C_{60}F_{36}$ was prepared, and purified by HPLC as described previously.[2,3] This involved preliminary purification (using a 4.6 mm × 25 cm Cosmosil Buckyprep column) with toluene as eluent to remove $C_{60}F_{18}$. The residual material was then rechromatographed using, in turn, toluene–hexane (50 : 50), toluene–hexane (10 : 90) and hexane (all 1 ml min^{-1} flow rates). Full details of the peaks obtained are given in ref. 3, and only those of fractions which contained oxygenated material are described here. Some material appears to temporarily bind to the column (causing reduction in retention times), and this can bleed into fractions of subsequent injections. The origin of the oxygenated species is largely due to traces of moisture in the solvents, large quantities of which are used in the HPLC separations. Consequently, changes in composition tend to occur on recycling, hence the separations could probably be improved by working with entirely moisture-free conditions. This has not been possible at this stage, but our present purpose is to identify the species that are present, and thus to provide insight into the reactivity of the fluorofullerenes.

Results and discussion

The main species present in each mass spectrum are shown in bold in the Tables. During EI mass spectrometry, some elimination (either of HF or H_2O) may occur, hence some of the species shown may be produced by these eliminations rather than being present initially. Species of identical mass also appear in different fractions, and these may be isomers arising from the two isomers of the $C_{60}F_{36}$ precursor. Nevertheless the results indicate the main processes involved, and pinpoint the areas in which work, aimed at obtaining larger quantities of material, should be directed.

HPLC

(1) Toluene eluent. The peak of 3.5 min retention time was collected for reprocessing under (**2**).

(2) Toluene–hexane eluent (50 : 50). The above fraction gave

Table 1 Species obtained from HPLC with toluene–hexane (50:50)[a]

Retention time/min	Mass/amu	Species	Figure no.
9–12	928	$C_{60}(CF_3)_3(H)$?	1 (inset)
	1360	$C_{60}F_{32}O_2$	
	1378	$\mathbf{C_{60}F_{32}O(OH)_2}$	
	1380 (main)	$\mathbf{C_{60}F_{33}O{\cdot}OH}$	
13.8	1360	$C_{60}F_{32}O_2$	1
	1380 (main)	$\mathbf{C_{60}F_{33}O{\cdot}OH}$	
	1396	$\mathbf{C_{60}F_{33}O_2OH}$	
	1412 (trace)	$C_{60}F_{33}O_3OH$	
21	927	$C_{60}(CF_3)_3$ (dimer?)	

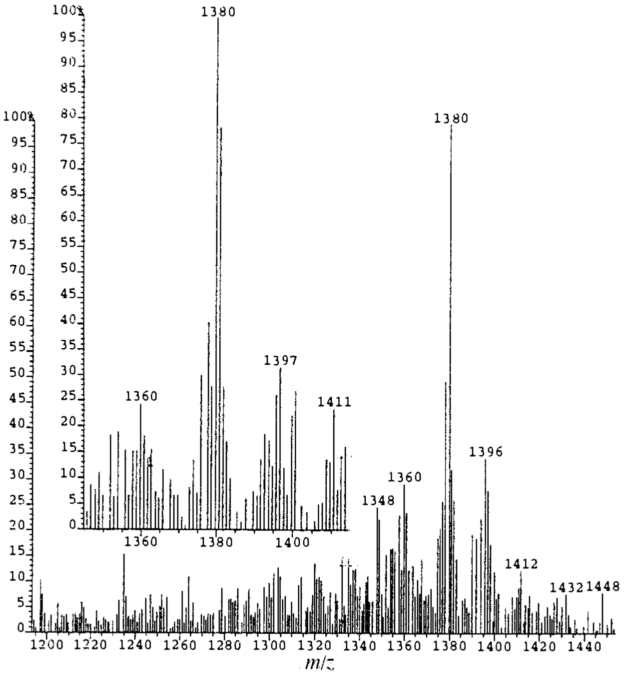


Fig. 1 EI mass spectrum (70 eV) of the 13.8 min eluent (50:50 toluene–hexane, 1 ml min^{-1}); inset shows the spectrum of the 9–12 min eluent

peaks with retention times of 3.6 and 4.7 min (combined for reprocessing to obtain $C_{60}F_{36}$),[3] 5.9 and 7.3 min [combined for reprocessing under (**3**)], 12 min (broad) and 21 min.

The 12 min peak was reprocessed with this solvent to give (after removal of fore-run material) a broad peak (with a sharp superimposed one) of 9–12 min retention and a sharp peak of 13.8 min retention time. Details are given in Table 1.

