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Evidence for the S_N2' mechanism in hydrolysis of $C_{60}F_{48}$: origin of the stability of trannulenes

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The products of hydrolysis of $C_{60}F_{48}$ (which contains six isolated double bonds) by either aq. acetone or aq. THF show that no more than twelve fluorines are replaced through nucleophilic substitution, as predicted by the recently identified S_N2' mechanism. Subsequent HF elimination gives fragments containing a maximum of six epoxide oxygens. Calculated heats of formation of models for the possible initial hydroxy derivatives indicate that there is little energetic discrimination between them, so that a complex mixture is likely to be formed. Overall the data show that hydrolytic degradation of fluorofullerenes is less severe than believed previously, requires a specific motif, and explains the low susceptibility of $C_{60}F_{18}$ towards hydrolysis and the high stability of trannulenes.

Introduction

In the presence of a co-solvent, fluorofullerenes react readily with water (nucleophilic substitution),[1] the co-solvent being necessary because the fluorofullerenes are hydrophobic. The mechanism of the substitution has, until very recently, been uncertain, though an S_N2' mechanism was conjectured at an early stage.[2,3] A puzzling feature had been the fact that although some fluorines in fluorofullerenes are clearly replaced by OH groups, only a few fluorines appear to react.[4] Surprising too was the apparent stability of $C_{60}F_{18}$ towards moisture, and the high stability of trannulenes.[5]

The answer to this mechanistic conundrum was provided recently by the discovery that both the C_3 and C_1 isomers of $C_{60}F_{36}$, but not the *T* isomer, readily undergo hydrolysis to form isomers of $C_{60}F_{35}OH$ (Figs. 1 and 2). Moreover, the structural characterisation of these latter showed that both are formed by S_N2' substitution, and that the essential motif for the nucleophilic substitution is the presence of at least one fluorine adjacent to the end of an isolated double bond (where OH attack occurs), with at least one fluorine (which becomes eliminated) adjacent to the other end; the reaction will take place faster if two fluorines are adjacent to the attack site.[6] This is illustrated in Fig. 3.

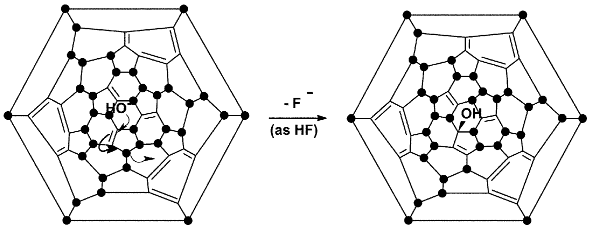

Fig. 1 S_N2' mechanism for the conversion of $C_3C_{60}F_{36}$ into a C_1 isomer of $C_{60}F_{35}$; ● = F.

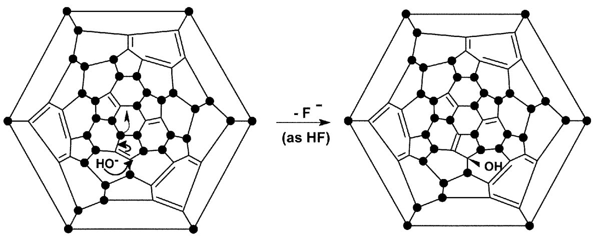

Fig. 2 S_N2' mechanism for the conversion of $C_1C_{60}F_{36}$ into a C_1 isomer of $C_{60}F_{35}OH$; ● = F.

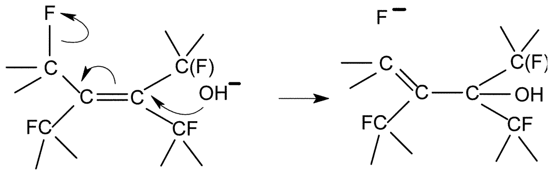

Fig. 3 Motif required for substitution of F by OH in fluorofullerenes; the fluorine in parentheses is not essential but increases the substitution rate.

The possible practical applications of fluorofullerenes, stimulated us into examining the generality of our conjecture that the motif in Fig. 3 is the factor that determined their stabilities or otherwise. As a first step we decided to investigate the stability of $C_{60}F_{48}$ which exists as three isomers, two enantiomers (*RR* and *SS*) and a *meso* form, each of which contains six such motifs;[7] the *RR* isomer is shown in Fig. 4.

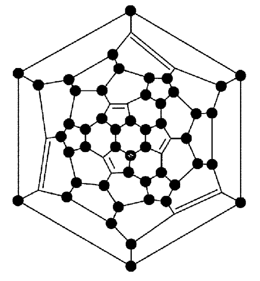

Fig. 4 The *RR* isomer of $C_{60}F_{48}$; ● = F.

