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Reductive Defluorination of Aqueous Perfluorinated Alkyl Surfactants: Effects of Ionic Headgroup and Chain Length

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Perfluorinated chemicals (PFCs) are distributed throughout the environment. In the case of perfluorinated alkyl carboxylates and sulfonates, they can be classified as persistent organic pollutants since they are resistant to environmentally relevant reduction, oxidation, and hydrolytic processes. With this in mind, we report on the reductive defluorination of perfluorobutanoate, PFBA ($C_3F_7CO_2^-$), perfluorohexanoate, PFHA ($C_5F_{11}CO_2^-$), perfluorooctanoate, PFOA ($C_7F_{15}CO_2^-$), perfluorobutane sulfonate, PFBS ($C_4F_9SO_3^-$), perfluorohexane sulfonate, PFHS ($C_6F_{13}SO_3^-$), and perfluorooctane sulfonate, PFOS ($C_8F_{17}SO_3^-$) by aquated electrons, e_{aq}^-, that are generated from the UV photolysis ($\lambda = 254$ nm) of iodide. The ionic headgroup ($\text{-}SO_3^-$ vs $\text{-}CO_2^-$) has a significant effect on the reduction kinetics and extent of defluorination (F index $= -[F^-]_{produced}/[PFC]_{degraded}$). Perfluoroalkylsulfonate reduction kinetics and the F index increase linearly with increasing chain length. In contrast, perfluoroalkylcarboxylate chain length appears to have a negligible effect on the observed kinetics and the F index. H/F ratios in the gaseous fluoro-organic products are consistent with measured F indexes. Incomplete defluorination of the gaseous products suggests a reductive cleavage of the ionic headgroup occurs before complete defluorination. Detailed mechanisms involving initiation by aquated electrons are proposed.

Introduction

Fluorinated chemicals (FCs) such as fluorotelomer alcohols, partially fluorinated amphiphiles, perfluoroalkyl carboxylates, and perfluoroalkylsulfonates have been widely used for and/or in the production of inert polymers such as Teflon, waterproofing textiles, protective coatings on metals, aqueous film-forming foams (AFFFs), semiconductor etching, and as lubricants. Atmospheric oxidation[1,2] and biotransformation[3,4] can convert partially fluorinated chemicals into environmentally persistent perfluorochemicals (PFCs). For example, perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) have been detected globally in surface waters[5,6] due to atmospheric[7] and oceanic transportation.[8]

Perfluorochemicals are chemically inert due to relatively high organic bond strengths (e.g., 413.0 kJ/mol for $F_3C{-}CF_3$; 530.5 kJ/mol for $F{-}C_2F_5$)[9] and fluorine's electronegativity making them resistant to conventional advanced oxidation processes (AOPs).[10−13] For example, hydroxyl radical ($^{\bullet}OH$) with a reduction potential of $E° = 2.73$ V[14] reacts with a typical hydrocarbon octanoate with a second-order rate constant that is $>10^9$ M^{-1} s^{-1};[15] however, the corresponding second-order rate constants, when the compounds are perfluorinated, have an upper limit of $<10^5$ M^{-1} s^{-1} (e.g., PFOA and PFOS).[16] Direct electron transfer oxidation processes (e.g., $S_2O_8^{2-}$/UV[13] and $PW_{12}O_{40}^{3-}$/UV[12]) and aqueous pyrolysis (i.e., sonolysis)[17,18] have shown to be more effective for PFC remediation. Perfluorocarboxylate reaction rate constants with sulfate radical ($SO_4^{\bullet -}$) are estimated to be on the order of 10^4 M^{-1} s^{-1},[19,20] orders of magnitude lower than the sulfate radical constants with hydrocarbons.[21]

Reductive remediation of perfluorocarboxylates and perfluorosulfonates is feasible.[22−24] For example, PFOS and PFHS can be reduced by elemental iron (Fe(0), $E = -0.447$ V)[14] in water under extreme conditions (350 °C, 20 MPa).[23,24] Aromatic,[25,26] benzylic,[27] olefinic,[28,29] and tertiary[30−32] fluoroorganics readily undergo reductive defluorination by chemical and electrochemical methods. Studies on linear fluorochemicals containing only secondary[20] and primary[33] C−F bonds are limited due to low ($E < -2.7$ V) reduction potentials.[34,35] Reductive fluoride elimination is influenced by a number of chemical properties such as C−F bonding character (e.g., σ vs π character),[26] electron density,[36] redox potential,[35] anion radical stability,[25] ionic headgroup,[16] $-(CF_2)_n-$ chain length,[20] and electron-donating reagent strength.[37] The activation energies of aqueous electron reactions with halo-organics are invariable and small (6 to 30 kJ/mol) due to tunneling effects.[38] However, fluoroorganic reduction rates are lower than other organohalogens since fluorine has no low-lying vacant d orbital to accept an electron. Low PFC water solubility has limited most reductive defluorination studies to organic solvents.[39]

A systematic study on the reductive remediation of aqueous PFCs ($C_3F_7CO_2^-$, $C_5F_{11}CO_2^-$, $C_7F_{15}CO_2^-$, $C_4F_9SO_3^-$, $C_6F_{13}SO_3^-$, and $C_8F_{17}SO_3^-$) has yet to be completed. We here utilize the aquated electron (e_{aq}^-, $E°_{aq/e} = -2.9$ V), a powerful

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TABLE 1: Apparent First-Order Rate Constants, Quantum Yields, and F Indexes for the Decomposition of Perfluoroalkylcarboxylates and Perfluoroalkylsulfonates by Aqueous Iodide Photolysis[a]

