Efficient mineralization of a novel fluorotelomer surfactant, 2H,3H,3H,5H,5H,6H,6H-4-thia-perfluoro(2-methyl)-1-dodecanoic acid, in superheated water induced by a combination of potassium permanganate and dioxygen

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ABSTRACT

Mineralization of a fluorotelomer surfactant containing a C_6F_{13} end-group (FSC), in hot and superheated water was studied. The process was optimized by variation of parameters such as temperature and the presence or absence of O_2, Ar, $KMnO_4$ and $K_2S_2O_8$. Treatment of FSC with a combination of $KMnO_4$ and O_2 efficiently decomposed the surfactant to F^-, SO_4^{2-}, and CO_2. Specifically, when aqueous FSC (34.8 μmol) and $KMnO_4$ (0.50 mmol) were reacted at 350 °C for 18 h under O_2 (13.6 mmol), the F^-, CO_2, and SO_4^{2-} yields reached 82, 84, and 97%, respectively, that is, most of fluorine, carbon, and sulfur atoms were mineralized. 1H-Perfluoroalkanes ($C_nF_{2n+1}H$, n = 1~6) were detected as minor products in the gas phase, in amounts that decreased with increasing reaction time. Taken together, these major and minor products accounted for 96% of the fluorine, 97% of the sulfur, and 91% of the carbon atoms in the initial FSC. The in situ formed MnO_2 dominantly acted as the oxidizing agent for the mineralization of FSC.

Keywords:

Fluorotelomer

Surfactant

Decomposition

Superheated water

Permanganate

Oxidation

1. Introduction

Organofluorine compounds, which are thermally and chemically stable, show a high surface activity and do not absorb light [1, 2]. Among them, compounds consisting of a perfluoroalkyl group (C_nF_{2n+1}–, where n = approx. 4 to 14) and an acid end group (COOH or SO_3H) have been used as industrial surfactants in applications that involve severe chemical and thermal conditions, which are incompatible with conventional hydrocarbon agents [3, 4]. While these chemicals are used as niche products, some of them showed environmentally negative features. Representatively, perfluorooctanesulfonic acid and perfluorooctanoic acid ($C_8F_{17}SO_3H$, PFOS and $C_7F_{15}COOH$, PFOA, respectively) and their derivatives, which had been used for several decades, exhibit high environmental persistence [5–7], bioaccumulation, and non-ignorable toxicity. Therefore, international regulations (including voluntary restraints) for their manufacturing, uses, export/import have been issued from the mid-2000s and it is still of concern [8]. After the negative features of these compounds were revealed, over two hundred scientific reports that described decomposition methods of these compounds in water appeared, as summarized by recent review papers [9–11].

Fluorochemical surfactants used in industry are not limited in such perfluorinated alkyl compounds [3, 4, 6, 12, 13]. Derivatives with a perfluoroalkyl group that connects to ethylene unit (–CH_2CH_2–), i.e., compounds bearing $C_nF_{2n+1}C_2H_4$– group, are also used as surfactants for surface modification and other purposes. They are classified as fluorotelomer related products [14], and any species containing C_8F_{17}, $C_8F_{17}C_2H_4$– or higher groups have been restricted by the Stockholm Convention in 2019 at the same time as PFOA because they have possibility to generate PFOA when they degrade [8].

While many reports on the decomposition methods for PFOS and PFOA have been published, only a few ones focus on the decomposition of these fluorotelomers: by use of UV light irradiation [15], ball milling [16], heating with peroxodisulfate (persulfate, $S_2O_8^{2-}$) [17], oxidation with boron-doped diamond electrode [18], advanced oxidation processes [19], TiO_2 photocatalyst [20], and biodegradation [21–23]. Furthermore, the majority of the previous studies were performed to investigate whether they could transform into PFOA in the environment and did not necessarily aim to achieve mineralization (i.e. decomposition to F^- ions) of these compounds in view of the waste treatment. Although the hydrocarbon telomers seem to decompose readily compared to perfluorinated compounds because of the weak C–H bond (its dissociation energy is 337 kJ/mol, which is smaller than that of the C–F bond, 536 kJ/mol), their complete mineralization is still challenging.

Under the circumstances, development of an effective method to mineralize these compounds would be of interest. In addition, the generated F^--containing solutions could be treated with Ca^{2+} to generate harmless CaF_2 [24, 25]. CaF_2 is the raw material for producing hydrofluoric acid required for fluorination reactions. Because the global supply of mined high-purity fluorspar, the mineral form of CaF_2, is limited (hugest reserves are in China, Mexico, and South Africa [26]), such a treatment process would have the added benefit of recycling of fluorine element.

Hence, the objective of this study deals with the mineralization of 2H,3H,3H,5H,5H,6H,6H-4-thia-perfluoro(2-methyl)-1-dodecanoic acid (FSC, Fig. 1), a novel fluorotelomer surfactant, in two different conditions: i) in hot water (70–90 °C) with peroxodisulfate and ii) in superheated water (200–350 °C) with $KMnO_4$. FSC is an alternative surfactant to PFOS and PFOA and is successfully used for preparing spherical wormhole-like mesoporous silica for applications in the field of catalysts [27].

Decontamination methods using peroxodisulfate is a powerful tool for the treatment of a broad range of organic compounds in water [28]. Indeed, PFOA and analogues were efficiently mineralized in hot water (80 °C) by addition of peroxodisulfate [29]. Superheated water (subcritical water, pressurized hot water) is a liquid state water at temperature ranging between 100 °C and 374 °C (the critical temperature). Reactions using superheated water are recognized to be environmentally benign [30–32], because of water's high diffusivity, low viscosity, and high hydrolyzing power [33]. In view of water as a reaction medium, its nontoxicity and abundance are also attractive. Although reactions in superheated water can generate toxic COF_2, it is readily transformed into CO_2 and HF under the reaction conditions, which is not the case for COF_2 generated during pyrolysis of fluorinated compounds. Furthermore, $KMnO_4$, a harmless oxidizing agent, is employed at tap water manufacturing facilities to treat metal compounds, preventing undesired disinfection products (e.g., trihalomethanes) [34]. So far, there have been only three reports that described $KMnO_4$-induced superheated water treatment: destructions of acetic acid [35], poly(vinylidene fluoride) [–$(CH_2CF_2)_n$–] [36], and ionic liquids bearing perfluorinated anions [37].

2. Materials and methods

2.1. Materials

99.999% O_2 and 99.9% Ar for the degradation reactions and standard gas mixtures, 1.00 % CO_2 in N_2 and 0.971% trifluoromethane (or fluoroform, CF_3H) in N_2 for the quantification of gas-phase products were supplied by Nissan Tanaka (Saitama, Japan). 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-octanethiol and 2-(trifluoromethyl)acrylic acid (or 2-(trifluoromethyl)prop-2-enoic acid) were obtained from Elf Atochem (now Arkema, Pierre Benite, France) and Tosoh

Finechem Corp. (Shunan, Japan), respectively. Pentafluoroethane (C_2F_5H, 99%), 1H-heptafluoropropane (C_3F_7H, 97%), 1H-nonafluorobutane (C_4F_9H, 99%), 1H-perfluoropentane ($C_5F_{11}H$, 98%), and 1H-perfluorohexane ($C_6F_{13}H$, 98%) were manufactured at SynQuest Labs (Alachua, FL, USA). For the measurement of gas chromatography-mass spectrometry (GC/MS), standard mixtures of each 1H-perfluoroalkane and Ar were prepared by removing an aliquot of 1H-perfluoroalkane from the reagent bottle with a gas-tight syringe, injecting it into an evacuated glass sampling bottle (1000 mL, GL Sciences, Tokyo, Japan), and filling the bottle with Ar to normal pressure. Solvents and reagents not specifically mentioned above were supplied by FUJIFILM Wako Pure Chemical (Osaka, Japan).

