Formation of $C_{60}F_{48}$ and fluorides of higher fullerenes

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The effect of contact times and temperatures on fluorination of [60]fullerene by fluorine gas has been analysed by Knudsen cell mass spectrometry. The main product ranges from $C_{60}F_{38/40}$ (4 h, 70 °C) to $C_{60}F_{48}$ (16 h, 315 °C), showing that some control of product according to conditions is possible. The IR spectrum for $C_{60}F_{48}$ (which is white, and crystallises from chloroform or dichloromethane as large colourless prisms) shows fine structure with sharp bands at 1238, 1215, 1199, 1170, 1142, 1126, 771, 754, 724, 650 and 603 cm^{-1}. The ^{19}F NMR spectrum ($CDCl_3$) duplicates precisely that reported in the literature, but couplings not previously observed are evident by 2D (COSY) analysis, thereby confirming further the structure. Fluorination of a sample containing [70]- and higher fullerenes gives rise to $C_{70}F_{44-56}$, $C_{78}F_{54-60}$ and $C_{84}F_{56-62}$. $C_{60}F_{48}$ is stable towards chlorinated hydrocarbons, but is rapidly degraded by THF, ether and acetone. With benzene and alkylbenzenes, coloured charge transfer-complexes are formed which exhibit a bathochromic shift with increased alkyl substitution of the benzene ring; from toluene solution thick, red needles may be obtained and these slowly become colourless on standing as toluene is lost from the lattice.

Introduction

There have been many studies of fluorination of fullerenes[1] but thus far only two derivatives have been isolated and characterised. $C_{60}F_{48}$ has been prepared by fluorination of [60]fullerene with a mixture of fluorine and sodium fluoride at 250 °C for 20 h, extraction of the product with $CFCl_3$ and further fluorination of the extract at 275 °C for 30 h. The ^{19}F NMR spectrum of the product indicated a single structural isomer (two chiral forms of D_3 symmetry)[2] but some of the anticipated F–F couplings were absent, rendering the structure assignment less secure. $C_{60}F_{36}$ has been prepared by fluorinating [60]fullerene with MnF_3 (330 °C, 24 h, *in vacuo*).[3] The ^{19}F NMR spectrum indicates that it consists of four isomers.[3]

A major problem in fluorination of fullerenes is that fluorine-resistant solvents do not dissolve fullerenes to any appreciable extent. Accordingly, most studies have been carried out using solid fullerene. This however incurs another problem, namely that the very close packing of the fullerene molecules (especially [60]fullerene), renders it difficult for fluorine to penetrate the lattice. This has been strikingly demonstrated by the completely unchanged recovery of a significant amount of [60]fullerene from a solid sample that had been exposed to fluorine gas at 70 °C for four days.[4] This feature also accounts for fluorination of [70]fullerene occurring more rapidly than [60]fullerene (poorer packing) and the fact that impure [60]fullerene fluorinates faster than pure material (compare refs. 5 and 6). We have now carried out (*a*) a systematic analysis of the effect of varying reaction time and temperature on fluorination of [60]fullerene by fluorine gas, in order to ascertain the minimum conditions needed to achieve a given fluorination level, and (*b*) used a mixture of [60]- and higher fullerenes in order to obtain the first data on fluorination of the latter.

Experimental

Prior to fluorination, the [60]fullerene samples were heated for 6 h at 160 °C to remove traces of solvent. Fluorination was carried out with fluorine gas (containing up to 10% of HF and some traces of O_2). The product was weighed after each fluorination and the sample placed in a Knudsen cell contained within a magnetic sector MI-1201 mass spectrometer operated under EI conditions (70 eV). The mass spectrum was recorded, the sample was removed and fluorinated further, under the conditions listed in the footnote to Fig. 1. The spectra and chemical analyses for sample D were identical to those for a further sample, obtained by heating directly for 16 h at 315 °C *i.e.* without the intermediate heating stages. These latter samples were white and chemical analysis indicated the stoichiometric formula $C_{60}F_{48\pm1}$. The IR spectra (below) showed a complete absence of bands due to unreacted [60]fullerene. Fluorination of the mixed fullerene samples was carried out in the same way. $C_{60}F_{48}$ crystallises readily from either chloroform or dichloromethane as large (3–5 mm) colourless prisms, and from toluene as thick, red needles.

