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Reductive Defluorination of Perfluorooctane Sulfonate

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Perfluorooctane sulfonate (PFOS) is under increased scrutiny as an environmental pollutant due to recent reports of its worldwide distribution, environmental persistence, and bioaccumulation potential. The susceptibility of technical PFOS and PFOS branched isomers to chemical reductive dehalogenation with vitamin B_{12} (260 μM) as catalyst and Ti(III)-citrate (36 mM) as bulk reductant in anoxic aqueous solution at 70 °C and pH 9 was evaluated in this study. Defluorination was confirmed by fluoride release measurements of 18% in technical PFOS, equivalent to the removal 3 mol F^-/mol PFOS, and 71% in PFOS branched isomers equivalent to the removal of 12 mol F^-/mol PFOS. Degradation of PFOS was further confirmed by monitoring the disappearance of PFOS compounds with reaction time by suppressed conductivity ion chromatography, LC-MS/MS, and ^{19}F NMR studies. The PFOS compounds differed in their susceptibility to reductive degradation by vitamin B_{12}/Ti(III) citrate. Chromatographic peaks corresponding to branched PFOS isomers disappeared whereas the peak corresponding to linear PFOS was stable. To our knowledge this is the first report of reductive dehalogenation of PFOS catalyzed by a biomolecule.

Introduction

Perfluorooctane sulfonate (PFOS, $C_8F_{17}SO_3H$) and related derivatives have been used for decades in a wide variety of industrial and consumer-based products ranging from surfactants, firefighting foams, to coatings (*1*). PFOS has been detected globally in human blood samples and wildlife tissues, including biota from pristine areas (*2–5*). Recent evidence indicates that PFOS is a persistent toxic pollutant that accumulates in higher organisms and could pose a potential human health risk (*6, 7*). These findings have prompted environmental regulatory agencies and the industry to initiate the phase out of PFOS manufacture (*8*).

Currently, little is known about the environmental sources and pathways of exposure of perfluoroalkyl compounds (PFAS). The widespread occurrence of PFOS and related substances in the environment could be attributed to the release during manufacture, use, and disposal of industrial and consumer products as well as transformation of their precursors (*9*). Studies suggested that the presence of PFAS in the remote regions is likely to occur through atmospheric or ocean water transport of volatile PFAS precursors (fluorotelomer and fluorosulfoamido alcohols), which are ultimately transformed to stable perfluorooctanoic acid (PFOA) and PFOS, respectively (*9, 10*). A study evaluating the fate of 171 perfluorinated substances using the biodegradation prediction software engine (CATABOL) estimated that 27% and 17% of the perfluorinated sulfonic acid and carboxylic acid containing compounds would be degraded to PFOS and PFOA, respectively (*11*). Dispersion of PFOS and derivatives in the environment could also occur via surface water, indoor air, and dust and adsorption to sediments and sludge (*7*).

The development of treatment techniques to decompose PFOS is crucial to reduce and eliminate the environmental release of this ubiquitous pollutant. To date neither biodegradation nor chemical degradation of PFOS under ambient conditions has been observed. PFOS displays an outstanding resistance against chemical and biological degradation. The recalcitrance has been attributed to the stability of the strong covalent carbon−fluorine bonds, the rigidity of the perfluoroalkyl chain, and the lack of reactive substituents in the PFOS molecule (*12*).

There are only two studies published on the degradation of perfluorooctane sulfonate in water. Moriwaki and coworkers (*13*) reported the breakdown of PFOS by ultrasonic irradiation. PFOA and short-chain perfluorinated carboxylic compounds were the products of the reaction. The decomposition of PFOS using zerovalent iron in subcritical water was examined by Hori et al. (*14*). The authors suggested that PFOS adsorbed on the iron surface was thermally decomposed, and F^- ion was slowly released. No organic degradation products were detected.

In the quest for PFOS biotransformation, microbial reductive dehalogenation should be considered. Reductive dehalogenation is an important mechanism contributing to the biodegradation of highly chlorinated compounds such as trichloroethylene and perchloroethylene, respectively (*15*). Most known reductive dehalogenases are dependent on the corrinoid cofactor, vitamin B_{12} (cyanocobalamin). This cobalt-containing cofactor catalyzes reductive dehalogenation in vitro when supplied with an appropriate reducing agent such as Ti(III) (*16*).

