General and Inorganic Chemistry

Progress in fullerene fluorination

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Fluorofullerenes hold the promise of being useful synthetic intermediates, because of the ease with which they undergo nucleophilic substitution. However, the progress in this field has been hampered by the difficulty in controlling fluorination for the preparation of fluorofullerenes of either low, or specific fluorine content. In this paper, previous work is described together with the latest developments involving the use of metal fluorides as fluorinating species. The availability of specific fluorofullerenes has made it possible to make the first detailed studies of the nucleophilic substitution reactions.

Key words: fluorofullerenes, nucleophilic substitution; fluorination of fullerenes, metal fluorides; fullerene hydroxides; fullerene oxides.

Fluorinated fullerenes as lubricants

The paper reporting the correct interpretation of the 720 amu peak in the mass spectrum of laser-vaporized carbon[1] contained the speculation that fully fluorinated [60]fullerene might be a potent lubricant. However, this conjecture did not take account of the rigidity of the fullerene cage, a consequence of which is that there is very little possibility of C—C bond twisting[2] to relieve the eclipsing strain, which, by contrast, is responsible for the high stability of Teflon. The eclipsing strain is calculated therefore to result in lengthening of the C—F bond to 1.672 Å[3] and its 15% weakening compared to the C—F bond in CF_4.[4] Thus it is very difficult to fully fluorinate [60]fullerene, and the mass spectra of the products from a number of studies involving fluorination of C_{60} by fluorine gas have a maximum intensity around $C_{60}F_{46}$—$C_{60}F_{48}$.[5—10] Thereafter the yields fall off dramatically with increasing fluorine content with only small traces of $C_{60}F_{60}$ being evident.[11] Fluorination of C_{60} under more drastic conditions, for example, by fluorine with UV irradiation[7] or by krypton difluoride in HF[12]* yields species up to $C_{60}F_{78}$ indicating that the cage ruptures. It is clear that the goal of obtaining a stable fully fluorinated fullerene cage will not be realized at present. This problem is compounded by the chemical reactivity of fluorofullerenes, which is considered in the next section. However, other highly fluorinated fullerenes of different structure (fluoroalkylfullerenes) can be produced, and their potential has yet to be fully explored.

Fluorofullerenes as synthons: nucleophilic substitution

Though the fluorofullerenes proved to be disappointing as potential lubricants, they may prove to be useful synthons, because of their relatively high solubility, and the ease with which they undergo nucleophilic substitu-

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* The KrF_2/HF fluorination procedure was developed at the I. V. Kurchatov State Scientific Center of the Russian Federation (Moscow).

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tion. This latter feature was discovered accidentally as a result of ^{19}F NMR investigation of the fluorinated fullerene dissolved in either acetone or THF. These solutions showed that a sharp single line around −151 ppm, indicative of a highly symmetrical species (such as $C_{60}F_6$, $C_{60}F_{20}$, $C_{60}F_{60}$, *etc.*),[13] was superimposed upon a broad band between −135 and −175 ppm due to the mixture of fluorinated fullerenes. The observation has subsequently been confirmed by other authors.[11] A second single line was also observed around −190 ppm attributed to HF, thought initially to have arisen as a by-product in the fluorination process. If the solutions were allowed to remain in the NMR tube, a further line developed at around −123 ppm, indicating that it was due to NaF arising from reaction of the HF with sodium ions in the glass of the NMR tube. To confirm this, a spectrum of NaF was needed, but none of this material was available immediately in the laboratory. I therefore added sodium carbonate to the NMR solution, hoping to convert the HF to NaF and to my surprise, the broad band in the ^{19}F NMR spectrum disappeared as well as that due to HF (and the peak at −123 ppm was intensified). This disappearance evidently was due to very rapid nucleophilic substitution, which contrasts with the high stability of alkyl fluorides toward nucleophiles, and is indicative of the very high electron-withdrawing capability of the fullerene cage.

The question then arose as to why solid samples of fluorofullerenes were reasonably stable in (moist) air. It seemed likely that this was due to the hydrophobic nature of the fluorofullerenes. Thus a suspension of fluorofullerene in water showed no visible sign of reaction, but when THF was added as cosolvent, an immediate and exothermic reaction took place, and substantial quantities of HF were produced. This explained the origin of the HF noted above, *i.e.*, it was produced by reaction with traces of water in the THF.[14] It also explained why the mass spectrum of fluorinated fullerene under FAB (fast atom bombardment) conditions using *m*-nitrobenzylamine as the matrix showed masses considerably in excess of that which would be possible even for $C_{60}F_{60}$.[13] This matrix is a nucleophile and replaces some of the F atoms producing compounds with substantially larger masses.[14] The ease of nucleophilic substitution also accounts, in part at least, for the presence of oxygenated species in the products of fullerene fluorination.[10,15] Traces of water or other oxygenated solvents occluded in the fullerene will react with the fluorinated material. There is also the possibility that oxygen, which is known to be trapped by the fullerene lattice,[16] forms epoxides in a process which may be enhanced by the radical conditions that are involved in the fluorination by the fluorine gas.

The utilization of the nucleophilic reactivity of fluorofullerenes would seem to be best if fullerenes of (a) specific, and (b) low fluorine content are prepared. However, early studies indicated the difficulty associated with this goal, because complex mixtures of fullerenes fluorinated to various (and high) levels of fluorine incorporation are normally obtained. The availability of so many reaction sites in, *e.g.*, [60]fullerene means that this problem is an order of magnitude greater than that, say, encountered in derivatizing benzene by substitution. The customary way of overcoming such difficulties is either to use a deficiency of reagent, or to use a very dilute solution of the fullerene. Neither of these strategies works with fullerene for three reasons.

(1) Once the addition has taken place the remaining double bonds in the corresponding hexagon become more localized, thereby facilitating further addition.

