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Chemical Fragmentation of $C_{60}F_{48}$

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Complex mixtures of fused alicyclic fluorocarbons C_nF_m ($n = 16-30$, $m = 30-50$) were obtained during extensive fluorination of C_{60} beyond $C_{60}F_{48}$ using elemental fluorine at elevated temperatures (275−325 °C). Analysis of these fluorocarbon mixtures (performed by GC-MS and NMR) demonstrated that the distribution of individual fluorocarbons in these mixtures is not random. A plausible computational model of the chemical fragmentation process was developed.

1. Introduction

We have reported previously that attempts to fluorinate C_{60} beyond $C_{60}F_{48}$ with elemental fluorine employing UV irradiation resulted in rupture of the C_{60} framework with the formation of "hyperfluorinated" species.[1] Extensive fluorination of C_{60} at elevated temperatures has also been shown to lead to skeletal fragmentation with the formation of complex mixtures of fluorocarbons,[2,3] presumably via transient formation of $C_{60}F_{48}$. Cage-opened compounds have been detected in the products of fluorination of C_{60} by KrF_2 in liquid HF.[4] Here we report the results of destructive fluorination of C_{60} with F_2 as well as a plausible model of the fragmentation process.

2. Results and Discussion

Chemical fragmentation of transient $C_{60}F_{48}$ with elemental fluorine starts at temperatures above 275 °C and proceeds more rapidly at 300 °C and higher. At 300−325 °C the fluorination can be completed in 6−7 days (see Experimental Section). The DL/meso ratio of two principal $C_{60}F_{48}$ isomers[5] remains practically unchanged during the fluorination, indicating that fragmentation processes of DL and meso $C_{60}F_{48}$ proceed with comparable speeds. A typical ^{19}F NMR spectrum of residual $C_{60}F_{48}$ isolated at the midpoint of the reaction (2 days, 300 °C) is presented in Figure 1.

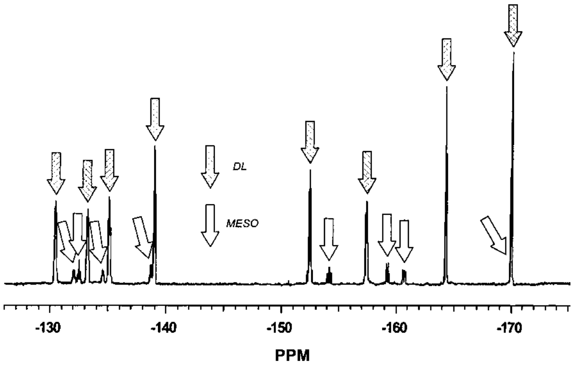

Figure 1. ^{19}F NMR spectrum of remaining $C_{60}F_{48}$ after 2 days of fluorination at 300 °C. Arrows indicate signals corresponding to the two major isomers of $C_{60}F_{48}$: meso (minor) and DL (major).

Fluorocarbon mixtures produced by extensive fluorination of C_{60} are colorless, transparent glasslike materials without odor and are relatively nonvolatile. They can be sublimed at elevated temperatures (>250 °C) which facilitates separation from $C_{60}F_{48}$ due to the differences in volatility. These fluorocarbon mixtures are very soluble in $CFCl_3$ and C_6F_6, but practically insoluble in most other common solvents. We observed only partial solubility in $CDCl_3$ (used to run solution ^{19}F NMR spectra). The solubility can be improved by adding small amounts of $CFCl_3$ to $CDCl_3$ or by heating the NMR samples to 50−60 °C.