It follows that $C_{60}F_{48}$ should readily undergo hydrolysis and that a maximum of six fluorines should be replaced through hydrolysis and we now show that this is the case. A consequence of the hydrolysis is that a fluorofullenol is produced initially, but this undergoes HF elimination to give an epoxide. Thus ultimately an oxygen is incorporated for every two fluorines that are lost, and from the number of oxygens present the original fluorine site occupancy can be determined (1 × O = 2 × F).

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Experimental

A sample of $C_{60}F_{48}$[7] (2 mg) was added to water, but no reaction ensued because of the hydrophobic nature of the fluorofullerene. Acetone was then added, whence solution was immediate. The mixture was left to stand for a few hours, concentrated to dryness, dissolved in toluene and examined by EI mass spectrometry. The crude mixture was subjected to HPLC (high pressure liquid chromatography) using a 10 × 250 mm Cosmosil Buckyprep column with toluene elution at a flow rate of 4.7 ml min^{-1}. Fractions were collected at 2.4–4.5 min, 5.9–6.5 min, 7.5 min and 9–11 min.

A further sample was also reacted with aq. THF, a mass spectrum being run on the crude product only.

Results and discussion

(a) Reaction with aqueous acetone

Mass spectra (EI, 70 eV, DCI probe with increasing probe temperature) were run on the crude product. Figs. 5 and 6 are the scans obtained with probe temperatures of *ca.* 250 and 400 °C, respectively; the former shows peaks with masses up to 1528 amu, whilst the latter reveals more of the less volatile, less fluorinated species. It is notable in particular in showing $C_{60}F_{18}O$ (1078 amu) and $C_{60}F_{18}O_2$ (1094 amu) as the ions of highest intensity. This feature duplicates the results obtained in an earlier hydrolysis experiment that involved a wide-ranging mixture of fluorinated [60]fullerenes, and provided in 1993, the very first indication of the existence of $C_{60}F_{18}$.[2] The dominance of this species from two very different starting materials clearly reflects the high stability of $C_{60}F_{18}$ and its oxide derivatives.

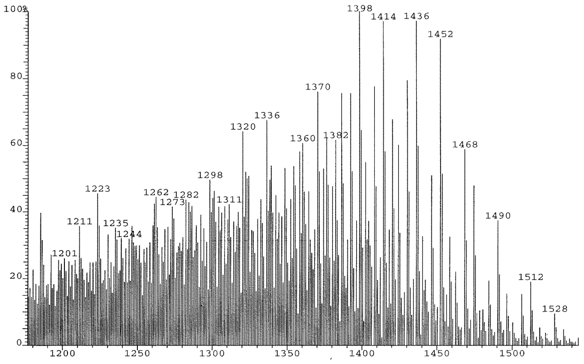


Fig. 5 EI mass spectrum (70 eV) of the $C_{60}F_{48}$ hydrolysis product; probe temp. *ca.* 250 °C.

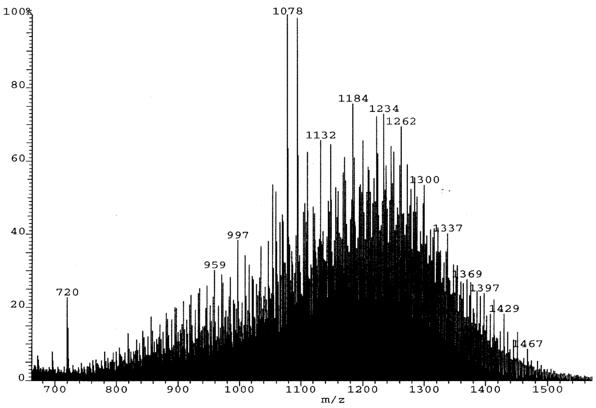


Fig. 6 EI mass spectrum (70 eV) of the $C_{60}F_{48}$ hydrolysis product; probe temp. *ca.* 400 °C.

Table 1 Species identified (EI mass spectrometry, probe temp. 250 °C) in hydrolysed $C_{60}F_{48}$ and the overall site occupancy

