Stability of Saturated and Unsaturated Perfluoroalkyl Telomer Acid Compounds as Reference Standards

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Introduction

Fluorotelomer alcohols are a group of products used in various commercial applications. These alcohols may escape into the environment where they can get oxidized or metabolized to fluorotelomer acids with eventual conversion into perfluoroalkanoic acids, for example perfluorooctanoic acid (PFOA).[1-4] To fully understand what is actually occurring in the environment, accurate analysis of fluorotelomer alcohols and acids present in environmental samples is needed and this requires the use of reference standard solutions.[5] However, since the saturated telomer acids can easily degrade to the corresponding unsaturated telomer acids,[6] difficulties arise in providing stable solutions of the former in suitable solvents for use as reference standards..

The objective of this work was to examine, carefully, the stability of these telomer acids when used as reference standard solutions. The facile degradation of saturated telomer acids reported earlier[6] has been confirmed and a method is suggested to stabilize these standards. We have also found, and identified, degradation products originating from unsaturated telomer acids in solution. This work may provide further insight into the behaviour of these telomer acids in the environment.

Experimental

LC/MS: LC/MS experiments were conducted on a Waters Acquity Ultra Performance LC attached to a Micromass Quattro micro API. Separations were performed on an Acquity UPLC BEH Shield RP_{18} column (1.7 um, 2.1 x 100 mm). Typical run conditions were 65% (80:20 MeOH: ACN) and 35% water, both containing 10 mM NH_4OAc at a flow rate of 300 uL/minute.

Experiment 1: An experiment was designed and conducted as outlined in Tables 1 and 2. A stock solution of FOEA in methanol was prepared at a concentration of 100ug/ml in a volumetric flask. Half the solution was then immediately transferred to a polyethylene vial. These solutions were immediately used to prepare the 8 solutions described in Table 1. The solutions were stored for 42 days at ambient temperature prior to the analyses reported in Table 1.

Experiment 2: FOEA was dissolved in water in the presence of sodium hydroxide at room temperature. After 5 days, the solution was analyzed by LC/MS.

Results and Discussion

The conversion of a saturated to an unsaturated telomer acid is easily achieved in the presence of base such as sodium hydroxide[7] (see figure 1). Indeed, it has been shown that saturated telomer acids such as 2-perfluorooctyl ethanoic acid (FOEA) can suffer conversion into 2H-perfluoro-2-decenoic acid (FOUEA) when simply dissolved in methanol.[6] Storage of these methanol solutions at lower temperatures slows down this elimination while dissolution in water appears[6] to stop it. The dehydrofluorination of FOEA in methanol could be due to one or several factors. The solvent medium may be basic enough to, or contains basic impurities that, promote the elimination of HF. The glass surface in contact with the stored solutions may also be able to induce degradation.

A designed experiment was conducted in which an eight-run pattern was used as a half factorial for four factors at two levels (see Table 1).[8] The four variables (factors) chosen are highlighted in Table 2 and were: methanol versus aqueous methanol; storage in glass versus polyethylene; concentration of 50ug/ml versus 5ug/ml; and the presence or absence of an acid (HF). The parameter measured (Y) was the ratio of signals FOEA/FOUEA as measured by LC/MS under SIR conditions for the fragment ions 477 and 457, respectively. The results are highlighted at the bottom of Table 1 and Figure 2. A plot of the results (Figure 2) shows a significant contrast between variable D and the other 6 columns. The measurements for these 6 columns (A, B, C, AB, BC, AC) could be considered as the noise from the experiment since they have values similar to each other. Therefore, storage in glass versus polyethylene (variable A), methanol versus aqueous methanol (variable B) and concentration (variable C) has no significant effect on the degradation of FOEA. The presence of HF (variable D) has a stabilizing effect for FOEA but the elimination process is still occurring.

