Mass Spectral Studies of Native and Mass-labeled Perfluorooctanesulfonamides

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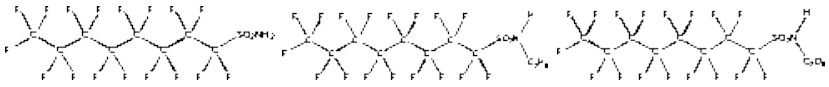
Introduction

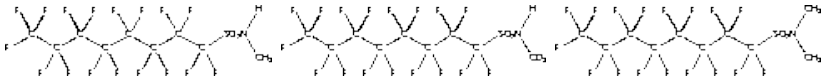
In recent years, concerns have been raised about the widespread distribution of fluorinated chemicals in the environment and their accumulation in humans.[1-4] There have been numerous studies aimed at the analysis of perfluorooctanesulfonamide (FOSA) in the environment but very few involving NMeFOSA or NEtFOSA. [5]The results of an investigation of the mass spectral behaviour of FOSA and NEtFOSA have been published.[6] In this work, a number of fragmentation pathways were proposed, but some gaps still remain. No similar study appears to have been reported for NMeFOSA. We have therefore synthesized samples of both native and mass-labeled NMeFOSA and NEtFOSA, and native NMe_2FOSA, and studied them by GC/MS in an attempt to further our understanding of their modes of fragmentation.The objective of this work was to carefully examine the mass spectrum of FOSA to elucidate the various possible fragmentation pathways accessible to this molecule under electron impact (EI) conditions.

Materials and Methods

Chemicals. Starting from commercially available material, and using a combinationof chromatography and crystallization techniques, we have obtained perfluorooctane-1-sulfonamide (1) free of all branched isomers. The N-alkylated perfluorooctane-1-sulfonamides (2-6) were produced from 1 via alkylation at nitrogen. The compounds were characterized by NMR spectroscopy on a Bruker 400MHz instrument using d_4-methanol as solvent.



FOSA (1) NEtFOSA (2) d-NEtFOSA (3)



NMeFOSA (4) d-NMeFOSA (5) NMe2FOSA (6)

High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) Experiments. The analyses were conducted on an Agilent 6890N (HRGC) coupled to a Waters Autospec Ultima (HRMS). The GC column used was a J&W DB-FFAP (30 m x 0.25 mm id x 0.25 µm film). All injections were performed in splitless mode with an injector temperature of 230 °C using helium as a carrier gas at a constant flow of 1 ml/min. The following temperature program was used: 100 °C (2 min), 10 °C/min to 230 °C, 230 °C (5 min). The transfer line and source were maintained at 230 °C. The HRMS was calibrated over a mass range of 50-550 Daltons at a resolution of 1000 using perfluorokerosene (PFK-H) prior to the injection of the sulfonamides.

Results and Discussions

Chromatographic Studies

The sulfonamides 1-6 were analyzed by HRGC/HRMS using electron impact ionization. The elution pattern of the sulfonamides on the DB-FFAP column follows closely the volatility of the compounds (order of elution: 6 > 5 ≥ 4 > 3 ≥ 2 > 1). As has been reported by others,[7] the deuterated compounds have a slightly shorter retention time than their

native counterparts.

Mass Spectral Studies

The mass spectrum of FOSA, using 50 eV ionization, is shown in Figure 1 and the fragments identified are summarized in Scheme 1. As indicated in the earlier work,[6] the molecular ion (m/z 499) is not detected (a weak signal, at m/z 500, corresponding to $[M+H]^+$, can be seen in Figure 1), while the observed fragments are of two types. After cleavage, the positive charge may reside either on a purely fluorocarbon residue or on a nitrogen-containing fragment. The latter gives $[O_2SNH_2]^+$, m/z 80, the base peak in the spectrum (Scheme 1, pathway B). Corresponding to the former, we find fragment ions assignable to the three series (Scheme 1, pathway A); C_nF_{2n+1} (n=1,2…6; m/z 69, 199, …319), C_nF_{2n-1} (n=3,4…8; m/z 131, 181…381), and C_nF_{2n-3} (n=3, 4…8; m/z 93, 143…343). The last series is of relatively low intensity compared to the other two, and was not previously reported.[6] One further fragment, at m/z 100, corresponds to $[C_2F_4]$Ÿ+. Fragment ions were also found at m/z 480, 416 and 64. It was suggested[6] that the first two are formed by loss of a fluorine atom and then SO_2 or $SONH_2$ from the molecular ion (Scheme 1, pathway C), but it was not possible to distinguish between the formulas $[F_{16}C_8NH_2]^+$ and $[F_{16}C_8O]^+$ for the ion at m/z 416. Product ion analysis (MS/MS) of the ion at m/z 416 showed a fragment at m/z 97, but distinction between the structures $[CF_2CFNH_2]$Ÿ+ and $[CF_2CFO]$Ÿ+ was not possible. As seen in Figure 1, a relatively weak signal appears at m/z 97. Further, although deuterium labeling experiments supported some contribution from the species $[OSNH_2]^+$ to the ion at m/z 64, a significant contribution of $[SO_2]$Ÿ+ to this fragment could not be ruled out. The results of our investigations on FOSA and its N-methyl and N-ethyl derivatives allow us to conclude that the fragments at m/z 416, 97 and 64 are mainly, if not exclusively, the nitrogen-containing species $[F_{16}C_8NH_2]^+$,$[F_2CCFNH_2]$Ÿ+ (Scheme 1, pathway C) and $[OSNH_2]^+$ (Scheme 1, pathway E), respectively.

