Environmental Fate of Polyfluorinated Chemicals

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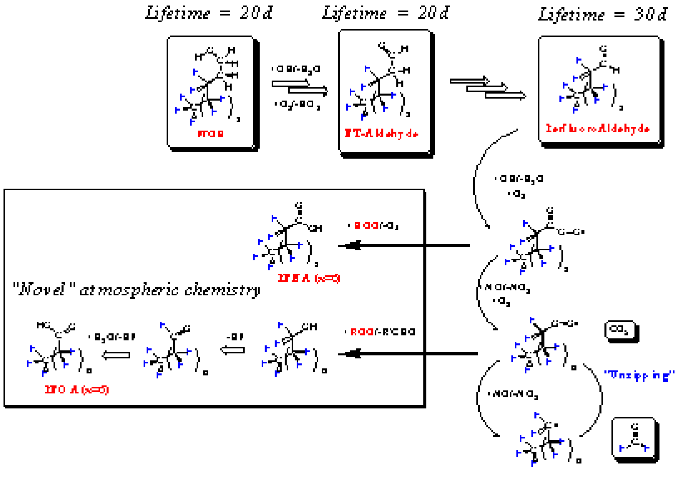
The chemical architecture of the carbon fluorine bond imparts unique and useful properties such that it is now widely utilized in both consumer and industrial applications. Fluorine is frequently incorporated into agrochemical, pharmaceutical, industrial, and consumer chemicals to enhance their stability, surface properties, or movement. The role fluorine plays in the environmental fate, persistence, and disposition of these chemicals is of significant interest to the public, industry, and government regulators. Our recent research, in this area, has probed the specific fate of polyfluorinated chemicals renowned for their surface active properties thus popular for use in textile, carpet, and paper products. The widespread dispersal of the perfluorinated anions, such as PFOS and PFNA are potentially related to these heavily used consumer products.

Our evolving theory is that polyfluorinated alcohol precursors are sufficiently volatile to escape from these consumer products and are persistent enough to be transported long distances. During their atmospheric residence these materials undergo oxidative processing and are degraded at least partially to yield the perfluorinated acids (PFAs). The PFAs are then deposited, through wet and dry deposition, widely in the environment, including remote Arctic regions, and subsequently enter the food chain. It is likely that partially degraded products will also enter the food chain and potentially be metabolized to the PFAs. The fluorotelomer alcohols (FTOHs) are potential volatile precursors for the perfluorinated carboxylic acids (PFCAs) while the polyfluorinated sulfamidoethanols would correspondingly yield the perfluorinated sulfonates such as PFOS. The talk will focus largely on the potential for conversion of FTOHs to explain the high concentrations of PFCAs in remote regions.

FTOHs and related chemistries function, once they are covalently appended to a polymer backbone, effectively to provide hydro- and lipophobic properties to surfaces. The basic structural element of FTOHs is represented by $CF_3CF_2(CF_2\text{-}CF_2)_xCH_2CH_2OH$ with the 8:2 FTOH having x=3. The relevant physical and chemical properties of the FTOHs are dominated by the perfluorinated alkyl tail. For instance, vapour pressures have been determined to range from ~15 to ~240 Pa (25 C) for the 8:2 FTOH with higher and lower values for the shorter and longer chains respectively; the reason for the large difference in measured values is unclear though all published values suggest FTOHs will primarily be in the gas phase.[1,2,3] These vapour pressures are higher than would be expected based on simple mass considerations if extrapolated from hydrocarbon alcohols. Combined with moderately low water solubilities (~150 mcg/L for the 8:2 FTOH) the high vapour pressures results in significant Henry's Law Constants. This property was utilized to investigate the presence of residual FTOHs in a number of fluorinated polymers and surfactants. The fluorinated materials were dispersed in a large volume of water which was then sparged with nitrogen to enhance the stripping of residual FTOHs. The FTOHs were trapped onto an XAD cartridge and subsequently analyzed by GC/MS. Data from a suite of fluorinated materials obtained from both commercial and industrial sources suggested the typical residual FTOH mean value to be a few %. This represents a potential significant source of fugitive emissions of FTOHs to the atmosphere since it would be a more direct route than degradation of the polymer linkage chemistry.[4.] The existence of a residual pool of FTOHs in fluorinated polymers (annual production ~13 million kg) combined with high vapour pressures lead us to develop methods to investigate their presence in atmospheric samples.

