



Photochemical decomposition of perfluorodecanoic acid in aqueous solution with VUV light irradiation

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ABSTRACT

The photochemical decomposition of perfluorodecanoic acid (PFDeA) in water in the presence of persulfate ion ($S_2O_8^{2-}$) and sulfur ion (S^{2-}) was investigated under vacuum ultraviolet (VUV) light irradiation. PFDeA was decomposed under VUV light irradiation. With the addition of $S_2O_8^{2-}$ or S^{2-} , the photo-decomposition and defluorination of PFDeA were enhanced significantly. Sulfate radical anion ($SO_4^{\bullet-}$) generated from photolysis of $S_2O_8^{2-}$ initiated PFDeA oxidation. While the S^{2-} ion, acting as a $\bullet OH$ scavenger, enhanced the role of reduction pathway induced by aqueous electrons (e_{aq}^-). The shorter-chain perfluorocarboxylic acids (PFCAs), formed in a stepwise manner from longer-chain PFCAs, were identified as products by HPLC/MS.

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1. Introduction

Perfluorinated compounds (PFCs), which have been extensively used for decades in a wide range of industrial products, have been detected in the environment globally [1,2]. Their environmental persistence and bioaccumulative potential probably have adverse effect on human health and ecosystem [2–6]. Due to their relatively high organic bond strength and their resistance to most conventional advanced oxidation processes resulting from fluorine's electron negativities, PFCs are chemically inert [7,8].

A few studies have investigated the chemical decomposition of PFCs in solutions. PFCs molecules are pyrolyzed in the interfacial region with high temperature caused by sonication [8]. The addition of some chemicals to thermolysis reaction system leads to an increase in the rate of PFCs oxidation, whereas the reaction temperature is much lower than the temperatures used for traditional treatment by subcritical ($\sim 300^\circ C$) or supercritical water ($> 374^\circ C$). For example, PFCs could be efficiently decomposed in hot water at a relatively lower temperature ($80^\circ C$) in the presence of $S_2O_8^{2-}$ [9]. In this case, $SO_4^{\bullet-}$, thermally obtained from $S_2O_8^{2-}$, can oxidize PFCs. Besides the oxidative path, reductive degradation pathway also plays an important role in PFCs decomposition. For instance, efficient ion-induced decompositions of PFCs using zerovalent iron in sub- and supercritical water have been observed [10,11].

It has been reported that the light-induced degradation methods in aqueous solutions such as direct photolysis [12], persulfate photolysis [5,13], photocatalysis [14,15] are more effective for perfluorocarboxylic acids (PFCAs). PFCAs are oxidized by one-electron transfer from PFCAs to the photoexcited species ($SO_4^{\bullet-}$ or $[PW_{12}O_{40}]^{3-\bullet}$) [4,14]. In addition, the inorganic oxidants, i.e. KIO_4 , $HClO_3$, $(NH_4)_2S_2O_8$, and $KBrO_3$, are used as an electron scavenger to suppress electron–hole recombination in TiO_2 photocatalytic system; substantially the reactivity of valence-band holes toward PFCs is augmented [16,17]. Reductive photo-decomposition of PFCs has been observed as well [18–20]. Photocatalyst [18,20] and aqueous electron (e_{aq}^-) are capable of completely dissociating PFCs via fluoride elimination. It has been reported that perfluorooctane sulfonate (PFOS) can be photocatalytically defluorinated by biomimetic reduction with vitamin B12 as catalyst and Ti (III)-citrate as a bulk electron source in anoxic aqueous solutions [18]. Aqueous electron (e_{aq}^-), a powerful one-electron reductant which is generated from the UV-KI photolysis via charge-transfer-to-solvent states, is able to decompose both PFOS and perfluorooctanoic acid (PFOA) [19].

Persulfate photolysis has been utilized to degrade PFOA [13]. Under vacuum ultraviolet (VUV) light irradiation, PFOA was decomposed through both photolysis and initiation of sulfate radical ($SO_4^{\bullet-}$). Since the PFDeA absorption of light is strong in the region from deep UV-region to 200 nm and weak in the region from 200 nm to visible light, we expect to utilize 185 nm light irradiation to excite PFDeA to direct photolysis, and employ inorganic compounds, such as $K_2S_2O_8$ and Na_2S , to enhance PFDeA decomposition. In the present work, PFDeA defluorination and degradation

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in solutions with $K_2S_2O_8$ or Na_2S under VUV light irradiation was studied, and the photochemical decomposition mechanism of PFDeA in the presence of $K_2S_2O_8$ and Na_2S was discussed.