PFC	formula	k (min^{-1})	QY	F index[b]
perfluorobutanoate, PFBA	$CF_3(CF_2)_2CO_2^-$	1.3×10^{-3}	7.1×10^{-4}	1.2
perfluorohexanoate, PFHA	$CF_3(CF_2)_4CO_2^-$	1.1×10^{-3}	6.9×10^{-4}	1.9
perfluorooctanoate, PFOA	$CF_3(CF_2)_6CO_2^-$	1.4×10^{-3}	6.4×10^{-4}	1.6
perfluorobutane sulfonate, PFBS	$CF_3(CF_2)_3SO_3^-$	4.0×10^{-4}	2.4×10^{-4}	2.5
perfluorohexane sulfonate, PFHS	$CF_3(CF_2)_5SO_3^-$	1.2×10^{-3}	5.7×10^{-4}	5.9
perfluorooctane sulfonate, PFOS	$CF_3(CF_2)_7SO_3^-$	3.0×10^{-3}	1.2×10^{-3}	9.2

[a] See Figure 3 for detailed experimental conditions. [b] $-[F^-]_{Produced}/[PFC^-]_{Degraded}$

reductant, to decompose a number of perfluoroalkyl carboxylates and perfluoroalkyl sulfonates of varying chain (hydrophobic tail) length (e.g., C_3 to C_8). Aquated electrons are generated from UV photolysis of aqueous iodide solutions via charge-transfer-to-solvent (CTTS) states.[40] The kinetics and mechanism of aqueous PFC reduction is significantly affected by ionic headgroup speciation and fluorinated tail length.

Experimental Details

PFOA ($C_7F_{15}CO_2NH_4$, 3M), PFHA ($C_5F_{11}CO_2H$, >97%, Fluka), PFBA ($C_3F_7CO_2H$, >98%, Aldrich), PFOS ($C_8F_{17}SO_3K$, 3M), PFHS ($C_6F_{13}SO_3K$, >98%, Fluka), and PFBS ($C_4F_9SO_3K$, 3M) were used as received. PFC stock solutions were prepared to be 500 mg/L, and the pH was adjusted to between 6 and 8 with HCl or NH_4OH. A 1 mol/L KI (Fisher) aqueous stock solution was freshly prepared every week and stored in the dark.

PFC and KI stock solutions were diluted with Milli-Q water to 30 mL. Photolysis was completed in a Pyrex glass reactor with a quartz window and irradiated with 254-nm light source (UVP, 8 W). Argon or air was continuously purged through the aqueous solution or through the headspace. An 0.5-mL sample aliquot was taken at different time points during photolysis and, if necessary, diluted prior to analysis. The incident photon flux was determined to be $5.17(\pm 0.06) \times 10^{-5}$ mol L^{-1} min^{-1} by iodide/iodate actinometry using the intrinsic quantum yield of iodide/iodate as a reference.[38]

Initial PFC and possible aqueous-phase intermediate analysis was completed by high-performance liquid chromatography/mass spectrometry (HPLC-MS, Agilent 1100 LC and Agilent Ion Trap) with a Betasil C18 column (Thermo-Electron) of dimensions 2.1 mm inside diameter, 100 mm length, and 5-μm particle size. A 2 mM aqueous ammonium acetate:methanol gradient mobile phase at a flow rate of 0.3 mL min^{-1} was used for separation. The samples were analyzed by the MS/MS (Agilent, MSD Trap) in negative mode monitoring for the molecular ions of PFOS ($m/z = 499$), PFHS ($m/z = 399$), and PFBS ($m/z = 299$), and decarboxylated ions of PFOA ($m/z = 369$), PFHA ($m/z = 269$), and PFBA ($m/z = 169$). The nebulizer gas pressure was 40 PSI, drying gas flow rate and temperature 9 L min^{-1} and 325 °C, the capillary voltage set at + 3500 V, and the skimmer voltage −15 V. HPLC analytical procedures are detailed elsewhere.[18]

Ion chromatography (Dionex DX-500) was used for the analysis of fluoride and other ionic intermediates. Aliquots (0.5 mL) were transferred from the reactor to disposable sample vials (PolyVial) and sealed with filter caps (PolyVial) and loaded onto an AS-40 autosampler. The 0.5-mL sample was injected, and anions were separated on an IonPac AS11-HC anion exchange column and quantified by conductivity measurement. Linear calibration curves were generated using standard solutions of sodium fluoride, sodium sulfate, and sodium formate at concentrations varying from 1 to 200 μM.

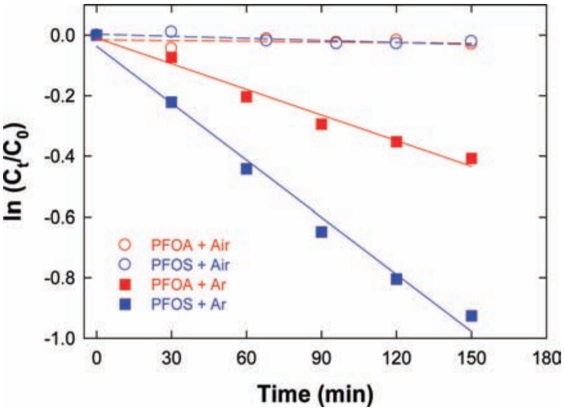


Figure 1. Time profiles of PFOX (X = A and S for carboxylate and sulfonate, respectively) degradation during $\lambda = 254$ nm irradiation of an aqueous KI-PFOX solution in the presence and absence of oxygen (i.e., air vs Ar). PFOS and PFOA are identically 100 ppb, i.e., $[PFOA]_0 = 0.24\ \mu M$; $[PFOS]_0 = 0.20\ \mu M$; $[KI]_0 = 10$ mM.