(2) The molecules pack together so well that fluorine is unable to penetrate the fullerene lattice. Consequently, the outer layer of molecules becomes highly fluorinated before the inner ones are even touched. Thus if [60]fullerene is exposed to dilute fluorine at room temperature for a day or so, the product consists of highly fluorinated fullerene, and completely unchanged material.[10] The packing is much better in pure [60]fullerene than in a mixture of [60]- and [70]fullerenes, which accounts for the more rapid fluorination of the latter[5] compared to the former.[13] I likewise attributed the more rapid fluorination of [70]fullerene compared to [60]fullerene* to the poorer packing in the former compared to the latter.[17] Similar conclusions have also been reached by other researchers.[18]

(3) No solvent that is resistant to fluorination will dissolve fullerene.

Nevertheless, substantial progress has been made toward the goals of preparing specifically fluorinated fullerenes and those of lower content of fluorine, as described below.

Fluorofullerene $C_{60}F_{48}$

A typical mass spectrum of the product obtained by fluorinating [60]fullerene with fluorine gas at 70 °C is shown in Fig. 1. Clearly, a wide range of fluorinated fullerenes are obtained, and this is indicated also by the IR spectrum which shows a broad band centered around 1150 cm^{-1} (Fig. 2, *a*). If, however, the fluorination is carried out in a two-step process at 275 °C in the presence of NaF, then a pure white product is obtained, the mass spectrum of which indicated it to be $C_{60}F_{48}$. This work thus was a significant step forward, and moreover, the ^{19}F NMR spectrum (Fig. 3, *a*) gave just eight sharp lines. Nine distinct structures (excluding enantiomers) could give such a pattern,[19] but from connectivities established by a 2D(COSY) NMR spectrum, only the structure shown in Fig. 4 (which also shows the assignment of the fluorine atoms to signals shown in Fig. 3, *a*) is consistent with the spectrum observed. Nevertheless some couplings were missing,

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* A. Brisdon, J. H. Holloway, E. G. Hope, and R. Taylor, unpublished results.

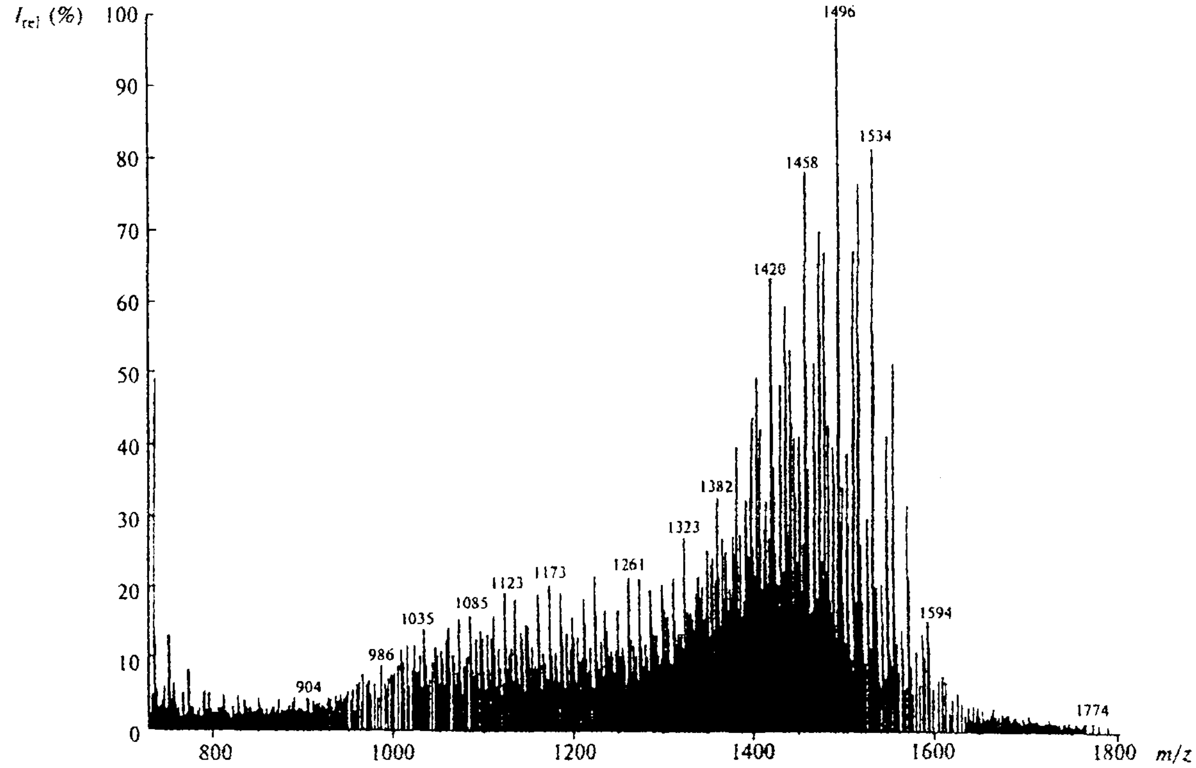

Fig. 1. Mass spectrum of the product of fluorinating [60]fullerene with F_2 gas at 70 °C.

causing some concern about the structure.[12] However, an improved method of formation has more recently been found; this method included monitoring with mass spectrometry the extent of fluorine gas fluorination as a function of the reaction temperature.[20] Thus one-step fluorination at 315 °C was found to produce pure $C_{60}F_{48}$. The ^{19}F NMR spectrum of this sample (Fig. 3, *b*) duplicates quite remarkably the earlier spectrum; 2D (COSY) NMR analysis revealed some of the connectivities missing in the original analysis, and these are shown in Fig. 3. The IR spectrum for this material shows fine structure (Fig. 2, *b*).

It should be noted that the structure shown in Fig. 4 is chiral and thus each half of the molecule which is bisected by the plane orthogonal to the C_3 axis may be either *R* or *S*. This leads to three diastereoisomers (*RR*, *SS*, and *RS*) for $C_{60}F_{48}$ of which the two enantiomeric pairs are symmetrical and give rise to the observed NMR spectrum. There is insufficient symmetry* in the *meso* form to give peaks of sufficient intensity for analysis; they are likely to be responsible for the identical background peaks observed in both spectra (see Figs. 3, *a*, *b*).