2.2. Synthesis of FSC

3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-octanethiol (1 eq., 5.00 g, 13.2 mmol), 2-(trifluoromethyl)acrylic acid (1 eq., 1.84 g, 13.2 mmol), and azobisisobutyronitrile (AIBN, 0.05 eq., 0.11 g, 0.7 mmol) were heated at reflux in MeCN (20 mL) for 16 h. The reaction mixture was concentrated under vacuum, added by 1,1,1,3,3-pentafluorobutane (50 mL), and washed with water (6 × 50 mL). The organic phase was dried with $MgSO_4$ and filtered, and the filtrate was concentrated by means of a rotary evaporator to afford FSC as a yellow oil (85 % yield), the structure of which was confirmed by ^{1}H and ^{19}F NMR, as shown in Figs. S-1 and S-2 in Supplementary Material (SM), respectively. The solubility of FSC in water is very low. We observed that FSC is soluble at least up to 126 mg L^{-1}.

2.3. Reactions in hot water containing $S_2O_8^{2-}$

The procedure for degradation reactions by use of $S_2O_8^{2-}$ was similar as that of the reactions of PFOA and other perfluoroalkanoic acids (perfluorocarboxylic acids, $C_nF_{2n+1}COOH$) [29]. Specifically, FSC (29.7 μmol) and aqueous $K_2S_2O_8$ (0.50 mmol in 10 mL, i.e., the concentration was 50 mM) were placed in a gold container (24.6 mL, 2.8 cm i.d.), which was then fitted into a 35-mL stainless-steel autoclave. Here, FSC was only slightly soluble in aqueous $K_2S_2O_8$. The gold container was used to suppress contamination of the reaction mixture with autoclave material. After being pressurized to 0.6 MPa O_2, the autoclave was capped and then heated in an oil bath at the desired temperature (70–90 °C) for 6 h. After being removed from the oil bath, the autoclave was cooled to 25 °C with ice water. The gas in the autoclave was transferred into a sampling bag and characterized by GC. Finally, the cap was removed from the autoclave, and the reaction solution in the gold container was collected and analyzed by ion-chromatography.

2.4. Reactions in superheated water containing $KMnO_4$

All reactions were performed in an autoclave (35 mL volume) with a cap, both of which were made of stainless-steel. A thermocouple enabled to monitor the temperature. The cap was joined to one pressure-resistant needle valve that was joined to a gas cylinder and another that was joined to a pressure meter and a gas collecting port. A gold container (25 mL volume, 2.8 cm i.d.) was placed in the autoclave and charged with 10 mL of aqueous $KMnO_4$ and FSC (34.8–35.4 μmol). At this stage, FSC was not completely soluble in the aqueous phase. The autoclave was pressurized with O_2 (0.6–1.6 MPa; 5.1–13.6 mmol), sealed, and then heated to the planned temperature (200–350 °C) at approximately 10 °C min^{-1}. When the reaction temperature had been maintained for the desired amount of time, the autoclave was immediately cooled to 25 °C. The gas phase, which was recovered in a sampling bag, was subjected to GC and GC/MS. Then,

the autoclave was opened, and the mixture inside was collected and centrifuged. The liquid was characterized by ion chromatography and HPLC/MS. The precipitate was dried overnight under vacuum at room temperature, and its X-ray diffraction pattern and X-ray photoelectron spectrum were measured. We also performed control reactions without $KMnO_4$ and reactions under Ar instead of O_2.

2.5. Analytical procedures

The major gas-phase products were quantified on a GC 323 instrument (GL Sciences) with thermal conductivity detection (temperature, 130 °C). An activated carbon column (60/80 mesh, 2.17 mm i.d., 2 m length, the column oven temperature, 110 °C) was employed. The carrier gas was Ar, and the injection port was maintained at 150 °C. Minor gas-phase products were characterized by a GC/MS system (QP2010 SE, Shimadzu, Kyoto, Japan) equipped with a fused-silica capillary column (Rt-Q-BOND; Restek, Bellefonte, PA, USA). The carrier gas was He, and the injection port was heated at 120 °C. The sample was injected in split mode (20/1), and the system was operated in full-scan mode. The temperature program was as follows: hold at 30 °C for 5 min, ramp to 200 °C at 20 °C min^{-1}, and hold at 200 °C for 20 min.

An ion chromatograph (IC-2001; Tosoh, Tokyo, Japan) equipped with an analytical column (Tosoh TSKgel Super IC-Anion, the column oven temperature, 40 °C) was employed to quantify the amounts of F^- and SO_4^{2-} in the reaction solutions. The mobile phase was an aqueous solution composed of 6 mM sodium tetraborate, 15 mM boric acid, and 0.2 mM sodium hydrogen carbonate; and flowed at 0.8 mL min^{-1}. HPLC/MS enabled us to quantify FSC in the reaction solutions. The instrument was an LCMS-2010 EV (Shimadzu) equipped with an analytical column (TSKgel ODS-100H, Tosoh). The mobile phase was 60:40 (volume ratio) MeCN/pure

water at 0.8 min^{-1}. A typical mass chromatogram (*m*/z = 519, corresponding to $[C_6F_{13}C_2H_4SCH_2CH(CF_3)COO]^-$, i.e., deprotonated FSC) and a calibration curve based on the peak intensity are shown in Fig. S-3 in SM. An electrospray ionization MS system (in the absence of the column in the above-described HPLC/MS) was used to detect any species remaining in the reaction solutions, with methanol as the mobile phase (0.2 mL min^{-1}). Selected sample solutions were subjected to another ion chromatography to detect short-chain perfluoroalkanoic acids (such as CF_3COOH). For these analyses, the injection volume was 10 μL, a TSKgel OApak-A (Tosoh) column was used, and the mobile phase was aqueous phthalic acid (10 mM) at 1.0 mL min^{-1}.

The F^- and CO_2 yields were calculated by means of Eqs. 1 and 2, respectively:

F^- yield (%) = [(moles of F^- formed)/(moles of F atoms in initial FSC)] × 100 (1)

CO_2 yield (%) = [(moles of CO_2 formed)/(moles of C atoms in initial FSC)] × 100 (2)

Details of quantification conditions of major products, F^- and SO_4^{2-} by ion-chromatography and CO_2 by gas-chromatography with thermal conductivity detection, are listed in Tables S-1 and S-2 in SM.

3. Results and discussion

3.1. Synthesis of FSC

First, FSC surfactant was prepared by a radical addition of the fluorinated mercaptan 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanethiol) onto 2-trifluoromethacrylic acid [27] (Scheme 1).

3.2. Reactions in hot water containing $S_2O_8^{2-}$

The F^- and CO_2 amounts produced by reactions of FSC in hot water containing 50 mM $K_2S_2O_8$ at 70, 80, and 90 °C are listed in Table 1. We previously reported that C5–C9 perfluoroalkanoic acids such as PFOA effectively decompose into F^- and CO_2 at around 80 °C [29]. For example, when $C_6F_{13}COOH$ in 50 mM aqueous $K_2S_2O_8$ is heated at 80 °C with 50 mM $K_2S_2O_8$ for 6 h, F^- and CO_2 are obtained in 75.7 and 77.9% yields, respectively. In this previously reported system, 80 °C was suitable to achieve efficient mineralization of these compounds because at this temperature, $S_2O_8^{2-}$ decomposes to two sulfate anion radicals ($2SO_4^{\bullet-}$), which have high oxidizing ability. The $SO_4^{\bullet-}$ radical is reduced to SO_4^{2-}, and the perfluoroalkanoic acid undergoes oxidation accompanied by a carbon–carbon bond cleavage between the perfluoroalkyl group and carboxyl group, in a process similar to Kolbe electrolysis [29, 38]. In contrast, at higher temperature, the mineralization extent decreases because $SO_4^{\bullet-}$ is consumed by other reactions, such as reaction with water. In both thermal- [29] and photochemical [39] reactions, 50 mM was the most desired $K_2S_2O_8$ concentration to mineralize perfluoroalkanoic acids in water: $K_2S_2O_8$ is not fully soluble at further higher concentration.

