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Efficient mineralization of hydroperfluorocarboxylic acids with persulfate in hot water

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ABSTRACT

The persulfate ($S_2O_8{}^{2-}$)-induced decomposition of hydroperfluorocarboxylic acids (H-PFCAs), that is, $HC_nF_{2n}COOH$ ($n = 4$, 6, and 8), in hot water was investigated, and the results were compared with the results for perfluorocarboxylic acids (PFCAs). This is the first report on the use of hot water to decompose H-PFCAs, which are being developed as alternative surfactants to environmentally persistent and bioaccumulative PFCAs. Although H-PFCAs showed almost no decomposition in hot water at 80 °C in the absence of $S_2O_8{}^{2-}$, the addition of $S_2O_8{}^{2-}$ to the reaction solution led to efficient mineralization to F^- ions, with F^- yields [(moles of F^-)/(moles of fluorine in initial H-PFCAs)] of 96.7–98.2% after 6 h of treatment. The decomposition of H-PFCAs induced by $S_2O_8{}^{2-}$ also proceeded even at 60 °C, at which the initial decomposition rates were 7.1–12.7 times those for the corresponding PFCAs. The reaction mechanism can be explained by nucleophilic substitution by $SO_4{}^{\bullet -}$ at the carbon atom attached to the ω-H atom of the H-PFCAs, followed by formation of perfluorodicarboxylic acids ($HOOCC_{n-1}F_{2n-2}COOH$), which react with $SO_4{}^{\bullet -}$ to give shorter-chain perfluorodicarboxylic acids; this process eventually resulted in complete mineralization to F^- ions.

1. Introduction

Perfluorocarboxylic acids ($C_nF_{2n+1}COOH$, PFCAs) such as perfluorooctanoic acid ($C_7F_{15}COOH$, PFOA) have recently received much attention because they are ubiquitous environmental contaminants [1–3]. These chemicals have been used as products and as raw materials for surfactants, surface treatment agents, and so on because of their high surface-active effect, high thermal and chemical stability, and high light transparency [2]. After it became clear that these chemicals persist and bioaccumulate in the environment, a provisional health advisory value for PFOA was issued [4], and efforts to eliminate these chemicals from products and facility emissions are proceeding [5]. In parallel with the effort to eliminate PFOA and other bioaccumulative PFCAs, there have been efforts to develop alternatives to these chemicals.

Hydroperfluorocarboxylic acids (H-PFCAs; $HC_nF_{2n}COOH$), ω-hydroperfluorocarboxylic acids in which a fluorine atom of the terminal trifluoromethyl group in PFCAs has been replaced by a hydrogen atom, are among the alternatives being developed [6]. H-PFCAs are likely to decompose more easily than corresponding PFCAs because the former have a carbon–hydrogen bond. However, the decomposition of H-PFCAs has not been reported; no one has confirmed that these chemicals do in fact decompose more easily than PFCAs. Decomposition of these chemicals to F^- ions would be desirable because there is a well-established waste-treatment process based on reaction with Ca^{2+} to form the environmentally harmless CaF_2, which is a raw material for hydrofluoric acid, which faces an increasing global demand. Therefore, the development of decomposition technology for these chemicals at sites where they are emitted in large quantities is important because such technology would not only reduce the environmental impact of the fluorochemicals but also contribute to the recycling of a fluorine resource.

PFCAs and related chemicals are generally stable: conventional methods for wastewater treatment, such as the use of Fenton's reagent ($Fe^{2+} + H_2O_2$) and H_2O_2 + UV light irradiation, are not applicable, because aqueous OH radicals are only slightly reactive toward PFCAs [7–9].

We previously reported that PFCAs such as PFOA are efficiently decomposed to F^- ions in hot water at 80 °C in the presence of persulfate ($S_2O_8{}^{2-}$) [10]: the thermolysis of $S_2O_8{}^{2-}$ produces sulfate radical anions ($SO_4{}^{\bullet -}$), which can act as strong oxidants to decompose PFCAs. In this reaction system, the relatively low temperature of 80 °C is essential; a higher temperature, such as 150 °C, is unsuitable because most of the $SO_4{}^{\bullet -}$ is consumed by reaction with hot water. We also reported that PFCAs are efficiently decomposed to F^- ions by $SO_4{}^{\bullet -}$ produced by UV light irradiation of $S_2O_8{}^{2-}$ [11]. Recently, $SO_4{}^{\bullet -}$ was applied to the decomposition of polychlori-

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nated biphenyls [12] and chlorophenols [13,14], at which the $SO_4^{\bullet -}$ was obtained from reactions of $S_2O_8^{2-}$ or peroxymonosulfate with metal ions.

Herein we report the decomposition of typical H-PFCAs, that is, $HC_nF_{2n}COOH$ ($n = 4, 6, 8$), with $S_2O_8^{2-}$ in hot water at low temperatures (60 and 80 °C). The decomposition efficiency and the decomposition mechanisms of the H-PFCAs are compared with those of the corresponding PFCAs.