In early studies,* attempts had been made to use ^{13}C NMR spectroscopy to analyze fluorofullerenes, but unfortunately, this work gave just broad featureless spectra, attributed to the inability to decouple from fluorine. Very recently, the solid-state ^{13}C NMR spectrum (magic angle spinning) of $C_{60}F_{48}$ has been obtained,** and this shows just two equal intensity peaks in the sp^2-carbon region (~143 and 147 ppm), as required by the structure (and also by the eight plausible isomers[19]). Such spectra are complicated by fluorine coupling, but will become of increasing value as fluorine-decoupling facilities become more widely available. Eight pairs of lines are also evident in the sp^3 region due to the eight unique C atoms which are coupled to the attached F atoms; the coupling constants are about 230 Hz in each case. All of the lines are broadened due to the long-range coupling with nearby fluorines.

The strong electron-withdrawing capacity of $C_{60}F_{48}$ means that it readily participates in charge transfer. This is readily seen, for example, on dissolving $C_{60}F_{48}$ in toluene, whence a bright-red solution is immediately obtained. Conversely, a solution in hexafluorobenzene is colorless, while a benzene solution is yellow, and in general the bathochromic shift parallels the electron-donating ability of the substituents in the aromatic ring.[20]

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* The symmetry of the chiral (D_3) and achiral (S_6) forms of this isomer of $C_{60}F_{48}$ indicates that in both cases, the molecules contain eight non-equivalent groups of F atoms (six fluorines in each group), and, hence, it cannot account for the low intensity of signals in the NMR spectrum of the *meso*-form. (*Note of the scientific editor.*)

* R. Taylor, J. H. Holloway, and E. G. Hope, unpublished results.

** V. I. Privalov, unpublished results.

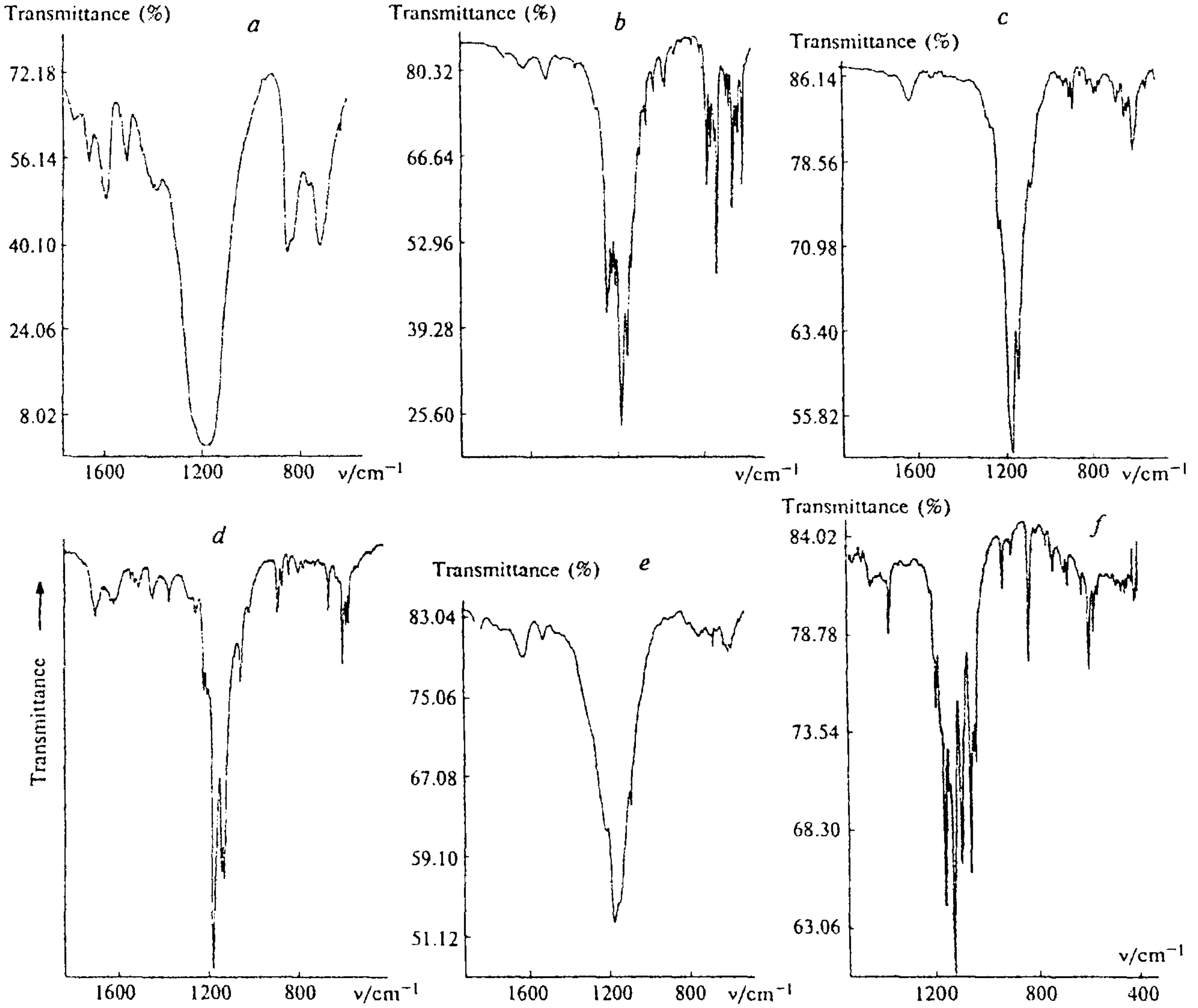

Fig. 2. IR spectra of (*a*) the material giving the mass spectrum shown in Fig. 1; (*b*) $C_{60}F_{48}$; (*c*) $C_{60}F_{36}$ (C_3 isomer); (*d*) $C_{60}F_{36}$ (*T* isomer); (*e*) $C_{70}F_{36/38/40}$; (*f*) $C_{60}F_{18}$.