Under some conditions, mass loss was recorded, attributed to cage degradation to give fluorocarbons such as CF_4, C_2F_6 and C_3F_8. These were detected in the samples by EI mass spectrometry (VG Autospec, 70 eV) and could arise from entrapment in the fullerene lattice (it is well known that solvents and gases, *e.g.* oxygen are so entrapped)[7] but degradation during mass spectrometry cannot be ruled out. Mass loss increased significantly if fluorination was attempted for increased reaction times. It is possible that cage degradation of the higher fullerenes is more rapid since they are, for example, less stable towards hydrogenation, a much less aggressive reaction.[8]

Results and discussion

Mass spectra

Fig. 1(*a*)–(*d*) show the EI mass spectra for samples (A–D) fluorinated at increasing time and temperature, and the increasing extent of fluorination along this series is apparent. Sample D is evidently $C_{60}F_{48}$ of high purity.

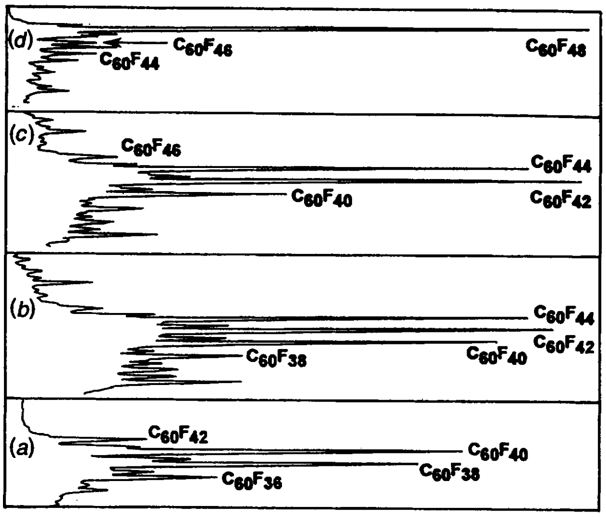

Fig. 1 EI mass spectra for the products (A–D) of fluorination of [60]fullerene under increasingly vigorous consecutive conditions: (*a*) A, 70 °C, 4 h; (*b*) B, a further 5 h at 220 °C; (*c*) C, a further 11 h at 275 °C; (*d*) D, a further 3 h at 315 °C