2. Experimental

2.1. Materials

Potassium persulfate (>99.0%) was purchased from Wako Pure Chemical Industries (Osaka, Japan) and used as received. 5H-Perfluoropentanoic acid (HC_4F_8COOH, >97%), 7H-perfluoroheptanoic acid ($HC_6F_{12}COOH$, >98%), 9H-perfluorononanoic acid ($HC_8F_{16}COOH$, >98%), perfluoroazelaic acid ($HOOCC_7F_{14}COOH$, >96%), and dodecafluorosuberic acid ($HOOCC_6F_{12}COOH$, >98%) were obtained from SynQuest Laboratories (Alachua, FL, USA). Heptafluorobutyric acid (C_3F_7COOH, >99%), nonafluoropentanoic acid (C_4F_9COOH, >98%), undecafluorohexanoic acid ($C_5F_{11}COOH$, >98%), and perfluorononanoic acid ($C_8F_{17}COOH$, >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.

2.2. Reaction procedures

A stainless steel pressure-resistant reactor (35.1 mL volume) equipped with a thermocouple and a stainless steel screw cap was used. The screw cap was connected to a pressure gauge for measuring the pressure in the reactor and to a sampling port for analyzing gas products. A gold vessel (24.6 mL, 2.8 cm i.d.) was fitted into the reactor to prevent contamination from the reactor material. In a typical run, an aqueous (Milli-Q) solution (10 mL) of an H-PFCA or a PFCA (3.71–3.92 μmol, 371–392 μM) and $K_2S_2O_8$ (50 μmol–0.50 mmol, 5.0–50.0 mM) was introduced into the gold vessel, and the reactor was pressurized to 0.65 MPa with synthetic air and sealed. The reactor was placed in an oven, and the reactor temperature was raised to the desired reaction temperature (60 or 80 °C) and then held constant for a specified time (e.g., 6 h), after which the reactor was quickly cooled to room temperature using ice water. Control reactions were performed in the absence of $K_2S_2O_8$. The gas phase was subjected to gas chromatography/mass spectrometry (GC/MS) and GC. The aqueous phase was subjected to ion-chromatography, ion-exclusion chromatography, high-performance liquid chromatography (HPLC), electrospray ionization (ESI) mass spectrometry, and LC/MS.

We also used Fenton's reagent to attempt to decompose an H-PFCA: an aqueous solution (22 mL; initial pH, 2.3) containing $HC_6F_{12}COOH$ (123 μmol, 5.58 mM), H_2O_2 (1.0 M), and $FeSO_4{\cdot}7H_2O$ (4.92 mM) was mixed in an oxygen atmosphere for 17 h in the dark at room temperature. After the reaction, the gas and the aqueous phases were analyzed.

2.3. Analysis

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, Tosoh Corp.), 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}.

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 determine whether H-PFCAs or PFCAs with short ($<C_4$) chains were formed in the aqueous phase. The mobile phase was phthalic acid (10 mM) at a flow rate of 0.6 mL min^{-1}, and a typical sample injection volume was 5 μL.

The reaction substrates were quantified by HPLC with conductometric detection; 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 (45–65 vol.% of methanol), and the separation column was a Tosoh TSKgel Super ODS column (4.6 mm i.d., 10 cm length × 2). When the sample injection volume was 30 μL and the mobile phase was a mixture of methanol/aqueous NaH_2PO_4 (55:45, v/v), the limits of detection (mg L^{-1}), which were calculated from a signal-to-noise ratio of 3, were 1.54, 0.57, and 0.22 for $HC_8F_{16}COOH$, $HC_6F_{12}COOH$, and HC_4F_8COOH, respectively.

An ESI-mass spectrometry system (LCMS-2010 EV, Shimadzu, Kyoto, Japan) was used to identify the intermediates in the aqueous phase. Analyses were carried out in negative ion mode, and the electrospray probe voltage was 4.50 kV. Reaction samples were delivered to the electrospray probe using acetonitrile as a mobile phase at a flow rate of 0.2 mL min^{-1}. LC/MS measurements were also carried out: a separation column (TSKgel ODS-80TSQA, Tosoh Corp.) was added to the above ESI-mass spectrometry system, and the mobile phase was a 50:50 (v/v) mixture of methanol and aqueous CH_3COONH_4 (1 mM, adjusted pH 4.0 with acetic acid).

The GC/MS system consisted of a gas chromatograph (HP5890, Hewlett-Packard, Wilmington, DE, USA) with a Poraplot Q column (0.32-mm i.d., 25-m length; Chrompack, Bergen op Zoom, The Netherlands), a mass spectrometer (HP 5972A), and a workstation (HP G1034CJ). The carrier gas was He, and the electron impact source was operated at 70 eV. The analyses were conducted in full-scan mode (m/z 1.2–200) to survey the products. A GC system (GC 323, GL Sciences, Tokyo, Japan) consisting of an injector (150 °C), a column oven (50 °C), and a thermal conductivity detector (130 °C), was also used: the column was an active carbon column (60/80 mesh, 2.17-mm i.d., 2-m length), and the carrier gas was argon.