In the current study, we have found that when FSC was treated with hot water containing 50 mM $K_2S_2O_8$ at 70 °C for 6 h, virtually no mineralization proceeded. The F^- and CO_2 yields were only 1 and 2%, respectively (Table 1, entry 1). At this temperature, the SO_4^{2-} amount was 336 μmol, which corresponds to 34% [= 336/(500 × 2)] of the sulfur atoms in the initial $S_2O_8^{2-}$ amount (0.50 mmol) [note that although each FSC molecule contains one sulfur atom, the amount (29.7 μmol) was much lower than that (1000 μmol) in the initial $S_2O_8^{2-}$]. That is, while

FSC little mineralized, $S_2O_8^{2-}$ was consumed. Although we did not quantify $S_2O_8^{2-}$ in the reaction solution because $S_2O_8^{2-}$ cannot be detected by conventional ion-chromatography, $S_2O_8^{2-}$ and SO_4^{2-} are known to be the only stable sulfur species and the total S atom content [moles of ($S_2O_8^{2-}$ × 2 + SO_4^{2-})] was constant and the same as the initial value (moles of initial $S_2O_8^{2-}$ × 2) during the decomposition of perfluoroalkanoic acids in water [39]. Therefore, 34% SO_4^{2-} yield suggested that 66 % of the initial $S_2O_8^{2-}$ remained. Rising the reaction temperature to 80 °C increased the F^- and CO_2 yields to 16 and 6 %, respectively (Table 1, entry 2). However, the SO_4^{2-} amount was 766 μmol, which corresponds to 77% yield, suggesting that the remaining $S_2O_8^{2-}$ percentage was only 23%. At 90 °C, the CO_2 yield increased to 12% but the F^- yield did not increase (14%) (entry 3). These yields suggest that a CF_3 group on C2 position and adjacent non-fluorinated moiety decomposed (if the CF_3 group decomposed into F^-, the yield should be 19% (= 3/16; one FSC molecule has 16 fluorine atoms). However, the SO_4^{2-} amount at 90 °C was 974 μmol, which means 97% of the sulfur atoms in the initial $S_2O_8^{2-}$ amount. This result indicates that the majority of $S_2O_8^{2-}$ was consumed (the remaining ratio was estimated to be 3% only). Therefore, we concluded that no further increase in FSC mineralization could be expected under these conditions, Hence, it was of interest to explore reactions of FSC in superheated water containing $KMnO_4$. One reason for the low reactivity against $S_2O_8^{2-}$ is likely the poor solubility of FSC in water.

3.3. Reactions in superheated water

The F^- and CO_2 amounts formed by reactions of FSC at 300 °C for 6 h in superheated water under several combinations between coexisting gas (either O_2 or Ar, initial amount, 5.1 mmol) and $KMnO_4$ (initial amount, 0.50 mmol) are summarized in Table 2. In all cases, no FSC

remained. For the reaction under O_2 without any $KMnO_4$, the F^- and CO_2 yields were both 20% (entry 1). This result suggests that the decomposition of FSC was almost limited to the CF_3 group at C2 and adjacent non-fluorinated moiety. Compared to these yields, the SO_4^{2-} yield (Eq. 3; each FSC molecule contains one sulfur atom. *Note*: the calculation of the SO_4^{2-} yield is different from that using $S_2O_8^{2-}$ as described above) was higher (55%, entry 1), indicating that the carbon–sulfur bond in FSC was cleaved more easily.

$$SO_4^{2-} \text{ yield (\%)} = [(\text{moles of } SO_4^{2-} \text{ formed})/(\text{moles of S atom in initial FSC})] \times 100 \quad (3)$$

For a reaction in the presence of $KMnO_4$ under Ar, the F^- yield was enhanced to 35% (entry 2), suggesting that in addition to the CF_3 group at C2, the C_6F_{13} group also decomposed partially. The SO_4^{2-} yield increased to 88%, indicating that oxidative decomposition around the sulfur atom in FSC was accelerated. The CO_2 yield remained low (19%).

When FSC was decomposed under O_2 without any $KMnO_4$, the pH of the resulting solution was 2.4; whereas for a similar reaction with $KMnO_4$ under Ar [initial pressure, 0.6 MPa (5.1 mmol)], it increased up to 8.0. Under the latter conditions, OH^- ions were released (Eq. 4):

$$4KMnO_4 + 2H_2O \rightarrow 4MnO_2 + 3O_2 + 4KOH \quad (4)$$

When the pH of the aqueous system was approximately 5–11, some of the CO_2 molecules existed in the form of HCO_3^- in water [40]. Therefore, in these cases, the CO_2 yield calculated from the amount of gas-phase CO_2 did not accurately reflect the mineralization extent of the carbon atoms in FSC. As discussed in section 3.4, when pH is 3.8, the CO_2 amount in the

reaction solution could be negligible, referring Henry's law constant and the dissociation constant.

Results of the reactions under O_2 without $KMnO_4$ and those with $KMnO_4$ (0.50 mmol) under Ar are compared at several reaction temperatures (Fig. 2). For both conditions, F^-, SO_4^{2-} and CO_2 amounts were similar at each temperature. However, at all tested temperatures, the reactions with $KMnO_4$ (0.50 mmol) under Ar (Figs. 2c and 2d) gave higher F^- and SO_4^{2-} amounts and yields than those released from reactions under O_2 in the absence of $KMnO_4$ (Figs. 2a and 2b).

Reaction of FSC with $KMnO_4$ under O_2 produced the highest F^- yield (52 ± 1%) at 300 °C (Table 2, entry 3). This finding demonstrates that not only the CF_3 group at C2 but also the C_6F_{13} group began to decompose. Under these conditions, the SO_4^{2-} yield was 100%, indicating that the sulfur atom in FSC was quantitatively mineralized. The pH value of the solution was 7.7 while the CO_2 yield increased to 31 ± 1%.

Because the combination of $KMnO_4$ and O_2 effectively mineralized FSC, we examined this mixture in more details as described in section 3.4. In all reactions listed in Table 2, trace amounts of 1H-perfluoroalkanes were detected in the gas phase (Table 2). It was of interest to optimize the reaction conditions to achieve a high mineralization efficiency while suppressing the formation of 1H-perfluoroalkanes, which are quite stable, some of them having high global warming potentials [41]. For example, CF_3H has a global warming potential of 12400 (for one hundred years) [42] and emissions of such a gas in East Asia have been gradually increasing since 2010 [43].

3.4. Reactions in superheated water containing both $KMnO_4$ and O_2

The first experiments used FSC (initial amount, 34.8 μmol) at 350 °C for 6 h under O_2 (13.6 mmol, ca 391-fold excess of FSC) while varying the initial $KMnO_4$ amount (Fig. 3). These experiments revealed that the F^- amount increased as the $KMnO_4$ amount increased up to 0.50 mmol (ca. 14-fold molar excess of FSC), after which the F^- amount remained essentially unchanged (Fig. 3a). When the $KMnO_4$ amount was 1.0 mmol, the F^- content was 422 μmol, or a 76% F^- yield. CO_2 was the major gas-phase product, and the amount increased as the initial $KMnO_4$ amount was increased (Fig. 3a). Small 1H-perfluoroalkane amounts were also found in the gas phase (Fig. 3b). It is worth noting that increasing the $KMnO_4$ amount from 0.25 mmol to 1.0 mmol reduced the CF_3H amount, which reveals that CF_3H could be decomposed in such a present reaction system. A reaction without any $KMnO_4$ was also performed. The released F^-, CO_2, and SO_4^{2-} amounts were 160, 199, and 17.0 μmol, which correspond to 29, 48, and 49% yields, respectively (Table 3, entry 1). The mineralization of FSC did not proceed effectively in the absence of $KMnO_4$.