Bright-red needles are deposited from the toluene solution, but single crystal X-ray diffraction analysis is impossible, because the crystals comprised a mixture of diastereomers. On standing, these crystals slowly become colorless as the toluene evaporates.

The structure of $C_{60}F_{48}$ raises significant questions concerning the method of its formation. Thus is the structure obtained simply by stepwise addition of fluorine, with passage through intermediate structures or is rearrangement involved at a late stage whereby a kinetically produced product converts to a thermodynamically more stable one? Some clue to this may be provided by elucidation of the structures of intermediate products. The first indication that such may exist came as a result of accidental addition of methanol to fluorinated [60]fullerene during mass spectrometry studies. This produced a considerable increase in the number of oxygen atoms attached to the fullerene cage (see below), and it was noticeable that the peaks due to $C_{60}F_{36}O$, $C_{60}F_{18}O$, and $C_{60}F_{18}O_2$ were of higher intensities than other peaks.[10,15] This provided the first indication that fluorination paralleled hydrogenation, because the comparable $C_{60}H_{36}$ and $C_{60}H_{18}$ are dominant species in hydrogenation of [60]fullerene.[21] Similar peaks in the 18/36 F region (especially of the monooxides) were also evident from the work of Chowdhury *et al.*[8]

The goal therefore was to try to make these new species and the major breakthrough came through the introduction by Boltanina *et al.*[22] of fluorination of fullerenes by metal fluorides.

Fluorination with metal fluorides

The key to the success of this method is twofold. First, by carrying out exploratory experiments using a Knudsen cell within a mass spectrometer and monitor-

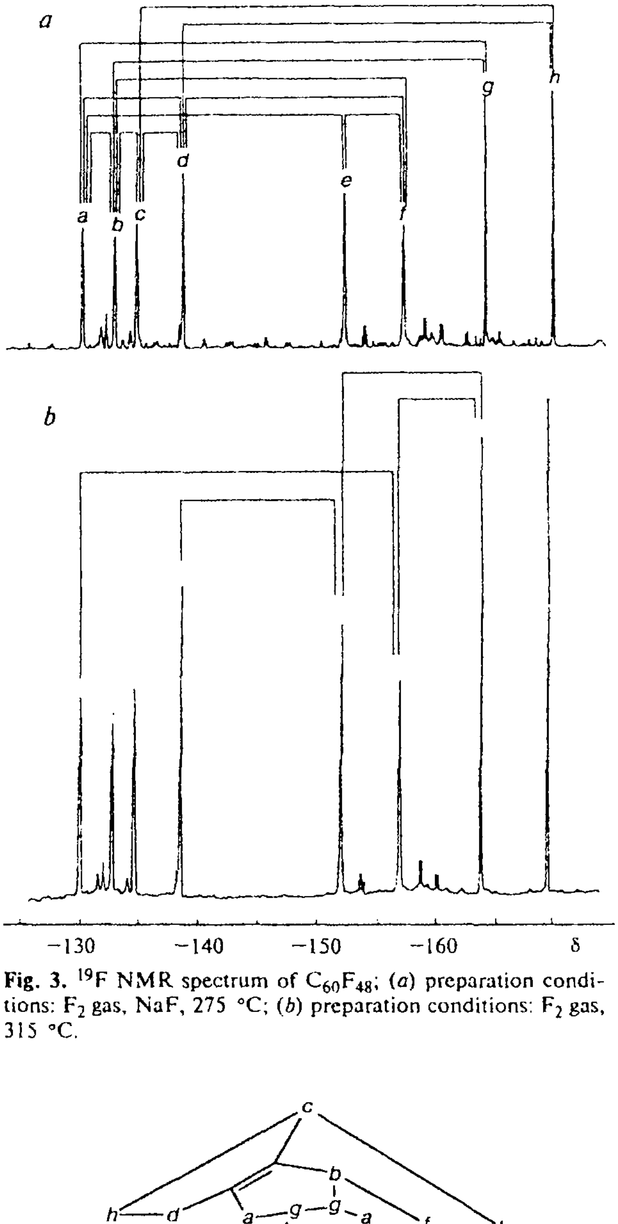

Fig. 3. ^{19}F NMR spectrum of $C_{60}F_{48}$; (*a*) preparation conditions: F_2 gas, NaF, 275 °C; (*b*) preparation conditions: F_2 gas, 315 °C.

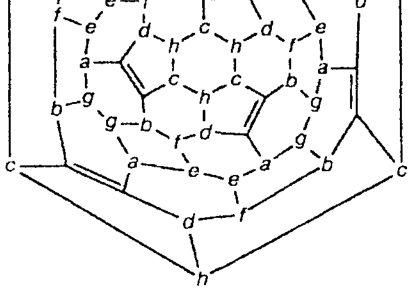

Fig. 4. Schlegel diagram of $C_{60}F_{48}$.

ing the products according to variations in temperature, the optimum conditions for macroscopic bench-scale preparation can be found. Second, the difficulties that are associated with fluorination by fluorine gas, namely, excessive fluorination of the fullerene, are avoided, because of the volatility of the fluorofullerenes compared to the parent molecules. Since the reactions are carried out under vacuum, the fluorofullerenes are pumped away from the metal fluoride and are condensed in a cold zone, and no further fluorination can take place. Each metal fluoride has a different temperature at which it yields its fluorine, and because the volatility of the fluorofullerenes increases with fluorine content, it then becomes a matter only of using the appropriate metal fluoride and temperature to obtain a particular derivative. The potency of the fluorides as fullerene fluorinating species was shown to decrease in the sequence $CoF_3 > MnF_3 > FeF_3$.[22]

