

**Atmospheric lifetime and oxidation products of N-ethyl perfluorobutylsulfonamide (C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>N(H)CH<sub>2</sub>CH<sub>3</sub>).**

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**Introduction**

Perfluorooctane sulfonate (PFOS) is a ubiquitous environmental contaminant that is detectable in wildlife and humans around the globe<sup>1-3</sup>. Some of the highest concentrations ever measured for PFOS are in polar bear liver samples collected in the Arctic<sup>4</sup>, making PFOS the most prominent organohalogen contaminant in polar bears compared to individual polychlorinated biphenyl (PCB) congeners and chlorinated pesticides<sup>4</sup>. These findings are remarkable because such locations are far from known source(s) of PFOS, and the physical properties of PFOS do not make it an obvious candidate for long-range transport in the atmosphere.

A novel class of perfluorooctylsulfonamides (C<sub>8</sub>F<sub>17</sub>SO<sub>2</sub>N(R<sup>1</sup>)(R<sup>2</sup>)) was previously detected in the atmosphere<sup>5</sup>, and we hypothesized that these may serve as "PFOS precursors" - which through atmospheric transport and oxidation would lead to the deposition of PFOS at remote global locations. Here we present results from smog chamber experiments with the model compound *N*-ethyl perfluorobutylsulfonamide (NEtFBSA; C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>N(H)CH<sub>2</sub>CH<sub>3</sub>), thus representing the first gas phase kinetic and product studies ever reported for a sulfonamide or a perfluoroalkylsulfonyl derivative. The implications for global dissemination of PFOS are discussed.

**Experimental Methods**

Experiments were performed in a 140-liter Pyrex reactor interfaced to a Mattson Sirius 100 FTIR spectrometer. The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL), which were used to photochemically initiate the experiments. Chlorine atoms were produced by photolysis of molecular chlorine. OH radicals were produced by the photolysis of CH<sub>3</sub>ONO in the presence of NO in air. Reaction rates were determined by the relative rate technique.

The loss of NEtFBSA and the reference compound(s) were monitored by FTIR spectroscopy using an infrared path length of 27 m and a resolution of 0.25 cm<sup>-1</sup>. NEtFBSA is a semi-solid at room temperature and was introduced into the chamber by slowly passing a fraction of the diluent gas over the sample. Where necessary, the concentration of NEtFBSA in the chamber was calculated by actively sampling 5L of chamber air onto XAD cartridges (Amberlite XAD-2, 400/200 mg) and by liquid chromatography tandem mass spectrometry (LC/MS/MS) analysis of the methanol eluent.

Initial concentrations of the gas mixtures for Cl atom relative rate experiments were 1.7-4.7 mTorr of NEtFBSA, 3-15 mTorr of the reference compounds (C<sub>2</sub>H<sub>5</sub>Cl or CH<sub>3</sub>OCHO), and 98-102 mTorr of Cl<sub>2</sub> in 700 Torr of either N<sub>2</sub> or air diluent. In the OH radical experiments the initial reagent concentrations were 5-8 mTorr of the reference compound (C<sub>2</sub>H<sub>2</sub>), 100-300 mtorr of CH<sub>3</sub>ONO, and 0-28 mTorr NO in 700 Torr of air diluent. Cl experiments were performed at 296 K, while OH reaction experiments were performed at 301 K.