Next, we explored the effect of the O_2 amount on the F^-, SO_4^{2-}, and CO_2 formations during reactions of FSC with 0.50 mmol $KMnO_4$ (ca. 14-fold molar excess of FSC) for 6 h (Figs. 4a and 4b). These experiments revealed that F^- and CO_2 formation was elevated when the O_2 amount was increased. When the initial O_2 amount was 13.6 mmol, the F^- content was 417 ± 20 μmol (entry 2 in Table 3), which corresponds to 75 ± 4 % yield. Under the same conditions, the CO_2 content in the gas phase reached 308 ± 28 μmol, which corresponds to 74 ± 7 % yield. The pH of the solution at the end of the reaction was 3.8. Under the conditions, we estimated the CO_2 amount present in the reaction solution as follows. The Henry's law constant (H) of CO_2 is 3.3×10^{-4} mol m^{-3} Pa^{-1} [44]. The CO_2 partial pressure [$P(CO_2)$] of the collected gas after the autoclave was released to normal pressure was 2.85 ± 0.21 kPa (= 1.01×10^5 Pa × $(2.82 \pm 0.21) \times 10^{-2}$; the

CO_2 concentration in the collected gas phase was 2.82 ± 0.21 % by gas chromatography). Therefore, the CO_2 concentration in the reaction solution was 0.94 ± 0.07 mM [= $H \times P(CO_2)$]. This concentration and the reaction solution volume (10 mL) indicated that the CO_2 amount present in the reaction solution was 9.4 ± 0.7 μmol. This value was only ca. 3% of the CO_2 amount (308 ± 28 μmol) present in the gas phase. Furthermore, the p*K*a (6.35, first dissociation step) [45] and the pH (3.8) indicated that most CO_2 molecules are not dissociated in the reaction solution ($[HCO_3^-]/([H_2CO_3] + [CO_2]) = 4.47 \times 10^{-7}$).

Therefore, the presence of CO_2 in the reaction solution could be quasi-negligible, relative to that in the gas phase.

The SO_4^{2-} content was 32.6 ± 1.0 μmol (entry 2 in Table 3), which indicated the yield was almost quantitative (94 ± 3%). Small amounts (0.1~15 μmol) of 1H-perfluoroalkanes were also detected (Fig. 4c). The CF_3H content gradually decreased when that of O_2 increased to 13.6 mmol.

Fig. 5a exhibits time courses of the formation of F^- and SO_4^{2-} and CO_2, when FSC was heated with 0.50 mmol $KMnO_4$ under O_2 (13.6 mmol) at 350 °C. The F^- and CO_2 amounts were enhanced by time. The F^- and SO_4^{2-} ions efficiently formed from the initial period such as 2 h. After 18 h, these amounts were 459 and 33.6 μmol, corresponding to 82 and 97% yields, respectively. This F^- yield is the highest value among those tested in the present study. The released CO_2 gradually increased with increasing time, and reached 349 μmol after 18 h, corresponding to 84% yield. In the gas phase, 1H-perfluoroalkane traces were detected (Fig. 5c), reaching maxima at ca. 6 h, and then decreased after prolonged time. The fluorine recovery—[(total moles of F atoms in F^- and 1H-perfluoroalkanes after reaction)/(moles of F atoms in FSC before reaction)]—at 18 h was calculated to 96% (See Mass balance calculations in SM). The

carbon recovery—[(total moles of C atoms in CO_2 and 1H-perfluoroalkanes after reaction)/(moles of C atoms in FSC before reaction)]—was 91% (See Mass balance calculations in SM). That is, most of the fluorine and carbon contents in the initial FSC could be accounted for F^-, CO_2, and 1H-perfluoroalkanes. The carbon recovery (91%) was lower than the fluorine recovery (96%).

Sulfur recovery was almost quantitative (97%, See Mass balance calculations in SM). The reaction solution after 18 h was analyzed by ion-chromatography, but did not reveal any short-chain perfluoroalkanoic acids such as CF_3COOH. However, when the reaction solution was characterized by electrospray ionization mass spectrometry, which is more sensitive than the above technique, a peak with a *m*/*z* signal of 131, corresponding to $[CF_3COO + H_2O]^-$, was detected (Fig. 6), indicating the presence of traces of CF_3COOH.

3.5. Proposed reaction mechanism

To monitor the fate of $KMnO_4$, X-ray diffraction was achieved on the precipitates recovered after the reaction of FSC containing 0.50 mmol $KMnO_4$ under O_2 (initial amount, 13.6 mmol) at 350 °C for 2, 6 and 18 h (Fig. 7). The patterns did not display any diffraction peaks originating from $KMnO_4$, while peaks assigned to MnO_2 only were detected. This result is unsurprising because reports on the decomposition of persistent chemicals by treatment with $KMnO_4$ in superheated water [35–37] have indicated that $KMnO_4$ is converted to MnO_2 (Eq. 4), which then acts as the oxidizing agent. In the present system, it had been unclear whether most of the MnO_4^- was transformed into MnO_2 before the FSC starts to decompose, because large amounts of F^- ions formed even after short reaction periods (such as 2 h, Fig. 5a). Nevertheless, during the period when the 1H-perfluoroakane amounts decreased (after 6 h, Fig. 5b), $KMnO_4$ had already

been converted into MnO_2. To clarify the role of the in situ formed MnO_2 on the mineralization of FSC in more detail, a two-stage reaction was performed. i) First, aqueous $KMnO_4$ (0.50 mmol in 10 mL) without FSC was heated at 350 °C for 2 h with O_2 (initial amount 13.6 mmol). This reaction period was enough to convert $KMnO_4$ into MnO_2 (Fig. 7a). ii) After the autoclave was cooled, FSC (37.5 μmol) was added to the reaction mixture in the autoclave. The vessel was then pressurized with O_2 (13.6 mmol) and reacted at 350 °C for 6 h. This two-stage operation efficiently released F^- (475 μmol, 72 % yield), SO_4^{2-} (35.3 μmol, 94% yield), and CO_2 (353 μmol, 78% yield) (Table 3, entry 3). These yields were similar to the corresponding yields obtained from the reaction where both FSC and $KMnO_4$ were charged initially, pressurized with O_2 (13.6 mmol), and then heated at 350 °C for 6 h (Table 3, entry 2). This result clearly indicates that the in situ formed MnO_2 dominantly acts as the oxidizing agent for the FSC mineralization.

The observed high fluorine (96%) and sulfur (97%) recoveries mentioned above indicate that the F^- and SO_4^{2-} concentrations in the reaction solution do not meaningfully decrease by the adsorption of these ions on the in situ formed MnO_2 surface. Of course, it is not surprising that traces of the fluorine component are detected on the formed MnO_2 surface by means of a sensitive analytical method. In fact, after 18 h-reaction, the collected precipitate was analyzed by X-ray photoelectron spectroscopy and the F(1s) spectrum displayed a peak around 684 eV, which corresponds to F^- (Fig. S-4 in SM). In contrast, the spectrum did not show any peak assigned to carbon-fluorine bond (if the bond was present, the peak would appear at ~689 eV). This result is consistent with the fact that FSC was efficiently mineralized by this treatment.

On the basis of our observations of the products generated under the reactions described herein, as well as from the literature, FSC decomposes according to the suggested process displayed in Scheme 2.

When FSC was heated in superheated water containing $KMnO_4$ under an excess O_2, the thioether bond (C-S-C) in the non-fluorinated moiety can be oxidized to give a sulfone structure (C-SO_2-C). This transformation is supported by the oxidation of common thioethers with electrophilic oxygen such as H_2O_2 [46]. Further oxidation around S atom is likely to lead to a fluorotelomer sulfonate, $C_6F_{13}CH_2CH_2SO_3^-$. Actually, the formation of fluorotelomer sulfonate from sulfone homologue is reported in the electrochemical degradation for fluorotelomers [18]. The sulfonate derivative induced desulfonation, which releases C_6F_{13}• radical, SO_4^{2-}, and CO_2. The degradation steps of FSC until here seem to proceed easily because the SO_4^{2-} yield in the present system reached almost 100% as described above.