The gaseous fluoro-compound intermediates produced were analyzed by gas chromatography (GC) MS. The reactor headspace was continuously purged with argon. The purge gas containing the reaction intermediates was circulated over a thermal desorption tube (CarboTrap, Supelco) to adsorb the intermediates. After completion of the reaction, the purge gas was turned off and the tubes were sealed to atmosphere. The analysis consisted of thermal desorption of the adsorbed intermediates from the tube and analysis of the desorbed gases by GC-MS (Agilent 6890 GC and 5973 MSD) using electron-impact (EI, 80 eV) ionization. Fluorochemical intermediates were identified by searching the spectra for characteristic ions such as $m/z = 69$, the trifluoromethyl anion.

Results and Discussion

Figure 1 shows the time course for the reductive decomposition of PFOS and PFOA during the photolysis ($\lambda = 254$ nm) of an aqueous iodide solution in the presence of argon and air ($[PFOS]_i = 0.20\ \mu M$, $[PFOA]_i = 0.24\ \mu M$, $[I^-]_i = 10$ mM). The quantum yield for the generation of aquated electrons from iodide photolysis at 248 nm (eq 1) is 28%.[39] In the presence of air, PFOS and PFOA are not degraded due to the rapid reaction ($k_3 = 1.9 \times 10^{10}$ M^{-1} s^{-1})[15] of the aquated electron with dissolved oxygen (~0.2 mM) (eq 3)

$$I^- + h\nu \rightarrow I^{-*}_{CTTS} \rightarrow I^\bullet + e^-_{aq} \tag{1}$$

$$e^-_{aq} + I^\bullet \rightarrow I^- \tag{2}$$

$$e^-_{aq} + O_2 \rightarrow O_2^- \tag{3}$$

$$e^-_{aq} + PFOX^- \rightarrow PFOX^{\bullet 2-} \tag{4}$$

However, in the presence of Ar (i.e., in the absence of air) PFOS and PFOA initial decomposition (eq 4, where X = S and A for sulfonate and carboxylate, respectively) follows pseudo-first-order kinetics. Under these conditions, the rate of PFOS reduction is two times greater than that of PFOA ($k_{app}^{-PFOS} = 6.5 \times 10^{-3}$ min^{-1}; $k_{app}^{-PFOA} = 2.9 \times 10^{-3}$ min^{-1}). The relative photoreduction rates ($k_{app}^{-PFOS}/k_{app}^{-PFOA}$) are consistent with those observed in pulse radiolysis[16] where k_4^{-PFOS} and k_4^{-PFOA} for reduction by aquated electrons are reported to be 7.3×10^7 and 5.1×10^7 M^{-1} s^{-1}, respectively. A more recent laser flash photolysis study[20] reported $k_4^{-PFOA} = 1.7 \times 10^7$ M^{-1} s^{-1}.

The quantum yields for the photoreduction of PFOS and PFOA are 11.8×10^{-4} and 6.4×10^{-4}, respectively. The relatively low quantum yields (~0.1%) indicate that there are quenching reactions for aquated electrons. Photodetachment of an aquated electron produces iodine atom ($I^{\bullet}$, eq 1). $I^{\bullet}$ complexes with a neighboring iodide forming the diiodide radical anion ($I_2^{\bullet-}$, eq 5,5′) with an equilibrium constant, $K_5 > 1.2 \times 10^4$. The complexation is diffusion controlled and $[I^-]_{ss} \gg [e^-]_{ss}$ such that $R_5 > R_2$ and $[I_2^{\bullet-}]/[I^{\bullet}] = 120$. The diffusion-controlled reaction ($k_6 = 3.2 \times 10^9$ M^{-1} s^{-1}) between two $I_2^{\bullet-}$ molecules (eq 6) produces triiodide (I_3^-) and I^-

$$I^{\bullet}+I^{-}\leftrightarrow I_2^{\bullet-} \tag{5,5′}$$

$$I_2^{\bullet-}+I_2^{\bullet-}\rightarrow I_3^{-}+I^{-} \tag{6}$$

Aquated electron quenching may occur via $I^{\bullet}$ carriers (eq 7) or by way of hydrogen production (eq 8)

$$e_{aq}^{-}+I_2^{\bullet-}/I_3^{-}\rightarrow I^{-}/I_2^{\bullet-}+I^{-} \tag{7}$$

$$e_{aq}^{-}+H^{+}\rightarrow H^{\bullet} \qquad H^{\bullet}+e_{aq}^{-}+H^{+}\rightarrow H_2 \tag{8}$$

As shown in Figure 2a, the steady-state triiodide concentration, $[I_3^-]_{ss}$, is almost negligible in aqueous solutions without PFOX (i.e., in the absence of dissolved oxygen) and increases to micromolar levels upon addition of PFOX suggesting the $I^{\bullet}$ carrier quenching is the predominant mechanism. pH changes during photolysis (Figure 2b) is consistent with $I^{\bullet}$ carrier quenching of aquated electrons. $H^{\bullet}$, intermediates in eq 8, may also be quenched by $I^{\bullet}$ carriers. For comparison, in the absence of PFOX and oxygen, pH increases to and is sustained at 8 immediately after light irradiation probably due to proton consumption by e_{aq}^- (eq 8). The PFOA photolysis also continuously increases the pH, although this is not obvious in Figure 2b. For example, a comparison of the absolute change in proton concentration is made after 3 min of photolysis, and $\Delta[H^+]$(no PFOX) = -4.7×10^{-7} M; $\Delta[H^+]$(PFOS) = -2.9×10^{-7} M; and $\Delta[H^+]$(PFOA) = -4.6×10^{-6} M. The greater absolute change during PFOA photolysis is a result of the initial pH of the PFOA solution being ca. 2 orders of magnitude less than the PFOS solution, which will increase the absolute rate of reactions such as eq 8, which consume protons. The pH during PFOS photolysis decreases shortly after the initial increase, $t > 3$ min. The bell-shaped pH change during PFOS photolysis is ascribed to the initial proton consumption by eq 8 and subsequent interruption of eq 8 by reaction of aqueous electrons with PFOS reduction intermediates with concomitant fluoride production (i.e., pK_a(HF) = 3.45). The constant rise in pH during PFOA photolysis suggests analogous reduction intermediates are not produced.