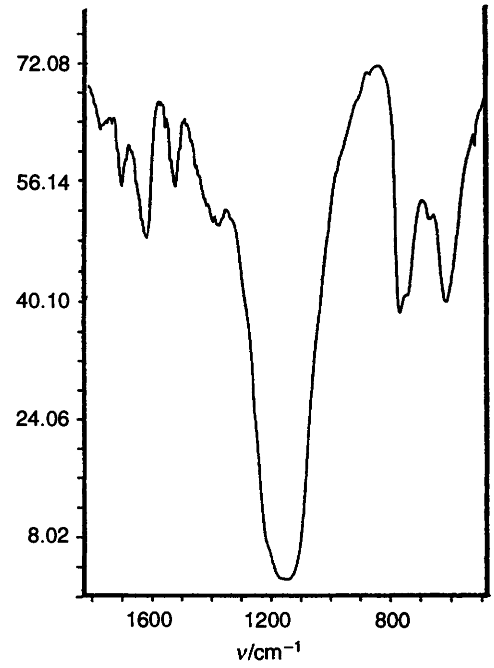

Fig. 2 IR spectrum (KBr) for sample A

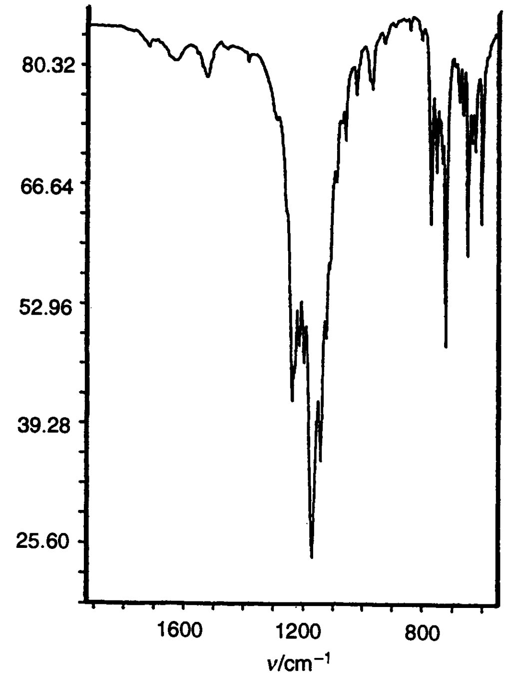

Fig. 3 IR spectrum (KBr) for sample D

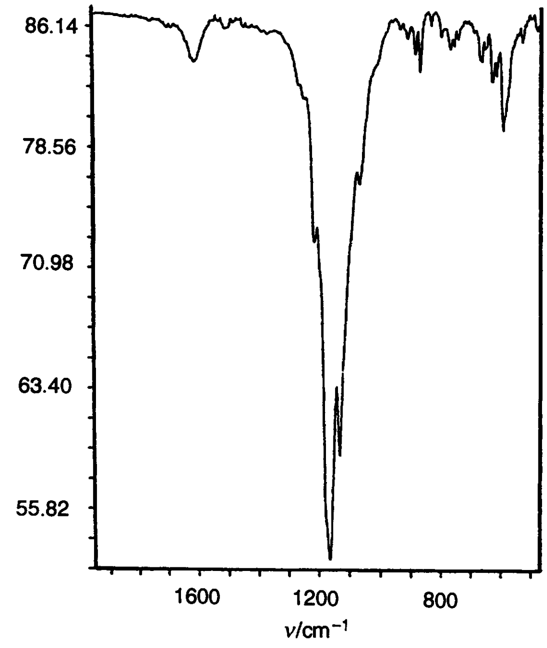

Fig. 4 IR spectrum for $C_{60}F_{36}$

IR spectra

IR spectra for fluorinated [60]fullerene reported previously showed broad bands centred at *ca.* 1148 or 1165 cm^{-1},[5,6] due to a mixture of products being obtained. In the present work (KBr disc), we find increasing sharpness of the spectra as the range of fluorinated products decreases. Fig. 2 shows the spectrum for sample A and Fig. 3 shows the spectrum for sample D. The presence of sharp bands (at 1238, 1215, 1199, 1170, 1142, 1126, 771, 754, 724, 650 and 603 cm^{-1}) is consistent with the presence of a single component. The spectrum may be compared with that (Fig. 4) of the recently isolated[3] $C_{60}F_{36}$ which shows sharp bands at 1160 and 1132 cm^{-1}. These IR spectra now provide a convenient means of assessing the purity and structure of fluorinated [60]fullerene.

Recently, the IR spectrum was calculated for the two lowest energy isomers of $C_{60}F_{48}$, namely the D_3 enantiomers, and the S_6 *meso*-form, using an MNDO-based method.[9] This predicted a main band at *ca.* 1300 cm^{-1} which is considerably higher than the value (*ca.* 1150 cm^{-1}) invariably obtained in fullerene fluorination. However, this discrepancy may aid refinement of subsequent theoretical methods, and in particular the magnitude of the frequency scaling factors[9] needed.

