Chapter 2

Treatment Technologies for Aqueous Perfluorooctanesulfonate (PFOS) and Perfluorooctanoate (PFOA)

Abstract

Fluorochemicals (FCs) are oxidatively recalcitrant and thus environmentally persistent and resistant to most conventional treatment technologies. FCs have unique physiochemical properties derived from fluorine being the most electronegative of elements. Recent concern has grown over the FCs perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA), as they have been detected globally in the hydrosphere, atmosphere, and biosphere. Halting further fluorochemical release into the environment will require improved containment during application and manufacturing processes and remediation of the primary sources such as manufacturing waste. Removal technologies such as reverse osmosis, nanofiltration, and activated carbon can remove FCs from water. Incineration of the concentrated waste is required for complete fluorochemical destruction. Recently, a number of alternative technologies for on-site FC decomposition have been reported. The fluorochemical degradation technologies span a range of chemical processes including direct photolysis, photocatalytic oxidation, photochemical oxidation, photochemical reduction, thermally induced reduction, and sonochemical pyrolysis. We review these FC degradation technologies in terms of kinetics, mechanism, energetic cost, and applicability. The optimal PFOS/PFOA remediation method is strongly dependent upon the initial FC concentration, background organic and metal concentration, and available degradation time.

Introduction

Fluorochemicals (FCs) have a wide variety of applications such as inert, nonstick polymers (e.g., telfon), water- and stain- proof coatings for paper and textiles (e.g., Scotchguard), oxidative protective coatings on metals, inert surfactants for semi-conductor etching, aqueous film forming foams (AFFFs), and thermally stable lubricants. The diverse FC applications are due to the unique physiochemical properties[1-3] gained upon replacing the majority of the hydrogens in an organic with fluorines. Organic poly-, and moreso, per-, fluorination yields a more thermally stable (i.e., C_2H_5-H 101 kcal/mol vs. C_2F_5-F 127 kcal/mol, and CF_3-CF_3 99 kcal/mol vs. CH_3-CH_3 89 kcal/mol), a more oxidatively resistant (i.e., $F + e \rightarrow F-$, $E_0 = 3.6$ V)[4], and a weakly polarizable (i.e., $\alpha_{PFOS} = 3.2$ Å^3 vs. $\alpha_{SDS} = 12.4$ Å^3)[5] organic. The thermal and oxidative resistance from fluorination makes fluorochemicals useful for extreme applications such as high-temperature lubricants and AFFFs. The relatively low perfluorochemical polarizability makes fluorochemicals useful for non-stick, protective coatings.

The physiochemical properties of fluorochemicals make them difficult to treat using most conventional remediation strategies[6-8]. Perfluorochemicals (PFCs), organics with all of their hydrogens replaced by fluorines, are particularily recalcitrant and environmentally persistent. For example, atmospheric lifetimes of perfluorinated gases have been estimated to be > 1000 years.[9] Recently, concern has increased over the environmental impact of perfluorinated surfactants such as perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS), or PFOX where (X = S or A). Perfluorinated surfactants have a perfluorinated carbon tail, which preferentially partitions out of the aqueous phase, and an ionic headgroup, which preferentially partitions in to the aqueous phase. Due to their biphasic or surfactant nature, they tend to accumulate at the air-water interface[10-13]. PFOX has been observed to primarily accumulate in the hydrosphere[14-34] and the biosphere[22,24,35-59]. PFOX is released to the environment primarily during manufacturing and coating processes[60], as well as from use of FC-based products[61-65]. PFOX can be indirectly created via atmospheric[66-68], aquatic[69], or biologic transformation[70-74] of fluorotelomer alcohols[75] and fluoroalkylsulfonamides[76,77]. Recent data suggests the phasing-out of the production of PFOS and PFOA in 2000 by 3M[78] and later by DuPont has reduced their proliferation in the environment[53,66,77,79]. It has been recently shown that landfill leachate from primary fluorochemical disposal sites may also be a source of PFCs tin the environment[80], which is currently treated with granular activated carbon post-WWTP.

The very dilute (i.e., ppt or pM) hydrosphere concentrations of PFOS and PFOA make remediation of the perfluorinated surfactants previously released to and distributed in the environment difficult using most conventional technologies[81]. The onsite control of the primary FC discharges from their primary source (i.e., concentrated manufacturing effluents) is a more viable approach. A number of fluorochemical, specifically PFOS and PFOA, treatment technologies have been evaluated in the literature. Granular activated carbon has been shown to be effective at removing PFOA and PFOS at ppb levels from relatively clean water (i.e., post-WWTP)[6,82] and is utilized today. The activated carbon must then be incinerated[83] to destroy the adsorbed fluorosurfactants. A fraction of the fluorochemicals entering the WWTP will adsorb to the sludge[7,84,85] where anaerobic digestion has a minimal effect on their concentration[86]. The digested sludge may subsequently be disposed of in a landfill, allowing the adsorbed fluorochemicals to be re-released into the environment.

Most conventional degradation technologies are ineffective for the *in situ* degradation of aqueous PFOS and PFOA, since they are inherently recalcitrant to chemical and microbiological treatment[7,8,86–89]. Advanced oxidation processes (AOPs)[90], which utilize the hydroxyl radical,—such as alkaline ozonation, peroxone (i.e., a mixture of O_3 and H_2O_2), or Fenton's reagent (i.e., H_2O_2 and Fe^{2+} salts)—have been shown to be relatively ineffective for PFOA and PFOS destruction[91–93]. A number of photolytic methods, such as direct photolysis[93–99], persulfate photolysis[94,100–102], alkaline isopropanol photolysis[99] ,and photocatalysis[93,103–107] have shown varying degrees of efficacy on higher concentrations of perfluorocarboxylates. Reduction by elemental iron under near super-critical water conditions has been shown to be possible for PFOS degradation. Ultrasonic irradiation of aqueous solutions of PFOS and PFOA[92] has been observed to degrade these compounds. Recently it has been reported that PFOS and PFOA are completely mineralized during this process[108] and that sonolysis can be used effectively for environmentally relevant concentrations and matrices.

We will now overview these techniques in more detail in terms of their viability to remediate and degrade aqueous PFOS and PFOA. These techniques will be reviewed in terms of their reaction conditions, degradation kinetics, degradation products and energy requirements. The techniques will be initially divided into four treatment groups: conventional, oxidative, reductive, and thermal. It is likely that the optimal treatment technology will be highly dependent on initial PFOX concentration (i.e., high for manufacturing waste or low for environmental distribution) and the matrix in question.

Tertiary Water Treatment

Conventional wastewater treatment techniques[109], such as trickling filtration, activated sludge, anaerobic digestion, and chlorination have been reported to have little effect on

PFOA and PFOS mass flows (i.e, $[\mathrm{PFOX}]_{\mathrm{WWTP,influent}} \approx [\mathrm{PFOX}]_{\mathrm{WWTP,effluent}}$[7,8,80,110,111]). Microbial communities can not metabolize PFOS and PFOA[86–89]. In some cases, PFOS and PFOA concentrations were greater in the WWTP effluent as compared to the influent[7,8] which suggest microbial transformation[7,8,111] of fluorosulfonamides such as FOSE and FOSA to PFOS[70–73,110]and fluorotelomer alcohols to PFOA[112], or the release of residual PFOX from disposed products[110]. Incineration[113] of sludge containing PFCs[84,111] is effective for the complete destruction of fluorochemicals and fluoropolymers. Tertiary water treatment technologies such as granular activated carbon (GAC)[6], ion-exchange[82], and reverse osmosis[114,115] have been shown to be effective in removing PFOS from water. GAC[6,80] is currently utilized to remove PFCs from WWTP effluent and effectively removes > 90% of PFOS and PFOA. PFOX equilibrium adsorption to various surfaces is lower than observed for organics of similar molecular weight[116,117]. The adsorption process is observed to be kinetically slow[116]. Isopropanol as a co-solvent was shown to have a deleterious effect on reverse osmosis for the removal of PFOS[114]. In all tertiary treatment cases, a subsequent destruction step such as incineration is required for complete perfluorochemical remediation.

PFOX Oxidation

Perfluorinated chemicals such as PFOS and PFOA are recalcitrant towards oxidation due to the complete substitution of fluorine (C-F bond) for hydrogen (C-H bond). Fluorine is the most electronegative of elements and will retain its electrons (i.e., will resist oxidation) at all cost. Fluorine is nearly always found in the (-1) oxidation state with the only exception being F_2 where its oxidation state is (0). The fluorine atom is the most powerful inorganic oxidant known, with a reduction potential of 3.6 V (eq. 2.1)[4] and thus it is thermodynamically unfavorable to create the fluorine atom with any other one-electron oxidant.

$$F\cdot + e^- \rightarrow F^- \ (E^0 = 3.6 \text{ V}) \qquad (2.1)$$

Perfluorination will also reduce the oxidizability of the ionic headgroup ($-SO_3^-$ for PFOS and $-CO_2^-$ for PFOA) since it inductively reduces headgroup electron density. Thus PFOX are quite resistant to oxidation as compared with their alkyl analogs.

Advanced Oxidation Processes—Oxygen-Containing Radicals

For particularily recalcitrant organics, advanced oxidation processes which utilize the hydroxyl radical, ozone, or O-atom are a viable solution[90,118–120]. Hydroxyl radical can be generated through hydrogen peroxide photolysis[121], ozonation[122,123], photo-Fenton's[124], sonolysis[125], and peroxone chemistry[126]. A hydroxyl radical normally reacts with saturated organics through an H-atom abstraction to form water (eq. 2.2) and will react with unsaturated organics primarily via an addition reaction. The hydroxyl radical reacts with most aliphatic and aromatic organics at near diffusion-controlled rates[127]. At environmentally relevant pHs, PFOS and PFOA contain no hydrogens to abstract, thus the hydroxyl radical must act through a direct electron transfer to form the less thermodynamically favored hydroxyl ion (eq. 2.3).

$$HO\cdot + e^- \rightarrow H_2O \ (E^0 = 2.7 \text{ V}) \qquad (2.2)$$

$$HO\cdot + e^- \rightarrow HO^- \ (E^0 = 1.9 \text{ V}) \qquad (2.3)$$

Thus the perfluorination or substitution of all of the organic hydrogens for fluorines in PFOS and PFOA renders these compounds inert to advanced oxidation techniques[91]. The addition of H_2O_2 is detrimental to the photolytic degradation of PFOA by competitively adsorbing photons[93]. An upper limit for the second-order rate of HO· + PFOA has been estimated to be $k_{HO\cdot + PFOA} \leq 10^5 \text{ M}^{-1} \text{ s}^{-1}$; multiple orders of magnitude slower than the reaction of hydroxyl radical with most hydrocarbons[127]. The futility of conventional advanced oxidation for the degradation of PFOS and PFOA is noted in the use of perfluorinated compounds to enhance advanced oxidation of other organics. PFOS is used as an additive to increase aqueous solubility of PAHs[128,129], enhancing their degradation by UV-H_2O_2. PFOS has also been utilized as a TiO_2 surface coating to increase adsorption of PCBs[130] and chlorinated aromatics[106], leading to enhanced oxidation rates. Biphasic water-perfluorocarbon systems have been utilized to increase organic ozonation rates[131] by increasing dissolved ozone concentrations. Convential advanced oxidation methods utilizing oxygen-based radicals are not practical methods for the decomposition of perfluorochemicals.

Persulfate Photolysis—Sulfate Radical Oxidation

Persulfate photolysis has been utilized for the oxidative degradation of a number of organics[132–136]. Persulfate photolysis[137] or thermolysis[138] generates two sulfate radicals, $SO_4\cdot^-$, (eq. 2.4). The sulfate radical is an oxidizing radical that reacts by a direct one-electron transfer to form sulfate (eq. 2.5). The sulfate radical has a one-electron reduction potential of 2.3 V[4], making it a stronger direct electron transfer oxidant than the hydroxyl radical.

$$S_2O_8^{2-} + h\nu\ (< 270\ \text{nm})\ /\ \Delta \rightarrow 2\ SO_4\cdot^- \qquad (2.4)$$

$$SO_4\cdot^- + e^- \rightarrow SO_4^{2-}\ \ (E^0 = 2.3\ \text{V}) \qquad (2.5)$$

Persulfate photolysis has been utilized to degrade a number of perfluoroalkylcarboxylates of various chain length[94,100–102]. PFOA degradation by sulfate radical oxidation has achieved minimum half-lives on the order of 1 hour, with fluoride accounting for 15% of the total fluorine over the same period of time ($[\text{PFOA}]_i$ = 1.35 mM, $[S_2O_8^{2-}]$ = 50 mM, 9000 W L^{-1}, Xe-Hg lamp, 4.7 atm O_2)[94,100]. The percent of total fluorine as fluoride can be used as a measure of PFOA mineralization.

A reaction mechanism for the sulfate radical mediated degradation of perfluoroalkylcarboxylates was proposed by Kutsuna and Hori[102]. The initial degradation is postulated to occur through an electron transfer from the carboxylate terminal group to the sulfate radical (eq. 2.6). The oxidized PFOA subsequently decarboxylates to form a perfluoroheptyl radical (eq. 2.7), which reacts quantitatively with molecular oxygen to form a perfluoroheptylperoxy radical (eq. 2.8). The perfluoroheptylperoxy radical will react with another perfluoroheptylperoxy radical in solution, since there are no reductants present to yield two perfluoroalkoxy radicals and molecular oxygen (eq. 2.9). The perfluoroheptyloxy has two branching pathways: unimolecular decomposition to yield the perfluorohexyl radical and carbonyl fluoride (eq. 2.10), or an H-atom abstraction from an acid such as HSO_4^- to yield perfluoroheptanol (eq. 2.12). The perfluorohexyl radical formed in eq. 10 will react with O_2 (eq. 2.9) and resume the radical 'unzipping' cycle. The COF_2 will hydrolyze to yield CO_2 and two HF (eq. 2.11). The perfluoroheptanol from eq. 2.12 will unimolecularly decompose to give the perfluoroheptylacyl fluoride and HF (eq. 2.13). Perfluoroheptyl acyl fluoride will hydrolyze to yield perfluoroheptanoate (eq. 2.14).

$$CF_3(CF_2)_6COO^- + SO_4\cdot^- \rightarrow CF_3(CF_2)_6COO\cdot + SO_4^{2-} \qquad (2.6)$$

$$CF_3(CF_2)_6COO\cdot \rightarrow CF_3(CF_2)_5CF_2\cdot + CO_2 \qquad (2.7)$$

$$CF_3(CF_2)_5CF_2\cdot + O_2 \rightarrow CF_3(CF_2)_5CF_2OO\cdot \qquad (2.8)$$

$$CF_3(CF_2)_5CF_2OO\cdot + R_FOO\cdot \rightarrow CF_3(CF_2)_5CF_2O\cdot + R_FO\cdot + O_2 \qquad (2.9)$$

$$CF_3(CF_2)_5CF_2O\cdot \rightarrow CF_3(CF_2)_4CF_2\cdot + COF_2 \qquad (2.10)$$

$$COF_2 + H_2O \rightarrow CO_2 + 2\ HF \qquad (2.11)$$

$$CF_3(CF_2)_5CF_2O\cdot + HSO_4^- \rightarrow CF_3(CF_2)_5CF_2OH + SO_4^{\cdot -} \quad (2.12)$$

$$CF_3(CF_2)_5CF_2OH \rightarrow CF_3(CF_2)_5COF + HF \quad (2.13)$$

$$CF_3(CF_2)_5COF + H_2O \rightarrow CF_3(CF_2)_5COO^- + HF + H^+ \quad (2.14)$$

During photolysis, Kutsuna and Hori observed the pH decrease to < 3, due to HF production making eq. 2.12 the major branching pathway (75%). The shorter chain carboxylates produced will be just as recalcitrant as PFOA.