3. Results and discussion

3.1. Persulfate-induced decomposition of H-PFCAs at 80 °C

The time course of the reaction of aqueous $HC_8F_{16}COOH$ and $S_2O_8^{2-}$ (130 molar excess relative to $HC_8F_{16}COOH$) at 80 °C is shown in Fig. 1. $HC_8F_{16}COOH$ rapidly disappeared from the HPLC chromatogram within 0.5 h of the treatment, and F^- and CO_2 were the main products in the aqueous and gas phases, respectively. After $HC_8F_{16}COOH$ disappeared, the amounts of F^- and CO_2 continued to increase, which indicates that reaction intermediates decomposed to F^- and CO_2 during this period. After 6 h, the F^- amount reached 61.6 μmol, which corresponds to a F^- yield [(moles of F^- formed)/(moles of fluorine in initial $HC_8F_{16}COOH$, i.e., moles of initial $HC_8F_{16}COOH \times 16$)] of 98.2% (Table 1, entry 1). This result clearly indicates that the fluorine content in $HC_8F_{16}COOH$ was successfully mineralized.

In the absence of $S_2O_8^{2-}$, virtually no reaction occurred: 97.0% of the initial $HC_8F_{16}COOH$ remained in the aqueous phase, and the F^- yield was only 0.02% after 6 h (Table 1, entry 2). These results clearly indicate that $SO_4^{\bullet -}$ acted as an oxidant to decompose $HC_8F_{16}COOH$.

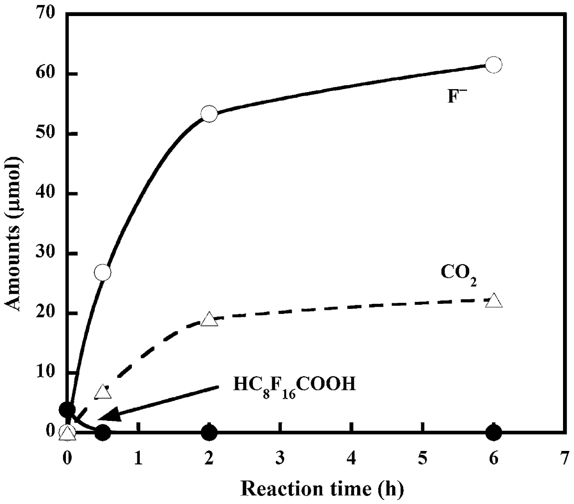

Fig. 1. Time course of $HC_8F_{16}COOH$ decomposition in hot water (80 °C) containing $S_2O_8^{2-}$: detected molar amounts of $HC_8F_{16}COOH$, F^-, and CO_2. An aqueous solution (10 mL) containing $HC_8F_{16}COOH$ (3.92 μmol, 392 μM) and $S_2O_8^{2-}$ (0.50 mmol, 50.0 mM) was introduced in the reactor, the reactor was pressurized with synthetic air (0.65 MPa), and the reactor temperature was raised to 80 °C and held constant for 0.5–6 h.

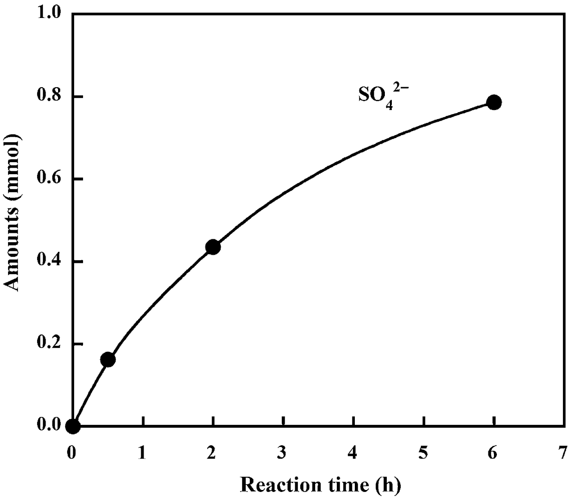

Fig. 2. Reaction-time dependence of the amounts of SO_4^{2-} detected during the decomposition of $HC_8F_{16}COOH$ with $S_2O_8^{2-}$. Reaction conditions were the same as in Fig. 1.

In accordance with the oxidative decomposition of $HC_8F_{16}COOH$, $SO_4^{\bullet-}$ is expected to be reduced to SO_4^{2-}. Consistent with this expectation, SO_4^{2-} accumulated in the aqueous phase, and the amount increased with reaction time (Fig. 2) while the decomposition of $HC_8F_{16}COOH$ and the formation of F^- and CO_2 proceeded efficiently (Fig. 1). After 6 h, the amount of SO_4^{2-} in the aqueous phase was 0.79 mmol. The initial amount of $S_2O_8^{2-}$ was 0.50 mmol; therefore, 79% of the sulfur content in initial $S_2O_8^{2-}$ was transformed to SO_4^{2-} during this period.

We carried out the decomposition reaction with the other H-PFCAs, that is, $HC_6F_{12}COOH$ and HC_4F_8COOH, at a constant reaction time of 6 h at 80 °C. The results are summarized in Table 1 (entries 3–6) together with the data obtained in the absence of $S_2O_8^{2-}$. Without $S_2O_8^{2-}$, almost all (98.0–99.7%) of the substrates remained in the aqueous phase, and there was no formation of F^- and CO_2 (entries 4 and 6). In contrast, in the presence of $S_2O_8^{2-}$, no substrates remained in the aqueous phase, and the F^- yields reached 97.8% and 96.7% for $HC_6F_{12}COOH$ and HC_4F_8COOH, respectively (entries 3 and 5). Therefore, $S_2O_8^{2-}$ led to efficient mineralization of these H-PFCAs.

