Background

Perfluorocarboxylic acids (PFCAs) have become ubiquitous in the environment. Atmospheric degradation of fluorotelomer alcohols (FTOAs), volatile precursors to the perfluorocarboxylic acids, including perfluorocarboxylic acid (PFOA) in Arctic animals. The abundance of water (gas, liquid, and solid) in the atmosphere could be significant. The gas phase reaction of CxF2x+1CHO (x=1,3,4) and HO2 radicals offers a qualitative explanation for the presence of long-chain perfluorinated aldehydes, including perfluorooctanoic acid (PFOA) in Arctic animals.

Abstract

Smog chamber/FITR techniques were used to study the Cl atom and OH radical initiated oxidation of perfluorinated aldehyde hydrates, CxF2x+1CHOH (x=1,3,4) in 700 Torr of Ar/N2/O2 diluent. It was established that reaction of the hydrate with OH radicals gives CxF2x+1COOH radical which reacts with O3 to give CxF2x+1COOOH (and HO2) in 100% molar yield.

Rate constants of k(CxF2x+1CH(OH)2 +Cl ) = (5.92 ± 0.88) x 10-13 cm3 molecule-1 s-1 leads to an estimate of reaction with OH radicals. Assuming an atmospheric lifetime for CxF2x+1CHOH, it is known that the gas phase reaction of CxF2x+1C(O)O2 (formed during the atmospheric degradation of CxF2x+1CHO) with HO2 radicals offers a qualitative explanation for the presence of PFCAs observed in the environment (yields of 8-38%, Sulbaek Andersen et al. J. Phys. Chem., 2004, 108, 6325).

Evaluating the Rate of Hydration

Smog chamber relative rate techniques were used to study the kinetics of reactions of Cl atoms and OH radicals with CxF2x+1CHOH. It was established that CF3CHOH has stable hydrates of the formula CxF2x+1CHOH.

The length of the molecule had no discernable impact on the reaction. This seems reasonable based on expectations that the CxF2x+1CHOH group will not react with OH atoms, and that its influence on the reactivity of the –CHOH group will not change markedly upon increasing “x”.

Conclusions

In the atmosphere, the oxidation of CxF2x+1CHOH is initiated by reaction with OH radicals. Cl atoms and OH radicals react with CxF2x+1CHOH via the same mechanism and give the same radical products.

In this study we determine that CxF2x+1CHOH have an atmospheric lifetime of approximately 6 months with respect to reaction with OH radicals. In the Cl initiated oxidation of CxF2x+1CHOH, only one product, CF3COOH, was found and in a yield which was indistinguishable from 100%.

Given the structural similarity of CF3CHOH to longer chain perfluorinated aldehyde hydrates, the atmospheric oxidation mechanism for CF3CHOH is likely to be similar to the longer chain perfluorinated aldehyde hydrates.

It is known that the gas phase reaction of CxF2x+1C(O)O2 (formed during the atmospheric degradation of CxF2x+1CHO) with HO2 radicals offers a qualitative explanation for the presence of PFCAs observed in the environment (yields of 8-38%, Sulbaek Andersen et al. J. Phys. Chem., 2004, 108, 6325).

We show herein that hydration and subsequent reaction with OH radicals in the atmosphere could potentially enhance the production of PFCAs during the atmospheric degradation of CxF2x+1CHO.

The rate of hydration needs to be further evaluated to access the importance of hydration as an atmospheric loss mechanism for CxF2x+1CHO.

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