Persulfate photolysis in liquid carbon dioxide/water mixtures[101] has been reported to be a good medium for the degradation of longer chain carboxylic acids normally insoluble in water. Through kinetic modeling of batch reactions, the second-order rate constants of the sulfate radical with various chain-length perfluorocarboxylates have been determined to be on the order of 10^4 M^{-1} s^{-1} [102], consistent with a flash photolysis study[139] which measured sulfate radical reaction with trifluoroacetate to be 1.6 x 10^4 M^{-1} s^{-1}. A relatively slow rate when compared to second-order rates of the sulfate radical with hydrocarbons; short-chain alcohols and carboxylic acids are at the lower end with reaction rates on the order of 10^6 M^{-1} s^{-1} and aromatic organics are at the upper end with reaction rates being diffusion controlled, 10^9-10^{10} M^{-1} s^{-1} [140]. The presence of any other dissolved organic species with aqueous PFOA will competitively inhibit degradation. Persulfate photolysis would be a practical technique for the degradation of 'pure' aqueous PFOA. When other organics are present, significant PFOA degradation will only occur when the PFOA concentration greatly exceeds the total organic concentration ($[PFOA]/[Org]_{total} > 100$). Persulfate photolysis under the previously stated conditions would be a viable decomposition method for perfluoroalkylcarboxylates of all chain lengths, since they have similar second-order kinetics with the sulfate radical[102].

Direct UV Photolysis

Photolysis is chemical bond-breaking driven by light. UV-Vis light adsorption yields an electronically excited molecule. An electronically excited molecule has a bonding (molecular) or non-bonding (atomic) electron promoted to an anti-bonding orbital. An electronically excited molecule is more susceptible to chemical reaction and may open new chemical reaction pathways unavailable to the ground state species. Terrestrial solar-driven photolytic processes require utilization of 290–600 nm photons, due to atmospheric absorption of higher energy light. Organics with large chromophores can be directly photolyzed by solar irradiation[141,142]. Simulated sunlight applied to aqueous solutions of PFOS[97], PFOA[98], and N-EtFOSE[143] for 30 days had no effect on their concentration ($[FC]_i = 100\ \mu M$, $\lambda = 290\text{-}600$ nm, 10 W, 5 W/L). The 8:2 fluorotelomer alcohol did not significantly degrade under direct photolysis[144].

Ultraviolet-C (UV-C, $\lambda < 300$ nm) and vacuum ultraviolet (VUV, $\lambda < 200$ nm) have been utilized for a number of disinfection and advanced oxidation processes[90]. UV-C, generated by a black or germicidal lamp ($\lambda = 250 \pm 10$ nm), is primarily used for indirect photolyses (e.g., persulfate photolysis), disinfection, and in some cases direct photolysis[145]. VUV irradiation is of high enough energy to photodissociate water into an H-atom and HO· (eq. 2.15) with a quantum yield of 0.3 at 185 nm[146,147].

$$H_2O + h\nu\ (\lambda < 200\ \text{nm}) \rightarrow H\cdot + HO\cdot \tag{2.15}$$

VUV has a very short liquid penetration depth (< 100 μm) due to the strong adsorption by water yielding a strongly oxidizing region near the lamp surface. Organic degradation during VUV photolysis is primarily via HO oxidation[148–150]. Hori et al.[93] reported on the photolytic degradation of PFOA which occurred with a half-life of 24 hrs ($[PFOA]_i =$

1.35 mM, 200 W Xe-Hg lamp, 22 mL, 4.8 atm O_2). The primary photoproducts were shorter chain carboxylic acids with fluoride accounting for 15% of the decomposed PFOA fluorine after 24 hours. Aqueous PFOA VUV photolysis[94,151] proceeds at a faster rate, having a photolysis half-life of 90 minutes ($[PFOA]_i = 100\ \mu M$, $\lambda = 254$ nm w/ minor 185 nm, 15 W, 800 mL, pH 3.7, 40 °C, N_2) with fluoride accounting for 12% of the degraded PFOA fluorine. The gas-phase VUV photolysis of trifluoroacetic acid yields CO_2, CF_3, and H-atom as predominant photoproducts (eq. 2.16)[152]. Aqueous PFOA will be dissociated into its ion products at pH 3.7, and direct photolysis will be of the PFOA anion (eq. 2.17), which may unimolecularily decompose to a perfluoro alkyl anion, CO_2 and an aqueous electron which will protonate under the experimental conditions (eq. 2.18).

$$CF_3COOH + h\nu\ (\lambda = 172\text{ nm}) \rightarrow CF_3COOH^* \rightarrow CF_3\cdot + CO_2 + H\cdot \qquad (2.16)$$

$$CF_3(CF_2)_6COO^- + h\nu\ (\lambda < 220\text{ nm}) \rightarrow CF_3(CF_2)_6COO^{-*} \qquad (2.17)$$

$$CF_3(CF_2)_6COO^{-*} + H^+ \rightarrow CF_3(CF_2)_6\cdot + CO_2 + H\cdot \qquad (2.18)$$

The hydroxyl radical concentration in the region near the VUV lamp surface may be great enough to also lead to PFOA oxidation and perfluoroalkyl radical formation. Since the photolysis conditions are anoxic (i.e., N_2 atmosphere) the perfluoroalkylradical will react at diffusion-controlled rates with HO produced via water photolysis to form the perfluoroalkyl alcohol (eq. 2.19).

$$CF_3(CF_2)_6\cdot + HO\cdot \rightarrow CF_3(CF_2)_6OH \qquad (2.19)$$

The overall degradation mechanism will occur through similar reactions, as seen in persulfate photolysis (eqs. 2.7–2.14), to yield a perfluoroalkyl carboxylate (PFAC) one -CF_2- unit shorter than the initial species. The produced PFAC will undergo photolysis until the perfluorinated tail is completely unzipped. PFOS photolytic degradation has also been reported[99] and has a slower photolysis rate, half-life of 5.3 days, than PFOA under similar conditions ($[PFOS]_i = 40\ \mu M$, $\lambda = 254$ nm, 32 W, 750 mL, 36–that 40 °C, N_2). Shorter chain perfluorocarboxylates and perfluoroalkyl alcohols were detected as reaction intermediates. After 50% of the PFOS is decomposed, fluoride accounts for 59% of the decomposed PFOS fluorine. The greater fluoride mass balance than observed with PFOA is likely due to faster photolysis rates of the PFAC intermediates than of the initial PFOS. Direct photolysis of PFOS and PFOA will be negligible under environmental conditions. Higher energy UV and VUV photolysis can degrade PFOX. Competitive UV light absorption by solvent and other matrix components will limit photolysis rates.

Phosphotungstic Acid Photocatalysis

Phosphotungstic acid, $H_3PW_{12}O_{40}$, is a heteropolyacid or polyoxometalate that has been utilized for photocatalytic degradation of contaminants[153,154] and as an electron shuttle[155–157]. $PW_{12}O_{40}^{3-}$ is the predominant form when pH < 2 and absorbs light with $\lambda < 390$ nm. Upon light adsorption, $PW_{12}O_{40}^{3-}$ enters a photo-excited state enhancing its oxidation strength (eq. 2.20).

$$PW_{12}O_{40}^{3-} + h\nu\ (< 390\ \text{nm}) \rightarrow PW_{12}O_{40}^{3-}{*} \qquad (2.20)$$

PFOA[93], PFPA[104], and TFA[158] have been reported to be decomposed by $H_3PW_{12}O_{40}$ photocatalysis. PFOA has half-life of 24 hours during phosphotungstic acid photolysis ($[PFOA]_i = 1.35$ mM, $[H_3PW_{12}O_{40}] = 6.7$ mM, pH < 2, 9000 W L^{-1}, Xe-Hg lamp, 4.8 atm O_2). After 24 hours of photolysis when 50% of the PFOA is degraded, fluoride accounts for 20% of the total fluorine. The extent of fluoride production is similar to that observed during persulfate photolysis, suggesting a similar degradation mechanism where the carboxylate headgroup is oxidatively removed and a shorter-chain perfluoroalkylcarboxylate is formed.

Hori et al.[104] proposed that $PW_{12}O_{40}^{3-}$ photocatalytic PFOA decomposition involves a photo-Kolbe type mechanism where PFOA first complexes with $PW_{12}O_{40}^{3-}$ (eq. 2.21) and upon photon adsorption an electron is directly transferred from PFOA to $PW_{12}O_{40}^{3-}$ (eq. 2.22)[104]. Similar to the sulfate radical mechnism, PFOA will decarboxylate to form the perfluoroheptyl radical. Oxygen is essential to the photocatalytic cycle in that it accepts an electron from the reduced phosphotungstic acid, $PW_{12}O_{40}^{4-}$, (eq. 2.23) returning it to its photoactive state.

$$CF_3(CF_2)_6COO^- + PW_{12}O_{40}^{3-} \rightarrow CF_3(CF_2)_6COO^- \cdots PW_{12}O_{40}^{3-} \qquad (2.21)$$

$$CF_3(CF_2)_6COO^- \cdots PW_{12}O_{40}^{3-} + h\nu\ (< 390\ \text{nm}) \rightarrow CF_3(CF_2)_5CF_2\cdot + CO_2 + PW_{12}O_{40}^{4-} \qquad (2.22)$$

$$PW_{12}O_{40}^{4-} + O_2 \rightarrow PW_{12}O_{40}^{3-} + O_2\cdot^- \qquad (2.23)$$

The superoxide produced in eq. 20.13 will protonate when pH < 2 to the hydroperoxy radical (eq. 2.24) which can act as a reductant for pefluoroalkylperoxy (eq. 2.25) and perfluoroalkoxy radicals (eq. 2.26). The perfluoroalkylhydroperoxide produced in eq. 25 will likely photolyze to a perfluoroalkoxy radical and a hydroxyl radical (eq. 2.27).

$$H^+ + O_2\cdot^- \leftrightarrow HO_2\cdot \qquad (2.24)$$

$$CF_3(CF_2)_5CF_2OO\cdot + HO_2\cdot \rightarrow CF_3(CF_2)_5CF_2OOH + O_2 \qquad (2.25)$$

$$CF_3(CF_2)_5CF_2O\cdot + HO_2\cdot \rightarrow CF_3(CF_2)_5CF_2OH + O_2 \qquad (2.26)$$

$$CF_3(CF_2)_5CF_2OOH + h\nu \rightarrow CF_3(CF_2)_5CF_2O\cdot + HO\cdot \qquad (2.27)$$

The subsequent reactions of the various perfluoroalkyl radicals are analogous to those found in the sulfate radical PFOA decomposition mechanism, eq. 2.7–2.14. Due to the slow phosphotungstic-acid-mediated PFOA decomposition kinetics, perfsulfate photolysis would be a preferred perfluoroalkylcarboxylate oxidation technique since it operates by a similar mechanism and its degradation rate is at least an order of magnitude faster. Phosphotungstic acid has also been shown to enhance the TiO_2 photocatalytic degradation rates of PFOA[105] by acting as both an electron shuttle from TiO_2 to O_2 and as a photocatalyst.

TiO_2 Photocatalysis

TiO_2 photocatalysis has been shown to degrade a large number of pollutants through oxidative and reductive pathways[159]. The TiO_2 photocatalytic degradation of a number of perfluoroalkyl carboxylates and perfluoroalkylsulfonates was investigated[105] and was observed to be effective for the degradation of the carboxylates but not the sulfonates. The observation is consistent with investigations of PFOS as an inert, reusable TiO_2 surface coating[106,107,130] to enhance adsorption of hydrophobic contaminants onto TiO_2 ,where PFOS was stable to photolysis periods of up to 30 hours. The TiO_2 photocatalytic degradation of PFOA was reported to be quite slow, requiring 60 hours of UV photolysis to achieve 50% mineralization ($[PFOA]_i = 4.4$ mM, $[TiO_2]_i = 2.0$ g L^{-1}, pH = 1, O_2, $\lambda =$ 310–400 nm, 1500 W L^{-1}). Photonic efficiencies were determined to be less than 1.0×10^{-5}. The degradation mechanism is postulated to occur via a photo-Kolbe mechanism, similar to phosphotungstic acid[104], since rates increase with decreasing pH from 2.4 to 1.0[160]. The pKa of PFOA is estimated to be -0.5[1]. The degradation mechanism involves adsorption of PFOA onto the TiO_2 and direct oxidation by a TiO_2 valence band hole (eq. 2.28).

$$>TiOH\cdot^{+}\ (h_{vb}^{+}) + >CF_3(CF_2)_6COO^{-} \rightarrow >TiOH + CF_3(CF_2)_5CF_2\cdot + CO_2 \qquad (2.28)$$

The subsequent perfluoroalkyl radical reactions will be analogous to those observed during phosphotungstic acid photocatalysis due to the presence of oxygen. Thus, due to kinetic considerations, persulfate photolysis is a more viable perfluoroalkylcarboxylate oxidation technique.