^{19}F NMR spectra of the fluorocarbon mixtures produced from extensive fluorination of C_{60} display features typical of fluorocarbon mixtures. Thus, fluorine spectra consist of two very broad peaks (−205 to −170 ppm, CF and −160 to −110 ppm, CF_2) and one relatively sharp peak (−81 ppm, CF_3). Integration of these spectral regions indicated the approximate ratio 3 CF: 5 CF_2: 0.2 CF_3 or ∼37% CF, ∼61% CF_2, and ∼2% CF_3 based on total fluorinated-carbon content. A similar result was found for the fluorination of other carbon-rich materials under similar conditions.[6]

Additional NMR analysis of the fluorocarbon mixtures was performed using solid state ^{19}F-^{13}C CP/MAS ^{13}C NMR spectroscopy.[7] That spectrum consists of two broad, partially resolved bands centered at 96 and 116 ppm, corresponding to CF and CF_2 resonances, respectively. Integration indicated the approximate elemental formula $[(CF)_2(CF_2)_3]_n$, assuming that the fluorine atoms in CF- and CF_2 groups have similar relaxation characteristics. CF_3 groups were not detected by this method due to the low signal-to-noise ratio.

The elementary composition of fragmentation products was further elucidated by GC-MS performed using the electron capture (EC) ionization mode. EC was chosen because perfluorocarbons (PFCs) have high electron affinities and easily produce negative ions. In addition, EC is "softer" than electron ionization (EI), i.e., it results in significantly less fragmentation within the mass spectrometer. It therefore allows observation

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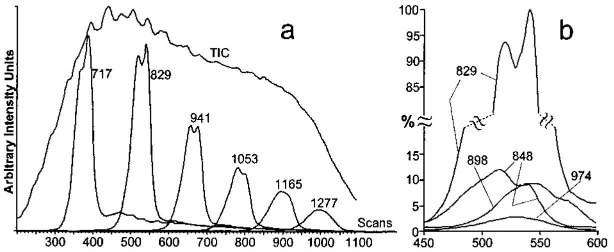


Figure 2. (a) Total ion current and selected single-ion chromatograms of the fluorocarbon mixture produced by extensive fluorination of C_{60} for 7 days at 300−325 °C. The *m*/*z* values of the selected ions are shown for each trace. (b) Expanded traces of the *m*/*z* 829 ion and of selected odd-electron species which coelute from the gas chromatograph. The latter are possible molecular anion precursors to the *m*/*z* 829 fragment. Note that the middle 60% of the *y*-axis has been omitted to better display the traces.

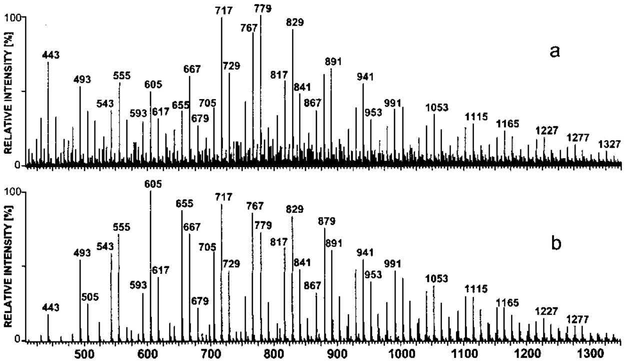
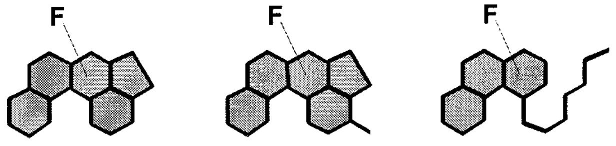


Figure 3. (a) Cumulative mass-spectrum of the fluorocarbon mixture produced by extensive fluorination of C_{60} for 7 days at 300−325 °C. (b) Simulated mass spectrum produced by applying the FORTRAN program described in the text.

of intact molecular anions ($M^{\bullet}$), whereas molecular cations ($M^{\bullet+}$) are seldom seen in EI spectra of this class of compound.[4]

For a typical GC−MS run, the total ion current and selected single-ion chromatograms are displayed in Figure 2a. Examination of individual spectra from this run indicated that the fluorocarbon mixture is composed of thousands of individual compounds which elute sequentially (but with strong overlap) from the gas chromatograph. However, the distribution of the individual products in these mixtures is not random. Figure 3a shows the cumulative spectrum of the GC−MS run from which peaks were chosen for presentation in Figure 2a. Thus, fragment peaks with *m*/*z* 717, 829, 941, etc. are distinctively salient, probably indicating that the corresponding molecular anions from which they were generated exist in greater relative abundance than other components of the mixture.

