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# Direct fluorination of fullerenes †

O V Boltalina, N A Galeva

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**Abstract. Data on the synthesis of a new class of fluorocarbon compound, fluorofullerenes, by reactions of $C_{60}$, $C_{70}$, their mixtures and higher fullerenes with molecular fluorine are surveyed. The physicochemical and thermodynamic properties are presented for pure $C_{60}F_{48}$, which is the only compound formed selectively in direct fluorination of $C_{60}$, and for fluorofullerene mixtures. The bibliography includes 70 references.**

## I. Introduction

Very few naturally occurring compounds of fluorine exist, these are primarily mineral inorganic compounds. The unique properties inherent in fluorine and its compounds [1, 2] have served as the basis for the development of new modern technologies and a large number of fluorine-containing materials both in organic and inorganic chemistry.[3, 4]

The interest in the reaction of molecular fluorine with the new form of carbon, *viz*., fullerenes, is undoubtedly due to the widely known useful properties of the products of direct fluorination ‡ of graphite, such as high thermal stability (up to 400 °C) of graphite fluorides $(CF)_n$ and $(C_2F)_n$, the possibility of using fluorine-intercalated graphites $C_xF$ with high degrees of fluorination as cathodic materials for lithium batteries, as well as the good antifriction properties of these compounds.[5, 6]

On the one hand, the polyhedral clusters of carbon, fullerenes, can be regarded as inorganic compounds, as this is an allotropic modification of carbon. On the other hand, fullerenes can be placed among organic compounds, as their behaviour in chemical transformations is similar to that of unsaturated hydrocarbons. Formally, $C_{60}$ and $C_{70}$ fullerenes have 30 and 35 double bonds, respectively.

Owing to delocalisation of the π-electron density, fullerenes undergo both addition to the double bonds and electrophilic addition with the intermediate formation of charge transfer complexes and, eventually, various derivatives. The $C_{60}$ fullerene can add up to 24 chlorine or bromine atoms or methyl groups. As the size of the functional groups being added decreases, their number increases; for example, hydrogenation of $C_{60}$ can result in $C_{60}H_{36}$.

What is the maximum number of addends in the case of fluorine? On the one hand, the van der Waals radius of fluorine (1.35 Å) is greater than that of hydrogen (1.2 Å), and on the other hand, fluorine forms stronger bonds with carbon. The authors of theoretical work [7–9] published before experiments on hydrogenation and halogenation of fullerenes were carried out had predicted that the completely fluorinated fullerene $C_{60}F_{60}$ would be stable. However, in this case, the steric interaction of the adjacent fluorine atoms would result in elongation of the carbon – carbon bonds in the fullerene framework to 1.67 Å,[10] as well as in a decrease in the C – F bond energy by 15% in comparison with that of the C – F bond in $CF_4$.[11] The authors of yet another theoretical work [12] noted that the formation of the $C_{60}F_{60}$ molecule is possible provided that steric strain is relieved by distortion of the carbon framework with retention of the icosahedral symmetry. It was anticipated that, owing to its unique spherical symmetry, perfluorofullerene would possess good lubricating properties, similarly to graphite fluorides. It did not take the experimenters too long to answer these questions, and as early as in 1991, the first study was published [13] dealing with the synthesis of highly fluorinated fullerene by the reaction of $C_{60}$ with molecular fluorine. It was shown that addition of 36 (as in the reaction with hydrogen) or more fluorine atoms can occur. Thus, a new line of research, *i.e*., studies on the fluorination of fullerenes, appeared in fluorine chemistry.

This review is aimed at generalisation of the literature data available since 1991 and the own author's results concerning fluorination of fullerenes with molecular fluorine. We intentionally limit ourselves to direct fluorination reactions. First, the reaction of $F_2$ with fullerenes drew the highest attention of researchers in 1991 – 96; these were the peak years in the activity of scientific groups in the USA, Great Britain, France and Japan, who were experienced in direct fluorination and possessed the corresponding experimental equipment. Second, direct fluorination reactions are well-developed technological processes that have been implemented in large-tonnage manufacture of various fluorine-containing products. If areas of fluorofullerene application demanding their production on a relatively large scale are

**O V Boltalina, N A Galeva** Department of Chemistry, M V Lomonosov Moscow State University, Leninskie Gory, 119899 Moscow, Russian Federation. Fax (7-095) 939 12 40. Tel. (7-095) 939 53 73.
E-mail: OVB@capital.ru (O V Boltalina)

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† To the cherished memory of V F Bagryantsev.

‡ The term 'direct fluorination' designates the reaction involving molecular fluorine, as it is generally accepted in the literature (see *e.g*. Ref. 4).

found, it is the reactions with molecular fluorine that can prove to be the most efficient and economically sound.

We leave the studies on the alternative methods for fullerene fluorination, including the reactions with fluorides of transition metals, noble gases, *etc*., outside the scope of this review; these studies have been covered in recent reviews.[14,15] The authors of almost all pioneering publications of the early 1990s used samples obtained by direct fluorination of $C_{60}$ or $C_{60}/C_{70}$ mixtures to study the physical and chemical properties of fluorofullerenes. On the other hand, despite the abundance of original works published in this period, neither detailed analysis of the results obtained nor coordination of the data obtained by different authors regarding the composition and properties of fluorination products have been carried out to date.

## II. Synthesis of fluorofullerenes

### 1. Direct fluorination of $C_{60}$ and $C_{60}/C_{70}$

The first synthetic study[13] on fullerene fluorination was carried out soon after the development of the procedure for their synthesis in macroscopic quantities. Selig *et al*.[13] studied the fluorination of fullerenes using a Sartorius magnetic balance, which allowed them to detect the changes in the sample weight to within 0.1 mg. The samples were kept in a fluorine atmosphere for at least 20 h to attain a constant weight. The largest weight gain occurred within the first several minutes, after which the absorption of fluorine markedly retarded. The electron impact (EI) mass spectrum (70 eV) of the yellowish-brown reaction product with the composition $F:C_{60} = 38$ (the composition was determined by measurement of the weight gain and by titrimetry) contained peaks corresponding to the $C_{60}F_{30-44}$ molecules, the most intense peak being due to the $C_{60}F_{36}$ molecule. It should be noted that Selig *et al*.,[13] who used an IR cell for the fluorination, observed accumulation of $CF_4$ during the reaction ($\nu_{C-F} = 1283\ cm^{-1}$). It was shown[16] that fluorination of fullerenes with molecular fluorine is accompanied by side reactions to give perfluoroalkanes $C_nF_{2n+2}$ ($n = 1-4$). The mass spectrum of a gas phase sample taken directly from the reactor zone during the experiment (Fig. 1) showed, in addition to the $F_2^+$ ions, the presence of $C_nF_k^+$ ions ($n = 1-4$, $k = 1-9$).

In 1991, a paper by Holloway *et al*.[17] was published. Direct fluorination of $C_{60}$ fullerene at 70 °C was monitored for several days. Three to four days after the beginning of fluorination, the black $C_{60}$ powder underwent an abrupt colour change to dark-brown; this colour remained apparently unchanged for another three to four days and then abruptly changed to light-brown. Subsequent fluorination resulted in gradual decolourising of the sample to white eventually. The stepwise change in the colour of the powder during the reaction was considered as evidence for consecutive addition of fluorine atoms to the fullerene molecule. It was assumed that the two intermediates (dark- and light-brown) were stable, partially fluorinated fullerene derivatives, $C_{60}F_6$ and $C_{60}F_{42}$, while the white powder was $C_{60}F_{60}$. The formation of $C_{60}F_{60}$ was proven by NMR spectroscopy [the $^{19}F$ NMR spectrum contained one intense band with a chemical shift ($\delta$) of $-150.5$ ppm]. On the other hand, analysis of the mass spectra of the white powder showed peaks corresponding to species with compositions ranging from $C_{60}F_6$ to $C_{60}F_{42}$; however, species with higher fluorine contents ($> 42$) were not found.

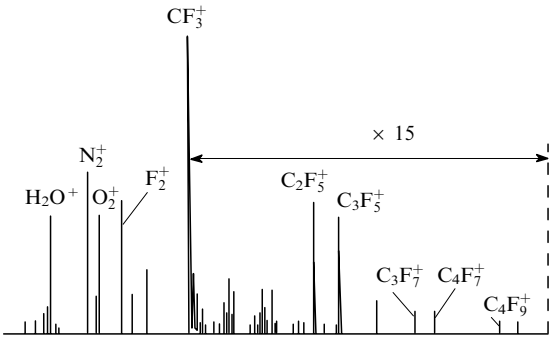



**Figure 1.** Mass spectra of a gas phase sample taken from the reactor during the reaction of fullerenes with molecular fluorine.

Tuinman *et al*.[18] performed the fluorination of fullerenes in various temperature and time modes using reaction vessels made of different materials (Pyrex, quartz, steel). For example, the following procedure was described: through a tube with an inserted capillary containing the fullerene, helium was first passed at 160 °C at a flow rate of 50 ml $min^{-1}$ for two hours in order to remove traces of moisture and then fluorine was passed at a flow rate of 1 ml $min^{-1}$ together with helium. When the temperature was increased, no visible changes in the sample occurred until helium feeding to the reactor was stopped (at 210 °C); as this was done, the volume of the powder increased and its colour changed from black to yellow. Then the temperature was increased to 275 °C and fluorine was passed for additional 4 h (the temperature was not further increased because of the vigorous reaction of fluorine with quartz). According to mass spectroscopic data, the main products, *viz*., white powders, were mixtures of fluorofullerenes $C_{60}F_{38-46}$ (Fig. 2); however, no perfluorinated fullerene $C_{60}F_{60}$ was detected, the maximum degree of fluorination being 48 (the $C_{60}F_{48}$ molecule). It was noted that molecules containing more than 48 fluorine atoms were not formed upon longer treatment of fullerenes with fluorine.

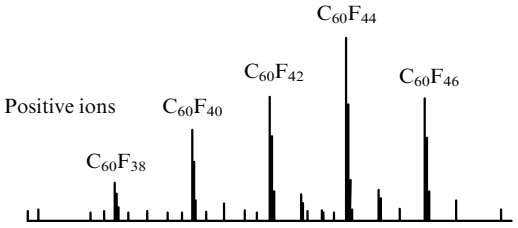



**Figure 2.** Electron impact mass spectra (70 eV) of a sample synthesised by Tuinman *et al*.[18]

Kniaz *et al*.[19] monitored the course of $C_{60}$ fluorination using a Sartorius balance. The most intense peak in the mass spectrum of the air-stable yellowish-white reaction product corresponded to the $C_{60}F_{40}$ molecule. In addition, a $10^{-5}$ times less intense peak corresponding to the $C_{60}F_{60}$ molecule was observed. In order to improve the quality, the resulting product was sublimed at 300 °C; this gave a yellow sublimate and a white non-volatile residue which included black grains of amorphous carbon. Unlike the spectra of the starting sample, the mass spectra of the sublimate and the residue did not display peaks corresponding to the highly fluorinated $C_{60}F_x$ molecules ($x > 48$). The absence of these peaks was explained by the liberation of molecular fluorine from $C_{60}F_x$ ($x > 48$) during sublimation.