While the reactions of $HC_nF_{2n}COOH$ (n = 4, 6, and 8) with $S_2O_8^{2-}$ (0.50 mmol; 50.0 mM) were proceeded, the pH values were decreased from 3.3–3.4 to 1.5–1.6 after 6 h.

3.2. Decomposition of H-PFCAs at 60 °C

In the above reactions, samples were heated at 80 °C in the presence of a large excess of $S_2O_8^{2-}$ (50.0 mM; 130 molar excess relative to the substrates). Under these conditions, the reactions were so rapid that the H-PFCAs disappeared from the aqueous phase within 0.5 h. To investigate the decomposition of H-PFCAs in the presence of $S_2O_8^{2-}$ in detail, we carried out the reactions under milder conditions (reaction temperature, 60 °C; initial amount of $S_2O_8^{2-}$, 50 μmol; concentration, 5.0 mM). The time course of the reaction of aqueous $HC_8F_{16}COOH$ at 60 °C is shown in Fig. 3. Under these conditions, the decomposition of $HC_8F_{16}COOH$ and simultaneous formation of F^- and CO_2 were observed. In the absence of $S_2O_8^{2-}$, $HC_8F_{16}COOH$ did not decompose, whereas when $S_2O_8^{2-}$ was present, the amount of $HC_8F_{16}COOH$ decreased linearly with time, and the decrease in the substrate amount was accompanied by the formation of F^- and CO_2 (Fig. 3). We used the initial rate of decomposition of $HC_8F_{16}COOH$, the slope taken from this period, as a measure of the reactivity, and the initial rates for various H-PFCAs,

Table 1
Decomposition of H-PFCAs and PFCAs in hot water (80 °C) in the presence or absence of $S_2O_8^{2-}$ [a].

Entry	Substrate [initial amount (μmol)]	Initial $S_2O_8^{2-}$ (mmol)	Remaining substrate (μmol) [%][b]	F^- (μmol) [yield (%)][c]	CO_2 (μmol) [yield (%)][d]
1	$HC_8F_{16}COOH$ [3.92]	0.50	n.d.[e] [0]	61.6 ± 0.2[f] [98.2]	22.3 ± 0.3[f] [63.2]
2	$HC_8F_{16}COOH$ [3.70]	0	3.59 [97.0]	0.01 [0.02]	0.38 [1.1]
3	$HC_6F_{12}COOH$ [3.86]	0.50	n.d. [0]	45.3 [97.8]	18.0 [66.6]
4	$HC_6F_{12}COOH$ [3.86]	0	3.78 [98.0]	n.d. [0]	n.d. [0]
5	HC_4F_8COOH [3.75]	0.50	n.d. [0]	29.0 [96.7]	14.1 [75.2]
6	HC_4F_8COOH [3.67]	0	3.66 [99.7]	n.d. [0]	n.d. [0]
7	$C_8F_{17}COOH$ [3.85]	0.50	n.d. [0]	48.3 [73.8]	19.0 [54.8]
8	$C_8F_{17}COOH$ [3.77]	0	3.73 [98.9]	0.03 [0.05]	0.68 [2.00]
9	$C_6F_{13}COOH$ [3.74]	0.50	n.d. [0]	36.8 [75.7]	20.4 [77.9]
10	$C_6F_{13}COOH$ [3.74]	0	3.68 [98.4]	n.d. [0]	n.d. [0]
11	C_4F_9COOH [3.74]	0.50	n.d. [0]	30.2 [89.7]	15.4 [82.4]
12	C_4F_9COOH [3.74]	0	3.73 [99.7]	n.d. [0]	n.d. [0]

[a] An aqueous solution (10 mL) of substrate with or without $S_2O_8^{2-}$ was heated at 80 °C under air for 6 h.
[b] Remaining substrate (%) = [(moles of remaining substrate)/(moles of initial substrate)] × 100.
[c] F^- yield (%) = [(moles of F^- formed)/(moles of fluorine in initial substrate)] × 100.
[d] CO_2 yield (%) = [(moles of CO_2 formed)/(moles of carbon in initial substrate)] × 100.
[e] n.d = not detected.
[f] Errors shown here were ascribed to replicate experiments.

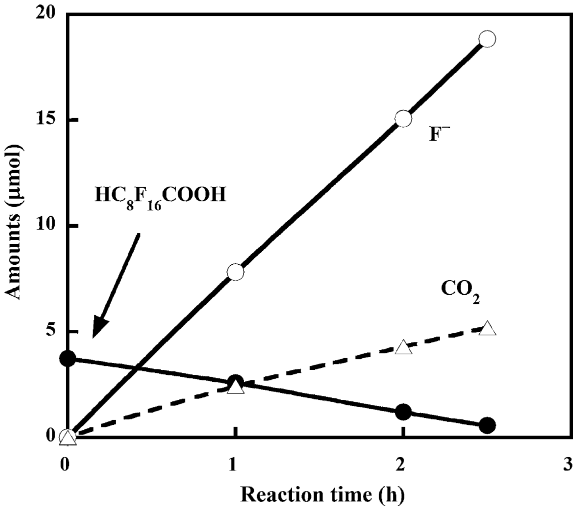

Fig. 3. Time course of $HC_8F_{16}COOH$ decomposition in hot water (60 °C) containing $S_2O_8^{2-}$: detected molar amounts of $HC_8F_{16}COOH$, F^-, and CO_2. An aqueous solution (10 mL) containing $HC_8F_{16}COOH$ (3.73 μmol, 373 μM) and $S_2O_8^{2-}$ (50 μmol, 5.0 mM) was introduced in the reactor, the reactor was pressurized with synthetic air (0.65 MPa), and the reactor temperature was raised to 60 °C and held constant for 1–2.5 h.

