J. Am. Chem. Soc. **1993,** *115,* 5885–5886

Hyperfluorination of Buckminsterfullerene: Cracking the Sphere

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Received March 10, 1993

The discovery of techniques for the large-scale preparation of fullerenes[1] has given chemists access to starting materials with previously unobtainable carbon templates. The known chemistry of these hollow carbon molecules is expanding rapidly.[2] However, the chemistry under investigation is limited to those unique carbon cages originally generated in the fullerene synthesis. A simple way to obtain variations on these closed carbon cages, *e.g.*, "bucky-sponges" or "bucky-bowls", might entail controlled isomerization of the fullerene skeleton. Our recent experiments on the fluorination of C_{60} (carried out in pursuit of mass spectrometric confirmation of $C_{60}F_{60}$[3]) led to the observation of hyperfluorinated fullerenes reported here. This observation indicates "cracking" of the C_{60}-skeleton without loss of carbon atoms, *i.e.*, isomerization to yield new carbon-cage configurations.

Previously, mass spectrometry of product mixtures generated by direct fluorination of C_{60} has shown that $C_{60}F_{2n}$, with n = 18–23, are the major products of the reaction.[4,5] Higher degrees of fluorination are also observed, but only at greatly reduced signal intensity. Thus, Chowdhury and Cox have identified $C_{60}F_{58}^{\bullet+}$ and $C_{60}F_{60}^{\bullet+}$ at 0.02% and 0.002% of base intensity, respectively.[6]

By contrast, the mass spectra of samples obtained by passing F_2 gas over a fluorofullerene sample with simultaneous UV irradiation[7] show $C_{60}F_{48}$ to be the major constituent, with reasonably intense peaks for higher degrees of fluorination (Figure 1). The intensity of $C_{60}F_{60}^{\bullet+}$ is ~1.3% of the base peak. More surprisingly, the $C_{60}F_{2n}^{\bullet+}$ series continues well beyond n = 30. This is clearly discernable in the inset of Figure 1. The salient $C_{60}F_{2n}^{\bullet+}$ peaks are real, as attested by their signal/noise ratios (≥2 in all cases) and the intensity of the ^{13}C-isotope peaks (70–80% *vs* 66% theoretical). To our knowledge, this is the first report of substituted fullerenes with a larger number of substituents than the formal number of surface valences available.

The relatively high noise level observed in the inset of Figure 1 is peak-at-every-mass *chemical noise* which waxes and wanes in concert with the $C_{60}F_{2n}$ signals as the sample evaporates from the direct exposure sample holder. These "noise" peaks probably constitute fragments of higher molecular weight compounds,[4,5] indicating that even higher degrees of fluorination were attained in the chemical reaction than are apparent in the displayed mass spectra. Salient peaks between the $C_{60}F_{2n}^{\bullet+}$ signals correspond to previously recognized oxygenated species and mass spectral fragments.[5,6,8] Thus, the two most intense peaks between $C_{60}F_{58}$ and $C_{60}F_{60}$ (see Figure 1 inset) appear at m/z 1838 ($C_{60}F_{58}O^{\bullet+}$) and 1848 ($C_{59}F_{60}^{\bullet+}$; probably due to loss of CO from $C_{60}F_{60}O^{\bullet+}$ [5]).

The observation of $C_{60}F_{2n}$ molecular ions with $n > 30$ has significant structural implications. All previous reports of the preparation of highly substituted C_{60} have tacitly assumed that the basic skeletal structure remains intact. This allows up to 60 "free valences" which could, in principle, be occupied by 60 substituents, one at each carbon. "Persubstitution" of buckminsterfullerene implies 60 substituents on the intact skeleton and no π-bonds. "Hypersubstitution" of C_{60} (*i.e.*, more than 60 substituents, as observed in Figure 1), *requires* dissolution of some of the skeletal σ-bonds. The combined intensity of peaks ascribable to hyperfluorinated products (*i.e.*, $C_{60}F_{2n}^{\bullet+}$; $n > 30$) observed in Figure 1 is estimated to be 1.2–1.5% of the sum of all $C_{60}F_{2n}^{\bullet+}$ intensities.