It is known that fluoride anion can behave as a weak base.[9] Thus, the addition of HF, while rendering the medium acidic, also introduced fluoride anion which could itself act as a dehydrofluorination agent. A separate experiment was conducted where a reduced amount of HF was used to stabilize the FOEA. The results are shown in Figure 3. We can observe that the rate of degradation is reduced when the concentration of HF is lower, possibly indicating that fluoride anion (F-) can promote the dehydration of HF. Figure 3 also shows that storage at 4°C further reduces the dehydrofluorination rate. Additional work is underway in an effort to confirm these results and to determine the optimum level of HF. The effect of acids other than HF and the use of solvents other than methanol are currently being examined.

It should be noted that the response factors for FOUEA are much larger than for FOEA. Indeed, the response factor for FOUEA relative to FOEA, as measured under our conditions and with our instrument, was approximately 2:1 under SIR (457 vs 477). The response factor increased to approximately 4.5:1 with selected MRM transitions (457 → 393 vs 477 → 393).

Unsaturated telomer acids such as FOUEA are much more stable compounds than their saturated counterparts. However, it is known[10] that unsaturated telomer acids can react with MeOH in the presence of base to form methoxy-substituted unsaturated telomer acids (see Figure 4). When FOUEA is stored in methanol at a concentration of 50ug/ml, formation of the methoxy adduct can be observed by LC/MS. This formation is slow as conversion was measured at about 1% per year at ambient temperature. Storage at 4°C is recommended for these unsaturated telomer acids in methanol in order to further reduce the rate of formation of the methoxy-adduct.

The reaction between the unsaturated telomer acid and methanol led us to the idea that a similar reaction may be possible with water. Indeed, when FOUEA is treated with aqueous base (experiment 2), a signal having the characteristics of the gem-diol (see Figure 5a) can be detected by LC/MS. One can envision a mechanism whereby this gem-diol could decompose to PFOA and acetic acid[4] (see Figure 5b). However, PFOA was not detected in our reaction mixture.

It is apparent that saturated telomer acids undergo facile dehydrofluorination in the presence of base. Analytical laboratories need to be careful in avoiding basic work-ups if the objective is to analyze for saturated telomer acids. Because of this, it is plausible that these compounds will be difficult to find in the environment and the biota due to their facile degradation. We are aware of two studies seeking the presence of saturated telomer acids; one study found saturated telomer acids in the waters of lake Winnipeg[6] but a second study was unsuccessful in detecting saturated telomer acids in fish tissues originating from the Great Lakes.[11]

Table 1. Pattern of 8-run design expanded to show interaction columns for Experiment 1

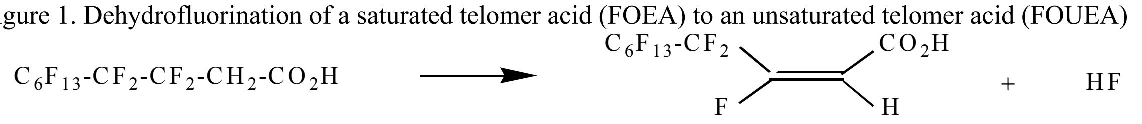
Experiment	A[a]	B[a]	C[a]	AB	BC	AC	D[a]	Y[b]
a	-	-	-	+	+	+	-	0.7
b	-	-	+	+	-	-	+	9.0
c	-	+	-	-	+	-	+	1.8
d	-	+	+	-	-	+	-	0.8
e	+	-	-	-	-	+	+	2.5
f	+	-	+	-	+	-	-	0.2
g	+	+	-	+	-	-	-	1.2
h	+	+	+	+	+	+	+	2.4
Total	-6.0	-6.1	6.2	7.9	-8.5	-5.6	12.8	
Effect on Y[b] (factor interaction)	-1.5	-1.5	1.6	2.0	-2.1	-1.4	3.2	

[a] See Table 2 for description of variables A, B, C and D
[b] Y ≡ signal intensity ratio of FOEA/FOUEA under SIR conditions (477/457)

Table 2. The four variables chosen for the designed study (Experiment 1)

Variable	+	-
A ≡ Storage	Glass	Polyethylene
B ≡ Solvent	Methanol	Aqueous methanol
C ≡ Concentration	50ug FOEA / ml	5ug FOEA / ml
D ≡ Acid	HF	No acid

