Separation and Fluorine Nuclear Magnetic Resonance Spectroscopy (19F-NMR) Analysis of the Individual Branched Isomers Present in Technical Perfluorooctanesulfonic Acid (PFOS)

Gilles Arsenault[1], Robert McCrindle[2], Brock Chittim[1], Alan McAlees[1]

[1]Wellington Laboratories
[2]University of Guelph

Introduction

The production of perfluoroalkylsulfonate derivatives via electrochemical fluorination is not a clean process but rather gives a complex mixture.[1,2] The presence of C_8 isomers in commercial perfluorooctanesulfonate (PFOS) is evidenced by their partial separation by liquid chromatography (LC), resulting into two broad peaks.[3-5] In other studies, PFOS appears as a broad signal.[6,7]

Indeed, commercial perfluorooctanesulfonyl fluoride (PFOF), and derived products, are mixtures of ~70% linear and ~30% branched isomers as measured by ^{19}F NMR spectroscopy.[8,9] This study allowed quantification of the individual normal chain (**7**), isopropyl branched (**6**), alpha branched (**1**), *t*-butyl branched (**8**) and internal *gem*-dimethyl branched (**9**) isomers. Apparently, in this study it was not possible to quantify the individual internal CF_3 branched isomers (**2**, **3**, **4**, **5**), presumably due to overlap of their NMR spectra.

The objective of this work was to isolate individual isomers present in a mixture prepared from technical perfluorooctanesulfonic acid (PFOS) and characterize their structures by ^{19}F NMR. As a result, the quantification of the individual internal CF_3 branched isomers present in technical PFOS proved possible.

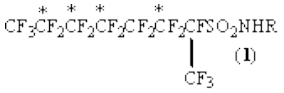
Experimental

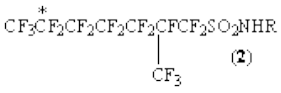
A commercial sample of PFOF was converted to secondary sulfonamides (PFOSamide) using benzylamine and the resulting mixture separated by a combination of crystallisation and preparative-scale HPLC. A set of six fractions was obtained, each containing a different isomer as the major component accompanied by smaller amounts of up to four further isomers. The normal chain sulphonamide was purified to better than 99%. The ^{19}F-NMR spectra of these PFOSamide isomers were run on a 400 MHz Bruker instrument using d_4-methanol as solvent and hexafluorobenzene as an internal standard (set at -169.00 ppm).[10]

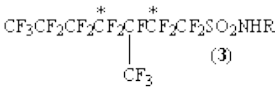
Results and Discussions

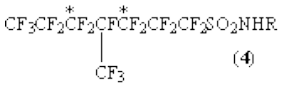
The structures of the various PFOSamideisomers analyzed by ^{19}F-NMR are shown in Scheme 1. Only isomers **1-7** were individually concentrated and characterized by ^{19}F-NMR (see Table 1).

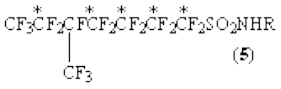
Scheme 1: Structures of the 7 major PFOSamide isomers (* signifies that the signal exists as a clearly resolved AB quartet; R = benzyl group)

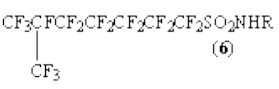

(1)

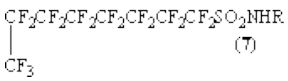

(2)

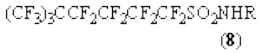

(3)


(4)


(5)


(6)


(7)


(8)

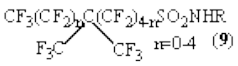

(9)

Table 1: ^{19}F-NMR of the of the 7 major isomers separated from a technical mixture of PFOSamide

Compound[a]	C-1	C-2	C-3	C-4	C-5	C-6	C-7	Branched CF_3
1	-172.20	-117.81[b] -117.51	-124.43	-126.25[b] -126.05	-127.41[b] -127.27	-131.00[b] -130.88	-86.03	-75.24
2	-108.00	-186.80	-116.40	-124.30	-127.04	-130.80	-85.98	-74.74
3	-116.13	-115.10[b] -114.85	-189.68	-116.83[b] -116.39	-125.18	-130.62	-85.86	-75.12
4	-117.62	-123.01	-116.53[b] -116.30	-190.03	-117.37[b] -117.01	-128.87	-85.79	-75.12
5	-117.30[b]	-124.32[b]	-124.84[b] -124.71	-117.79[b] -117.68	-189.81	-121.11[b] -120.88	-85.17	-75.55
6	-117.85	-125.03	-125.90	-125.26	-119.54	-190.74	-76.90[c]	-76.90[c]
7 (linear)	-117.84	-125.08	-126.31	-126.41	-126.58	-127.40	-130.95	(-86.02)[d]

a The numbering of the carbon chain is as follows: C(7)-C(6)-C(5)-C(4)-C(3)-C(2)-C(1)-SO_2NHR

b AB pattern observed due to chirality in the structure

c These signals are the equivalent trifluoromethyl groups on the isopropyl moiety

d This actually is the terminal CF_3 in **7**

Isomers **1** and **3**-**7** were each enriched to the point where the NMR signals attributable to the major isomer were distinct and easily assignable. As an example, the partial spectra of isomers **1**, **3** and **5** are shown in Figures 1, 2 and 3. Assignments of the **$\underline{CF_3}CF_2$**, **$(\underline{CF_3})_2CF$** and **CF** signals were straightforward as much data exists concerning their chemical shift values[11] and they are well resolved from the CF_2 signals observed in the region of -115 to -130 ppm. Isomer **2** was only seen as a minor component in a fraction enriched in **5**.