2. Materials and methods

2.1. Materials

Perfluorobutanoic acid (PFBA, C4, 99%), perfluoropentanoic acid (PFPeA, C5, 97%), perfluoroheptanoic acid (PFHpA, C7, 96%), perfluorooctanoic acid (PFOA, C8, 96%), perfluorononanoic acid (PFNA, C9, 99%), and perfluorodecanoic acid (PFDeA, C10, 98%) were purchased from Aldrich Chemical Co. (New Jersey, USA). Perfluorohexanoic acid (PFHxA, C6, 97%) was purchased from Sigma–Aldrich Chemical Co. (Tokyo, Japan). PFCs-free deionized water, HPLC-grade methanol, and analytical-grade reagents of ammonium acetate, sulfide sodium, and persulfate potassium were employed in our studies.

2.2. Photoreactor

The photochemical decomposition experiments were conducted in a tubular glass reactor with an inner diameter of 55 mm and a length of 800 mm. A 23 W low-pressure mercury lamp (ZW23D15W-Z436, China) emitted at both 254 nm and 185 nm was used to provide VUV illumination (hereafter referred to as VUV) with a light intensity of 62–69 $mW\ cm^{-2}$. The lamp with a quartz envelope was placed in the center of the reactor. The reaction temperature was kept constant at 30 °C by a cooling water jacket around the reactor. 500 mL of 0.1 mM (51.4 $mg\ L^{-1}$) PFDeA aqueous solution was filled into the reactor. Gas was continuously bubbled into the reactor through a porous glass plate at a flow rate of 100 $mL\ min^{-1}$.

2.3. Analysis

The concentrations of F^- and SO_4^{2-} in aqueous solution were determined by an ion-chromatography system (DX-120, DIONEX) consisting of a manual sample injector (sample injection volume: 20 μL), a degasser, a pump, a separation column (4.6 mm i.d., 25 cm length, TSKgel Super IC-Anion, Japan), a column oven (40 °C), and a conductivity detector with a suppressor device. The mobile phase, a solution of Na_2CO_3 (1.7 mM) and $NaHCO_3$ (1.8 mM), was pumped into the system at a rate of 1.35 $mL\ min^{-1}$. The limits of detection (LOD) of F^- and SO_4^{2-} ions were both 0.01 $mg\ L^{-1}$.

The concentrations of PFDeA and the formed PFCAs were analyzed by an Agilent 1100 high-performance liquid chromatograph (HPLC, Agilent Technology, USA) coupled with a Trap-XCT ion-trap mass spectrometer (Applied Biosystems, Foster City, CA). 5 μL of the sample was injected into a Luna C18 column (100 \times 2.0 mm, 5 μm , Phenomenex, USA). A gradient mobile phase, consisting of a mixture of 1 mM ammonium acetate (pH 6.0) and methanol, was employed at a flow rate of 200 $\mu L\ min^{-1}$. The operating gradient was from 40% to 60% methanol within 2 min, from 60% to 75% methanol within 3 min, then at 75% methanol for 13 min, followed by a 1-min washing with 60% methanol, and then reverted to initial conditions. The total running time was 20 min, with an equilibration time of 6 min between two successive samples. Detection was operated in the negative electrospray ionization mode using multiple reactions monitoring (MRM). The optimized conditions were: nebulizer gas pressure of 40 psi, drying nitrogen gas temperature of 350 °C, drying nitrogen gas flow rate of 10 $L\ min^{-1}$, capillary voltage of +1500 V, and the skimmer cone voltage of –40 V. Selected ion monitoring (SIM) mode was employed for the identification of PFCs, and quantization was monitored as

$[M-H]^-$ plus $[M-COOH]^-$ ions for C4–C10 PFCAs in the single MS mode.