(*i*) *The* 9–12 *min fraction.*—The species identified here (inset, Fig. 1 and Table 1) provide the first evidence for the replacement of fluorine by OH, conjectured earlier[1] and only the second example[4] of a fullerene diol [$C_{60}F_{32}O(OH)_2$, 1378 amu]. Loss either of water from the diol or of HF from $C_{60}F_{33}O{\cdot}OH$ (1380 amu), possibly during mass spectrometry, accounts for the formation of the dioxide, $C_{60}F_{32}O_2$ (1360 amu). (The peaks of higher mass in the spectrum gave poor isotope patterns and no clear indication of any particular species.) Although hydroxy groups are usually not detected in EI mass spectrometry of fullerenols, the recent observation of $C_{70}Ph_9OH$ by EI mass spectrometry[5] shows that, as in the present case, it is possible in some cases.

(*ii*) *The* 13.8 *min fraction.*—This fraction also showed the above noted 1360/1380 amu peaks (Fig. 1), despite the longer retention time. The differences may be due to derivation from the two isomers of $C_{60}F_{36}$ which themselves have markedly different retention times.[3] The spectra of both this fraction and the previous one showed a pronounced peak at 928 amu, which could be $C_{60}(CF_3)_3H$ arising from cage fragmentation which is known to give CF_3-containing species.[1]

Table 2 Species obtained from HPLC with toluene–hexane (10:90)[a]

Retention time/min	Mass/amu	Species	Figure no.
8.1	1360	$C_{60}F_{32}O_2$	2
	1366	$C_{60}F_{34}$	
	1380 (main)	$\mathbf{C_{60}F_{33}O{\cdot}OH}$	
	1382	$\mathbf{C_{60}F_{34}O}$	
	1420	$\mathbf{C_{60}F_{36}O}$	
12.0	1354	$C_{59}F_{34}$	3
	1382 (main)	$\mathbf{C_{60}F_{34}O}$	
	1402	$\mathbf{C_{60}F_{35}OH}$	
	1404	$\mathbf{C_{60}F_{36}}$	
	1420 (trace)	$C_{60}F_{36}O$	
20.0	1344	$C_{60}F_{32}O$	4
	1354	$C_{59}F_{34}$	
	1360	$C_{60}F_{32}O_2$	
	1382 (main)	$\mathbf{C_{60}F_{34}O}$	
	1402	$\mathbf{C_{60}F_{35}OH}$	
24.5–28.5	1304	$C_{58}F_{32}$	Not shown
	1332	$C_{59}F_{32}O$	
	1360	$\mathbf{C_{60}F_{32}O_2}$	
	1380 (main)	$\mathbf{C_{60}F_{33}O{\cdot}OH}$[b]	
	1382	$\mathbf{C_{60}F_{34}O}$	
	1400 (trace)	$C_{60}F_{34}(OH)_2$[b]	
	1402 (trace)	$C_{60}F_{35}OH$	

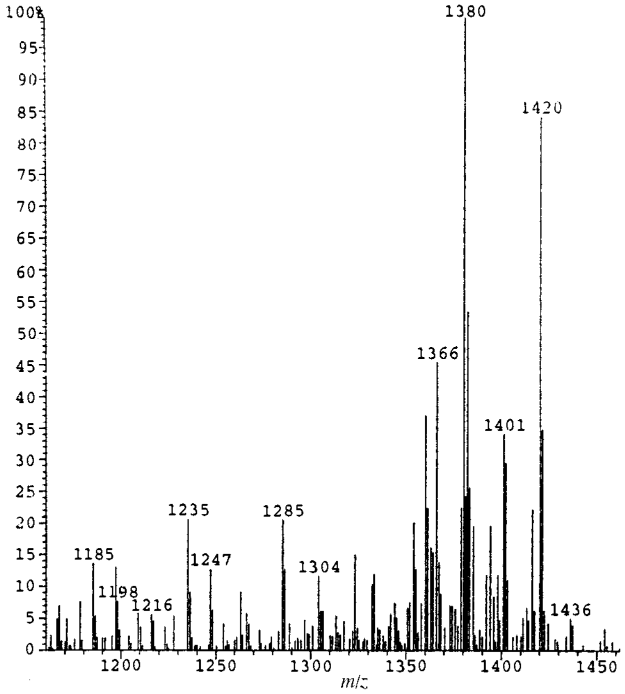


Fig. 2 EI mass spectrum (70 eV) of the *ca.* 8 min eluent (after further recycling) (10:90 toluene–hexane, 1 ml min^{-1})

(*iii*) *The* 21 *min fraction.*—This was recycled to give a fraction of 20.8 min retention time which showed a pronounced peak (with a good isotope pattern) in the mass spectrum at 927 amu. This species is evidently related to that at 928 amu noted under 2(*ii*) and could for example be the $C_{60}(CF_3)_3^{\bullet}$ radical produced under ms conditions from a dimer precursor. We hope subsequently to produce larger quantities of this material to facilitate positive identification.