Okino *et al*.[20–23] determined the composition of fluorofullerenes by X-ray photoelectron spectroscopy (XPS) in thin films obtained by deposition of $C_{60}$ on nickel plates which were then treated with fluorine under the same conditions as the $C_{60}$ powders (Table 1). The XPS data are in good agreement with mass spectroscopic data. For example, a sample with the composition $F:C_{60} = 45$ (XPS data) contained $C_{60}F_{44}$ and $C_{60}F_{46}$ as the major components. It should be noted that the X-ray photoelectron spectra of the samples with low fluorine content ($F:C_{60} < 20$) contained peaks belonging to the $C_{60}$ fullerene and $C_{60}F_x$ fluorofullerene ($x \approx 40$) phases. It was assumed that even short-term fluorination converts a fraction of fullerene molecules to derivatives with high fluorine content, whereas the data of chemical analysis and XPS of the $C_{60}F_x$ samples, where $x < 20$,

**Table 1**. Conditions used for the synthesis of fluorofullerenes and their characteristics.

| $C_{60}$ sample | Fluorination conditions | | | Reaction product according to data | | | Ref. |
|---|---|---|---|---|---|---|---|
| | time /h | $T$ /°C | $p$ /atm | CA | MS | XPS | |
| Film | 4 | 200 | 1 | – | $C_{60}F_{42-46}$ | $C_{60}F_{45}$ | 20 |
| | 24 | 150 | 1 | – | – | $C_{60}F_{40}$ | 20 |
| | ~288 | 70 | 1 | – | – | $C_{60}F_{20}$ | 20 |
| | ~336 | 70 | 1 | $C_{60}F_9$ | – | $C_{60}F_{22}$ | 20 |
| Sample weight | 4 | 200 | – | $C_{60}F_{45}$ | – | – | 21 |
| | ~672 | 200 | – | – | – | – | 21 |
| See [a] | 30 | 48–72 | 225 [b] | – | $C_{60}F_{45}$ | $C_{60}F_{44-48}$ | 22 |
| | 48 | 100 | – | – | – | – | 23 |

**Note**. The following designations are used: CA is chemical analysis; MS is mass spectroscopy; XPS is X-ray photoelectron spectroscopy. [a] Sample weight 30 mg; [b] mm Hg.

showed only the presence of unreacted $C_{60}$ together with highly fluorinated molecules.

Hamwi *et al.*[24,25] fluorinated $C_{60}$ using a setup made of Monel and steel. A fullerene powder was placed in an aluminium boat; the reaction was carried out at 20–300 °C, either under static conditions ($p$ = 1–5 atm) or in a stream of fluorine (the flow rate was 2 ml $min^{-1}$) for 10–336 h. Thermogravimetric analysis showed that fluorofullerenes started to decompose at 180 °C. For this reason, the reaction at temperatures above 180 °C was stopped at the instant when the product weight started to decrease. This resulted in a series of differently coloured powders (from black to pale yellow). The maximum weight gain recorded for one of the samples corresponded to the stoichiometry $F:C_{60}$ = 58.5. On the other hand, without mass spectroscopic analysis, it is difficult to make reliable conclusions on the actual presence of molecules with such a high fluorine content.

Short-term reactions of the same compounds gave fluorofullerenes with low fluorine stoichiometric factors (*e.g.*, $C_{60}F_9$), as determined from weight gain. According to IR spectroscopic and X-ray diffraction data, these samples contained only the non-fluorinated fullerene, while the $^{19}F$ NMR spectrum exhibited one broad peak, which proved the presence of fluorine in the products.[25]

It was found[24,25] that $C_{60}/C_{70}$ fullerene mixtures are more reactive than $C_{60}$ fullerene. For example, the reaction of $C_{60}/C_{70}$ with fluorine at room temperature for 4 h resulted in an increase in the sample weight; however, the weight of pure $C_{60}$ samples did not change upon longer treatment (48 h) under the same conditions. Fluorination of $C_{60}/C_{70}$ at 300 °C for 4 h afforded a pale yellow product with the ratio $F:C_{60}$ = 44, whereas for pure $C_{60}$, it took 8 h to attain the same degree of fluorination.

Bagryantsev *et al.*[16] fluorinated a $C_{60}/C_{70}$ fullerene mixture and found that if the reaction temperature is raised from 70 to 315 °C, the content of fluorofullerenes with higher degrees of fluorination gradually increases. The $C_{60}F_x$ ($x$ = 38, 40) and $C_{60}F_{48}$ fluorofullerenes were the main components among the products obtained at 70 and 315 °C, respectively. The trend towards higher degrees of fluorination at elevated temperatures was also observed in the case of $C_{60}$ fullerene (Table 2). For example, the $C_{60}F_{46}$ fluorofullerene with a small admixture of $C_{60}F_{44}$ and $C_{60}F_{48}$ was the main reaction product at 275 °C. Fluorination of $C_{60}$ at 315 °C under dynamic conditions resulted in a mixture of fluorofullerenes, in which $C_{60}F_{48}$ was the major product, $C_{60}F_{46}$ was a minor product, whereas the content of $C_{60}F_{44}$ was insignificant. Figure 3 shows a diagram demonstrating the effect of fluorination time of $C_{60}$ at 315 °C on the $C_{60}F_{48}$ content in the resulting samples. Repeated fluorination increased the $C_{60}F_{48}:C_{60}F_{46}$ ratio but also resulted in an appreciable loss of the original fluorofullerene due to thermal destruction (partial burning and sublimation); according to mass spectroscopic data, the content of the main product ($C_{60}F_{48}$) was as high as 95%. Fluorination at higher temperatures (up to 355 °C) for 2–3 h resulted in ~ 90% of $C_{60}F_{48}$; the reaction yield was > 80% in most cases. This procedure was beneficial regarding the reaction time and the consumption of reactants.

A study of the effect of the method of feeding fluorine to the reactor showed that the reaction under dynamic conditions in the absence of flashes mostly gave two components, *viz.*, $C_{60}F_{48}$ and

**Table 2**. Experimental data on the fluorination of fullerenes with molecular fluorine and composition of the products obtained.[16]

| Starting compound | Mode | $T_{max}$ /°C | $\omega$ (%) [a] | Ratio $F:C_{60}$ in the products according to data | | | | Composition according to mass spectroscopy data | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | see [b] | CA | XPS | NMR | $C_{60}F_{44}$ | $C_{60}F_{46}$ | $C_{60}F_{48}$ | $F:C_{60}$ (see [c]) |
| $C_{60}$ (see [d]) | dynamic | 275 | 94 | 43 | 46 ± 1 | – | 46.0 ± 0.5 | 16 | 77 | 4.3 | 45.77 |
| $C_{60}$ | quasi-static | 315 | 70 | 22 | 44 ± 1 | 44 ± 2 | – | 19 | 50 | 13 | 45.45 |
| $C_{60}F_x$ [e] | " | 315 | – | – | – | – | – | 3.2 | 32 | 63 | 47.23 |
| $C_{60}F_x$ [e] | static | 315 | – | – | – | – | – | 6.9 | 33 | 51 | 46.40 |
| $C_{60}F_x$ [e] | dynamic | 315 | – | – | 48 ± 1 | 46 ± 2 | – | 0 | 3.8 | 95 | 47.92 |
| $C_{60}$ | " | 315 | 56 | 10 | 48 ± 1 | – | – | 14 | 33 | 49 | 46.53 |
| $C_{60}$ | " | 315 | 88 | 38 | 49 ± 1 | – | – | 1.5 | 29 | 68 | 47.37 |
| $C_{60}$ (see [d]) | " | 340 | 88 | 37.4 | – | – | – | 0 | 13 | 85 | 47.74 |
| $C_{60}$ (see [d]) | " | 340 | 80 | 31.1 | – | – | – | 0 | 10 | 88 | 47.79 |
| $C_{60}$ | " | 350 | 51 | 6.1 | 49 ± 1 | – | – | 0 | 6.3 | 91 | 47.87 |
| $C_{60}$ | " | 350 | 84 | 34 | – | – | 48.0 ± 0.5 | 4.7 | 12 | 81 | 47.52 |

[a] The reaction yield ($\omega$) was calculated using the formula: $\omega = (m_{exp}/m_{theor}) \times 100\%$, where $m_{exp}$ and $m_{theor}$ are the $C_{60}F_{48}$ masses; [b] the calculation is based on the weight gain; [c] the measurement accuracy is ±0.02; [d] $F_2$ diluted with 90 vol.% Ar was used; [e] the fluorination of fluorofullerenes $C_{60}F_x$ was carried out successively in quasi-static, static and dynamic modes.

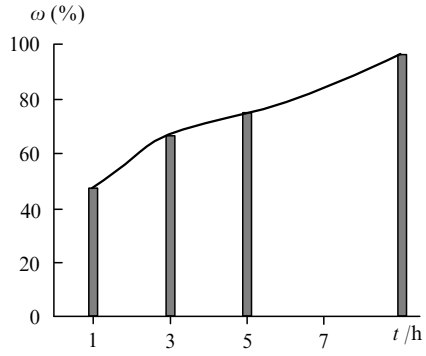



**Figure 3.** Effect of time ($t$) of $C_{60}$ fluorination with molecular fluorine at 315 °C on the $C_{60}F_{48}$ content ($\omega$) in the samples synthesised.

$C_{60}F_{46}$. The product obtained under quasi-static conditions (Fig. 4) contained $C_{60}F_x$ fluorofullerenes, where $x = 40-48$, and an admixture of the $C_{60}F_{44}O$ and $C_{60}F_{46}O$ oxyfluorides (empirical formula $C_{60}F_{45.45}O_{0.05}$). It is evident from Fig. 4 that the absorption of fluorine at low temperatures (up to 110 °C) virtually does not occur (section *I*). In section *II*, starting from 110 °C, noticeable fluorine absorption at a specified, constant rate of heating was observed. The rate of fluorine absorption in the temperature range from 160 to 31 ° C (section *III*) was almost constant. When the temperature was maintained constant (section *IV*, 315 °C), noticeable fluorine absorption ceased.