Figure 1. Dehydrofluorination of a saturated telomer acid (FOEA) to an unsaturated telomer acid (FOUEA)



FOEA FOUEA

Figure 2. Plot for the designed experiment

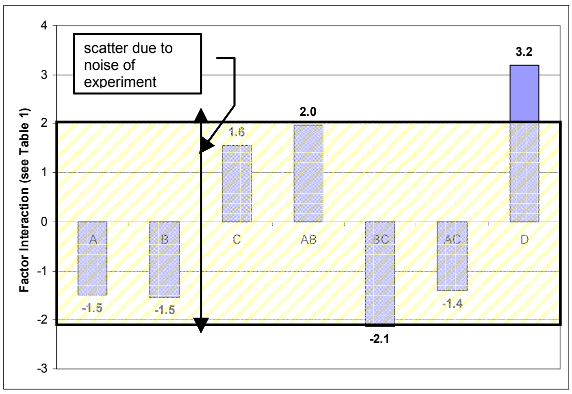


Figure 3. Dehydrofluorination rates for FOEA under different conditions

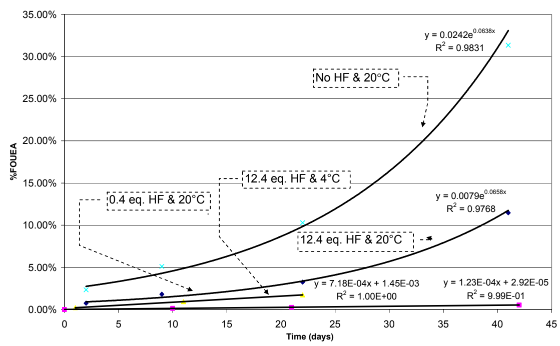


Figure 4. Reaction of FOUEA with methanol

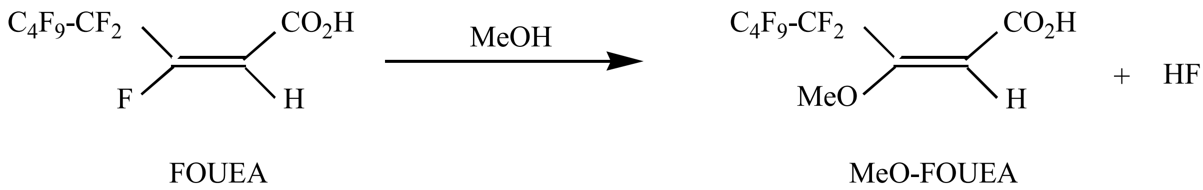
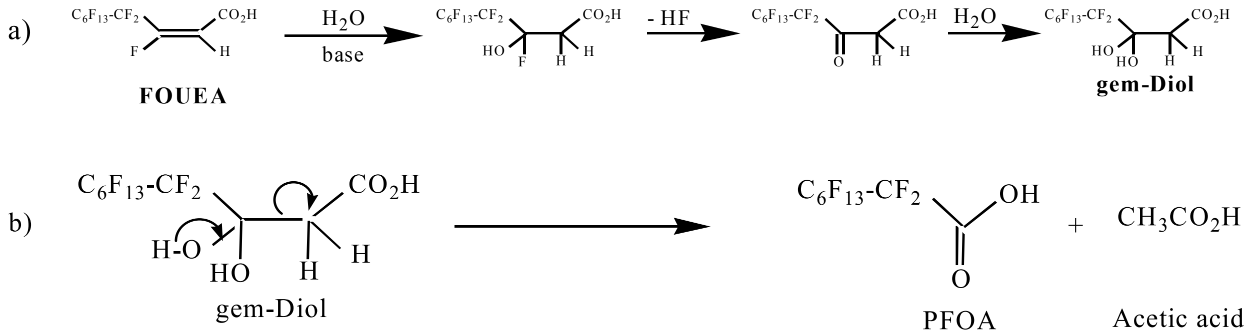


Figure 5. Reaction of FOUEA with water and a potential pathway to formation of PFOA



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