The TiO_2 photocatalytic degradation of PFOA is slightly enhanced by the addition of phosphotungstic acid[161] or by electrophotocatalysis utilizing TiO_2 with a sub-monolayer Ni-Cu coating[103]. The phosphotungstic acid addition was completed under the same conditions as listed above TiO_2 photocatalysis. The optimal phosphotungstic acid concentration was 0.5 mM, yielding a degradation rate twice as fast as TiO_2 alone; at higher concentrations the degradation rate began to decrease. The PFOA half-life during TiO_2/Ni-Cu photocatalysis was 90 min with fluoride accounting for 5% of the total fluorine ($[PFOA]_i = 50\ \mu M$, $\lambda = 254$ nm, 90 W L^{-1}, air). A direct comparison between the TiO_2 and TiO_2/Ni-Cu systems is not easy due to the variations between $[PFOA]_i$, power density and wavelength used. A rough analysis yields a power density normalized absolute rate of TiO_2/Ni-Cu to be 7.4 times faster than TiO_2 alone. Applying a potential of -0.1 V to the TiO_2/Ni-Cu system decreases the half-life by a factor of two, 45 minutes, and increases the fluoride yield at the half-life to 20% of the total fluorine. The authors state that PFOA is photoreductively degraded, yet the majority of the fluorine is accounted for by shorter chain perfluoroalkylcarboxylates, which would suggest an oxidative mechanism. A reductive mechanism would be expected to defluorinate rather than decarboxylate. Electrochemistry using a boron-doped diamond electrode has also been shown to degrade PFOA[162].

Fe(II)/Fe(III) Photocatalysis

Photolysis of Fe(III)-carboxylate complexes involves charge transfer from the carboxylate functional group to the Fe(III). For example, ferrioxalate photolysis[163–166] will yield two CO_2 molecules under oxic conditions and is commonly used as a chemical actinometer. Perfluoroalkylcarboxylates (C_2-C_5) have been observed to decompose during UV photolysis in the presence of Fe(III)[167] ($[PFC]_i = 67.3$ mM, $[Fe^{3+}]_i = 5.0$ mM, pH = 1.5, 4.9 atm O_2, Xe-Hg Lamp, 9000 W L^{-1}). The Fe(III) photolysis PFC degradation half-life is approximately 20 hours with fluoride accounting for 45% of the total fluorine after 50% of the PFC is degraded. The fluoride yield is nearly double that of other PFC direct electron transfer oxidations. Low pH aqueous iron photolysis can also initiate indirect oxidations through photo-Fenton chemistry[124]. Fe(III)-perfluorocarboxylate photochemistry is postulated to react by chemistry similar to the analogous hydrocarbons. Initially, aqueous Fe(III) will complex with the PFAC (eq. 2.29). Fe(III)-PFAC UV photon adsorption results in a charge transfer from the PFAC to the Fe(III) yielding Fe(II), CO_2 and a perfluoroalkylradical (eq. 2.30). The perfluoroalkyl radical will follow the chemistry observed in other oxic systems as well as additional oxidative chemistry due to Fenton chemistry. The O_2 reduction by Fe(II) will regenerate Fe(III) (eq. 2.31).

$$CF_3(CF_2)_3COO^- + Fe^{3+} \rightarrow [CF_3(CF_2)_3COO^-Fe^{3+}]^{2+} \qquad (2.29)$$

$$[CF_3(CF_2)_3COO^-Fe^{3+}]^{2+} + h\nu\ (\lambda < 300\text{ nm}) \rightarrow CF_3(CF_2)_2CF_2\cdot + CO_2 + Fe^{2+} \qquad (2.30)$$

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2\cdot^- \qquad (2.31)$$

The photolytic Fe(III) degradation of PFCs follows a similar mechanism as the other oxidative degradations, in that an electron is removed directly from the carboxylate group leading to decarboxylation and formation of a shorter chain PFAC through a series of subsequent reactions.

PFOX Reduction

PFOS and PFOA oxidation is slow due to the high electronegativity of the fluorine atoms coating the carbon chain. Per- and poly-halogenation is a common chemical attribute found in environmentally persistent pollutants as they are oxidatively protected. For example, the Stockholm Convention greatly restricted the use of the most persistent organic pollutants (POPs) such as chlordane, DDT, hexachlorobenzene, polychlorinated biphenyls, and polychlorinated dioxins. All of these organics were partially chlorinated with $0.3 < Cl/C < 1.2$ and $<Cl/C> = 0.63$. For comparison, PFOS and PFOA have a F/C ~ 2 and fluorine is more electronegative than chlorine. PFOS is being reviewed for addition to the Stockholm Convention POP list along with organics such as polybrominated diphenyl ethers, hexachlorocyclohexane, and endosulfan[168]. Reductive dehalogenation[169–174] has been utilized to remediate persistent halogenated organic contamination, leading to an increased susceptibility to oxidation and thus reduction of their environmental persistence. Once dehalogenation is complete, the organic ceases to be further reduced. A subsequent oxidative, microbial, or pyrolytic/combustion step is required to completely mineralize the reduced halo-organic.

Reductive remediation of perfluorocarboxylates and perfluorosulfonates is feasible[99,175,176]. For example, PFOS can be reduced by elemental iron, Fe(0), in water under high-temperature, high-pressure conditions (e.g., 350 ^{o}C, 20 MPa)[176]. Unsaturated per- and poly-fluoroorganics (i.e., those containing aromatic, benzylic, olefinic, and tertiary functional groups) will readily reductively defluorinate[177–182]. Fluoroorganics containing only secondary and primary C-F bonds are difficult to defluorinate due to low reduction potentials ($E < -2.7$ V)[183,184]. Only the aqueous electron and elemental alkali and alkaline metals have lower standard reduction potentials. Reductive defluorination kinetics are influenced by a number of FC chemical properties[178,179,183,185–187] and electron-donating strength of the reductant[188]. For example, branched PFOX is observed to have faster reduction kinetics than linear PFOX[99,189].

Sub-Critical Elemental Iron Reduction

Elemental iron, Fe(0), is a reductant and has been utilized for remediation of natural water halocarbon contamination due to iron's natural abundance and nontoxicity. Fe(0) has a reduction potential of - 0.447 V (eq. 2.32) and has been shown to reduce a large number of halocarbons[169,190,191].

$$Fe^0 \rightarrow Fe^{2+} + 2\ e^-,\ E_0 = 0.447 \qquad (2.32)$$

Fe(0) reactive barriers have been applied in the field to degrade chlorinated solvents and other chemicals in groundwater[192–194]. Recently, nano-Fe(0) has become popular due to the increased reactive surface area and thus reduction kinetics[173,174,195]. Alternatively, bimetallic systems using metals such as Pt(0), Ni(0), or Pd(0) at percent levels with Fe(0) have also shown faster reduction kinetics[196–198] and are postulated to be H-atom production catalysts[199,200]. The application of sub-critical water with the Fe(0) has been used to enhance reaction rates and mass transfer for remediation of soils and sediments[170,172,201]. Sub-critical Fe(0) has been shown to degrade PFOS[176], PFHS[175], and shorter-chain perfluoroalkylsulfonate components of an anti-reflective coating ($[PFOS]_i$ = 370 μM, [Fe(0)] = 50 g L^{-1}, 350 ^oC, 200 atm, Ar). The sub-critical Fe(0) PFOS degradation half-life is 45 minutes, with fluoride accounting for 55% of the total fluorine after 6 hours. No shorter-chain carboxylic acids were observed suggesting that reductive defluorination is the primary degradation mechanism. Application of a subsequent oxidation step could completely mineralize PFOX.

UV-KI Photolysis—Aqueous Electron Reduction

The aqueous electron is a powerful one-electron reductant, E = -2.87 V[4]. The aqueous electron is characterized by an electron surrounded by a shell of 5 water molecules, and is also known as the hydrated or aquated electron[202]. The aqueous electron can reduce most halogenated contaminants at near diffusion-controlled rates[127,171,203–206]. Electron tunneling leads to activation energies for reaction with halogenated organics that are invariable and small (6 to 30 kJ/mol)[207]. Reaction rates of the aqueous electron with fluorinated compounds have been reported[178,179,186,187,208]. Organic fluoro-saturation decreases aqueous electron reduction kinetics, since fluorine doesn't have any low-lying vacant d-orbital to accept an electron. As fluoro-saturation increases the rates tend to decrease (i.e., rates are fastest for tertiary fluorocarbons, then secondary, then primary).

Aqueous electrons can be produced by radiolytic[209], photolytic[210], chemical[127], and direct injection[211] methods. In surface waters, the photolysis of humic materials[212–214] and hard-UV photolysis of water[202] are the most common sources of natural aqueous electrons which have a steady-state concentration of 10^{-15} M. Second-order reaction rates of aqueous electrons with perfluorocarboxylates have been determined to be on the order of 10^7 $M^{-1}s^{-1}$ using pulse radiolysis and flash photolysis methods[186,187]. This is the fastest reported second-order rate constant of these perfluorocarboxylates with any chemical species (e.g., $k_{PFOS+HO\cdot} \sim k_{PFOS+SO4\cdot-} \sim 10^4$ M^{-1} s^{-1}). Pulse radiolysis experiments[186] reported $k_{PFOS+e}(M^{-1}\ s^{-1}) > k_{PFOA+e}(M^{-1}\ s^{-1})$, suggesting sulfur-containing PFOS is easier to reduce. Batch reactions utilizing the aquated electron (e_{aq}^-, $E°_{aq/e} = -2.9$ V), produced by iodide photolysis, are observed to decompose both PFOS and PFOA ($[PFOS]_i = [PFOA]_i = 200$ nM, $[I^-] = 10$ mM, $\lambda = 254$ nm, 40 W L^{-1}, Ar). Aquated electrons are generated from UV-photolysis of aqueous iodide solutions via charge-transfer-to-solvent (CTTS) states (eq. 2.33).

$$I^- + h\nu \rightarrow I^{-*}_{CTTS} \rightarrow I\cdot + e^-_{aq}\ (QY_{\lambda=248\ nm} = 0.286)^{215} \qquad (2.33)$$

Fluoride is produced as a nonstoichiometric product, 10% for PFOA and 50% for PFOS, and thus the initial PFOX molecule is degraded but not completely destroyed by aqueous-electron-based reductive methods. Prior to complete defluorination, the ionic headgroup is reductively cleaved to yield an unsaturated, gaseous fluorochemical. The process is photocatalytic, as I-atom carriers (i.e., $I^{\bullet}$, $I_2^{\bullet-}$, $I_3^{\bullet-}$) and aqueous iodofluorocarbons will readily react with reducing species such as e_{aq}^-, $H^{\bullet}$ to regenerate I^-, the photo-active species.

Perfluoroalkyl carboxylate or sulfonate ($C_nF_{2n+1}X^-$; n = 8, X = SO_3 for PFOS; n = 7, X = CO_2 for PFOA) reaction with the aquated electron, e_{aq}^-, yields the corresponding radical anion ($C_nF_{2n+1}X^{\bullet 2-}$, eq. 2.34). The radical anion will quickly decompose via fluoride elimination in an aqueous environment to yield a perfluoroalkyl radical ($C_nF_{2n}X^{\bullet -}$, eq. 2.35). The electrophilic perfluoroalkyl radicals will oxidize iodide to yield the perfluoroalkyl carbanion ($C_nF_{2n}X^{2-}$, eq. 2.36). Perfluoroalkyl radicals may also react with e_{aq}^- to also yield an aqueous perfluoroalkyl carbanion which will protonate (eq. 2.37), or with $I^{\bullet}$ carriers (i.e., $I^{\bullet}$, $I_2^{\bullet-}$, $I_3^{\bullet-}$) to yield a perfluoroalkyl iodide ($C_nF_{2n}IX^-$, eq. 2.38). The perfluoroalkyl iodide may be converted back to a perfluoroalkyl radical via photolytic homolysis of the C-I bond (eq. 2.39), or by reaction with e^-_{aq} to yield the radical and I^- (eq. 2.40). 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. 2.41).

$$C_nF_{2n+1}X^- + e_{aq}^- \rightarrow C_nF_{2n+1}X^{\bullet 2-} \tag{2.34}$$

$$C_nF_{2n+1}X^{\bullet 2-} \rightarrow C_nF_{2n}X^{\bullet -} + F^- \tag{2.35}$$

$$C_nF_{2n}X^{\bullet -} + I^- \rightarrow C_nF_{2n}X^{2-} + I^{\bullet} \tag{2.36}$$

$$C_nF_{2n}X^{\bullet -} + e_{aq}^- \rightarrow C_nF_{2n}X^{2-} \tag{2.37}$$

$$C_nF_{2n}X^{\bullet -} + I^{\bullet} \leftrightarrow C_nF_{2n}IX^- \tag{2.38}$$

$$C_nF_{2n}IX^- + e_{aq}^- \rightarrow C_nF_{2n}X^{\bullet -} + I^- \tag{2.39}$$

$$C_nF_{2n}X^{2-} + H^+/H_2O \rightarrow C_nF_{2n}HX^- \qquad (2.40)$$

$$C_nF_{2n}X^{\bullet -} + H^{\bullet} \rightarrow C_nF_{2n}HX^- \qquad (2.41)$$

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 than the initial defluorination step[181]. After partial reductive defluorination of PFOX, the ionic headgroup is cleaved. Ionic headgroup cleavage yields a neutral, polyfluorinated organic, which preferentially partitions to the gas-phase. The gaseous fluoroorganic could be completely destroyed using thermal or plasma techniques.