(3) Toluene–hexane eluent (10:90). The combined peaks of 5.9 and 7.3 min retention time from (**2**), were rechromatographed with this solvent to give peaks of 8.1, 12.0, 19.5–20.0, 24.5 and 28.5 min retention times. Details are given in Table 2.

(*i*) *The* 8.1 *min peak.*—This (major fraction) was colourless, and was recycled to give a cluster of three peaks at *ca.* 8 min retention time and a broad peak of 20 min retention time [described under (*iii*) below]. The mass spectrum (Fig. 2 and Table 1) indicated that three main components are present,

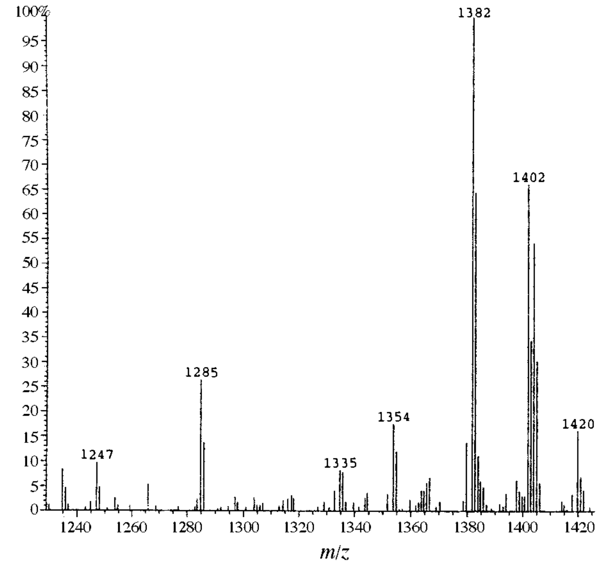


Fig. 3 EI mass spectrum (70 eV) of the 12 min eluent (10 : 90 toluene–hexane, 1 ml min^{-1})

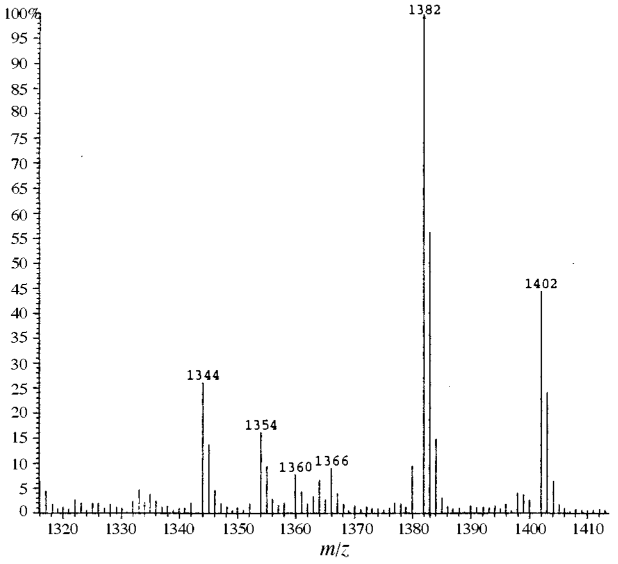


Fig. 4 EI mass spectrum (70 eV) of the 20 min eluent (10 : 90 toluene–hexane, 1 ml min^{-1})

$C_{60}F_{33}O{\cdot}OH$ (1380 amu), $C_{60}F_{34}O$ (1382 amu) and $C_{60}F_{36}O$ (1420 amu). The IR spectrum showed strong bands at 3425 (consistent with the presence of $C_{60}F_{33}O{\cdot}OH$) and 1724 cm^{-1}, respectively; blank runs confirmed that the OH band did not arise from moisture in the KBr. A medium-intensity peak was also obtained at 1291 cm^{-1} (C–O stretch).

