Efficient Decomposition of Environmentally Persistent Perfluorocarboxylic Acids by Use of Persulfate as a Photochemical Oxidant

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Photochemical decomposition of persistent perfluorocarboxylic acids (PFCAs) in water by use of persulfate ion ($S_2O_8^{2-}$) was examined to develop a technique to neutralize stationary sources of PFCAs. Photolysis of $S_2O_8^{2-}$ produced highly oxidative sulfate radical anions ($SO_4^{\bullet-}$), which efficiently decomposed perfluorooctanoic acid (PFOA) and other PFCAs bearing C_4–C_8 perfluoroalkyl groups. The major products were F^- and CO_2; also, small amounts of PFCAs with shorter than initial chain lengths were detected in the reaction solution. PFOA at a concentration of 1.35 mM (typical of that in untreated wastewater after an emulsifying process in fluoropolymer manufacture) was completely decomposed by a photochemical system with 50 mM $S_2O_8^{2-}$ and 4 h of irradiation from a 200-W xenon–mercury lamp. The initial PFOA decomposition rate was 11 times higher than with photolysis alone. All sulfur-containing species in the reaction solution were eventually transformed to sulfate ions by this method. This method was successfully applied to the decomposition of perfluorononanoic acid contained in a floor wax solution.

Introduction

Perfluorocarboxylic acids (PFCAs) and perfluorosulfonic acids and their salts have been widely used as emulsifying agents in polymer synthesis and as surface treatment agents in photolithography, paper coatings, and waxes and polishes (*1–3*). As the use of these perfluorinated acids has increased, some of them, such as perfluorooctanoic acid (C_7F_{15}COOH; PFOA) and perfluorooctanesulfonate ($C_8F_{17}SO_3^-$; PFOS), have recently been detected in environmental waters, wildlife, and humans (*4–8*). Analytical studies have revealed their bioaccumulation, with longer-chain compounds being more bioaccumulative (*9–11*), and their toxicological properties are being clarified (*9–14*). Recently, PFCAs bearing C_8–C_{10} perfluoroalkyl groups, which are more bioaccumulative than

PFOA, were detected in wildlife at higher concentrations than PFOA (*15*). These anthropogenic compounds, whose high stability is ascribed to their C–F bonds, have no known natural decomposition processes. When the compounds are boiled in nitric acid or sulfuric acid, no sign of C–F bond cleavage is observed (*1, 2*). To thermally decompose them, high temperatures (~1200 °C) are required (*3*). Therefore, the development of techniques for decomposing them (as waste, especially in wastewater) to harmless species under mild conditions is desirable as a measure against stationary sources (e.g., manufacturing, processing, and waste sites) (*7, 14*). Ideally, the method would involve cleavage of the C–F bonds to form F^- ions, because F^- ions readily combine with Ca^{2+} to form environmentally harmless CaF_2.

The heterogeneous photocatalyst TiO_2 has been widely studied for the decomposition of air and water pollutants (*16, 17*). However, the reactivity of TiO_2 toward PFCAs is estimated to be very low, because $OH^\bullet$ radicals in aqueous solution are hardly reactive to PFCAs such as trifluoroacetic acid (*18, 19*). So far, heteropolyacid $H_3PW_{12}O_{40}$ has been the only photocatalyst reported to decompose PFCAs (*20–23*).

Persulfate ion ($S_2O_8^{2-}$) is not a photocatalyst. However, it is an attractive candidate to photochemically decompose PFCAs because photolysis of $S_2O_8^{2-}$ produces two sulfate radical anions ($SO_4^{\bullet-}$) with quantum efficiency of unity (eq 1), and the formed $SO_4^{\bullet-}$ can act as a strong oxidant in aqueous systems (*24, 25*):

$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^{\bullet-} \qquad (1)$$

There have been a few examples of photochemical systems using $S_2O_8^{2-}$ to help decompose environmentally harmful compounds (*26–28*). However, in such systems, $S_2O_8^{2-}$ was mostly used as an electron-trapping agent to suppress hole-electron recombination in the TiO_2 photocatalytic system; substantially, the reactivity of $SO_4^{\bullet-}$ toward substrate was ignored.

Here we show the effective photochemical decomposition of PFOA and other PFCAs bearing C_4–C_9 perfluoroalkyl groups using $S_2O_8^{2-}$. By use of this system, PFCAs were effectively decomposed to F^- and CO_2, and all of the initial $S_2O_8^{2-}$ was transformed to SO_4^{2-}, for which there is a well-established waste treatment process. Finally, we applied this method to the decomposition of perfluorononanoic acid (C_8F_{17}COOH; PFNA) contained in a floor wax solution as an example of wastewater treatment.