While the non-fluorinated moiety decomposes, a CF_3• radical is also released from C2. The C_6F_{13}• radical likely reacts with O_2 and water to form $C_6F_{13}OH$. Because perfluoroalcohols are unstable [47, 48], $C_6F_{13}OH$ releases into HF and $C_5F_{11}COF$ acid fluoride (Eq. 5), which can be hydrolyzed to produce the corresponding $C_5F_{11}COOH$ perfluoroalkanoic acid [49] (Eq. 6).

$$C_6F_{13}OH \rightarrow C_5F_{11}COF + HF \quad (5)$$

$$C_5F_{11}COF + H_2O \rightarrow C_5F_{11}COOH + HF \quad (6)$$

The sequence of these steps results in the CF_3COOH formation, the shortest perfluoroalkanoic acid which was consistently detected by electrospray ionization mass spectrometry. The stepwise degradation of perfluoroalkanoic acid via the formation of shorter-chain analogues as shown here has been frequently described in the literature [10, 11, 18, 29, 39].

According to the same mechanism, CF_3COOH decomposes into CO_2 and HF via the formation of CF_3OH. The $CF_3^{\bullet}$ radical, released from C2 also reacts onto O_2 and H_2O to generate CF_3OH that is further transformed into CO_2 and HF via COF_2. Recently, decomposition of persistent chemicals in superheated water in the presence of alkali reagent was reported [50, 51]. When such a system is applied to perfluoroalkanesulfonic acids, the perfluoroalcohol formation seems to be accelerated [50]. If the reaction solution is highly basic, such a possibility should be accounted.

In addition to the above decomposition processes, which produce the major products, processes that form the minor products, the 1H-perfluoroalkanes, may also occur. The released $C_6F_{13}^{\bullet}$ radical reacts with H_2O to yield $C_6F_{13}H$. The formation of 1H-perfluoroalkanes during reactions of perfluorinated compounds in superheated water was reported, where the hydrogen atoms in 1H-perfluorolkanes arise from water [29, 52]. When $KMnO_4$ and O_2 were present, $C_6F_{13}H$ could be transformed into $C_6F_{13}OH$, which decomposed into $C_5F_{11}COF$ as described above. Likewise, the shorter-chain 1H-perfluoroalkanes ($C_5F_{11}H$ to CF_3H) could be produced as byproducts after carbon–carbon bond cleavage between the perfluoroalkyl and the carboxyl groups. This is consistent with a previous study reporting that heating PFOA at ~300 °C in a glass tube underwent decarboxylation to form CO_2 and 1H-perfluoroalkanes [53].

There have been several reports on the superheated water decomposition of perfluorinated surfactants [50, 54–58]. Among them, the destruction that proceeded by oxidative way has been quite rare [56]. On the other hand, to our knowledge, the present report on the oxidative decomposition of FSC is the first example for the degradation of fluorotelomer surfactant in superheated water. Direct comparison on the reactivity of the present FSC and perfluorinated molecules is difficult because of a few examples. Accumulation of the data for superheated water

reactions of both perfluorinated and fluorotelomer surfactants is thus desired, as further investigations.

4. Conclusions

A fluorotelomer surfactant (FSC) was involved in reactions in hot water (70–90 °C) with $S_2O_8^{2-}$ anions or in superheated water with $KMnO_4$. This examination is the first report on the degradation of FSC. Hot water under the former conditions was not efficient to mineralize FSC. Decomposition of FSC molecule occurred only around CF_3 group at C2. FSC was only slightly soluble in aqueous $K_2S_2O_8$ and its low solubility of FSC in water may be the reason for its low reactivity. In contrast, under the latter conditions, the mineralization moiety was extended to C_6F_{13} group, and it mineralized greater by increasing the O_2 amount. Specifically, when FSC was treated with 0.50 mmol $KMnO_4$ under O_2 (13.6 mmol) at 350 °C for 18 h, the F^- and SO_4^{2-} yields in the reaction solution and that of CO_2 in the gas phase reached 82, 97, and 84%, respectively. These are optimized conditions to release F^- ions. In addition to these major products, gas-phase 1H-perfluoroalkanes ($C_nF_{2n+1}H$, n = 1~6) were also produced. After reaction of FSC for 18 h, the carbon, fluorine, and sulfur recoveries were calculated to be 91, 96, and 97%, respectively. Accompanying the reactions, MnO_4^- was converted into MnO_2, and the in situ formed MnO_2 dominantly acts as the oxidizing agent for the mineralization of FSC.

Extension of this methodology (superheated water reaction in the presence of both $KMnO_4$ and O_2) to other organofluorine compounds and surfactants and scale-up of the reaction system are further planned in our laboratory.

Acknowledgments

The authors thank the Japan Society for the Promotion of Science for a grant (JSPS KAKENHI no. JP18H03402) and Elf Atochem and Tosoh Finechem Corp. for supplying free reactants.

Declarations of interest

None.

Appendix A. Supplementary data

Supplementary data (^{1}H and ^{19}F NMR spectra, quantification conditions of major products, mass chromatogram of FSC solution, calibration curve for the quantification of FSC, mass balance calculations, and XPS spectrum) associated with this article can be found, in the online version, at https://doi.org/10.1016/jcej.

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Table 1

Product yields of obtained by reaction of FSC in hot water with $S_2O_8^{2-}$[a]

Entry	Temperature (°C)	F^- (μmol) [yield (%)]	CO_2 (μmol) [yield (%)]	SO_4^{2-} (μmol) [yield (%) based on S atoms in $S_2O_8^{2-}$][b]
1	70	4.9 [1]	6.3 [2]	336 [34]
2	80	75.6 [16]	21.4 [6]	766 [77]
3	90	65.1 [14]	43.1 [12]	974 [97]

[a] Initial FSC amount, 29.7 μmol; reaction solution volume, 10 mL; initial $K_2S_2O_8$ amount, 0.50 mmol (50 mM as concentration); reaction time, 6 h.

[b] Based on the sulfur amount (1000 μmol) in the initial $S_2O_8^{2-}$. Although FSC molecule contains one sulfur atom, the amount (29.7 μmol) was much lower than the amount (1000 μmol) from $S_2O_8^{2-}$. Even if the initial sulfur atom of FSC is included in the yield calculation, the SO_4^{2-} yields become almost similar values. *Note*: the calculation of the SO_4^{2-} yield is different from that using $KMnO_4$ as described in the later sections.

Table 2

Products obtained by reaction of FSC under several combinations between O_2, $KMnO_4$ and Ar (300 °C, 6 h)

Entry	Initial $KMnO_4$ (mmol)	Coexisting gas (mmol)	Initial FSC (μmol)	F^- (μmol) [yield (%)]	CO_2 (μmol) [yield (%)]	SO_4^{2-} (μmol) [yield (%)]	1H-perfluoroalkanes in the gas phase (μmol)
1	none	O_2 (5.1)	30.1	95.4 [20]	71.4 [20]	16.5[55]	CF_3H (0.7), C_2F_5H (0.3), C_3F_7H (1.3), C_4F_9H (1.1), $C_5F_{11}H$ (1.3), $C_6F_{13}H$ (0.5)
2	0.50	Ar (5.1)	34.2	193 [35]	78.0 [19]	30.2[88]	CF_3H (15.2), C_2F_5H (4.0), C_3F_7H (0.8), C_4F_9H (4.1), $C_5F_{11}H$ (2.4), $C_6F_{13}H$ (0.1)
3	0.50	O_2 (5.1)	35.4	293 ± 2 [52 ± 1]	132 ± 4 [31 ± 1]	35.3 ± 0.2 [100]	CF_3H (14.8 ± 0.9), C_2F_5H (2.7 ± 1.3), C_3F_7H (1.0), C_4F_9H (4.9 ± 0.2), $C_5F_{11}H$ (2.3 ± 0.3), $C_6F_{13}H$ (0.1)