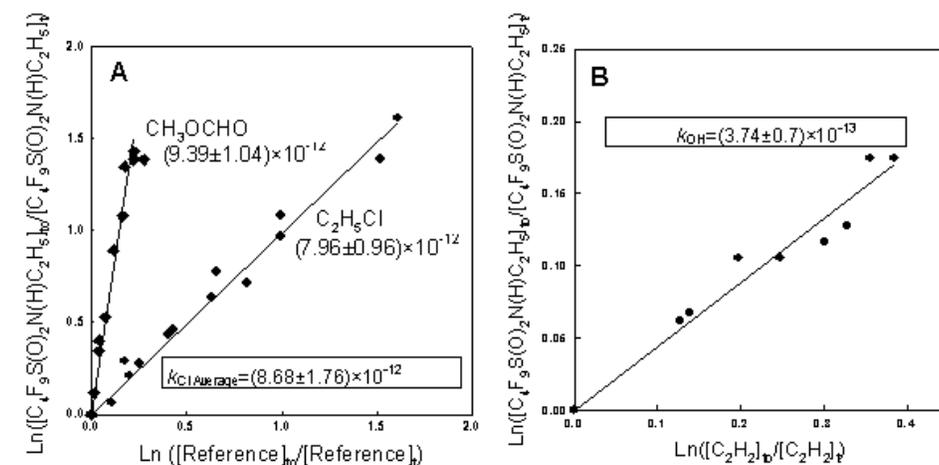
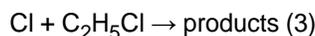
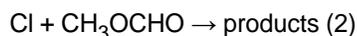
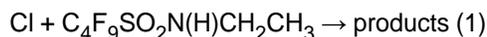
Reference compounds were obtained from commercial sources at purities > 99% and were subjected to repeated freeze-pump-thaw cycling before use. NEtFBSA was not available commercially, and was synthesized in our laboratory by reaction of dried C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>F and ethyl amine in diethyl ether, followed by distillation of the product C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>N(H)CH<sub>2</sub>CH<sub>3</sub>.

In smog chamber experiments it is important to check for unwanted loss of reactants and products via photolysis, dark chemistry, and heterogeneous reactions. Control experiments were performed in which mixtures of reactants (except Cl<sub>2</sub> or CH<sub>3</sub>ONO) in N<sub>2</sub> were let to stand in the dark for 20 min, followed by direct UV irradiation for another 20 min. There was no discernable loss of reactants or reference compounds in these control experiments, indicating that direct photolysis

and heterogeneous reactions are not a significant complication in the present work. Quoted uncertainties for the rate constants are two standard deviations from least squares regressions.

## Results

Relative rate study of the reaction of Cl atoms with NEtFBSA. The kinetics of reaction (1) were measured relative to reactions (2) and (3).



**Figure 1. Relative kinetics for the gas phase oxidation of NEtFBSA by (A) chlorine and (B) hydroxyl radical. Rate constant units are  $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ .**

Figure 1a shows the loss of NEtFBSA versus loss of the reference compounds following the UV irradiation of NEtFBSA/Cl<sub>2</sub>/reference mixtures in air or N<sub>2</sub> diluent.

There was no discernable effect of diluent gas on the kinetic data, and the experimental data was combined. The lines through the data in Figure 1a are linear least squares fits to the combined data sets which give values of  $k_1/k_2 = 6.71 \pm 0.74$  and  $k_1/k_3 = 0.99 \pm 0.12$ . Using  $k_2 = 1.4 \times 10^{-12}$  and  $k_3 = 8.04$

$\times 10^{-12}$ , we derive  $k_1 = (9.39 \pm 1.04) \times 10^{-12}$  and  $(7.96 \pm 0.96) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. Within the experimental uncertainty, results obtained using these two different reference compounds were indistinguishable, indicating the absence of significant systematic errors in the present work. We choose to cite a final value for  $k_1$  which is the average of the two determinations together with error limits which encompass the extremes of the individual determinations. Hence,  $k_1 = (8.68 \pm 1.76) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

Relative rate study of the reaction of OH radicals with NEtFBSA. Initial relative rate experiments to measure the OH radical rate constant required long irradiation times, suggesting relatively slow kinetics, however we were unable to analyze the data due to apparent non-linearity; whereby the kinetics seemed to slow down, relative to the reference compound, in later stages of the experiments. We later determined that this phenomenon was attributable to the propensity of NEtFBSA to partition to the walls of the chamber at lower temperatures and to come off the walls at higher temperatures. This problem was overcome by performing the experiments in a preheated chamber (301 K), rather than starting the experiment at room-temperature and having the temperature slowly increase throughout the experiment. Linear results were obtained in experiments whereby the chamber was filled with test substance/diluent at room temperature and by subsequently irradiating the chamber until the temperature stabilized at  $301 \pm 1 \text{ K}$ . The reference compound and methyl nitrite were then added and the experiment proceeded as usual. Subsequent irradiations maintained the temperature of the chamber.