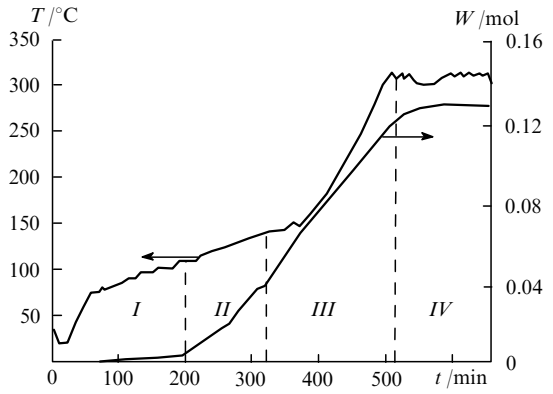



**Figure 4.** Changes in the temperature and in the fluorine amount absorbed ($W$) during the fluorination of $C_{60}$ under quasi-static conditions.

Matsuo *et al.*[26] fluorinated $C_{60}$ using various methods: with molecular fluorine, with a mixture of fluorine and hydrogen fluoride, with molecular fluorine under UV irradiation, and by passing a stream of fluorine through a $CFCl_3$ solution of fullerene (Table 3). The last-mentioned technique, which is the only reported example of liquid-phase fluorination where a low degree of fluorination is attained, might be a promising method for the synthesis of fluorofullerenes with low fluorine contents. However, the methods which were used to analyse the products do not allow unambiguous conclusions to be made about the actual molecular composition of the fluorides, in particular, about the formation of products with low fluorine content. In general, the molecular formulae established for the fluorofullerenes were in agreement with the data reported by other investigators. For example, the largest degree of fluorination was attained when UV irradiation was used (see also the data in Ref. 27).

Chilingarov *et al.*[28] studied $C_{60}$ fluorination under conditions of a mass spectroscopic experiment where molecular fluorine was fed from a cylinder into an effusion cell. The temperature (500–800 K) and the reaction time, as well as the fluorine pressure ($10^{-4}-10^{-5}$ atm) were varied. In the $F_2$ (gas) – $C_{60}$ (solid) system, only molecules with an even number of fluorine atoms, $C_{60}F_{2n}$ ($2 < 2n < 44$), were formed. The composition of the gas phase was largely temperature-dependent: an increase in temperature shifted the distribution of ions in the mass spectrum towards smaller masses. For example, the following major products were obtained: $C_{60}F_{38}$ at 510 K, $C_{60}F_8$ at 760 K, and $C_{60}F_2$ and $C_{60}F_4$ at 800 K. Longer reaction times at 745 and 800 K increased the content of $C_{60}F_{18}$ and $C_{60}F_{22}-C_{60}F_{46}$, respectively. A search for conditions for selective synthesis of a certain fluorofullerene in the gas phase was performed. For example, the maximum yield of $C_{60}F_{18}$ (50%) was attained if the reaction was carried out for 20 h at 720 K and at a fluorine pressure of $2\times10^{-4}$ atm in the presence of $NiF_2$. In the presence of $MnF_2$ (10 h, 615 K, $p_{F_2} = 2\times10^{-4}$ atm), up to 90% of $C_{60}F_{36}$ was formed. No study of solid-phase fluorination products, which could be obtained, *e.g.*, by condensation from the gas phase, was carried out.[28] Therefore, it is impossible to estimate the applicability of the above approach for the selective synthesis of macroscopic quantities of fluorofullerenes.

Thus, the studies on direct fluorination of fullerenes described in this Section showed that

(1) the reaction with molecular fluorine occurs readily and the products of fullerene fluorination can form even at room temperature;

(2) as a rule, mixtures of fluorofullerenes $C_{60}F_n$ with a wide range of compositions are formed ($9 \leqslant n \leqslant 54$, see Ref. 25); the samples with fluorine content $n < 36$ are mixtures of highly fluorinated products ($36 \leqslant n \leqslant 48$) and unreacted $C_{60}$ (the higher the content of the latter in the mixture, the smaller the stoichiometric coefficient for the fluorine atom);

(3) fluorofullerene molecules from $C_{60}F_2$ (see Ref. 28) to $C_{60}F_{102}$ were detected in the gas phase.[27]

The studies were carried out in the temperature range of 20–300 °C (on increasing the temperature above 300 °C, either no noticeable weight gain in the sample occurred or fluorine reacted vigorously with the reactor material); $C_{60}F_{44}$ and $C_{60}F_{46}$ were the main fluorination products at 275–300 °C.[16]

## 2. Fluorination of fullerene bromo and chloro derivatives

In order to obtain fullerene derivatives with low fluorine content, an attempt was made to fluorinate bromo and chloro fullerene derivatives such as $C_{60}Br_{24}$, $C_{60}Br_8$, $C_{60}Br_6$ and $C_{60}Cl_{24}$ with

**Table 3**. Conditions of the synthesis of fluorofullerenes from $C_{60}$ and their characteristics.[26]

| Fluorinating agent | Time /days | $T$ /°C | Ratio F : $C_{60}$ in the products according to data | | | Product colour |
|---|---|---|---|---|---|---|
| | | | see [a] | CA | XPS | |
| $F_2$ | 11.5–27 | 20–90 | 40 | 41 | 45 | – |
| $F_2$ – HF | 12–35 | 20–85 | – | 42–45 | – | – |
| $F_2$ under UV irradiation (254 nm) | 11–14 | 20–70 | >45 | 47–52 | – | yellowish-white |
| $F_2$ (see [b]) | 0.2–14 | 20–65 | – | 27–33 | – | – |

[a] The calculation is based on the weight gain; [b] the stream of fluorine was passed through a $CFCl_3$ solution of $C_{60}$;

molecular fluorine.[29] The idea was to perform the reaction in two stages: in the first step, fluorine had to add to the carbon atoms unoccupied by bromine or chlorine, while in the second stage, due to the lower strength of the C–Cl and C–Br bonds with respect to the C–F bond, abstraction of $Br_2$ and $Cl_2$ on heating was expected giving rise to fluorofullerenes with a low fluorine content. However, the reaction of $C_{60}Br_{24}$ with molecular fluorine resulted in complete displacement of bromine even without additional heating to give fluorofullerenes with variable composition up to $C_{60}F_{44}$ with predominant formation of $C_{60}F_{36}$. Fluorination of $C_{60}Br_8$ gave $C_{60}F_{36}$; the resulting product contained mostly $C_{60}F_{18}$ as well as mono- and dioxides of fluorofullerenes. As in the reaction of $C_{60}$ fullerene with gaseous fluorine, fluorine compounds with an even number of fluorine atoms in the molecule were formed.

### 3. Synthesis of pure fluorofullerenes by direct fluorination

The use of the reaction of $C_{60}$ with molecular fluorine for the synthesis of fluorofullerenes with a particular number of fluorine atoms was first reported by Gakh *et al.*[30] Fluorination was carried out in two stages. A stream of molecular fluorine ($\upsilon$ = 1.3 ml min$^{-1}$) was passed over a mixture of $C_{60}$ with NaF at 250 °C for 20 h, then the product was extracted with $CFCl_3$ and dried; a new portion of NaF was added, and the mixture was again treated with a stream of $F_2$ (275 °C, 30 h). After extraction and drying, the composition of the sample was determined by mass spectroscopic analysis using field desorption for ionisation. The intensity of the ion corresponding to the $C_{60}F_{48}$ molecule was 69% of the overall intensity of the ions corresponding to the $C_{60}F_{2n}$ molecules ($2n \leqslant 48$). A study of the $^{19}F$ NMR spectrum of a sample with a sufficiently high content of $C_{60}F_{48}$ allowed the researchers to suggest the molecular structure of $C_{60}F_{48}$ (see Section III.5).

Considerable progress[16, 31, 32] in the synthesis of pure $C_{60}F_{48}$ (with > 95% of $C_{60}F_{48}$ in the samples) was attained in studies of the dependence of the composition of the products of $C_{60}$ fluorination with molecular fluorine on the temperature (70–355 °C) and on the reaction conditions. At each intermediate step before the next increase in the temperature, the molecular composition was determined by high-temperature mass spectroscopy with electron impact ionisation and evaporation of samples from the effusion cell. The fluorination products had the form of white powders stable in air for at least three years. The molecular structure of the $C_{60}F_{48}$ fluorofullerene obtained by this method was identical to that reported by Gakh *et al.*[30]

### 4. Fluorination of $C_{70}$ and higher fullerenes

The fluorination of $C_{60}/C_{70}$ mixtures resulted in a series of products $C_{70}F_n$, where $n$ = 48 (see Ref. 24) and 54 (see Ref. 18) for the components with the maximum dergee of fluorination. The reaction of pure $C_{70}$ with fluorine resulted in mixtures of fluorides containing mainly $C_{70}F_{40}$ (see Ref. 13), $C_{70}F_{38}$ (see Ref. 16) and $C_{70}F_{54}$ (see Ref. 31). In these mixtures, $C_{70}F_{46}$ (see Ref. 13), $C_{70}F_{48}$ (see Ref. 16) and $C_{70}F_{56}$ (see Ref. 31), respectively, had the maximum degrees of fluorination. Experiments carried out successively at 250, 280 and 350 °C showed an increase in the degree of fluorination with increase in temperature. However, even at 350 °C, the fluorination product was a mixture of compounds from $C_{70}F_{38}$ to $C_{70}F_{56}$ (Fig. 5).[16]

The only reference to the fluorination of higher fullerenes with molecular fluorine can be found in the paper by Bagryantsev *et al.*[31] The mass spectrum of the product of fluorination of a fullerene mixture containing small amounts of $C_{76}$ and $C_{84}$ showed the presence of $C_{76}F_{54}$ and $C_{84}F_n$ ($n$ = 56–62). The reaction was carried out under the same conditions as the fluorination of $C_{70}$ to give $C_{70}F_{56}$.[31]

Thus, the maximum number of fluorine atoms that can be added to $C_{60}$ and $C_{70}$ (48 and 56, respectively) corresponds to 80%

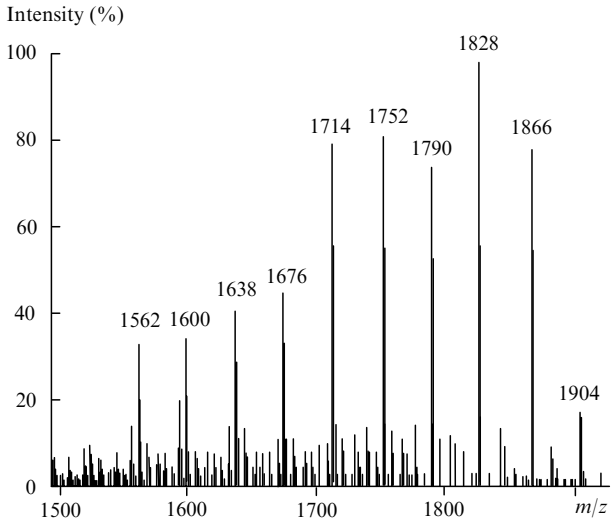



**Figure 5.** Electron impact mass spectrum of a $C_{70}F_n$ sample ($n$ = 38–56) synthesised at 350 °C. The maximum degree of fluorination corresponds to $C_{70}F_{56}$ (1904 amu) and the most intense peak corresponds to 1828 amu, *i.e.*, $C_{70}F_{52}$.

occupation of the reaction sites in fullerene molecules. More extensive fluorination on treatment of fullerenes with molecular fluorine at temperatures of up to 350 °C is probably hampered by the inaccessibility of the remaining double C=C bonds because of steric hindrance caused by the size of the fluorine atoms and the rigidity of the spherical carbon skeleton. Pure fluorides of the $C_{70}$ fullerene will probably be hardly accessible due to the lower symmetry of $C_{70}$ in comparison with $C_{60}$. In the case of heavy fullerenes, the prospects for the synthesis of pure compounds are also complicated by the existence of geometrical isomers.

