

# ANALYSIS OF PERFLUOROALKYL ANION FRAGMENTATION PATHWAYS FOR LINEAR AND BRANCHED PERFLUOROCTANOIC ACIDS (PFOA) DURING LC/ESI-MS/MS

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## Introduction

- LC-electrospray ionization-MS (LC/ESI-MS) and LC/ESI-MS/MS can be considered as the current standard for analysis of anionic perfluorinated compounds.<sup>1</sup>
- The belief by many is that the perfluoroalkyl anion fragments by 'unzipping' to produce C<sub>n</sub>F<sub>2n</sub> species.<sup>2</sup>
- Initial analysis in our laboratory of the mass spectrum of MPFOA indicated that the fragmentation mechanism of a perfluoroalkyl anion is more complex than one involving simple sequential loss of neutral C<sub>n</sub>F<sub>2n</sub> fragments.
- Indeed, recent work<sup>3</sup> has shown that the fragmentation mechanism of linear perfluoroalkyl carboxylic acids involves, after initial decarboxylation, rapid fluorine shifts, which generate a series of new anions prior to secondary and tertiary fragmentation.

## Objective

- To develop a fundamental understanding of the fragmentation mechanism for the perfluoroalkyl anions generated from perfluoroalkyl carboxylates under LC/ESI-MS/MS conditions.
- To extend the investigation of perfluoroalkyl fragmentation to branched PFOA isomers.

## Experimental

**Chemicals**: The branched isomers of PFOA were obtained from Wellington Laboratories.

**LCMS/MS**: The analyses were conducted on a Waters Acquity Ultra Performance LC interfaced to a Micromass Quattro *micro* atmospheric pressure ionization (API) mass spectrometer (MS) in negative-ion electrospray mode. Tune parameters were optimized to promote the in-source fragmentation of each individual isomer from [R<sub>1</sub>-CO<sub>2</sub>]<sup>-</sup> to [R<sub>1</sub>]<sup>-</sup>. Product ion experiments were then carried out on [R<sub>1</sub>]<sup>-</sup> (argon collision gas ~ 3.5e-3 mbar; cone voltage: 15V – 30V; collision energies: 15eV – 25eV).

## Results and Discussions

### Fragmentation of LPFOA

- The study was performed on the various branched isomers of PFOA shown in Figure 1.
- As expected, based on results of the previous study, LPFOA produces secondary daughter ion fragments at m/z 119, m/z 169 and m/z 219 (see figure 2). Note that no signals were detected at m/z 269 (from primary carbanions 1a and 1g, see Figure 3) nor at m/z 69 consistent with the lower stability of primary carbanions.
- The secondary daughter ion fragments produced for each PFOA isomer is shown in Figure 2.

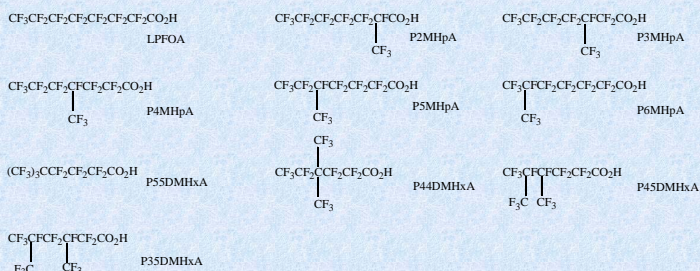


Figure 1. Structures of the perfluoroalkane carboxylic acids

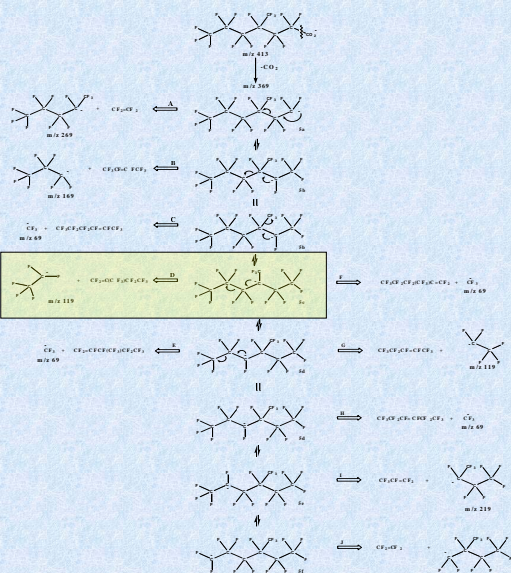


Figure 3. Fragmentation pathway for P4MHpA

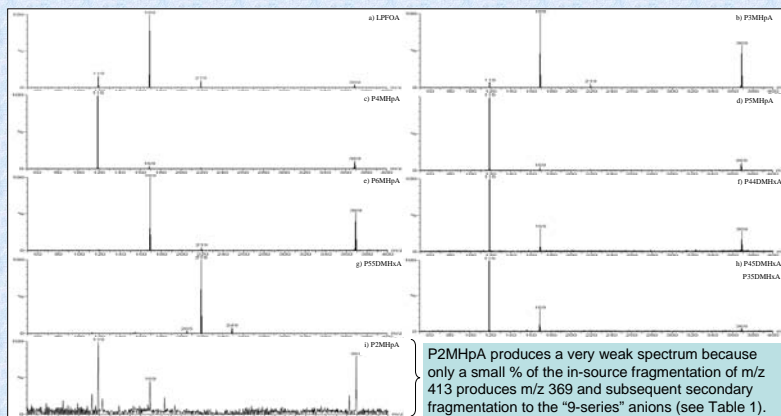


Figure 2. LC/ESI-MS/MS: Secondary daughter ion scan from m/z 369

## Results and Discussion (con't)

### Fragmentation of branched PFOA isomers

- As an example, the fragmentation of P4MHpA will be outlined:
    - Primary fragmentation (decarboxylation) produces the fragment m/z 369.
    - Rapid fluorine migration produces various anions (see figure 3).
    - It is known that order of stabilities of perfluoro carbanions is 3° > 2° > 1°. Therefore, fragment 5c containing the 3° carbanion (figure 3, highlighted) is expected to contain the highest equilibrium population. Consequently, upon secondary fragmentation, the strongest signal is m/z 119.
  - The other branched PFOA isomers follow the same pattern of fragmentation through a tertiary carbanion, except for P2MHpA.
  - P2MHpA shows minimal signs (see Figure 2) of the typical fragments m/z 369/219/169/119/etc but instead produces unique anions at m/z 85 [CF<sub>3</sub>O]<sup>-</sup> and m/z 63 [FCO]<sup>-</sup>. This crowded carboxylate anion prefers to attack the neighboring alpha-CF<sub>3</sub> instead of decarboxylating.
- Relative response factors**
- The SIR relative response factor for the individual PFOA isomers are shown in Table 1.
  - Certain isomers showed significant reduction in their SIM response factors relative to LPFOA because of facile in-source fragmentation.
  - The spectrum of P2MHpA is extremely weak because of the lack of "9-series" fragments.

Table 1. SIM response factors for the various branched PFOA isomers relative to linear PFOA (LPFOA)

Isomer	P2MHpA	P3MHpA	P4MHpA	P5MHpA	P6MHpA	P55DMHxA	P44DMHxA	P45DMHxA	P35DMHxA
%Relative response factor (m/z 413)	1	40	90	110	100	90	50	75	36
%Relative response factor (multi-channel SIM: 413/369/269/219)	1	107	100	104	86	109	98	103	78

## References

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