While it is certain that the peaks above $C_{60}F_{60}$ in Figure 1 represent transformed C_{60} skeletons, peaks below that point need not necessarily represent the intact skeleton exclusively.[9] The smooth transition between that section of the spectrum where skeletal disruption *may* exist (*i.e.*, below $C_{60}F_{62}$) and that section where it *must* exist (*i.e.*, above $C_{60}F_{60}$) implies that the transition occurs at a lower degree of fluorination, perhaps signaled by the abrupt intensity decline after $C_{60}F_{48}$. Of course, any of the peaks may encompass isomeric mixtures of different skeletal structures. Tandem mass spectrometry may assist in structure analysis of individual mixture components, if structure-specific fragmentations can be identified.[10] This possibility is being explored.

The reaction mechanism of skeletal disruption (cracking) is unclear. It may occur through addition of photochemically generated fluorine radicals to an already strained fluorinated fullerene system, with the added strain leading to cracking. Calculations have shown that persubstitution of the intact skeleton is unlikely to occur, due to the steric interaction.[11] Alternately, photochemical isomerization of $C_{60}F_{2n}$ may generate "cracked-sphere" isomers which have fewer rings and more double bonds than the "intact-sphere" isomers, thus making them amenable to further fluorination without introducing significant additional steric strain. Dixon has calculated that one such isomer of $C_{60}F_{48}$[12] is 451 kcal/mol more stable than its "intact" symmetrical counterpart.[11] The possibility of photochemical isomerization of $C_{60}F_{48}$ leading to the hyperfluorinated products described here is attractive, not only because of the greater thermodynamic stability of the rearranged product but also because it correlates with the presumed transition point from the intact to the cracked fullerene cage, as suggested by Figure 1 and discussed previously.

Further investigation of this reaction and its unusual hyper-

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[7] Pure C_{60} (100 mg) was mixed with NaF (7.0 g), placed in a quartz tube, and dried at 150 °C in a flow of N_2. The N_2 flow was replaced with one of pure F_2 (1 mL/min), and the tube was heated at 250 ± 5 °C for 14 h, to give a $CFCl_3$-soluble product (185 mg). A portion of this product (50 mg) was further fluorinated for 24 h in a quartz tube at 85 °C with pure F_2 and simultaneous UV irradiation (500-W Hanovia medium-pressure lamp), affording the final product (43 mg).

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[9] A recent report of C_{60} skeletal rupture with the incorporation of only two substituents is based on the reaction of C_{60} with singlet oxygen: Talliani, C.; Ruani, G.; Zamboni, R.; Danieli, R.; Rossini, S.; Denisov, V. N.; Burlakov, V. M.; Negri, F.; Orlandi, G.; Zerbetto, F. *J. Chem. Soc., Chem. Commun.* **1993**, 220.

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[12] The isomer in question is spherical and contains eight benzene rings (each fluorinated at the 1, 3, and 5 positions) which are connected by CF_2-bridges at the 2, 4, and 6 positions. Thus, the isomer has 24 double bonds and 8 six-membered and 6 sixteen-membered rings. The intact buckminsterfullerene skeleton has 12 five-membered and 20 six-membered rings and 6 double bonds for $C_{60}F_{48}$.