## III. Methods of study and physical properties of fluorofullerenes

### 1. IR spectroscopy

The IR spectroscopic data for fluorofullerenes are reported in many papers. As the compositions of fluorofullerene samples are known, one can follow a correlation between the vibration frequency of the C–F bonds and the fluorine content in the samples. For example, the broad unresolved band at 1148–1165 cm$^{-1}$ typical of fluorofullerene mixtures $C_{60}F_x$ ($36 \leqslant x \leqslant 48$)[13, 19] shifts towards 1170–1176 cm$^{-1}$ for the pure $C_{60}F_{48}$ fluorofullerene.[16] A similar shift of bands with increase in the fluorine content was also observed in the case of fluorinated graphite: 1110–1120 cm$^{-1}$ for fluorine-intercalated graphite with the composition $C_2F$ (see Ref. 26) and 1220 cm$^{-1}$ for graphite fluorides $(CF)_n$, $(C_2F)_n$.[33, 34]

The main distinction of the IR spectra of pure $C_{60}F_{48}$ from those of fluorofullerene mixtures is that fine structure in the region of C–F vibrations and a group of intense bands in the region of 600–800 cm$^{-1}$ are displayed (see Refs 26, 32). One can see in Fig. 6 that the most intense peaks at 650 and 723 cm$^{-1}$ are characteristic only of the $C_{60}F_{48}$ fluorofullerene but are absent from the IR spectrum of a $C_{60}F_{46}$ sample. Evidently, the bands in this spectrum region can serve as 'fingerprints' of pure $C_{60}F_{48}$. The IR spectra for certain $C_{60}F_{48}$ isomers were calculated in a theoretical study,[35] but no detailed assignment of the normal vibration modes has been carried out to date.

IR spectroscopic data for some $C_{60}F_x$ fluorofullerene samples are presented in Table 4.

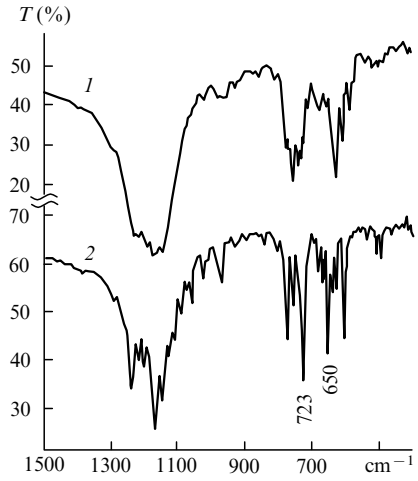



**Figure 6.** IR spectra of fluorofullerene samples: $C_{60}F_{46}$ (*1*) and $C_{60}F_{48}$ (*2*).[32]

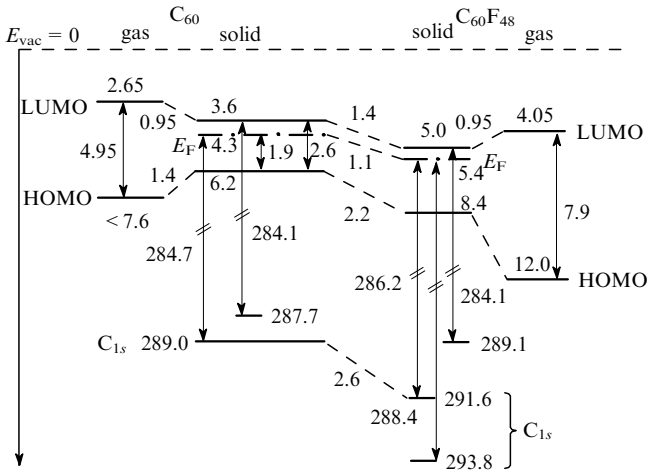



**Figure 7.** Energy diagram for the $C_{60}$ and $C_{60}F_{48}$ molecules in the gas and solid phases[36] (the HOMO value was changed in accordance with the data in Refs 37 and 38).

**Table 4**. IR spectroscopic data for some samples of $C_{60}F_x$ fluorofullerenes.

| $x$ | Vibration frequencies /cm$^{-1}$ | Ref. |
|---|---|---|
| 36 (see [a]) | 1164, 1133 | 34 |
| $6 \leqslant x \leqslant 42$ | 1148 | 17 |
| $38 \leqslant x \leqslant 48$ | 1150, 750, 510 | 18 |
| $30 \leqslant x \leqslant 44$ | 1165 | 13 |
| 47 | 1168 | 24 |
| 27 – 52 | 1150, 750, 600 | 26 |
| 48 | 1170, 1141, 755, 736, 723, 650, 604 | 31 |

[a] The fluorofullerene was synthesised in the reaction with manganese trifluoride.

## 2. Electronic structure and electrochemical properties

The electronic structure of fluorinated fullerenes differs from the electronic structure of the original fullerenes. The high electronegativity of fluorine decreases both the LUMO and the HOMO energies, thus the electron affinity and the first ionisation potential of $C_{60}F_x$ and $C_{70}F_x$ increase in comparison with those of $C_{60}$ and $C_{70}$. Obviously, the changes in the electronic potentials occurring due to transformation of fullerenes to fluoro derivatives affect their electrochemical and photoelectrochemical behaviour. Data on the electronic structures of the $C_{60}F_{48}$ and $C_{60}$ molecules obtained by XPS, from the near fine structure and from the near-edge X-ray absorption fine structure spectra (NEXAFS) are presented in Fig. 7.

It was found[36] that the work functions for $C_{60}F_x$ are 5.6, 5.2 and 5.4 eV for $x = 30$, 36 and 48, respectively. This is considerably higher than the work functions for organic compounds (usually, 4.1 – 5.0 eV) and for $C_{60}$ fullerene (4.7 eV[39]), which points to strong electron-withdrawing properties of fluorofullerenes.

The addition of fluorine to fullerene shifts the bands in the absorption spectra from 1.8 eV for $C_{60}$ fullerene to 6.4 eV for $C_{60}F_x$ ($42 \leqslant x \leqslant 48$).[40]

Many researchers have studied fluorofullerenes by XPS,[25,26,41–43] but the data of different authors are in poor agreement due to the use of different types of X-ray radiation, different calibrations of the instruments and different substrate materials. In certain cases, surface charging and a shift of the absolute energy scale were observed, which complicated considerably the interpretation of the spectra and made it difficult to obtain reliable data on the composition of the fluorofullerene samples and on the chemical shifts. According to some data of multicomponent photoelectron $C_{1s}$ spectra,[22,25,41,42] destruction processes take place on a sample surface exposed to hard X-radiation, which is accompanied by a flow of high-energy electrons. In addition, it was found[26] that the relative intensity of peaks in the photoelectron spectra depended on the duration of the exposure of samples to X-radiation. This was explained by the destructive effect of the electron flux. For example, according to the data reported by Matsuo *et al.*[26] the $C_{60}$ : F ratio was 42 after irradiation of a fluorofullerene sample for 33 s, while an increase in the irradiation time to 750 s decreased the content of fluorine to $C_{60}$ : F = 38.

The use of electron-free synchrotron radiation (40 – 500 eV) made it possible to prevent the destruction of the fluorofullerene surface layer and to eliminate the charge accumulation on the sample surface. The photoelectron spectra obtained under these conditions[43] displayed peaks at 287.2 and 284.9 eV, which were interpreted as the energies of the 1*s* electrons of the carbon atoms ($E_b$) involved in the formation of the C – F and C – C bonds, respectively (Fig. 8 *a*). Similar two-component $C_{1s}$ spectra were also obtained in other studies.[26,36,45,46] The two lines in the $F_{1s}$

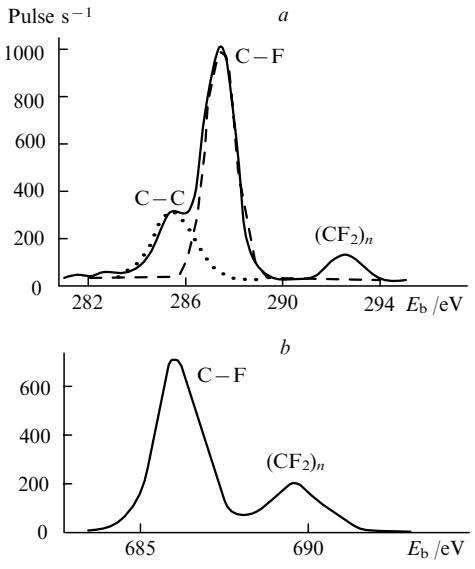



**Figure 8.** X-Ray photoelectron spectra of $C_{60}F_{48}$: (*a*) spectrum of carbon 1*s* electrons; (*b*) spectrum of fluorine 1*s* electrons excited by X-ray radiation of Al$K\alpha_{1,2}$ with Teflon as the standard.[44]

photoelectron spectrum of $C_{60}F_{48}$ fluorofullerene (Fig. 8 *b*) at 685.9 and 689.5 eV represent two states of fluorine, namely, those in fluorofullerene and in Teflon, respectively.

In certain studies, the XPS method was used to determine the compositions of the samples obtained (see Tables 1, 2). However, the accuracy of these estimates is insufficient, ±2 fluorine atoms per fullerene molecule.

It is well known that, depending on the fluorine content in fluorine-intercalated graphite $C_xF$, the nature of the C–F bond changes from ionic to partially ionic (or partially covalent).[5] The $F_{1s}$ photoelectron spectra of $C_xF$ compounds with low fluorine content display one peak at 684.5 eV; this corroborates the existence of only one type of fluorine atoms in the compound, which are in the same electronic state as those in metal fluorides (for instance, the peak at 685.6 eV represents LiF[22]). It is believed[5] that intercalated fluorine atoms distributed between carbon layers undergo ionisation and interact with the $C_x^{\delta+}$ polycation.

The increase in $x$ in $C_xF$ to 10 is accompanied by some delocalisation of the electron density, hence the C–F bond cannot be considered as purely ionic. The $F_{1s}$ spectrum displays a peak at 685.7–685.8 eV. Subsequent increase in the fluorine content in $C_xF$ produces a second peak in the $C_{1s}$ spectrum, which is explained by a covalent contribution to the energy of the fluorine–carbon bond. Thus, the $C_xF$ compounds with the composition $2 \leqslant x \leqslant 4$ contain fluorine–carbon bonds of two types: ionic and partially ionic (or partially covalent). The observed chemical shifts in the photoelectron spectra are listed in Table 5.