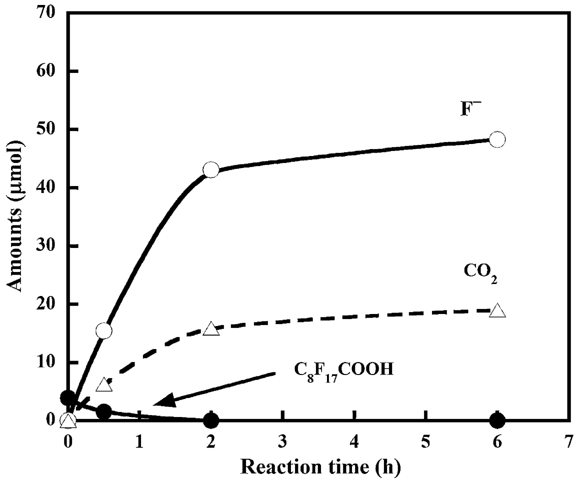

Fig. 4. Time course of $C_8F_{17}COOH$ decomposition in hot water (80 °C) containing $S_2O_8^{2-}$: detected molar amounts of $C_8F_{17}COOH$, F^-, and CO_2. The reaction conditions were the same as those described in Fig. 1, except that $C_8F_{17}COOH$ (3.85 μmol, 385 μM) was used as the substrate.

along with other decomposition data, are summarized in Table 2, together with other H-PFCAs. The initial decomposition rates for $HC_8F_{16}COOH$, $HC_6F_{12}COOH$, and HC_4F_8COOH were nearly identical (1.08–1.28 μmol h^{-1}; entries 1–3), which indicates that the reactivities of these H-PFCAs were almost the same; that is, the reactivity was little influenced by the carbon-chain length.

3.3. *Comparison of H-PFCAs with PFCAs*

We compared the $S_2O_8^{2-}$-induced decomposition of H-PFCAs with that of the corresponding PFCAs. Fig. 4 shows the time course of $C_8F_{17}COOH$ decomposition in hot water at 80 °C with $S_2O_8^{2-}$ (50.0 mM) under the same experimental conditions used for $HC_8F_{16}COOH$ (Fig. 1). $C_8F_{17}COOH$ was efficiently decomposed to F^- and CO_2, as previously reported for PFOA decomposition [10]. In addition to $C_8F_{17}COOH$, $C_6F_{13}COOH$ and C_4F_9COOH also completely disappeared after 6 h, and F^- and CO_2 were formed in yields of 73.8–89.7% and 54.8–82.4%, respectively (Table 1, entries 7, 9, and 11). In contrast, in the absence of $S_2O_8^{2-}$, almost all (98.4–99.7%) of the initial amounts of the PFCAs remained in the aqueous phase, and F^- and CO_2 did not form meaningfully (entries 8, 10, and 12).

The F^- yield from each of the H-PFCAs was higher than that from the corresponding PFCAs: for example, 98.2% for $HC_8F_{16}COOH$ (entry 1) compared to 73.8% for $C_8F_{17}COOH$ (entry 7), and 97.8% for $HC_6F_{12}COOH$ (entry 3) compared to 75.7% for $C_6F_{13}COOH$ (entry 9). This result indicates that mineralization by $S_2O_8^{2-}$ proceeded faster for H-PFCAs than for the corresponding PFCAs. The difference between the $S_2O_8^{2-}$ reactivities of H-PFCAs and PFCAs was more obvious at 60 °C and with a smaller amount of $S_2O_8^{2-}$. The reaction-time dependence of the decomposition of $C_8F_{17}COOH$ in hot water at 60 °C in the presence of $S_2O_8^{2-}$ (5.0 mM) is shown in Fig. 5, together with that of $HC_8F_{16}COOH$. Whereas $HC_8F_{16}COOH$ decomposed efficiently at an initial decomposition rate of 1.28 μmol h^{-1} (Table 2, entry 1), $C_8F_{17}COOH$ decomposed much more slowly (Fig. 5a), at an initial decomposition rate of 0.18 μmol h^{-1} (Table 2, entry 4), which was 14% of that of the rate for $HC_8F_{16}COOH$. Although small amounts of F^- and CO_2 were detected during the reaction of $C_8F_{17}COOH$ (Fig. 5b and c), the amounts were one order of magnitude smaller than the amounts for $HC_8F_{16}COOH$ over the duration of the reaction: for example, the yields of F^- and CO_2 at 3 h were 4.08% and 3.98% (Table 2, entry 4), whereas those for $HC_8F_{16}COOH$ at the shorter reaction time of 2.5 h were 31.5% and 15.5%, respectively (Table 2, entry 1). The same tendency was also observed for $C_6F_{13}COOH$ and C_4F_9COOH: the initial decomposition rates for $C_6F_{13}COOH$ and C_4F_9COOH were both 0.09 μmol h^{-1}

Table 2
Decomposition of H-PFCAs and PFCAs in hot water (60 °C) in the presence of $S_2O_8^{2-}$ [a].