Group	Species	N^a	Mass	Species	N^a
1534	$C_{60}F_{42}O$	44	1430	$C_{60}F_{34}O_4$	42
1528	$C_{60}F_{40}O_3$	46	1424	$\mathbf{C_{60}F_{32}O_6}$	44
1518	$C_{60}F_{42}$	42	1420	$C_{60}F_{36}O$	38
1512	$C_{60}F_{40}O_2$	44	1418	$C_{60}F_{35}O.OH$	38
1506	$C_{60}F_{38}O_4$	46	1414	$C_{60}F_{34}O_3$	40
1500	$\mathbf{C_{60}F_{36}O_6}$	48	1408	$C_{60}F_{32}O_5$	42
1496	$C_{60}F_{40}O$	42	1404	$C_{60}F_{36}$	36
1490	$C_{60}F_{38}O_3$	44	1402	$C_{60}F_{35}OH$	36
1484	$C_{60}F_{36}O_5$	46	1398	$C_{60}F_{34}O_2$	38
1480	$C_{60}F_{40}$	40	1392	$C_{60}F_{32}O_4$	40
1474	$C_{60}F_{38}O_2$	42	1386	$\mathbf{C_{60}F_{30}O_6}$	42
1468	$C_{60}F_{36}O_4$	44	1382	$C_{60}F_{34}O$	36
1462	$\mathbf{C_{60}F_{34}O_6}$	46	1376	$C_{60}F_{32}O_3$	38
1458	$C_{60}F_{38}O$	40	1370	$C_{60}F_{30}O_5$	40
1452	$C_{60}F_{36}O_3$	42	1364	$C_{60}F_{33}OH$	34
1446	$C_{60}F_{34}O_5$	44	1360	$C_{60}F_{32}O_2$	36
1442	$C_{60}F_{38}$	38	1336	$C_{60}F_{29}O_3.OH$	36
1440	$C_{60}F_{37}OH$	38	1320	$C_{60}F_{29}O_2.OH$	34
1436	$C_{60}F_{36}O_2$	40			

[a] Site occupancy.

The lower temperature scan is of greater relevance to interpretation of the hydrolysis results, because the more highly fluorinated fullerenes are more volatile. This scan will therefore contain more of the species that have lost less fluorine *via* direct fragmentation as opposed to fluorine loss by hydrolysis. We have therefore collated (Table 1) all the species that are validated by the presence of isotopic lines, and show that no more than six oxygen atoms are present.

Thus it is seen that no more than six oxygens are present arising from the conjectured S_N2' hydrolysis, and these are found in four species (bold in Table 1). One is derived from the original $C_{60}F_{48}$, and three fragments result from normal stepwise F_2 loss. We do not see $C_{60}F_{46}O$, which would be produced by the initial substitution, but fragments *viz* $C_{60}F_{42}O$, $C_{60}F_{40}O$, $C_{60}F_{38}O$, $C_{60}F_{36}O$ and $C_{60}F_{34}O$, are clearly evident. In a few cases the hydroxy fragments obtained prior to subsequent HF elimination can be seen.

In an attempt to isolate some of the components, HPLC separation was carried out and produced four broad fractions (see Experimental section). These however either did not contain single species, or contained components that were very unstable. The main features of the mass spectra for each fraction are as follows:

9–11 Min fraction. The highest mass peak was 1468 amu ($C_{60}F_{36}O_4$), and the most intense peak was $C_{60}F_{26}O_2$ (1246 amu). Other prominent species were $C_{60}F_{28}O_2$ (1284 amu), $C_{60}F_{30}O_2$ (1322 amu), $C_{60}F_{26}O_3$ (1262 amu), $C_{60}F_{30}O_3$ (1300 amu) and $C_{60}F_{32}O_3$ (1338 amu).

7.5 Min fraction. In lower temperature scans of this fraction, hydroxy-containing species were dominant, in particular $C_{60}F_{40}O(OH)_2$ (1530 amu, highest mass component), $C_{60}F_{38}O(OH)_2$ (1492 amu), $C_{60}F_{36}O(OH)_2$ (1454 amu) and $C_{60}F_{35}O_2OH$ (1434 amu); $C_{60}F_{38}O_3$ (1490 amu), and $C_{60}F_{36}O_2$ (1436 amu) were also pronounced.

At higher temperature scans, the most intense peak is for $C_{60}F_{18}O$ (1078 amu) with that for $C_{60}F_{18}O_2$ (1094 amu) being also substantial, as seen for the unprocessed material. They are however, *not* present in the sample prior to mass spectroscopic analysis, because the HPLC retention time is far shorter than the known values under the conditions used, for these compounds.[8] They must therefore be produced by fragmentation of a less stable precursor.

A significant peak in the lower temperature scan is at 790 amu (52%). This has often been seen in the products of fullerene fluorination, and in some cases may be due to $C_{60}CF_3H$, but in the present instance can only be due to $C_{60}F_2O_2$, confirmed by peaks for $C_{60}O$ (736 amu, 100%) and $C_{60}O_2$ (752 amu, 47%).