Alkaline 2-Propanol Photolytic Reduction

Photolysis of alkaline 2-propanol will catalytically yield the isopropyl radical through various radical chain initiation and propagation steps. The isopropyl radical has been reported to dechlorinate PCBs and pesticides[216–218]. Photolytic production of a strong one-electron oxidation, $Ox^{\bullet}$, will abstract an H-atom from 2-propanol to yield the isopropyl radical (eq. 2.38)[4], $(CH_3)_2COH$, which under alkaline conditions will deprotonate to yield (eq. 2.39)[219], $(CH_3)_2CO^{\bullet -}$, a stronger reductant (eqs. 2.40–2.41).

$$(CH_3)_2CHOH + Ox^{\bullet} \rightarrow (CH_3)_2COH + Ox^- \qquad (2.38)$$

$$(CH_3)_2COH \leftrightarrow (CH_3)_2CO^{\bullet -} + H^+ \text{ (pKa = 12.03)} \qquad (2.39)$$

$$(CH_3)_2CO + e_{aq}^- + H^+ \rightarrow (CH_3)_2COH \text{ (E = -1.4 V)} \qquad (2.40)$$

$$(CH_3)_2CO + e_{aq}^- \rightarrow (CH_3)_2CO^{\bullet -} \text{ (E = -2.1 V)} \qquad (2.41)$$

UV photolysis of alkaline 2-propanol[99] has been observed to decompose PFOS with a pseudo-first-order half-life of 17.8 hours ($[PFOS]_i = 40\ \mu M$, $[NaOH]_i = 90$ mM, $\lambda = 254$

nm, 43 W L^{-1}, T = 38-50 °C, N_2). The branched PFOS isomers degraded faster than the linear isomers consistent with electrochemical perfluoroorganic reduction where increased PF branching yielded easier reductions[183,184]. The primary product observed during the reduction is $NaF_{(s)}$. Similar to aqueous electron reduction, perfluoroalkyl carboxylate or sulfonate ($C_nF_{2n+1}X^-$; n = 8, X = SO_3 for PFOS; n = 7, X = CO_2 for PFOA) reaction with $(CH_3)_2CO^{\bullet-}$ yields the perfluoroalkyl radical and fluoride (eq 2.42). The produced perfluoroalkyl radical will then abstract an H-atom from 2-propanol to propagate the radical chain (eq. 2.43). Radical chain termination would occur via reaction of two radicals (eq. 2.44).

$$(CH_3)_2CO^{\bullet-} + C_nF_{2n+1}X^- \rightarrow (CH_3)_2CO + C_nF_{2n}X^{\bullet-} + F^- \qquad (2.42)$$

$$C_nF_{2n}X^{\bullet-} + (CH_3)_2CHOH \rightarrow C_nF_{2n}HX^- + (CH_3)_2COH \qquad (2.43)$$

$$C_nF_{2n}X^{\bullet-}/(CH_3)_2CO^{\bullet-} + C_nF_{2n}X^{\bullet-} \rightarrow \qquad (2.44)$$

The radical chain mechanism makes alkaline 2-propanol an efficient PFOS degradation technology. A degradation mass balance has yet to be completed.

B_{12} Mediated Reduction

Vitamin B_{12} is a class of cobalamins, a cobalt ion complexed tetrapyrrole or corrin ring, which in certain forms are metabolically active coenzymes that catalyze rearrangement and methylation reactions[220]. Various B_{12} cofactors have been shown effective for the dechlorination of a number of organics such as PCE, TCE, CCl_4, and HCB[221–224]. The complexed cobalt ion is reduced to active Co(I) through two one-electron transfers (eqs. 2.45–2.46)[225,226] which can be completed in aqueous solution using Ti(III)-citrate as a bulk reductant (eq. 2.47)[227].

$$B_{12a}[Co(III)] + e^- \rightarrow B_{12r}[Co(II)] \quad (E^0 = -0.11\text{ V, pH} = 9) \qquad (2.45)$$

$$B_{12r}[Co(II)] + e^- \rightarrow B_{12s}[Co(I)] \quad (E^0 = -0.85\text{, pH} = 9) \qquad (2.46)$$

$$\text{Ti(III)-cit} \rightarrow \text{Ti(IV)-cit} + e^- \quad (E^0 = -0.7,\ pH = 9) \tag{2.47}$$

The B_{12}-Co(I) has been postulated to reduce TCE by two mechanisms: an outer-sphere one-electron transfer[223,228] yielding chloride and a radical (eq. 2.48), followed by decay of the radical (eq. 2.49)

$$B_{12}\text{-Co(I)} + Cl_2C{=}CHCl \rightarrow B_{12}\text{-Co(II)} + ClC{=}CHCl + Cl^- \tag{2.48}$$

$$ClC{=}CHCl \rightarrow ClC{\equiv}CH + Cl\cdot \tag{2.49}$$

or a nucleophilic attack by B_{12}-Co(I), one of the strongest known nucleophiles[229], yielding a carbanion[222,224] (eq. 2.50) which is transformed to the reduced form (eq. 2.51).

$$B_{12}\text{-Co(I)} + Cl_2C{=}CHCl \rightarrow B_{12}\text{-Co(III)}Cl_2CCHCl^- \tag{2.50}$$

$$B_{12}\text{-Co(III)}Cl_2CCHCl^- + e^- + H^+ \rightarrow B_{12}\text{-Co(II)} + ClHC{=}CHCl + Cl^- \tag{2.51}$$

The overall TCE B_{12} reduction mechanism eventually yields acetylene as a final product.

Vitamin B_{12} has recently been shown to be an effective electron transfer mediator for the reduction of PFOS[189], with Ti(III)-citrate used as the bulk electron source ($[PFOS]_i$ = 332 μM, [Ti(III)-cit] = 36 mM, 70 °C, pH = 9.0). Reduction kinetics were determined to be 12.3 times faster for branched PFOS ($\tau_{1/2}$ = 33 hrs) then linear PFOS ($\tau_{1/2}$ = 410 hrs). The faster kinetics for the branched form are consistent with reduction potentials increasing as branching increases[183,184]. The branched form of PFOS gave a greater F^- yield per PFOS degraded, $[F^-]/[PFOS]_{br,deg} = 12$ vs. $[F^-]/[PFOS]_{lin,deg} = 3$, implying a change in the overall reduction mechanism. Ti(III)-citrate was also observed to reduce PFOS, but at a significantly lower rate than when using B_{12} as a electron transfer mediator. As with the Fe(0) reduction of PFOS and PFHS, a greater-than-standard temperature is required to drive the reaction on a reasonable time scale. The ability of

B_{12} to reduce PFOS, suggests that it may be possible for anaerobic bacteria to decompose perfluorochemicals and that it is more likely for them to degrade nonlinear PFCs.

PFOX Thermolysis

The high-temperature processing of organic materials will lead to pyrolytic reactions in the absence of oxygen and combustion reactions in the presence of oxygen. The thermolysis of fluorochemicals has been documented experimentally under more controlled conditions to determine individual reaction kinetics and mechanisms[230–241] and under more industrial conditions to test incinerability[83,111,113] or other thermal degradation processes[242]. A comprehensive experimental and theoretical database of C_1 and C_2 fluorochemical pyrolytic and combustion mechanisms, thermochemistry, and kinetics has been reported[243]. Fluorochemical C-C bonds (100 kcal/mol) in a fluorochemical will break prior to C-F bonds (120 kcal/mol) to yield fluoroalkyl radicals. The fluoroalkyl radical produced will be electrophilic and less stable towards thermal decomposition than the parent compound. Pyrolysis of longer perfluorochemical chains will tend to yield tetrafluoroethene, C_2F_4, difluorocarbene, CF_2, and the trifluoromethyl radical, CF_3 as the primary C_1 and C_2 products. Under combustion conditions, these radicals are readily transformed into CO, CO_2, and HF [243]

Thermal degradation of solid PFOA and PFOS salts[244–246] and gaseous PFOA (acid and ammonium salts)[230,247] has been reported. The primary products during the thermolysis of perfluoroalkylcarboxylates are the analogous 1H-perfluoroalkane for the salts (NH_4^+, H^+, eq. 2.52)[230,245,247], and the perfluoroolefin as well as the acyl fluoride and the anhydride for metal salts (Na^+, K^+, Ca^{2+}, etc.)[245]. A similar mechanism may be expected for perfluoroalkylsulfonates (eq. 2.53), as the C-S bond has been observed to be mostly broken during PFOS pyrolysis[248].

$$CF_3(CF_2)_6COO^-NH_4^+{}_{(s\ or\ g)} + \Delta \rightarrow CF_3(CF_2)_5CF_2H_{(g)} + CO_{2(g)} + NH_{3(g)} \qquad (2.52)$$

$$CF_3(CF_2)_7SO_3^-K^+{}_{(s\ or\ g)} + \Delta \rightarrow CF_3(CF_2)_5CF{=}CF_{2(g)} + SO_{3(g)} + K^+F^-{}_{(s)} \qquad (2.53)$$

A C-C bond breaking mechanism may also be the initial unimolecular decomposition step as observed in perfluorohexane pyrolysis[231]. A comparison of the extent of pyrolysis of similar carboxylate and sulfonate salts[246] reveals temperatures required for equivalent sulfonate salt decomposition to be 100 to 200 K greater than the corresponding carboxylate salt. The acid and ammonium salts are thermally converted to 1H-perfluoroalkane[245–247] and have a significantly lower decomposition temperature since no C-F bonds are broken. Thermolysis in the presence of ethylene glycol also primarily produces the1H-perfluoroalkane[245] suggesting that the perfluoroalkylanion is a weaker acid ($pKa_{HOCH2CH2OH}$ = 14.2).The produced perfluoroolefin or 1H-perfluoroalkane will undergo further pyrolytic reactions to eventually yield C_2F_6 and C_2F_4[231,243]. If water and/or oxygen are present, the primary end-products will be CO, CO_2, and HF.

Incineration

Combustion is the most common thermal treatment of waste. Incineration, a combustion-based process, is one of the oldest chemical destruction techniques and today the waste heat from incineration can be converted usable energy. Incineration involves heating a substance to >1000 ^{o}C for at least 2 s. Incineration is commonly used in countries where land is scarce and solid waste must be thermally processed, > 95%, prior to landfill disposal. The test for determining the applicability of incineration for a chemical is to detemine the temperature at which > 99% of a chemical is destroyed after 2 s of applied heat. A number of fluorochemicals have been tested for incinerability. A fluorotelomer based acrylic polymer was found to be > 99% destroyed at 950 ^{o}C as a free polymer and at 700 ^{o}C when coated on a fabric[113]. Carbon tetrafluoride, CF_4, one of the most recalcitrant fluorochemicals, will be > 99% destroyed under incinerator conditions[83]. CF_4 has an estimated atmospheric lifetime of > 50,000 years with the dominant degradation pathway being diffusion into high-temperature incinerators and power plants[249]. Laboratory scale studies have shown PFOS and perfluorosulfonamides to be > 99% destroyed at 600 ^oC[248,250]. Gas-phase NMR studies have determined the > 99% destruction temperature for various PFOA salts to be in the range of 300–350 ^oC[230,247]. Therefore, incinerator conditions will be sufficient to completely destroy fluorochemicals in polymer, coating, and monomer forms. Incineration is most energy efficient for solid wastes, since all the heat will go into destroying the contaminant in question. Highly concentrated aqueous fluorochemical solutions and fluorochemicals adsorbed to a solid matrix could also be incinerated, but energy will be wasted on destroying the matrix.

Sonochemistry

Sonochemistry is the driving of chemical reactions by application of an acoustic field to a solution[251–253]. The chemistry is generated by acoustic cavitation of microscopic bubbles and has been utilized for the decomposition of a number of aqueous chemical contaminants[254–258] including chlorocarbons[259–261] and perfluorocarbons[92,262]. Application of ultrasonic field to an aqueous solution initially nucleates cavitation bubbles which will undergo stable and transient bubble collapse events[251,263–266]. Transiently collapsing bubbles generate the observed chemistry. After expanding to a radial maximum, transient bubbles undergo a quasi-adiabatic compression and the PdV energy is converted into kinetic energy of the trapped gas molecules. Transient bubble collapses generate average vapor temperatures near 5,000 K[267,268] and much higher bubble vapor core temperatures (> 10,000 K), which generate sonoluminescence[269,270]. Hot vapor will collide with the collapsing bubble wall; transfer of heat from the vapor to the bubble wall will generate interfacial temperatures measured to be at least 800 K[251,255]. Water vapor within the collapsing bubble will pyrolyze to yield an H-atom and a hydroxyl radical (eq. 2.54), the hydroxyl eventually pyrolyzes as well to yield an O-atom and an H-atom (eq. 2.55)[251].

$$H_2O + \Delta \rightarrow HO\cdot + H\cdot \tag{2.54}$$

$$HO\cdot + \Delta \rightarrow O + H\cdot \tag{2.55}$$

The radicals produced will react preferentially with chemicals partitioning to the bubble gas-phase. A fraction of the radicals will be transported to the bubble interface and a smaller fraction to the bulk aqueous phase where they can react with aqueous contaminants. Chemicals preferentially partitioning to the bubble vapor will decompose via pyrolytic and combustion reactions[259]. Hydrocarbon surfactants will degrade via hydroxyl radical oxidation at the interface[271]. Surfactants that are difficult to oxidize, such as PFOS and PFOA, will pyrolytically decompose at the bubble-water interface[92].

Sonochemistry has been observed to degrade PFOS and PFOA[92] with the primary ionic products being fluoride and sulfate ($[PFOS]_i$ = 20 μM, f = 200 kHz, 200 W, 3 W/cm^2, 20 ^{o}C, argon). Under these conditions the sonochemical half-life of PFOA was 22 minutes and of PFOS was 43 minutes. The initial decomposition step was determined to occur at the bubble-water interface. Time-dependent product analyses during PFOS and PFOA sonolysis was used to investigate the mechanism and kinetics of the overall degradation process ($[PFOS]_i$ = 10 μM, f = 358/618 kHz, 250 WL, 6.4 W/cm^2, 10 ^{o}C, argon)[262]. Under these conditions, the decomposition half-life was reduced to 17 and 26 minutes for PFOA and PFOS, respectively. The nearly immediate production of mineralized fluorine (fluoride), sulfur (sulfate), and carbon (CO and CO_2) products after decomposition of the initial perfluorinated surfactant implies that sonochemical PFOS/PFOA mineralization (i.e., conversion to inorganic products) has overall kinetics similar to the decomposition of the perfluorinated surfactant (eq. 2.56),

$$\frac{-d[PFOX]}{dt} = \frac{d\{Mineralization\}}{dt} \tag{2.56}$$

or that the primary intermediates produced from PFOS and PFOA sonolysis have much shorter half-lives than their parent surfactants. Assuming that the initial decomposition step is pyrolytic, the primary fluorochemical intermediates are expected to be perfluoroolefins and 1H-perfluoroalkanes, eqs. 2.52–2.53. The high Henry's constants[3] of the primary fluorochemical intermediates favor partitioning into the bubble vapor ,where they will be pyrolyzed into their C_1 fluororadical constituents (eq. 2.57)[231,272].

$$CF_3(CF_2)_5CF_2H_{(g)} + \Delta \rightarrow CF_3 + 5\ {:}CF_2 + CF_2H \tag{2.57}$$

The C_1 fluororadicals will subsequently react with H_2O, HO·, H·, and O-atom in the bubble vapor to yield CO, CO_2, and HF[243]. More recent studies have shown that perfluorochemical adsorption to acoustically cavitating bubble interfaces is enhanced when the bubble interfaces are lightly populated. The adsorption enhancements increase the effective concentration of dilute perfluorochemical solutions by 1–2 orders of magnitude. Sonochemical degradation studies on groundwater containing perfluorochemicals have shown that organic content has only minimal effects on decomposition rates, even when organic concentrations are many orders of magnitude greater than fluorochemical concentrations, due to preferential adsorption of PFCs to the bubble-water interface.