3. Results

3.1. Photolytic decomposition of PFDeA

Photolytic decomposition experiments of PFDeA solution were conducted under VUV irradiation in nitrogen, oxygen, and air atmospheres, respectively. Fig. 1 shows the degradation ratio [(moles of decomposed PFDeA)/(moles of initial PFDeA)] and the defluorination ratio [(moles of F^- formed)/(moles of fluorine content in initial PFDeA)] of PFDeA VUV decomposition within 360-min under different atmospheres. The extent of PFDeA decomposition was significant in photolysis reaction system. The concentration of PFDeA decreased over time. Reaction atmosphere had little influence on PFDeA photolysis. Nearly 60% of the initial PFDeA was photo-decomposed after 360-min irradiation, and the defluorination ratio of PFDeA was nearly 16%. Formation rates of F^- were the same (about 0.17–0.19 $mg\ L^{-1}\ min^{-1}$) under these three types of atmospheres.

3.2. Photochemical decomposition of PFDeA with $K_2S_2O_8$

Compared to direct photolysis, the addition of $K_2S_2O_8$ significantly enhanced PFDeA decomposition under oxygen. The degradation ratio and defluorination ratio of PFDeA in the presence of $K_2S_2O_8$ as a function of VUV light irradiation time were shown in Fig. 2. The addition of $K_2S_2O_8$ to VUV system greatly exhibited rapid reactivity with PFDeA. The concentrations of undecomposed PFDeA after 360-min reaction were below the limit of detection, and large amounts of F^- formed with yields greater than 30%. When the initial amount of $K_2S_2O_8$ rose from 0.1 to 5 mM, no significant changes in degradation and defluorination ratios occurred, and formation rates of F^- were stable in the range of 0.41–0.43 $mg\ L^{-1}\ min^{-1}$. As the indicative of photochemical reactivity, the decomposition rate constant of PFDeA, obtained by the slope of this period, was about $4.48 \times 10^{-3}\ mg\ L^{-1}\ min^{-1}$. The corresponding value for the formation rate of F^- was about $4.00 \times 10^{-3}\ mg\ L^{-1}\ min^{-1}$. In the aqueous solution with initial $[S_2O_8^{2-}]$ of 0.1, 1 and 5 mM, the $[SO_4^{2-}]$ reached 0.2, 2 and 10 mM, respectively, after 360-min irradiation. These data indicate that all sulfur species in this reaction system eventually transformed to SO_4^{2-} .

3.3. Photochemical decomposition of PFDeA with Na_2S

When the reaction was carried out in the presence of Na_2S under nitrogen atmosphere (Fig. 3), the trends of PFDeA decomposition and F^- formation were similar to those of reactions in the presence of $K_2S_2O_8$ under oxygen atmosphere. Compared to direct photolysis, the addition of Na_2S significantly enhanced PFDeA decomposition. The amount of PFDeA decreased linearly within 120-min irradiation. The decomposition rate constants of PFDeA (with 0, 0.1, 1, and 5 mM Na_2S), obtained by the slope of this period, were 1.92×10^{-3} , 2.98×10^{-3} , 3.03×10^{-3} , and $2.12 \times 10^{-3}\ mg\ L^{-1}\ min^{-1}$, respectively. The corresponding values for formation rates of F^- were 1.97×10^{-3} , 4.95×10^{-3} , 5.01×10^{-3} , and $2.38 \times 10^{-3}\ mg\ L^{-1}\ min^{-1}$, respectively.

The PFDeA decomposition rate constant was significantly influenced by the initial concentration of Na_2S . The photochemical reactivity increased with $[Na_2S]$. When 0.1 mM Na_2S was added into solution, the degradation rate constant of PFDeA was nearly 2 times higher than that of direct photolysis. However, further increase in initial $[Na_2S]$, PFDeA decomposition rate decreased significantly. Analysis of the changes in S^{2-} ions during the reaction period showed that S^{2-} converted into SO_4^{2-} when 0.1 mM Na_2S

