Pergamon

Tetrahedron Letters 42 (2001) 7137–7139

TETRAHEDRON
LETTERS

'Fluorine dance' on the fullerene surface

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Received 30 July 2001; accepted 9 August 2001

Abstract—A facile fluorine migration process ('fluorine dance') leads to the formation of the most thermodynamically stable isomers during the high temperature fluorination of [60]fullerene. © 2001 Elsevier Science Ltd. All rights reserved.

The high temperature fluorination of C_{60} with elemental fluorine leads predominantly to the formation of two (out of $>10^7$ possible) closely related isomers of $C_{60}F_{48}$.[1a] The major isomer is an enantiomer pair (the DL-form) of D_3 symmetry, and the minor isomer is achiral (the *meso*-form) exhibiting S_6 symmetry.[1a–c] Because elemental fluorine reactions are usually non-regioselective, the high degree of product selectivity in this case is remarkable, and has not thus far been adequately explained. Here we report new experimental data that demonstrate a facile migration of fluorine atoms ('fluorine dance') on the fullerene surface during the reaction. This 'fluorine dance' results in the formation of the equilibrated mixture of the most thermodynamically stable isomers.

$C_{60}F_{48}$ is not the only fluoro[60]fullerene that can be produced selectively by high temperature fluorination of C_{60}. Using appropriate solid fluorinating agents, one isomer of $C_{60}F_{18}$ (using K_2PtF_6) and a mixture of several $C_{60}F_{36}$ isomers (using MnF_3) have been selectively synthesized.[2a–f] The structure of $C_{60}F_{18}$ has been unambiguously established by single-crystal X-ray,[2a] and that of the major C_3 isomer of $C_{60}F_{36}$ is discussed in detail in the previous communication.[2f] Interestingly, the known structures of $C_{60}F_{18}$ and the major C_3 isomer of $C_{60}F_{36}$ are 'incompatible' with that of *meso*/DL $C_{60}F_{48}$, i.e. the highest fluorinated species cannot be derived by simple addition of fluorine molecules over the residual double bonds of either of the lower fluorinated ones.[1a,2a,2f,3]

Two possible explanations can account for this observation: the known 'lower' fluoro[60]fullerenes are not intermediates in the formation of 'higher' ones; or rearrangements of fluorine atoms occur during the high temperature fluorination. The possibility of such rearrangements has been suggested in the past, but then abandoned in later publications.[2d,4] If no fluorine migration occurs during the reaction, then further fluorination of $C_{60}F_{36}$ should yield novel isomers of $C_{60}F_{48}$. Given these structural constrains, and prompted by our interest in the synthesis of new fluoro[60]fullerenes, we investigated the high temperature fluorination of $C_{60}F_{36}$ isomers.

The reaction[5] did not produce novel isomers of $C_{60}F_{48}$. Instead, the ^{19}F NMR spectra of $C_{60}F_{48}$ samples result-

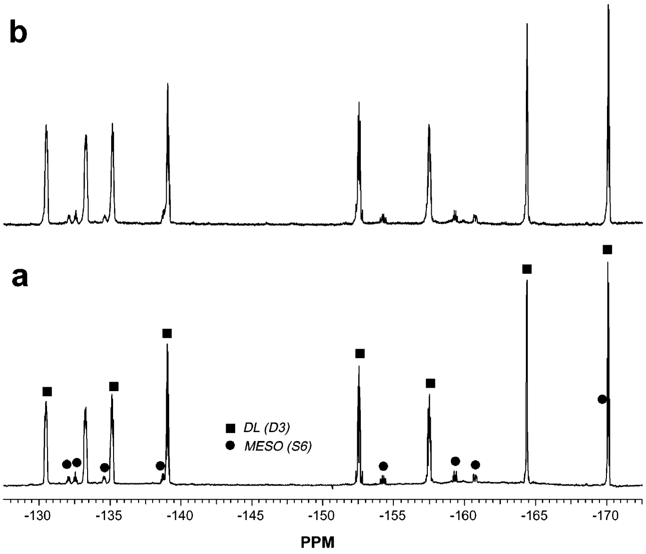

Figure 1. ^{19}F NMR spectra ($CDCl_3$) of DL/*meso* $C_{60}F_{48}$ produced by fluorination of C_{60} (a) and $C_{60}F_{36}$ (b).

Keywords: C_{60}; fluorination; halogen dance; $C_{60}F_{48}$.

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PII: S0040-4039(01)01475-7

ing from the fluorination of C_{60} and $C_{60}F_{36}$ under identical conditions were essentially indistinguishable (Fig. 1). Repeated experiments performed in different fluorination systems (to rule out accidental cross-contamination of $C_{60}F_{48}$ samples) produced the same results. Moreover, fluorination of $C_{60}F_{16–42}$ mixtures (produced by incomplete fluorination of C_{60} with either F_2 or XeF_2) led to identical $C_{60}F_{48}$ samples. These observations point to a rapid fluorine migration on the [60]fullerene surface during fluorination, resulting in formation of the equilibrated mixture of the thermodynamically most stable $C_{60}F_{48}$ isomers, regardless of the composition of the starting material(s). As expected for a thermodynamically controlled process, the selectivity of the fluorination process (measured as the *meso*/DL ratio) decreases with increasing temperature, from 10–12% at 275°C to 14–16% at 300°C. Below 250°C, the samples of $C_{60}F_{48}$ were contaminated with less fluorinated products. Above 320°C, the yield was negatively affected by chemical fragmentation.[1b]