2D ^{19}F-^{19}F COSY experiments were performed on the isomers to aid in the unambiguous assignment of the CF_2 signals. The strong correlations found in the COSY experiments are for fluorines separated by two carbon bonds, since four-bond ($4J_{FF}$) couplings constants are generally around 10Hz while vicinal coupling constants ($3J_{FF}$) are near zero.[12,13]

A number of the CF_2 signals found in the ^{19}F-NMR spectra of isomers **1**-**5** appear as distinct AB quartets. These

isomers have a chiral center located at the CF carbon attached to the internal CF_3. CF_2 groups directly attached to the chiral CF moiety for isomers **1**,**3**,**4**,**5** appear as AB quartets since this chirality makes the geminal fluorines non-equivalent. This behaviour has been observed previously with cyclic perfluoroalkanes.[14] In some isomers, the chirality is transferred down the perfluoroalkyl chain making most of the geminal CF_2s non-equivalent (as indicated in Scheme 1 and Table 1). It appears likely that rigidity of the perfluoroalkyl chain[15,16] permits the transfer of non-equivalence down the chain.

One striking observation made for these AB quartets is that the lower field doublet is always broader and therefore shorter. Presumably, the non-equivalent fluorine at lower field has greater through space interaction with the neighboring fluorines than its geminal counterpart.

Terminal CF_3 in isomer **5** is unique in that it shows a multiplet of 8 lines (intensity ratio 1:5:11:15:15:11:5:1) whereas all other similar isomers show a broadened triplet. This multiplet is due to couplings to the lone beta fluorine ($4J_{FF}$ = 13.6 Hz) and the five gamma fluorines ($5J_{FF}$ = 6.8 Hz). Large through-space $5J_{FF}$ coupling has previously been seen with similar fluorinated structures.[14]

^{19}F-NMR analysis of technical potassium PFOS and integration of specific isolated signals (**1**: C-1; **2**: branched CF3, C-1, C-2; **3**: C-6, C-3; **4**: C-7, C-2, C-6; **5**: branched CF3, C-7, C-6; **6**: C-7, C-3, C-6; **7**: C-8; **8**: *t*-butyl group at -66.4 ppm: and **9**: *gem*-dimethyl groups at -70.0 ppm) has permitted quantification of the nine isomers shown in Scheme 1 and the data are summarized in Table 2. The sum of these individual values matches closely that reported earlier using NMR,[8,9] except here, we are able to give the individual percentage of each internal CF_3 branched isomer. Note that, while there are small chemical shift differences between ^{19}F signals for potassium PFOS isomers and the corresponding amides, this did not cause any problems with assignment of the former.

Table 2. Percent concentration of the various isomers present in commercial potassium PFOS as measured by ^{19}F-NMR spectroscopy

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Our work	1.9%	1.9%	5.0%	4.8%	6.2%	10.8%	68.9%	0.2%	0.3%
Literature[8,9]	1.6%	17.0%				10.3%	70.0%	0.23%	0.15%

Reference

1. 3M Company. “The Science of Organic Fluorochemistry.” 1999. US EPA Public Docket OPPT-2002-0043-0006.

2. 3M Company. “Sulfonated Perfluorochemicals in the Environment: Sources, Dispersion, Fate and Effects.” 2000. US EPA Public Docket OPPT-2002-0043-0005.

3. C.Kubwabo, N.Vais and F.M.Benoit, J.Environ.Monit., 2004. 6, 540-545.

4. Z.Kuklenyik, J.A.Reich, J.S.Tully, L.L.Needham and A.M.Calafat, Environ.Sci.Technol., 2004. 38, 3698-3704.

5. M.Takino, S.Daishima and T.Nakahara, Rapid Commun. Mass Spectrom., 2003. 17, 383-390.

6. C.A.Moody, J.W.Martin, W.C.Kwan, D.C.G.Muir and S.A.Mabury, Environ.Sci.Technol., 2002. 36, 545-551.

7. K.J.Hansen, H.O.Johnson, J.S.Eldridge, J.L.Butenhoff and L.A.Dick, Environ.Sci.Technol., 2002. 36, 1681-1685.

8. J.W.Martin, K.Kannan, U.Berger, P.De Voogt, J.Field, J.Franklin, J.P.Giesy, T.Harner, D.C.G.Muir, B.Scott, M.Kaiser, U.Jarnberg, K.C.Jones, S.A.Mabury, H.Schroeder, M.Simcik, C.Sottani, B.Van Bavel, A.Karrman, G.Lindstrom and S.Van Leeuwen, Environ.Sci.Technol., 2004. 38, 248A-255A.