NMR spectra

(*a*) In $CDCl_3$. Fig. 5 shows the Schlegel diagram for $C_{60}F_{48}$ reported previously, the original notation being retained for convenience.[2] Fig. 6(*a*) shows the NMR spectrum reported in that paper (solvent not stated), and this may be compared with our spectrum [$CDCl_3$ as solvent, Fig. 6(*b*)], whence it is evident that the agreement is quite remarkable, even down to fine detail in the background.

In the original analysis all of the 1,2-couplings predicted by the structure (a–e, a–g, b–f, b–g, c–h, d–f, d–h, e–f) were observed. However, of the 1,3 couplings predicted (*a–b*, *a–d*, a–f, *b–c*, b–d, b–e, *c–d*, d–e, e–g, f–g, f–h) only those italicised were detected.[2] We have measured the 2D COSY spectrum for $C_{60}F_{48}$ and find that the couplings a–f, d–e, e–g and f–g are also present (Fig. 7) which lends further support to the proposed structure.

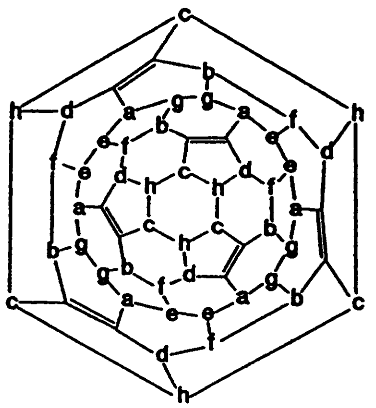

Fig. 5 Schlegel diagram for $C_{60}F_{48}$ with notation as in ref. 2

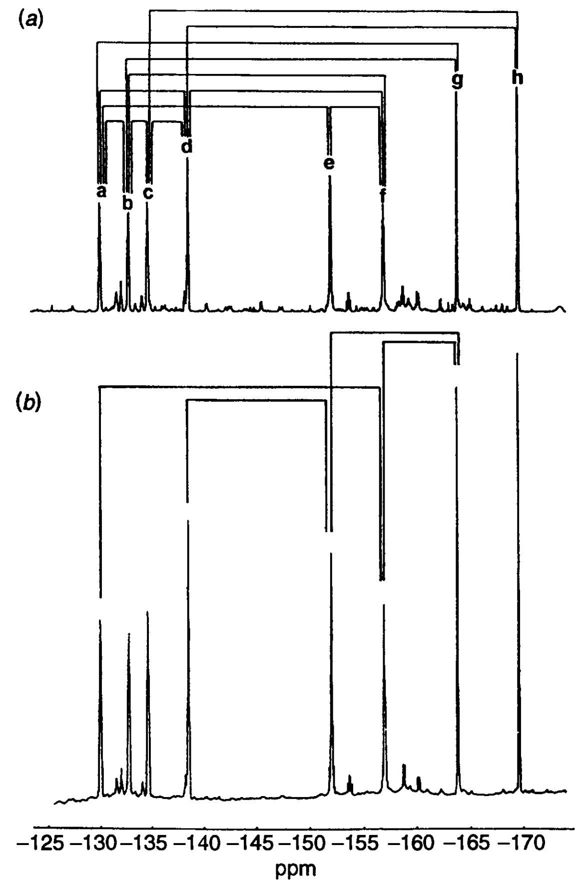

Fig. 6 ^{19}F NMR spectrum for $C_{60}F_{48}$: (*a*) literature[2] spectrum; (*b*) this work ($CDCl_3$). The additional couplings detected in this work are shown in the lower spectrum.

(*b*) In dichloromethane. The ^{19}F NMR spectrum obtained using dichloromethane as solvent, was not significantly different from that obtained using $CDCl_3$.

(*c*) In toluene. A solution of $C_{60}F_{48}$ in toluene is deep red, due to formation of a charge transfer complex (see below), and from this solution red crystals may be obtained. On standing they lose their colour as solvent is lost, and $C_{60}F_{48}$ is regenerated. The ^{19}F NMR spectrum of the red solution is however similar to that obtained using $CDCl_3$, the peaks being shifted downfield by *ca.* 1 ppm.

