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Efficient decomposition of perfluoroether carboxylic acids in water with a combination of persulfate oxidant and ultrasonic irradiation

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ABSTRACT

The decomposition of perfluoroether carboxylic acids $CF_3OC_2F_4OCF_2COOH$, $CF_3OC_2F_4OC_2F_4OCF_2COOH$, $CF_3OC_3F_6COOH$, $C_2F_5OC_2F_4OCF_2COOH$, and $C_4F_9OC_2F_4OC_2F_4OCF_2COOH$ and perfluoroalkylether sulfonates $C_2F_5OC_2F_4SO_3^-$ and $C_3F_7OC_2F_4SO_3^-$ in water with a combination of persulfate oxidant and ultrasonic irradiation was investigated. In the absence of persulfate, the perfluoroether acids decomposed quite slowly. For example, the pseudo-first-order rate constants for the decomposition of perfluoroether carboxylic acids ranged from 2.03×10^{-2} to 3.34×10^{-2} h^{-1}. After 24 h, 44.2–58.0% of the initial concentrations (ca. 50 μM) of the substrates remained, and the F^- yields were 27.7–59.7%. In contrast, the addition of persulfate dramatically accelerated the reactions. When 10 mM persulfate was used, the pseudo-first-order rate constants for the decomposition of perfluoroether carboxylic acids were 2.5–3.9 times those in the absence of persulfate. However, the addition of persulfate did not enhance the decomposition of perfluoroalkylether sulfonates. Enhancement of the perfluoroether carboxylic acid decomposition can be explained by acceleration of substrate decarboxylation, induced by sulfate radical anions formed from the persulfate during ultrasonic irradiation.

1. Introduction

Fluorochemical surfactants have been widely used in industry owing to their high surface-active effect, high thermal and chemical stability, and high light transparency [1]. After it became clear that perfluorocarboxylic acids ($C_nF_{2n+1}COOH$) and perfluoroalkyl sulfonates ($C_nF_{2n+1}SO_3^-$) are ubiquitous environmental contaminants and that the species with long perfluoroalkyl chains, such as perfluorooctanoic acid ($C_7F_{15}COOH$, PFOA) and perfluorooctanesulfonate ($C_8F_{17}SO_3^-$, PFOS) bioaccumulate [2–4], efforts to eliminate the use of these species in industry began [5,6]. In parallel with the effort to eliminate these chemicals in industry, there have been efforts to develop environmentally benign alternatives.

Perfluoroether acids, such as nonafluoro-3,6-dioxaheptanoic acid ($CF_3OC_2F_4OCF_2COOH$, NFDOHA), in which ether linkages are inserted in the perfluoroalkyl chains of the molecules so that they contain only short perfluoroalkyl ($\leq C_4$) groups, are among the recently developed alternatives [7,8]. Although perfluoroether acids are likely to decompose more easily than conventional perfluorocarboxylic acids or perfluoroalkyl sulfonates because they have ether linkages, few reports have focused on their decomposition behavior. The decomposition of a perfluoroether carboxylic acid ($C_2F_5OC_2F_4OCF_2COOH$) by a heteropolyacid photocatalyst [9], decomposition of perfluoroether carboxylic acids by persulfate ($S_2O_8^{2-}$, peroxodisulfate) in hot water [10], and decomposition of perfluoroalkylether sulfonates in subcritical water in the presence of oxygen have been reported [11]. If perfluoroether acids are to be used more widely, waste-treatment techniques will have to be established. Decomposition of fluorochemicals to F^- ions at sites where the chemicals are emitted in large quantities would be desirable because there is a well-established waste-treatment process for F^- ions based on reaction with Ca^{2+} to form the environmentally harmless CaF_2, demand for which is increasing because it is a raw material for the production of hydrofluoric acid. Thus the development of such a method would allow for the recycling of a fluorine resource.

We previously reported that perfluorocarboxylic acids and perfluoroether carboxylic acids are efficiently decomposed to F^- ions in hot water in the presence of $S_2O_8^{2-}$ [10]: the thermolysis of $S_2O_8^{2-}$ produces sulfate radical anions ($SO_4^{\bullet -}$), which act as strong oxidants to decompose the substrates. We also reported that perfluorocarboxylic acids are efficiently decomposed to F^- ions by $SO_4^{\bullet -}$ produced by UV irradiation of $S_2O_8^{2-}$ [12]. The reactivity of $SO_4^{\bullet -}$ obtained from the reactions of $S_2O_8^{2-}$ or peroxomonosulfate with metal ions has also been used to decompose polychlorinated biphenyls [13] and phenols [14].