The reactivity of OH radicals towards NEtFBSA (4) was studied relative to reaction with acetylene (5).



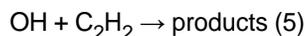
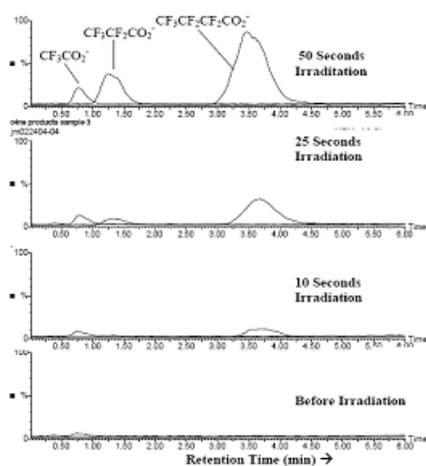


Figure 1b shows the loss of NEtFBSA versus loss of the reference compound upon exposure to OH radicals. The line through the data is the linear least squares fit to the combined data set which give a values of  $k_4/k_5 = 0.44 \pm 0.09$ . Using  $k_5 = 8.5 \times 10^{-13}$ , and considering the experimental uncertainties, we derive  $k_4 = (3.74 \pm 0.7) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

Product Study by FTIR. Replicate product studies, initiated by chlorine atoms, were analyzed by FTIR.  $\text{COF}_2$  and  $\text{SO}_2$  were the sole products that could be confirmed in FTIR spectra.  $\text{COF}_2$  and  $\text{SO}_2$  shared very similar temporal profiles, such that they were formed only in small quantities until the majority of NEtFBSA was consumed, followed by a dramatic increase thereafter. Once the spectral features of  $\text{COF}_2$  and  $\text{SO}_2$  were subtracted, a residual spectrum remained. The residual product(s) increased almost linearly until ~80-90% of the starting material had been depleted. Taken together, this suggests that the initial oxidation products were more persistent than NEtFBSA, and secondary reactions, including unzipping of the fluorinated chain to yield  $\text{COF}_2$ , proceeded only after NEtFBSA was largely consumed. Furthermore, the mechanism(s) of primary oxidation are likely localized to the alkyl portion of the molecule, rather than interaction with sulphur or nitrogen which could presumably lead to evolution of  $\text{COF}_2$  or  $\text{SO}_2$ .



**Figure 2. Production of perfluoroalkyl carboxylate products in a chlorine atom product study with NEtFBSA.**

Product Study by LC/MS/MS. Another product study was performed in the same manner as for FTIR data collection (chlorine atoms only), except that air was pumped quantitatively from the smog chamber onto XAD cartridges to allow for off-line extraction and analysis by LC/MS/MS. One XAD sample was a blank taken from the chamber filled with air only, and this showed no trace of starting material or of the major products. A second XAD sample was a pre-irradiation sample, collected after filling the chamber with air, chlorine gas, and NEtFBSA, but before the fluorescent blacklamps were turned on (e.g.  $t=0$ ). This sample was used to calculate a starting NEtFBSA concentration of 4.7 mTorr. Three product samples were collected on XAD at times corresponding to 20, 47, and 92% loss of starting material, as determined by FTIR (collected at  $t=10, 25,$  and  $50$  s total irradiation time, respectively).