Here we report the defluorination of technical PFOS and branched PFOS isomers by biomimetic reduction with vitamin B_{12} as catalyst and Ti(III)-citrate as a bulk reductant in anoxic aqueous solutions.

Materials and Methods

Chemicals. Perfluorooctane sulfonic acid potassium salt (98% purity) was purchased from SynQuest Laboratories (Alachua, FL). Titanium(III) chloride (15% solution in HCl), vitamin B_{12} (99.0%), and perfluorooctanoic acid, PFOA, (96%) were supplied by Sigma-Aldrich (St. Louis, MO). 4′-(Trifluoromethoxy)-acetanilide (97% purity) was obtained from Matrix Scientific (Columbia, SC). HPLC-grade acetonitrile, methanol, and boric acid (99.5%) were purchased from Mallinckrodt Chemicals (Phillispsburg, NJ).

Identification and Quantification of Structural PFOS Isomers. Linear and branched structural isomers of technical perfluorooctane sulfonate acid potassium salt were identified based on tandem mass spectrometry (MS/MS) spectral data obtained by high-performance liquid chromatography coupled to MS/MS as suggested by Langlois and co-workers (*17*). The composition of structural perfluorooctane sulfonate (PFOS, $C_8F_{17}SO_3H$) isomers in the technical salt was determined by HPLC-suppressed conductivity detection and HPLC-MS/MS. The amount of the branched PFOS isomers

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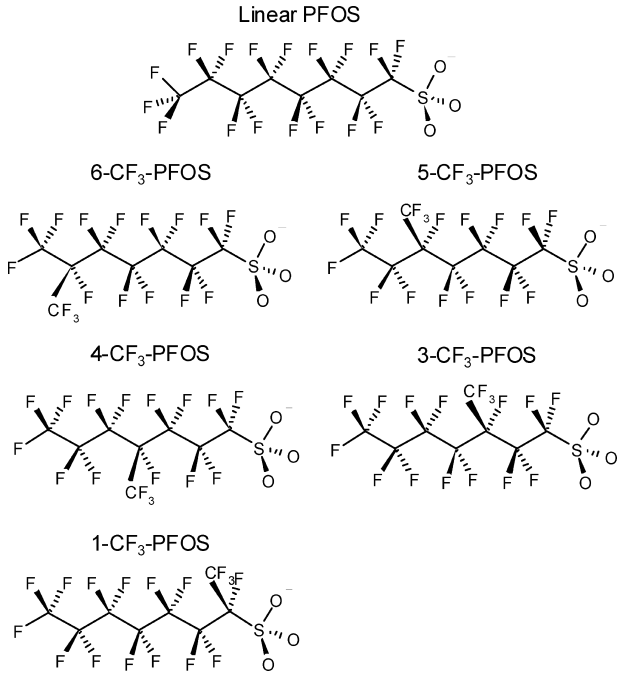

FIGURE 1. Chemical structure of linear PFOS and branched isomers, perfluoroisopropyl (6-CF_3-PFOS), 5-perfluoromethyl (5-CF_3-PFOS), 4-perfluoromethyl (4-CF_3-PFOS), 3-perfluoromethyl (3-CF_3-PFOS), and 1-perfluoromethyl (1-CF_3-PFOS).

TABLE 1. Percent Concentration of Technical PFOS Based on LC-MS/MS Studies

PFOS	composition (%)
1-CF_3-PFOS	8.7
3- and 4-CF_3-PFOS	2.7
5- and 6-CF_3-PFOS	13.2
linear PFOS	75.4

was calculated by relating the areas of the branched PFOS isomers peaks to the total area of all PFOS peaks, and it was found to be 24.6%. This observation was further confirmed by first-principle calculations performed in models of the linear and branched structural isomers of the compound. The chemical structure of the identified PFOS isomers and their abundance in the technical PFOS is shown in Figure 1 and Table 1, respectively. Linear PFOS and 1-perfluoromethlyl-PFOS (1-CF_3-PFOS) were chromatographically separated. 3-Perfluoromethyl- and 4-perfluoromethyl-PFOS (3- and 4-CF_3-PFOS) as well as 5-perfluoromethyl- and 6-perfluoroisopropyl-PFOS (5- and 6-CF_3-PFOS) coeluted as two different peaks.