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The use of ultrasonic irradiation to induce reactions is recognized as an innovative technique, allowing decomposition of environmental contaminants in water [15,16]. Decomposition by ultrasonic irradiation is mainly due to cavitation: the sudden collapse of cavitation bubbles gives rise to localized, transient high temperatures (several thousand degrees) and high pressures (several hundred atmospheres), which lead to the decomposition of organic molecules via reaction with hydroxyl radicals formed from pyrolysis of water or via direct pyrolysis [16,17]. Ultrasonic irradiation has been used to decompose PFOS and PFOA to F^- ions in pure water [18,19], and the use of the process to treat landfill groundwater and aqueous film-forming foams has been investigated [20,21].

Although the ultrasonic reaction technique is powerful, it is energy intensive because sonication is relatively inefficient with respect to total input energy and is uneconomical when used alone [15,16]. Therefore, combination of this technique with other types of energy, such as chemical oxidants, would be attractive for reduction of the total input energy.

In this study, we combined $S_2O_8^{2-}$ as an oxidant and ultrasonic irradiation to efficiently decompose five perfluoroether carboxylic acids (NFDOHA, $CF_3OC_2F_4OC_2F_4OCF_2COOH$, $CF_3OC_3F_6COOH$, $C_2F_5OC_2F_4OCF_2COOH$, $C_4F_9OC_2F_4OC_2F_4OCF_2COOH$) and two perfluoroalkylether sulfonates ($C_2F_5OC_2F_4SO_3^-$, $C_3F_7OC_2F_4SO_3^-$). The effectiveness of this combination is reported.

2. Materials and methods

2.1. Materials

Potassium persulfate (>95%) was purchased from Wako Pure Chemical Industries (Osaka, Japan) and used as received. NFDOHA (>98%), perfluoro-3,6,9-trioxadecanoic acid ($CF_3OC_2F_4OC_2F_4OCF_2COOH$, >98%), perfluoro(4-methoxybutanoic) acid ($CF_3OC_3F_6COOH$), perfluoro-3,6,9-trioxatridecanoic acid ($C_4F_9OC_2F_4OC_2F_4OCF_2COOH$, >98%), and the potassium salt of pefluoro(2-ethoxyethane)sulfonate ($C_2F_5OC_2F_4SO_3^-$) were purchased from SynQuest Laboratories (Alachua, FL, USA). Difluoro[1,1,2,2-tetrafluoro-2-(pentafluoroethoxy)ethoxy] acetic acid (undecafluoro-3,6-dioxaoctanoic acid, $C_2F_5OC_2F_4OCF_2COOH$, 99%) and the potassium salt of perfluoro(2-propoxyethane)sulfonate ($C_3F_7OC_2F_4SO_3^-$) were supplied by Asahi Glass Company (Tokyo, Japan).

2.2. Reaction procedures

The reaction apparatus consisted of a stainless steel ultrasonic reactor (8 L, 28 kHz, 200 W), a pump, and a cooling bath (Fig. 1). The reactor was a conventional ultrasonic cleaner (SC-208, SMT, Tokyo, Japan). The sample solution in the reactor was circulated by a pump through stainless steel tube connected to the reactor and immersed in cooling bath. The circulation flow rate was 15 L min^{-1}, and the reaction temperature was maintained at 28 °C.

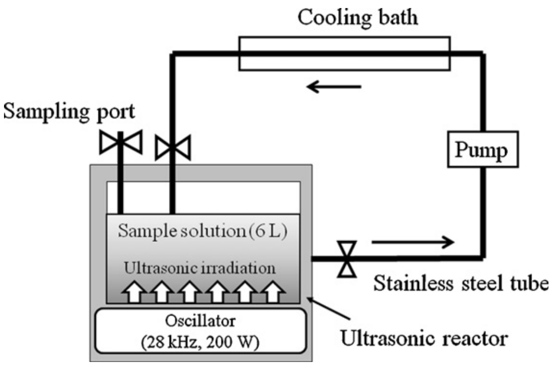

Fig. 1. Schematic diagram of the apparatus for ultrasonic reaction.

In a typical run, an aqueous solution (6 L) of a perfluoroether acid (ca. 50 μM) and $K_2S_2O_8$ (10 mM) was introduced into the reactor, and the reactor was sealed. After the sample solution was circulated for 1 h, ultrasonic irradiation was started. The reaction was carried out in air atmosphere, unless otherwise noted. Some reactions were carried out under argon: argon gas was bubbled into the reaction solution prior to the reaction and then introduced into the gas phase during the reaction. During the reaction, a few milliliters of the sample solution was extracted from the reactor through a sampling port.