The spectrum in Figure 1 shows two additional relatively strong peaks at m/z 82 and 66. The first of these we ascribe to the fragment $[F_2CNH_2O]^+$ (Scheme 1, pathway F) since N-alkyl sulfonamides show a strong signal corresponding to the appropriate $[F_2C(NRR')O]^+$ ion. The second, at m/z 66, appears to belong to a series of fragments differing in mass by 50 amu (CF_2), and terminating with the ion m/z 416 mentioned above (Scheme 1, pathway D). This series corresponds to ions of formula $[(CF_2)_nNH_2]^+$ (n=1,2…..8; m/z 66, 166…..416) formed by the net fragmentations $M^+ - SO_2 - C_xF_{2x+1}$ (x= 0, 1 …..7). The m/z 66 peak is the strongest in the series, followed by that at m/z 416, while the remainder are relatively weak. In particular the signals at m/z 116 and 166 are barely distinguishable from the background.

In the earlier work, [6] a cyclic structure with a ten -membered ring was proposed for the ion m/z 480 (Scheme 2, pathway C) on the basis of the observation that MS/MS of the ion at m/z 416 (presumed to be derived from m/z 480 by loss of SO_2) gave a fragment m/z 97 (identified as $[CF_2CFNH_2]$Ÿ+ above), but none corresponding to $[CF3]^+$, m/z 69. However, preferred formation of such a thermodynamically unfavorable ring seems highly unlikely. Further, if, as seems likely, the cationic charge is retained preferentially on the nitrogen -containing fragment after cleavage of the m/z 416 species, then significant amounts of $[CF_3]^+$ may not be formed. A possible alternative to the m/z 97 fragmen is outlined is Scheme 2, pathway C ′. Formation of intermediate species m/z 480 and 416 could involve initial formation of a molecular radical cation (m/z 499) by loss of an electron from the sulfonamide function, intramolecular displacement of an α fluorine atoms by the nitrogen to give a kinetically favorable three -membered ring species, m/z 480, with a sultam structure, and loss of SO_2 to give an acyclic cation, m/z 416. Subsequent preferential loss of the $F_3C(CF_2)_5$Ÿ radical would give the resonance stabilized radical ion, m/z 97. Note that the spectrum in Figure 1 also shows very weak signals at m/z 147 and 197, perhaps corresponding to losses of $F_3C(CF_2)_4$Ÿ and $F_3C(CF_2)_3$Ÿ from the m/z 416 ion. As indicated in Scheme 3, several alternative ring structures can be drawn for an ion with m/z 480, and indeed, one or more of these may give rise to the observed peak in Figure 1, with the m/z 416 fragment coming from a less stable isomer such as that suggested above (Scheme 2, pathway C).

Three-membered ring intermediates may also be suggested to rationalize the formation of three major fragments at the low -mass end of the spectrum in Figure 1. Thus, intramolecular attack of nitrogen in the molecular radical cation at the α-carbon with displacement of the $F_{15}C_7$Ÿ radical rather than FŸ to give the intermediate sultam cation $[F_2CSO_2NH_2]^+$, m/z 130 (Scheme 2, pathway D1), followed by loss of SO_2 would give the $[F_2C{=}NH_2]^+$ ion, m/z 66. Intramolecular attack at the α-carbon by oxygen rather than nitrogen (Scheme 2, pathway E) with displacement of the $F_{15}C_7$Ÿ radical, would give an isomeric m/z 130 cationic intermediate $[F_2CSONH_2O]^+$, which could subsequently lose F_2CO to generate the ion $[OSNH_2]^+$, m/z 64. Alternatively, the three -membered ring intermediate may rearrange to the four -membered ring species $[OF_2CNH_2SO]^+$ (Scheme 2, pathway F), which may lose F_2CO or SO to generate the ions $[OSNH_2]^+$, m/z 64, or $[OF_2CNH_2]^+$, m/z 82, respectively.