(*ii*) *The* 12.0 *min peak.*—The spectrum of this fraction (Fig. 3 and Table 2) also shows the replacement of F by OH and subsequent elimination of HF ($C_{60}F_{36}$, 1404 amu→$C_{60}F_{35}OH$, 1402 amu→$C_{60}F_{34}O$, 1382 amu). Fragmentation involving CO loss from the latter produces $C_{59}F_{34}$ (1354 amu). The IR spectrum differed from that of the previous fraction in showing an intense OH band at 3435 cm^{-1}, but a weak 1719 cm^{-1} band. This suggests that $C_{60}F_{35}OH$ (1402 amu) is the main component, and that $C_{60}F_{34}O$ (1382 amu) is produced here by HF loss in the mass spectrometer.

(*iii*) *The* 20 *min peak.*—The mass spectra of both the 20 min peaks obtained from either the initial separation, or from recycling the 8 min peak, were identical (*e.g.* Fig. 4) as were the IR spectra (*e.g.* Fig. 5). The mass spectrum suggests that this component is $C_{60}F_{35}OH$, which fragments under EI conditions to $C_{60}F_{34}O$ (Table 2). However, the IR spectra showed only a very weak OH band, but a strong band at 1728 cm^{-1}, as well as a strong C–H stretch (which may derive partly from lattice-trapped solvent, a common property of fullerenes). Accurate mass measurement of the peak at 1402 amu gave 1401.945 amu (*cf.* 1401.947 amu required); the alternative $C_{60}F_{32}O_7$, with an improbable 46 site occupancies, requires 1401.917 amu and may be discounted.

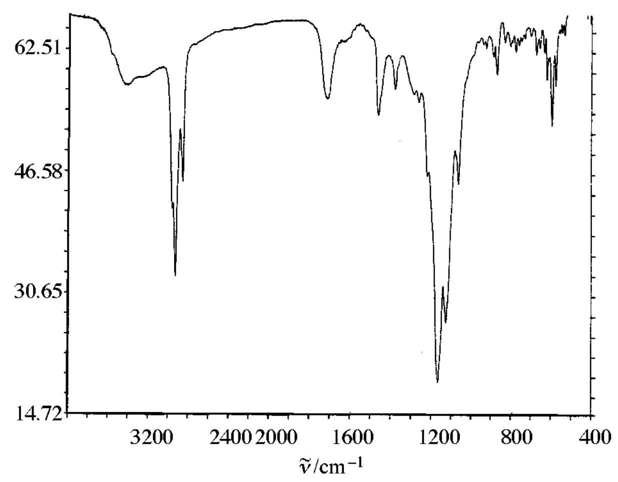


Fig. 5 IR spectrum of the 20 min eluent (10 : 90 toluene–hexane, 1 ml min^{-1})

(*iv*) *The* 24.5–28.5 *min peaks.*—These broad peaks were combined. The mass spectrum (not shown) demonstrates the difficulty of precise identification of the components. Thus although at various probe temperatures a peak at 1360 amu due to $C_{60}F_{32}O_2$ was consistently present, this was accompanied at lower temperatures by peaks at 1382 ($C_{60}F_{34}O$) and 1402 amu ($C_{60}F_{35}OH$), and at higher temperatures by peaks at 1380 ($C_{60}F_{33}O{\cdot}OH$) and 1400 amu [$C_{60}F_{34}(OH)_2$] (Table 2). These variations arise from a combination of volatility and stability differences. The IR spectrum showed a broad band at 3399 cm^{-1} and one at 1728 cm^{-1}.

(4) Hexane eluent. A fraction that eluted in 3–5 min in each of the previous solvents, consisted mainly of two isomers of $C_{60}F_{36}$ which eluted at 24.9 and 33.2 min after rechromatography in hexane.[3] The other components consist largely of either traces of higher oxides derived from $C_{60}F_{36}$ or of oxides/hydroxides derived from more highly fluorinated [60]fullerene (Table 3 and Figs. 6–9). Because these all have shorter elution times than those isolated using the previous solvents, when eluting with these they were removed in the early fractions. The parallel between early elution and higher site occupancy is a feature of the Cosmosil Buckyprep column (see *e.g.* ref. 6).

Relative HPLC retention times

Although it is difficult to draw comprehensive conclusions regarding the HPLC retention times of all of the identified components because of the fragmentation under EI conditions, some provisional general patterns have emerged as follows:

1. Whilst previous work showed that $C_{60}F_{36}$ elutes faster than $C_{60}F_{18}$,[8] this now appears to reflect a general trend of more highly fluorinated fullerenes eluting faster than less highly fluorinated ones. Thus, with toluene–hexane (10 : 90), $C_{60}F_{34}$ elutes in 9 min whereas the $C_{60}F_{36}$ isomers elute in less than 5 min, whilst with hexane $C_{60}F_{38}$ elutes in 9 min whereas $C_{60}F_{36}$ requires 19–23 min.