The extracted sample solutions were subjected to ion chromatography, high-performance liquid chromatography (HPLC), and liquid chromatography/mass spectrometry (LC/MS). Reactions either in the absence of $S_2O_8^{2-}$ or in the absence of ultrasonic irradiation were also performed.

2.3. Analysis

An ion chromatography system (IC-2001, Tosoh, Tokyo, Japan) consisting of an automatic sample injector (30-μL injection volume), a degasser, a pump, a guard column, a separation column (TSKgel Super IC-Anion, 4.6-mm i.d., 15-cm length, Tosoh), a column oven (40 °C), and a conductivity detector with a suppressor device was used to measure the F^- 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 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 (55–75 vol.% of methanol), and the separation column was a Tosoh TSKgel Super ODS column (4.6-mm i.d., 10-cm length × 2).

An LC/MS system (LCMS-2010 EV, Shimadzu, Kyoto, Japan) with a separation column (TSKgel ODS-80TSQA) was also used to identify the intermediates in the reaction solutions. The mobile phase was a 50:50 v/v mixture of methanol and aqueous CH_3COONH_4 (1 mM, adjusted to pH 4.0 with acetic acid), and the flow rate was 0.2 mL min^{-1}. Analyses were carried out in negative-ion mode, and the electrospray probe voltage was 4.50 kV.

3. Results and discussion

3.1. Decomposition of NFDOHA

First, we examined the decomposition of a typical perfluoroether carboxylic acid (NFDOHA) with either $S_2O_8^{2-}$ or ultrasonic irradiation alone (Fig. 2). We previously reported that perfluorocarboxylic acids and perfluoroether carboxylic acids are efficiently decomposed in hot water (80 °C) with 50 mM $S_2O_8^{2-}$ [10]. In the present system, the reaction temperature was maintained at 28 °C, and the initial concentration of $S_2O_8^{2-}$ was 10 mM. Under these conditions, almost no decomposition of NFDOHA occurred without ultrasonic irradiation. After 24 h, 98.5% of the initial NFDOHA (initial concentration, 50.7 μM) remained (Fig. 2a, A), and no F^- was formed (Fig. 2b, A). In contrast, ultrasonic irradiation in the absence of $S_2O_8^{2-}$ led to partial decomposition of NFDOHA. The decrease in the NFDOHA concentration during the initial irradiation period followed pseudo-first-order kinetics (Fig. 2c) with a rate constant of 3.34×10^{-2} h^{-1} (Table 1, entry 1). After 24 h of irradiation, 44.3% of the NFDOHA remained; that is, 55.7% of the initial NFDOHA was consumed (Fig. 2a, B). Simultaneously,