Reaction of the initial perfluorinated alkyl carboxylate or sulfonate with e_{aq}^- yields the corresponding radical anion ($C_nF_{2n+1}X^{\bullet 2-}$; $n = 8$, X = SO_3 for PFOS$^{\bullet 2-}$; $n = 7$, X = CO_2 for PFOA$^{\bullet 2-}$, eq 4). The radical anion will quickly decompose via fluoride elimination[27,41] to yield the perfluoroalkyl radical ($C_nF_{2n}X^{\bullet -}$, eq 9)

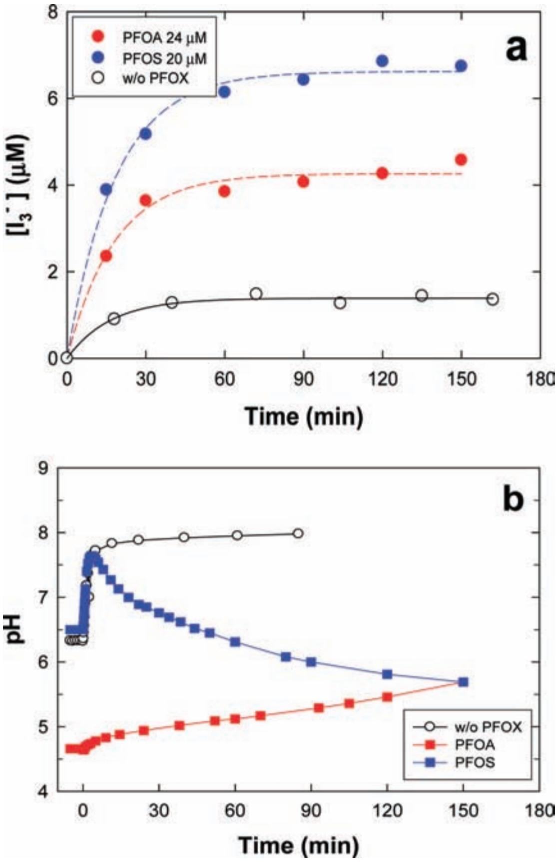


Figure 2. Time profiles of (a) triiodide production and (b) pH change during the photolysis of aqueous iodide-PFOX solutions. $[PFOS]_0 = 20$ μM; $[PFOA]_0 = 24$ μM; $[KI]_0 = 10$ mM; $\lambda = 254$ nm and in the presence of Ar.

$$C_nF_{2n+1}X^{\bullet 2-}\rightarrow C_nF_{2n}X^{\bullet -}+F^{-} \tag{9}$$

$$C_nF_{2n}X^{\bullet -}+e_{aq}^{-}\rightarrow C_nF_{2n}X^{2-} \tag{10}$$

$$C_nF_{2n}X^{\bullet -}+I^{\bullet}\underset{h\nu}{\rightleftharpoons} C_nF_{2n}IX^{-} \tag{11}$$

$$C_nF_{2n}IX^{-}+e_{aq}^{-}\rightarrow C_nF_{2n}X^{\bullet -}+I^{-} \tag{12}$$

$$C_nF_{2n}X^{2-}\rightarrow C_nF_{2n-1}X^{-}+F^{-} \tag{13}$$

$$C_nF_{2n}X^{2-}+H^{+}/H_2O\rightarrow C_nF_{2n}HX^{-} \tag{14}$$

$$C_nF_{2n}X^{\bullet -}+H^{\bullet}\rightarrow C_nF_{2n}HX^{-} \tag{15}$$

The electrophilic perfluoroalkyl radicals[42−44] may react further with e_{aq}^- to yield carbanions ($C_nF_{2n}X^{2-}$, eq 10) or with $I^{\bullet}$ carriers (i.e., $I^{\bullet}$, $I_2^{\bullet -}$, $I_3^{\bullet -}$) to yield the perfluoroalkyl iodide carboxylate or sulfonate ($C_nF_{2n}IX^-$, eq 11). The perfluoroalkyl iodide carboxylates and sulfonates will be converted back to perfluoroalkyl radicals via photolytic homolysis of the C−I bond (eq 11) or via reaction with e_{aq}^- to yield the radical and I^- (eq 12).[45] In organic solvents, the carbanion undergoes an intramolecular defluorination to give an olefin (eq 13).[27,35] However, in the presence of water, the carbanion, which is a strong base, will be protonated. An overall H/F exchange may also occur via reaction of a fluoroalkyl radical anion ($C_nF_{2n}X^{\bullet -}$) with an $H^{\bullet}$ (eq 15). If an H/F exchange product retains the anionic carboxylate or sulfonate terminal group, it will remain in the aqueous phase and proceed through sequential H/F exchanges. Subsequent e_{aq}^- reductions with partially defluorinated intermediates ($C_nF_{2n}IX^-$, $C_nF_{2n-1}X^-$ or $C_nF_{2n}HX^-$) should be faster

