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Light-induced degradation of perfluorocarboxylic acids in the presence of titanium dioxide

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Abstract

The UV-photon-induced degradation of heptafluorobutanoic acid was investigated in acidic aqueous solutions in the presence of titanium dioxide. Heptafluorobutanoic acid could be degraded with this photocatalyst in a light-induced reaction generating carbon dioxide and fluoride anions. Carbon dioxide evolution in a significant amount occurred only in the presence of molecular oxygen and the photocatalyst.

The light-induced degradation of trifluoroacetic acid, pentafluoropropanoic acid, nonafluorobutanoic acid, pentadecafluorooctanoic acid, nonafluorobutanesulfonic acid, and heptadecafluorooctanesulfonic acid in the presence of titanium dioxide was also studied. The perfluorocarboxylic acids under investigation are degraded to generate CO_2 and fluoride anions while both perfluorinated sulfonic acids are persistent under the experimental conditions employed in this study.

For all compounds photonic efficiencies of the mineralization reaction were estimated to be smaller than 1×10^{-5}.

To increase the photocatalytic activity mixed systems containing homogeneous phosphotungstic acid and heterogeneous titanium dioxide catalysts were also investigated. In the mixtures of these two photocatalysts, the formation rate of CO_2 increased with illumination time.

Keywords: Photocatalysis; Titania; Phosphotungstic acid; Heptafluorobutanoic acid

1. Introduction

Water soluble poly- and perfluorinated surfactants and their building blocks cause serious environmental problems. Therefore, there is a growing interest in the development of technologies to treat wastewater polluted with these substances. However, only a few investigations concerning the chemical or photochemical degradation of poly- and perfluorinated carboxylic acids or sulfonic acids in aqueous phases were published (Maruthamuthu et al., 1995; Mas et al., 1997; Hori et al., 2003a,b, 2004a,b, 2005a,b, 2006; Moriwaki et al., 2005; Schröder and Meesters, 2005).

Starting about three decades ago, titanium dioxide mediated photocatalytic degradation reactions have been investigated as a possible method for the treatment of wastewater polluted with organic pollutants (Hoffmann et al., 1995). Many halogenated organic compounds can be degraded photocatalytically (Hoffmann et al., 1995), but Mas et al. (1997) have shown that trifluoroacetic acid (TFA) can not be decomposed by titanium dioxide mediated photocatalysis (Théron et al., 1999, 2001) and TFA resists hydroxyl radical attack in aqueous solution (Maruthamuthu et al., 1995).

On the other hand, the light-induced degradation of such perfluorocarboxylic acids as TFA, pentafluoropropanoic acid (PFPA), heptafluorobutanoic acid (HFBA), nonafluoropentanoic acid (NFPA), and pentadecafluorooctanoic acid (PFOA) in aqueous solutions in the presence

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of phosphotungstic acid (12-tungsto(VI) phosphoric acid, $H_3PW_{12}O_{40}$) was recently reported by Hori et al. (2003a,b, 2004a,b). Perfluorocarboxylic acids in aqueous solutions were effectively degraded under UV-irradiation in the presence of molecular oxygen, and phosphotungstic acid acting as a homogeneous photocatalyst. The authors suggest that the degradation reaction is initiated by a Kolbe-like decarboxylation of the perfluorocarboxylic acid to form a perfluoroalkyl radical (Eq. (1)). In a following reaction step, the initially formed perfluoroalkyl radical containing two or more carbon atoms is converted to a perfluorocarboxylic acid shortened by one CF_2-unit thus releasing two fluoride anions (Eq. (2)). Mechanistic details are still unrevealed but it seems that the oxygen in the newly formed perfluorocarboxylic acid originates from water and not from molecular oxygen (Hori et al., 2004b)

$$\begin{aligned} \mathrm{F{-}(CF_2)_{\mathit{n}}CF_2COO^-} &\underset{-\mathrm{e}^-}{\rightarrow} \mathrm{F{-}(CF_2)_{\mathit{n}}CF_2COO^{\cdot}} \\ &\underset{-\mathrm{CO_2}}{\rightarrow} \mathrm{F-(CF_2)_{\mathit{n}}CF_2^{\cdot}} \end{aligned} \tag{1}$$

$$\mathrm{F-(CF_2)_{\mathit{n}}CF_2^{\cdot}} \xrightarrow[-2\mathrm{F}^-]{+2[\mathrm{O}],+[\mathrm{H}],+2\mathrm{e}^-} \mathrm{F-(CF_2)_{\mathit{n}}COOH} \tag{2}$$

Hori et al. (2004b, 2005a) reported also the light-induced degradation of PFOA and other perfluorinated carboxylic acids in aqueous solutions containing H_2O_2 or $K_2S_2O_8$ acting as oxidants. The persulfate anion, $S_2O_8^{2-}$, is decomposed by photolysis yielding two sulfate radical anions, $SO_4^{\cdot-}$. The formed $SO_4^{\cdot-}$ is acting as an oxidant in aqueous solutions and reacts with PFOA via electron transfer (Hori et al., 2005a) according to Eq. (1).