LC/MS analysis of product samples revealed several other products that were distinguishable by their retention times, product ion scans, and/or accurate mass determination. The primary products of chlorine atom initiated oxidation were a ketone:  $\text{C}_4\text{F}_9\text{SO}_2\text{N}(\text{H})\text{COCH}_3$ , aldehyde #1:  $\text{C}_4\text{F}_9\text{SO}_2\text{N}(\text{H})\text{CH}_2\text{CHO}$ , and a product identified as  $\text{C}_4\text{F}_9\text{SO}_2\text{N}(\text{C}_2\text{H}_5\text{O})^-$  by high resolution MS – but whose structure remains tentative. Another reaction product, aldehyde #2:  $\text{C}_4\text{F}_9\text{SO}_2\text{N}(\text{H})\text{CHO}$ , was also observed and was presumed to be a secondary

oxidation product of the ketone and aldehyde #1. LC/MS/MS also indicated that a major product in all samples was the perfluorobutylsulphonamide (i.e.  $\text{C}_4\text{F}_9\text{SO}_2\text{NH}_2$ ), however this product was later synthesized and the spectrum collected by FTIR did not confirm its formation *in situ* until very late in the experiments. Therefore, its detection by LC/MS/MS was largely an artefact of the analytical conditions.

Perfluorobutanesulfonate was not detected above the level of the blank in any sample, however, three perfluoroalkyl carboxylates were detected above the level of the blank in Sample 1, 2, and 3; perfluorobutanoic acid (PFButA), perfluoropropionic acid (PFPropA), and trifluoroacetic acid (TFA) (Fig 2). The concentration of each acid increased with continued irradiation, and in Sample 3 each acid accounted for 0.33, 0.11, and 0.09% of the molar balance, respectively.

These results suggest that NEtFBSA is persistent enough to allow for substantial long-range transport. These results can be extrapolated to predict that the analogous perfluorooctyl species, *N*-ethyl perfluorooctylsulfonamide, could also undergo long-range transport, but a more detailed examination of their respective water solubilities and vapour pressures will allow a more accurate prediction of their tropospheric lifetimes. Other perfluoroalkylsulfonamides containing additional alkyl and/or alcohol moieties are expected to be more reactive than NEtFBSA. The products observed did not support a mechanism for the gas-phase production of perfluoroalkylsulfonates, however production of perfluorocarboxylic acids was observed, and this is consistent with their formation in similar fluorotelomer alcohol product studies<sup>6</sup>. A future product study should be conducted using hydroxyl radical, which is expected to be the primary mode of degradation in the troposphere for such substances. The observed primary and secondary oxidation products may be deposited to aquatic

and terrestrial ecosystems where they could then be further degraded to perfluoroalkyl sulfonates and amides through other biotic or abiotic degradation mechanisms.

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### References

- (1) Giesy, J. P.; Kannan, K. *Environ. Sci. Technol.* 2001, **35**, 1339-1342.
- (2) Hansen, K. J.; Clemen, L. A.; Ellefson, M. E.; Johnson, H. O. *Environ. Sci. Technol.* 2001, **35**, 766-770.
- (3) Kannan, K.; Corsolini, S.; Falandysz, J.; Fillmann, G.; Kumar Kurunthachalam, S.; Loganathan Bommanna, G.; Mohd Mustafa, A.; Olivero, J.; Van Wouwe, N.; Yang Jae, H.; Aldoust Kenneth, M. *Environ. Sci. Technol.* 2004, **38**, 4489-4495.
- (4) Martin, J. W.; Smithwick, M. M.; Braune, B. M.; Hoekstra, P. F.; Muir, D. C. G.; Mabury, S. A. *Environ. Sci. Technol.* 2004, **38**, 373-380.
- (5) Martin, J. W.; Muir, D. C. G.; Solomon, K. R.; Moody, C. A.; Ellis, D. A.; Kwan, W.; Mabury, S. A. *Anal. Chem.* 2001, **74**, 584-590.
- (6) Ellis, D. A.; Martin, J. W.; De Silva, A. O.; Mabury, S. A.; Hurley, M. D.; Andersen, M. P. S.; Wallington, T. J. *Environ. Sci. Technol.* 2004, **38**, 3316-3321.