Experimental Section

Materials. Potassium persulfate (>99.0%) was purchased from Wako Pure Chemical Industries (Osaka, Japan) and used as received. Trifluoroacetic acid (CF_3COOH, >99.0%), pentafluoropropionic acid (C_2F_5COOH, >98%), heptafluorobutyric acid (C_3F_7COOH, >99%), nonafluoropentanoic acid (C_4F_9COOH, >98%), undecafluorohexanoic acid (C_5F_{11}COOH, >98%), and PFNA (>95%) were purchased from Tokyo Kasei Kogyo Co. (Tokyo, Japan). Tridecafluoroheptanoic acid (C_6F_{13}COOH, >96%) and PFOA (>95%) were obtained from Wako Pure Chemical Industries.

Photochemical Procedures. A cylindrical pressure-resistant Inconel reactor (176-mL volume, 5.9-cm i.d.; Nitto Koatsu Co., Tsukuba, Japan) equipped with a sapphire window (4.0-cm i.d.) was used. The inner wall of the reactor was coated with poly(tetrafluoroethylene). A gold vessel (105 mL, 5.5-cm i.d.), which is stable to highly acidic solutions, was introduced into the reactor. In a typical run, an acidic (pH 3.0–3.1) aqueous solution (22 mL) containing PFOA

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(29.6 μmol; 1.35 mM) and $K_2S_2O_8$ (0.14–1.10 mmol; 6.4–50.0 mM) was poured into the gold vessel. The initial PFOA concentration was in the concentration range present in untreated wastewater after an emulsifying process in fluoropolymer manufacture. After the reactor was bubbled and then pressurized to 0.48 MPa with oxygen gas, the solution was irradiated with UV–visible light from a xenon–mercury lamp (200 W, L20001-01L, San-Ei Electric Co., Osaka, Japan). For the light irradiation, a water filter and an optical-quartz glass fiber were used. In all runs, the reaction temperature was held constant at 25 °C. After irradiation, the pressure was released, and gas was collected in a sampling bag and subjected to gas chromatography/mass spectrometry (GC/MS) and GC measurements. Gas volume was measured by an integrating flowmeter. The reaction solution was analyzed by ion chromatography, ion-exclusion chromatography, high-performance liquid chromatography (HPLC), and electrospray ionization (ESI) mass spectrometry.

Analytical Procedures. An ion-chromatography system (IC-2001, Tosoh Corp., Tokyo, Japan) consisting of an automatic sample injector (30-μL injection volume), a degasser, a pump, a guard column (TSKguard column Super IC-A, 4.6-mm i.d., 1.0-cm length; Tosoh Corp.), a separation column (TSKgel Super IC-Anion, 4.6-mm i.d., 15-cm length), a column oven (40 °C), and a conductivity detector with a suppressor device was used to measure the F^- and SO_4^{2-} concentrations. The mobile phase was an aqueous solution containing $Na_2B_4O_7$ (6 mM), H_3BO_3 (15 mM), and $NaHCO_3$ (0.2 mM), and the flow rate was 0.8 mL min^{-1}. The limits of detection (LODs), which were calculated from a signal-to-noise (S/N) ratio of 3, were 0.74 and 2.62 μg L^{-1} for F^- and SO_4^{2-}, respectively.

An ion-exclusion chromatograph system consisting of a guard column (TSKgel OApak-P, 7.8-mm i.d., 1.0-cm length; Tosoh Corp.), a separation column (TSKgel OApak-A, 7.8-mm i.d., 30-cm length; Tosoh Corp.), a pump, a column oven (40 °C), and a conductivity detector was used to measure the concentrations of short-chain PFCAs (CF_3COOH to C_3F_7-COOH). The mobile phase was phthalic acid (10 mM) with a flow rate of 0.6 mL min^{-1}, and typical sample injection volume was 5 μL. The LODs (S/N = 3) (injected at 5 μL) were 0.27, 0.28, and 0.81 mg L^{-1} for CF_3COOH, C_2F_5COOH, and C_3F_7COOH, respectively.

The concentrations of longer-chain PFCAs (C_4F_9COOH to PFNA) were measured by an HPLC system with conductometric detection (IC-2001, Tosoh Corp.); the column was a Tosoh TSKgel Super-ODS (4.6-mm i.d., 10-cm length × 2), and the mobile phase was a mixture of methanol and aqueous NaH_2PO_4 (20 mM, adjusted to pH 3.0 with H_3PO_4) at several mixing ratios with a flow rate of 0.4 mL min^{-1}. When the sample injection volume was 30 μL, the LODs (milligrams per liter, S/N = 3) were as follows: 0.30 and 0.63 for C_4F_9-COOH and $C_5F_{11}COOH$ [mobile phase 55:45 (v/v) methanol/aqueous NaH_2PO_4]; 0.18, 0.15, 0.63, and 0.57 for $C_5F_{11}COOH$, $C_6F_{13}COOH$, PFOA, and PFNA [65:35 (v/v) methanol/aqueous NaH_2PO_4]; and 0.14, 0.20, and 0.33 for $C_6F_{13}COOH$, PFOA, and PFNA [70:30 (v/v) methanol/aqueous NaH_2PO_4], respectively. Details of the HPLC method are described elsewhere (29).