PFOX Degradation Technology Summary

In Tables 2.1 & 2.2 we have compiled the aqueous PFOX degradation parameters for the most viable techniques: reactions conditions, initial concentrations, degradation kinetics, degradation products, and energy required to reduce the initial PFOX concentration by 50% and the energy required per μmole. However, neither the absolute or normalized energy is optimal for comparison of the reviewed techniques. As $[PFOX]_i$ increases, the inherent efficiency of any chemical process will also increase if the concentration is below kinetic saturation. For example, see the data on UV-KI or sonolytic degradation of PFOX at $[PFOX]_i$ = 200 nM vs. 20 μM. In both cases for PFOS and PFOA the absolute amount of energy required for 50% degradation decreases by 45–75% upon decreasing $[PFOX]_i$. However, since the concentration decreases by 2 orders of magnitude, the energy required to degrade a μmole of PFOX will increase by at least an order of magnitude.

In terms of reaction conditions, the techniques with no chemical additives such as photoelectrocatalysis, sonolysis, and direct photolysis are advantageous. Although, the sulfate (persulfate), $TiO_{2(s)}$, iron (Fe(0), Fe^{2+}/Fe^{3+}), and iodide (UV-KI) are relatively innocuous and shouldn't be an environmental issue. Sub-critical Fe(0) has safety implications of operating under high-pressure, high-temperature conditions.[273] Acoustic and UV-based systems will require reactor cooling.

A comparison of degradation kinetics will be headgroup dependent (i.e, PFOS and PFOA have dissimilar degradation rates). PFOA is more kinetically susceptible to oxidative, and photolytic processes, whereas PFOS is more susceptible to reductive processes. Both PFOS and PFOA are susceptible to sonolysis, a thermal-based process. For example, PFOA has a degradation half-life less than 60 minutes by direct photolysis (λ = 195 nm), persulfate photolysis (λ = 254 nm), photoelectrocatalysis, and sonolysis, and PFOS has a degradation half-life under 60 min for sub-critical Fe(0) and sonolysis. Sonolysis is the only technique that has been shown to quickly degrade both as it can create incinerator level temperatures, if only for a short (ns) period of time. Kinetics will be of importance in flowing systems where the aqueous PFOX will only be in the reactor for a finite period. Whereas there are batch reactor cases (e.g., manufacturing waste) where treatment time is not a factor and the kinetics will be relatively unimportant.

PFOX degradation products are dependent upon whether the technique used is oxidative, reductive or thermal. Thermal methods, such as sonolysis and incineration, have a distinct advantage. PFOX is sonolytically mineralized to F^-, SO_4^{2-}, CO, and CO_2 nearly immediately after the initial degradation step. Thus PFOX sonolytic mineralization efficacy is equivalent to its degradation efficacy. Reductive methods, such as sub-critical Fe(0), UV-KI, and UV-NaOH-IPA, will to some extent defluorinate PFOS and PFOA. Defluorination will yield either an olefin or a hydride which will be easier to oxidize than PFOX. However, even partially fluorinated species have long environmental lifetimes. For example, fluoroform, CF3H, has an atmospheric lifetime of 250–390 years.[274] Direct photolytic and oxidative processes are weakest in terms of degradation products. Oxidation of PFOX cleaves the headgroup and after a series of subsequent reactions the highest yield product is a perfluorocarboxylate with one less -CF_2- group, which is just as recalcitrant as the initial compound. For example, persulfate photolysis is one of the most energy-efficient processes for PFOA degradation, but would require approximately 50x more energy to completely mineralize PFOA, which is similar to the energy requirement for sonolytic mineralization.

As discussed earlier, it is difficult to directly compare energetic efficiencies due to factors such as initial concentration used and whether interest is in initial PFOX degradation or complete mineralization. Tables 2.1 & 2.2 can be used for a rough measure of which treatment technology is energetically viable. The PFOX treatment technology utilized will strongly depend on the situation in question and the desired results. For example, our group has shown that sonolysis is a viable method for the degradation of PFOX in groundwater, even though they were at relatively low concentrations, 100 ppb, as compared to other matrix components. This is a result of PFOX being strong surfactants and thus will preferentially adsorb to the bubble-water interface, the active site in sonolysis, over other chemical species. Redox and photolytic methods would have a much greater loss of efficacy when utilized to degrade PFOX in groundwater due to reactive radical scavenging by NOM, dissolved and solid metals, and co-contaminants.

It is of note that none of the reviewed methods approaches the normalized energy for production of PFOX. The concentration effect (i.e., production concentrations are much greater than waste/water concentrations) is a major factor in this deficiency. Assuming C-F bond formation is the most energetically consuming step in producing PFOS, we will make a rough estimate of energy per μmole to produce PFOS. Electrochemical conversion of octanesulfonyl fluoride to perfluorooctane sulfonyl fluoride is completed in concentrated HF with an applied voltage of 4-7 V, 2 electrons are required to convert C(-I)-H to C(+I)-F, and there are 17 C-F bonds in PFOS. Thus approximately 1.31–2.28 x 10^4 kJ mol^{-1} or 1.31–2.28 x 10^{-2} kJ μmol^{-1} is necessary to create PFOS—a value orders of magnitude greater than the energy required for sonolytic mineralization of 10 μM PFOS: 95 kJ μmol^{-1}. Therefore, investigations into the energy usage optimization of the currently reviewed methods, as well as research into new techniques for aqueous PFOX removal or degradation, would be fruitful in reducing the overall environmental impact of this class of chemicals. Hybrid methods containing two or more of the previously stated techniques are likely to be viable solutions. For example, we have found that the iron and DOC levels in leachate reduce the PFOS and PFOA sonolytic degradation rates by factors of four and three, respectively. However, the sonozone process[275–278], the simultaneous application of ozone and ultrasound, nearly rectifies the rates to those observed under pristine conditions. Further investigations are needed into novel oxidative and reductive techniques as well as hybrid (synergistic) remediation techniques to degrade particularly recalcitrant pollutants such as aqueous PFOS and PFOA.

.

Tables

Table 2.1. Summary of technologies for aqueous PFOA degradation

Technique	Conditions	Power/Vol.	k(lab)[a]	Product[b]	Energy[c]	Ref.
UV Direct Photolysis	1.35 mM PFOA $\lambda = 220–460$ nm	22 mL 200 W	0.69 d^{-1} $\tau_{1/2} = 1440$ min	33% F^- 38% CO_2 65% PFacids	792,000 kJ (1,170 kJ/µmol)	93
UV Phosphotungstic Photocatalysis	1.35 mM PFOA $\lambda = 220–460$ nm 0.48 MPa O_2 6.6 mM PTA	22 mL 200 W	2.0 d^{-1} $\tau_{1/2} = 500$ min	30% F^- 25% CO_2 70% PF acids	276,000 kJ (410 kJ/µmol)	93
TiO_2 Photocatalysis	1.0 mM PFOA $\lambda = 310–400$ nm pH 2–3 0.1 g TiO_2	50 mL 75 W	0.69 d^{-1} $\tau_{1/2} = 1440$ min	50% F^- 50% CO_2	132,000 kJ (265 kJ/µmol)	161
UV Direct Photolysis	50 µM PFOA $\lambda = 185$ nm	1000 mL 23 W	0.017 min^{-1} $\tau_{1/2} = 41$ min	10% F^- 90% PFacids	49 kJ (1 kJ/µmol)	94
UV Persulfate Photolysis	50 µM PFOA $\lambda = 254$ nm 1.5 mM $S_2O_8^{2-}$	1000 mL 23 W	0.012 min^{-1} $\tau_{1/2} = 58$ min	5% F^- 95% PFacids	69 kJ (1.2 kJ/µmol)	94
UV Persulfate Photolysis	1.35 mM PFOA $\lambda = 220–460$ nm 0.48 MPa O_2 pH 2–3 10 mM $S_2O_8^{2-}$	22 mL 200 W	0.69 h^{-1} $\tau_{1/2} = 58$ min	12% F^- 85% PFacids	33,600 kJ (50 kJ/µmol)	100
Photocatalysis TiO_2/Ni-Cu	50 µM PFOA $\lambda = 254$ nm	250 mL 23 W	0.0077 min^{-1} $\tau_{1/2} = 90$ min	10 % F^- 90% PFacids	500 kJ (20 kJ/µmol)	103
Photoelectro-catalysis TiO_2/Ni-Cu	50 µM PFOA $\lambda = 254$ nm -0.1 V	250 mL 23 W	0.015 min^{-1} $\tau_{1/2} = 45$ min	20% F^- 80% PFacids	250 kJ (10 kJ/µmol)	103
Persulfate Photolysis	2.5 mM PFBA $\lambda = 254$ nm 50 mM $S_2O_8^{2-}$	200 mL 60 W	0.0096 min^{-1} $\tau_{1/2} = 72$ min	~ 10^4 $M^{-1}s^{-1}$[d] $SO_4^{\cdot -}$ + $PFBA^-$	1300 kJ (1.0 kJ/µmol)	102
Hydrogen Peroxide	2.5 mM PFBA $\lambda = 254$ nm	200 mL 60 W	3.0e-5 min^{-1} $\tau_{1/2} = 23100$ min	n/a	420000 kJ (320 kJ/µmol)	102

Photolysis	250 mM H_2O_2					
Flash Photolysis	5e-5 M $Fe(CN)_6$ 0.02–0.1 M PFOA	266 nm 10 ns 3 mJ/pulse	$\sim 10^7$ $M^{-1}s^{1d}$	n/a	n/a	187
Sonolysis	20 μM PFOA f = 354 kHz	150 W 600 mL	0.018 min^{-1} $\tau_{1/2}$ = 39 min	95% F^-	670 kJ (67 kJ/μmol)	279
Sonolysis	200 nM PFOA f = 354 kHz	150 W 600 mL	0.047 min^{-1} $\tau_{1/2}$ = 15 min	95% F^-	260 kJ (1300 kJ/μmol)	279
UV-KI Photolysis	20 μM PFOA λ = 254 nm	1.5 W 30 mL	0.0014 min^{-1} $\tau_{1/2}$ = 500 min	10% F^- gaseous fluoroalkanes	1500 kJ (150 kJ/μmol)	
UV-KI Photolysis	200 nM PFOA λ = 254 nm	1.5 W 30 mL	0.0025 min^{-1} $\tau_{1/2}$ = 280 min	10% F^- gaseous fluoroalkanes	820 kJ (8200 kJ/μmol)	
Ferro-photolysis	2.5 mM $Fe_2(SO_4)_3$ 67 mM PFBA λ = 220–460 nm	200 W 105 mL	0.028 h^{-1} $\tau_{1/2}$ = 1490 min	45% F^- 55% short chains	89400 kJ (2.7 kJ/ μmol)	167

Table 2.2. Summary of technologies for aqueous PFOS degradation

Technique	**Conditions**	**Power/Vol.**	**k(lab)**[a]	**Products**[b]	**Energy**[c]	**Ref.**
Sub-Critical Fe(0)	370 μM PFOS 0.5 g Fe(0) 350 °C, 20 MPa	10 mL	$0.013\ \text{min}^{-1}$ $\tau_{1/2} = 53$ min	50% F^-	2,000 kJ (11 kJ / μmol)	176
UV Direct Photolysis	40 μM PFOS $\lambda = 254$ nm	32 W 750 mL	$0.13\ \text{day}^{-1}$ $\tau_{1/2} = 7700$ min	71% F^- 90% SO_4^{2-}	17,000 kJ (850 kJ / μmol)	99
UV Alkaline IPA Photolysis	40 μM PFOS $\lambda = 254$ nm	32 W 750 mL	$0.93\ \text{day}^{-1}$ $\tau_{1/2} = 1070$ min	$NaF_{(s)}$	2,500 kJ (125 kJ / μmol)	99
Sonolysis	20 μM PFOS f = 354 kHz	150 W 600 mL	$0.011\ \text{min}^{-1}$ $\tau_{1/2} = 63$ min	95% F^- 100% SO_4^{2-}	945 kJ (95 kJ / μmol)	279
Sonolysis	200 nM PFOS f = 354 kHz	150 W 600 mL	$0.023\ \text{min}^{-1}$ $\tau_{1/2} = 30$ min	95% F^- 100% SO_4^{2-}	450 kJ (4500 kJ/μmol)	279
UV-KI Photolysis	20 μM PFOS $\lambda = 254$ nm [KI] = 10 mM	1.5 W 30 mL	$0.002\ \text{min}^{-1}$ $\tau_{1/2} = 350$ min	50% F^- 50% fluoroalkanes	960 kJ (96 kJ / μmol)	
UV-KI Photolysis	200 nM PFOS $\lambda = 254$ nm [KI] = 10 mM	1.5 W 30 mL	$0.008\ \text{min}^{-1}$ $\tau_{1/2} = 87$ min	50% F^- 50% fluoroalkanes	260 kJ (1250 kJ/μmol)	

References

(1) Goss, K. U. *Environ. Sci. Technol.* **2008**, *42*, 456.

(2) Goss, K. U.; Bronner, G. *J. Phys. Chem. A* **2006**, *110*, 9518.

(3) Goss, K. U.; Bronner, G.; Harner, T.; Monika, H.; Schmidt, T. C. *Environ. Sci. Technol.* **2006**, *40*, 3572.

(4) Wardman, P. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1637.

(5) 3M Company. *The Science of Organic Fluorochemistry*; Docket AR226-0547; Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency: Washington, D.C., 1999; p. 12.

(6) 3M Company. *Removal of PFOA with Granular Activated Carbon: 3M Wastewater Treatment System Monitoring*; Docket AR226-1699; Office of Pollution Prevention & Toxics, U.S. Environmental Protection Agency: Washington, D.C., 2004; p 5.

(7) Sinclair, E.; Kannan, K. *Environ. Sci. Technol.* **2006**, *40*, 1408.

(8) Schultz, M. M.; Higgins, C. P.; Huset, C. A.; Luthy, R. G.; Barofsky, D. F.; Field, J. A. *Environ. Sci. Technol.* **2006**, *40*, 7350.

(9) Morris, R. A.; Miller, T. M.; Viggiano, A. A.; Paulson, J. F.; Solomon, S.; Reid, G. *J. Geophys. Res.—Atmos.* **1995**, *100*, 1287.

(10) Shinoda, K.; Hato, M.; Hayashi, T. *J. Phys. Chem.* **1972**, *76*, 909.

