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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 $HC_8F_{16}COOH$ × 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 $HC_8F_{16}COOH$.