ESI mass spectrometry was used to identify the products in the reaction solution. The system used (Kansai University) was a triple-stage quadrupole mass spectrometer (TSQ700, Finnigan MAT, San Jose, CA). Analyses were carried out in negative ion mode. The electrospray potential was −4.5 kV against the counter electrode of a heated capillary. The capillary was used to aid desolvation of electrosprayed droplets. Ions entered the vacuum system through a skimmer cone. The cone voltage was 20 V. The capillary temperature was set to 150 °C, because the loss of CO_2 from $C_7F_{15}COO^-$ was markedly observed at higher temperatures such as 250

°C. Reaction samples were diluted with acetonitrile (1000-fold by volume) and were electrosprayed at a flow rate of 10 μL min^{-1}.

A GC/MS system consisting of a gas chromatograph (HP5890, Hewlett-Packard, Wilmington, DE) with a column (Poraplot Q, 0.32-mm i.d., 25-m length, Chrompack, Bergen op Zoom, The Netherlands), a mass spectrometer (HP 5972A), and a workstation (HP G1034CJ) was used to identify the products in the gas phase. The carrier gas was He. The oven temperature was held constant at 30 °C. The sample gas (30 μL) was introduced into the GC/MS system in splitless mode. The injector temperature was held constant at 120 °C, and the electron impact (EI) source was operated at 70 eV.

Quantification of CO_2 was carried out by a GC system (GC 323, GL Sciences, Tokyo, Japan) with an active carbon column (60/80 mesh, 2.17-mm i.d., 2-m length, 110 °C) and a thermal conductivity detector. The sample injection mode was splitless, and the injection volume was 0.4 mL. The LOD (S/N = 3) for CO_2 was 94.1 ppmv.

Quantification of PFNA in floor wax was performed by HPLC with conductometric detection and LC/MS/MS (MS/MS = electrospray/tandem mass spectrometry). Conditions for LC/MS/MS were identical with that reported elsewhere (29), except for the ammonium acetate (2 mM)/methanol mobile-phase gradient: 10% methanol, increased to 30% at 0.1 min, 75% at 7 min, and 100% at 10 min, maintained until 12 min, and returned to the original conditions at 20 min. PFNA was determined by monitoring product ion of m/z 419 from primary ion m/z 463.

Wax Sample Treatment. The decomposition of PFNA contained in floor wax solution was examined as an example of PFCA decomposition in wastewater. The colloidal white-colored wax contained not only PFNA but also many other compounds and sediments; therefore, solid-phase extraction by InertSep RP-1 cartridges (250 mg/6 mL; GL Sciences, Tokyo, Japan) was performed to clean up and concentrate PFNA prior to HPLC analysis.

To quantify PFNA in the wax itself, the wax (0.50 g) was diluted to 50 mL with water. The cartridges were preconditioned with methanol (10 mL), followed by water (10 mL). After preconditioning, the aqueous wax solution was passed through the cartridge at a rate of 1 mL min^{-1}. The PFNA was then eluted from the cartridge with methanol (5 mL). The eluted solution was concentrated under argon to 1 mL and then subjected to HPLC with conductometric detection. In this manner, the PFNA concentration in the wax (before dilution) was determined to be 75.4 mg L^{-1}. The above procedure was also taken for aqueous solution (0.50 mL) of PFNA (112 mg L^{-1}) instead of the wax, and good recovery was obtained (101%, n = 4, relative standard deviation = 3.7%). Quantification of PFNA in the wax was also performed by LC/MS/MS and use of different solid-phase extraction media (Oasis HLB cartridges, 200 mg/6 mL; Waters Corp., Milford, MA), and a similar value, 74.5 mg L^{-1}, was obtained.