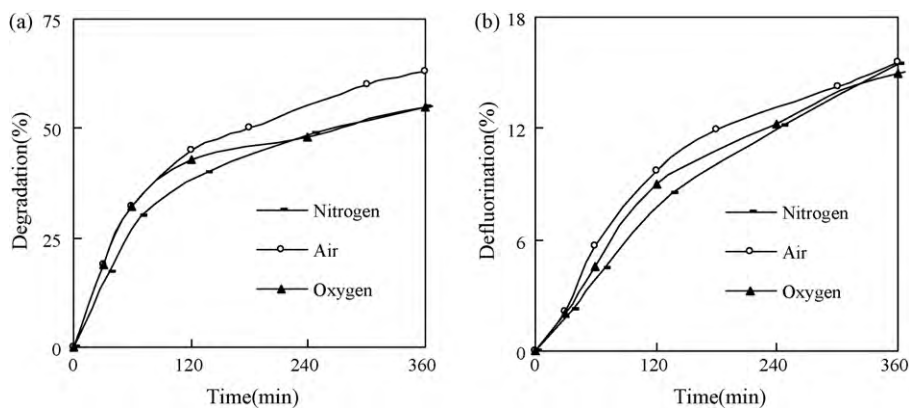


Fig. 1. The degradation (a) and defluorination (b) ratios of PFDeA with VUV light irradiation under nitrogen, oxygen, and air atmosphere.

was added. And the SO_4^{2-} ions yield (the molar ratio of total sulfur content in SO_4^{2-} ions to total initial sulfur content in Na_2S) was 98%. When 1 mM and 5 mM Na_2S were added, the SO_4^{2-} ions yields were about 70% and 58%, respectively. The decrease could be explained by that some of S^{2-} ions were oxidized to SO_4^{2-} by oxidants, i.e. $\cdot\text{OH}$ radicals, while the others reacted with H^+ and H^{\cdot} and formed H_2S gas.

3.4. Intermediate products during PFDeA photochemical decomposition

Although the photochemical decomposition of PFDeA had higher rate than that of direct photolysis, similar product distributions were found in these two systems. Other than F^- and

shorter-chain PFCAs, no other byproduct was detected in solution, indicating that the photochemical reaction was very selective. The formation of shorter-chain PFCAs was identified and quantified by HPLC/MS. The external standards were used to confirm the results. The identified intermediate products of PFDeA decomposition were shorter-chain PFCAs including PFNA ($\text{C}_8\text{F}_{17}\text{COO}^-$), PFOA ($\text{C}_7\text{F}_{15}\text{COO}^-$), PFHpA ($\text{C}_6\text{F}_{13}\text{COO}^-$), PFHxA ($\text{C}_5\text{F}_{11}\text{COO}^-$), PFPeA ($\text{C}_4\text{F}_9\text{COO}^-$), and PFBA ($\text{C}_3\text{F}_7\text{COO}^-$). The total recoveries of F (molar ratio of total F content in F^- and short-chain PFCAs formed and in unchanged PFDeA to that in the PFDeA before irradiation) were in the range of 93.6–105%.

The changes in PFCAs concentration during PFDeA photochemical decomposition in the presence of 1 mM $\text{K}_2\text{S}_2\text{O}_8$ (a) and Na_2S (b) are shown in Fig. 1S. When 1 mM $\text{K}_2\text{S}_2\text{O}_8$ was added, the con-

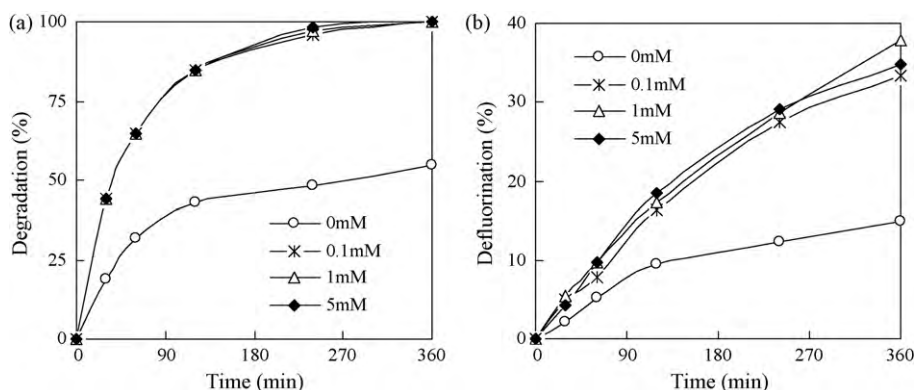


Fig. 2. The degradation (a) and defluorination (b) ratios of PFDeA in the presence of $\text{K}_2\text{S}_2\text{O}_8$ with VUV light irradiation under oxygen atmosphere.