9. 3M Company. “Fluorochemical Isomer Distribution by 19F-NMR Spectroscopy.” 1997. US EPA Public Docket AR226-0564.

10. G.Cornelissen, P.C.M.Van Noort, G.Nachtegaal and A.P.M.Kentgens, Environ.Sci.Technol., 2000. 34, 645-649.

11. F.J.Weigert and K.J.Karel, J. Fluorine Chem., 1987. 37, 125-149.

12. A.A.Ribeiro and K.Umayahara, Magn. Reson. Chem., 2003. 41, 107-114.

13. J.L.Battiste, N.Jung and R.A.Newwark, J.Fluorine Chem., 2004. 125, 1331-1337.

14. T.A.Kestner, J.Fluorine Chem., 1987, 36, 77-82.

15. D.A.Ellis, K.A.Denkenberger, T.E.Burrow and S.A.Mabury, J.Phys. Chem. A, 2004. 10099-10106.

16. S.S.Jang, M.Blanco, W.A.Goddard III, G.Caldwell and R.B.Ross, Macromol. 2003. 36, 5331-5341.

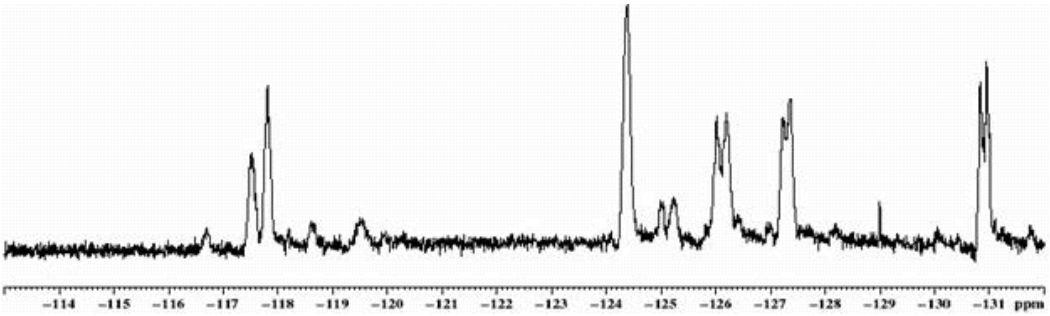


Figure 1. ^{19}F-NMR of Isomer **1** for the CF_2 region (trace amount of **6** present)

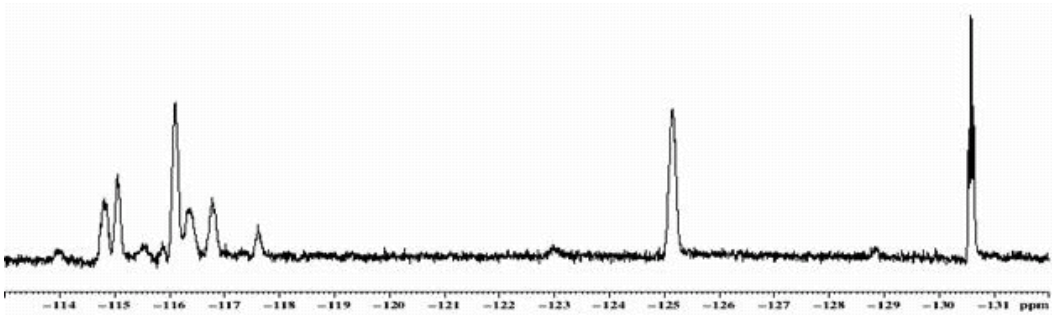


Figure 2. ^{19}F-NMR of Isomer **3** for the CF_2 region (trace amount of **4** present)

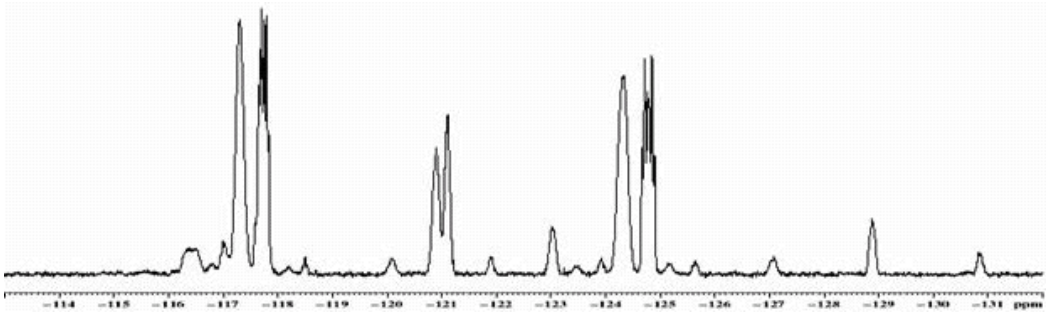


Figure 3. ^{19}F-NMR of Isomer **5** for the CF_2 region (trace amount of **2** and **4** present)