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

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Introduction

- Fluorotelomer alcohols are a group of compounds used in various commercial products from which they may escape into the environment and then get oxidized or metabolized to fluorotelomer acids.
- To fully understand what is actually occurring in the environment, accurate analysis of fluorotelomer alcohols and acids in environmental samples is needed and this requires the use of reference standard solutions.[1]
- The facile degradation of saturated to unsaturated telomer acids has been reported.[2]

Objective

- The objective of this work was to examine carefully the stability of these telomer acids in solutions when prepared for use as reference standards in analytical methods.
- This work may provide further insight into the behaviour of these telomer acids in the environment.

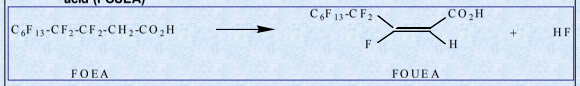
Experimental

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 RP18 column (1.7 um, 2.1 x 100 mm). Typical run conditions were 65% (80:20 MeOH: ACN) and 35% water, both with 10 mM NH4OAc at a flow rate of 300 uL/minute.
The 8:2 saturated telomer acid (FOEA) was used in this study.

Results and Discussions

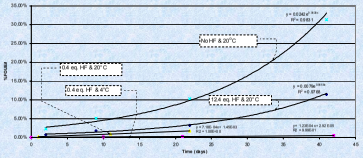
- The conversion of a saturated to an unsaturated telomer acid is easily achieved in the presence of a base such as sodium hydroxide[3] (see figure 1).

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



- Initial studies in methanol indicated that the presence of HF had a stabilizing effect for FOEA but the elimination process was still occurring (see figure 2).

Figure 2. Comparison of dehydrofluorination rates for FOEA with varying amounts of HF in Methanol



- It is known that fluoride anion can behave as a weak base[4]. Thus, the addition of HF, while rendering the medium acidic, also introduces fluoride anion which could itself act as a dehydrofluorination agent.

References

[1]Martin JW, Kannan K, Berger U, De Voogt P, Field J, Franklin J, Giesy JP, Harner T, Muir DCG, Scott B, Kaiser M, Jarnberg U, Jones KC, Mabury SA, Schroeder H, Simcik M, Sottani C, Van Bavel B, Karrman A, Lindstrom G and Van Leeuwen S. *Environ.Sci.Technol.* 2004; 38, 248A-255A.
[2]Loewen M, Halldorson T, Wang F and Tomy G. *Environ.Sci.Technol.* 2005; 39, 2944-2951.
[3]Achilefu S, Mansuy L, Selve C and Thiebaut. *J.Fluorine Chem.* 1995; 70, 19-26.
[4]Clark JH. *Chem. Rev.* 1980; 80, 429-452.
[5]Zuczek C, Gerardin-Charbonnier C, Rocca S, Thiebaut S and Selve C. *J.Fluorine Chem.* 1999; 99, 41-49.

Results and Discussions (continued)

- Since the rate of dehydrofluorination of the saturated telomer acids in the presence of HF was still unacceptable, more studies were conducted to find conditions to further reduce the rate of this decomposition.
- A study comparing the effects of different acids in methanol showed that trifluoroacetic acid (TFA) and HCl were the best of those tested in stabilizing the saturated telomer acids (see figure 3).

Figure 3a. Comparison of dehydrofluorination rates for FOEA in the presence of various acids at 22ºC

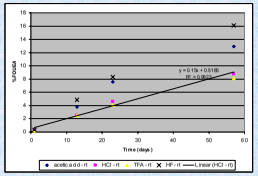


Figure 3b. Comparison of dehydrofluorination rates for FOEA in the presence of various acids at 4ºC

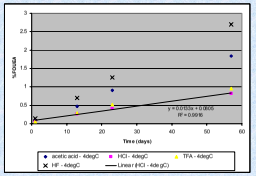
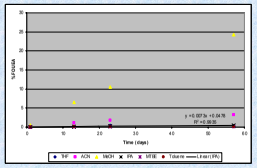


Figure 4. Comparison of dehydrofluorination rates in various solvents at ambient temperature (22ºC)



- The stabilization trend observed of HCl ~ TFA > acetic acid > HF indicates that decreased basicity of the anion leads to a decrease in dehydrofluorination.
- A comparison of different solvents showed that isopropanol (IPA) was the best LC solvent for stabilizing the saturated telomer acid (see figure 4).
- It appears that the dielectric constant of the solvent may be a factor that influences the stability of the saturated telomer acid (see Table 1).

Table 1. Dielectric constants of the various solvents

Solvent	Type	Dielectric Constant
Acetonitrile (ACN)	Aprotic	36.6
Methanol (MeOH)	Protic	33
Isopropanol (IPA)	Protic	18.3
Tetrahydrofuran (THF)	Aprotic	7.5
Methyl tert-butyl ether (MTBE)	Aprotic	4.5
Toluene	Aprotic	2

Results and Discussions (continued)

- Interestingly, the type of glass in which the solutions are stored was also shown to have an effect on the stability of the saturated telomer acids (see figure 5).
- These results indicate that the basicity of the glass has an impact on the dehydrofluorination rates of the saturated telomer acids.

Figure 5. Effect of glass type on dehydrofluorination rates in MeOH at ambient temperature (22ºC)

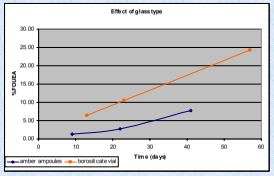
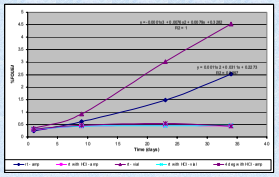


Figure 6. Rate of dehydrofluorination in IPA with/without HCl and at 22ºC or 4ºC

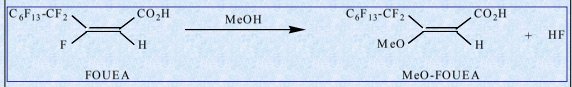


- Solutions prepared in IPA containing a small amount of HCl show very good stability against dehydrofluorination (see figure 6). As expected, solutions without HCl showed poor stability. Solutions without HCl and in clear borosilicate glass showed the highest rates of dehydrofluorination.

Comment on the stability of unsaturated telomer acids

- It is known[5] that unsaturated telomer acids can react with MeOH in the presence of a base to form methoxy-substituted unsaturated telomer acids (see Figure 7).

Figure 7. Reaction of FOUEA with methanol



- Indeed, when FOUEA is stored in methanol at a concentration of 50ug/ml, formation of the methoxy adduct does occur as evidenced by LC/MS. This formation is slow, with conversion being measured at about 1% per year at ambient temperature. Storage at 4°C is recommended for solutions of these unsaturated telomer acids in methanol in order to further reduce the rate of formation of the methoxy-adduct.

Conclusions

- Solutions of saturated telomer acids are best kept in IPA in the presence of trace amounts of HCl.
- Analytical laboratories have to be careful how they handle both reference standard solutions and environmental samples if they wish to analyze for saturated telomer acids.