Fluorofullerene $C_{60}F_{36}$

Reaction of [60]fullerene with MnF_3 in a Knudsen cell showed that $C_{60}F_{36}$ is produced as the main product. Macroscopic production was achieved by heating the two reagents to 330 °C for 24 h under vacuum (0.1 mbar) in a tube leading to a cold zone; this yielded a pale yellow product which gave approximately 30 lines in a ^{19}F NMR spectrum. Sublimation of the product gave a white material and a less volatile yellow residue. The ^{19}F NMR spectrum of the white material (Fig. 5, *a*), now reduced to only 12 lines, and 2D (COSY) NMR analysis indicated the presence of four main components, one of which gave a 1 : 1 : 1 peak intensity, attributed provisionally to the *T* isomer, predicted by calculations to be of high stability.[22]

However, this interpretation created a problem in that the remaining peaks could not be assigned to any isomer of known symmetry or high predicted stability. Moreover, further work involving HPLC purification of this product showed that all the twelve peaks had identical intensities, which did not vary with sample or treatment. Clearly this component is *one* isomer, and calculations indicate that it has C_3 symmetry.[23] Further HPLC work resulted in the isolation of a second, more polar (and minor) isomer, which gives the 1 : 1 : 1 ^{19}F NMR peak pattern (Fig. 5, *b*) required of the *T* isomer. This material is that producing peaks *E* in the preliminary publication.[22] Both isomers contain the known $C_{60}F_{18}$ motif (see below), which further supports their characterization. The mass and IR spectra of the major and minor components are given in Figs. 6, *a*, *b* and 2, *c*, *d*, respectively.

A significant (and very reproducible) feature of the mass spectrum of the crude material is the fragmentation pattern showing peaks (amu) 1385 ($C_{60}F_{35}$, F loss), 1382 ($C_{60}F_{34}O$, arising either by F_2 loss from $C_{60}F_{36}O$ traces, or by HF loss from $C_{60}F_{35}OH$ produced *via* nucleophilic substitution), 1366 ($C_{60}F_{34}$, F_2 loss) and most notably, peaks at 1335 and 1285 due to loss of CF_3 and a further CF_2. The appearance of these latter two

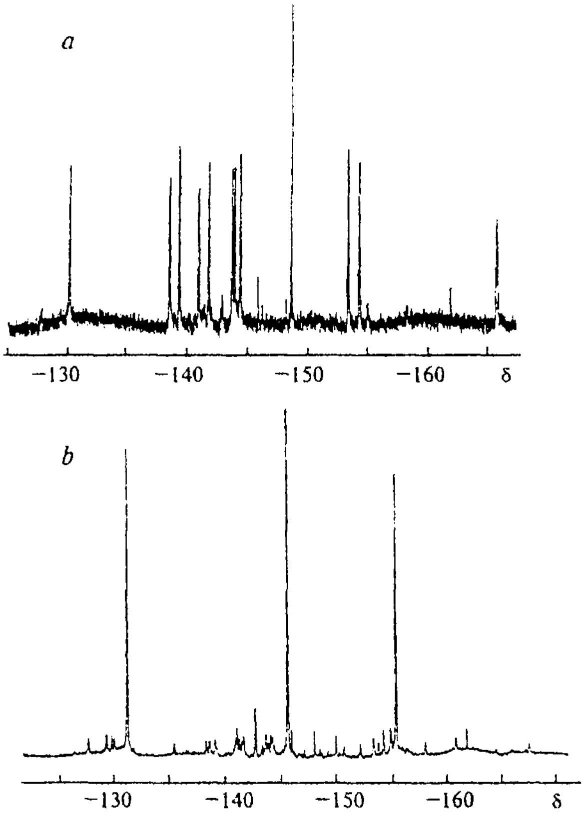

Fig. 5. ^{19}F NMR spectra of $C_{60}F_{36}$: (*a*) major C_3 isomer; (*b*) minor *T* isomer.

peaks has been a constant feature of mass spectra of fluorofullerenes[5,15].* It might be presumed that the peak due to the loss of CF_3 means that $C_{60}F_{36}$ has an open cage. However, if this were so there would need to be *two* such groups present and a peak in the mass spectrum at 1266 due to loss of both groups would be evident, but this is not the case. Moreover, no CF_3 groups are detectable by ^{19}F NMR. The fragmentation pattern differs markedly from that for $C_{60}F_{18}$, which is described below.

Fluorofullerenes $C_{70}F_{36/38/40}$

Fluorination of [70]fullerene with MnF_3 under the conditions used for the preparation of $C_{60}F_{36}$ produced a mixture of $C_{70}F_{36}$, $C_{70}F_{38}$, and $C_{70}F_{40}$, with the middle product being the most abundant, as shown by the mass spectrum (Fig. 7). This parallels precisely the observation in the hydrogenation of [70]fullerene,[24] providing strong evidence that the hydrogenated and fluorinated compounds are isostructural. The ^{19}F NMR spectrum consists of very many lines, which it has, as yet, not been possible to resolve. Likewise the IR spectrum showed a fairly broad band in the C—F stretching region (Fig. 2, *e*).[22] In due course it may become possible to separate the components by HPLC and thereby establish the actual structure for $C_{70}F_{36}$, various possibilities for which have been proposed by analogy with $C_{70}H_{36}$.[21,25] On a Cosmosil Buckyprep column (toluene as the eluent) the $C_{70}F_{36-40}$ mixture elutes slightly faster than $C_{60}F_{36}$; this parallels the behavior of the corresponding hydrofullerenes.