Purification of PFOS Isomers and Linear PFOS. A solution containing technical PFOS (0.5 mM) and carbonate buffer (85 mM) was centrifuged (10000 rpm, 10 min). The linear PFOS compound precipitates under these conditions while the branched PFOS isomers remain in solution. The supernatant consisting of branched PFOS isomers (94.2%) and traces of linear PFOS was employed in further experiments.

Reductive Defluorination. Reductive defluorination of technical PFOS (332 μM) and reductive defluorination of the purified mixture of branched PFOS isomers (54 μM) by vitamin B_{12} (260 μM) and Ti(III)-citrate (36 mM) in a carbonate buffer (85 mM) was examined in batch assays at pH values ranging from 7.0 to 9.0. The Ti(III)-citrate solution was prepared as described by Holliger et al. (*18*). The pH of this solution was adjusted with concentrated NaOH to pH values ranging from 8.0 to 9.0. All experiments were set up in triplicate in an anaerobic box, utilizing 37 mL serum bottles sealed with viton stoppers and aluminum crimp caps and wrapped with aluminum foil to prevent decomposition of vitamin B_{12} by light. The flasks were incubated at 30, 50, or 70 °C under static conditions. After various time intervals, samples of the liquid medium were analyzed for fluoride using a VWR SympHony fluoride-selective combination electrode. Several control flasks lacking either vitamin B_{12} and/or Ti(III)-citrate or supplied with cobalt(II) in lieu of vitamin B_{12} were run in parallel. If evidence of fluoride release was obtained, selected samples were analyzed by HPLC-suppressed conductivity ion chromatography, ^{19}F NMR, and/or LC-MS/MS. Solid phase extraction (SPE) procedures were conducted to remove interferences and concentrate analytes when required.

Cleanup and Concentration of Samples. SPE cartridges (3 mL, 500 mg ODS-C18, Agilent Technologies, DE) mounted on a vacuum manifold were conditioned with 6 mL of MeOH, followed by 6 mL of deionized water. The desired volume of sample was loaded at 1 mL min^{-1}. SPE cartridges were rinsed with 4 mL of deionized water and then centrifuged (10000 rpm, 10 min) prior elution. Analytes were eluted with 4 mL of methanol and collected in clean Nalgene flasks. Solutions for chromatographic analysis were spiked with known concentrations of internal standard (PFOA, 31 μM) to determine recovery efficiencies. Recovery efficiencies of 104.0 $\pm$ 14.1% for triplicate samples were obtained.

^{19}F NMR. Analysis of technical PFOS and fluoride ion by ^{19}F NMR was performed by a method adapted from Moody et al. (*19*). Samples were dissolved in 90% H_2O/10% CD_3OD or in 90% CH_3OH/10% CD_3OD (0.7 mL) containing chromium acetylacetonate ($Cr(acac)_3$) (4 mg mL^{-1}) as the relaxation agent and the internal standard, 4′-(trifluoromethoxy)-acetanilide (4-TFMeAc, 140 mg L^{-1}), and then the samples were analyzed in 5 mm tubes. ^{19}F NMR spectra were acquired at 22 °C on a Varian Unity-300 spectrometer operating at a ^{19}F frequency of 282.208 MHz using a 5 mm four-nucleus (^{31}P, ^{13}C, ^{19}F, ^{1}H) probe. Acquisition involved a relaxation delay of 1.44 s followed by a 90° pulse (16.2 μs) and a Hahn echo with an echo delay of 100 μs, with 16384 complex data points and a spectral width of 33333 Hz. The acquisition time for all samples was 32.5 min. A 10 Hz line broadening was applied before zero filling to 32768 data points and Fourier transform. Baseline correction was performed using a fifth-order polynomial, and chemical shifts were referenced to the internal standard at −58.08 ppm (*20*).