(*d*) In diethyl ether. If the spectrum of $C_{60}F_{48}$ is run in diethyl ether, then some of the fine structure is lost, and a sharp peak develops at −153.5 ppm, together with a broad one at *ca.* −189 ppm due to HF formation, this latter arising from nucleophilic substitution (*cf.* ref. 10). If water is added to this solution, then all of the original structure is lost and sharp singlets appear at −152.2, −152.3 and −152.4 ppm, with two very minor peaks in between.

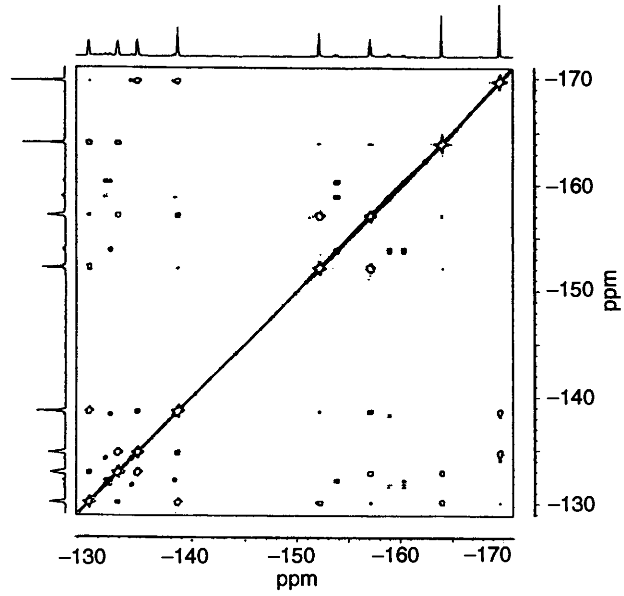

Fig. 7 2D COSY spectrum for $C_{60}F_{48}$

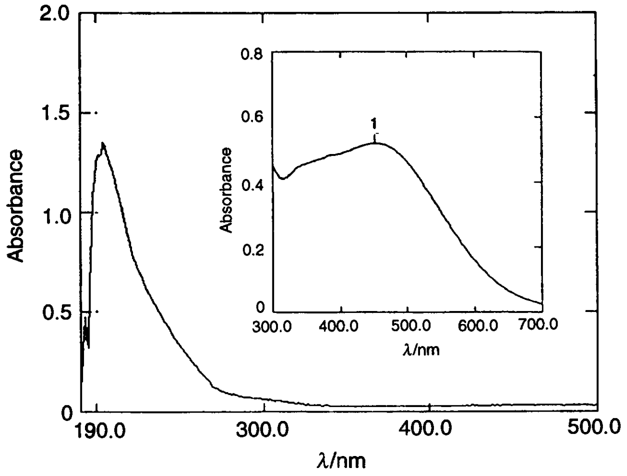

Fig. 8 UV-VIS spectrum for $C_{60}F_{48}$ in hexane; inset shows charge-transfer spectrum in toluene

(*e*) In acetone. Virtually all of the original structure is lost, but no peaks develop apart from the broad peak at *ca.* −189 ppm due to HF formation as above.

(*f*) In THF. All of the original structure is completely lost, and two sharp peaks develop at −154.8 and −155.3 ppm. A THF solution of $C_{60}F_{36}$ exhibits the same behaviour, the original fine structure[3] being lost completely, and a sharp peak develops at −152.4 ppm (together with a small one at −145.6 ppm).

We hope in due course to be able to investigate these degradation reactions in more detail.

UV-VIS spectrum

$C_{60}F_{48}$ is soluble in hexane and gives rise to the spectrum shown in Fig. 8, with $\varepsilon_{max} = 22\,000\ dm^3\ mol^{-1}\ cm^{-1}$ at 204 nm.