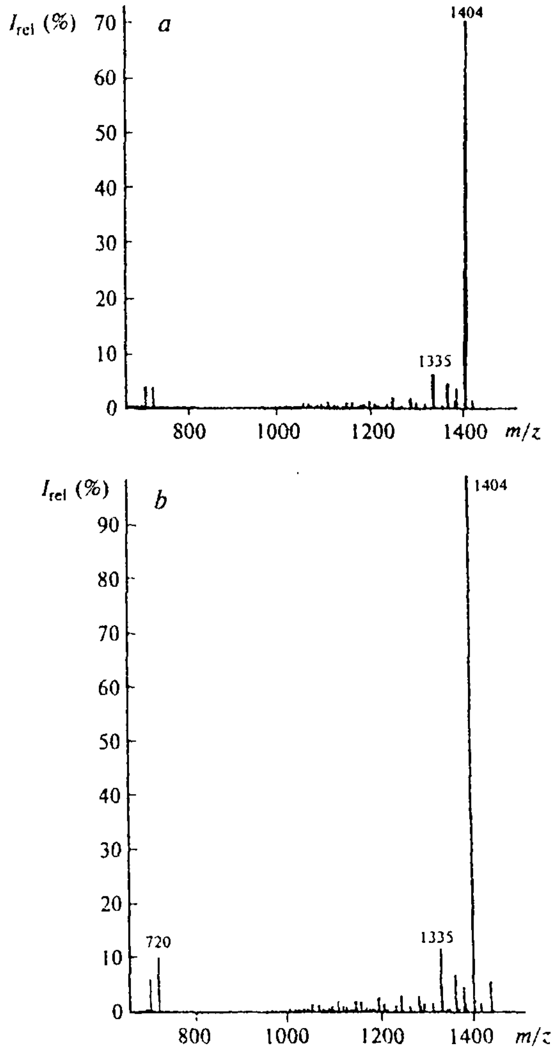

Fig. 6. Mass spectra of $C_{60}F_{36}$: (*a*) major C_3 isomer; (*b*) minor *T* isomer.

Fluorofullerene $C_{60}F_{18}$

HPLC separation (Cosmosil Buckyprep, toluene as the eluent) of the products obtained from fluorination of [60]fullerene by MnF_3 gives a small amount of a compound eluting after $C_{60}F_{36}$. This proved to be $C_{60}F_{18}$, which has been prepared in a larger quantity by fluorinating [60]fullerene with K_2PtF_6 at 500—600 K for 8 h

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* A. Brisdon, J. H. Holloway, E. G. Hope, and R. Taylor, unpublished results.

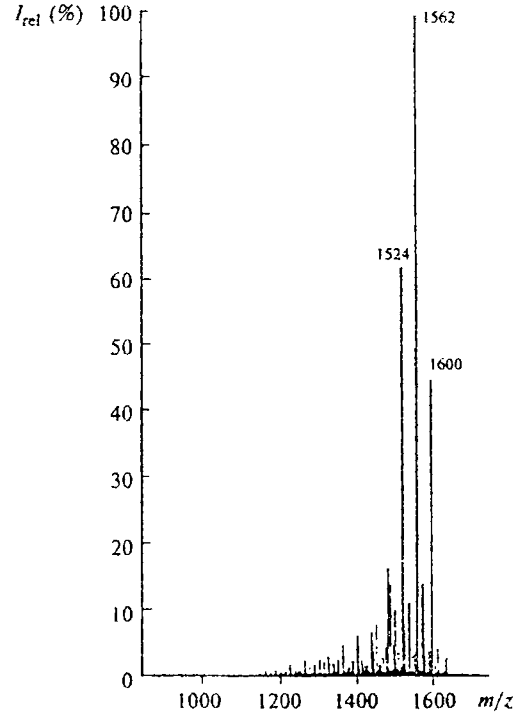


Fig. 7. Mass spectrum of the $C_{70}F_{36/38/40}$ mixture.

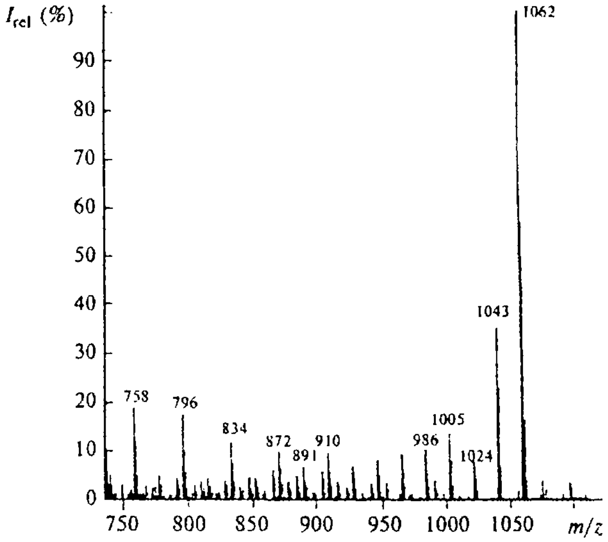


Fig. 8. Mass spectrum of $C_{60}F_{18}$.

in a Knudsen cell incorporated within a mass spectrometer.[26] The product is a yellow-green microcrystalline solid, readily soluble in hexane, toluene, chloroform, and other solvents; it is less volatile and much more polar than $C_{60}F_{36}$. The latter property is a result of the concentration of fluorine at one end of the molecule.

The fragmentation pattern in the mass spectrum (Fig. 8) is quite different from that considered above for $C_{60}F_{36}$. While there is more fragmentation than in the case of $C_{60}F_{36}$, this may be entirely due to the lower volatility of $C_{60}F_{18}$, thereby requiring a higher temperature of the probe. Here there is no loss of CF_3 or CF_2 groups, but instead a regular loss of fluorine down to $C_{60}F_8$, and thereafter the fluorines are lost in pairs.[26]

The ^{19}F NMR spectrum of $C_{60}F_{18}$ consists of four lines in a 1 : 2 : 2 : 1 intensity ratio (Fig. 9), consistent only with a structure with C_{3v} symmetry (Fig. 10),[26] which significantly is isostructural with $C_{60}H_{18}$,[27] and is a substructure of both C_3 and T isomers of $C_{60}F_{36}$. The IR spectrum (Fig. 2, *f*) contains many sharp lines indicative of a single isomer.