Matsuo *et al.*[26] compared the photoelectron spectra of fluorofullerene, fluorine-intercalated graphite $C_2F$ and graphite fluorides $(C_2F)_n$ and $(CF)_n$ (Fig. 9). It is important that the high-energy peak for $C_{60}F_{43}$ fluorofullerene (291.1 eV) is located approximately between the corresponding peaks of $C_2F$ and graphite fluorides, whence the authors conclude that the degree of covalency of the C–F bond in fluorofullerene is intermediate between those of the C–F bonds in $C_2F$ intercalates and in graphite fluorides.

The differences between the electron binding energies ($\Delta E_b$) in carbon atoms with different chemical environments were compared;[26] the difference is manifested in the $C_{1s}$ photoelectron spectra as two peaks. It was concluded that the greater $\Delta E_b$, the more ionic and less covalent the C–F bond. For example, $\Delta E_b$ for $C_{60}F_{33}$ and $C_{60}F_{31}$ samples is smaller than that for fluorine-intercalated graphite $C_2F$ and larger than that for graphite fluoride $(C_2F)_n$, which suggests that the C–F bond in fluorofullerene has an intermediate character between covalent and semi-ionic. Comparison of the $\Delta E_b$ values in the $C_{1s}$ spectra in $C_{60}F_{48}$ fullerene (1.8 eV) and in the spectra of fluorine-intercalated graphite (2.6 eV) and graphite fluorides (1.9 eV) showed that the C–F bond in $C_{60}F_{48}$ is covalent. The average $\Delta E_b$ values were 2.2–2.4 eV (see Table 5).

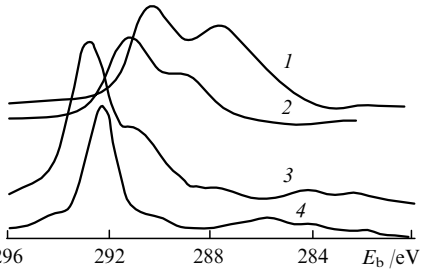



**Figure 9.** X-Ray photoelectron spectra of carbon 1*s* electrons in fluorine-intercalated graphite $C_2F$ (*1*), $C_{60}F_{43}$ fluorofullerene (*2*) and graphite fluorides $(C_2F)_n$ (*3*) and $(CF)_n$ (*4*).[26]

The electrochemical behaviour of fluorofullerenes was first studied by cyclic voltammetry. Holloway *et al.*[17] studied the electrochemical reduction of $C_{60}F_{48}$ in a $CH_2Cl_2$ solution and detected the reaction products using a mass spectrometer. It was shown that the reduction of $C_{60}F_{48}$ occurs reversibly and that the reduction potential of $C_{60}F_{48}$ is 1.38 V higher than that of $C_{60}$. This agrees completely with the fact that the electron affinity of fluorinated fullerenes is about 1.5 eV higher than that of fullerenes. Based on the mass spectra obtained using the electro-spray method, it was concluded[47] that the electrochemical reduction mechanism includes a series of consecutive reactions of electron transfer and abstraction of fluorine atoms.

A study of the electrochemical properties of fluorofullerenes in solid electrolytes based on polyphosphazine derivatives doped with $Li^+$ was carried out.[48] The cathodic mixture contained a fluorofullerene, graphite and the electrolyte in the mass ratio

**Table 5**. X-Ray photoelectron spectroscopy data for fluorine-intercalated graphite, graphite fluorides and fluorofullerenes.

| Compound [a] | $E_b(F_{1s})$ /eV | $E_b(C_{1s})$ /eV | | $\Delta E_b(C_{1s})$ /eV | Ref. |
|---|---|---|---|---|---|
| | | C–C | C–F | | |
| $C_xF$ ($20 < x$) | 684.5 | 284.6 | – | – | 5 |
| $C_xF$ ($4 < x < 10$) | 685.7–685.8 | 284.1 | – | – | 5 |
| $C_xF$ ($2 \leqslant x \leqslant 4$) | 686.0–687.1 | 284.1–284.6 | 286.8–288.0 | 2.7–3.4 | 5 |
| $C_2F$ | 687 | 287.5 | 290.1 | 2.6 | 26 |
| $C_4F$ | – | 283.4 | 286.6 | 3.2 | 26 |
| $(C_2F)_n$ | 690 | 290.8 | 292.7 | 1.9 | 26 |
| $(CF)_n$ | 689.6 | – | 290.4 | – | 33 |
| $C_{60}$ | – | 284.6 | – | – | 22 |
| $C_{60}$ | – | 284.7 | – | – | 37 |
| $C_{60}F_{48}$ | – | 286.2 | 288.4 | 2.2 | 37 |
| $C_{60}F_x$ ($x$ = 44, 46, 48) | – | 284.9 | 287.2 | 2.3 | 43 |
| $C_{60}F_{47}$ | – | 288.5, 290.7, 293.3 | – | – | 26 |
| $C_{60}F_{43}$ | – | 288.9 | 291.1 | 2.2 | 26 |
| $C_{60}F_x$ ($x$ = 31, 33) | – | 288.0 | 290.4 | 2.4 | 26 |
| $C_{60}F_x$ | 688 | 284.6 | 289.5 | 4.9 | 42 |
| $C_{60}F_{48}$ | – | 291.5 | 293.5 | 2.0 | 45 |
| $C_{60}F_{48}$ | 685.9 | 285.6 | 287.4 | 1.8 | 46 |
| $C_{60}F_x$ ($x$ = 40–48) | – | 286.8 | 289.3 | 2.5 | 46 |

[a] The sample composition is given in accordance with original work.

1 : 1 : 2. The voltammograms of $C_{60}F_x$ and $C_{70}F_x$ fluorofullerenes in solid-phase lithium batteries showed peaks at potentials of 3.1 and 3.4 V relative to the $E(Li^+/Li)$ potential, which corresponded to irreversible reduction of $C_{60}F_x$ and $C_{70}F_x$. After two voltammetric cycles, XPS showed a decrease in the relative intensity of the signal at 289 eV in the $C_{1s}$ spectrum for the carbon atoms involved in the C–F bonds and the appearance of a new signal at 685 eV in the $F_{1s}$ spectrum. This is evidence for irreversible reduction of C–F bonds during the experiment and the formation of LiF. Similar experiments with fluorinated graphite $(CF)_n$ showed that its reduction potential is 0.5 V more negative than that of fluorofullerene. This implies that the C–F bond in the $C_{60}F_x$ molecule is reduced more readily than the C–F bond in $(CF)_n$. It was assumed that reduction of fluorofullerenes under galvanostatic conditions is homogeneous, unlike the heterogeneous reduction of graphite fluoride $(CF)_n$.

The electrochemical behavior of fluorofullerenes the synthesis of which is described in Section II and Table 3 was studied as a function of the elementary composition (from $C_{60}F_{15}$ to $C_{60}F_{47}$).[49] It was shown that the reduction potentials of fluorofullerenes approach the reduction potential of $C_{60}$ fullerene as the fluorine content decreases.

## 3. Crystal structure

The structure of $C_{60}$ fullerene at room temperature is described by a face-centred cubic (FCC) lattice with the parameter $a = 14.17$ Å; the distance between the neighbouring $C_{60}$ molecules is 10.02 Å, and the density is 1.72 g cm$^{-2}$ (which corresponds to $1.44 \times 10^{21}$ molecules cm$^{-2}$).[10]

Data of numerous X-ray diffraction studies (see, *e.g.*, Refs 19, 20, 50–53) indicate that at room temperature, the products of fullerene fluorination have the same FCC lattice (Table 6) as the matrix compound $C_{60}$ but with an increased spacing. The increase in the distance between two neighbouring molecules following fluorination manifests itself as a shift of diffraction lines to smaller reflection angles: the first maximum is at $2\Theta = 9°$,[13] which is much smaller than for crystalline $C_{60}$. Some papers reported the absence of crystallinity, especially for samples obtained at rather low temperatures.[20,24,25] The diffraction pattern usually contained two diffuse peaks indicating the absence of long-range order, characteristic of crystals.

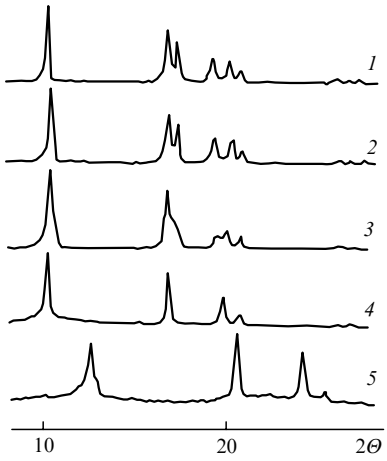



**Figure 10.** X-Ray diffraction patterns of samples with increasing contents of $C_{60}F_{48}$ (*1–3*), $C_{60}F_{46}$ fluorofullerene (*4*) and $C_{60}$ fullerene (*5*).[46]

The *a* parameters for fluorofullerene samples obtained by different research groups and described by a FCC lattice range from 16.98 (see Ref. 20) to 17.6 Å,[24] which approximately corresponds to an increase in the molecular volume by a factor of 1.8 relative to that of $C_{60}$.[50]

Due to the replacement of the short double bonds by longer single bonds, the radius of the carbon cage in a fluorofullerene molecule increases by 1% (from 3.53 to 3.56 Å)[47] with respect to that of $C_{60}$, or by 10% according to other data.[21] Representing a fluorofullerene molecule by two concentric spheres which correspond to the positions of the carbon and fluorine atoms (the C–F bond length is 1.36 Å) and considering that fluorination results in an increase in the radius of the carbon cage by 10%, Okino *et al.*[21] calculated the X-ray spectra for $C_{60}F_{45}$ and $C_{70}F_{32}$ samples.

Kniaz *et al.*[19,51] studied a sublimed fluorofullerene powder; the most intense peak in its mass spectrum was that of $C_{60}F_{40}$. It was shown that it contained 60% of a FCC phase and 40% of a hexagonal phase (see Table 6) and had a higher degree of crystallinity than unsublimed fluorofullerene.

