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## POTENTIAL SOURCES OF ENVIRONMENTALLY RELEVANT IMPURITIES FOUND IN TECHNICAL MIXTURES OF PFOS AND PFOA REPLACEMENT PRODUCTS

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### Introduction

The industrial synthesis of per- and poly-fluorinated compounds has historically been conducted using either Simons electrochemical fluorination (ECF) or the telomerization process. It is well known that products produced using ECF contain a mixture of branched and linear isomers, as well as other by-products, whereas telomerization produces an isomerically pure product.<sup>1</sup> Isomer profiling of perfluorinated compounds in environmental samples has been used as a tool for predicting both the production method as well as probable exposure pathways.<sup>2</sup> Industrial manufacture of both perfluorooctanesulfonyl fluoride (PFOSF) based products and perfluorooctanic acid (PFOA) occurred primarily through ECF production until this process was voluntarily phased-out in 2002. Since then, most of the commercially produced per- and poly-fluoroalkyl based products have been synthesized using telomerization.<sup>3</sup>

Research into the environmental fate and health effects of per- and poly-fluorinated substances (both branched and linear) is on-going.<sup>4</sup> Current environmental levels, global demand, and potential human exposure have placed an emphasis on the importance of monitoring, toxicity research, and source identification. More than 200,000 tons of fluorinated materials are produced annually for the fluoropolymer industry with applications ranging from corrosive chemical processing to stain repellency.<sup>5</sup> The production of almost all fluoropolymers requires the use of PFOA, or a suitable analogue, as a processing aid.<sup>6</sup> At current levels of production, even relatively minor impurities become relevant potential environmental contaminants. Furthermore, PFOS, a common breakdown product of substituted sulfonamides which are widely used in commercial applications, has also had extensive application in metal plating processes.<sup>7</sup>

Over the past few years, industry stewardship programs have prompted the removal of PFOS and PFOA from industrial production processes. However, commercial demand resulted in the use of replacement fluorinated materials such as 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid (GenX or HFPO-DA), 2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethanesulfonic acid (F-53b), and 3H-perfluoro-3-((3-methoxy-propoxy)propanoic acid) ammonium salt (ADONA).<sup>7,8</sup> The objective of this work was to investigate the impurities in technical mixtures of PFOS and PFOA replacement products and compare them to historically produced ECF PFOS and PFOA. Due to length restrictions, only F-53b will be addressed in this abstract.

### Materials and Methods

A technical grade commercial sample, specified as being for electroplating use only, of F-53b was obtained from Alfa Chemistry (Stony Brook, NY, USA). Fractionation and purification was completed at Wellington Laboratories Inc. using proprietary methods. LC/MS experiments were conducted on a Waters Acquity Ultra Performance Liquid Chromatograph (LC) interfaced to a Micromass Quattro micro API triple quad mass spectrometer (MS). Separations were performed on a Waters Acquity BEH Shield RP18 column (1.7  $\mu\text{m}$ , 2.1 x 100 mm) using gradient elution. MS data were collected in full scan mode using negative-ion electrospray ionization.

### Results and discussion

Although the telomerization process does not result in the generation of significant levels of branched isomers during production, it is not exempt from side reactions. Since this process involves the free radical addition of a telogen to an unsaturated taxogen (commonly tetrafluoroethylene, TFE), it is possible for multiple products to be produced with the most common variants having a difference of one or more  $\text{CF}_2\text{CF}_2$  units. Figure 1 illustrates the telomerization processes that have been used to produce F-53b.<sup>9</sup>

The purity of the commercial sample of F-53b was determined by dissolution in methanol and analysis using LCMS (percentages were calculated assuming equal response factors due to a lack of analytical

standards). The sample was found to contain only 77% of the expected C<sub>8</sub> compound (m/z 531) with the major impurity (20%) differing by 100 Daltons (one CF<sub>2</sub>CF<sub>2</sub> unit; m/z 631). It is interesting to note that some of the minor impurities (totaling 0.5%) exhibited a difference of 50 Daltons (a CF<sub>2</sub> unit).