Table 3

Products obtained by reactions of FSC in the presence of O_2 (13.6 mmol) at 350 °C for 6 h

Entry	Initial $KMnO_4$ (mmol)	Initial FSC (μmol)	F^- (μmol) [yield (%)]	CO_2 (μmol) [yield (%)]	SO_4^{2-} (μmol) [yield (%)]	1H-perfluoroalkanes in the gas phase (μmol)
1	none	34.8	160 [29]	199 [48]	17.0 [49]	CF_3H (1.3), C_2F_5H (1.6), C_3F_7H (2.7), C_4F_9H (6.3), $C_5F_{11}H$ (5.1), $C_6F_{13}H$ (1.6)
2	0.50	34.8	417 ± 20 [75 ± 4]	308 ± 28 [74 ± 7]	32.6 ± 1.0 [94 ± 3]	CF_3H (9.5 ± 1.5), C_2F_5H (3.1 ± 0.5), C_3F_7H (1.1 ± 0.2), C_4F_9H (3.6), $C_5F_{11}H$ (4.4 ± 0.6), $C_6F_{13}H$ (0.4)
3[a]	0.50	37.5	475 [72]	353 [78]	35.3 [94]	CF_3H (1.8), C_2F_5H (2.3), C_3F_7H (2.2), C_4F_9H (4.6), $C_5F_{11}H$ (4.7), $C_6F_{13}H$ (0.7)

[a] Two-stage reaction. i) An aqueous solution of $KMnO_4$ (0.50 mmol in 10 mL) without FSC was heated at 350 °C for 2 h in the presence of O_2 (initial amount 13.6 mmol). ii) After the autoclave was cooled, FSC was added to the reaction mixture, and the autoclave was pressurized with O_2 (13.6 mmol) and then heated at 350 °C for 6 h.

99

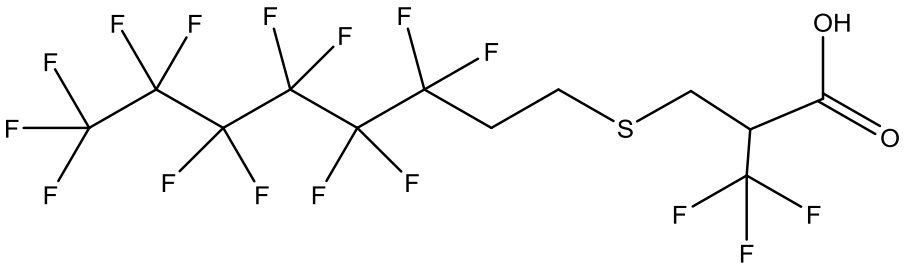
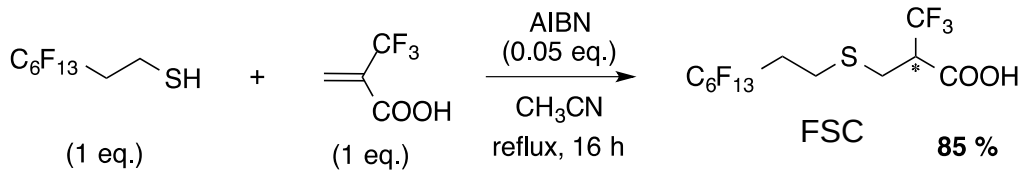


Fig. 1. Structure of 2H,3H,3H,5H,5H,6H,6H-4-thia-perfluoro(2-methyl)-1-dodecanoic acid (FSC)



Scheme 1. Radical addition of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanethiol onto 2-trifluoromethacrylic acid initiated by AIBN.

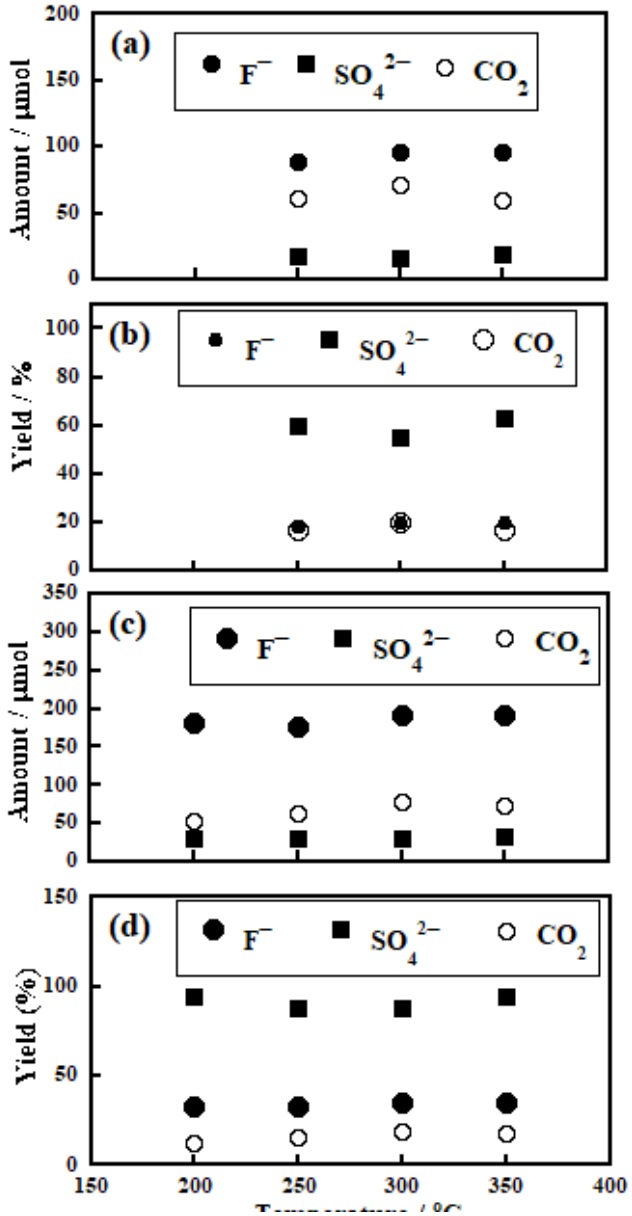


Fig. 2. Effect of temperature on (a) F^- and SO_4^{2-} amounts formed in the reaction solution and CO_2 amount produced in the gas phase and (b) their corresponding yields upon reaction of FSC (initial amount, 30.1 μmol) under O_2 (5.1 mmol) in the absence of $KMnO_4$ and (c) effect of temperature on F^- and SO_4^{2-} amounts formed in the reaction solution and CO_2 amount produced in the gas phase and (d) their corresponding yields upon reaction of FSC (initial amount, 34.2 μmol) in the presence of $KMnO_4$ (0.50 mmol) under Ar. Each reaction time was 6 h.