**Table 6**. Lattice parameters, the number of molecules in a unit cell and the density of fluorofullerenes at room temperature.

| Compound | Lattice type | Lattice parameters /Å | | *z* | $V_{cell}/z$ /Å$^3$ | $d_{calc}$ [a] /g cm$^{-3}$ | Ref. |
|---|---|---|---|---|---|---|---|
| | | *a* | *c* | | | | |
| $C_{60}$ | FCC | 14.17 | | 4 | 711 | 1.681 | 10 |
| $C_{60}F_{45}$ (see [b]) | FCC | 17.07 | | 4 | 1250 | 2.093 | 20 |
| $C_{60}F_{40}$ (see [b]) | FCC | 16.98 | | 4 | 1224 | 2.009 | 20 |
| $C_{60}F_{20}$ (see [b]) | FCC | 17.3 | | 4 | 1294 | 1.412 | 20 |
| $C_{60}F_{22}$ (see [b]) | FCC | 17.3 | | 4 | 1294 | 1.412 | 20 |
| $C_{60}F_{54}$ (see [c]) | FCC | $17.60 \pm 0.15$ | | 4 | 1363 | 2.128 | 24 |
| $C_{60}F_{53}$ (see [b]) | FCC | 17.21 | | 4 | 1274 | 2.252 | 25 |
| $C_{60}F_{48}$ | FCC | 17.27 | | 4 | 1288 | 2.105 | 47 |
| $C_{60}F_{40}$ (see [d]) | BCT-40% | 11.85 | 19.28 | 2 | 1354 | – | 19, 51 |
| | FCC-60% | 16.677 | | 4 | 1160 | – | 19, 51 |
| $C_{60}F_{46}$ (see [d]) | FCC | 17.158(3) | | 4 | 1263 | 2.096 | 46 |
| $C_{60}F_{48}$ (see [d]) | BCT | 11.852(8) | 17.91(1) | 2 | 1258 | 2.155 | 46 |
| | FCT | 16.75 | 17.9 | 4 | 1256 | 2.096 | 46 |
| $C_{60}F_{48}$ (see [d]) | BCT | 11.859(3) | 17.83(2) | 2 | 1254 | 2.162 | 52 |
| $C_{60}F_{46}$ (see [d]) | FCC | 17.24(1) | | 4 | 1281 | 2.116 | 52 |
| $C_{60}F_{48}$ (see [d]) | orthorhombic | 12.06(3) [e] | 12.21(4) | 1 | 1398 | 1.939 | 53 |

**Note**. The following designations are used: FCC is face-centred cubic lattice, BCT is body-centred tetragonal lattice, and FCT is face-centred tetragonal lattice; [a] $d_{calc} = M/(VN_A)$, where *M* is molecular mass, *V* is the cell volume, $N_A$ is the Avogadro number; [b] composition was determined by photoelectron X-ray spectroscopy; [c] composition was determined from the weight gain; [d] composition corresponds to the most intense peak in the mass spectrum; [e] lattice parameter *b* is equal to 37.97(8) Å.

It was found [46] that at room temperature, $C_{60}F_{48}$ has a body-centred tetragonal cell with the parameters $a = 11.852(8)$ and $c = 17.91(1)$ Å. It was assumed previously [53] that the $C_{60}F_{48}$ structure can be described by an orthorhombic cell (see Table 6). Comparison of X-ray diffraction data for fluorofullerene samples with different molecular compositions (Fig. 10) shows that, where a mixture of fluorofullerenes with averaged composition is concerned, the crystal structure corresponds to an FCC lattice similar to that of $C_{60}$, whereas the $C_{60}F_{48}$ fullerene has a body-centred tetragonal lattice.

## 4. NMR spectroscopy

**$^{19}$F NMR of solutions**. The NMR method was first employed to study the products of fullerene fluorination back in 1991.[17] The $^{19}$F NMR spectra of solutions of fluorofullerenes in acetone or tetrahydrofuran exhibit singlet peaks with chemical shifts of $-150.5$ and $-152.7$ ppm. It was suggested [17] that either one or both peaks were due to the $C_{60}F_{60}$ molecule in which all fluorine atoms are equivalent. However, the mass spectra of these samples did not show the presence of $C_{60}F_{60}$.

Some $^{19}$F NMR spectra had a signal at $-188$ ppm, due to the hydrogen fluoride resulting from the reactions of fluorides with the residual water in acetone.[17] It has been found [54] that the integral intensity of the $^{19}$F NMR signal of the fluoride ion in THF depends on the amount of water in THF.

Kniaz *et al.*[19] have employed the $^{19}$F NMR method to study acetone solutions of the product of fluorination of $C_{60}$, the product of its sublimation at 300 °C and the non-volatile residue after sublimation. The $^{19}$F NMR spectra thus obtained were identical to those reported in the study cited above.[17] Analysis of the initial fluorofullerene by mass spectroscopy showed that the intensity of the peak due to the $C_{60}F_{60}$ molecule was $10^5$ times lower than that of the most intense peak, which corresponded to the $C_{60}F_{40}$ molecule. After sublimation, the mass spectra of neither the sublimate nor the residue exhibited signals for $C_{60}F_n$, where $n \geqslant 50$. The researchers explained this outcome by assuming that less stable, higher fluorofullerenes were destroyed during sublimation to give $F_2$ or $CF_4$. It was found that the NMR signal intensity passes through a maximum (corresponding to the composition $C_{60}F_{36}$) as fullerene gets saturated with fluorine. Hence, the signal at $-149$ ppm could belong to yet another highly symmetrical molecule, $C_{60}F_{36}$.

The $^{19}$F NMR spectrum of a THF solution of fluorofullerene (prepared [17] by direct fluorination of $C_{60}$) studied by Boltalina *et al.*[55] looked like those reported previously.[17, 19, 54] Unlike earlier studies, in this study, the solution was analysed by mass spectroscopy. The spectra contained intense peaks in the region of small masses (which were not identified) but no signals corresponding to fluorofullerenes. This outcome may be due to the chemical interaction of fluorofullerene with the solvent; this would account for the fact that the data obtained by NMR spectroscopy for solutions of fluorofullerenes in THF or acetone do not agree with the data obtained by other methods which do not require dissolution of samples.

The line occurring at $\sim -150$ ppm in the $^{19}$F NMR spectrum of a THF or acetone solution of fluorofullerenes can apparently be attributed to the product of decomposition of fluorofullerenes accompanied not only by the loss of fluorine but also by destruction of the carbon skeleton. The composition of the products of reactions between THF or acetone and fluorofullerenes $C_{60}F_x$ has not yet been identified. To eliminate the influence of solvents, NMR studies of solid samples should be carried out.

**$^{19}$F NMR of solid samples**. Static $^{19}$F NMR spectra of solid $C_{60}F_n$ fluorofullerenes have been reported.[24, 25] The spectra consist of one broad line with $\delta$ $-153$ ppm and the half-width $\Delta\nu_{1/2} = 60-120$ ppm (Fig. 11). The $\delta$ values observed in the NMR spectra of a black sample (the mass spectrum of which exhibited ions corresponding to $C_{60}$, $C_{70}$ and low-fluorine fluorofullerenes) and of a pale-yellow sample consisting mainly of fluorofullerenes were identical. The NMR spectra differed only in the $\Delta\nu_{1/2}$ value, which was 115 ppm for the pale-yellow sample and 140 ppm for the black one. Fluorination of $C_{60}$ with molecular fluorine for two weeks at room temperature gave a light-brown fluorofullerene, which was then sublimed at 150 °C. The $^{19}$F NMR spectrum of this sample exhibited a narrow peak at $-155$ ppm with $\Delta\nu_{1/2} = 8$ ppm. It was suggested [25] that this peak width corresponded to highly symmetrical molecules such as $C_{60}F_{60}$ or $C_{60}F_{36}$. The spectra of some fluorofullerene samples sublimed at 110 °C and 150 °C had an additional signal with $\delta = -133$ ppm; this was attributed to the presence of oxyfluorides $C_{60}F_{60-2y}O_y$. Unfortunately, the researchers did not investigate the composition of the samples; therefore, the reliability of the conclusions drawn cannot be judged.

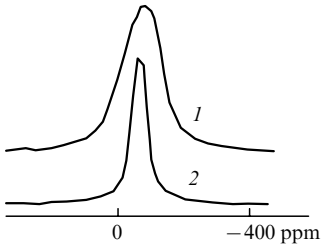



**Figure 11.** $^{19}$F NMR spectrum (relative to $CF_3CO_2H$) of solid samples of $C_{60}F_n$ fluorofullerenes at 20 (*1*) and 300 °C (*2*).[35, 36]

**$^{13}$C NMR**. A solid sample having $C_{60}F_{46}$ as the major component (according to the data of mass spectroscopy) was studied by $^{13}$C NMR.[41] The technique of $^{13}C-{}^{19}F$ polarisation exchange showed that the sample was a mixture of compounds differing from one another in molecular motion parameters. For one of the components characterised by fast molecular re-orientations (similar to those observed in plastic crystals), the ratio of the $sp^2 : sp^3$ resonance lines was found to be 14 : 46, *i.e.* it complied with the stoichiometry $C_{60}F_{46}$, determined from the mass spectroscopy data. The resonance lines of the $sp^2$-hybridised carbon atoms occurred in the region of 140.0 – 142.5 ppm, while those of $sp^3$ carbon were manifested at 86 – 90 ppm. However, in addition to the lines assigned to $C_{60}F_{46}$, the $^{13}$C NMR spectrum exhibited a broad band at 118 ppm having $\Delta\nu_{1/2} = 40$ ppm and an intensity of 20±10% of the total peak intensity. The dynamics of cross-polarisation of this line indicated that the other component of the sample comprises molecules immobile in the solid phase.

## 5. Molecular structure of $C_{60}F_{48}$

Experimental data on the structure of $C_{60}F_{48}$ were first obtained by Gakh *et al.*[30] Mass-spectroscopic analysis of the specimen they studied (the procedure of the synthesis is described in Section II.3) showed that the intensity of the ion derived from the $C_{60}F_{48}$ molecule amounted to 69% of the total intensity of ions derived from $C_{60}F_{2n}$ ($2n \leqslant 48$). The $^{19}$F NMR spectrum of a solution of this sample in the $CFCl_3 - CDCl_3$ mixture exhibited eight main lines with equal intensities (Fig. 12). It was found [30] that this spectrum can be attributed to 14 isomers of $C_{60}F_{48}$ including optical isomers which contain eight groups of equivalent fluorine atoms. Using $^{19}$F (COSY) homonuclear correlation spectroscopy, a two-dimensional spectrum of $C_{60}F_{48}$ was recorded,[30] in which the cross-peaks were due to the spin – spin scalar interactions of the fluorine nuclei in the system. Based on this spectrum, the molecular structure of the fluorofullerene shown in Fig. 13 *a* was proposed. The use of homonuclear two-dimensional $^{19}F-{}^{19}F$ COSY spectroscopy for $C_{60}F_{48}$ [31] revealed additional cross-peaks, which were consistent with the proposed structure.[30] Note that Boltalina *et al.*[31] fluorinated a fullerene extract ($C_{60} : C_{70} = 3 : 1$) and, according to mass spectrometry, the fluorination product contained up to 30% of $C_{70}F_x$ ($x = 44-56$) and traces of fluorinated higher fullerenes ($C_{76}F_y$ and $C_{84}F_z$). However, these impurities barely influenced the NMR spectral pattern.