LC-MS/MS. Mass spectrometry analysis was conducted by a method described by Langlois et al. (*17*). HPLC-MS/MS measurements were performed on a Magic 2002 (Michrom Biosciences, Inc.)/Thermoelectron LCQ Classic HPLC-MS system. Chromatographic separation was conducted on a MagicMS C18 microbore column (5 μm, 200 Å, 1 × 150 mm). The mobile phase consisted of a buffer solution (10 mM NH_4OAc in H_2O) and methanol. A gradient program with 5% B to 90% B in 35 min was used to elute the components of the samples with a flow rate of 50 μL min^{-1}, temperature of 40 °C, and injection volume of 25 μL. Negative ionization was employed to detect fluorinated sulfonates and acids. Tandem MS/MS was also applied to get structural information on selected ions (e.g., on m/z 499, $CF_3(CF_2)_7SO_3^-$). Helium was used as a collision gas and a 35% relative collision energy was applied in the MS/MS experiments. MS/MS spectra were recorded within a mass range of m/z 75–1000 using a scan time of 0.2 s.

HPLC-Suppressed Conductivity Ion Chromatography. PFOS compounds were quantified by a HPCL system with suppressed conductivity detector (ICS-3000 ion chromatography system, DIONEX, Sunnyvale, CA). The chromatograph was equipped with an autosampler (injection volume 5 μL), a pump, a degasser, a guard column, and a separation column (Acclaim Polar Advantage II, C18, 4.6 mm i.d., 25 cm length)

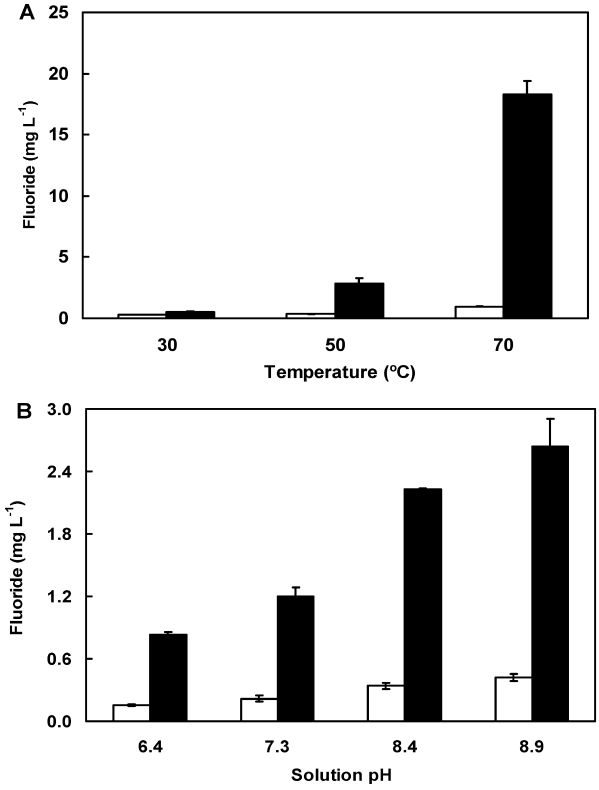

FIGURE 2. Effect of temperature at pH 9.0 (A) and effect of solution pH at 30 °C (B) on the biomimetic reductive dehalogenation of technical PFOS with vitamin B_{12} and Ti(III) citrate at day 7 and 36, respectively: control samples (PFOS + Ti(III) citrate) (white bars); treatment samples (PFOS + Ti(III) citrate + vitamin B_{12}) (black bars). Error bars (shown if larger than the symbols) represent standard deviations of triplicate assays.

operating at 35 °C. A mixture of 20 mM boric acid (pH 8.0) and 95% acetonitrile was used as the mobile phase at a flow rate of 1 mL min^{-1}. The ratio of boric acid to acetonitrile varied with the linear gradient program: from 0 min, 75:25 v/v, to 13.2 min, 45:55 v/v. The detection limit of branched PFOS isomers and linear PFOS was 1 mg L^{-1} based on a signal-to-noise ratio of 3. Since purified PFOS isomers are not available, the analytical sensitivity (peak height related to the concentration) was assumed to be the same for the different PFOS isomers.

Results and Discussion

The chemical reductive dehalogenation of technical PFOS with vitamin B_{12} and Ti(III) citrate was evaluated in this study. The impact of temperature, solution pH, vitamin B_{12}, and Ti(III) citrate dosages were assessed to determine the optimal treatment conditions. Figure 2 shows the fluoride release results obtained in experiments conducted at different temperature and pH values. The rate of PFOS degradation increased considerably with increasing temperature. An increase in temperature from 30 to 70 °C resulted in a 37-fold increase in the reaction rate. Raising the reaction pH from 7.5 to 9.0 also had a positive impact on the rate of PFOS defluorination, although less marked compared to the results obtained at high temperature. The effectiveness of vitamin B_{12} in catalyzing the reduction of PFOS was also evaluated at 30 °C (data not shown). Concentrations ranging from 20 to 1000 μM were tested, and 260 μM was found to be the optimum catalyst concentration. Increasing the Ti(III) citrate dosages from 10 mM to 36 mM also lead into a 6-fold increase in the kinetics of PFOS degradation at 30 °C (data not shown).

