ATMOSPHERIC CHEMISTRY OF PERFLUOROALKYSULFONAMIDES: KINETIC AND PRODUCT STUDIES OF THE OH AND CI ATOM INITIATED OXIDATION OF N-ETHYL PERFLUOROBUTYLSULFONAMIDE (C₄F₉SO₂N(H)CH₂CH₃).

J.W. Martin*, D.A. Ellis†, and S.A. Mabury†, M. D. Hurley† and T. J. Wallington†,

†Department of Chemistry, University of Toronto, 80 St. George St., Toronto, ON, Canada M5S 3H6
‡Ford Motor Company, SRL-3083, PO Box 2053, Dearborn, MI 48121-2053, USA
*Current address: Department of Public Health Sciences, University of Alberta, 10-102 Clinical Sciences Bldg., Edmonton, AB, Canada T6G 2G3

Abstract

Perfluorocyclodecanes (C₉F₁₈NOK₉) are present in the atmosphere and may via atmospheric transport and oxidation, contribute to perfluorocarboxylic acid (PFCA) and perfluorocarboxylate (PFOS) pollution in remote locations. Smog chamber experiments using the perfluorocyclodecanes analog: N-ethyl perfluorobutyrsulfonamide (NEtFBASA: C₄F₉SO₂N(H)CH₂CH₃) were performed to assess this possibility. Using relative rate methods, rate constants for reactions of NEtFBASA with chlorine atoms and OH radicals were determined as kCl = (8.68 ± 1.71) × 10⁻¹² and kOH = (3.4 ± 0.2) × 10⁻¹³ cm³ molecule⁻¹ s⁻¹. Similar modeling exercises suggest that reaction with OH radicals will dominate removal of perfluorooctylsulfonamides from the gas-phase (wet and dry deposition will not be important).

The atmospheric lifetime of NEtFBASA with respect to reaction with OH radicals is approximately 60 days allowing substantial long-range atmospheric transport. The primary products of chlorine atom initiated oxidation were: the ketone C₄F₉SO₂N(H)CH₂CHO, and a product identified as C₄F₉SO₂NH₂Cl. Perfluorobutanoic acid, perfluoropropionic acid, and trifluoroacetic acid. Taken together, results suggest a plausible route by which perfluorooctylsulfonamides may serve as atmospheric sources of PFCA's, including perfluorobutanoic acid.

Experimental Methods

Relative Rate Experiments

- C₄F₉SO₂N(H)CH₂CH₃ + reactant/reference/air mixtures were irradiated to study C radical kinetics (1)
- C₄F₉SO₂N(H)CH₂CH₃ + Cl⁻ → Cl⁻ + C₄F₉SO₂N(H)CH₂CHO (2)
- C₄F₉SO₂N(H)CH₂CH₃ + HCl⁻ → Cl⁻ + C₄F₉SO₂N(H)CH₂CH₂Cl (3)

OH + C₄F₉SO₂N(H)CH₂CH₃ → products (4)
OH + C₄F₉SO₂N(H)CH₂CH₃ → products (5)

Conclusions

The atmospheric lifetime of NEtFBASA with respect to reaction with OH radicals is approximately 60 days allowing substantial long-range atmospheric transport.

The primary products of chlorine atom initiated oxidation were: the ketone C₄F₉SO₂N(H)CH₂CHO, and a product identified as C₄F₉SO₂NH₂Cl. Perfluorobutanoic acid, perfluoropropionic acid, and trifluoroacetic acid were detected in all samples.

Results suggest a plausible route by which perfluorocyclodecanes may serve as atmospheric sources of PFCA's, including perfluorobutanoic acid.

Acknowledgments

The Natural Science and Engineering Research Council (NSERC) of Canada is thanked for funding this research through a postdoctoral fellowship grant (Martin). Funding for materials, supplies, and support was provided through an NSERC Discovery Grant and Strategic Grant (Mabury). Student travel assistance was provided by a Florida Student Travel Award (Benskin). This poster was prepared by Jonathan Benskin (University of Alberta).

Figure 2A. Loss of NEtFBASA versus loss of the reference compound upon exposure to OH radicals in separate experiments.

Figure 2B. Combined data for loss of NEtFBASA versus loss of the reference compound following the UV irradiation of NEtFBASA/Cl⁻ reactant/reference/air mixtures were irradiated to +Cl⁻/-HCl⁻.

Figure 3. Increasing production of perfluorooctanoic acid (PFCA) in the irradiation of NEtFBASA. Individual chromatograms are normalized to the same y-axis scale.

Figure 1. The appearance of (A) CO₂, (B) SO₂, and (C) "residual products" relative to the starting concentration of NEtFBASA in Torr/mTorr, or arbitrary units as a function of the disappearance of NEtFBASA in two replicate experiments (A and B). The residual product features increased linearly with the loss of starting material, at which point the residual features began to decrease and SO₂ and CO₂ evolution increased rapidly thereafter.