To decompose PFNA in the wax photochemically, an aqueous solution (22 mL) containing the wax (0.44 g) and $K_2S_2O_8$ (1.10 mmol; 50.0 mM) was introduced into the reactor. The concentration of PFNA in the reaction solution was 1.51 mg L^{-1} (3.25 μM). Then the solution was irradiated for 12 h in the same manner as described above. After irradiation, the precipitate that formed was removed by centrifugation (3000 rpm, 10 min). A portion of the liquid phase (15 mL) was diluted to 50 mL with water. The diluted solution was passed through the preconditioned InertSep RP-1 cartridge, eluted by methanol, and concentrated to 1 mL in the manner described above. Finally, the concentrated solution was analyzed by HPLC, and PFNA was quantified.
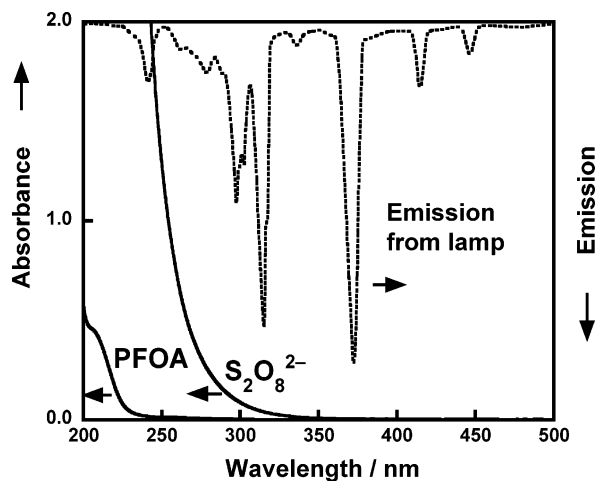
FIGURE 1. Wavelength distribution for absorption of PFOA (1.35 mM in water) and of $S_2O_8^{2-}$ (50.0 mM in water) and emission from the xenon–mercury lamp. The concentrations of PFOA and $S_2O_8^{2-}$ were the same as in subsequent photochemical reactions (Figure 2). The path length for measurement of the absorption spectra was 1.0 cm.
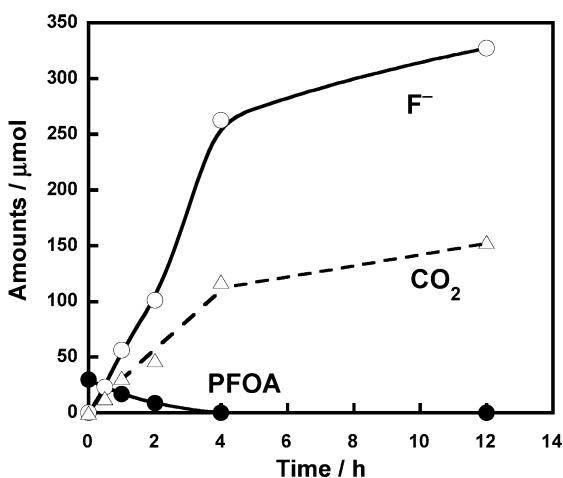

FIGURE 2. Irradiation-time dependence of PFOA decomposition with $S_2O_8^{2-}$: detected molar amounts of PFOA, CO_2, and F^-. An aqueous solution (22 mL) containing $S_2O_8^{2-}$ (1.10 mmol; 50.0 mM) and PFOA (29.6 μmol; 1.35 mM) was irradiated with a xenon–mercury lamp under oxygen (0.48 MPa).

Results and Discussion

Decomposition of PFOA. In our reaction conditions, an aqueous solution containing PFOA and $S_2O_8^{2-}$ was irradiated with UV–visible light from a xenon–mercury lamp through a water filter. Figure 1 shows wavelength distribution for absorption of PFOA and of $S_2O_8^{2-}$ and emission from the lamp. Under these conditions, the lamp emits mainly 220–460-nm light. Since PFOA absorbs from the deep-UV region to 220 nm and has a weak, broad absorption to ~270 nm, whereas $S_2O_8^{2-}$ absorbs from the deep-UV region to 350 nm, we observed $S_2O_8^{2-}$ to be the dominant absorbing species in our reaction conditions.

We determined the irradiation-time dependence of the photoreaction using a 37-fold molar excess of $S_2O_8^{2-}$ over PFOA (Figure 2). The amount of PFOA decreased with irradiation, and F^- and CO_2 were found as products in the liquid and gas phases, respectively. After 4 h of irradiation, PFOA disappeared on the HPLC chromatogram (LOD was 0.20 mg L^{-1} = 0.48 μM; 1.06×10^{-8} mol in the 22 mL reaction solution). On the other hand, the production of F^- and CO_2 still continued after 4 h, indicating that species other than
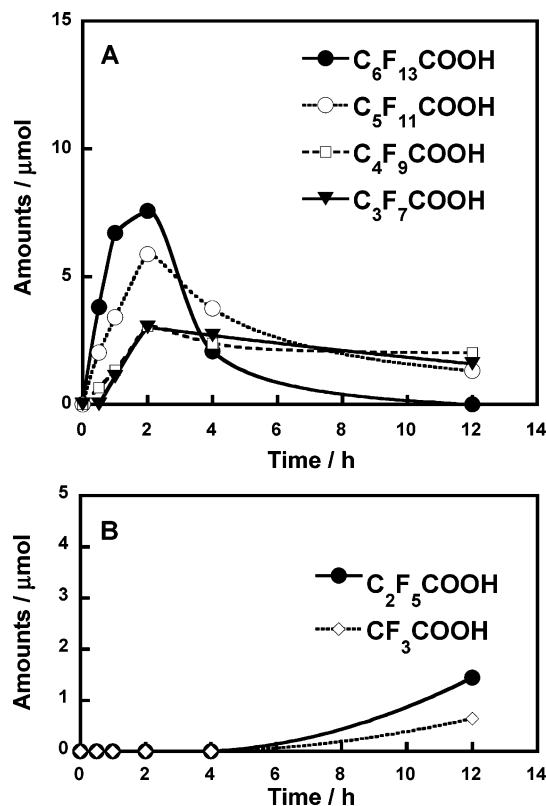