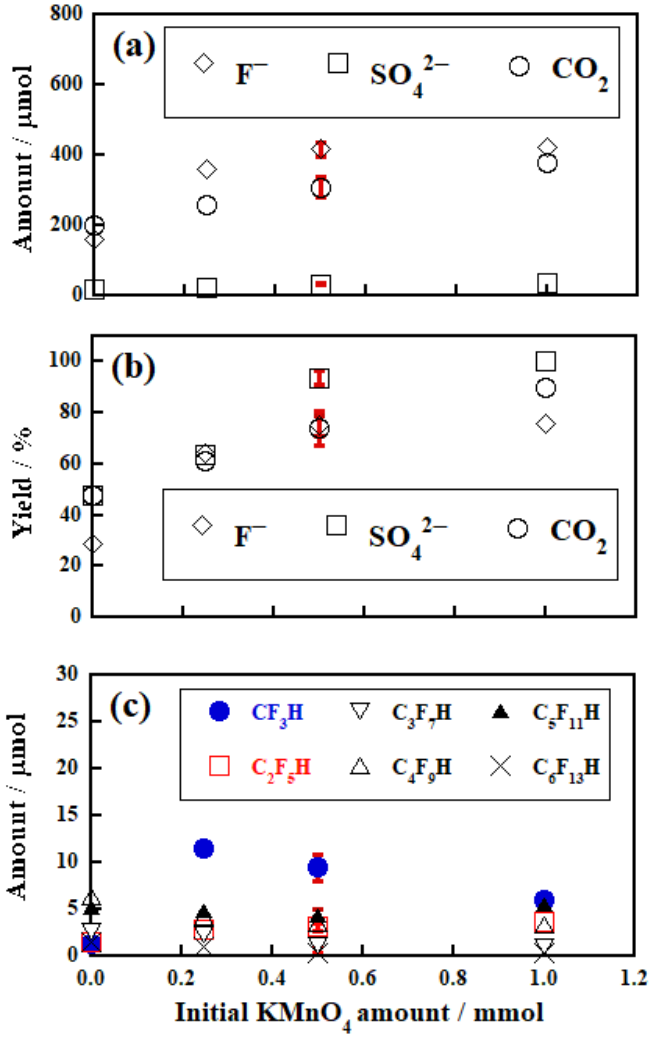


Fig. 3. Effect of initial $KMnO_4$ amount on (a) F^- and SO_4^{2-} amounts formed in the reaction solution and CO_2 amount released in the gas phase and (b) their corresponding yields and (c) 1H-perfluoroalkane amounts in the gas phase upon reaction of FSC (initial amount, 34.8 μmol) at 350 °C for 6 h under O_2 (13.6 mmol). Error bars at the initial $KMnO_4$ 0.50 mmol were obtained from two reactions under the same conditions.

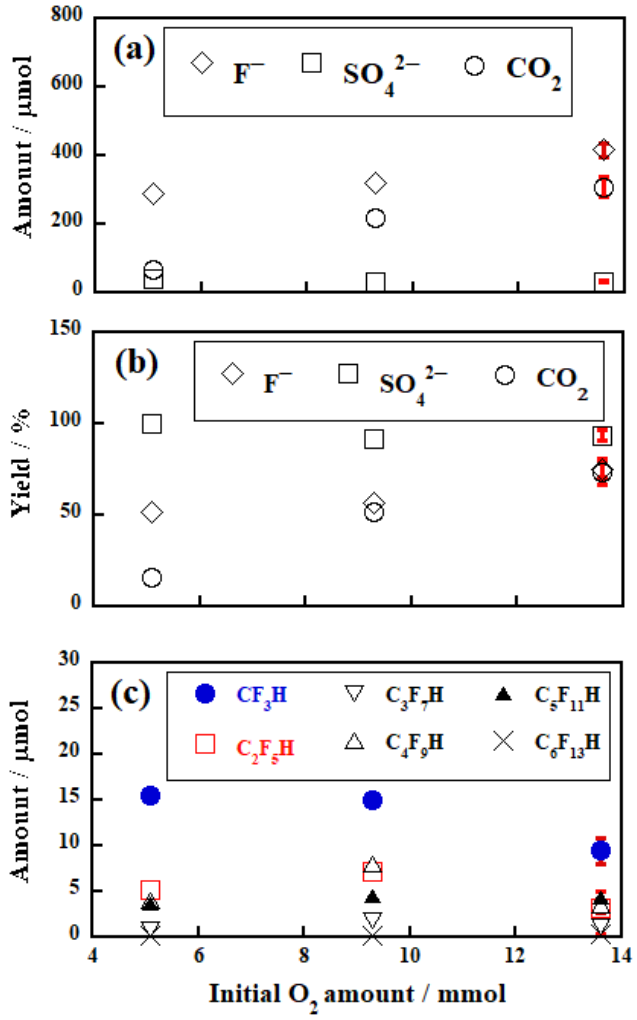


Fig. 4. Effect of initial O_2 amount on (a) F^- and SO_4^{2-} amounts formed in the reaction solution and CO_2 amount produced in the gas phase and (b) their corresponding yields and (c) amounts of 1H-perfluoroalkanes in the gas phase upon reaction of FSC (initial amount, 34.8 μmol) at 350 °C for 6 h containing $KMnO_4$ (initial amount, 0.50 mmol). Error bars at the initial O_2 13.6 mmol were obtained from two reactions under the conditions.

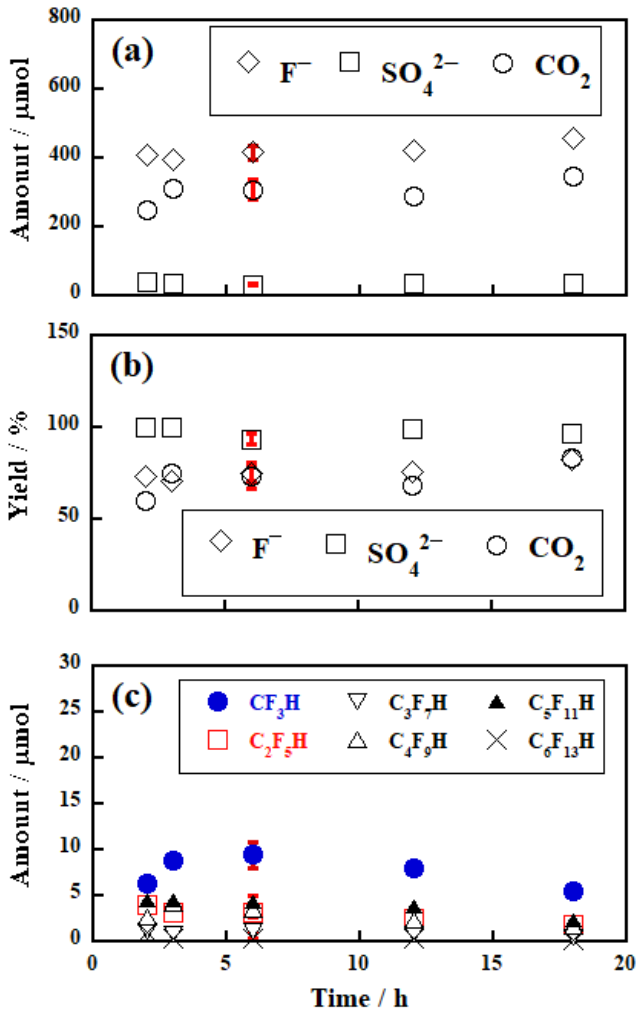


Fig. 5. Effect of reaction time on (a) F^- and SO_4^{2-} amounts formed in the reaction solution and CO_2 amount released in the gas phase and (b) their corresponding yields and (c) amounts of 1H-perfluoroalkanes in the gas phase upon reaction of FSC (initial amount, 34.8 μmol) at 350 °C containing $KMnO_4$ (initial amount, 0.50 mmol) under O_2 (initial amount, 13.6 mmol). Error bars at 6 h were obtained from two reactions under the same conditions.

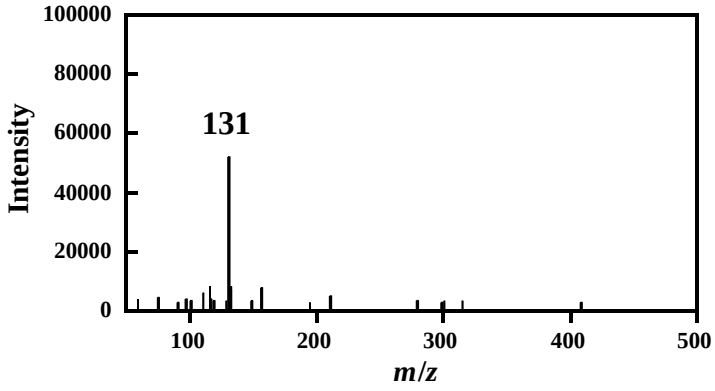


Fig. 6. Electrospray ionization mass spectrum of solution obtained by reaction of FSC (initial amount, 34.8 μmol) at 350 °C in the presence of $KMnO_4$ (initial amount, 0.50 mmol) under O_2 (initial amount, 13.6 mmol) for 18 h.