We can suggest two possible routes to these odd chain length by-products. (1) If the TFE contains a hexafluoropropene impurity, this 3 carbon unit could be incorporated occasionally into the telomerization reaction sequence. However, if this was the dominant formation process, one would expect to see multiple isomers since branching would occur at random points along the perfluoroalkyl chain, but only one dominant isomer was observed. (2) The telomerization precursor (ICF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F) may contain some of the shorter analogue (ICF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F) formed as outlined in Figure 2. This reaction pathway is supported by the presence of the m/z 497 impurity (1.5%) which may form by insertion of CF<sub>2</sub>O instead of CF<sub>2</sub>CF<sub>2</sub> during the telomerization process. Unfortunately, the third most abundant impurity with a mass-to-charge ratio of 623 (0.6%) has yet to be identified.

A comparison of F-53b (77% C<sub>8</sub> isomer) to ECF produced PFOS (typically a mixture of branched and linear isomers with an overall PFOS content of 80%) highlights the importance of knowing the relative toxicity of the branched and linear isomers. Although the telomerization process produces mainly one isomer per homologue group, a significant percentage of the technical mixture of F-53b is composed of impurities formed during the reaction process and these impurities are just as likely to be released into the environment as the target compound.

#### References

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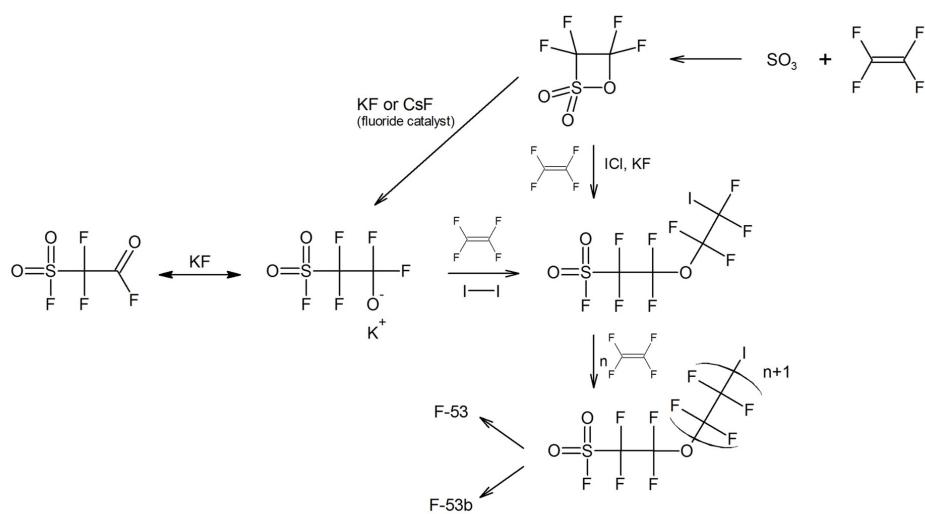


Figure 1: The production of F-53 and F-53b using the telomerization process.

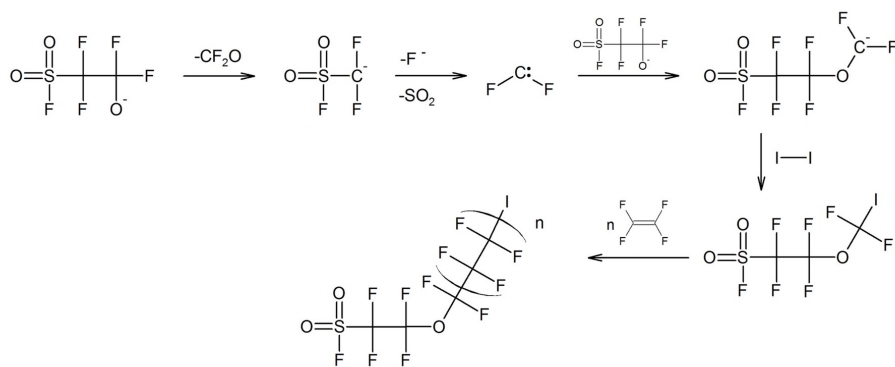


Figure 2: Possible synthetic route to by-product formation during the telomerization process.