The existing literature implies that the fluorine dance is probably applicable for other highly fluorinated fullerenes, such as $C_{60}F_{36}$. Similar to $C_{60}F_{48}$, the synthesis of $C_{60}F_{36}$ yields a mixture of the most thermodynamically stable isomers with a ratio of major C_3 and minor T isomers compatible with the calculated thermodynamic stabilities.[6a–c] In addition, there is a note in the literature[2d] that C_3 $C_{60}F_{36}$ can be prepared from C_{3v} $C_{60}F_{18}$, which is only possible via migration of fluorine atoms.[3]

The migration of halogen atoms other than fluorine (commonly referred to as 'halogen dance' in the literature) is frequently observed in reactions of iodine-, bromine-, and, to some extent, chloro-aromatic compounds.[7a–e] Halogen dance in aliphatic systems is also documented, but these examples are relatively rare.[7f] In contrast, fluorine migration is a much less common phenomenon presumably due to the strength of the carbon–fluorine bond (470 kJ/mol compared to 350 for C–Cl, 290 for C–Br and 230 for C–I).[8a] The migration typically involves high-energy intermediates such as cations, carbenes and radicals, or excited molecules (photochemical reactions).[8b–k] The presence of double bonds and aromatic rings seems to facilitate this process. Both 1,3-sigmatropic and 1,5-sigmatropic shifts and fluoride ion-promoted migration mechanisms are also discussed in the literature.[8a,9b]

Thermal rearrangements in perfluorocyclohexenes involving fluorine migration were first reported more than 50 years ago.[9a] Typically, they require high temperatures (500–550°C) and in many cases involve a catalytic source of fluoride ions.[9b] The major differences between those reactions and the fluorine dance on the fullerene surface are the high yield (above 70%) and the high specificity (two isomers out of $>10^7$ possibilities) at relatively low temperatures (275–300°C) in the latter case.

The fluorine dance phenomena allows accurate prediction of the structures of the 'higher' fluoro[60]fullerenes based on calculations at the AM1 level, since the initial fluorination pattern is irrelevant, and the most thermodynamically stable isomers are the ones actually produced. In fact, all known isomers of $C_{60}F_{48}$ and $C_{60}F_{36}$, and even their relative abundances were accurately predicted using such calculations.[6b,c] Although structure/stability relationships in higher fluoro[60]fullerenes are complicated due to significant distortion of the carbon framework, and can only be dissected by proper computational methods, there are simple structural similarities between major $C_{60}F_{36}$ and $C_{60}F_{48}$ isomers. In each, isolated double bonds are distributed in such a way as to maximise the number of pentagons that have a double bond on the edge. This similarity provides the basis for a trivial explanation of the 'magic' fluorination numbers 36 and 48. The parent [60]fullerene has 12 five-member rings. In $C_{60}F_{36}$ each of the 12 pentagons has one double (or aromatic) bond (12 in total). In $C_{60}F_{48}$ only a half of the pentagons have double bonds (six in total). The observed distribution of double bonds in $C_{60}F_{36}$ and $C_{60}F_{48}$ could be further attributed to greater repulsions experienced by fluorines on fullerene pentagons compared with those on hexagons. The 'fluorine density' (number of fluorines per unit area) in a fully fluorinated five-member ring is higher by ~26% than that in a fully fluorinated six-member ring (the area of an equilateral polygon being equal to $ns^2/(4\tan(180/n))$, where n = number of sides; s = length of side). This simple model proved to be useful for initial-guess purposes.[1a,6c]

Examination of CPK models of $C_{60}F_{48}$ and $C_{60}F_{36}$ (Fig. 2) further shows why steric interactions play a dominant role in determining relative thermodynamic stabilities of the isomers. Both molecules, but especially $C_{60}F_{48}$, are crowded due to multiple interactions between fluorine atoms.[1c,10a,b] For $C_{60}F_{48}$, experimental and theoretical data indicate very short non-bonded distances between fluorine atoms (an average 2.2 Å compared to typical 2.9 Å).[1c,10b–d]

The specific structural features of highly fluorinated fullerenes outlined above are believed to be largely responsible for the ease of fluorine migration in these compounds. Due to their carbon-cage framework, both $C_{60}F_{36}$ and $C_{60}F_{48}$ are thermally stable and easily withstand prolonged heating at 300°C without degradation. At the same time carbon–fluorine bonds are relatively weak,[10e] which facilitates fluorine migration. The presence of residual double bonds (and benzene rings in

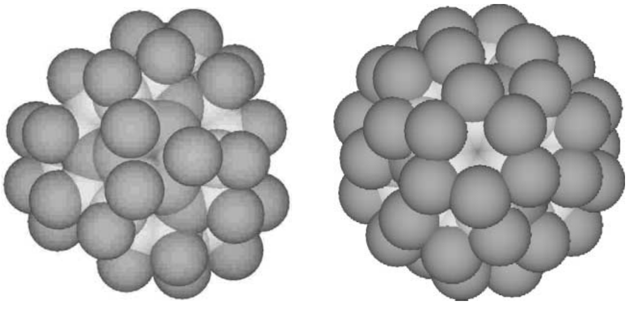

Figure 2. CPK models of C_3 $C_{60}F_{36}$ (left) and D_3 $C_{60}F_{48}$ (right).

$C_{60}F_{36}$) could also be a contributing factor for the fluorine dance process.[8a]

In summary, we discovered a facile fluorine migration process—the 'fluorine dance'—accompanying high temperature fluorination of C_{60} (or $C_{60}F_{36}$) and leading to DL/*meso* $C_{60}F_{48}$. This discovery provides a rational basis for understanding the unusual regioselectivity of this reaction. The possibility of a fluorine dance in other fluoro[60]fullerenes is also explored.

Acknowledgements

The research was sponsored by the IPP program, US Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

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