This compound is the fluorofullerene of lowest fluorine content that has so far been either made or characterized. Further work is in hand to reduce the fluorine content even lower.[23]

Fluorination of bromo- and chlorofullerenes

An alternative approach has been explored with the objective of obtaining fullerenes of lower fluorine content when fluorinating with either fluorine gas or xenon difluoride.[28] This approach is based on the fact that the bromo- and chlorofullerenes are much less thermally stable than fluorofullerenes. Thus it was anticipated that by fluorinating these derivatives, many of the sites would be unavailable for fluorination, and then the other halogens could subsequently be removed by controlled heating. Fluorination of $C_{60}Cl_{24}$, $C_{60}Cl_6$, $C_{60}Br_{24}$, $C_{60}Br_8$, and $C_{60}Br_6$ was therefore attempted.

Fluorination of $C_{60}Br_6$ (F_2 gas) was unsuccessful in this respect, though evidence for the formation of $C_{60}Br_2O_n$ (n = 2 to 4) was obtained. Fluorobenzene derivatives were also produced, as a result of fluorination of benzene which becomes trapped in the lattice of $C_{60}Br_6$ formed upon bromination of [60]fullerene in benzene.[29] Interestingly, whereas fluorination of benzene is normally explosively fast, it is benign when trapped in the fullerene lattice.

According to EI mass spectroscopy, fluorination of $C_{60}Br_8$ (F_2 gas) affords fluorinated species up to $C_{60}F_{36}$ with, most notably, $C_{60}F_{18}$ and its mono- and dioxide as the most abundant ones (*cf.* Ref. 15). However, heating to remove the Br atoms resulted in decomposition to unidentified components.

Fluorination of $C_{60}Br_{24}$ (F_2 gas) indicated that the overall objective was achieved, because the mass spectrum showed significant peaks up to *ca.* $C_{60}F_{26}$ with only minor ones of higher mass. Preliminary experiments suggested that controlled loss of halogen could be achieved by heating.

Fluorination of either $C_{60}Cl_6$ or $C_{60}Cl_{24}$ with xenon difluoride did not lead to identifiable products, but fluorination of $C_{60}Cl_{24}$ with IF_5 indicated (FAB mass spectrum) that some of the chlorines had been replaced by fluorines, as well as fluorines being added to the cage.

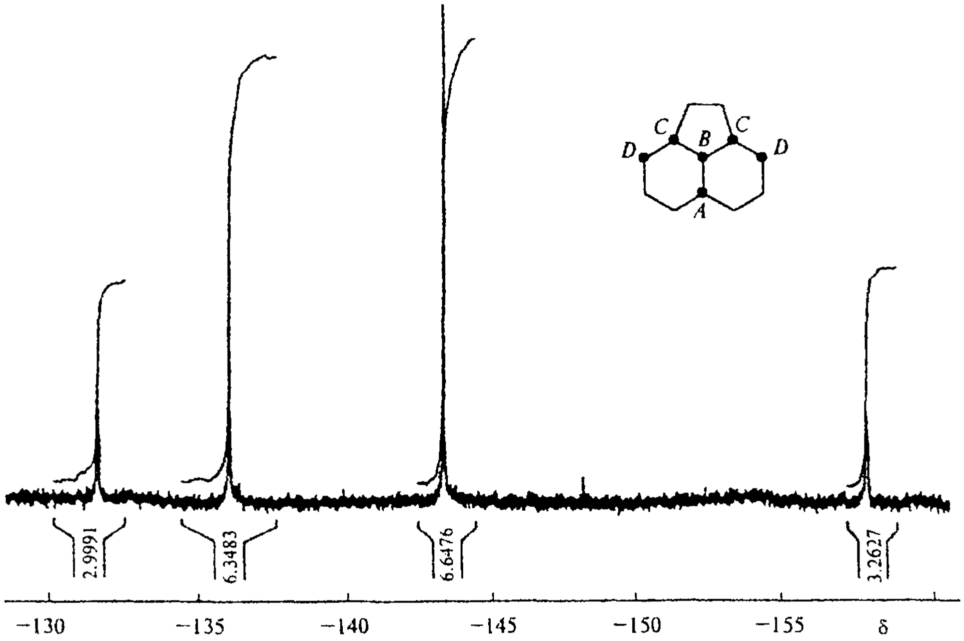


Fig. 9. ^{19}F NMR of $C_{60}F_{18}$.

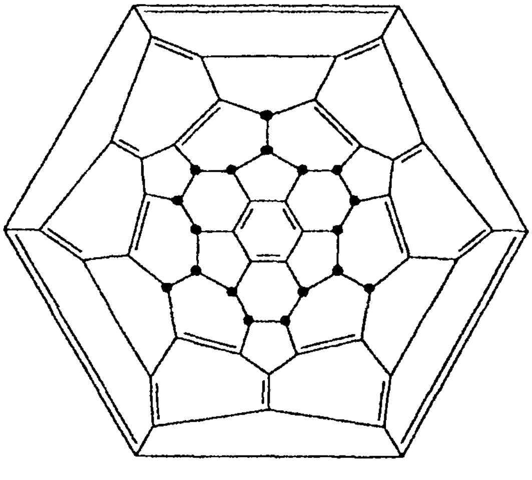
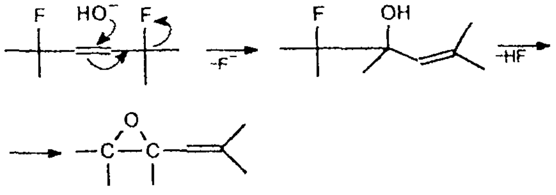


Fig. 10. Schlegel diagram showing the structure of $C_{60}F_{18}$.

Nucleophilic substitution: fullerene oxides

The presence of mono-oxygenated species in the products of fluorinating fullerenes was an early observation.[6] Since the extent of oxide formation varied with the material used for the fluorination vessel, the presence of oxygen (or water) absorbed on the surface was indicated to be at least partly responsible. Later work showed that five[8] and up to eighteen[10,15] O atoms were attached to fluorofullerenes, and a mechanism involving nucleophilic addition of water followed by elimination of HF was proposed (Scheme 1).[15] This process requires that the oxygen is present as an epoxide, so that one O atom replaces two F atoms, and it is interesting that this requirement indicated that up to 58 sites are fluorinated in the original material.[8,15] As noted above, the reaction of fluorinated [60]- and [70]fullerenes with aqueous methanol revealed the formation of derivatives containing as many as eighteen O atoms attached to the cages.