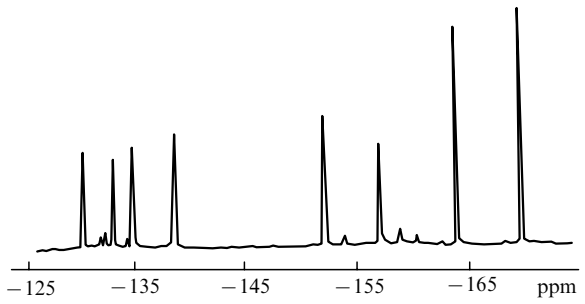



**Figure 12.** $^{19}$F NMR spectrum of a solution of $C_{60}F_{48}$ in the $CFCl_3-CDCl_3$ system.[30]

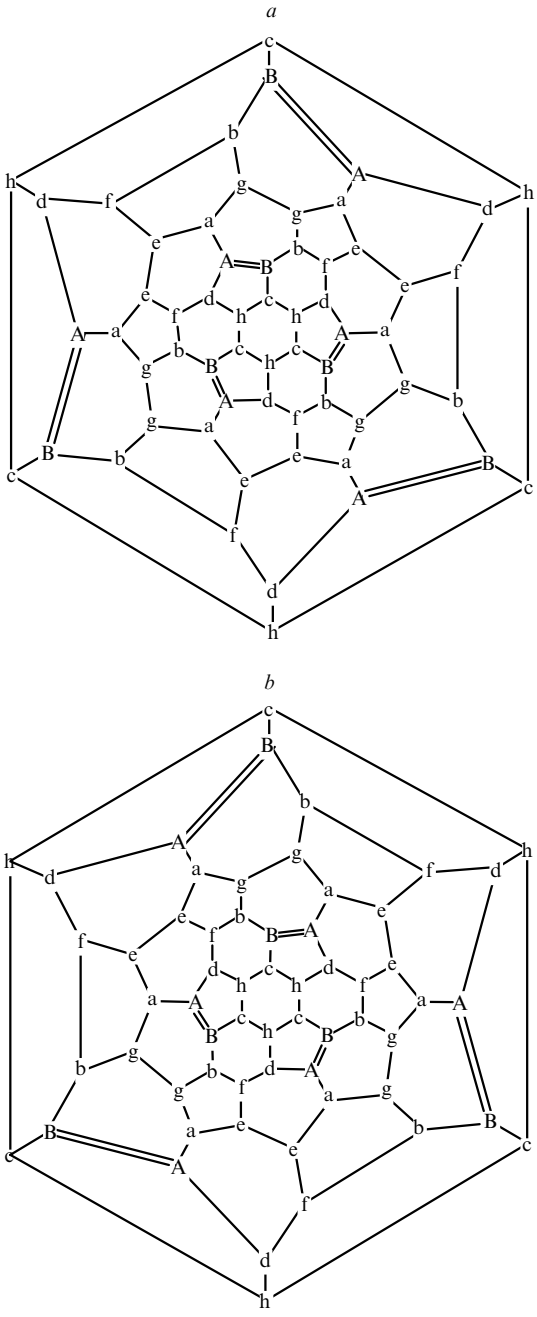



**Figure 13.** Schlegel diagrams for optical isomers of the $C_{60}F_{48}$ molecule with $D_3$ symmetry (*a*)[30] and with $S_6$ symmetry (*b*).[35,36] The atoms equivalent in symmetry are denoted by the same characters, (*a*–*f*) for F atoms and A and B for C atoms.

Semi-empirical quantum-mechanical calculations for the relative stability of nine isomers of $C_{60}F_{48}$, namely, five chiral pairs with $D_3$ symmetry and four meso forms with $S_6$ symmetry, have shown[35] that two of these isomers, namely, those presented in Fig. 13, are more stable than any other isomer by at least 175 kJ mol$^{-1}$. In addition, the difference between the energies of formation of these isomers is negligibly small and amounts to 2 kJ mol$^{-1}$. In view of the size of the molecular system in question and the degree of uncertainty inherent in semi-empirical methods, these isomers can be regarded isoenergetic. The double bonds in them are located only at the edges shared by pentagons and hexagons in the carbon cage (see Fig. 13). The presence of a double bond at an edge shared by two hexagons increases the energy of formation of $C_{60}F_{48}$ by 174.7 kJ mol$^{-1}$. Conjugation of double bonds is a destabilising factor, which increases the $\Delta_f H$ value by 500 kJ mol$^{-1}$ with respect to that of the most stable isomer.

Since the shape of fluorofullerene molecules is nearly spherical, it would be natural to expect molecular mobility in the crystalline phase similar to that observed for $C_{60}$ fullerene.[10] Figure 14 presents the variation of the static $^{19}$F NMR spectra of fluorofullerenes *vs*. temperature. These data (Fig. 14 *a*) indicate that, as the temperature decreases to 320 K and below, the velocity of re-orientation of the $C_{60}F_{48}$ molecules in the fluorofullerene crystal lattice smoothly decreases, and at temperatures below 260 K, the rotational re-orientation of molecules stops on the NMR time scale, the spectrum exhibiting one broad line with $\Delta\nu_{1/2}$ = 40 000 Hz. At temperatures above 320 K, the $C_{60}F_{48}$ molecules rotate isotropically, the velocity of rotation being sufficient for observing the fine structure in the signals of the two groups of fluorine atoms in fluorofullerene molecules.[56]

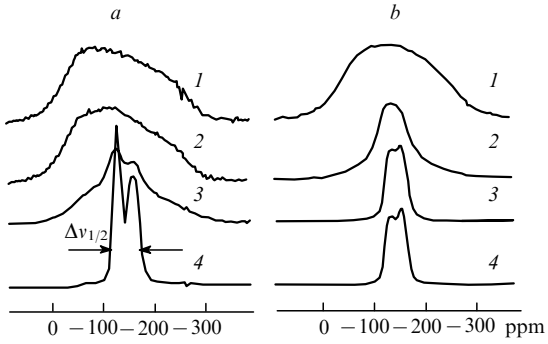



**Figure 14.** Variation of the static $^{19}$F NMR spectrum of crystalline $C_{60}F_{48}$ (*a*) and $C_{60}F_{46}$ (*b*) fluorofullerenes as a function of temperature /K: (*1*) 200, (*2*) 260, (*3*) 300, (*4*) 340.

The high-resolution $^{19}$F NMR spectrum of a polycrystalline sample of $C_{60}F_{48}$ consists of eight lines with equal intensities, which correspond to eight groups of magnetically non-equivalent fluorine atoms in the $C_{60}F_{48}$ molecule. It should be noted that the chemical shifts of these lines[56] virtually coincide with the chemical shifts observed in the $^{19}$F NMR spectrum recorded for a solution of $C_{60}F_{48}$ in $CDCl_3$.[30] Thus, the crystal lattice does not exert significant influence, compared to the influence of the solvent, on the $^{19}$F chemical shifts of $C_{60}F_{48}$. The four groups of low-intensity lines (< 10% of the total intensity of peaks) observed in the spectra of both solutions and solid samples can apparently be assigned to $C_{60}F_{2n}$ impurities ($2n < 48$) or to other $C_{60}F_{48}$ isomers.

The high-resolution $^{13}$C NMR spectra of a $C_{60}F_{48}$ sample exhibit two equally intense lines in the region of signals corresponding to $sp^2$ carbon atoms, pointing to the presence in the $C_{60}F_{48}$ molecule of two magnetically non-equivalent groups of carbon atoms not attached to fluorine atoms.[56] In accordance with the $^{19}$F NMR spectrum, the region of signals of the $sp^3$

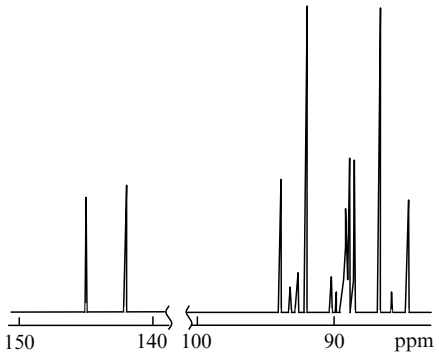



**Figure 15.** $^{13}C$ NMR $\{^{1}H, ^{19}F\}$ spectrum of a solution of $C_{60}F_{48}$ in $CDCl_3$ (recorded by Prof. T Ono, Japan).

carbon nuclei should contain eight peaks corresponding to eight magnetically nonequivalent groups of carbon atoms attached to fluorine atoms. However, the spectral pattern was fairly complex because each of the eight expected lines was split due to the scalar $^{13}C-^{19}F$ spin–spin interaction. The complex multiplet was resolved by using equipment for C–F decoupling (Fig. 15). It is worth noting that $^{13}C$ NMR data obtained by other investigators [41] only pointed out the presence of non-resolved broad bands in the regions of $sp^2$ and $sp^3$ carbon signals.

Thus, the compound $C_{60}F_{48}$ has been studied comprehensively by NMR spectroscopy; it was found that the isomeric purity of this compound prepared by direct fluorination of $C_{60}$ reaches 90%, which is a startling result if one recalls that tens of thousands geometrical isomers of $C_{60}F_{48}$ can theoretically exist. To elucidate the molecular structure more precisely (to choose between the most probable structures, $D_3$ and $S_6$), experimental and theoretical data of IR and Raman spectroscopy and crystallography should be resorted to. Additional experiments are needed including the synthesis of $C_{60}F_{48}$ with an endohedral $^{3}He$ atom and subsequent analysis of the chemical shifts in the $^{3}He$ NMR spectra.

## IV. Chemical properties of fluorofullerenes

Fluorocarbon polymers such as Teflon are known to be exceptionally chemically inert, being able to react slowly only with liquid sodium metal. This is due to the great strength of the C–F bond (460–540 kJ mol$^{-1}$), the non-polar character of this bond and the rigidity of carbon chains covered by a shell of fluorine atoms. A similar type of behaviour could have been expected of fluorofullerenes. However, fluorofullerenes were found to exhibit oxidative properties. A typical feature of fluorinated fullerene derivatives is high reactivity. Strong repulsion of fluorine atoms from one another is supposed to be the driving force of reactions. The C–F bond length in fluorofullerenes is 1.49 Å;[23] for comparison, this bond length in aliphatic fluorocarbons is 1.38 Å.[4] Correspondingly, the energy of the C–F bond in fluorofullerenes is 150–250 kJ mol$^{-1}$ lower than that in aliphatic fluorocarbons. According to both kinetic and thermodynamic factors, fluorofullerenes have lost the intertness of the C–F bond, typical of fluorocarbons; fluorine can be transferred to electron-saturated compounds and electrons can be captured from some reagents such as benzene.