Entry	Substrate (initial amount, μmol)	Remaining substrate (μmol) [%][b]	F^- (μmol) [yield (%)][c]	CO_2 (μmol) [yield (%)][d]	Short-chain PFCAs (amount, μmol)	Initial decomposition rate of substrate (μmol h^{-1})[e]
1	$HC_8F_{16}COOH$ (3.73)	0.56 [15.0][f]	18.8 [31.5][f]	5.20 [15.5][f]	–	1.28
2	$HC_6F_{12}COOH$ (3.80)	1.08 [28.4][f]	14.6 [32.0][f]	4.89 [18.4][f]	–	1.08
3	HC_4F_8COOH (3.75)	0.90 [24.0][f]	14.5 [48.3][f]	4.99 [26.6][f]	–	1.14
4	$C_8F_{17}COOH$ (3.88)	3.38 [87.1][g]	2.69 [4.08][g]	1.39 [3.98][g]	PFOA (0.10), $C_6F_{13}COOH$ (0.02)[g]	0.18
5	$C_6F_{13}COOH$ (3.71)	3.43 [92.5][g]	0.66 [1.37][g]	0.58 [2.23][g]	$C_5F_{11}COOH$ (0.08)[g]	0.09
6	C_4F_9COOH (3.82)	3.46 [90.6][g]	0.72 [2.09][g]	0.94 [4.92][g]	C_3F_7COOH (0.22)[g]	0.09

[a] An aqueous solution (10 mL) of substrate with $S_2O_8^{2-}$ (50 μmol, 5.0 mM) was heated at 60 °C under air.
[b] Remaining substrate (%) = [(moles of remaining substrate)/(moles of initial substrate)] × 100.
[c] F^- yield (%) = [(moles of F^- formed)/(moles of fluorine in initial substrate)] × 100.
[d] CO_2 yield (%) = [(moles of CO_2 formed)/(moles of carbon in initial substrate)] × 100.
[e] The initial decomposition rate was taken from the initial period when the substrate amount decreased linearly with respect to time.
[f] Reaction time, 2.5 h.
[g] Reaction time, 3 h.

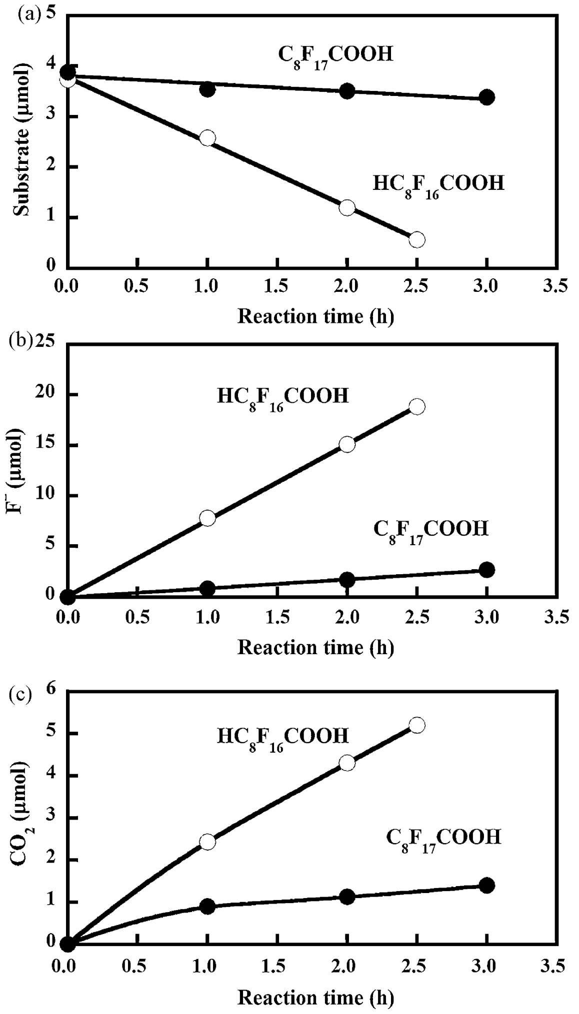

Fig. 5. Reaction-time dependence of the decomposition of $C_8F_{17}COOH$ in hot water (60 °C) containing $S_2O_8{}^{2-}$, along with data for $HC_8F_{16}COOH$ under the same reaction conditions for comparison: (a) $C_8F_{17}COOH$, (b) F^-, and (c) CO_2. The reaction conditions were the same as those described in Fig. 3, except that $C_8F_{17}COOH$ (3.88 µmol, 388 µM) was used as the substrate.

(Table 2, entries 5 and 6), whereas those for $HC_6F_{12}COOH$ and HC_4F_8COOH were 1.08 and 1.14 µmol h^{-1}, respectively (Table 2, entries 2 and 3). Thus, the initial decomposition rates for all H-PFCAs tested here were 7.1–12.7 times as high as those for the corresponding PFCAs.