Scheme 1



In the introduction, the rapidity of nucleophilic substitution of fluorofullerenes was indicated. A study of the effects of various nucleophiles revealed a substantial difference in the speed of replacement of the fluorines, according to the known nucleophilicity of the reagents.[14] Thus whereas a weak nucleophile such as sodium acetate produced only 15% fluorine replacement after 550 h, the reaction with sodium methoxide in methanol or diethylamine was very rapid with substantial amounts of the fluorine being replaced within 1 h at room temperature. Thereafter, the replacement slows down, due probably to both increased steric hindrance arising from the presence of the bulkier nucleophiles on the cage, and the decreased electron-withdrawing effect of the system as the fluorines are replaced. Reactions with various organolithium reagents or Grignard reagents are also very fast.[14]

The availability now of *specific* fluorinated fullerenes marks a significant step forward in the ability to study the nucleophilic substitution. Some preliminary work involving reaction with water[23] is described here. Progress has also been enhanced by use of Cosmosil columns which readily separate the oxygenated species from the unreacted material. A regime in which the initial separation is carried out with toluene followed by various toluene—hexane mixtures, and eventually hexane, has proved crucial. It is also possible to take advantage of the fact that the oxides are more soluble in hexane than the fluorinated precursors, thereby facilitating a partial preliminary separation.

Thus, it has been possible to separate and partially characterize the following species:

(1) $C_{60}F_{35}OH$ (1402 amu) due to replacement of one fluorine in $C_{60}F_{36}$ by OH;

(2) $C_{60}F_{34}(OH)_2$ (1400 amu) due to replacement of two fluorines in $C_{60}F_{36}$ by OH;

(3) $C_{60}F_{34}O$ (1382 amu) due to the loss of HF from $C_{60}F_{35}OH$. This species is usually present in $C_{60}F_{36}$ (unless freshly prepared and purified);

(4) $C_{60}F_{33}(OH)O$ (1380 amu) due to replacement of one fluorine in $C_{60}F_{34}O$ by OH;

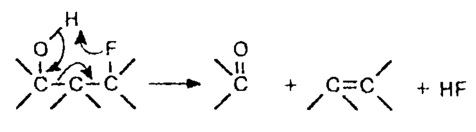
(5) $C_{60}F_{32}O_2$ (1360 amu) due to loss either of HF from $C_{60}F_{33}(OH)O$ or two HF molecules from $C_{60}F_{34}(OH)_2$;

(6) $C_{60}F_{33}(OH)_3$ (1398 amu) due to replacement of three fluorines in $C_{60}F_{36}$ by OH groups.

Various other ions are detected by mass spectrometry due, it is believed, to loss of F_2 from the above compounds, for example, $C_{60}F_{31}(OH)_3$ (1376 amu), $C_{60}F_{32}O$ (1344 amu), and $C_{60}F_{29}(OH)O$ (1304 amu). Also detected is $C_{60}F_{36}O$ (1420 amu) which could in principle be derived from traces of $C_{60}F_{38}$ (1442 amu) but these species are not seen together which makes this possibility less likely.

Of particular interest is the loss of CO from $C_{60}F_{32}O_2$ giving $C_{59}F_{32}O$ (1332 amu). Loss of CO from an epoxide has been observed previously in the mass spectrum of the epoxide derivative of the cyclopentadiene adduct with [60]fullerene.[30] One cannot dismiss entirely the possibility that the epoxides are in fact cage-opened ketones. The IR spectra of $C_{60}F_{34}O$, run as a solution in either toluene or chloroform, showed bands in the 1717—1720 cm^{-1} region, characteristic of C=O. A conceivable mechanism for the formation of ketonic $C_{60}F_{34}O$ could be *via* acid-catalyzed elimination of water from diol $C_{60}F_{34}(OH)_2$; a related mechanism has been proposed to account for the detection by IR of carbonyl from fullerenols in the presence of acid.[31] An alternative mechanism that could produce a carbonyl group from a single loss of HF from $C_{60}F_{35}OH$ is a six-center elimination (Scheme 2), and this would give a cage-opened product.

Scheme 2



Further work will be needed to determine the structure of oxygenated fullerenes. It is possible that both epoxide and ketonic structures are present. Notably, substantial quantities of (more polar) $C_{60}F_{18}O$ are produced in the preparation of $C_{60}F_{18}$,[23] and it is not certain that this is obtained from a $C_{60}F_{20}$ precursor *via* nucleophilic substitution.

* * *

I first met Mark Vol'pin in September 1990, just four weeks after I had isolated (on August 23; from soot prepared by Jonathan Hare, Harry Kroto's research student) the very first pure samples of C_{60} and C_{70} ever obtained, discovered their colors, and obtained the definitive structural-characterizing ^{13}C NMR spectra.[32] I took these samples with me on a scheduled visit to the A. N. Nesmeyanov Institute of Organoelement Compounds (where I also gave the first fullerene lecture in Russia), and they elicited great interest not only from Prof. Vol'pin but also from other researchers at the Institute (Dr. E. Gal'pern and Prof. D. Bochvar), who published the definitive MO calculations for these compounds back in 1973.[33] Prof. Vol'pin's interest in intercalated carbon made him particularly aware of the significance of the discovery, and I took back to Sussex some of this carbon, which we had hoped could be examined in an arc-discharge apparatus modified to use carbon powder (and thereby perhaps prepare endohedral fullerenes). Alas, we were unable to proceed with the construction of the required apparatus. Prof. Vol'pin maintained a continuing interest in fullerenes (our last meeting was at the International Workshop on Fullerenes and Atomic Clusters (IWFAC) in 1995), and it is a fitting tribute that fullerene research continues at the A. N. Nesmeyanov Institute of Organoelement Compounds.

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