



# Kinetics and mechanism insights into the photodegradation of hydroperfluorocarboxylic acids in aqueous solution

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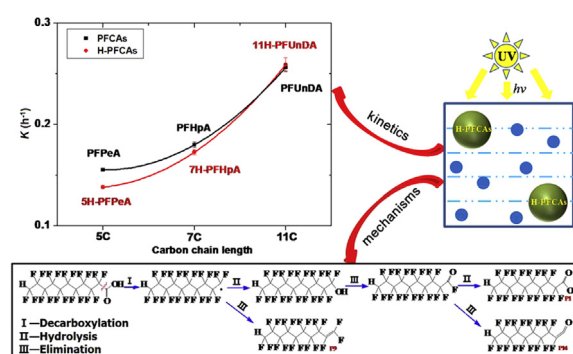
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## HIGHLIGHTS

- Pseudo-first-order rate coefficient of H-PFCAs increase with carbon chain length.
- H-PFCAs degrade slightly slower than corresponding PFCAs.
- High pH and humic acid was not favorable for H-PFCAs photodegradation.
- The inhibitory effect of three inorganic ions was  $\text{NO}_3^- > \text{CO}_3^{2-} > \text{HCO}_3^-$ .
- $\text{HC}_{10}\text{F}_{20}\text{COOH}$  photolysis involve decarboxylation, defluorination, elimination.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Keywords:

Hydroperfluorocarboxylic acids  
Photodegradation  
Kinetics  
Product identification

## ABSTRACT

Hydroperfluorocarboxylic acids (H-PFCAs) have attracted worldwide attention for their potential use as alternatives to perfluorocarboxylic acids (PFCAs). Decomposition of these chemicals is of great significance due to their possible environmental risks. In this work, the photodegradation of typical H-PFCAs ( $\text{HC}_n\text{F}_{2n}\text{COOH}$ ,  $n = 4, 6, 10$ ) in water by a 500 W mercury lamp was systematically examined. We found that the photodegradation of H-PFCAs all followed pseudo-first-order kinetics, and the photoreactivity increased with carbon chain length. The degradation pseudo-first-order rate coefficients of H-PFCAs were slightly slower than the corresponding PFCAs. The decomposition efficiency of  $\text{HC}_{10}\text{F}_{20}\text{COOH}$  was enhanced by lowering pH, but inhibited by the presence of humic acid. Three common inorganic ions showed inhibitory effect on  $\text{HC}_{10}\text{F}_{20}\text{COOH}$  photodegradation, with the order of  $\text{NO}_3^- > \text{CO}_3^{2-} > \text{HCO}_3^-$ . This is because these anions have different light absorption, making less light available for compound degradation. As a photosensitizer,  $\text{Fe}^{3+}$  had an obvious promoting effect on the reaction. According to the products identified by mass spectrometry analysis, decarboxylation, defluorination and elimination reaction were mainly involved in the photodegradation of  $\text{HC}_{10}\text{F}_{20}\text{COOH}$ . Toxicity predictions by ECOSAR program showed that photolysis can reduce the aquatic toxicity of  $\text{HC}_{10}\text{F}_{20}\text{COOH}$ . This work could provide useful information for developing a simple and effective technology to treat H-PFCAs in water.

## 1. Introduction

Perfluorocarboxylic acids (PFCAs) are a class of ubiquitous

environmental persistent organic pollutants that have attracted worldwide attention [1–3]. These compounds are widely used as emulsifying agents, wax additives, surfactants, surface treatment agents, fire

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retardants, and so on, due to their high surface-active effect, excellent thermal and chemical stability, and high light transparency [4–8]. They have been detected in various environmental matrices including waters, sediments, dust, and wildlife [9,10]. Recent studies indicated that long-chain PFCAs can accumulate in human body [11,12] and thus pose a risk to human health [13]. Although shorter-chain PFCAs ( $\leq C7$ ) are less bioaccumulative, they are still persistent to natural degradation processes [14]. Considering the potential hazards of these chemicals, the alternatives of PFCAs have been developed for industrial applications.