Charge-transfer spectra

Solutions of $C_{60}F_{48}$ in some aromatic hydrocarbons are coloured due to the formation of charge-transfer complexes, and the absorption maxima show a bathochromic shift with increasing electron supply in the aromatic ring. Thus a solution in hexafluorobenzene is colourless, in benzene it is yellow ($\varepsilon_{max} = 1530\ dm^3\ mol^{-1}\ cm^{-1}$ at 428 nm), in toluene deep

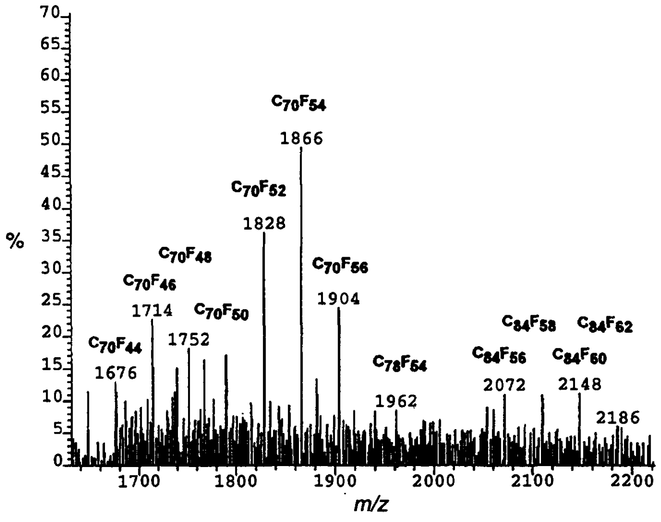

Fig. 9 Mass spectrum of fluorinated [60]fullerene (containing small amounts of [70]- and higher fullerenes) after heating with methanol

orange–red ($\varepsilon_{max} = 7100$ dm^3 mol^{-1} cm^{-1} at 454 nm, inset of Fig. 8), and magenta in mesitylene (ε_{max} at 538 nm); the extinction coefficient could not be measured accurately in mesitylene because of low solubility. The solution in mesitylene lost colour on standing for a few days in air, due, we presume, to a slow reaction with impurities present; the other solutions showed no spectral changes. The charge-transfer complex in toluene appears to be fairly resistent to hydrolysis, for, on addition of water, the colour was lost only over a period of many weeks.

Fluorinated [70]- and higher fullerenes

Previously, [70]fullerene has been variously reported to produce $C_{70}F_{44}$,[11] $C_{70}F_{46}$,[6] $C_{70}F_{48}$[4] and $C_{70}F_{54}$[12] as the most highly fluorinated species. In the present work we find a new upper level of fluorination in the detection of $C_{70}F_{56}$ (Fig. 9); $C_{70}F_{54}$ was usually the most abundant species. It may be significant that $C_{60}F_{48}$ and $C_{70}F_{56}$ each represent 80% site occupancy, and this probably represents the maximum level that can be achieved before steric crowding begins seriously and adversely to affect stability. In the case of hydrogenation, this level is reached at a lower level of site occupancy, because of the lower strength of the C–H bond compared to the C–F bond.

There have been no previous reports of the fluorination of higher fullerenes. Recently, hydrogenation of higher fullerenes showed $C_{70}H_{50}$, $C_{78}H_{48}$ and $C_{84}H_{52}$ to be formed under conditions whereby [60]fullerene gave $C_{60}H_{36}$ and [70]fullerene gave $C_{70}H_{40}$.[8] From the work described above, fluorination to a higher level of site occupancy could be expected, and this is found, with $C_{78}F_{54}$ and $C_{84}F_{56-62}$ being evident in the mass spectrum (Fig. 9). Although these species were not detectable in as-prepared samples, they were detected after heating the $C_{60}F_{48}$ product under reflux for 6 h with methanol. This may have selectively reacted with the fluorinated species of the lower fullerenes, thereby reducing the vapour pressure of the latter and so enabling detection of the less volatile components by mass spectrometry.

Acknowledgements

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