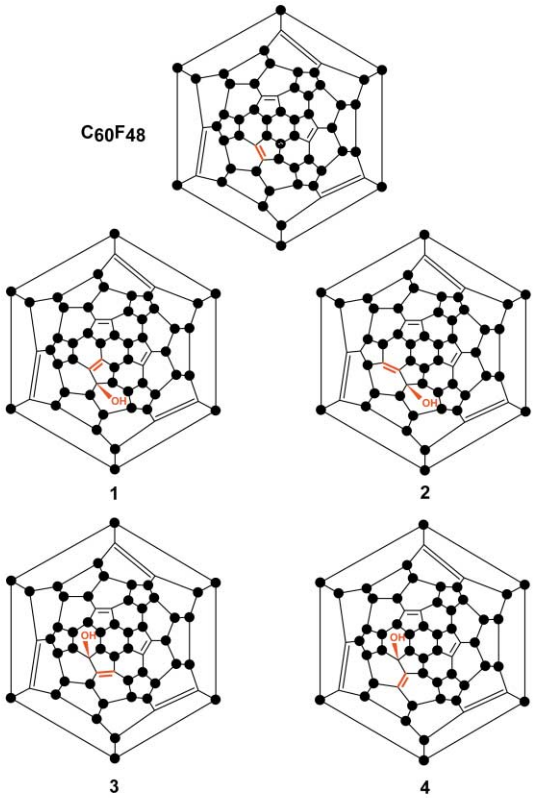


Fig. 7

Evidently $C_{60}F_2O_2$ has a particularly stable structure (as yet unassigned).

5.9–6.5 Min fraction. The highest mass peak is at 1490 amu, and again the 1078/1094 amu peaks are intense as is that for $C_{60}F_2O_2$ (100%) together with $C_{60}O$ (736 amu, 67%) and $C_{60}O_2$ (752 amu, 23%).

(b) Reaction with aqueous THF

A mass spectrum was run on the crude product only. The products were largely similar to those noted above, prominent fragments/species being: $C_{60}F_{38/36/34/32}O_4$ (1506, 1468, 1430, 1392 amu), $C_{60}F_{36/34/32/30}O_5$ (1484, 1446, 1408, 1370 amu), $C_{60}F_{32/30}O_6$ (1424, 1386 amu), $C_{60}F_{35/33}OH$ (1402, 1364 amu).

These results confirm clearly that only six oxygens are introduced into the molecule (*i.e.* twelve fluorines only are replaced) in accordance with the mechanism proposed. The result is significant because it indicates that the 'Achilles heel' of fluorofullerenes with regard to applications, namely the susceptibility to nucleophilic substitution, may not be as severe as believed originally.[1]

Theoretical calculations

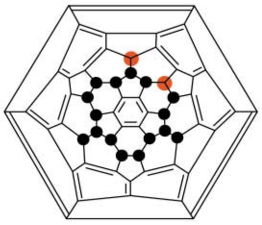
There are six equivalent double bonds in $C_{60}F_{48}$ and the hydroxy group can attack at either end on any one of these, causing elimination of fluorine in two ways at the other end. In order to determine if there is any preference for the initial attack–elimination we have calculated heats of formation (B3LYP/6-31G*) for each of the four possible products. Fig. 7 shows those obtained from attack at one of the six equivalent double bonds in the *RR* isomer. The relative heats of formation (kcal mol^{-1}) for these are: **1**, 3.2; **2**, 9.0; **3**, 3.3; **4**, 0 (• = F). For the RS isomer the corresponding relative values are closely similar. These values predict little discrimination but isomer **4** has a small energetic advantage. These small differences, coupled with the initial presence of three isomers, means that up to twelve hydroxy derivatives are feasible. Consequently, separation and analysis of them would be very difficult especially since they are likely to have similar polarities. Note too that each hydroxy derivative can undergo HF elimination in two different ways.

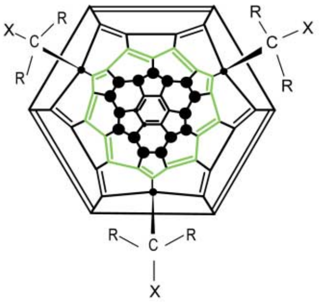
Overall these results provide further clarification of the structural characteristics that lead to hydrolytic degradation of fluorofullerenes, the limits of such degradation, and suggest a greater probability of finding useful applications for fluorofullerenes than at one time envisaged.

Reactivity of $C_{60}F_{18}$ and stability of trannulenes

The substitution pattern of $C_{60}F_{18}$ is now explained by these data. There are only two fluorine positions (red in **6**) that can be substituted according to the principles we describe, and this is found in practise.[5,9]

For trannulenes (*e.g.* **7**), the motif required for substitution is seen to be absent, and moreover, the double bonds in the vicinity of the fluorine atoms are highly delocalised and unavailable for ready participation in the mechanism shown in Fig. 3. Substitution of any of the 15 fluorine atoms can only occur under forcing conditions, if at all.





(**6**, ● = replaceable F) (**7**, annulene chain in green)

Notes and references

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