Hydroperfluorocarboxylic acids (H-PFCAs;  $HC_nF_{2n}COOH$ ) have been considered as the alternatives to PFCAs, in which a fluorine atom of the terminal trifluoromethyl group has been replaced by a hydrogen atom. Theoretically, H-PFCAs that contain a carbon–hydrogen bond are likely to decompose more easily than PFCAs. At present, there are two researches on the decomposition of H-PFCAs [4,15]. Hori et al. examined the decomposition of H-PFCAs ( $HC_nF_{2n}COOH$ ,  $n = 4, 6, 8$ ) with persulfate ( $S_2O_8^{2-}$ ) in hot water, and found that  $S_2O_8^{2-}$  could induce efficient mineralization of H-PFCAs to  $F^-$  ions [4]. At the conditions of  $\sim 380 \mu\text{mol/L}$  substrate,  $5.0 \text{ mmol/L}$   $S_2O_8^{2-}$  and  $60^\circ\text{C}$ , the initial decomposition rates of H-PFCAs were 7.1–12.7 times those for the corresponding PFCAs [4]. Then, they investigated the photocatalytic mineralization of H-PFCAs ( $HC_nF_{2n}COOH$ ,  $n = 4, 6$ ) with heteropolyacid ( $H_4SiW_{12}O_{40}$ ) photocatalyst, and UV-Visible light irradiation (wavelength  $> 290 \text{ nm}$ ) from a 200 W xenon–mercury lamp efficiently decomposed H-PFCAs to  $F^-$  and  $CO_2$  [15]. In the reaction solutions containing  $5 \text{ mmol/L}$  substrate and  $0.5 \text{ mmol/L}$  catalyst, the decomposition rate constants of H-PFCAs were 1.8–2.5 times higher than those for the corresponding PFCAs [15]. Both of these two works revealed that H-PFCAs can degrade more quickly than corresponding PFCAs. However, whether this situation still holds true for direct photodegradation remains unknown.

In recent years, photochemical methods have attracted much research interests around the world due to the advantages of high-efficiency and low secondary pollution [8,16]. To date, many efforts have been devoted to the photolysis of PFCAs. For example, Tang et al. found that perfluorooctanoic acid (PFOA) could be efficiently degraded in the UV-Fenton system, and the PFOA removal was 95% within 5 h [17]. Hori et al. have revealed that a 200 W xenon-mercury lamp can efficiently decompose PFCAs bearing C4–C8 perfluoroalkyl groups by use of  $50 \text{ mmol/L}$   $S_2O_8^{2-}$  [18]. It was reported that the PFOA decomposition and defluorination efficiencies by the UV/Cu–TiO<sub>2</sub> system reached 91% and 19%, respectively, after 12 h of reaction [19]. Compared with these photochemical and photocatalytic oxidation methods, direct photolysis which requires no addition of oxidants/catalysts is convenient and inexpensive. Giri et al. demonstrated that PFOA degradation was greatly enhanced by the combined UV photolysis (185 nm + 254 nm) with almost complete PFOA removal in 4 h [20]. Qu et al. showed that nearly complete removal of PFCAs (C4–C12) was achieved after 16 h of irradiation by a medium-pressure mercury lamp [1]. However, current knowledge on the decomposition efficiencies and mechanisms of H-PFCAs in a simple photolysis system is still lacking.

In this work, we systematically studied the Hg lamp induced photodegradation of typical H-PFCAs ( $HC_nF_{2n}COOH$ ,  $n = 4, 6, 10$ ) for the first time, in order to examine the degradation and transformation of these chemicals by direct photolysis. The objectives of this study are: (i) compare the photodegradation of H-PFCAs with corresponding PFCAs to reveal the difference in reaction rates, (ii) evaluate the effects of solution pH, humic acid (HA) and inorganic ions ( $Cl^-$ ,  $SO_4^{2-}$ ,  $CO_3^{2-}$ ,  $HCO_3^-$ ,  $NO_3^-$ ,  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Cu^{2+}$ , and  $Fe^{3+}$ ) on H-PFCAs photodegradation, (iii) elucidate reaction pathways of  $HC_{10}F_{20}COOH$  by identifying the degradation products with liquid chromatography–time-of-flight–mass spectrometry (LC-TOF-MS) and gas chromatography–mass spectrometry (GC-MS), (iv) evaluate the toxicity of reaction products to three aquatic organisms (fish, daphnid and green algae) by ECOSAR program. This work may provide useful information for the

environmental elimination of H-PFCAs.