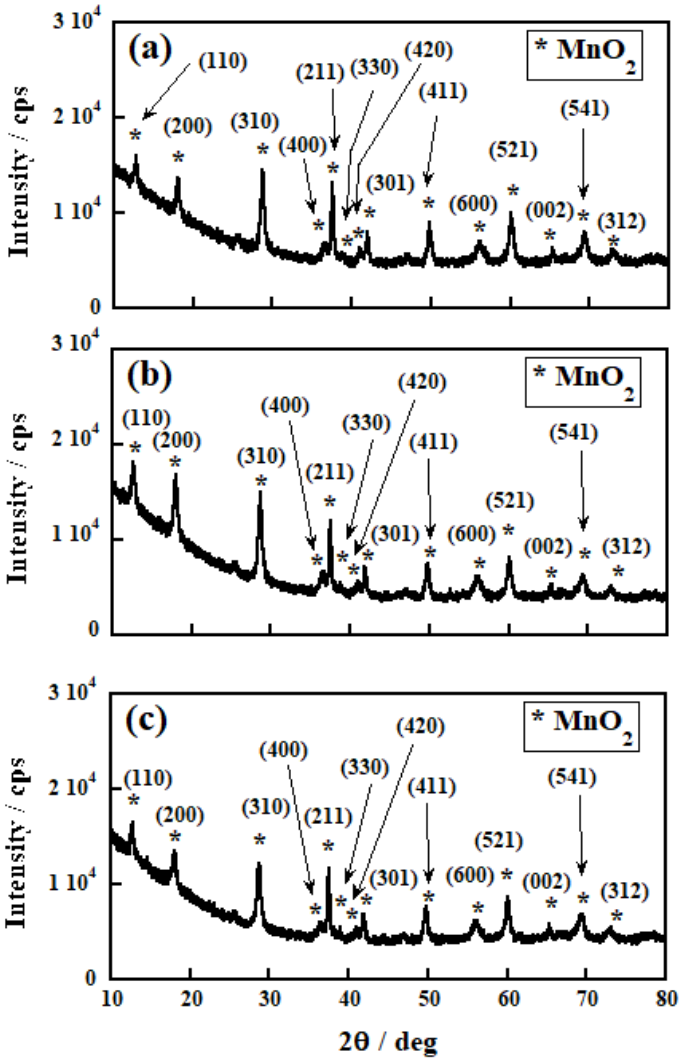
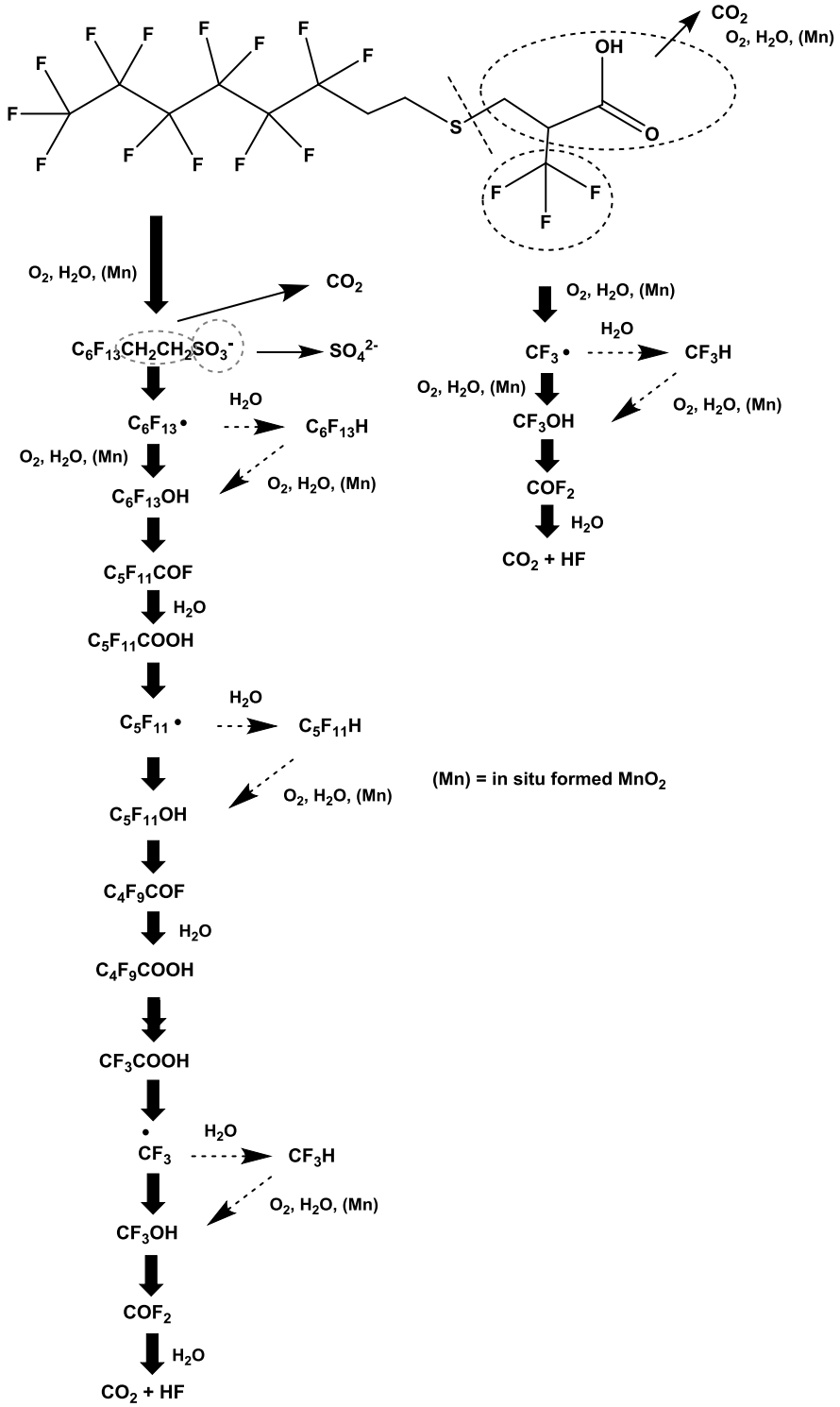


Fig. 7. X-ray diffraction patterns for precipitates collected after reactions of FSC (initial amount, 34.8 μmol) in the presence of $KMnO_4$ (initial amount, 0.50 mmol) under O_2 (initial amount, 13.6 mmol) at 350 °C for (a) 2, (b) 6, and (c) 18 h.


F
F
F
F
F
F
F
F
F
F
F
F
F
F
S
OH
O
CO2
O2, H2O, (Mn)
F
F
F
O2, H2O, (Mn)
CO2
C6F13CH2CH2SO3-
SO4 2-
C6F13 •
H2O
C6F13H
O2, H2O, (Mn)
O2, H2O, (Mn)
C6F13OH
C5F11COF
H2O
C5F11COOH
C5F11 •
H2O
C5F11H
O2, H2O, (Mn)
C5F11OH
C4F9COF
H2O
C4F9COOH
CF3COOH
• CF3
H2O
CF3H
O2, H2O, (Mn)
CF3OH
COF2
H2O
CO2 + HF
O2, H2O, (Mn)
CF3 •
H2O
CF3H
O2, H2O, (Mn)
O2, H2O, (Mn)
CF3OH
COF2
H2O
CO2 + HF
(Mn) = in situ formed MnO2

Scheme 2. Proposed decomposition mechanism for FSC in superheated water in the presence of both $KMnO_4$ and O_2.