We have also considered other possible pathways (summarized in Schemes 3, 4 and 5) to explain additional observed signals. Initial formation of 3-to-6-membered rings would be expected to be more favourable than closure to larger ring sizes and would explain the formation of most fragments found in Figure 1.

Summary

A thorough analysis of the mass spectrum of FOSA has been completed. New fragmentation pathways are proposed to explain the identity of the fragments found in the EI spectra of this and some related perfluorinated sulfonamides.

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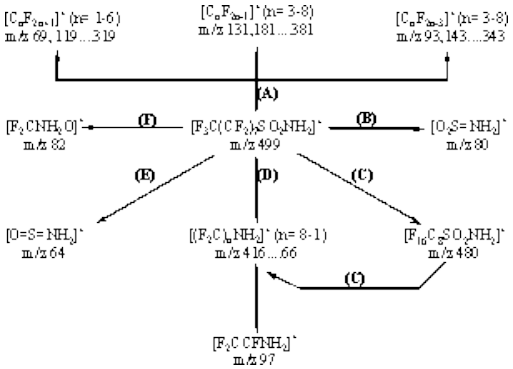
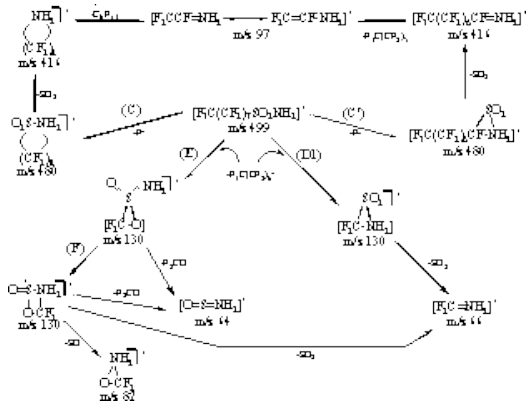
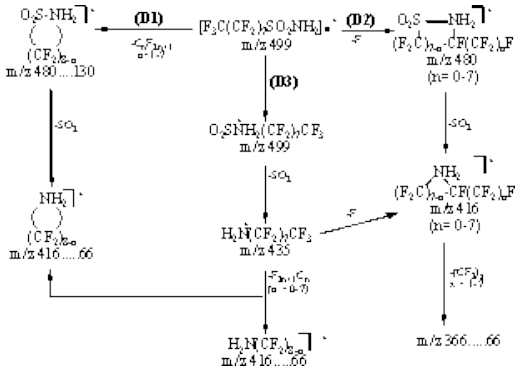
Scheme 1



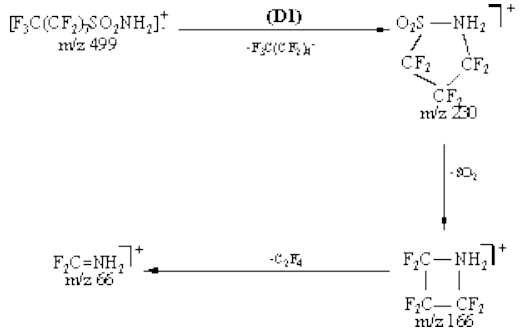
Scheme 2



Scheme 3



Scheme 4



Scheme 5

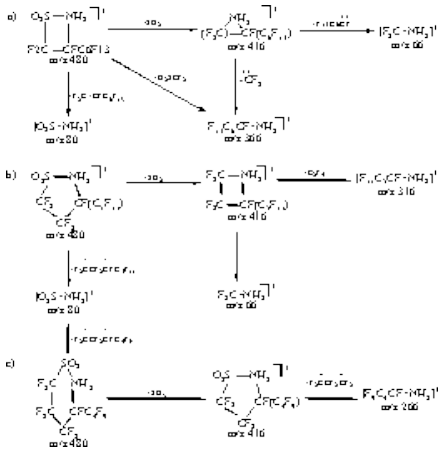


Figure 1. Mass Spectrum of FOSA at 50eV