(11) Lopez-Fontan, J. L.; Sarmiento, F.; Schulz, P. C. *Colloid Polym. Sci.* **2005**, *283*, 862.

(12) Lu, J. R.; Ottewill, R. H.; Rennie, A. R. *Colloid Surf. A—Physicochem. Eng. Asp.* **2001**, *183*, 15.

(13) Simister, E. A.; Lee, E. M.; Lu, J. R.; Thomas, R. K.; Ottewill, R. H.; Rennie, A. R.; Penfold, J. *J. Chem. Soc.—Faraday Trans.* **1992**, *88*, 3033.

(14) Boulanger, B.; Peck, A. M.; Schnoor, J. L.; Hornbuckle, K. C. *Environ. Sci. Technol.* **2005**, *39*, 74.

(15) Boulanger, B.; Vargo, J.; Schnoor, J. L.; Hornbuckle, K. C. *Environ. Sci. Technol.* **2004**, *38*, 4064.

(16) Hansen, K. J.; Johnson, H. O.; Eldridge, J. S.; Butenhoff, J. L.; Dick, L. A. *Environ. Sci. Technol.* **2002**, *36*, 1681.

(17) Harada, K.; Saito, N.; Sasaki, K.; Inoue, K.; Koizumi, A. *Bull. Environ. Contam. Toxicol.* **2003**, *71*, 31.

(18) Kim, S. K.; Kannan, K. *Environ. Sci. Technol.* **2007**, *41*, 8328.

(19) McLachlan, M. S.; Holmstrom, K. E.; Reth, M.; Berger, U. *Environ. Sci. Technol.* **2007**, *41*, 7260.

(20) Moody, C. A.; Hebert, G. N.; Strauss, S. H.; Field, J. A. *J. Environ. Monit.* **2003**, *5*, 341.

(21) Moody, C. A.; Martin, J. W.; Kwan, W. C.; Muir, D. C. G.; Mabury, S. C. *Environ. Sci. Technol.* **2002**, *36*, 545.

(22) Schultz, M. M.; Barofsky, D. F.; Field, J. A. *Environ. Eng. Sci.* **2003**, *20*, 487.

(23) Yamashita, N.; Kannan, K.; Taniyasu, S.; Horii, Y.; Petrick, G.; Gamo, T. *Mar. Pollut. Bull.* **2005**, *51*, 658.

(24) 3M Company. *Sulfonated perfluorochemicals in the environment: Sources, dispersion, fate and effects*; Docket AR226-0620; Office of Pollution Prevention & Toxics, U.S. Environmental Protection Agency: Washington, D.C., 2000; p 51.

(25) Armitage, J.; Cousins, I. T.; Buck, R. C.; Prevedouros, K.; Russell, M. H.; MacLeod, M.; Korzeniowski, S. H. *Environ. Sci. Technol.* **2006**, *40*, 6969.

(26) Saito, N.; Harada, K.; Inoue, K.; Sasaki, K.; Yoshinaga, T.; Koizumi, A. *J. Occup. Health* **2004**, *46*, 49.

(27) Schultz, M. M.; Barofsky, D. F.; Field, J. A. *Environ. Sci. Technol.* **2004**, *38*, 1828.

(28) Scott, B. F.; Moody, C. A.; Spencer, C.; Small, J. M.; Muir, D. C. G.; Mabury, S. A. *Environ. Sci. Technol.* **2006**, *40*, 6405.

(29) Scott, B. F.; Spencer, C.; Mabury, S. A.; Muir, D. C. G. *Environ. Sci. Technol.* **2006**, *40*, 7167.

(30) Senthilkumar, K.; Ohi, E.; Sajwan, K.; Takasuga, T.; Kannan, K. *Bull. Environ. Contam. Toxicol.* **2007**, *79*, 427.

(31) So, M. K.; Miyake, Y.; Yeung, W. Y.; Ho, Y. M.; Taniyasu, S.; Rostkowski, P.; Yamashita, N.; Zhou, B. S.; Shi, X. J.; Wang, J. X.; Giesy, J. P.; Yu, H.; Lam, P. K. S. *Chemosphere* **2007**, *68*, 2085.

(32) So, M. K.; Taniyasu, S.; Yamashita, N.; Giesy, J. P.; Zheng, J.; Fang, Z.; Im, S. H.; Lam, P. K. S. *Environ. Sci. Technol.* **2004**, *38*, 4056.

(33) Yamashita, N.; Kannan, K.; Taniyasu, S.; Horii, Y.; Okazawa, T.; Petrick, G.; Gamo, T. *Environ. Sci. Technol.* **2004**, *38*, 5522.

(34) Yamashita, N.; Taniyasu, S.; Petrick, G.; Wei, S.; Gamo, T.; Lam, P. K. S.; Kannan, K. *Chemosphere* **2008**, *70*, 1247.

(35) Calafat, A. M.; Kuklenyik, Z.; Caudill, S. P.; Reidy, J. A.; Needham, L. L. *Environ. Sci. Technol.* **2006**, *40*, 2128.

(36) Calafat, A. M.; Needham, L. L.; Kuklenyik, Z.; Reidy, J. A.; Tully, J. S.; Aguilar-Villalobos, M.; Naeher, L. P. *Chemosphere* **2006**, *63*, 490.

(37) Martin, J. W.; Whittle, D. M.; Muir, D. C. G.; Mabury, S. A. *Environ. Sci. Technol.* **2004**, *38*, 5379.

(38) 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.

(39) Giesy, J. P.; Kannan, K. *Environ. Sci. Technol.* **2001**, *35*, 1339.

(40) Holmstrom, K. E.; Jarnberg, U.; Bignert, A. *Environ. Sci. Technol.* **2005**, *39*, 80.

(41) Houde, M.; Balmer, B. C.; Brandsma, S.; Wells, R. S.; Rowles, T. K.; Solomon, K. R.; Muir, D. C. G. *Environ. Toxicol. Chem.* **2006**, *25*, 2405.

(42) Houde, M.; Martin, J. W.; Letcher, R. J.; Solomon, K. R.; Muir, D. C. G. *Environ. Sci. Technol.* **2006**, *40*, 3463.

(43) Kannan, K.; Choi, J. W.; Iseki, N.; Senthilkumar, K.; Kim, D. H.; Masunaga, S.; Giesy, J. P. *Chemosphere* **2002**, *49*, 225.

(44) Kannan, K.; Corsolini, S.; Falandysz, J.; Fillmann, G.; Kumar, K. S.; Loganathan, B. G.; Mohd, M. A.; Olivero, J.; Van Wouwe, N.; Yang, J. H.; Aldous, K. M. *Environ. Sci. Technol.* **2004**, *38*, 4489.

(45) Kannan, K.; Corsolini, S.; Falandysz, J.; Oehme, G.; Focardi, S.; Giesy, J. P. *Environ. Sci. Technol.* **2002**, *36*, 3210.

(46) Kannan, K.; Koistinen, J.; Beckmen, K.; Evans, T.; Gorzelany, J. F.; Hansen, K. J.; Jones, P. D.; Helle, E.; Nyman, M.; Giesy, J. P. *Environ. Sci. Technol.* **2001**, *35*, 1593.

(47) Kannan, K.; Newsted, J.; Halbrook, R. S.; Giesy, J. P. *Environ. Sci. Technol.* **2002**, *36*, 2566.

(48) Kannan, K.; Tao, L.; Sinclair, E.; Pastva, S. D.; Jude, D. J.; Giesy, J. P. *Arch. Environ. Contam. Toxicol.* **2005**, *48*, 559.

(49) Nakata, H.; Kannan, K.; Nasu, T.; Cho, H. S.; Sinclair, E.; Takemura, A. *Environ. Sci. Technol.* **2006**, *40*, 4916.

(50) Olsen, G. W.; Church, T. R.; Larson, E. B.; van Belle, G.; Lundberg, J. K.; Hansen, K. J.; Burris, J. M.; Mandel, J. H.; Zobel, L. R. *Chemosphere* **2004**, *54*, 1599.

(51) Olsen, G. W.; Church, T. R.; Miller, J. P.; Burris, J. M.; Hansen, K. J.; Lundberg, J. K.; Armitage, J. B.; Herron, R. M.; Medhdizadehkashi, Z.; Nobiletti, J. B.; O'Neill, E. M.; Mandel, J. H.; Zobel, L. R. *Environ. Health Perspect.* **2003**, *111*, 1892.

(52) Olsen, G. W.; Huang, H. Y.; Helzlsouer, K. J.; Hansen, K. J.; Butenhoff, J. L.; Mandel, J. H. *Environ. Health Perspect.* **2005**, *113*, 539.

(53) Olsen, G. W.; Mair, D. C.; Reagen, W. K.; Ellefson, M. E.; Ehresman, D. J.; Butenhoff, J. L.; Zobel, L. R. *Chemosphere* **2007**, *68*, 105.

(54) Sinclair, E.; Mayack, D. T.; Roblee, K.; Yamashita, N.; Kannan, K. *Arch. Environ. Contam. Toxicol.* **2006**, *50*, 398.

(55) Smithwick, M.; Mabury, S. A.; Solomon, K. R.; Sonne, C.; Martin, J. W.; Born, E. W.; Dietz, R.; Derocher, A. E.; Letcher, R. J.; Evans, T. J.; Gabrielsen, G. W.; Nagy, J.; Stirling, I.; Taylor, M. K.; Muir, D. C. G. *Environ. Sci. Technol.* **2005**, *39*, 5517.

(56) Taniyasu, S.; Kannan, K.; Horii, Y.; Hanari, N.; Yamashita, N. *Environ. Sci. Technol.* **2003**, *37*, 2634.

(57) Tomy, G. T.; Budakowski, W.; Halldorson, T.; Helm, P. A.; Stern, G. A.; Friesen, K.; Pepper, K.; Tittlemier, S. A.; Fisk, A. T. *Environ. Sci. Technol.* **2004**, *38*, 6475.

(58) Van de Vijver, K. I.; Hoff, P. T.; Das, K.; Van Dongen, W.; Esmans, E. L.; Siebert, U.; Bouquegneau, J. M.; Blust, R.; De Coen, W. M. *Mar. Pollut. Bull.* **2004**, *48*, 992.

(59) Verreault, J.; Berger, U.; Gabrielsen, G. W. *Environ. Sci. Technol.* **2007**, *41*, 6671.

(60) Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H. *Environ. Sci. Technol.* **2006**, *40*, 32.

(61) Kubwabo, C.; Stewart, B.; Zhu, J. P.; Marro, L. *J. Environ. Monit.* **2005**, *7*, 1074.

(62) Moriwaki, H.; Takata, Y.; Arakawa, R. *J. Environ. Monit.* **2003**, *5*, 753.

(63) Ellis, D. A.; Mabury, S. A.; Martin, J. W.; Muir, D. C. G. *Nature* **2001**, *412*, 321.

(64) Tittlemier, S. A.; Pepper, K.; Seymour, C.; Moisey, J.; Bronson, R.; Cao, X. L.; Dabeka, R. W. *J. Agric. Food Chem.* **2007**, *55*, 3203.

(65) Begley, T. H.; White, K.; Honigfort, P.; Twaroski, M. L.; Neches, R.; Walker, R. A. *Food Addit. Contam.* **2005**, *22*, 1023.

(66) Young, C. J.; Furdui, V. I.; Franklin, J.; Koerner, R. M.; Muir, D. C. G.; Mabury, S. A. *Environ. Sci. Technol.* **2007**, *41*, 3455.

(67) D'Eon, J. C.; Hurley, M. D.; Wallington, T. J.; Mabury, S. A. *Environ. Sci. Technol.* **2006**, *40*, 1862.

(68) Martin, J. W.; Ellis, D. A.; Mabury, S. A.; Hurley, M. D.; Wallington, T. J. *Environ. Sci. Technol.* **2006**, *40*, 864.

(69) 3M Company. *Study of the Stability of MeFOSEA in Aqueous Buffers*; Docket AR226-0380; Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency: Washington, D.C., 1999; p. 69.

(70) Tomy, G. T.; Tittlemier, S. A.; Palace, V. P.; Budakowski, W. R.; Braekevelt, E.; Brinkworth, L.; Friesen, K. *Environ. Sci. Technol.* **2004**, *38*, 758.

(71) Xu, L.; Krenitsky, D. M.; Seacat, A. M.; Butenhoff, J. L.; Anders, M. W. *Chem. Res. Toxicol.* **2004**, *17*, 767.

(72) *Additional Characterization of Metabolites of T-6292, T-6293 and T-6294 from Rat and Human Hepatocytes*; Docket AR226-0163; Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency: Washington, D.C., 1998; p. 69.

(73) *Effect of N-Alkyl Perfluorooctylsulfonamides on Mitochondrial Bioenergetics In Vitro*; Docket AR226-0166; Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency: Washington, D.C., 1998; p. 10.

(74) Hagen, D. F.; Belisle, J.; Johnson, J. D.; Venkateswarlu, P. *Anal. Biochem.* **1981**, *118*, 336.

(75) 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.

(76) Stock, N. L.; Lau, F. K.; Ellis, D. A.; Martin, J. W.; Muir, D. C. G.; Mabury, S. A. *Environ. Sci. Technol.* **2004**, *38*, 991.

(77) Shoeib, M.; Harner, T.; Vlahos, P. *Environ. Sci. Technol.* **2006**, *40*, 7577.

(78) 3M Company. *Phase-out Plan for POSF-Based Products* Docket AR226-0588; Office of Pollution Prevention & Toxics, U.S. Environmental Protection Agency: Washington, D.C., 2000; p. 11.

(79) Yarwood, G.; Kemball-Cook, S.; Keinath, M.; Waterland, R. L.; Korzeniowski, S. H.; Buck, R. C.; Russell, M. H.; Washburn, S. T. *Environ. Sci. Technol.* **2007**.

(80) *Investigation of Perfluorochemical (PFC) Contamination in Minnesota Phase 1*; Senate Environment Committee: Minnesota, 2006; p. 79.

(81) Schwarzenbach, R. P.; Escher, B. I.; Fenner, K.; Hofstetter, T. B.; Johnson, C. A.; von Gunten, U.; Wehrli, B. *Science* **2006**, *313*, 1072.

(82) Lampert, D. J.; Frisch, M. A.; Speitel, G. E. *Practice Periodical of Hazardous, Toxic and Radioactive Waste Management* **2007**, *11*.

(83) Tsang, W.; Burgess, D. R.; Babushok, V. *Combustion Science and Technology* **1998**, *139*, 385.