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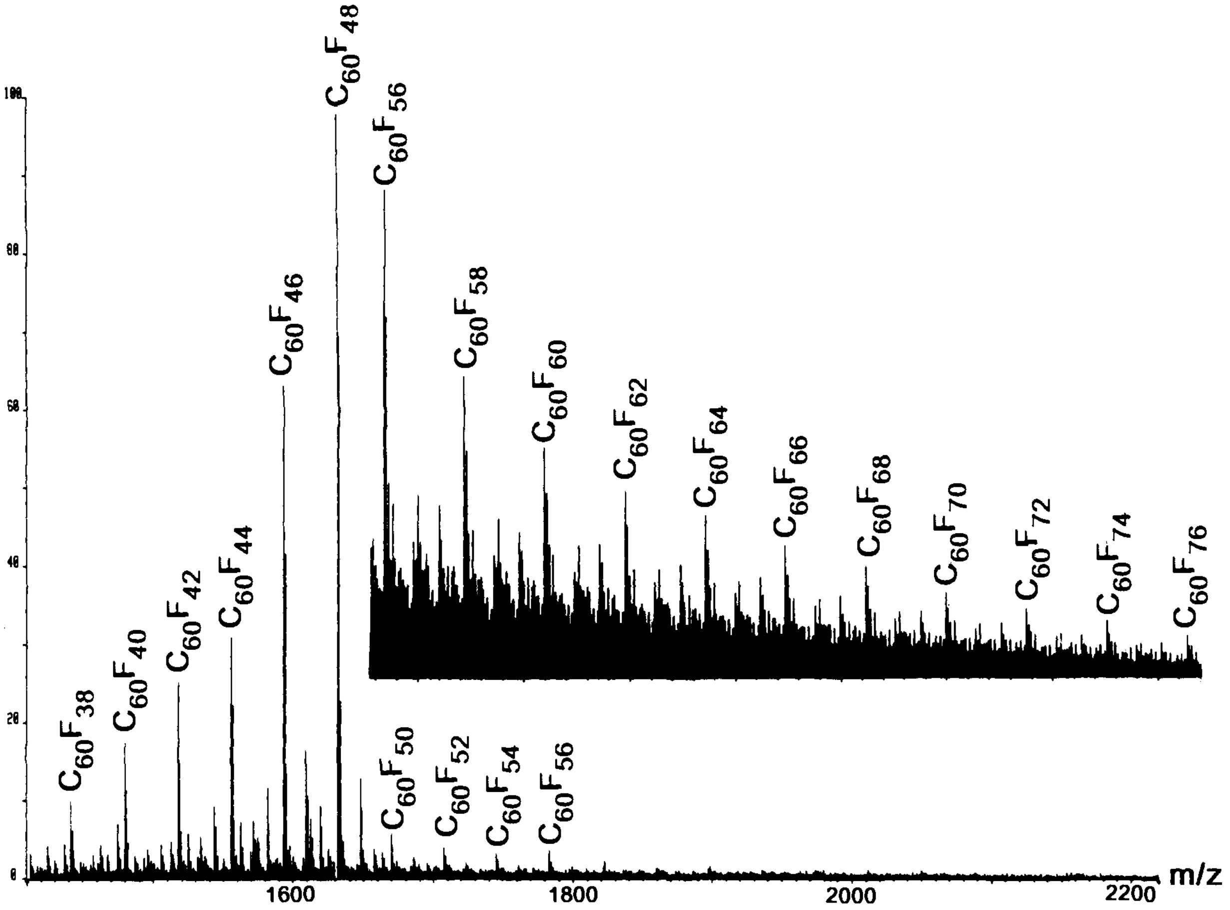

Figure 1. Electron ionization mass spectra of material obtained by passing fluorine gas over a previously fluorinated C_{60} sample for 24 h while irradiating both with a medium-pressure mercury-arc lamp. The inset is a multichannel acquisition[5] used to obtain more reliable relative intensities for the weaker region of the spectrum. The intensity of $C_{60}F_{60}^{\bullet+}$ is ~1.3% that of $C_{60}F_{48}$.

fluorinated fullerene products will establish whether practical applications exist, *e.g.*, preparative access to novel cage skeletons via the "standard" fullerenes.

Note Added in Proof: Based on experiments conducted subsequent to submission of this manuscript, it seems less likely that hyperfluorination proceeds via the intermediacy of the $C_{60}F_{48}$ isomer described in ref 12. Thus, electron capture mass spectra of hyperfluorinated C_{60} spanning a wider mass range (to *m/z* 3000) showed $C_{60}F_{2n}$ peaks with continuously decreasing intensity up to $C_{60}F_{102}$. Significantly there was no intensity increase at $C_{60}F_{96}$, as would be expected if the eight benzene rings of that "cracked" $C_{60}F_{48}$ isomer had been fluorinated.

Also, collision-induced dissociation spectra of $C_{60}F_{46}$, $C_{60}F_{48}$, $C_{60}F_{50}$, and $C_{60}F_{52}$ are essentially identical to that previously observed for $C_{60}F_{44}$.[5] If $C_{60}F_{50}$ and $C_{60}F_{52}$ had structures incorporating benzene rings connected by CF_2 groups (as the structure described in ref 12 does) the CID spectra would be expected to display enhanced loss of C_6F_x, C_7F_x, and C_8F_x fragments, which they do not.

Acknowledgment. This publication is based upon work performed through the ORNL Director's Research Development Program and research sponsored by the Office of Health and Environmental Research, U.S. Department of Energy under contract No. DE-AC0584OR21400 with Martin Marietta Energy Systems. The UTK Chemistry Mass Spectrometry Center is funded by the Science Alliance, a State of Tennessee Center of Excellence.