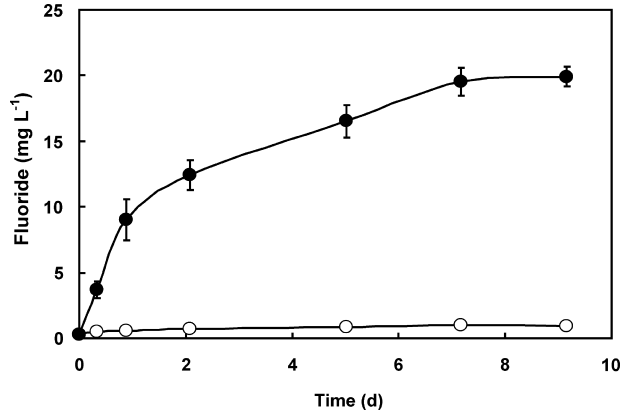

FIGURE 3. Time course of fluoride release of technical PFOS during the biomimetic reductive dehalogenation with vitamin B_{12} (260 μM) and Ti(III) citrate (36 mM) at 70 °C and solution pH 9.0 monitored by the fluoride-selective electrode: control samples (PFOS + Ti(III) citrate) (○); treatment samples (PFOS + Ti(III) citrate + vitamin B_{12}) (●). Error bars (shown if larger than the symbols) represent standard deviations of triplicate assays.

Figure 3 shows the time course of fluoride release of technical PFOS during the chemical reductive dehalogenation with vitamin B_{12} (260 μM) and Ti(III) citrate (36 mM) at 70 °C and solution pH 9.0. After 7 days, 18% PFOS defluorination was observed, equivalent to the removal of three fluorine atoms per mol of PFOS. ^{19}F NMR of the aqueous phase confirmed the presence of inorganic fluoride ions. The signal corresponding to fluoride ion appeared at −120.72 ppm. All chemical shifts were relative to the internal standard 4-TFMeAc (−58.08 ppm).

No significant reduction of PFOS was observed in the absence of either vitamin B_{12} or Ti(III) citrate, nor in controls in which vitamin B_{12} was replaced with cobalt(II) or in controls with Ti(IV)- in lieu of Ti(III)-citrate. These results indeed suggest that both the reducing agent and the biomolecule play a key role in the dehalogenation of perfluorooctane sulfonate. Monitoring the degradation of technical PFOS by suppressed conductivity ion chromatography, LC-MS/MS and ^{19}F NMR studies revealed that PFOS compounds differed in their susceptibility to reductive degradation by vitamin B_{12}/Ti(III) citrate. Chromatographic peaks corresponding to branched PFOS isomers disappeared whereas the peak corresponding to linear PFOS was stable.

The PFOS-based substances are commercially synthesized by electrochemical fluorination or telomerization processes. In the electrochemical fluorination, perfluoroalkyl isomers with linear and branched arrangements are formed as well as homologues with different chain lengths (*12*). In fact, technical PFOS used by industry is often a mixture of linear and branched structural isomers, with the latter making 20 to 30% of the total mass (*21–23*). ^{19}F NMR and LC-MS/MS studies revealed that the PFOS material used in our study contained 24.6% branched isomers, consisting chiefly of the following: perfluoromonomethyl and perfluoroisopropyl isomers: 3-CF_3-PFOS, 4-CF_3-PFOS (peak I in LC-MS/MS trace, Figure 5A), 5-CF_3-PFOS, 6-CF_3-PFOS (peak II), and 1-CF_3-PFOS (peak III). Ab initio DFT calculations were performed to determine the relative stability of the various isomers (Table S1 in Supporting Information). The calculations were conducted at the B3LYP/6-31++G(d,p) level as implemented in the GAUSSIAN03 computational package (*24*). Cluster models were employed to simulate the linear structure and the branched PFOS isomers in the acid form in the gas phase (i.e., isolated molecules) which, in a first stage of the theoretical study, were fully optimized. A further vibrational analysis of the optimized clusters confirmed that all structures corresponded to systems of minimum energy. The relative