(84) Higgins, C. P.; Field, J. A.; Criddle, C. S.; Luthy, R. G. *Environ. Sci. Technol.* **2005**, *39*, 3946.

(85) Schroder, H. F. *J. Chromatogr. A* **2003**, *1020*, 131.

(86) Hollingsworth, J.; Sierra-Alvarez, R.; Zhou, M.; Ogden, K. L.; Field, J. A. *Chemosphere* **2005**, *59*, 1219.

(87) Key, B. D.; Howell, R. D.; Criddle, C. S. *Environ. Sci. Technol.* **1998**, *32*, 2283.

(88) 3M Company. *Biodegradation studies of fluorocarbons—III*; Docket AR226-0489; Office of Pollution Prevention & Toxics, U.S. Environmental Protection Agency: Washington, D.C., 1978; p. 19.

(89) 3M Company. *Biodegradation studies of Fluorocarbons*; Docket AR226-0058; Office of Pollution Prevention & Toxics, U.S. Environmental Protection Agency: Washington, D.C., 1994; p. 4.

(90) Oppenlander, T. *Photochemical Purification of Water and Air*; Wiley-VCH: Weinheim, 2003.

(91) Schroder, H. F.; Meesters, R. J. W. *J. Chromatogr. A* **2005**, *1082*, 110.

(92) Moriwaki, H.; Takagi, Y.; Tanaka, M.; Tsuruho, K.; Okitsu, K.; Maeda, Y. *Environ. Sci. Technol.* **2005**, *39*, 3388.

(93) Hori, H.; Hayakawa, E.; Einaga, H.; Kutsuna, S.; Koike, K.; Ibusuki, T.; Kiatagawa, H.; Arakawa, R. *Environ. Sci. Technol.* **2004**, *38*, 6118.

(94) Chen, J.; Zhang, P. *Water Sci. Technol.* **2006**, *54*.

(95) Chen, J.; Zhang, P.; Liu, J. *Journal of Environmental Sciences—China* **2007**, *19*.

(96) Yamamoto, T.; Noma, Y.; Sakai, S.; Shibata, Y. *Environ. Sci. Technol.* **2007**.

(97) 3M Company. *Summary of Photolysis Studies using Simulated Sunlight on the Potassium Salt of Perfluorooctanesulfonic Acid*; Docket AR226-0056; Office of Pollution Prevention & Toxics, U.S. Environmental Protection Agency: Washington, D.C., 1978; p. 17.

(98) 3M Company. *FC-143 Photolysis Study using Simulated Sunlight*; Docket AR226-0490; Office of Pollution Prevention & Toxics, U.S. Environmental Protection Agency: Washington, D.C., 1979; p. 15.

(99) Yamamoto, T.; Noma, Y.; Sakai, S. I.; Shibata, Y. *Environ. Sci. Technol.* **2007**, *41*, 5660.

(100) Hori, H.; Yamamoto, A.; Hayakawa, E.; Taniyasu, S.; Yamashita, N.; Kutsuna, S.; Kiatagawa, H.; Arakawa, R. *Environ. Sci. Technol.* **2005**, *39*, 2383.

(101) Hori, H.; Yamamoto, A.; Kutsuna, S. *Environ. Sci. Technol.* **2005**, *39*, 7692.

(102) Kutsuna, S.; Hori, H. *Int. J. Chem. Kin.* **2007**, 276.

(103) Chen, J.; Zhang, P. Y.; Zhang, L. *Chem. Lett.* **2006**, *35*, 230.

(104) Hori, H.; Hayakawa, E.; Koike, K.; Einaga, H.; Ibusuki, T. *J. Mol. Catal. A—Chem.* **2004**, *211*, 35.

(105) Dillert, R.; Bahnemann, D.; Hidaka, H. *Chemosphere* **2007**, *67.*

(106) Yuan, Q.; Ravikrishna, R.; Valsaraj, K. T. *Sep. Purif. Technol.* **2001**, *24.*

(107) Hidaka, H.; Jou, H.; Nohara, K.; Zhao, J. *Chemosphere* **1992**, *25*, 1589.

(108) Vecitis, C. D.; Park, H.; Cheng, J.; Mader, B. M.; Hoffmann, M. R. *J. Phys. Chem. C* **2008**, *112*, 43, 16850.

(109) Sundstrom, D. W.; Klei, H. E. *Wastewater Treatment*; Prentice-Hall: Englewood Cliffs, 1979.

(110) Boulanger, B.; Vargo, J. D.; Schnoor, J. L.; Hornbuckle, K. C. *Environ. Sci. Technol.* **2005**, *39*, 5524.

(111) Loganathan, B. G.; Sajwan, K. S.; Sinclair, E.; Kumar, K. S.; Kannan, K. *Water Research* **2007**, *41*, 4611.

(112) DuPont. *Accelerated Biodegradation of 8-2 Telomer B Alcohol*; Docket AR226-1264; Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency: Washington, D.C., 2003; p. 45.

(113) Yamada, T.; Taylor, P. H.; Buck, R. C.; Kaiser, M. A.; Giraud, R. J. *Chemosphere* **2005**, *61*, 974.

(114) Tang, C. Y. Y.; Fu, Q. S.; Robertson, A. P.; Criddle, C. S.; Leckie, J. O. *Environ. Sci. Technol.* **2006**, *40*, 7343.

(115) Tang, C. Y.; Fu, Q. S.; Criddle, C. S.; Leckie, J. O. *Environ. Sci. Technol.* **2007**, *41*, 2008.

(116) Higgins, C. P.; Luthy, R. G. *Environ. Sci. Technol.* **2006**, *40*, 7251.

(117) Johnson, R. L.; Anschutz, A. J.; Smolen, J. M.; Simcik, M. F.; Penn, R. L. *J. Chem. Eng. Data* **2007**, *52*, 1165.

(118) Pera-Titus, M.; Garcia-Molina, V.; Banos, M. A.; Gimenez, J.; Esplugas, S. *Appl. Catal. B—Environ.* **2004**, *47*, 219.

(119) Andreozzi, R.; Caprio, V.; Insola, A.; Marotta, R. *Catal. Today* **1999**, *53*, 51.

(120) Legrini, O.; Oliveros, E.; Braun, A. M. *Chem. Rev.* **1993**, *93*, 671.

(121) Kochany, J.; Bolton, J. R. *Environ. Sci. Technol.* **1992**, *26*, 262.

(122) Hoigne, J.; Bader, H. *Water Research* **1983**, *17*, 173.

(123) Hoigne, J.; Bader, H. *Water Research* **1983**, *17*, 185.

(124) Zepp, R. G.; Faust, B. C.; Hoigne, J. *Environ. Sci. Technol.* **1992**, *26*, 313.

(125) Hua, I.; Hoffmann, M. R. *Environ. Sci. Technol.* **1997**, *31*, 2237.

(126) Acero, J. L.; Haderlein, S. B.; Schmidt, T. C.; Suter, M. J. F.; Von Gunten, U. *Environ. Sci. Technol.* **2001**, *35*, 4252.

(127) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.

(128) An, Y. J.; Jeong, S. W. *Journal of Colloid and Interface Science* **2001**, *242*, 419.

(129) An, Y. J.; Carraway, E. R.; Schlautman, M. A. *Water Research* **2002**, *36*, 300.

(130) Huang, Q.; Hong, C. S. *Chemosphere* **2000**, *41*.

(131) Gromadzka, K.; Swietlik, J. *Water Research* **2007**, *41*, 2572.

(132) Waldemer, R. H.; Tratnyek, P. G.; Johnson, R. L.; Nurmi, J. T. *Environ. Sci. Technol.* **2007**, *41*, 1010.

(133) Lau, T. K.; Chu, W.; Graham, N. J. D. *Environ. Sci. Technol.* **2007**, *41*, 613.

(134) Anipsitakis, G. P.; Dionysiou, D. D. *Environ. Sci. Technol.* **2004**, *38*, 3705.

(135) Anipsitakis, G. P.; Dionysiou, D. D. *Environ. Sci. Technol.* **2003**, *37*, 4790.

(136) Ball, D. L.; Edwards, J. O. *J. Am. Chem. Soc.* **1956**, *78*, 1125.

(137) Dogliott, L.; Hayon, E. *J. Phys. Chem.* **1967**, *71*, 2511.

(138) Kolthoff, I. M.; Miller, I. K. *J. Am. Chem. Soc.* **1951**, *73*, 3055.

(139) Maruthamuthu, P.; Padmaja, S.; Huie, R. E. *Int. J. Chem. Kin.* **1995**, *27*.

(140) Neta, P.; Huie, R. E.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1027.

(141) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*, *Second ed.*; Wiley: New York, 2003.

(142) Zepp, R. G.; Cline, D. M. *Environ. Sci. Technol.* **1977**, *11*, 359.

(143) 3M Company. *FM-3422: Photolysis Study using Simulated Sunlight*; Docket AR226-0363; Office of Pollution Prevention & Toxics, U.S. Environmental Protection Agency: Washington, D.C., 1981; p. 20.

(144) Gauthier, S. A.; Mabury, S. A. *Environ. Toxicol. Chem.* **2005**, *24*, 1837.

(145) Lee, C.; Choi, W.; Kim, Y. G.; Yoon, J. *Environ. Sci. Technol.* **2005**, *39*, 2101.

(146) Getoff, N.; Schenck, G. O. *Photochemistry and Photobiology* **1968**, *8*, 167.

(147) Fricke, H.; Hart, E. J. *J. Chem. Phys.* **1936**, *4*, 418.

(148) Oppenlander, T.; Gliese, S. *Chemosphere* **2000**, *40*, 15.

(149) Jakob, L.; Hashem, T. M.; Burki, S.; Guindy, N. M.; Braun, A. M. *Journal of Photochemistry and Photobiology A—Chemistry* **1993**, *75*, 97.

(150) Quici, N.; Litter, M. I.; Braun, A. A.; Oliveros, E. *Journal of Photochemistry and Photobiology A—Chemistry* **2008**, *197*, 306.

(151) Chen, J.; Zhang, P. Y.; Liu, J. *J. Environ. Sci* **2007**, *19*, 387.

(152) Osborne, M. C.; Li, Q.; Smith, I. W. M. *Physical Chemistry Chemical Physics* **1999**, *1*, 1447.

(153) Ozer, R. R.; Ferry, J. L. *Environ. Sci. Technol.* **2001**, *35*, 3242.

(154) Fox, M. A.; Cardona, R.; Gaillard, E. *J. Am. Chem. Soc.* **1987**, *109*, 6347.

(155) Lee, J.; Kim, J.; Choi, W. *Environ. Sci. Technol.* **2007**, *41*, 3335.

(156) Weinstock, I. A. *Chem. Rev.* **1998**, *98*, 113.

(157) Akid, R.; Darwent, J. R. *J. Chem. Soc.—Dalton Trans.* **1985**, 395.

(158) Hori, H.; Takano, Y.; Koike, K.; Takeuchi, K.; Einaga, H. *Environ. Sci. Technol.* **2003**, *37*, 418.

(159) Hoffmann, M. R.; Martin, S. T.; Choi, W. Y.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69.

(160) Kormann, C.; Bahnemann, D. W.; Hoffmann, M. R. *Environ. Sci. Technol.* **1991**, *25*, 494.

(161) Dillert, R.; Bahnemann, D.; Hidaka, H. *Chemosphere* **2007**, *67*, 785.

(162) Guan, B.; Zhi, J.; Zhang, X.; Murakami, T.; Fujishima, A. *Electrochem. Commun.* **2007**, *9*, 2817.

(163) Lee, J.; Seliger, H. H. *J. Chem. Phys.* **1964**, *40*, 519.

(164) Hatchard, C. G.; Parker, C. A. *Proceedings of the Royal Society of London Series A—Mathematical and Physical Sciences* **1956**, *235*, 518.

(165) Parker, C. A. *Proceedings of the Royal Society of London Series A—Mathematical and Physical Sciences* **1953**, *220*, 104.

(166) Allmand, A. J.; Webb, W. W. *Journal of the Chemical Society* **1929**, 1518.

(167) Hori, H.; Yamamoto, A.; Koike, K.; Kutsuna, S.; Osaka, I.; Arakawa, R. *Chemosphere* **2007**, *68*, 572.

(168)*http://chm.pops.int/Convention/POPsReviewCommittee/Chemicalsunderreview/tabid/242/language/en-US/Default.aspx*.

(169) Sayles, G. D.; You, G. R.; Wang, M. X.; Kupferle, M. J. *Environ. Sci. Technol.* **1997**, *31*, 3448.

(170) Yak, H. K.; Wenclawiak, B. W.; Cheng, I. F.; Doyle, J. G.; Wai, C. M. *Environ. Sci. Technol.* **1999**, *33*, 1307.

(171) Jones, C. G.; Silverman, J.; Al-Sheikhly, M.; Neta, P.; Poster, D. L. *Environ. Sci. Technol.* **2003**, *37*, 5773.

(172) Hinz, D. C.; Wai, C. M.; Wenclawiak, B. W. *J. Environ. Monit.* **2000**, *2*, 45.

(173) Zhang, W. X. *J. Nanopart. Res.* **2003**, *5*, 323.

(174) Wang, C. B.; Zhang, W. X. *Environ. Sci. Technol.* **1997**, *31*, 2154.

(175) Hori, H.; Nagaoka, Y.; Sano, T.; Kutsuna, S. *Chemosphere* **2008**, *70*, 800.

(176) Hori, H.; Nagaoka, Y.; Yamamoto, A.; Sano, T.; Yamashita, N.; Taniyasu, S.; Kutsuna, S.; Osaka, I.; Arakawa, R. *Environ. Sci. Technol.* **2006**, *40*, 1049.

(177) Macnicol, D. D.; Robertson, C. D. *Nature* **1988**, *332*, 59.

(178) Shoute, L. C. T.; Mittal, J. P.; Neta, P. *J. Phys. Chem.* **1996**, *100*, 11355.

(179) Shoute, L. C. T.; Mittal, J. P.; Neta, P. *J. Phys. Chem.* **1996**, *100*, 3016.

(180) Watson, P. L.; Tulip, T. H.; Williams, I. *Organometallics* **1990**, *9*, 1999.

(181) Combellas, C.; Kanoufi, F.; Thiebault, A. *Journal of Physical Chemistry B* **2003**, *107*, 10894.

(182) Corvaja, C.; Farnia, G.; Formenton, G.; Navarrini, W.; Sandona, G.; Tortelli, V. *J. Phys. Chem.* **1994**, *98*, 2307.