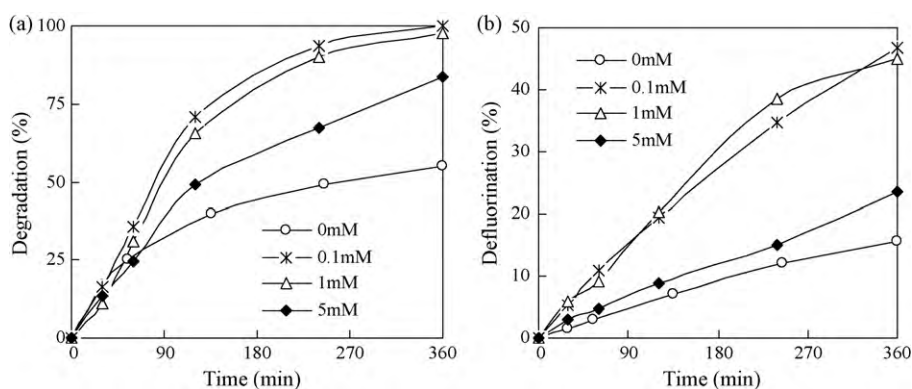


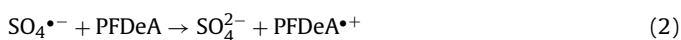
Fig. 3. The degradation (a) and defluorination (b) ratios of PFDeA in the presence of Na_2S with VUV light irradiation under nitrogen atmosphere.

centration of formed C7–C10 PFCAs firstly increased to a maximum and then decreased, whereas those of PFCAs bearing shorter perfluoroalkyl groups, such as, PFHxA, PFPeA and PFBA, increased with time. The PFNA and PFOA concentrations reached the maxima at around 120 min, while the highest PFHpA concentration was obtained at around 240 min. A fast yield rate of PFHxA was observed after 60 min of irradiation, followed by a slower process. When the reaction was carried out in the presence of Na₂S under nitrogen atmosphere, the products distribution was similar to that in the presence of K₂S₂O₈ under oxygen. No significant differences were observed in the formation of shorter-chain PFCAs.

4. Discussion

4.1. Photochemical decomposition of PFDeA with K₂S₂O₈

The reaction mechanism for sulfate radical mediated degradation of PFOA was proposed in previous researches [13]. The initial decomposition is postulated to occur through two branching pathways: direct photolysis yielding PFDeA^{•+} (Eq. (1)) and photochemical degradation through an electron transfer from PFDeA to the sulfate radical to form PFDeA[•] (Eq. (2)).



Excited PFDeA subsequently cleaves C–C bond between the C₉F₁₉ and COOH. The C₉F₁₉ radical in water produces thermally unstable alcohol C₉F₁₉OH, which undergoes HF elimination to form C₈F₁₇COF. This acid fluoride releases PFCAs with one less CF₂ unit, C₈F₁₇COOH, during hydrolysis process. Another reaction pathway was proposed by Kutsuna and Hori [21]. The C₉F₁₉[•] radical reacts with molecular oxygen to form C₉F₁₉COO[•] radical (Eq. (3)):



And then the C₉F₁₉COO[•] radical reacts with each other to yield perfluoroalkoxy radicals and molecular oxygen (Eq. (4)):



The perfluoroalkoxy has two branching pathways: unimolecular decomposition yielding C₈F₁₇[•] radical and carbonyl fluoride (Eq. (5)) or H-atom abstraction from an acid such as HSO₄⁻ yielding C₉F₁₉OH (Eq. (6)).