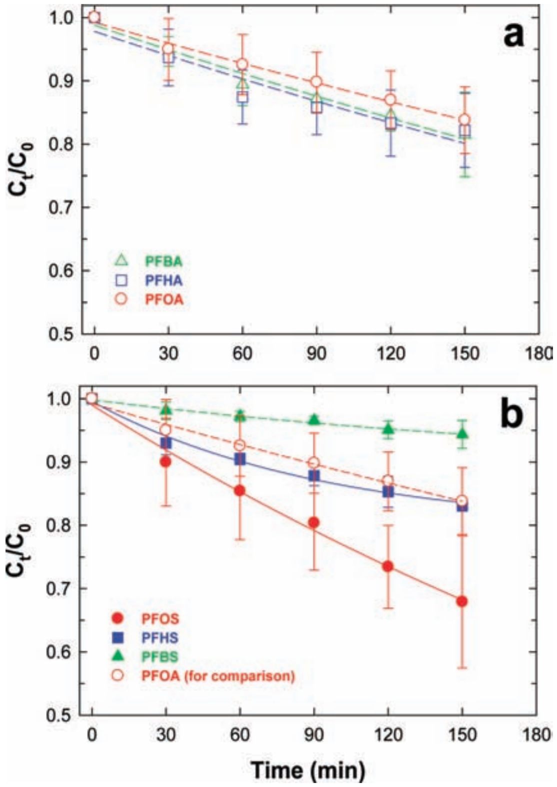


Figure 3. Time profiles of (a) PFXA (X = O, H, B) and (b) PFXS (X = O, H, B) degradation during $\lambda = 254$ nm irradiation of aqueous KI solution in the presence of Ar. All PFCs are identically 10 ppm, i.e., $[PFOS]_0 = 20\ \mu M$; $[PFHS]_0 = 25.1\ \mu M$; $[PFBS]_0 = 33.4\ \mu M$; $[PFOA]_0 = 24\ \mu M$; $[PFHA]_0 = 31.9\ \mu M$; $[PFBA]_0 = 46.0\ \mu M$; $[KI]_0 = 10$ mM.

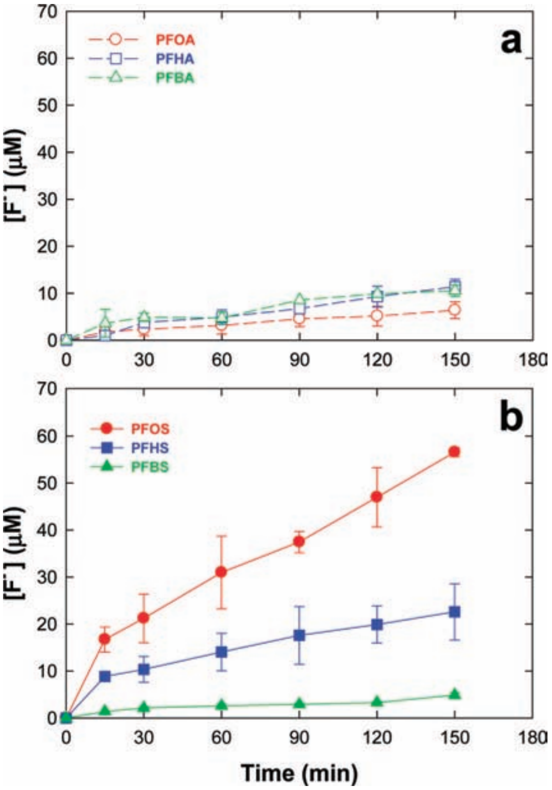


Figure 4. Time profiles of fluoride production during iodide and (a) PFXA (X = O, H, B) and (b) PFXS (X = O, H, B) photolysis. Experimental conditions are identical to those of Figure 3.

than the initial defluorination step.[27] For example, the reduction potentials and kinetics of fluorochemicals follow the order: 3° > 2° > 1°.[20,30−35] Also, C−F bond strength increases as the number of C−F bonds increases; $H_3C{-}F$ (107 kcal/mol), $H_2FC{-}F$ (109.6 kcal/mol), $HF_2C{-}F$ (114.6 kcal/mol), and $HF_3{-}F$ (116 kcal/mol).[9]

Shorter-chained PFCs (PFHS, PFBS, PFHA, and PFBA, where H = hexane and B = butane) were photolyzed under the same conditions. Parts a and b of Figure 3 show the time-dependent reactions of all six PFCs with photoproduced aquated electrons. The three perfluoroalkyl carboxylates have similar pseudo first-order degradation rates, $k_{app}^{-PFOA} \approx k_{app}^{-PFHA} \approx k_{app}^{-PFBA} \approx 1.3 \times 10^{-3}\ \text{min}^{-1}$ (Figure 3a), and the carboxylate kinetics are plotted on the sulfonate curve as a dashed line for comparison (Figure 3b). In contrast, the perfluoroalkyl sulfonates kinetics are dependent on chain length, $k_{app}^{-PFOS} > k_{app}^{-PFHS} > k_{app}^{-PFBS}$, and the rate decreases with decreasing chain length (3.0×10^{-3}, 1.2×10^{-3}, and $4.0 \times 10^{-4}\ \text{min}^{-1}$ for PFOS, PFHS, and PFBS, respectively). Accordingly, quantum yields for the degradation of the carboxylates are independent of chain length, i.e., PFBA (7.05×10^{-4}) ≈ PFHA (6.94×10^{-4}) ≈ PFOA (6.36×10^{-4}), whereas those for the sulfonates are chain-length dependent, i.e., PFOS (11.8×10^{-4}) > PFHS (5.71×10^{-4}) > PFBS (2.41×10^{-4}) (Table 1).

The aquated electron-mediated reduction of perfluorochemicals eventually eliminates fluoride (F^-) and thus fluoride measurements give insight into the overall mechanism and extent of reduction. The time-dependent F^- production during degradation of the perfluorocarboxylates and the perfluorosulfonates are shown in parts a and b of Figure 4, respectively. Similar to the decomposition kinetics, the perfluorocarboxylate F^- production has no chain length dependence ($[F^-] = 5{-}12\ \mu M$ at 2.5-h photolysis), whereas the perfluorosulfonate F^- production is dependent on chain length; F^- production decreases with decreasing chain length ($[F^-] = 58$, 23, and 5 μM at 2.5 h photolysis for PFOS, PFHS, and PFBS, respectively). The greater extent of defluorination and thus aquated electron consumption per fluorochemical (i.e., a single H/F exchange corresponds to the consumption of two electrons, overall eqs 9, 10, and 14) will reduce proton consumption via eq 8. Thus, change in pH may be used as an indicator of the extent of defluorination.

