Supporting Information

Accelerated Degradation of Perfluorosulfonates (PFSAs) and Perfluorocarboxylates (PFCAs) by UV/Sulfite+Iodide: Reaction Mechanisms and System Efficiencies

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Table of Contents

Detailed Information on Methods and Materials

Chemicals and the Preparation of PFAS Stock Solutions.

All the per- and polyfluoroalkyl substances (PFAS) were purchased from Acros Organics (AO), Alfa-Aesar (AA), MP Biomedicals (MP), Oakwood Chemicals (OC), and SynQuest Laboratories (SQ). Information on their names, abbreviations, purities, CAS numbers, and vendors are listed in **Table S1**. Other chemicals (sodium sulfite, sodium bicarbonate, sodium hydroxide, and potassium iodide) were purchased from Fisher Chemical. Stock solutions (10 mM for each PFAS) was prepared by dissolving individual PFAS chemicals in deionized water (generated by a Milli-Q system) containing 20 mM NaOH to fully deprotonate the carboxylic and sulfonic acids. All stock solutions were kept at room temperature (20 °C).

Table S1. All PFAS Chemicals Used in This Study.

	chemical name	abbreviation	C_nF_{2n+1} length (n)	purity (%)	CAS#	vendor
	PFCA, C_nF_{2n+1}−COOH or sodium salt					
1	Sodium trifluoroacetate	TFA	1	98	2923-18-4	AA
2	Perfluoropropionic acid	PFPrA	2	97	422-64-0	AO
3	Perfluorobutyric acid	PFBA	3	98	375-22-4	AO
4	Perfluoropentanoic acid	PFPeA	4	97	2706-90-3	AA
5	Perfluorohexanoic acid	PFHxA	5	97	307-24-4	OC
6	Perfluoroheptanoic acid	PFHpA	6	98	375-85-9	AA
7	Perfluorooctanoic acid	PFOA	7	96	335-67-1	AO
8	Perfluorononanoic acid	PFNA	8	97	375-95-1	SQ
	PFSA, C_nF_{2n+1}−SO_3H or potassium salt					
9	Potassium nonafluorobutanesulfonate	PFBS	4	98	29420-49-3	AA
10	Potassium perfluorohexanesulfonate	PFHxS	6	95	3871-99-6	SQ
11	Perfluorooctanesulfonic acid	PFOS	8	97	1763-23-1	SQ
	FTSA, C_nF_{2n+1}−CH_2CH_2−SO_3H					
12	1H,1H,2H,2H-Perfluorohexanesulfonic acid	4:2 FTS	4	97	757124-72-4	SQ
13	1H,1H,2H,2H-Perfluorooctanesulfonic acid	6:2 FTS	6	97	6164-3-49	SQ
14	1H,1H,2H,2H-Perfluorodecanesulfonic acid	8:2 FTS	8	97	39108-34-4	SQ
	Special structures					
15	Sodium Fluoroacetate	MFA		98	62-74-8	MP
16	Difluoroacetic acid	DFA		98	381-73-7	OC
17	2,3,3,3-Tetrafluoropropionic acid	CF_3−CFH−COOH		97	359-49-9	OC
18	3,3,3-Trifluoropropionic acid	CF_3−CH_2−COOH		97	2516-99-6	OC

Quantitation of Short-Chain PFCAs, Iodide, and Sulfite.

A Dionex ICS-5000 ion chromatography (IC) system was employed to measure the concentration of anions. The IC system was equipped with a conductivity detector, a suppressor (AERS 4 mm), and a Dionex ICS6000 EG eluent generator using an EGC 500 KOH cartridge. An IonPac AS11-HC analytical column (4 × 250 mm) in line with an AG11-HC guard column (4 × 50 mm) was used for anion separation.

Specific methods for each analyte are below:

- $CF_3CFHCOO^-$, $CF_3CH_2COO^-$, TFA, DFA, MFA, and acetate: Gradient, 1.0 mL min^{-1}, 1−40 mM KOH, 30°C, 68 minutes.

- PFPrA, I^-, and SO_3^{2-}: Gradient, 1.5 mL min^{-1}, 20−40 mM KOH, 30°C, 45 minutes.