FIGURE 3. Irradiation-time dependence of PFOA decomposition with $S_2O_8^{2-}$: detected molar amounts of PFCAs bearing (A) C_3–C_6 and (B) C_1–C_2 perfluoroalkyl groups. Reaction conditions were the same as in Figure 2.

PFOA continued to produce F^- and CO_2. After 12 h of irradiation, the yield of F^- [(moles of F^- formed)/(moles of initial PFOA $\times$ 15)] reached 73.8%. We detected not only F^- ions but also small amounts of shorter-chain PFCAs such as the one CF_2 unit-shortened PFCA ($C_6F_{13}COOH$) in the liquid phase (Figure 3A). The formation of $C_6F_{13}COOH$ was followed by more CF_2 unit-shortened species, $C_5F_{11}COOH$, C_4F_9COOH, and C_3F_7COOH. The amounts of these shorter-chain PFCAs reached maxima at 2 h. The total recovery of fluorine (i.e., molar ratio of total fluorine content in F^- and short-chain PFCAs formed and in unchanged PFOA to that in the PFOA before irradiation) was 99.1% at 2 h of irradiation. Likewise, total carbon recovery (i.e., molar ratio of total carbon content in CO_2 and short-chain PFCAs formed and in unchanged PFOA to that in the PFOA before irradiation) was 97.7%. Hence, the initial fluorine and carbon in PFOA can be almost completely accounted for by unchanged PFOA, F^-, CO_2, and short-chain PFCAs formed.

The formation of shorter-chain PFCAs was also confirmed by ESI mass spectral measurements, showing peaks corresponding to $[C_6F_{13}COO]^-$ (m/z 363) and $[C_5F_{11}COO]^-$ (m/z 313) (Figure 4). Further irradiation decreased the amounts of these shorter-chain PFCAs and increased formation of further shorter PFCAs (C_2F_5COOH and CF_3COOH; Figure 3B). These observations indicate that short-chain PFCAs form in a stepwise manner from longer-chain PFCAs.

GC/MS analysis of the gas phase indicated that this system produced no environmentally undesirable species such as CF_4 and CF_3H, which are stable species that have high global-warming potentials (at least 3900 and 9400 times as high as CO_2, respectively; 30). In contrast, CF_4 is often observed in the decomposition of perfluorinated compounds by extremely high energy techniques such as electron beam irradiation (31).
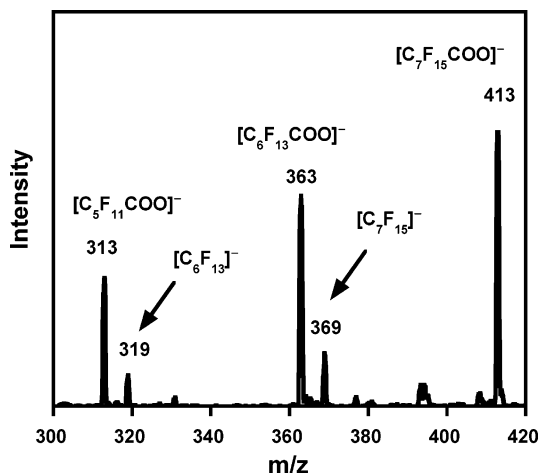
FIGURE 4. Typical ESI mass spectrum of the photochemical reaction solution. An aqueous solution (22 mL) containing $S_2O_8^{2-}$ (1.10 mmol; 50.0 mM) and PFOA (29.6 μmol; 1.35 mM) was irradiated with a xenon−mercury lamp under oxygen (0.48 MPa) for 2 h. The anions $[C_7F_{15}]^-$ and $[C_6F_{13}]^-$ were fragment species derived from $[C_7F_{15}COO]^-$ and $[C_6F_{13}COO]^-$, respectively.