Alternatively, the F^- yield can be evaluated using the F index (i.e., $-[F^-]_{produced}/[PFC]_{degraded}$). F indexes for all PFCs are observed to grow linearly over the course of the reaction. For the three carboxylates, the F index is between 1 and 2, suggesting a reductive mechanism independent of chain length (see Figure 5). For the sulfonates, the F-index is related to the number of carbons in the hydrophobic tail, with approximately one defluorination per carbon (i.e., 9, 6, and 3 for PFOS, PFHS, and PFBS, respectively). In both cases, defluorination is incomplete suggesting loss of partially defluorinated species to the gas phase, which implies loss of the sulfonate or carboxylate ionic headgroup prior to complete defluorination.

The data from Figures 3 and 4 has been compiled in Figure 5. $k_{app}^{-PFC}$and the F index for all six PFCs are plotted as a function of fluorocarbon chain length. It appears that the carboxylates have a similar degradation mechanism since both the kinetics and F indexes show no chain-length dependence. In contrast, the sulfonates have a distinct chain-length dependence with the apparent degradation rate constant and F index decreasing with decreasing chain length. Although there are only 3 data points for each, it is of note that the linear fits to the sulfonate rate constant and F index are nearly parallel. The F index is in

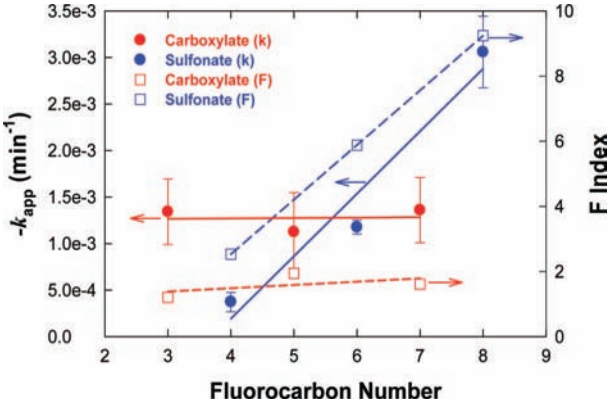


Figure 5. Effects of fluorocarbon number (chain length) on the degradation rates and the relative degree of defluorination (F index) during the photolysis of aqueous iodide−PFOX solutions. Experimental conditions identical to those of Figure 3.

agreement with the speciation of fluorochemical gases detected as reaction intermediates (Figure 6 and Table 2).

Gaseous intermediates produced during PFC reduction were trapped in thermal desorption tubes and analyzed by GC-MS. A number of intermediates were identified, which were composed of carbon, fluorine, hydrogen, and iodine (Figure 6 and Table 2). The perfluoroalkyl carboxylate gaseous intermediates were primarily composed of C−F bonds, consistent with F indexes. The perfluoroalkyl sulfonate intermediates had a greater degree of H/F exchange (i.e., degree of reduction), which is also consistent with F indexes for these compounds. The agreement between H/F exchange and the F index suggests initial defluorination is primarily followed by protonation of the carbanion intermediate (eq 14) or perfluororadical reaction with H atom (eq 15), with minor olefinization (eq 13). It is of note that the reduction products of the perfluorinated chemicals in aprotic solvents are primarily olefins. Also, the sulfonates have a larger number of unique gaseous intermediates as compared to the carboxylates. For example, PFOS has a more diverse set of intermediates ranging from C_1 to C_8 and 3 times the total number of intermediates as PFOA (Table 2).

A large majority of the gases produced are iodinated, and the noniodinated minority generally contains an olefin. On average, one $I^{\bullet}$ is incorporated into a single gaseous fluorinated intermediate suggesting partitioning out of solution quickly follows neutral fluororadical iodination. For example, the reaction of a fluoroalkyl radical ($R_F\bullet$) produced with $I^{\bullet}$ results in a product that has a high tendency to partition into the vapor phase (eq 16)

$$R_F^{\bullet} + I_{carrier}^{\bullet} \rightarrow R_FI_{(aq)} \rightarrow R_FI_{(g)} \qquad (16)$$

The absence of vapor-phase intermediates with higher degrees of iodination may be due to subsequent photolytic cleavage or