2. Oxygenated species elute less rapidly than their non-oxygenated precursors. This can be seen for example from comparison of the retention times of $C_{60}F_{38}$ and $C_{60}F_{36}O$ (Table 3).

3. Replacement of F by OH reduces the retention time. This can for example be seen by comparison of the retention times of $C_{60}F_{35}O{\cdot}OH$ and $C_{60}F_{36}O$ (Table 3).

Table 3 Species obtained from HPLC with hexane[a]

Retention time/min	Mass/amu	Species	Figure no.
5–6	**1404**, 1420, 1436, 1452, 1468, 1484	$C_{60}F_{36}O_n$ (n = 0–5)[c]	6
9	1442	$C_{60}F_{38}$	
11.5	1382	$C_{60}F_{34}O$	7
	1396	$C_{60}F_{33}O_2{\cdot}OH$	
	1402	$\mathbf{C_{60}F_{35}OH}$	
	1416	$C_{60}F_{34}O(OH)_2$	
	1454	$C_{60}F_{36}O(OH)_2$	
	1474	$\mathbf{C_{60}F_{38}O_2}$ **[or** $\mathbf{C_{60}F_{37}(OH)_3}$**]**	
14.1	1396	$C_{60}F_{33}O_2{\cdot}OH$	
	1398	$\mathbf{C_{60}F_{34}O_2}$	
	1418	$\mathbf{C_{60}F_{35}O{\cdot}OH}$	
	1436	$C_{60}F_{36}O_2$ [or $C_{60}F_{35}(OH)_3$]	
16.6	1380	$C_{60}F_{33}O{\cdot}OH$	8
	1382	$C_{60}F_{34}O$	
	1400	$C_{60}F_{34}(OH)_2$	
	1414	$C_{60}F_{34}O_3$	
	1416	$C_{60}F_{34}O(OH)_2$	
	1436	$C_{60}F_{36}O_2$	
	1454	$C_{60}F_{36}O(OH)_2$	
18.7	**1420**	$\mathbf{C_{60}F_{36}O}$	9

[a] The dominant species in each spectrum are in bold. [b] Obtained at a probe temperature of 250 °C. [c] The pentoxide probably fragments under EI conditions to give the other species. Fluorofullerenes with up to five oxygen atoms attached have been detected by mass spectrometry in earlier work.[7]

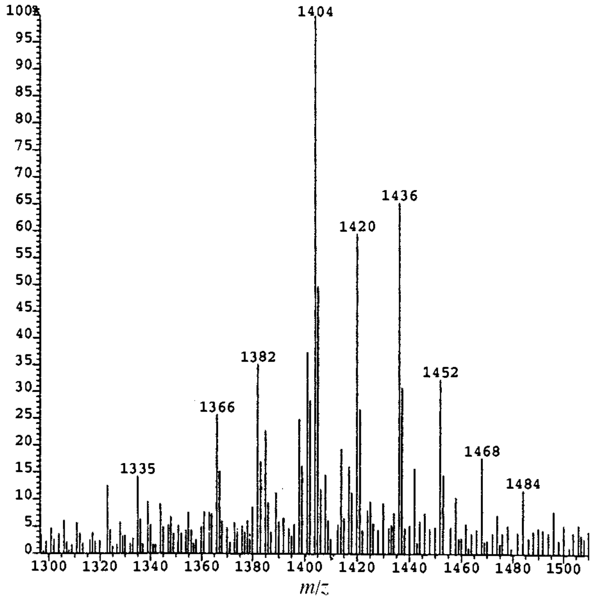


Fig. 6 EI mass spectrum (70 eV) of the 5–6 min eluent (hexane, 1 ml min^{-1})

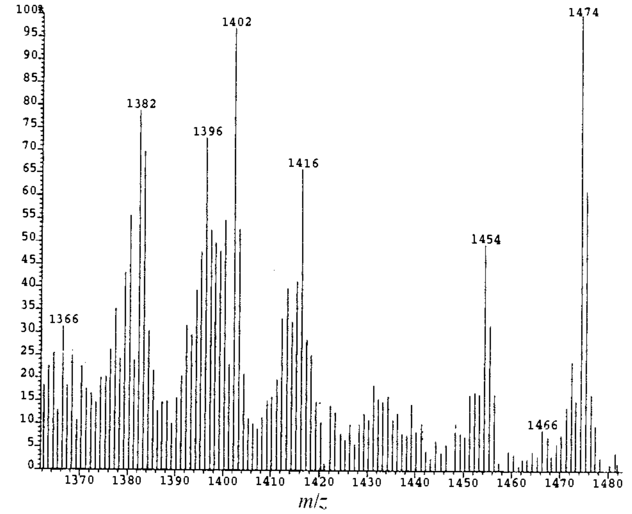


Fig. 7 EI mass spectrum (70 eV) of the 11.5 min eluent (hexane, 1 ml min^{-1})