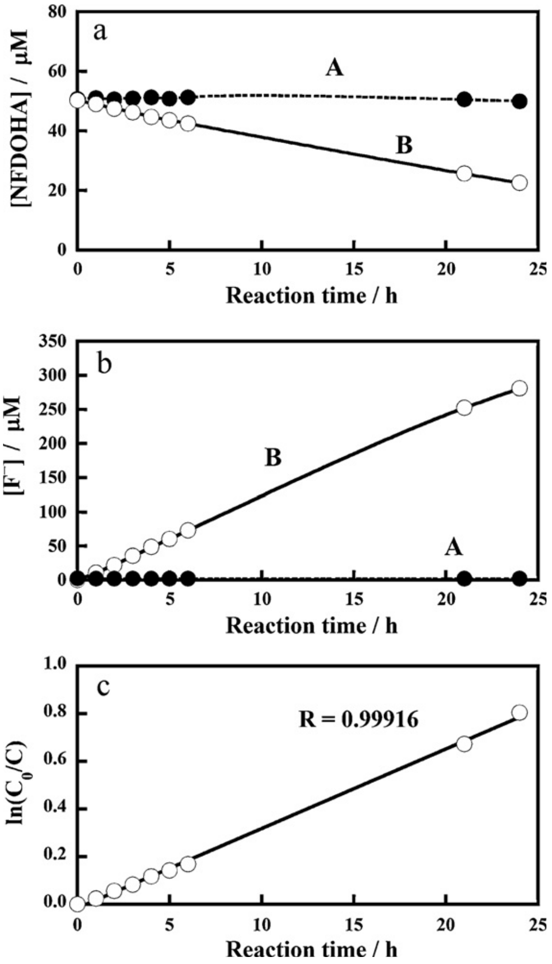

Fig. 2. Time courses of (a) concentration of remaining NFDOHA and (b) concentration of F^-: (A) an aqueous solution (6 L) containing NFDOHA (50.7 μM) and $S_2O_8^{2-}$ (10 mM) was maintained at 28 °C without ultrasonic irradiation; (B) an aqueous solution (6 L) containing NFDOHA (51.7 μM) without $S_2O_8^{2-}$ was maintained at 28 °C with ultrasonic irradiation. The reactions were carried out in air. Figure (c) shows plots of the first-order kinetics corresponding to the line B in (a) (ultrasonic irradiation without $S_2O_8^{2-}$; C, NFDOHA concentration; C_0, initial NFDOHA concentration; R, correlation coefficient).

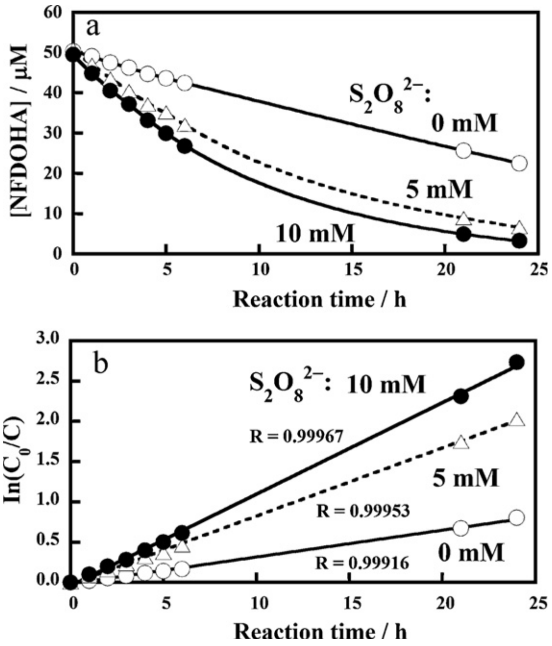

Fig. 3. (a) Effect of the initial $S_2O_8^{2-}$ concentration on the time course of NFDOHA concentration. An aqueous solution (6 L) containing NFDOHA (49.5–51.7 μM) and $S_2O_8^{2-}$ (0, 5, or 10 mM) was irradiated for 24 h. Figure (b) shows plots of the first-order kinetics (C, NFDOHA concentration; C_0, initial NFDOHA concentration; R, correlation coefficient).

F^- ions were formed (Fig. 2b, B) in a yield of 59.7% [=(moles of formed F^-)/(moles of fluorine content in initial NFDOHA, that is, moles of initial NFDOHA × 9)].

Next, we combined $S_2O_8^{2-}$ and ultrasonic irradiation. The time courses of the decrease in NFDOHA concentration at several $S_2O_8^{2-}$ concentrations (0, 5, and 10 mM) are shown in Fig. 3a, together with plots of the first-order kinetics (Fig. 3b). Increasing the initial concentration of $S_2O_8^{2-}$ clearly decreased the remaining NFDOHA concentration at all irradiation times, resulting in an increase in the pseudo-first-order rate constant from $3.34 \times 10^{-2}\,h^{-1}$ to $11.4 \times 10^{-2}\,h^{-1}$ (Table 1, entries 1–3). That is, the rate constant was 3.4 times that in the absence of $S_2O_8^{2-}$. When the initial concentration of $S_2O_8^{2-}$ was 10 mM, the concentration of

Table 1
Decomposition of perfluoroether acids induced by ultrasonic irradiation in the presence or in the absence of $S_2O_8^{2-}$.