FTOHs were first discovered in air samples from Toronto and a nearby rural location in 2001.[5] A more extensive sampling during November 2002 indicated FTOHs are widely observed across North America in the 10 to 100 pg/m^3 range while the sulfamidoethanols ranged from 15 to 1500 $pg/\ m^3$. The highest concentrations were observed in central Georgia, a state known for its large carpet industry.[6] Typically urban locations showed higher concentrations of fluoroalcohols than more rural locations. Sampling methods utilized high-vol air samplers outfitted with PUF:XAD:PUF sandwiches with subsequent analysis and identification provided by GC/MS in PCI and NCI modes.

Smog chamber studies, carried out with colleagues at Ford, indicated the FTOHs react primarily with OH leading to a lifetime on the order of 10 to 20 days, sufficient for significant long-range transport.[7] The sole degradation product is the FTOH aldehyde, also long-lived, which proceeds through successive OH initiated reactions to ultimately yield the FTOH acids, perfluorinated aldehydes, PFCAs (1 to 10%), and carbonyl fluoride as the dominant product.[8,9] The channels leading to PFCAs are highly dependent on the interplay between NOx and ROO species with urban areas projected to yield little to no PFCAs while rural and more remote areas will produce more significant conversions.[10,11] Interestingly, smog chamber results showed that fluorinated acids were produced for the all the possible chain lengths of a given FTOH. For instance the 8:2 FTOH generated the FTOH acid, PFNA and PFOA in roughly equivalent yield, and decreasing yields of the subsequent carbon chain length from the seven carbon PFHpA down to the two carbon TFA. Chain length had no influence on FTOH lifetime while shorter chain length yielded more efficient conversion to the PFCAs. Extensive smog chamber studies have provided a possible explanation for the production of PFCAs via atmospheric processing. An overall reaction scheme is proposed below.



where n=x-1, x-2, etc.

Long chain (9 to 14 carbons) PFCAs were first discovered in the livers of fish in a Toronto creek in the summer of 2001.[12] Once these PFCAs were added to the standard mix for analysis the PFCAs were shown to be present in the majority of biological samples tested and are particularly high in remote Arctic regions in species at the top of the food chain.[13,14,15] Interestingly, many biological samples, such as Polar Bear livers, shown an even:odd chain length pattern with the larger 'odd PFCA' appearing at higher concentrations than the next lower chain length 'even PFCA' (e.g. PFNA and PFOA). This could arise from the delivery of roughly equivalent quantities of the even and odd PFCAs to the region followed by food chain bioconcentration with the longer chain PFCA expected to reach higher concentrations.[16,17] The PFCA isomer signature analysis suggests a linear alkyl source thereby presumably ruling out an electrochemical process though further studies are underway to determine the extent of biological isomer discrimination.[18] Metabolism studies, in both microbes and rats, show analogous transformation pathways leading to PFCAs, as well as highly reactive intermediates.[19,20,21] These studies though indicate a biological route to the odd chain length PFCAs is unlikely since this would presumably require alpha oxidation which was, at most, minor in our rat studies.

Substantial evidence now supports an overall theory that FTOHs are a significant source of PFCAs to the remote environment and may be important in human exposures. Recommendations for solving this chemical pollution problem and the continued use of these useful materials include removing residual FTOHs prior to fluorinated polymer use, shortening the perfluorinated alkyl chain to lessen bioaccumulation potential, and strengthening linkage chemistry between the fluoro-alcohol and the polymer.

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