TABLE 1. Reaction Yields for Various Combinations between $S_2O_8^{2-}$, Light Irradiation, and Reaction Atmosphere[a]

entry	$S_2O_8^{2-}$	light irradiation	atmos- phere[b]	PFOA decomposition (%)	F⁻ yield[c] (%)	CO_2 yield[d] (%)
1	present[e]	present	O_2	100	59.1	49.8
2	present[e]	none	O_2	0	0	0
3	none	present	O_2	16.8	9.0	6.6
4	present[e]	present	Ar	96.6	52.3	43.3

[a] Reaction time was 4 h, initial amount of PFOA was 29.6 μmol, and the reaction solution volume was 22 mL. [b] Pressure was 0.48 MPa. [c] F⁻ yield = [(moles of F⁻ formed)/(moles of initial PFOA × 15)] × 100. [d] CO_2 yield = [(moles of CO_2 formed)/(moles of initial PFOA × 8)] × 100. [e] Amount of initial $S_2O_8^{2-}$ was 1.10 mmol.

We determined the reaction yields for various combinations of $S_2O_8^{2-}$, light irradiation, and reaction atmosphere (Table 1). In the absence of light irradiation, no reaction occurred (entry 2). When light was irradiated in the absence of $S_2O_8^{2-}$ (direct photolysis), PFOA decomposition, F⁻ formation, and CO_2 formation all markedly decreased (entry 3) compared to those in the presence of $S_2O_8^{2-}$ (entry 1). This observation clearly indicates that $SO_4^{\bullet-}$ reacts with PFOA:

$$SO_4^{\bullet-} + PFOA \rightarrow SO_4^{2-} + PFOA^{\bullet+} \qquad (2)$$
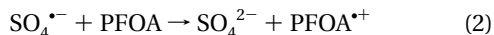
On the other hand, when the reaction was carried out in the presence of $S_2O_8^{2-}$ under argon (entry 4), the reaction yields of PFOA decomposition, F⁻ formation, and CO_2 formation were similar to those of reactions under oxygen (entry 1); also, no significant differences were observed in the formation of shorter-chain PFCAs (Table 2). Thus, the oxygen gas in the reaction system does not play a significant role in the PFOA decomposition system.

Effect of $S_2O_8^{2-}$ Concentration. The amount of PFOA decreased linearly with respect to irradiation time during a short initial period after irradiation started. We used the initial PFOA decomposition rate, the slope taken from this period, as a measure for the photochemical reactivity. We measured the effect of initial $S_2O_8^{2-}$ amount on the initial PFOA decomposition rate (Figure 5). The photochemical reactivity increased when the initial amount of $S_2O_8^{2-}$ was increased. When 0.59 mmol of $S_2O_8^{2-}$ (26.8 mM) was used, the decomposition rate was 11 times that for direct photolysis.

TABLE 2. Effect of Reaction Atmosphere on Photochemical Decomposition of PFOA with $S_2O_8^{2-}$: Detection of Short-Chain PFCAs as Minor Products[a]

entry	atmos- phere[b]	$C_6F_{13}COOH$ (μmol)	$C_5F_{11}COOH$ (μmol)	C_4F_9COOH (μmol)	C_3F_7COOH (μmol)
1	O_2	2.07	3.75	2.39	2.70
2	Ar	2.42	3.86	3.37	3.48

[a] Reaction time was 4 h. Initial amounts of PFOA and $S_2O_8^{2-}$ were 29.6 μmol and 1.10 mmol, respectively. Reaction solution volume was 22 mL. [b] Gas pressure was 0.48 MPa.
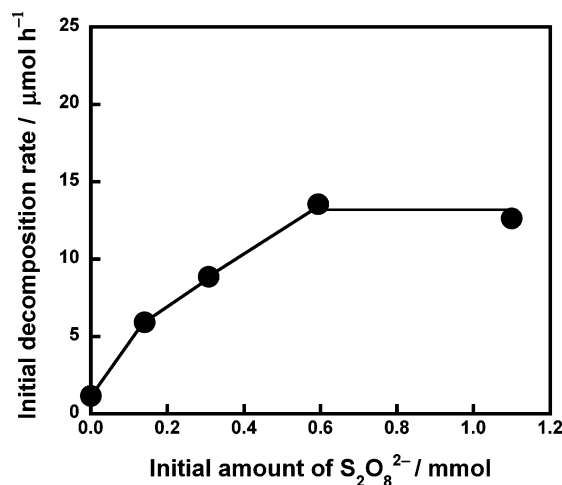

FIGURE 5. Effect of initial amount of $S_2O_8^{2-}$ on the initial decomposition rate of PFOA. An aqueous solution (22 mL) containing $S_2O_8^{2-}$ (0−1.10 mmol; 0−50.0 mM) and PFOA (29.6 μmol; 1.35 mM) was irradiated with a xenon−mercury lamp under oxygen (0.48 MPa). The initial decomposition rate of PFOA was taken from the initial period of irradiation when the decomposition amount of PFOA increased linearly with respect to time.