(183) Marsella, J. A.; Gilicinski, A. G.; Coughlin, A. M.; Pez, G. P. *J. Org. Chem.* **1992**, *57*, 2856.

(184) Pud, A. A.; Shapoval, G. S.; Kukhar, V. P.; Mikulina, O. E.; Gervits, L. L. *Electrochim. Acta* **1995**, *40*, 1157.

(185) Chen, X. D.; Lemal, D. M. *J. Fluor. Chem.* **2006**, *127*, 1158.

(186) Szajdzinska-Pietek, E.; Gebicki, J. L. *Res. Chem. Intermed.* **2000**, *26*, 897.

(187) Huang, L.; Dong, W. B.; Hou, H. Q. *Chem. Phys. Lett.* **2007**, *436*, 124.

(188) Ono, T.; Fukaya, H.; Hayashi, E.; Saida, H.; Abe, T.; Henderson, P. B.; Fernandez, R. E.; Scherer, K. V. *J. Fluor. Chem.* **1999**, *97*, 173.

(189) Ochoa-Herrera, V.; Sierra-Alvarez, R.; Somogyi, A.; Jacobsen, N. E.; Wysocki, V. H.; Field, J. A. *Environ. Sci. Technol.* **2008**, *42*, 3260.

(190) Johnson, T. L.; Scherer, M. M.; Tratnyek, P. G. *Environ. Sci. Technol.* **1996**, *30*, 2634.

(191) Roberts, A. L.; Totten, L. A.; Arnold, W. A.; Burris, D. R.; Campbell, T. J. *Environ. Sci. Technol.* **1996**, *30*, 2654.

(192) Puls, R. W.; Paul, C. J.; Powell, R. M. *Appl. Geochem.* **1999**, *14*, 989.

(193) Tratnyek, P. G.; Johnson, T. L.; Scherer, M. M.; Eykholt, G. R. *Ground Water Monit. Remediat.* **1997**, *17*, 108.

(194) Cantrell, K. J.; Kaplan, D. I.; Wietsma, T. W. *J. Hazard. Mater.* **1995**, *42*, 201.

(195) Liu, Y. Q.; Majetich, S. A.; Tilton, R. D.; Sholl, D. S.; Lowry, G. V. *Environ. Sci. Technol.* **2005**, *39*, 1338.

(196) Elliott, D. W.; Zhang, W. X. *Environ. Sci. Technol.* **2001**, *35*, 4922.

(197) Kim, Y. H.; Carraway, E. R. *Environ. Sci. Technol.* **2000**, *34*, 2014.

(198) Zhang, W. X.; Wang, C. B.; Lien, H. L. *Catal. Today* **1998**, *40*, 387.

(199) Bransfield, S. J.; Cwiertny, D. M.; Livi, K.; Fairbrother, D. H. *Appl. Catal. B—Environ.* **2007**, *76*, 348.

(200) Cwiertny, D. M.; Bransfield, S. J.; Livi, K. J. T.; Fairbrother, D. H.; Roberts, A. L. *Environ. Sci. Technol.* **2006**, *40*, 6837.

(201) Marshall, W. D.; Kubatova, A.; Lagadec, A. J. M.; Miller, D. J.; Hawthorne, S. B. *Green Chem.* **2002**, *4*, 17.

(202) Hart, E. J.; Anbar, M. *The Hydrated Electron*; John Wiley & Sons, Inc.: New York, 1970.

(203) Mezyk, S. P.; Helgeson, T.; Cole, S. K.; Cooper, W. J.; Fox, R. V.; Gardinali, P. R.; Mincher, B. J. *J. Phys. Chem. A* **2006**, *110*, 2176.

(204) Milosavljevic, B. H.; LaVerne, J. A.; Pimblott, S. M. *J. Phys. Chem. A* **2005**, *109*, 7751.

(205) Johnson, H. D.; Cooper, W. J.; Mezyk, S. P.; Bartels, D. M. *Radiat. Phys. Chem.* **2002**, *65*, 317.

(206) Nickelsen, M. G.; Cooper, W. J.; Secker, D. A.; Rosocha, L. A.; Kurucz, C. N.; Waite, T. D. *Radiat. Phys. Chem.* **2002**, *65*, 579.

(207) Rahn, R. O.; Stephan, M. I.; Bolton, J. R.; Goren, E.; Shaw, P.-S.; Lykke, K. R. *Photochem. Photobiol.* **2003**, *78*, 146.

(208) Anbar, M.; Hart, E. J. *J. Phys. Chem.* **1965**, *69*, 271.

(209) Czapski, G.; Schwarz, H. A. *J. Phys. Chem.* **1962**, *66*, 471.

(210) Matheson, M. S.; Mulac, W. A.; Rabani, J. *J. Phys. Chem.* **1963**, *67*, 2613.

(211) Hart, E. J.; Boag, J. W. *J. Am. Chem. Soc.* **1962**, *84*, 4090.

(212) Thomas-Smith, T. E.; Blough, N. V. *Environ. Sci. Technol.* **2001**, *35*, 2721.

(213) Hoigne, J.; Faust, B. C.; Haag, W. R.; Scully, F. E.; Zepp, R. G. *Acs Symposium Series* **1989**, *219*, 363.

(214) Zepp, R. G.; Braun, A. M.; Hoigne, J.; Leenheer, J. A. *Environ. Sci. Technol.* **1987**, *21*, 485.

(215) Lian, R.; Oulianov, D. A.; Crowell, R. A.; Shkrob, I. A.; Chen, X. Y.; Bradforth, S. E. *J. Phys. Chem. A* **2006**, *110*, 9071.

(216) Nishiwaki, T.; Usui, M.; Anda, K.; Hida, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 821.

(217) Yao, Y.; Kakimoto, K.; Ogawa, H. I.; Kato, Y.; Hanada, Y.; Shinohara, R.; Yoshino, E. *Chemosphere* **1997**, *35*, 2891.

(218) Hawari, J.; Demeter, A.; Samson, R. *Environ. Sci. Technol.* **1992**, *26*, 2022.

(219) Schwarz, H. A.; Dodson, R. W. *J. Phys. Chem.* **1989**, *93*, 409.

(220) Murakami, Y.; Kikuchi, J.; Hisaeda, Y.; Hayashida, O. *Chem. Rev.* **1996**, *96*, 721.

(221) Gantzer, C. J.; Wackett, L. P. *Environ. Sci. Technol.* **1991**, *25*, 715.

(222) Costentin, C.; Robert, M.; Saveant, J. M. *J. Am. Chem. Soc.* **2005**, *127*, 12154.

(223) Glod, G.; Angst, W.; Holliger, C.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1997**, *31*, 253.

(224) Wood, J. M.; Kennedy, F. S.; Wolfe, R. S. *Biochemistry* **1968**, *7*, 1707.

(225) Lexa, D.; Saveant, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 3220.

(226) Lexa, D.; Saveant, J. M.; Zickler, J. *J. Am. Chem. Soc.* **1977**, *99*, 2786.

(227) Zehnder, A. J. B.; Wuhrmann, K. *Science* **1976**, *194*, 1165.

(228) Shey, J.; van der Donk, W. A. *J. Am. Chem. Soc.* **2000**, *122*, 12403.

(229) Schrauze, G.N.; Deutsch, E.; Windgass, R.J.. *J. Am. Chem. Soc.* **1968**, *90*, 2441.

(230) Krusic, P. J.; Marchione, A. A.; Roe, D. C. *J. Fluor. Chem.* **2005**, *126*, 1510.

(231) Ainagos, A. F. *Kinet. Catal.* **1991**, *32*, 720.

(232) Hynes, R. G.; Mackie, J. C.; Masri, A. R. *J. Phys. Chem. A* **1999**, *103*, 54.

(233) Atkinson, B.; McKeagan, D. *Chem. Commun.* **1966**, 189.

(234) Bauer, S. H.; Hou, K. C.; Resler, E. L. *Phys. Fluids* **1969**, *12*, I125.

(235) Blake, P. G.; Tomlinso.A. D. *Journal of the Chemical Society B—Physical Organic* **1971**, 1596.

(236) Brown, C. E.; Smith, D. R. *Can. J. Chem.—Rev. Can. Chim.* **1988**, *66*, 609.

(237) Chowdhury, P. K. *J. Phys. Chem.* **1995**, *99*, 12084.

(238) Longfellow, C. A.; Smoliar, L. A.; Lee, Y. T.; Lee, Y. R.; Yeh, C. Y.; Lin, S. M. *J. Phys. Chem. A* **1997**, *101*, 338.

(239) Matula, R. A. *J. Phys. Chem.* **1968**, *72*, 3054.

(240) Millward, G. E.; Tschuiko.E. *J. Phys. Chem.* **1972**, *76*, 292.

(241) Tschuiko, E. *J. Chem. Phys.* **1968**, *49*, 3115.

(242) Lee, M. C.; Choi, W. *J. Ind. Eng. Chem.* **2004**, *10*, 107.

(243) Burgess, D. R.; Zachariah, M. R.; Tsang, W.; Westmoreland, P. R. *Prog. Energy Combust. Sci.* **1995**, *21*, 453.

(244) Lines, D.; Sutcliffe, H. *J. Fluor. Chem.* **1984**, *25*, 505.

(245) Lazerte, J. D.; Hals, L. J.; Reid, T. S.; Smith, G. H. *J. Am. Chem. Soc.* **1953**, *75*, 4525.

(246) Glockner, V.; Lunkwitz, K.; Prescher, D. *Tenside Surf. Det.* **1989**, *26*.

(247) Krusic, P. J.; Roe, D. C. *Anal. Chem.* **2004**, *76*, 3800.

(248) 3M Company. *Laboratory-Scale Thermal Degradation of Perfluorooctanyl Sulfonate and Related Substances*; Docket AR226-1366; Office of Pollution Prevention & Toxics, U.S. Environmental Protection Agency: Washington, D.C., 2003; p. 13.

(249) Ravishankara, A. R.; Solomon, S.; Turnipseed, A. A.; Warren, R. F. *Science* **1993**, *259*, 194.

(250) 3M Company. *Final Report—Laboratory-Scale Thermal Degradation of Perfluoro-Octanyl Sulfonate and Related Substances*; Docket AR226-1367; Office of Pollution Prevention & Toxics, U.S. Environmental Protection Agency: Washington, D.C., 2003; p. 142.

(251) Leighton, T. G. *The Acoustic Bubble*; Academic Press: London, 1994.

(252) Mason, T. J.; Lorimer, J. P. *Sonochemistry: theory, applications and uses of ultrasound in chemistry*; Halsted Press: New York, 1988.

(253) Suslick, K. S. *Ultrasound: Its Chemical, Physical, and Biological Effects;* VCH, New York, 1988.

(254) Destaillats, H.; Hung, H. M.; Hoffmann, M. R. *Environ. Sci. Technol.* **2000**, *34*, 311.

(255) Kotronarou, A.; Mills, G.; Hoffmann, M. R. *J. Phys. Chem.* **1991**, *95*, 3630.

(256) Vinodgopal, K.; Ashokkumar, M.; Grieser, F. *J. Phys. Chem. B* **2001**, *105*, 3338.

(257) Manousaki, E.; Psillakis, E.; Kalogerakis, N.; Mantzavinos, D. *Water Res.* **2004**, *38*, 3751.

(258) Petrier, C.; Lamy, M. F.; Francony, A.; Benahcene, A.; David, B.; Renaudin, V.; Gondrexon, N. *J. Phys. Chem.* **1994**, *98*, 10514.

(259) Hung, H. M.; Hoffmann, M. R. *J. Phys. Chem. A* **1999**, *103*, 2734.

(260) Jennings, B. H.; Townsend, S. N. *J. Phys. Chem.* **1961**, *65*, 1574.

(261) Petrier, C.; David, B.; Laguian, S. *Chemosphere* **1996**, *32*, 1709.

(262) Vecitis, C. D.; Park, H.; Cheng, J.; Mader, B. T.; Hoffmann, M. R. *J. Phys. Chem. A* **2008**, *112*, 4261.

(263) Suslick, K. S.; Hammerton, D. A.; Cline, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 5641.

(264) Price, G. J.; Ashokkumar, M.; Hodnett, M.; Zequiri, B.; Grieser, F. *J. Phys. Chem. B* **2005**, *109*, 17799.

(265) Sunartio, D.; Ashokkumar, M.; Grieser, F. *J. Am. Chem. Soc.* **2007**, *129*, 6031.

(266) Brennen, C. E. *Cavitation and Bubble Dynamics*; Oxford University Press: New York, 1995.

(267) Didenko, Y. T.; McNamara, W. B.; Suslick, K. S. *J. Am. Chem. Soc.* **1999**, *121*, 5817.

(268) Ciawi, E.; Rae, J.; Ashokkumar, M.; Grieser, F. *J. Phys. Chem. B* **2006**, *110*, 13656.

(269) Ashokkumar, M.; Grieser, F. *J. Am. Chem. Soc.* **2005**, *127*, 5326.

(270) Eddingsaas, N. C.; Suslick, K. S. *J. Am. Chem. Soc.* **2007**, *129*, 3838.

(271) Sostaric, J. Z.; Riesz, P. *J. Am. Chem. Soc.* **2001**, *123*, 11010.

(272) Kato, S.; Makide, Y.; Tominaga, T.; Takeuchi, K. *J. Phys. Chem.* **1987**, *91*, 4278.

(273) Kolaczkowski, S. T.; Plucinski, P.; Beltran, F. J.; Rivas, F. J.; McLurgh, D. B. *Chem. Eng. J.* **1999**, *73*, 143.

(274) Chang, M. B.; Chang, J. S. *Industrial & Engineering Chemistry Research* **2006**, *45*, 4101.

(275) Destaillats, H.; Colussi, A. J.; Joseph, J. M.; Hoffmann, M. R. *J. Phys. Chem. A* **2000**, *104*, 8930.

(276) Weavers, L. K.; Malmstadt, N.; Hoffmann, M. R. *Environ. Sci. Technol.* **2000**, *34*, 1280.

(277) Lesko, T.; Colussi, A. J.; Hoffmann, M. R. *Environ. Sci. Technol.* **2006**, *40*, 6818.

(278) Weavers, L. K.; Ling, F. H.; Hoffmann, M. R. *Environ. Sci. Technol.* **1998**, *32*, 2727.

(279) Vecitis, C. D.; Park, H.; Cheng, J.; Mader, B. T.; Hoffmann, M. R. *J. Phys. Chem. C* **2008**, *112*, 16850.