The possible "parent" molecular anions to these salient fragments can be inferred by searching for those higher mass, odd electron (i.e., even-numbered *m*/*z* value) signals in the spectrum which coelute with the fragment in question. Figure 2b shows an expanded section of 2a, with the single-ion traces of three even-numbered molecular anions, each of which may be contributing to the formation of the salient *m*/*z* 829 fragment. Thus, *m*/*z* 829 could be generated by loss of 19 Da ($F^{\bullet}$) from *m*/*z* 848, by loss of 69 Da ($CF_3^{\bullet}$) from 898, or by loss of 145 Da (CF_7; e.g., $CF_3^{\bullet} + 2F_2$) from 974. These three precursor-ion candidates have the elementary compositions $C_{20}F_{32}$, $C_{21}F_{34}$, and $C_{21}F_{38}$, respectively. While coelution is a necessary condition to establish the precursor/fragment relationship, it is not of itself a sufficient condition. In the absence of tandem mass spectrometry experiments, it cannot be established with certainty which (if any) of these precursor candidates are in fact contributing substantially to the *m*/*z* 829 signal in Figure 3a.



1 ($C_{20}F_{32}$) **2** ($C_{21}F_{34}$) **3** ($C_{21}F_{38}$)

Figure 4. Chemical structures of some $C_{20}F_{32}$, $C_{21}F_{34}$, and $C_{21}F_{38}$ isomers.

TABLE 1: Relative Signal Intensities Observed in the ^{19}F NMR Spectrum of the PFC Mixture and Those Expected from Structures 1, 2, and 3, Expressed as Percent of Total CF_x Signal

	observed	expected		
		1	2	3
CF	36.6	40.0	42.8	23.8
CF_2	61.0	60.0	52.4	71.4
CF_3	2.4	0.0	4.8	4.8

Detailed examination of the structural features associated with these candidates, and comparison with the NMR results discussed above, give some insight into which of them are more important. Drawings **1**−**3** (Figure 4) represent possible structures of the three precursor candidates whose single-ion traces are depicted in Figure 2b. Obviously, there are many other possible structures for each of the elementary compositions, but they must all comply with certain criteria, based on their origin. Thus, all viable alternatives to **1** must contain five rings ($C_{20}F_{32}$ demands five double bond equivalents, and survival of olefinic bonds is improbable given the reaction conditions). Furthermore, those rings must be arranged in a manner compatible with the C_{60} cage structure which was their origin.

Using these structures, the expected NMR integrated intensities for CF-, CF_2-, and CF_3 signals can be assessed, as in Table 1. Note that a 1:1 mixture of **1** and **2** produces nearly the correct proportions of CF, CF_2, and CF_3, whereas allowable isomers to structure **3** must *always* contain at least one CF_3 group, thus making the CF_3 content at least twice that observed in the ^{19}F NMR spectrum. The CF_2:CF ratio for **3** is also substantially different from the observed one. Rearranging the rings and the chain of **3** can bring the CF_2:CF ratio into compliance with the observed value, but only at the expense of making the CF_3 content even larger. Therefore, a combination of structures **1** and **2** (and their allowable isomers) seems to best fit the observed experimental GC-MS and NMR data. Structure **3** and its isomers are excluded as significant contributors to the *m*/*z* 829 fragment ion.

Generalizing the above discussion (which focused on the *m*/*z* 829 peak only), extensive fluorination of C_{60} seems to produce a mixture of relatively compact perfluorinated, fused polycyclic structures with few (and short) appended aliphatic chains. The observed carbon numbers range from 10 to 34 and the ring numbers from 2 to 9 (see Figure 3a). The fragments observed in the EC mass spectra represent predominantly loss of $F^{\bullet}$ and $CF_3^{\bullet}$ from the molecular anions. Such fragmentations in the EC spectra of cyclic PFCs are well documented.[8−11]

Having established that the chemical degradation of C_{60} under the influence of F_2 is not an entirely random process, the question of reaction mechanism arises. A simple suggestion for the mechanism entails a scissors-like "cutting" of the buckyball cage starting after the $C_{60}F_{48}$ level of fluorination, i.e., that level at which rupture is known to be initiated.[1] A cage with one of