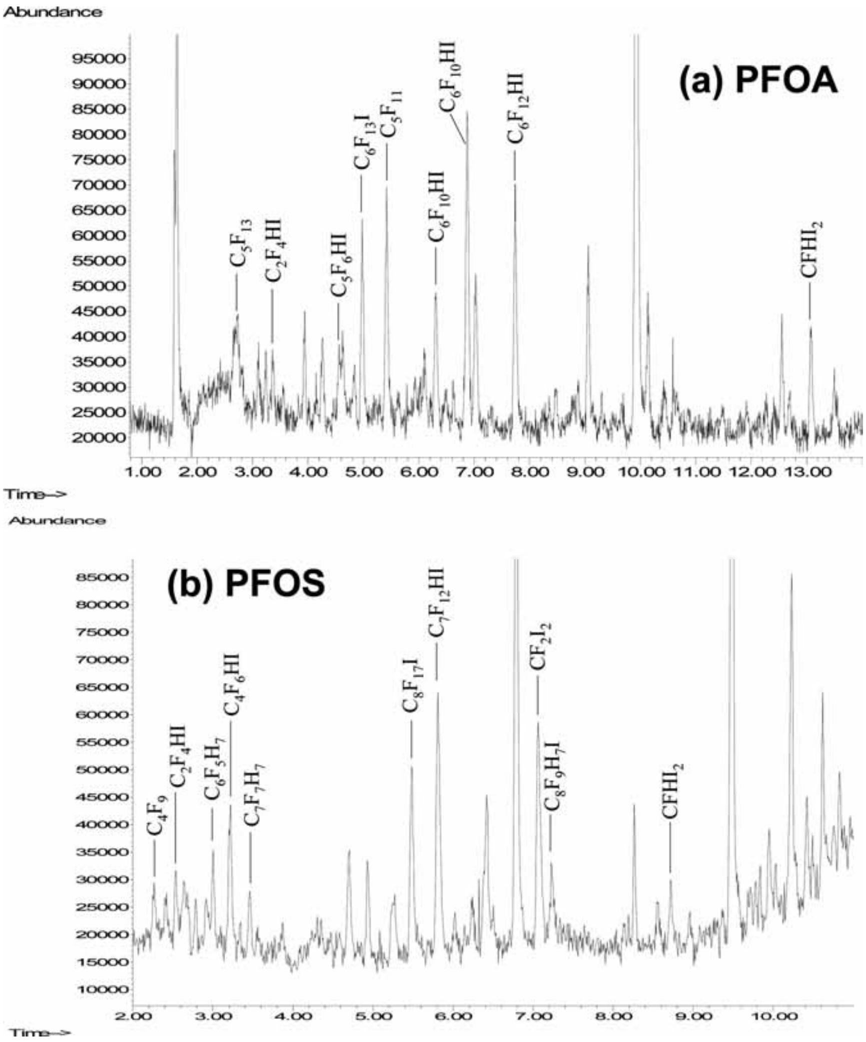


Figure 6. Primary gaseous intermediates collected during 2.5 h photolysis of aqueous iodide−PFC solutions. Experimental conditions identical to those of Figure 3. (a) Representative PFOA GC-MS spectrum. (b) Representative PFOS GC-MS spectrum.

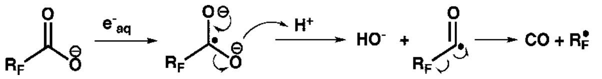
TABLE 2: Primary Gaseous Intermediates during 2.5 h of Iodide Photolysis of Perfluorinated Alkyl Carboxylate and Sulfonate Solution in Water

	PFBS $C_4F_9SO_3^-$		PFHS $C_6F_{13}SO_3^-$		PFOS $C_8F_{17}SO_3^-$	
no. of carbons	iodide	non-iodide	iodide	non-iodide	iodide	non-iodide
8					$C_8F_{17}I$ $C_8F_9H_8I$ $C_8F_9H_7I$ $C_8F_6H_3I$	$C_8F_{13}H_4$ $C_8F_{13}H_3$
7					$C_7F_{12}HI$ $C_7F_9H_6I$	$C_7F_7H_7$ $C_7F_6H_9$ $C_7F_4H_{10}$
6			$C_6F_{13}I$ $C_6F_{12}HI$ $C_6F_3H_8I$	$C_6F_7H_5$ $C_6F_5H_5$		$C_6F_5H_7$
5			C_5F_8HI C_5F_6HI $C_5F_4H_4I_2$ C_5FH_4I	$C_5F_2H_8$	$C_5F_7H_2I$ C_5F_3HI	
4		$C_4F_4H_4$	$C_4F_6H_3I$ C_4F_6HI $C_4F_5H_2I$	$C_4F_4H_4$	C_4F_6HI $C_4F_5H_2I$ C_4H_9I	C_4F_9 $C_4F_4H_2$
3	$C_3F_2I_2$ C_3F_2I C_3FH_2I C_3FHI		C_3F_6HI		C_3F_6HI $C_3F_4H_3I$	
2	C_2FI C_2H5I	$C_2F_3H_3$	$C_2F_4I_2$ $C_2F_3H_2I$ C_2H_5I C_2H_4I		C_2F_4HI $C_2F_3HI_2$ $C_2H_4I_2$ $C_2H_3I_2$ $C_2H_2I_2$ C_2H_5I	
1	CH_2I_2 CH3I		CF_2I_2 CH_3I		CF_2I_2 $CFHI_2$ CH_2I_2 CH_3I	

	PFBA $C_3F_7CO_2^-$		PFHA $C_5F_{11}CO_2^-$		PFOA $C_7F_{15}CO_2^-$	
no. of carbons	iodide	non-iodide	iodide	non-iodide	iodide	non-iodide
8						
7						
6					$C_6F_{13}I$ $C_6F_{12}HI$ $C_6F_{10}HI$	$C_6F_5H_7$
5					C_5F_6HI	C_5F_{13} C_5F_{11}
4			C_4F_9I			
3	C_3F_6HI			C_3F_9 C_3F_7		
2	C_2F_5I $C_2F_4I_2$ C_2F_4HI C_2H_6I				C_2F_4HI	
1	CH_3I		$CFHI_2$ CH_3I CH_2I_2		$CFHI_2$ CH_3I CH_2I_2	

reduction of C−I bonds by aquated electron (eqs 11 and 12, respectively) formed from the aqueous fluoro intermediates. It should be noted that a C−I bond (bond strength, 209 kJ/mol) is weaker than a C−F bond (bond strength, 460 kJ/mol). In addition, perfluorooctyl iodide ($C_8F_{17}I$) is observed as the heaviest intermediate during PFOS photolysis, whereas perfluorohexyl iodide ($C_6F_{13}I$), not $C_7F_{15}I$, is detected during PFOA photolysis. This suggests the presence of a transient perfluorooctyl radical ($C_8F_{17}^•$) intermediate during PFOS photolysis and perfluorohexyl radical ($C_6F_{13}^•$) generated from PFOA photolysis. The sulfonate elimination from an intact fluorocarbon tail is also observed during PFHS photolytic reduction (e.g., $C_6F_{13}I$, $C_6F_{12}HI$) and PFBS reduction (e.g., $C_4F_4H_4$). In addition, the loss of the carboxylate group plus a tail carbon is observed during PFHA photolysis (e.g., C_4F_9I). However, in the case of PFBA, a C_3 intermediate is detected.