The chemical properties of fluorofullerenes have been poorly studied yet. This is due to several reasons, namely, inaccessibility of macroscopic quantities of the compounds and the difficulty of the analysis of the reaction products (*i.e.* the formation of mixtures of compounds with closely similar properties).

It has been reported [57] that highly fluorinated fluorofullerenes enter into a number of oxidative reactions (with sodium iodide or isopropanol) and into fluorination reactions (with aromatic compounds in the presence of Lewis acids). Mixing a solution of a $C_{60}F_{44}-C_{60}F_{46}$ fluorofullerene mixture with 0.1 M NaI in acetone results in immediate evolution of iodine; after keeping the mixture for several hours at room temperature, a black precipitate is formed. Analysis of the reaction solution by mass spectroscopy shows the presence of fluorofullerenes with a fluorine content lower than that in the initial sample.

$$C_{60}F_n + NaI \longrightarrow I_2 + C_{60}F_m + NaF$$

$n = 44-46$, $m = 36-40$.

It was shown that fluorofullerenes react with bromides in a similar way. In the reaction with tetrabutylammonium bromide in chloroform, immediate evolution of bromine was observed.

The reaction with isopropanol proceeding on prolonged heating (85 °C) afforded 1.6 moles of acetone per mole of fluorofullerene.

$$C_{60}F_n + Me_2CH(OH) \longrightarrow Me_2CO + C_{60}F_m + HF$$

$n = 44-46$, $m = 36-40$.

The reaction of fluorofullerenes with benzene in the presence of $BF_3 \cdot Et_2O$ was studied. Mass-spectroscopic analysis of the reaction mixture, the colour of which slowly changed from yellow to brown, indicated the formation of fluorobenzene and the presence of fluorofullerenes with lower mass numbers. It was noted that degradation of fluorofullerenes $C_{60}F_x$ is accelerated as $x$ increases. Some reactions result in the formation of a black resin.

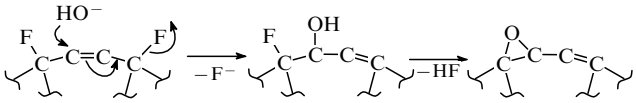
$$C_{60}F_n + PhH \longrightarrow PhF + C_{60}F_m + HF.$$

$n = 44-46$, $m = 36-42$.

It should be noted that even pyridine, which is well known to be inert towards electrophilic substitution, does react slowly with higher fluorofullerenes at elevated temperatures giving rise to 2-fluoropyridine (the yield reaches 10%).

Unfortunately, it cannot be understood from the results obtained what is the mechanism of these reactions, whether it is ionic (fluorine transfer) or radical (electron transfer). On the one hand, the predominant formation of biphenyl in the reaction of fluorofullerene with phenyllithium supports the radical mechanism, while, on the other hand, fluorination of pyridine is a typical ionic process (by analogy with the well known reactions of pyridine with other electrophilic fluorinating agents).

In one of the first publications dealing with fullerene fluorination,[58] it was noted that fluorination products tend to enter into a nucleophilic substitution reaction, namely, the $OH^-$ anion reacts with a double bond in fluorofullerene, then HF is eliminated and fluorofullerene oxide is produced.




As noted above, detailed investigation of the chemical properties of fluorofullerenes is possible only provided that individual compounds are available and their molecular structures and the degrees of purity are known. In the last two years, certain progress has been attained along this line. In particular, the isolation of pure $C_{60}F_{18}$ and of its oxo derivative $C_{60}F_{18}O$ are worthy of note.[59,60] An example of chemical transformation of individual fluorofullerenes is the reaction of $C_{60}F_{18}$ with benzene in the presence of $FeCl_3$, known as the Friedel–Crafts reaction, which resulted in the synthesis of $C_{60}F_{15}Ph_3$, called 'triumphene'.[61]

## V. Thermodynamic studies of the fluorofullerene $C_{60}F_{48}$

The thermodynamic properties of $C_{60}F_{48}$ known to date are summarised in Table 7.

The low-temperature heat capacity of $C_{60}F_{48}$ in the temperature range from 8 to 356 K was measured by adiabatic calorimetry.[62,65] These data were used to calculate the numerical values of

**Table 7**. Thermodynamic characteristics of $C_{60}F_{48}$.

| Characteristic | Value | Ref. |
|---|---|---|
| $C_{p,m}(298.15)$ /J K$^{-1}$ mol$^{-1}$ | $1365.2 \pm 2.7$ | 62 |
| $H^\circ_m(298.15) - H^\circ_m(0)$ /kJ mol$^{-1}$ | $192.48 \pm 0.83$ | 62 |
| $S^\circ_m(298.15) - S^\circ_m(0)$ /J K$^{-1}$ mol$^{-1}$ | $1137.2 \pm 5.7$ | 62 |
| $G^\circ_m(298.15) - H^\circ_m(0)$ /kJ mol$^{-1}$ | $146.6 \pm 2.9$ | 62 |
| $\Delta_f S^\circ_m(298.15)$ /J K$^{-1}$ mol$^{-1}$ | $-4071.6 \pm 5.8$ | 62 |
| $\Delta_s H^\circ_m(476)$ /kJ mol$^{-1}$ | $109 \pm 7$ | 63 |
| $\Delta_f H^\circ_m$(cryst.) /kJ mol$^{-1}$ | $-7563 \pm 166$ | 64 |
| $\Delta_f H^\circ_m$(gas) /kJ mol$^{-1}$ | $-7454 \pm 166$ | 64 |

the thermodynamic functions $H^\circ(T) - H^\circ(0)$, $S^\circ(T) - S^\circ(0)$ and $G^\circ(T) - H^\circ(0)$. The curve for the variation of the specific heat capacity of $C_{60}F_{48}$ as a function of temperature, presented in Fig. 16 displays a phase transition in the temperature range of 315–345 K ($T_{tr}$ = 329.6±0.4 K and $\Delta_{tr}H$ = 7.0±0.7 kJ mol$^{-1}$). According to NMR and X-ray diffraction data, this transition is due to the transformation of the ordered body-centred tetragonal phase into a face-centred cubic plastic phase.

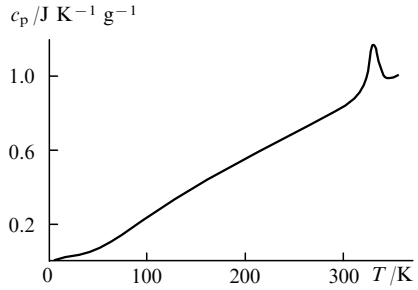



**Figure 16.** Specific heat capacity of $C_{60}F_{48}$ *vs.* temperature.[56]

The partial pressures of $C_{60}F_{48}$ have been measured in the temperature range of 395–557 K by high-temperature mass spectroscopy using $PbI_2$ and $C_{60}F_{36}$ as internal standards.[63] The researchers suggested calculating the partial pressures (in Pa) using the equation

$$\ln[p(C_{60}F_{48})] = -\frac{13\,146}{T} + 24.34.$$

The enthalpy of sublimation of $C_{60}F_{48}$ (see Table 7) calculated using the second law of thermodynamics is lower by 66 kJ mol$^{-1}$ than the enthalpy of sublimation of $C_{60}$ (175±3 kJ mol$^{-1}$), which is due to the smaller energy of intermolecular interactions in the fluorofullerene.

The energy of combustion of $C_{60}F_{48}$ for burning in a rotating bomb calorimeter (−24 638±163 kJ mol$^{-1}$) and the standard molar enthalpy of formation of $C_{60}F_{48}$ in the crystalline state have been determined [64] (see Table 7).

In 1992, the $\Delta_f H^\circ_m$(gas) values for $C_{60}F_{48}$ were estimated by semi-empirical MNDO and AM1 methods.[66] The values found for $C_{60}F_{48}$ isomers formed upon the addition of fluorine atoms to $C_{60}$ with and without rupture of the C–C bonds in the carbon cage were −7395 and −5508 kJ mol$^{-1}$, respectively. The former value is close to the enthalpy of formation found experimentally; however, in view of the molecular structure of fluorofullerene $C_{60}F_{48}$ now established (see Section IV), which rules out the presence of $=CF_2$ groups in the molecule, this appears to be an accidental coincidence.

The energy of the C–F bond in $C_{60}F_{48}$ calculated from experimental data [64] proved to be 36% lower than that in $CF_4$ (Fig. 17). The reason is elongation of the C–F bonds in $C_{60}F_{48}$ with respect to those in tetrafluoromethane, difluoroethane or difluorofullerene due to steric factors.

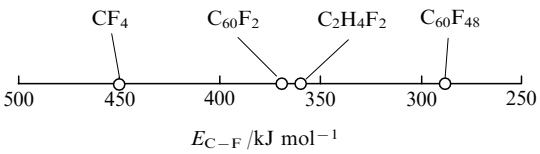



**Figure 17.** Energy of the C–F bond in some fluorocarbons.

## VI. Conclusion

In conclusion, we would like to mention some lines of investigation into direct fluorination of fullerenes which appeared recently and are, in our opinion, the most interesting and promising. In the near future, the search for the routes of the selective synthesis of fluorofullerenes, especially those with low fluorine contents (less than 36 fluorine atoms per fullerene molecule) would be continued. As shown above, no convincing evidence supporting the assumption that low-fluorine compounds can form in substantial amounts in the reaction of $F_2$ with fullerene can be found in the literature. Indirect data indicate that these compounds could be prepared by liquid-phase fluorination; however, exhaustive spectroscopic investigation of the reaction products is still to be performed.

Recent studies of Chilingarov *et al.*[28,67] in which fullerene mixed with transition metal difluorides is treated with molecular fluorine at elevated temperatures deserve attention. The use of transition metal difluorides as catalysts restricts substantially both the number of the products formed and the degree of saturation of fullerene molecules with fluorine. Nevertheless, it is still unclear whether this method would prove more efficient than the known solid-phase reactions involving trifluorides of metals of the first transition row.

Development of methods for purification and separation of fluorination products would remain among the most topical tasks. Attempts of using various methods for the separation of fluorofullerene mixtures resulting from direct fluorination have been reported in the literature. In particular, a technique used fairly often for this purpose is sublimation. However, these attempts have not yet been a success because the properties of compounds with close contents of fluorine (36 to 48 fluorine atoms per fullerene molecule) are close. Nevertheless, a series of recent publications dealing with chromatographic separation of several fluorofullerenes, their oxidised forms and even fluorofullerene isomers prepared by reactions with metal fluorides demonstrated high efficiency of this method as applied to the given class of compound.[68,69] The most impressive example is isolation of > 40 individual compounds from a $C_{70}F_x$ sample prepared by the reaction of $C_{70}$ with $MnF_3$. Among these 40 compounds, seven isomers of $C_{70}F_{36}$ alone were present.[70]

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