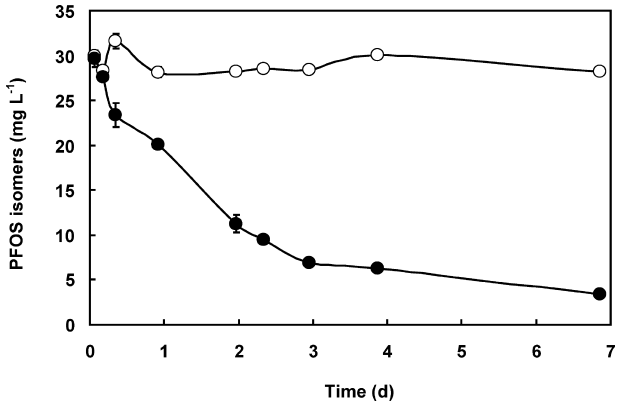

FIGURE 4. Time course for the disappearance of branched PFOS isomers in the chemical reductive dehalogenation with vitamin B_{12}/Ti(III) citrate based on suppressed conductivity ion chromatography analysis: control samples (PFOS + Ti(III) citrate) (○); treatment samples (PFOS + Ti(III) citrate + vitamin B_{12}) (●). Samples were incubated at 70 °C and pH 9.0 for 7 d. Error bars (shown if larger than the symbols) represent standard deviations of triplicate assays.

stability of the different structures was evaluated by comparing their corresponding Gibbs free energy calculated at standard conditions of temperature and pressure. The addition of the zero-point energy and the thermal effects to the electronic energy of each compound reveals that the linear structure is the most stable one followed by 1-CF_3-PFOS and 6-CF_3-PFOS with a difference in energy of ~0.3 and ~0.5 kcal mol^{-1}, respectively. The other branched isomers, namely, 3-CF_3-PFOS, 4-CF_3-PFOS, and 5-CF_3-PFOS, resulted in the less stable structures. The calculations established that the latter isomers have a similar Gibbs free energy, which differs from the most stable structure by about ~3 kcal mol^{-1}. These theoretical calculations are in agreement with experimental data obtained on the abundance of branched PFOS isomers in technical PFOS by LC-MS/MS studies (Table 1).

The branched PFOS isomeric fraction employed in the degradation studies was purified according to the protocol described in the Experimental Section. The susceptibility of these PFOS isomers to biomimetic reductive dehalogenation with vitamin B_{12} and Ti(III) citrate was evaluated at 70 °C and solution pH 9.0. The dehalogenation of the branched PFOS isomers was confirmed by fluoride release measurements, ^{19}F NMR, suppressed conductivity ion chromatography, and LC-MS/MS studies. Fluoride electrode measurements and ^{19}F NMR studies confirmed that the release of fluoride was significantly higher in branched PFOS isomers as compared to that in technical PFOS. After 5 days, 71% of the initial fluorine was released, equivalent to the removal of 12 mol of fluorine atoms per mole of branched PFOS, compared to only 3 mol of fluorine atoms per mole for the technical PFOS. Figure 4 shows the time course of branched PFOS isomer disappearance during dehalogenation based on ion chromatography analysis. The degradation of branched PFOS isomers followed pseudo-first-order kinetics with a reaction rate constant (K_1) of 0.0204 h^{-1}. This value is several orders of magnitude lower than the K_1 values commonly reported for chlorinated solvents known to be highly susceptible to reductive dehalogenation such as carbon tetrachloride and tetrachloroethylene (*25–27*). Nonetheless, the observed rate of PFOS degradation is faster compared to other persistent chlorinated pollutants. As an example, a K_1 value of 0.0017 h^{-1} has been reported for the reductive dehalogenation of *cis*-DCE by vitamin B_{12} (*26*); and K_1 values of 0.0026 and 0.0001 h^{-1} were observed for hexachlorobenzene and a polychlorinated benzene congener, respectively (*28*).