## 2. Materials and methods

### 2.1. Chemicals and reagents

H-PFCAs including 5H-perfluoropentanoic acid (5H-PFPeA,  $HC_4F_8COOH$ ), 7H-perfluoroheptanoic acid (7H-PFHpA,  $HC_6F_{12}COOH$ ) and 11H-perfluoroundecanoic acid (11H-PFUnDA,  $HC_{10}F_{20}COOH$ ), and the corresponding PFCAs were purchased from J&K Scientific Ltd. (Beijing, China), and they were used without purification. Humic acid (HA,  $> 99\%$  purity) was obtained from Aladdin (Shanghai, China). Stock solutions of these chemicals ( $400 \mu\text{mol/L}$ ) were prepared in methanol and stored at  $4^\circ\text{C}$  in dark. HPLC grade methanol and formic acid were obtained from Merck Company (Darmstadt, Germany). All other chemicals of analytical grade were purchased from commercial sources. Ultrapure water was obtained from a Milli-Q water purification system (Millipore Bedford, MA, USA).

### 2.2. Reaction procedures

The photolysis experiments were performed at room temperature in an XPA-1 photochemical reactor (Nanjing Xujiang Electromechanical Plant, China). The schematic diagram and the real picture of the photochemical reactor was shown in Figs. S1 and S2, respectively. The light source was a 500 W mercury lamp, which was vertically placed in a quartz cooling trap with circulating water to keep temperature constant. The emission spectrum of the lamp was reported in our previous work [1].  $40 \text{ mL}$  of reaction solutions ( $1 \mu\text{mol/L}$ ) were transferred into quartz tubes ( $25 \text{ mm i.d.} \times 18 \text{ cm}$ ) for irradiation, at a  $5 \text{ cm}$  distance to the mercury lamp. The light intensity at sample position is  $15 \pm 0.1 \text{ mW/cm}^2$ , as measured by a UV-A radiometer with 365 nm sensor (Photoelectric Instrument Factory of Beijing Normal University, China).

Direct dilution of the stock with ultrapure water will make the reaction solutions contain a certain amount of methanol (V/V, 0.25%). The results in Fig. S3 show that methanol have some inhibitory effect on the photodegradation of H-PFCAs. Thus, the experiments were proceeded with methanol-free test solutions using the following method:  $0.1 \text{ mL}$  of stock in each quartz tube was dried with a gentle nitrogen flow until the methanol was evaporated completely, and then the solute was dissolved in  $40 \text{ mL}$  of ultrapure water by ultrasonic.

To evaluate how pH affects chemical degradation, the initial pH was adjusted to  $\pm 0.1$  of the desired values (3.0, 5.0, 7.0, 9.0, and 11.0) by HCl and NaOH solution. In parallel experiments, certain concentrations of water components, such as humic acid, metal cations ( $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Cu^{2+}$ , and  $Fe^{3+}$ ) and inorganic anions ( $Cl^-$ ,  $SO_4^{2-}$ ,  $CO_3^{2-}$ ,  $HCO_3^-$ , and  $NO_3^-$ ) were added into the reaction solution to study their effects. At different time intervals (0, 0.5, 1, 2, 4, 6, 8, 10, and 12 h),  $600 \mu\text{L}$  of solutions were sampled for analysis. Each treatment was repeated three times.

### 2.3. Analysis

Concentrations of H-PFCAs were analyzed on an Agilent 1260 infinity high performance liquid chromatography (HPLC) coupled with an API 4000 triple quadrupole mass spectrometer (AB Sciex, Concord, ON, Canada). Chromatographic separation was achieved on a Thermo Hypersil BDS C18 column ( $2.1 \text{ mm} \times 100 \text{ mm}$ , particle size  $2.4 \mu\text{m}$ ) maintained at  $30^\circ\text{C}$ . The mobile phase consisting of 0.3% formic acid in water (A) and methanol (B) was eluted at a flow rate of  $0.2 \text{ mL/min}$ . The chemicals were measured in negative electrospray ionization mode using multiple reactant monitoring (MRM). The details of analysis conditions were shown in Text S1.

Identification of polar photoproducts was performed using the SPE-LC-MS method. All reaction solutions were purified by a solid phase

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