Entry	Substrate (initial conc., μM)	Initial $S_2O_8^{2-}$ conc. (mM)	Pseudo-first-order rate constant ($\times 10^{-2}\,h^{-1}$)	Remaining substrate conc. (μM)[a] [%][b]	F^- conc. (μM)[a] [yield, %][c]
1	NFDOHA (51.7)	0	3.34	22.9[44.3]	278[59.7]
2	NFDOHA (50.8)	5	8.48	6.67[13.1]	357[78.1]
3	NFDOHA (49.5)	10	11.4	3.21[6.5]	378[84.8]
4	NFDOHA (9.9)	10	10.1	0.57[5.8]	75.2[84.4]
5	NFDOHA (49.8)[d]	10	13.2	0.98[2.0]	329[73.4]
6	$CF_3OC_2F_4OC_2F_4OCF_2COOH$ (50.0)	0	2.03	29.0[58.0]	213[32.8]
7	$CF_3OC_2F_4OC_2F_4OCF_2COOH$ (49.5)	10	7.89	5.58[11.3]	355[55.2]
8	$CF_3OC_3F_6COOH$ (49.5)	0	2.54	26.8[54.1]	187[42.0]
9	$CF_3OC_3F_6COOH$ (49.8)	10	6.40	10.7[21.5]	312[69.6]
10	$C_2F_5OC_2F_4OCF_2COOH$ (58.5)	0	2.50	27.5[47.0]	349[54.2]
11	$C_2F_5OC_2F_4OCF_2COOH$ (58.3)	10	9.40	6.10[10.5]	391[61.0]
12	$C_4F_9OC_2F_4OC_2F_4OCF_2COOH$ (49.8)	0	3.33	22.0[44.2]	262[27.7]
13	$C_4F_9OC_2F_4OC_2F_4OCF_2COOH$ (47.8)	10	8.69	4.38[9.16]	365[40.2]
14	$C_2F_5OC_2F_4SO_3^-$ (49.6)	0	1.35	35.4[71.4]	169[37.9]
15	$C_2F_5OC_2F_4SO_3^-$ (49.6)	10	1.39	31.6[63.7]	156[34.9]
16	$C_3F_7OC_2F_4SO_3^-$ (49.5)	0	1.67	32.7[66.1]	83.5[15.3]
17	$C_3F_7OC_2F_4SO_3^-$ (49.5)	10	1.72	32.9[66.3]	93.9[17.2]

[a] Irradiation time, 24 h.
[b] Remaining substrate (%) = [(moles of remaining substrate)/(moles of initial substrate)] × 100.
[c] F^- yield (%) = [(moles of F^- formed)/(moles of fluorine content in initial substrate)] × 100.
[d] The reaction was carried out under argon.

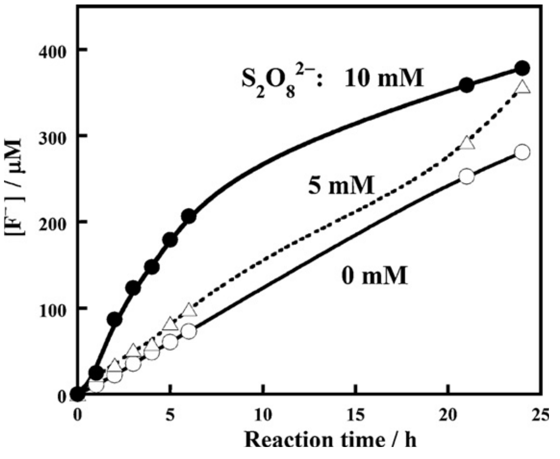

Fig. 4. Effect of the initial $S_2O_8^{2-}$ concentration on the time course of F^- concentration during the decomposition of NFDOHA. The reaction conditions were the same as those described in the caption of Fig. 3.

remaining NFDOHA after 24 h was 3.21 μM: 93.5% of the initial NFDOHA was consumed, which was 1.7 times the amount consumed in the absence of $S_2O_8^{2-}$.

Consistent with the increase in the consumption of NFDOHA, F^- formation increased with increasing $S_2O_8^{2-}$ concentration (Fig. 4). When the initial concentration of $S_2O_8^{2-}$ was 10 mM, the F^- concentration after 24 h reached 378 μM, which corresponds to a F^- yield of 84.8%, or 1.4 times the yield in the absence of $S_2O_8^{2-}$. The total recovery of fluorine (i.e., the molar ratio of the total fluorine content in the F^- and remaining NFDOHA to the fluorine content in the NFDOHA before reaction) was 91.3% after 24 h. Thus, the initial fluorine content in NFDOHA was well accounted for by F^- and unchanged NFDOHA, and the selectivity of the fluorine content in the consumed NFDOHA towards F^- [=(moles of F^-)/(moles of fluorine content in consumed NFDOHA)] was 90.7%.