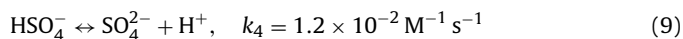
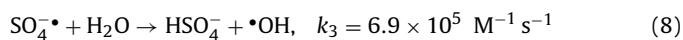
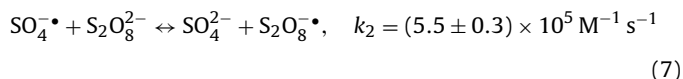


In the same way, the resulting intermediate products are decomposed and the PFCAs bearing shorter perfluoroalkyl groups are produced in a stepwise manner from PFCAs that bear longer perfluoroalkyl groups. Therefore, the photo-defluorination is a successive process.

In conclusion, direct VUV photolysis and photochemical decomposition proceed simultaneously in our system. Both PFDeA and S₂O₈²⁻ are photo-excited to excited state (PFDeA^{•+}) or reactive radicals under VUV irradiation. SO₄^{•-} radical, an oxidizing radical with one-electron reduction potential of 2.3 V [22], plays an important role in PFDeA oxidation.

No significant changes occurred when [K₂S₂O₈] rose from 0.1 mM to 1 mM and 5 mM. It indicates that the [K₂S₂O₈] does not play a substantial role in reaction system. The photo-decomposition rate of PFOA has been reported to increase with increasing initial [K₂S₂O₈] [14]; however, further increase in the initial [K₂S₂O₈] results in saturation, that is, no further increase in the PFOA decomposition rate. The saturation of the PFOA decomposition rate is

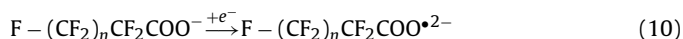
attributed to the saturation of SO₄^{•-} concentration. The rate constants of the saturation of SO₄^{•-} concentration by reaction with S₂O₈²⁻ and H₂O were calculated [23]



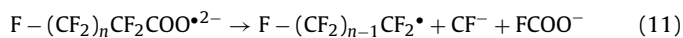
Under our reaction conditions, saturation of SO₄^{•-} concentration was also observed due to a higher rate constant of *k*₂ [S₂O₈²⁻] value (1.6 × 10⁷ M⁻¹ s⁻¹), calculated from [K₂S₂O₈] of 0.1 mM. Therefore, the tendency of PFDeA degradation rate to saturate at higher K₂S₂O₈ concentration can be explained by that the reaction of SO₄^{•-} with S₂O₈²⁻ occurs at higher concentrations, resulting in SO₄^{•-} concentration saturation.

4.2. Photochemical decomposition of PFDeA with Na₂S

PFDeA decomposition took place immediately under VUV light irradiation in the presence of Na₂S. The reaction yields were similar to those of direct VUV photolysis. However, the photochemical decomposition rate increased remarkably. Besides direct photolysis, another reaction mechanism plays an important role in PFDeA decomposition. In PFDeA structure, all C atoms, except the one on –COOH, are connected with F atoms. Fluorine, possessing the greatest electro-negativity relative to the other halogens, has the strongest inductive electron withdrawal ability. Therefore, a strong carbon–fluorine (C–F) covalent bond provides the thermal and chemical stability to PFCs and their derivatives. And thus it is difficult for C–F bond to be cleaved in oxidation way. e_{aq}⁻ is highly reductive and can reduce most halogenated compounds in photocatalytic process [24–28]. The e_{aq}⁻ reductive pathway is the only possible pathway for destruction to decompose PFCs since these compounds are inert towards holes and •OH [29]. The reaction mechanism for PFCAs with e_{aq}⁻ produced by photolysis of iodide, has been illustrated in previous study [19]. e_{aq}⁻ interacts with PFCAs by nucleophilic substitution. In summary, e_{aq}⁻ attacks the carbon atom in the aromatic ring and incorporates into the orbitals of the ring. The fluorine atom is capable of withdrawing electron due to its high electron affinity. The fluorine atom, instead of the carbon atom, is the reaction center when e_{aq}⁻ is approaching to PFCAs



And further dissociation yields C_nF_{2n} radical intermediate.



Similar reduction mechanism may occur in our reaction systems. Under nitrogen atmosphere, The C₉F₁₉ radical in water primarily forms thermally unstable alcohol C₉F₁₉OH. And the reaction (Eq. (3)) is restrained due to oxygen deficiency. In VUV/Na₂S system, S²⁻ ion, an electron donor, significantly reduces the undesired recombination of H⁺, •OH and e_{aq}⁻. Therefore, it could speculate that tendency of fluoride atom in PFDeA to accept an aqueous electron leads to the cleavage of C–F bond. In conclusion, the photochemical decomposition mechanism for PFDeA in the presence of Na₂S is presented in Fig. 4.