Quantitation of Long-Chain PFAS and Transformation Products.

PFAS parent compound quantitation. A high-performance liquid chromatography in line with a high-resolution quadrupole orbitrap mass spectrometer (HPLC-HRMS/MS, Q Exactive, Thermo Fisher Scientific) was used to monitor the concentration of PFAS parent compounds, with a detailed procedure fully described in our previous study.[1] Briefly, 2 μL sample was analyzed on a Hypersil GOLD column (particle size 1.9 μm, 100×2.1 mm, Thermo Fisher Scientific) and eluted with 10 mM ammonium acetate in nano-pure water (mobile phase A) and 10 mM ammonium acetate in methanol (mobile phase B) at a flow rate of 300 μL min^{-1}. The mobile phase gradient was set as follows: 95% A: 0−1 min, 95%−5% A: 1−6 min, 5% A: 6−8 min, and 95% A: 8−10 min. The MS spectra were obtained at the negative electrospray ionization (ESI) mode with a scan range of m/z 50−750 and a resolution of 70,000 at m/z 200. The MS data acquisition and analysis were performed with Xcalibur 4.0 (Thermo Fisher Scientific) with procedures described in our previous publications.[2-4]

Transformation products (TPs) identification. TPs were identified by Compound Discoverer (Thermo Fisher Scientific) with a suspect screening list. Suspect TP structures were examined based on the proposed PFAS degradation mechanism. The following four criteria were used to confirm the plausible TPs: (i) mass tolerance <5 ppm; (ii) isotopic pattern score >70%; (iii) peak area $>10^5$; (iv) peak area showing either an increasing trend or first showing an increasing trend then followed by a decreasing/stable trend over time.

Quality Assurance and Quality Control (QA/QC).

Before the measurement, the mass detector was calibrated using Pierce ESI Positive/Negative Ion Calibration Solutions (Thermo Scientific). The water matrix effects were evaluated by running a control experiment with a PFAS-free solution, which was then used to prepare the calibration standards. Eight points within the concentration range of 0.01−2 μM were included to prepare the standard series. No PFAS was detected in MilliQ water, pure methanol, and the matrix blank. Between each set of batch experiment samples, one MilliQ water blank was injected and checked for PFAS detection to avoid any carryover. The storage time for all samples before the measurement was less than three weeks at 4°C.

Fluoride Ion Quantitation.

The released fluoride (F^-) was measured using an ion-selective electrode (ISE, Fisherbrand Accumet) with a Thermo Scientific Orion Versa Star Pro meter. Each sample was added with an equal volume of total ionic strength adjustment buffer (TISAB for fluoride electrode, Thermo Scientific). The accuracy of F^- measurement was validated by IC in our previous work.[2, 3]

Texts S1 and S2 Referred to in the Main Text

Text S1. Rationales for the Kinetic Data Fitting Approach

We used $C/C_0>0.2$ data points for 1st-order fitting with the following reasons:

First, the ideal 1st-order reaction involving multiple reactants is rare. For an ideal 1st-order reaction, the same rate constant *k* applies regardless of the initial concentration C_0. However, most practical reactions that follow pseudo-first-order kinetics exhibit a lower *k* at a higher C_0. The kinetic fitting in this work was primarily conducted for engineering considerations. The detailed mechanism responsible for the pseudo-1st-order kinetics observed from UV/S+I warrants further research. Because *k* varies with the varying C_0, the use of concentrations in the bulk degradation range (e.g., C/C_0 from 1.0 to 0.2) for model fitting is much more meaningful than including the tail (e.g., C/C_0 from 0.01 to 0.0004) to represent the rate constant for a specific initial concentration C_0. In practice, 1st-order fittings involving very low C/C_0 values (e.g., 0.01, 0.003, 0.0004, etc.) usually overestimate the rate constant *k*. One could find that many of the bulk concentration data points (e.g., C/C_0 between 1.0 and 0.2) are above the fitted curve.

Second, due to the sensitivity of logarithmic functions, the concentration measurement using the tail such as from 99% to 99.96% removal (i.e., C/C_0 from 0.01 to 0.0004) will generate a significantly higher level of errors than using the bulk removal from 0% to 80% removal (i.e., C/C_0 from 1.0 to 0.2).