The enhancement of NFDOHA decomposition induced by the combination of $S_2O_8^{2-}$ and ultrasonic irradiation was also observed at a lower initial concentration of NFDOHA. Consistent with the pseudo-first-order kinetics observed for the decrease of NFDOHA, the rate constant, the ratio of remaining NFDOHA, and F^- yield after 24 h were almost unchanged when the initial NFDOHA concentration was changed (Table 1, entries 3 and 4). The effect of the reaction atmosphere on the decomposition by ultrasonic irradiation with $S_2O_8^{2-}$ was also examined. When the reaction was carried out under argon, the pseudo-first-order rate constant for the NFDOHA decrease was 13.2×10^{-2} h^{-1}, and the ratio of remaining NFDOHA and the F^- yield after 24 h were 2.0% and 73.4% (Table 1, entry 5). In contrast, the rate constant in air was 11.4×10^{-2} h^{-1}, and the ratio of remaining NFDOHA and the F^- yield after 24 h were 6.5% and 84.8% (Table 1, entry 3). The pseudo-first-order rate constant for the NFDOHA decrease was somewhat higher in argon than in air. A similar finding was also observed for sonochemical decomposition of PFOA and PFOS in pure water [18]. Argon gas has a higher polytropic index than air, which produces a higher temperature at the collapse of the cavitation bubbles during sonochemical reactions [22]. Our results were consistent with this phenomenon.

3.2. Application to other perfluoroether acids

We applied our method to perfluoroether carboxylic acids other than NFDOHA at a constant initial $S_2O_8^{2-}$ concentration of 10 mM. The results are summarized in Table 1, together with data obtained in the absence of $S_2O_8^{2-}$ (entries 6–13). In the absence of $S_2O_8^{2-}$, the pseudo-first-order rate constants for substrate decrease ranged from 2.03×10^{-2} to 3.33×10^{-2} h^{-1}, and 44.2–58.0% of the initial substrates remained after 24 h of irradiation (Table 1, entries 6, 8, 10, 12). In contrast, in the presence of $S_2O_8^{2-}$, the pseudo-first-order rate constants ranged from 7.89×10^{-2} to 9.40×10^{-2} h^{-1} (Table 1, entries 7, 9, 11, 13; that is, 2.5–3.9 times greater than those in the absence of $S_2O_8^{2-}$), and the ratios of remaining substrates after 24 h were 9.16–21.5% (that is, 0.19–0.40 times those in the absence of $S_2O_8^{2-}$). These results clearly indicate that the combination of $S_2O_8^{2-}$ and ultrasonic irradiation effectively decomposed these perfluoroether carboxylic acids.

We also attempted to decompose perfluoroalkylether sulfonates $C_2F_5OC_2F_4SO_3^-$ and $C_3F_7OC_2F_4SO_3^-$. Compared to the perfluoroether carboxylic acids, the perfluoroalkylether sulfonates decomposed slowly in the absence of $S_2O_8^{2-}$: the pseudo-first-order rate constants for $C_2F_5OC_2F_4SO_3^-$ and $C_3F_7OC_2F_4SO_3^-$ were 1.35×10^{-2} h^{-1} and 1.67×10^{-2} h^{-1}, respectively (Table 1, entries 14 and 16). The time courses of the $C_2F_5OC_2F_4SO_3^-$ and F^- concentrations, and plots of the first-order kinetics in the presence of $S_2O_8^{2-}$ (10 mM) are shown in Fig. 5a–c, respectively, together with the courses in the absence of $S_2O_8^{2-}$. In contrast to the perfluoroether carboxylic acids, the perfluoroalkylether sulfonates showed no significant differences in the time profiles of either the substrate or F^- concentration whether $S_2O_8^{2-}$ was present or not. The pseudo-first-order rate constant for the decrease of the substrate and the concentrations of F^- and remaining substrate after 24 h were also little affected by the presence of $S_2O_8^{2-}$ (Table 1, entries 14 and 15). The time profile of the $C_3F_7OC_2F_4SO_3^-$