In addition to the difference in the decomposition efficiency, we also observed another difference in the behavior of H-PFCAs and that of PFCAs. In the case of PFCAs, small amounts of short-chain PFCAs, that is, PFCAs with chain lengths shorter than the initial chain lengths, were detected in the reaction aqueous phase (Table 2, entries 4–6), whereas in the case of H-PFCAs, the corresponding species, that is, H-PFCAs with chain lengths shorter than the initial chain lengths, were not observed in the ESI-mass spectra or the HPLC chromatograms. This difference suggests that the decomposition mechanism of H-PFCAs differs from that of PFCAs.

3.4. Reaction mechanism

As described above, H-PFCAs showed high reactivity at the low temperature of 60 °C, whereas the reactivity of PFCAs was low at that temperature. In addition, decomposition of PFCAs formed shorter-chain PFCAs, whereas that of H-PFCAs did not form shorter-chain H-PFCAs. These observations led us to suppose that the reaction mechanisms for the two series of compounds differ considerably.

PFCAs are known to undergo little decomposition by conventional techniques such as treatment with Fenton's reagent ($Fe^{2+} + H_2O_2$) [8], irradiation with UV–vis light in the presence of H_2O_2 [7], and conventional TiO_2 photocatalysts [15,16], because the reactivity of OH radicals with PFCAs in water is low. In contrast, H-PFCAs have a carbon–hydrogen bond, which can be expected to react with OH radicals. Also, $SO_4{}^{\bullet-}$ reacts with water to form OH radicals, with a rate constant k[H_2O] of 460 s^{-1} [17] (Eq. (1)).

$$SO_4{}^{\bullet-} + H_2O \rightarrow HSO_4{}^- + OH^\bullet \tag{1}$$

To determine whether OH radicals generated from $SO_4{}^{\bullet-}$ and water might initiate the decomposition of H-PFCAs, we examined the reactivity of an H-PFCA ($HC_6F_{13}COOH$) with OH radicals produced from Fenton's reagent and found that treatment of $HC_6F_{12}COOH$ (123 µmol in 22 mL; 5.58 mM) with Fe^{2+} (4.90 mM) and H_2O_2 (1 M) for 17 h resulted in no decrease in the amount of $HC_6F_{12}COOH$. Therefore, OH radicals are unlikely to play a significant role at least in the initial decomposition step of H-PFCAs in the presence of $S_2O_8{}^{2-}$, although OH radicals may play some role in the transformation of reaction intermediates.

In the case of PFCAs, the mechanism of decomposition induced by $SO_4{}^{\bullet-}$ has been outlined as follows [10,11]: the oxidization of a PFCA ($C_nF_{2n+1}COOH$) by $SO_4{}^{\bullet-}$ causes decarboxylation that generates a perfluoroalkyl radical ($C_nF_{2n+1}{}^\bullet$). The perfluoroalkyl radical reacts with $SO_4{}^{\bullet-}$ to form $C_nF_{2n+1}OSO_3{}^-$. This unstable species easily undergoes hydrolysis to form $C_nF_{2n+1}OH$. The perfluoroalcohol undergoes HF elimination to form $C_{n-1}F_{2n-1}COF$. Hydrolysis of the acid fluoride generates a PFCA shortened by one CF_2 unit, that is, $C_{n-1}F_{2n-1}COOH$. The shortened PFCA is further decomposed by $SO_4{}^{\bullet-}$. Likewise, the decomposition of the shortened PFCAs proceeds via the formation of even shorter PFCAs.

We also expected the decomposition of H-PFCA to be initiated by oxidative decarboxylation. However, as described above, the formation of shorter-chain H-PFCAs was not observed; for example, no $HC_7F_{14}COOH$ was produced by decomposition of $HC_8F_{16}COOH$ in the presence of $S_2O_8{}^{2-}$. To determine the reaction intermediates for H-PFCAs, we employed ESI-mass spectrometry and LC/MS. When the reaction of $HC_8F_{16}COOH$ was carried out at 60 °C in the presence of $S_2O_8{}^{2-}$ (5.0 mM), the ESI-mass spectra of the reaction aqueous phase after 1 h showed peaks at m/z 445 and 439. The peak at m/z 445 corresponds to the anion of the initial substrate, that is, $[HC_8F_{16}COO]^-$, and the peak at m/z 439 corresponds to the anion of perfluorodicarboxylic acid $[HOOCC_7F_{14}COO]^-$. After 2 h, another peak appeared, at m/z 389. This m/z value corresponds to the anion of a shorter-chain perfluorodicarboxylic acid $[HOOCC_6F_{12}COO]^-$. These results indicate that perfluorodicarboxylic acids with various chain lengths were the reaction intermediates. We carried out LC/MS measurements and quantified $HOOCC_7F_{14}COOH$ in the reaction aqueous phase. The total-ion mass chromatogram for the reaction aqueous phase (2.5 h) of $HC_8F_{16}COOH$ with $S_2O_8{}^{2-}$ is shown in Fig. 6a. The peaks at 2.95 and 2.37 min correspond to $HOOCC_7F_{14}COOH$ and $HOOCC_6F_{12}COOH$, respectively, which were identified by use of standard samples (the retention time of $HC_8F_{16}COOH$ is 39.8 min so that the peak is not shown here). The peak X in Fig. 6a consist of several further shortened perflurodicarboxylic acids $HOOCC_nF_{2n}COOH$ (n = 2–5), because the mass spectrum showed peaks which correspond to their anions $[HOOCC_nF_{2n}COO]^-$ (n = 2–5) (Fig. 6b).