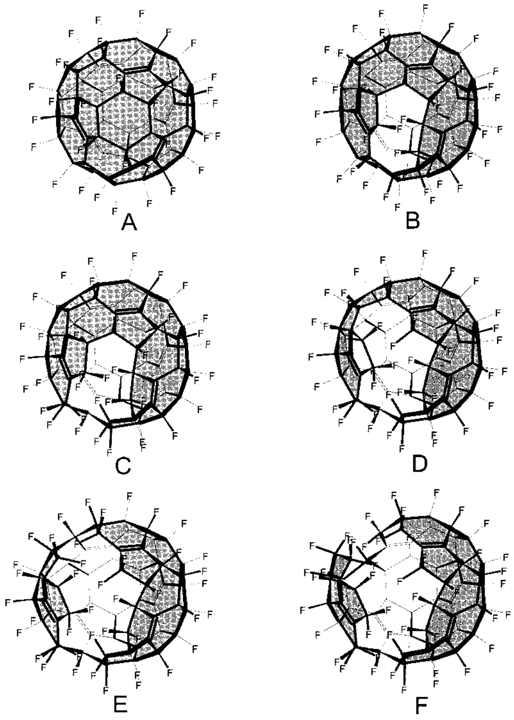


Figure 5. Proposed mechanism for the scissors-like rupture of the fullerene skeleton during extensive fluorination of C_{60} at elevated temperature. **A** ($C_{60}F_{48}$), **B** ($C_{60}F_{50}$), **C** ($C_{60}F_{52}$), **D** ($C_{60}F_{54}$), **E** ($C_{60}F_{56}$), and **F** ($C_{60}F_{58}$) represent successive phases of this "cracking" process.

the original C−C bonds broken will present weak spots along the periphery of the newly created macrocycle because the fluorines added at the ends of the now broken bond will exacerbate the already severe steric crowding. Under continued fluorination the "crack" will propagate by sequential fission of weakened bonds until a piece of the carbon skeleton is broken off. This becomes one of the fused cyclic structures that comprise the product mixture. An example of the proposed sequence of events is presented in Figure 5. In this figure structures **A** ($C_{60}F_{48}$), **B** ($C_{60}F_{50}$), **C** ($C_{60}F_{52}$), **D** ($C_{60}F_{54}$), **E** ($C_{60}F_{56}$), and **F** ($C_{60}F_{58}$) represent initial phases of this "cracking" process, leading finally to the formation of a "broken" piece **L** ($C_{20}F_{30}$, not shown).

To evaluate this hypothesis, we wrote a FORTRAN program to model the fragmentation process. It is known that skeletal rupture of the fullerene cage begins to occur after the $C_{60}F_{48}$ level of fluorination.[1] The computer model of the fragmentation process was developed under the assumption that the initial point of $C_{60}F_{50}$ framework rupture is random, but that subsequent bond dissolutions occur sequentially on the periphery of the macrocycle created by the previous C−C bond cleavages. Some directions of "crack" propagation are preferred, depending upon the perceived level of strain on each of the macrocycle bonds. Once expansion of the macrocycle has proceeded to the point where two pieces are separated, remaining polycyclic moieties connected only by an aliphatic chain are also considered separated and a bond in the chain connecting them is broken automatically. Fluorine atoms are added to fill all unoccupied valences of each of the "molecules" generated. Where applicable, a CF_3 group is subtracted to simulate fragmentation within the mass spectrometer.

Mass-dependent material losses are expected during the fluorination process described in the Experimental Section. Highly volatile materials will be swept out of the reaction tube during fluorination. Very nonvolatile materials will not undergo sublimation during the cleanup stage. Both types of reaction product will be lost to subsequent analysis. Therefore, the observed spectrum of recovered material (Figure 3a) is expected to be biased against the true reaction-product mixture at both ends of the spectrum. To simulate these expected real-world losses, the FORTRAN program applies mass dependent quadratic "intensity attenuations" to the generated spectrum.