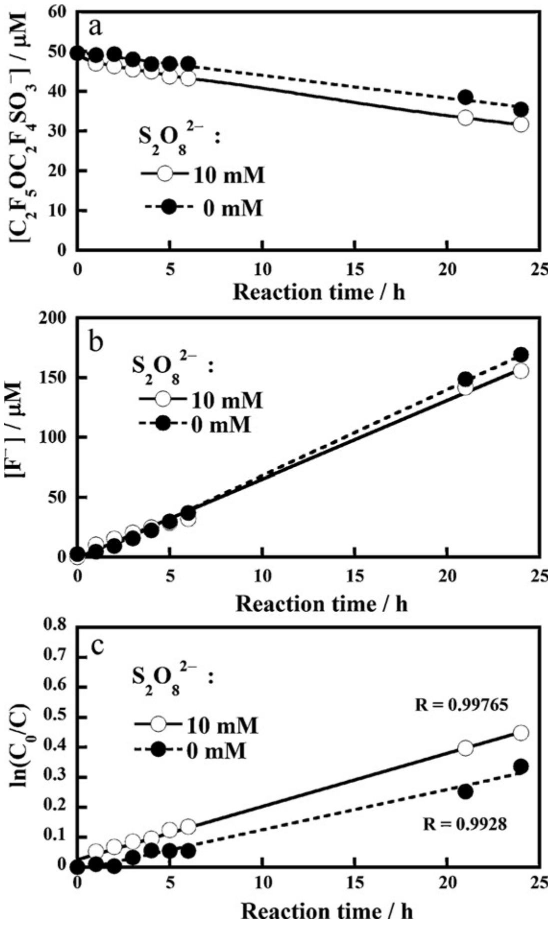

Fig. 5. Time courses of (a) $C_2F_5OC_2F_4SO_3^-$ concentration and (b) F^- concentration under ultrasonic irradiation with $S_2O_8^{2-}$. An aqueous solution (6 L) containing $C_2F_5OC_2F_4SO_3^-$ (49.6 μM) and $S_2O_8^{2-}$ (10 mM) was irradiated at 28 °C. The data obtained in the absence of $S_2O_8^{2-}$ are also shown. Figure (c) shows plots of the first-order kinetics (C, $C_2F_5OC_2F_4SO_3^-$ concentration; C_0, initial $C_2F_5OC_2F_4SO_3^-$ concentration; R, correlation coefficient).

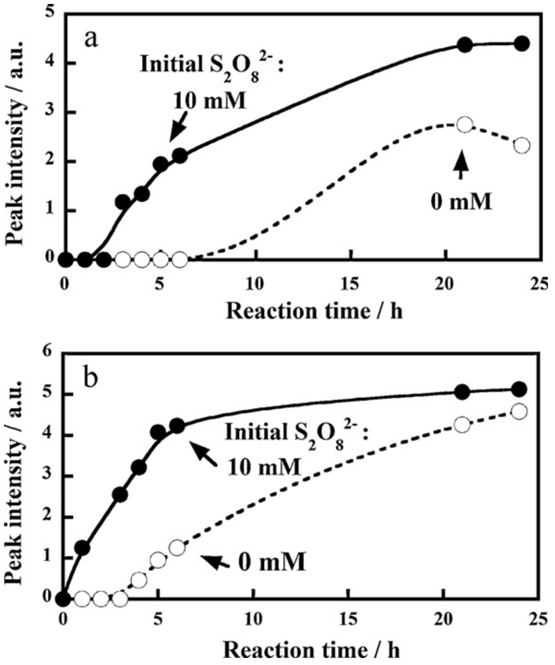

Fig. 6. Time courses of (a) LC/MS peak intensity for CF_3OCF_2COOH during decomposition of NFDOHA with and without $S_2O_8^{2-}$ (10 and 0 mM) and (b) LC/MS peak intensity for $C_2F_5OCF_2COOH$ during decomposition of $C_2F_5OC_2F_4OCF_2COOH$ with and without $S_2O_8^{2-}$ (10 and 0 mM). In (a), the initial concentrations of NFDOHA were 49.5 and 51.7 μM for the experiments with and without $S_2O_8^{2-}$, and in (b), the initial concentrations of $C_2F_5OC_2F_4OCF_2COOH$ were 58.3 and 58.5 μM for the experiments with and without $S_2O_8^{2-}$, respectively.

concentration in the presence of $S_2O_8^{2-}$ was also almost identical to that in the absence of $S_2O_8^{2-}$, and the pseudo-first-order rate constant and the concentrations of F^- and remaining substrate after 24 h were similar (Table 1, entries 16 and 17).

3.3. Reaction mechanism

As described above, $S_2O_8^{2-}$ clearly enhanced the decomposition of perfluoroether carboxylic acids but not perfluoroalkylether sulfonates. We analyzed the reaction solutions of several substrates by LC/MS to observe trace amounts of reaction intermediates. When NFDOHA was irradiated in the absence of $S_2O_8^{2-}$, the total-ion chromatogram of samples at long reaction times (21 and 24 h) showed a new species that yielded a peak at *m*/*z* 179, which corresponds to $CF_3OCF_2COO^-$, indicating that the new species was CF_3OCF_2COOH. That is, a C_2F_4O-unit-shortened homologue of NFDOHA was generated during the reaction. A similar phenomenon was reported previously for the sonochemical decomposition of PFOA [18]: perfluorocarboxylic acids with chain lengths shorter than PFOA were formed. The formation of the shortened compounds was explained by repetition of the decarboxylation and the oxidation of the resulting perfluoroalkyl radicals; the decarboxylation proceeded by pyrolysis at the interface between the cavitation bubbles and the surrounding water [18]. Such decarboxylation of perfluorocarboxylic acids can be induced not only by ultrasonic irradiation but also by direct photolysis [23].