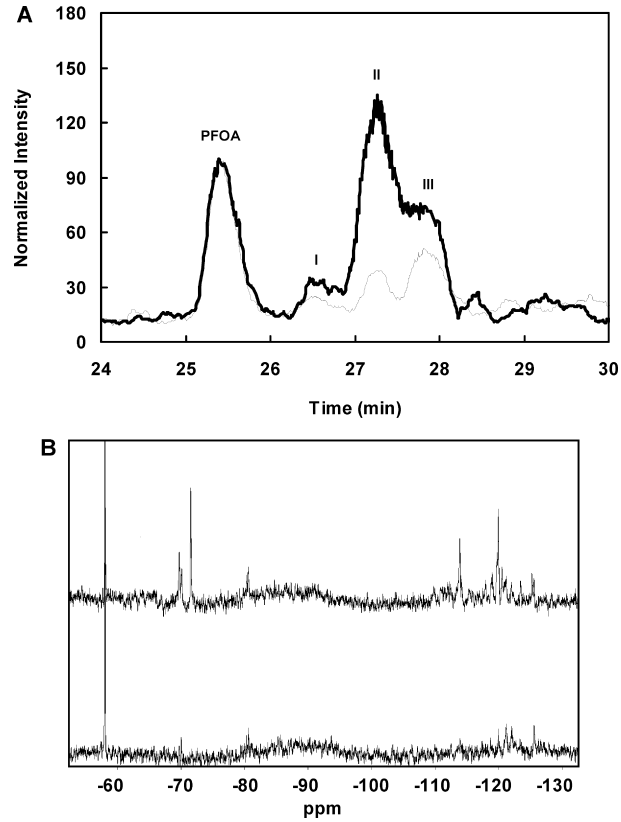

FIGURE 5. Biomimetic reductive dehalogenation of branched PFOS isomers at 70 °C and pH 9.0 at day 7. (A) LC-MS/MS chromatograms of branched PFOS isomers in control samples (PFOS + Ti(III) citrate) (thick line) and treatment samples (PFOS + Ti(III) citrate + vitamin B_{12}) (thin line). (B) ^{19}F NMR spectra of branched PFOS isomers in control (upper panel) and treatment samples (lower panel).

The LC-MS/MS chromatograms indicate removal of the isomers 5- and 6-CF_3-PFOS by 80 ± 1%, 3- and 4-CF_3-PFOS by 48 ± 1%, and 1-CF_3-PFOS by 44 ± 2% (Figure 5A). Isomer degradation was confirmed by the nearly complete disappearance of the signal corresponding to the branched CF_3 group and other organic fluorine signatures distinctive of the branched PFOS structures in ^{19}F NMR spectra (Figure 5B). These spectroscopic signals have been characterized and assigned for the individual branched PFOS isomers elsewhere (*29*).

As described previously, approaches involving cometabolic reductive dehalogenation are potentially promising for the degradation of perfluorinated surfactants. The reaction mechanism of vitamin B_{12}-catalyzed reductive dehalogenation, namely dechlorination, is poorly understood. The most commonly accepted models hypothesize that the attack involves radical intermediates (*16, 30*). Electron paramagnetic resonance (EPR) measurements conducted in this study have confirmed the formation of a vitamin B_{12} carbon-centered radical. The enhanced susceptibility of branched PFOS isomers as compared to linear PFOS to reductive dehalogenation may be related to the stabilizing effect of branched structures on radical intermediates resulting from the reductive attack. Tertiary radicals are widely known to be more stable than primary or secondary radicals (*31*). Moreover, steric hindrance caused by $-CF_3$ groups decreases the strength of the C−C bond in branched perfluoroalkanes (*32*). So presumably the reaction mechanism of reductive dehalogenation of branched PFOS isomers involves the cleavage of the most substituted C−C bond followed by rearrangements of intermediate radicals. Additional research needs to be conducted to understand the reaction mechanism of the

reductive dehalogenation of PFOS catalyzed by vitamin B_{12}/Ti(III) citrate.

To our knowledge this is the first report of reductive dehalogenation of PFOS catalyzed by a biomolecule. These results suggest that microbial transformation of some PFOS isomers might be possible in anaerobic environments. Furthermore, the observation that branched PFOS isomers are more prone to attack than linear PFOS provides clues for the design of more biodegradable perfluorinated chemicals.

Acknowledgments

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Supporting Information Available

One table with results from ab initio quantum mechanical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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