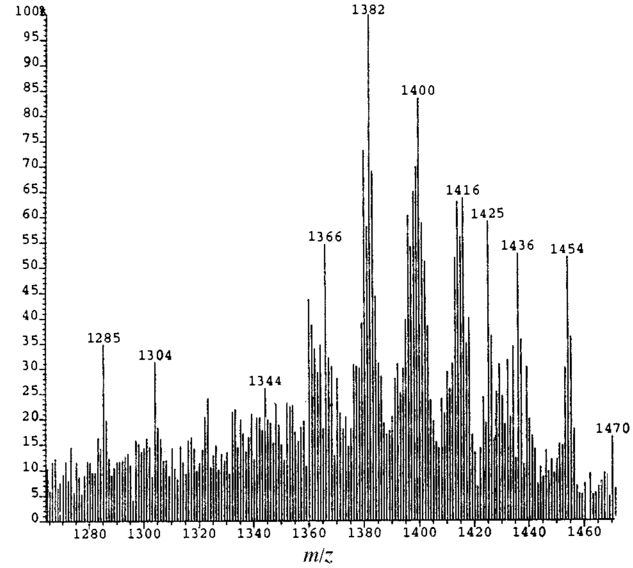


Fig. 8 EI mass spectrum (70 eV) of the 16.6 min eluent (hexane, 1 ml min^{-1})

Reaction sequence

The mass spectroscopy data indicate that the processes shown in Scheme 1 occur. They are divided into three sequences based upon either 36, 38, or 40 site occupancies, and the mass numbers are shown below the corresponding species (some species appear in spectra other than those shown in Figs. 1–4, 6–9).

The process of forming $C_{60}F_{34}O$ from $C_{60}F_{36}$ could be monitored. A ^{19}F NMR spectrum of the C_3 isomer of $C_{60}F_{36}$ in deuteriochloroform was obtained immediately after HPLC separation[3] and then after intervals of *ca.* 4 and 12 weeks (Fig. 10). The spectrum changes and by comparison with the ^{19}F NMR spectrum (Fig. 11) of a pure sample of isolate $C_{60}F_{34}O$, the peaks which increase with time are seen to be due to the formation of this oxide. A sample of pure $C_{60}F_{36}$ that was allowed to degrade with moisture showed the formation in the mass spectrum of peaks at 1402 amu due to $C_{60}F_{35}OH$ and 1382 amu due to $C_{60}F_{34}O$. Likewise two additional peaks appeared in the HPLC (*ca.* 90 : 10 toluene–hexane, 0.8 ml min^{-1}) at retention times ($C_{60}F_{36}$ = 4.1 min) of 6.1 and 7.6 min, attributable to these derivatives.

IR spectra and the nature of the oxides

Because of the very small amounts of material that were available in some cases, it proved necessary to run some IR spectra in toluene solution, using toluene as a blank. A preliminary spectrum obtained with $C_{60}F_{36}$ run either in KBr or in toluene showed that this technique was feasible, the spectra being identical apart from some non-cancelling and non-interfering bands in the C–H stretching region.

Notably, material indicated by mass spectrometry to contain oxide groups showed bands variously at 1717–1728 cm^{-1} (KBr), *e.g.* 1717 cm^{-1} for $C_{60}F_{34}O$ (Fig. 6); the bands are sharper in either toluene or chloroform as solvent. The possibility of interference from dioctyl phthalate plasticizer was ruled out since the toluene had been recovered many times *via* rotary evaporation (which removes dioctyl phthalate at an early stage), and the main band for this ester (1274 cm^{-1}) was absent. Assigning the bands to carbonyl in the 'oxide' would mean that the cage