The formation of CF_3OCF_2COOH from NFDOHA was greatly increased in the presence of $S_2O_8^{2-}$. When the initial concentration of $S_2O_8^{2-}$ was 10 mM, the peak corresponding to CF_3OCF_2COOH in the chromatogram appeared after 3 h of reaction, and the intensity of the peak increased markedly (Fig. 6a). In contrast, in the absence of $S_2O_8^{2-}$, the peak appeared only after 21 and 24 h. This result suggests that the transient high temperature ascribed to ultrasonic irradiation led to pyrolysis of $S_2O_8^{2-}$ to form $SO_4^{\bullet-}$, which efficiently caused the decarboxylation of NFDOHA. A similar mechanism occurs in the hot water reaction [10] and the photochemical reaction [12] in the presence of $S_2O_8^{2-}$.

In accordance with this oxidative decarboxylation mechanism, we expected $SO_4^{\bullet-}$ to be reduced to SO_4^{2-}. Consistent with this expectation, SO_4^{2-} accumulated in the reaction solution: after 24 h, the SO_4^{2-} concentration reached 1.02 mM.

What happened after the decarboxylation is not clear. If the reaction proceeds chemically, the following process, which is analogues to the mechanism proposed for the hot water reaction is plausible [10]. The formed $CF_3OC_2F_4OCF_2$ radical is oxidized to $CF_3OC_2F_4OCOO^-$, which undergoes further decarboxylation by $SO_4^{\bullet-}$ to form $CF_3OC_2F_4O$ radical. This radical may react with water to form $CF_3OC_2F_4OH$, which undergoes HF elimination to form CF_3OCF_2COF. Hydrolysis of the acid fluoride generates CF_3OCF_2COOH.

Similar results were also observed for the other perfluoroether carboxylic acids. For example, in the reaction of $C_2F_5OC_2F_4OCF_2COOH$, we detected $C_2F_5OCF_2COOH$, and the peak intensity in the total-ion chromatogram increased rapidly starting from the initial reaction period when the reaction was carried out in the presence of $S_2O_8^{2-}$ (Fig. 6b).

In contrast, the addition of $S_2O_8^{2-}$ did not enhance the decomposition of perfluoroalkyl sulfonates. This result indicates that $SO_4^{\bullet-}$ could not act as an oxidant to cleave the carbon–sulfur bond of these species and that the decomposition of perfluoroalkylether sulfonates may have proceeded by direct pyrolysis, in a mechanism similar to that for the sonochemical decomposition of PFOS [18,19].

4. Conclusions

We investigated the decomposition of perfluoroether carboxylic acids $CF_3OC_2F_4OCF_2COOH$ (NFDOHA), $CF_3OC_2F_4OC_2F_4OCF_2COOH$, $CF_3OC_3F_6COOH$, $C_2F_5OC_2F_4OCF_2COOH$, and $C_4F_9OC_2F_4OC_2F_4OCF_2COOH$ and perfluoroalkylether sulfonates $C_2F_5OC_2F_4SO_3^-$ and $C_3F_7OC_2F_4SO_3^-$ induced by a combination of $S_2O_8^{2-}$ and ultrasonic irradiation. In the absence of $S_2O_8^{2-}$, the decomposition of the perfluoroether carboxylic acids was slow: the pseudo-first-order rate constants for the decomposition ranged from 2.03×10^{-2} to 3.34×10^{-2} h^{-1}. After 24 h, 44.2–58.0% of the initial concentration (ca. 50 μM) of substrate remained, and the F^- yields were 27.7–59.7%. Addition of $S_2O_8^{2-}$ dramatically accelerated the reactions: when 10 mM $S_2O_8^{2-}$ was used, the pseudo-first-order rate constants for the decomposition of these substrates were 2.5–3.9 times those in the absence of $S_2O_8^{2-}$. The reactivity enhancement can be explained by acceleration of the decarboxylation of the substrates by sulfate radical anions generated from $S_2O_8^{2-}$. Consistent with this interpretation, enhancement of the decomposition by $S_2O_8^{2-}$ was not observed for perfluoroalkyl sulfonates $C_2F_5OC_2F_4SO_3^-$ and $C_3F_7OC_2F_4SO_3^-$.

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