However, further increase in the initial $S_2O_8^{2-}$ resulted in saturation, that is, no further increase in the PFOA decomposition rate. When the initial amount of $S_2O_8^{2-}$ was 0.59 mmol (26.8 mM), the transmittance of the initial reaction solution in the reactor at 254 nm (a maximum emission line of the lamp) was 35.8%, as calculated for an optical path of 0.9 cm in the reactor. Therefore, the saturation of the PFOA decomposition rate observed above 0.59 mmol of $S_2O_8^{2-}$ cannot be ascribed to the saturation of the light absorption ability. It was reported that $SO_4^{\bullet-}$ radical anions, produced by photolysis of $S_2O_8^{2-}$, react with $S_2O_8^{2-}$ to form SO_4^{2-} and $S_2O_8^{\bullet-}$ with a rate constant (k_3) of 5.5×10^5 M⁻¹ s⁻¹ under acidic conditions (pH 2) (32):

$$SO_4^{\bullet-} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\bullet-} \qquad (3)$$
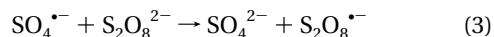
In addition, $SO_4^{\bullet-}$ radical anions react with water with a rate constant $k_4[H_2O]$ of 460 s⁻¹ (32):

$$SO_4^{\bullet} + H_2O \leftrightarrow HSO_4^- + OH^{\bullet} \leftrightarrow SO_4^{2-} + H^+ + OH^{\bullet} \quad (4)$$

For our reaction conditions, the $k_3[S_2O_8^{2-}]$ value was 1.47×10^4 s⁻¹, calculated from an initial $S_2O_8^{2-}$ amount of 0.59 mmol (26.8 mM). This value was much larger than $k_4[H_2O]$ (460 s⁻¹); therefore the reaction of $SO_4^{\bullet-}$ with water (eq 4) is negligible. Hence, the tendency of the PFOA decomposition rate to saturate at higher $S_2O_8^{2-}$ concentrations can be explained by the fact that the reaction of $SO_4^{\bullet-}$ with $S_2O_8^{2-}$ (eq 3) occurs at higher $S_2O_8^{2-}$ concentrations, resulting in saturation of $SO_4^{\bullet-}$ concentration.

TABLE 3. Photochemical Decomposition of PFCAs Bearing C_4-C_8 Perfluoroalkyl Groups[a]

entry	substrate (initial, μmol)	initial $S_2O_8^{2-}$ (mmol)	decomposed substrate (μmol) [yield, %][b]	F^- (μmol)	CO_2 (μmol)	short-chain PFCAs (μmol)
1	$C_6F_{13}COOH$ (29.3)	1.10	29.3 [100]	260	121	$C_5F_{11}COOH$ (1.96), C_4F_9COOH (2.78), C_3F_7COOH (8.69), C_2F_5COOH (4.48), CF_3COOH (2.42)
2	$C_6F_{13}COOH$ (29.7)	0	5.56 [18.7]	16.7	37.4	$C_5F_{11}COOH$ (3.00), C_4F_9COOH (1.10)
3	$C_5F_{11}COOH$ (29.4)	1.10	29.4 [100]	241	118	C_4F_9COOH (1.87), C_3F_7COOH (3.20), C_2F_5COOH (6.98), CF_3COOH (2.81)
4	$C_5F_{11}COOH$ (29.7)	0	3.55 [12.0]	7.1	20.0	C_4F_9COOH (3.06), C_3F_7COOH (1.10), C_2F_5COOH (0.27)
5	C_4F_9COOH (29.3)	1.10	28.9 [98.6]	200	98.7	C_3F_7COOH (1.87), C_2F_5COOH (3.33), CF_3COOH (3.11)
6	C_4F_9COOH (29.7)	0	4.63 [15.6]	14.7	16.0	C_3F_7COOH (3.31), C_2F_5COOH (1.40)
7[c]	PFNA (14.8)	1.10	14.8 [100]	187	104	$C_5F_{11}COOH$ (0.14), C_4F_9COOH (0.25), C_3F_7COOH (0.24), C_2F_5COOH (0.22), CF_3COOH (0.81)
8[c]	PFNA (15.0)	0	9.67 [64.5]	68.5	50.8	PFOA (3.86), $C_6F_{13}COOH$ (0.95), $C_5F_{11}COOH$ (0.52), C_4F_9COOH (0.29)

[a] An aqueous solution (22 mL) of substrate was irradiated with a xenon–mercury lamp under oxygen (0.48 MPa) for 12 h. [b] [(Moles of decomposed substrate)/(moles of initial substrate)] × 100. [c] The light intensity of the lamp was different from that for entries 1–6.
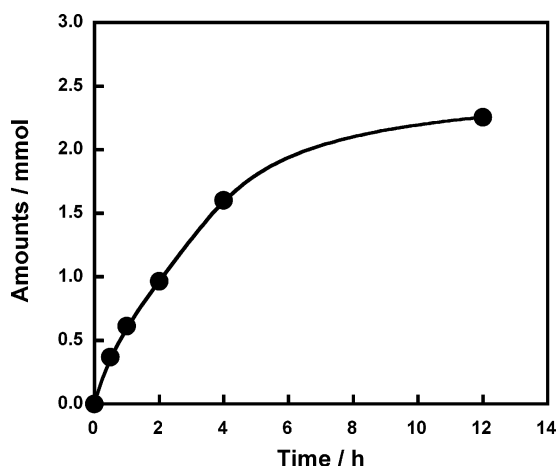

FIGURE 6. Irradiation-time dependence of the amounts of SO_4^{2-} detected during photochemical decomposition of PFOA with $S_2O_8^{2-}$. Reaction conditions were the same as in Figure 2.