The stability of fluorinated surfactants in advanced oxidation processes was investigated by Schröder and Meesters (2005). Using O_3, O_3/UV, or O_3/H_2O_2 a 2-perfluoroalkyl-ethanol-polyethoxylate (trade name: Fluowet OTN) was almost completely eliminated, but the fluorinated 1-hydroxyethane-2-perfluoroalkanes generated as primary degradation products resisted further oxidative treatment.

The sonochemical decomposition of perfluorooctanoic acid and perfluorooctane sulfonate was studied by Moriwaki et al. (2005). Under ultrasonic irradiation the authors observed the degradation of perfluorooctane sulfonate yielding perfluorooctanoic acid which is further decomposed by fission of C–C bonds of the perfluoroalkyl chain. No degradation of perfluorooctanoic acid and perfluorooctanesulfonate by Fenton's reagent was observed. From their observations, the authors concluded that not the attack of a hydroxyl radical but high temperatures and high pressures as produced by sonication are necessary prerequisities for the effective degradation of the perfluorinated acids under investigation.

From the observations cited above it seems to be likely, that the degradation of perfluorinated carboxylic acids is not initiated by hydroxyl radical attack but by direct electron transfer from the perfluorinated carboxylic acids to a suitable oxidizing species. This is a reaction pathway likewise known for the photocatalytic degradation of carboxylic acids in acidic media containing titanium dioxide (Sakata et al., 1984; Wolff et al., 1991; Serpone et al., 2005). Therefore, we have studied the light-induced degradation of HFBA in acidic solutions containing titanium dioxide and mixtures of titanium dioxide and phosphotungstic acid ($H_3PW_{12}O_{40}$). For comparison, the light-induced degradation of TFA, PFPA, NFBA, PFOA, nonafluorobutane-1-sulfonic acid (NFBS), and heptadecafluorooctanesulfonic acid (HFOS) in aqueous systems containing TiO_2 was investigated as well.

2. Experimental details

2.1. Chemicals

TFA (99%, Aldrich T62200), PFPA (97%; Aldrich 245917), HFBA (99%; Aldrich, 164194), NFPA (97%, Aldrich, 396575), PFOA (96%; Aldrich 171468), NFBS (97%; Aldrich, 562629), HFOS (TCI, H0781), 2-amino-2-hydroxymethyl-1,3-propanediol (tris(hydoxymethyl) aminomethane; Wako, 205-06271), boric acid (Wako, 021-02195), perchloric acid (Kanto, 32060-08), phthalic acid (Wako, 163-02462), sodium fluoride (99.99%; Merck), and titanium dioxide (Degussa P25) were used as received. 2-Tungsto(VI) phosphoric acid hydrate ($H_3PW_{12}O_{40} \cdot n\text{-}H_2O$; Sigma–Aldrich, P4006) was freeze-dried for 24 h prior to use.

All aqueous solutions and suspensions were prepared with deionized water (conductivity: $5\ \mu S\ m^{-1}$) prepared with an Autostill WG 222 (Yamato Scientific Co.).

2.2. Photochemical procedures

In typical photochemical experiments, the solutions of HFBA (4.4 mM) were prepared by dissolving 0.47 g (2.2 mmol) of the acid in 500 ml deionized water, 0.01 M, and 0.1 M perchloric acid, respectively. Aliquots of these solutions (50 ml) were transferred to the reaction vessels (Pyrex vials; outer diameter: 40.5 ± 0.1 mm, height: 127.8 ± 0.2 mm, volume: 123.7 ± 0.4 ml) containing TiO_2 (0.1 g). The mixtures were dispersed by sonication for about 5 min and sealed with butyl rubber septa and aluminium crimp caps. The reaction vessels were purged with oxygen or nitrogen gas for about 15 min and then illuminated under continuous magnetic stirring using a 75 W mercury lamp (Toshiba SHL-100UV-Q2) emitting light in the 310–400 nm range with an intensity of 1.4–2.1 $mW\ cm^{-2}$. In some experiments the light intensity was 5.7–7.2 $mW\ cm^{-2}$ in the 310–400 nm range. Photocatalyst-free samples were treated in the same way as controls.

2.3. Analytical procedures

Liquid samples were filtered twice through hydrophilic 0.20 μm PTFE syringe filter units (Advantec Dismic-25HP) prior to analysis. Carbon dioxide analysis was performed using a Shimadzu GC-8A gas chromatograph