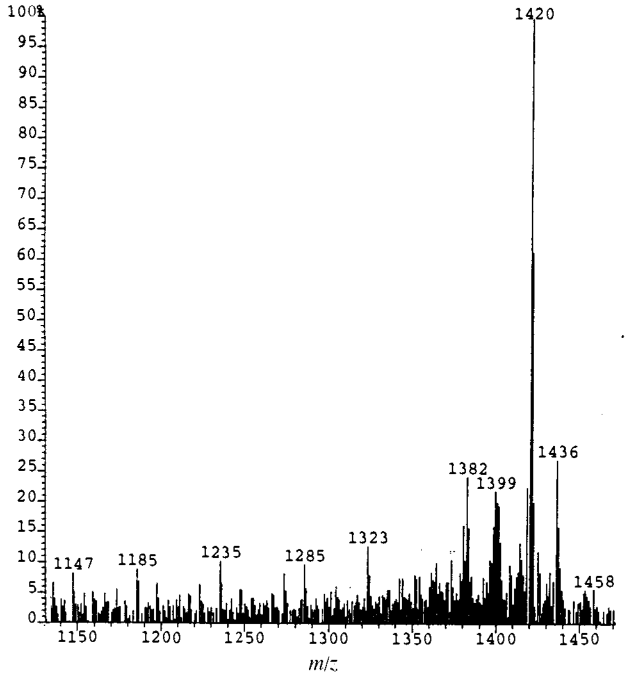
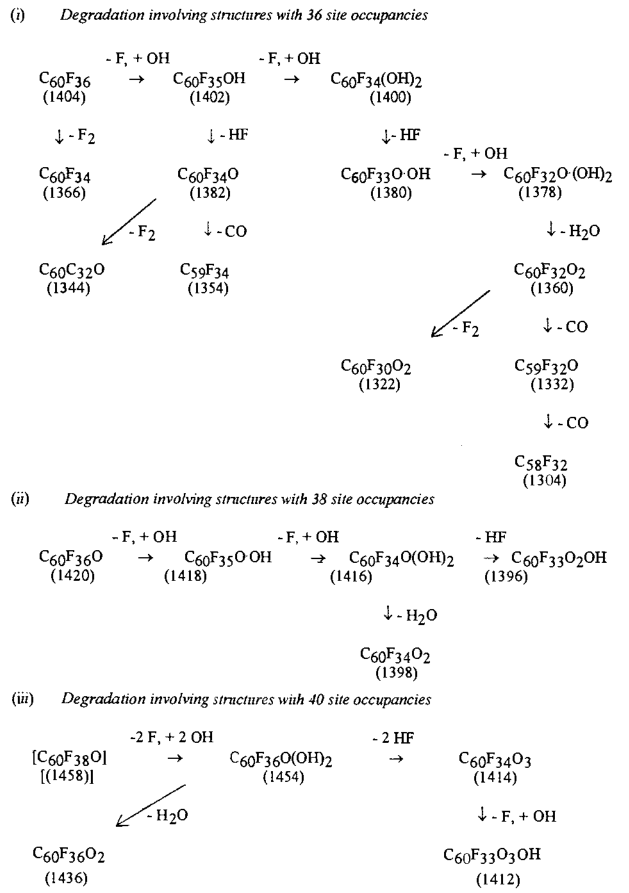


Fig. 9 EI mass spectrum (70 eV) of the 18.7 min eluent (hexane, 1 ml min^{-1})



Scheme 1 Nucleophilic substitution and elimination pathways

would have to be opened, which is irreconcilable with the occurrence of [60]fullerene from degradation in the EI mass spectrum. $C_{60}F_{18}O$ shows a band in this region, but a ketonic structure for this compound has been ruled out by structural characterisation, and likewise by degradation during EI mass spectrometry to [60]fullerene.[9] $C_{60}O$ itself does not show a band in the carbonyl region.[10] It seems probable that the band is a specific property of fluorofullerene epoxides, and it is noteworthy that of the 36 spectra reported for epoxides in a standard compilation,[11] some 45% showed a band (of variable intensity) between 1710 and 1735 cm^{-1}. No structural feature could be discerned from these data that would account for the appearance of this band for some epoxides but not for others.