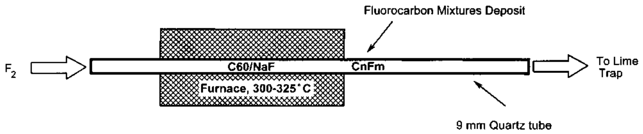


Figure 6. Schematic of an apparatus used for fluorination of C_{60}.

The final output of the program is formatted to produce a simulated mass spectrum which then can be manually compared with the experimental one. The simulated spectrum depicted in Figure 3b is the result of 20 000 passes through the program (i.e., it simulates the degradation of 20 000 $C_{60}F_{48}$ molecules by the proposed mechanism). The model spectrum closely approximates the observed one (Figure 3a), thus lending some credence to the proposed degradation mechanism.

3. Conclusions

In summary, we have demonstrated that C_{60} undergoes chemical fragmentation during extensive high-temperature fluorination via transient formation of $C_{60}F_{48}$ to yield complex mixtures of fused cyclic fluorocarbons C_nF_m, where n=10−34 and the number of rings (i.e., $(2n + 2 - m)/2$) ranges from 2 to 9. The distribution of the individual fluorocarbons in these mixtures is not random and can be simulated using an appropriate fragmentation model.

4. Experimental Section

Warning: Pure elemental fluorine is an extremely reactive and toxic gas. All experiments should be performed in a well-ventilated hood by properly trained personnel. Improper manipulation with 100% fluorine-containing equipment could result in fire, personal injury, or major chemical accident. General information regarding handling of 100% elemental fluorine can be obtain elsewhere.

General. All fluorination experiments were performed in the apparatus depicted in Figure 6. All reagents were obtained from commercial sources and were used as received without further purification. Elemental fluorine (Matheson Co., 10 L cylinder, 400 psi) was also used as received. GC−MS analysis was performed on a Hewlett-Packard 5890 gas chromatograph coupled to a VG-Analytical "ZAB" mass spectrometer (VG-Analytical, Manchester, England). ^{19}F NMR spectra were recorded on a Bruker MSL-400 (376.5 MHz) using a spectral width 332 ppm over 16 000 data points.

Fluorination of C_{60}. C_{60} (53 mg, 0.073 mmol) was mixed with 2.5 g of powdered NaF. The mixture was additionally ground in mortar. The mixture was then placed portion-wise in the center of the 9 mm quartz tube using two glass rods to press each added portions from both sides. The resulting pellet (3−4 cm long) was placed in the middle of the quartz tube and pressed again to be held in place by friction. Using Swagelock connectors the tube was placed between a fluorine/helium line at one end and a sequence of traps (cold, lime, and 5% aq. $NaHCO_3$) at the other. The tube was placed in a furnace and the air was replaced by the slow (3−5 mL/min) flow of helium. The tube was slowly (2−3 h) heated in a flow of helium to the appropriate temperature (250−300 °C) while avoiding quick temperature ramps which could result in cracking the pellet.

After reaching the working temperature, the flow of helium was replaced with a flow of elemental fluorine (1−2 mL/min), and fluorination was continued for 7 days at 300−325 °C. At that time fluorine gas was replaced with helium (2−3 mL/min) and heating was continued for an additional 16−20 h. During that time the heating zone was slowly moved 5−7 cm toward the exhaust end of the tube to allow separation of sublimed volatile perfluorocarbon products from the pellet. After completion of sublimation, oven heating was discontinued and the tube cooled to room temperature within 3−5 h. It is critical at this stage to avoid cracking of the pellet which could result in contamination of the sublimate with unreacted $C_{60}F_{48}$. After cooling, the tube was removed from the apparatus and cut into pieces to separate sublimed materials from the pellet. The sublimate was extracted by $CFCl_3$, the extract filtered from traces of inorganic materials and evaporated to dryness in a flow of He. The remaining glasslike material was dried for 16 h in vacuo at room temperature to remove traces of solvents. The yield of perfluorocarbon mixtures comprised 46 mg.

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Supporting Information Available: Source codes of the FORTRAN program. This material is available free of charge via the Internet at http://pubs.acs.org.

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