Firstly, the F atom is replaced with e_{aq}⁻ by nucleophilic substitution and the formed C₉F₁₈[•] radical intermediate reacts with •OH immediately to yield alcohol. Secondly, the thermally unstable alcohol (C₉F₁₈OH) undergoes HF elimination and forms C₈F₁₆COF. At last, the acid fluoride hydrolyzes to C₈F₁₇COOH (PFNA). In the same way, shorter-chain PFCAs are produced in a similar stepwise

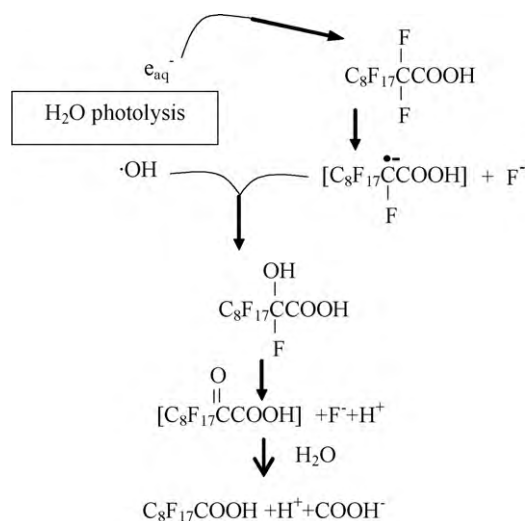


Fig. 4. PFDeA decomposition mechanism in the presence of Na_2S .

manner from longer-chain PFCAs. In VUV system, the degradation rate constants of PFDeA in the presence of Na_2S are lower than those of that in the presence of $\text{K}_2\text{S}_2\text{O}_8$ within 120-min VUV irradiation. However, the defluorination rate constants in the presence of Na_2S (0.1 mM and 1 mM) are higher than those for $\text{K}_2\text{S}_2\text{O}_8$. The higher defluorination rate constants of PFDeA can be explained by that F atom abstraction from PFDeA by e_{aq}^- greatly enhances PFDeA defluorination.

The reaction rate of PFDeA increases with $[\text{Na}_2\text{S}]$ until an optimal concentration is reached. Further increase in $[\text{Na}_2\text{S}]$ results in no further increase in PFDeA decomposition rate. When the initial amount of S^{2-} ions increases from 1 to 5 mM, the degradation ratio of PFDeA decreases from 97.46% to 83.72%. In this case, the reaction of $\cdot\text{OH}$ radicals with $\text{C}_n\text{F}_{2n}\cdot$ radical intermediate is inhibited by the competition of $\cdot\text{OH}$ radicals reacting with S^{2-} ions. In fact, the oxidative degradation (direct VUV photolysis) and reductive degradation (photochemical decomposition) pathways proceed simultaneously by oxidation and reduction mechanisms in VUV/ Na_2S system. However, which one is the more important pathway needs further study.

5. Conclusions

The addition of persulfate and sulfur ion is determinant to the PFDeA photolytic decomposition. Sulfate radicals, generated from persulfate photolysis, directly oxidizes PFDeA by a direct one-electron transfer from PFDeA to sulfate radical. C–C bond between C_9F_{19} and COOH is subsequently cleaved. The $\text{C}_9\text{F}_{19}\cdot$ radical reacts with $\cdot\text{OH}$ to form thermally unstable alcohol $\text{C}_9\text{F}_{19}\text{OH}$ or reacts with molecular oxygen to form $\text{C}_9\text{F}_{19}\text{COO}\cdot$ radical in the presence of oxygen. When sulfur ion is added into reaction system, S^{2-} ion, an electron donor, significantly reduces the undesired recombination of H^+ , $\cdot\text{OH}$ and e_{aq}^- . e_{aq}^- , a powerful one-electron reductant, can reduce PFOA through attacking the carbon atom in the aromatic ring followed by incorporation into the orbitals of the ring and the fluorine atom is capable of withdrawing electron and resulting in PFDeA defluorination.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.04.115.

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