Third, the choice of $C/C_0>0.2$ is empirical. Including a data point at $C/C_0=0.1$ generally does not cause a significant overestimation, but such data point is often not collected. In many cases, the data dropped from $C/C_0>0.2$ directly to $C/C_0<0.05$ in the next sample, which could cause a significant overestimation of the fitted *k* for C_0 and thus not used. We could also use a narrower range such as C/C_0 from 1.0 to 0.5, but the fitted *k* values do not have a significant difference from using C/C_0 from 1.0 to 0.2. The latter data set includes more data points.

Text S2. Extended discussion on the 10W:2000mL photoreactor setting.

The standard 18 W: 600 mL setting has an effective light path of 2.9 cm (determined by H_2O_2 photolysis),[5] whereas the actual thickness of solution in this reactor setting is 2.1 cm. The 10 W: 2000 mL configuration has a solution thickness of 4.5 cm. This thickness exceeds the effective light path, and the lamp power is even lower. However, both the elevated temperature (up to 36°C, no water cooling for the 10 W: 2000 mL reactor configuration) and the mixing by magnetic stirring could partially overcome the drawbacks upon exceeding the effective light path. Our lab is conducting systematic optimization of reactor settings and will report the comprehensive results in the near future.

Figure S1 Referred to in the Main Text

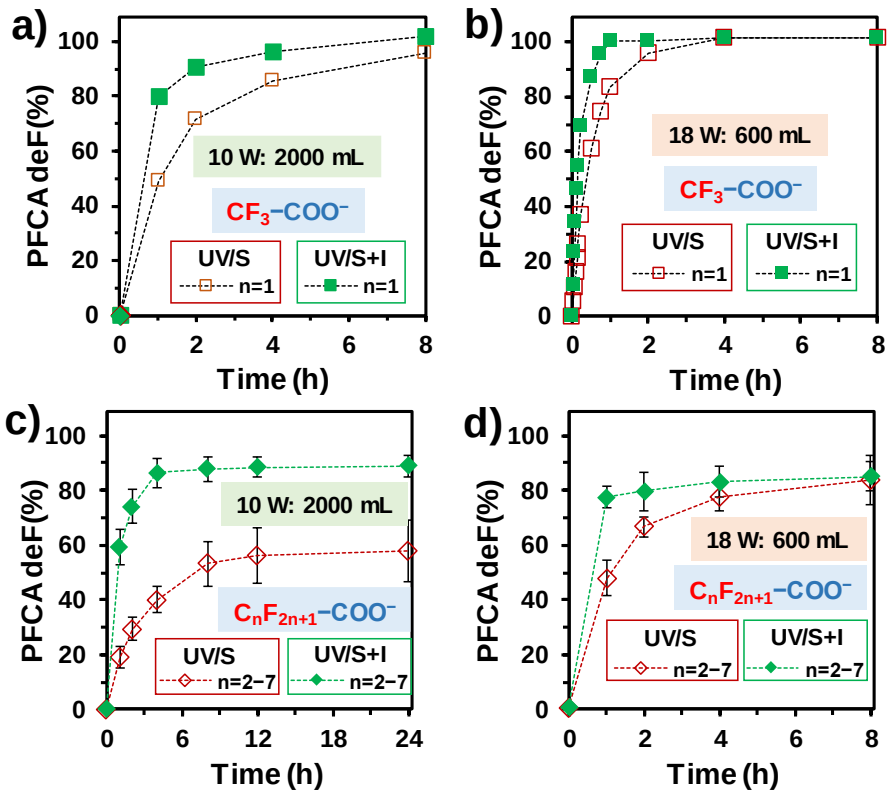

Figure S1. Defluorination of *n*=1 and *n*=2−7 PFCAs by UV/S (10 mM), and UV/S (10 mM) +I (2 mM) in two reactor configurations: (a+c) one 10 W lamp in 2000 mL water at 20−36℃ without cooling water and (b+d) one 18 W lamp in 600 mL at 20 ℃ with cooling water. Reaction conditions: individual PFAS (0.025 mM), $NaHCO_3$ (5 mM), pH 12.0, 254 nm irradiation. An extended discussion on the two reactor configurations is provided in **Text S2**.

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