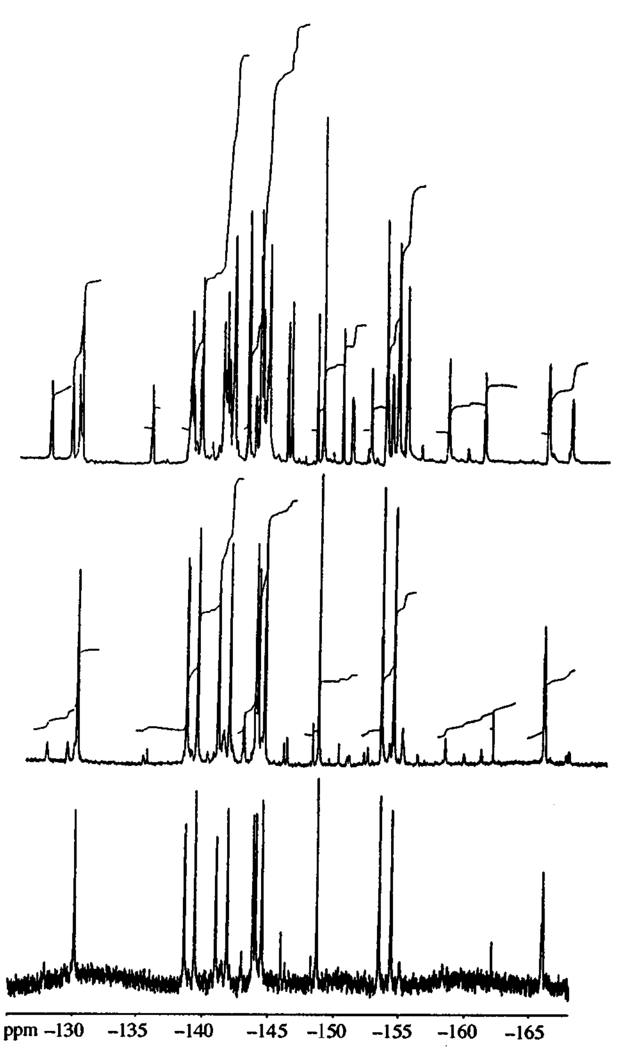


Fig. 10 ^{19}F NMR spectrum of $C_{60}F_{36}$ taken initially (lower spectrum) and after intervals of *ca.* 4 and 12 weeks

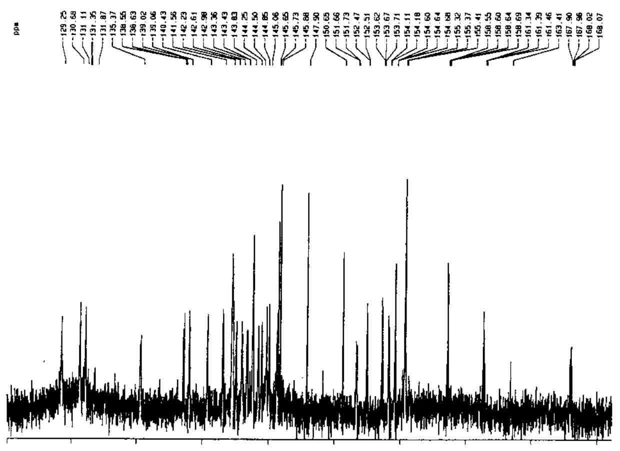
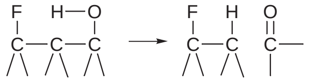


Fig. 11 ^{19}F NMR spectrum of HPLC-separated $C_{60}F_{34}O$

Our results provide confirmation of the facile replacement of fluorine in fluorofullerenes by nucleophiles,[1] in this case hydroxy groups. In the presence of a Lewis acid catalyst, replacement of fluorine by aryl nucleophiles is now known to occur *via* a direct substitution which must involve, albeit unexpectedly, formation of a cage carbocation.[12] However, in the absence of catalyst, as in the present reactions, the addition–elimination mechanism that we proposed earlier[1] may apply. Nucleophilic substitution was further demonstrated by adding a sodium carbonate solution to a sample of $C_{60}F_{36}$ in toluene and heating under reflux for a few minutes. The IR spectrum of the residue (neutralised with HCl and evaporated to dryness) showed complete removal of fluorine, the spectrum being typical of that for a fullerenol (broad bands at 3435, 1636, 1402 and 1104 cm^{-1}, *cf.* 3430, 1631, 1385, and 1090,[13] and the product was soluble in dilute HCl, a typical fullerenol property).

The presence of OH groups in the fluorohydroxyfullerenes was further indicated by ^1H NMR spectroscopy of a sample of 1402 amu ($C_{60}F_{35}OH$). This showed a sharp peak at δ 11.0, consistent with the presence of an OH group (especially in a strongly electron-withdrawing environment); there was also a broad band centred at δ 5.85, also indicative of an OH group (or groups). The occurrence of some tautomerism, driven by strain-relief (Scheme 2), could account for the appearance of carbonyl groups in the IR of some hydroxides. Loss of HF could then proceed *via* a *cis* β-elimination, but again would lead to a cage-opened product.



Scheme 2 Possible tautomerism in hydroxyfullerenes

In conclusion, our results show that the sequence of replacement of F by OH and subsequent elimination of HF is now well defined, and that separation of the products is possible using HPLC. With more refinement of this process it should be possible in due course to obtain substantial quantities of a range of fluorinated fullerene derivatives for definitive structural characterisation.

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