The time course of the amount of $HOOCC_7F_{14}COOH$ is shown in Fig. 7 (the reaction conditions were the same as those for the reaction shown in Fig. 3). The plot clearly indicates that $HOOCC_7F_{14}COOH$ was formed while $HC_8F_{16}COOH$ was decomposed (Fig. 3). Therefore, the initial decomposition step should be nucleophilic substitution of $SO_4{}^{\bullet-}$ at the carbon atom attached to

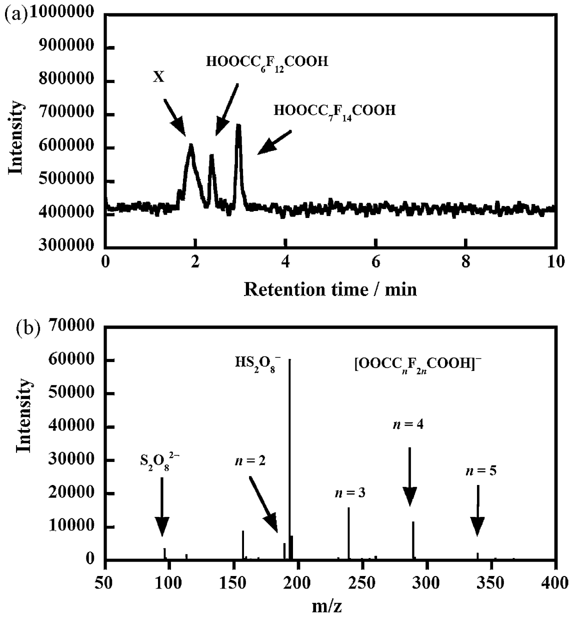

Fig. 6. LC/MS data for the reaction aqueous phase of $HC_8F_{16}COOH$ with $S_2O_8^{2-}$: (a) total-ion mass chromatogram and (b) mass spectrum for the peak X in a. The reaction conditions were the same as those described in Fig. 3, where the reaction time was 2.5 h.

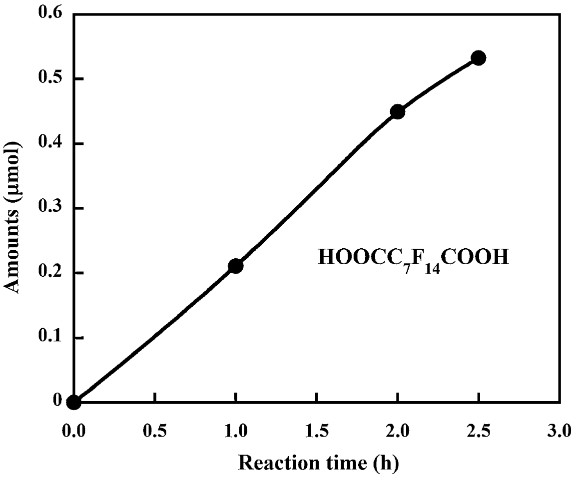

Fig. 7. Time course of the amount of $HOOCC_7F_{14}COOH$ formed in the decomposition of $HC_8F_{16}COOH$ in hot water (60 °C) containing $S_2O_8^{2-}$. The reaction conditions were the same as those described in Fig. 3.

the ω-H atom in the H-PFCA molecule, which releases F^- into the aqueous phase (Eq. (2)).

$$HC_8F_{16}COOH + SO_4^{\bullet -} \rightarrow O_3SOCHFC_7F_{14}COOH + F^- \qquad (2)$$

Next, the resulting species undergoes hydrolysis to form an alcohol, $HOCHFC_7F_{14}COOH$, and HSO_4^-. The alcohol undergoes HF elimination to form an aldehyde, $OHCC_7F_{14}COOH$, which is oxidized to a perfluorodicarboxylic acid, $HOOCC_7F_{14}COOH$, which was detected by LC/MS. The formed HSO_4^- is in equilibrium with SO_4^{2-} in water and was detected by ion-chromatography in the form of SO_4^{2-}. $HOOCC_7F_{14}COOH$ reacts with $SO_4^{\bullet -}$, in a manner similar to that described for the decomposition of PFCAs, via formation of further shortened pefluorodicarboxylic acids, which were detected by ESI-mass spectrometry and LC/MS.

4. Conclusion

We investigated the decomposition of H-PFCAs, that is, $HC_nF_{2n}COOH$ (n = 4, 6, and 8), in the presence of $S_2O_8^{2-}$ in hot water. The addition of $S_2O_8^{2-}$ to the reaction system of these H-PFCAs at 80 °C caused almost complete mineralization (F^- yields: ≈100%). The decomposition of H-PFCAs induced by $S_2O_8^{2-}$ proceeded even at 60 °C, at which temperature the initial decomposition rates were 7.1–12.7 times those for the corresponding PFCAs. The mechanism of H-PFCA decomposition differs from that of PFCAs: the former is initiated by the nucleophilic substitution of $SO_4^{\bullet -}$ at the carbon atom attached to the ω-H atom of the H-PFCA molecule, followed by formation of perfluorodicarboxylic acids, which react with $SO_4^{\bullet -}$ to give further shortened perfluorodicarboxylic acids, and the final result was complete mineralization. Decomposition of H-PFCAs by photochemical approaches is being investigated in our laboratory.

Acknowledgements

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