The detection of gaseous fluorochemical intermediates implies C−C bond scission within the carbon chain and/or cleavage of the ionic headgroup. There is evidence for both processes as shorter-chain products (C−C bond scission) and intact carbon chain products (headgroup cleavage) are observed. The minimal defluorination suggests that the carboxylate group is lost shortly after the initial reduction or simultaneously with the reduction. In the case of hydrocarbon carboxylates,[46] the aquated electron-mediated reduction occurs at the carbonyl group with subsequent loss of HO^- and CO, yielding an alkyl radical, or in this case a fluoroalkyl radical ($R_F^•$, eq 17).



(17)

However, there are no products with the complete carbon chain intact for the gaseous intermediates of PFOA and PFHA (Figure 6 and Table 2). Perfluoroalkylsulfonate reductive headgroup decomposition may be analogous to eq 17 yielding SO_2 rather than CO since gaseous intermediates with intact carbon chains are detected during iodide photolysis of PFBS, PFHS and PFOS.

Dissociative electron attachment of gaseous trifluoroacetic acid[47] yields CF_2^- and FCOOH as the lowest energy (∼1.4 eV) C−C scission products (eq 18). The production of CF_2 and FCOOH is one of the lowest energy (81 kcal/mol) thermal decomposition pathways for gaseous TFA as determined by ab initio calculations[48] due to the stability of difluorocarbene

$$CF_3COOH + e^-(\sim 1.4\,eV) \rightarrow CF_2^- + FCOOH \qquad (18)$$

The C_{n-2} perfluoroalkyliodides are observed as intermediates for PFOA, PFHA, PFBA suggesting $C_{n-2}F_{2n-4}^•$ as a radical intermediate. Following eq 18, a possible PFOA decomposition mechanism yielding a C_6 perfluoroalkyl radical is proposed (eq 19).

$$CF_3(CF_2)_7COO^- + e^-_{(aq)}(E^0 = -2.7\,V) \rightarrow CF_3(CF_2)_5CF_2\cdot + CF^- + FCOO^- \qquad (19)$$

The C_6 perfluoroalkylradical will react following eq 16 to produce $CF_3(CF_2)_5CF_2I$. CF^- will protonate and then likely insert into an I_2 carrier to form $CHFI_2$ (eq 20) and $FCOO^-$ will hydrate (eq 21).

$$CF^- + H^+ \rightarrow CHF + I_2/I_3^- \rightarrow CHFI_2 \qquad (20)$$

$$FCOO^- + H_2O \rightarrow HCO_3^- + H^+ + F^- \qquad (21)$$

The neutral products, $CF_3(CF_2)_5CF_2I$ and $CHFI_2$, are both observed as gaseous intermediates of PFOA-KI photolysis and a single F^- is produced per PFOA decomposed, consistent with PFOA's observed F index.

The gaseous KI photolysis products of the perfluoroalkylsulfonates and perfluoroalkylcarboxylates both consist of a number of shorter-chain fluorochemicals. The number of shorter-chain carboxylate products is relatively small, while shorter-chain FCs dominate the gaseous reaction product distribution for sulfonates. Density functional theory calculations of linear perfluorocarbon (nC_nF_{n+2}: $n = 2-8$) electron affinities indicate that the attached electron was localized on one of the centermost C−F bonds and that the electron affinity increased with increasing chain length.[49] We will assume a similar situation here for electron attachment to PFOS and propose plausible C−C bond scission mechanisms. The first possible mechanism will involve the unimolecular decomposition of the $CF_3(CF_2)_2CF_2{\cdot}^-(CF_2)_4SO_3^-$ produced via eq 9. If the radical anion were to complex with a proton, an intramolecular electron transfer could result in C−C bond scission (eq 22).

$$\begin{aligned}&CF_3(CF_2)_2CF_2^{\bullet -}(CF_2)_4SO_3^- + H^+ \rightarrow\\ &\quad CF_3(CF_2)_2CF_2^{\bullet -}H^+(CF_2)_4SO_3^- \rightarrow\\ &\quad\quad CF_3CF_2CHF_2 + {}^{\bullet}CF_2(CF_2)_3SO_3^- \qquad (22)\end{aligned}$$

The neutral perfluoroalkylhydride will partition to the gas-phase and the perfluoroalkylradical will proceed through previously stated radical reactions (eqs 10, 11, and 15). Another possible reductive C−C bond scission may involve the dianion produced in eq 10. The nucleophilic carbanion would intramolecularily attack a neighboring carbon to yield an olefin and a shorter chain carbanion, which would likely be located on the fragment, which does not include the ionic headgroup (eq 23).

$$\begin{aligned}&CF_3(CF_2)_3CF^-(CF_2)_3SO_3^- \rightarrow\\ &\quad CF_3CF_2CF_2^- + CF_2{=}CF(CF_2)_3SO_3^- \qquad (23)\end{aligned}$$

The carbanion produced in eq 23 will subsequently proceed through reactions 13, 14, and 22. The olefin may be oxidized by reaction with I_2 or any perfluoro-alkyl radicals present.

In summary, the nature of the ionic headgroup, either a carboxylate or sulfonate, has a significant effect on the kinetics and mechanism of perfluoro-alkyl surfactant reduction by aquated electrons. The fluorocarbon tail length of the perfluorinated alkyl sulfonates significantly affects the reduction rate and extent of defluorination, implying the existence of multiple reaction sites across the fluorocarbon tail. In contrast, perfluorinated alkyl carboxylates have invariable reaction rates with aquated electrons and similar degrees of defluorination implying a similar initial reaction site near the ionic headgroup. Ionic headgroup cleavage and partitioning of the subsequent neutral fluorochemical interrupts the aquated electron defluorination process. Thus, most intermediates are only partially fluorinated. Detailed studies utilizing a more quantitative intermediate analysis to better understand defluorination kinetics and mechanism are being investigated.

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