In the photochemical PFOA decomposition system with heteropolyacid $H_3PW_{12}O_{40}$ (23), the PFOA decomposition rate (the initial PFOA concentration was the same as our condition) was 2.9 times that for direct photolysis. Hence, the use of $S_2O_8^{2-}$ (11 times that for direct photolysis) was more efficient, although our method is not a photocatalytic system.

Fate of Sulfur Species. In our photochemical reaction system, $SO_4^{\bullet-}$ radical anions are formed from photolysis of $S_2O_8^{2-}$ (eq 1), which then react with PFOA. In such a system, SO_4^{2-} forms by one-electron transfer from PFOA to $SO_4^{\bullet-}$ (eq 2).

The irradiation-time dependence of the amounts of SO_4^{2-} detected during photochemical decomposition of PFOA (same experimental conditions as in Figures 2 and 3) was determined (Figure 6). As expected, SO_4^{2-} accumulated in the liquid phase and the amount increased with irradiation time, while PFOA decomposition and F^- and CO_2 formation also occurred. After 12 h of irradiation, the amount of SO_4^{2-} reached 2.26 mmol. The initial amount of $S_2O_8^{2-}$ was 1.10 mmol; therefore, the recovery of sulfur content was 103%. Thus, although $S_2O_8^{2-}$ radical anions may form at higher $S_2O_8^{2-}$ concentration (eq 3), all sulfur species used in this reaction were eventually transformed into SO_4^{2-}. The fate of PFOA$^{\bullet+}$ after an electron transfer with $SO_4^{\bullet-}$ (eq 2) is not clear; however, on the basis of the reported experimental results and on data from the literature (33, 34), it is possible to propose a mechanism. The first bond to be cleaved is the C–C bond between C_7F_{15} and COOH. The C_7F_{15} radicals in

water form the thermally unstable alcohol $C_7F_{15}OH$, which undergoes HF elimination to form $C_6F_{13}COF$ (33). This acid fluoride undergoes hydrolysis (34), resulting in the formation of the one CF_2 unit-shortened species $C_6F_{13}COOH$.

Other PFCAs and Wax Solution. We applied our method to other PFCAs bearing C_4-C_8 perfluoroalkyl groups at a constant irradiation time of 12 h. The results are summarized in Table 3, together with the data for direct photolysis. In each case, F^- and shorter-chain PFCAs were detected in the liquid phase, and CO_2 was detected in the gas phase. When $S_2O_8^{2-}$ was used, the decomposition yield of each substrate reached 100% (except for C_4F_9COOH, 98.6%). The effectiveness of $S_2O_8^{2-}$ is clear for each substrate. The amount of F^- formed by the reaction with $S_2O_8^{2-}$ for each substrate bearing C_4-C_6 perfluoroalkyl groups was 14–34 times higher than that obtained by the corresponding direct photolysis at the same initial substrate concentration and light intensity (entries 1–6).

As for PFNA decomposition in the wax solution, the concentration of PFNA in the reaction solution was 1.51 mg L^{-1} (3.25 μM) before irradiation. After 12 h of irradiation in the presence of $S_2O_8^{2-}$ (50.0 mM), the PFNA concentration in the reaction solution was determined to be 89 μg L^{-1} (0.19 μM) by HPLC with sample concentration by solid-phase extraction. Therefore, almost all (94%) of the initial PFNA was effectively removed from the reaction solution, despite the presence of other chemical species (resin, etc.) in the initial solution.

Our system is a simple photochemical system that allows effective decomposition of PFOA and other PFCAs in water, based on the high reactivity of $SO_4^{\bullet-}$ radical anions toward PFCAs. The $SO_4^{\bullet-}$ radical anions exist in aqueous-phase atmosphere such as in cloud droplets (35). Therefore, the high reactivity of $SO_4^{\bullet-}$ toward PFCAs in water may indicate the possibility for $SO_4^{\bullet-}$ serving as a tropospheric sink for PFCAs [gaseous reaction with $OH^{\bullet}$ radicals is a minor fate (36)]. Of course, such possibility should be evaluated by the reaction rate and tropospheric concentration levels of $SO_4^{\bullet-}$ and PFCAs.

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