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PAPER

Reductive degradation of perfluoroalkyl compounds with aquated electrons generated from iodide photolysis at 254 nm†

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The perfluoroalkyl compounds (PFCs), perfluoroalkyl sulfonates (PFXS) and perfluoroalkyl carboxylates (PFXA) are environmentally persistent and recalcitrant towards most conventional water treatment technologies. Here, we complete an in depth examination of the UV-254 nm production of aquated electrons during iodide photolysis for the reductive defluorination of six aquated perfluoroalkyl compounds (PFCs) of various headgroup and perfluorocarbon tail length. Cyclic voltammograms (CV) show that a potential of +2.0 V (vs. NHE) is required to induce PFC oxidation and −1.0 V is required to induce PFC reduction indicating that PFC reduction is the thermodynamically preferred process. However, PFCs are observed to degrade faster during UV(254 nm)/persulfate ($S_2O_8^{2-}$) photolysis yielding sulfate radicals ($E^\circ = +2.4$ V) as compared to UV(254 nm)/iodide (I^-) photolysis yielding aquated electrons ($E^\circ = -2.9$ V). Aquated electron scavenging by photoproduct triiodide (I_3^-), which achieved a steady-state concentration proportional to $[PFOS]_0$, reduces the efficacy of the UV/iodide system towards PFC degradation. PFC photoreduction kinetics are observed to be dependent on PFC headgroup, perfluorocarbon chain length, initial PFC concentration, and iodide concentration. From 2 to 12, pH had no observable effect on PFC photoreduction kinetics, suggesting that the aquated electron was the predominant reductant with negligible contribution from the H-atom. A large number of gaseous fluorocarbon intermediates were semi-quantitatively identified and determined to account for ~25% of the initial PFOS carbon and fluorine. Reaction mechanisms that are consistent with kinetic observations are discussed.

1. Introduction

Perfluoroalkyl compounds (PFCs), such as perfluorooctanoate ($PFOA$, $C_7F_{15}CO_2^-$) and perfluorooctane sulfonate ($PFOS$, $C_8F_{17}SO_3^-$), have been dispersed globally.^{1–4} Major issues^{3–13} related to the continued commercial use of highly perfluorinated chemicals need to be resolved, such as the development and demonstration of improved water treatment and *in situ* groundwater remediation technologies.^{9,12–14} PFCs have low vapor pressures, high acid dissociation constants (Table 1), and very high thermo-

chemical stabilities due to their intrinsic bond strengths (*e.g.*, 413.0 kJ mol^{−1} for F_3C-CF_3 and 530.5 kJ mol^{−1} for $F-C_2F_5$). The high C–F bond strengths contribute to their environmental persistence and lend a greater degree of resistance to conventional treatment approaches. In order to address this problem, a wide variety of alternative treatment technologies have been recently explored, including photolysis,¹⁵ persulfate photolysis,^{16–18} polyoxometalate photolysis,¹⁵ TiO_2 photocatalysis,^{19,20} iodide photolysis,^{21,22} Fe^0 reduction at sub- and supercritical conditions,²³ and sonolysis.^{12,24–30}

Based on these results, it appears that the PFC family of compounds may be more susceptible to reductive defluorination by electron-rich donors. However, reductive defluorination is most often studied in non-aquated solvents with easily-reduced unsaturated FCs.^{31–33} In general, saturated, linear PFCs are difficult to reduce due to their highly negative reduction potentials ($E^\circ < -2.0$ V).³⁴ For example, Hori *et al.* were able to reduce PFOS with elemental iron, Fe^0 ($E^\circ = -0.447$ V), but only at high temperatures and pressures (*i.e.*, 20 MPa, 350 °C).²³ In another study, Ochoa-Herrera *et al.*⁸ employed vitamin B₁₂ as an electron-transfer mediator and Ti(III)-citrate as a bulk reductant to reductively degrade PFOS. In particular, they compared the reduction rates of a linear PFOS and a branched PFOS and observed that the

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Table 1 The physicochemical properties of PFOA and PFOS

Property	PFOA, C ₇ F ₁₅ COOH	PFOS, C ₈ F ₁₇ SO ₃ H
Molecular weight	414 ⁵⁰	500; 538 for K ⁺ -salt
Melting point (°C)	45–50 ⁵⁰	>400 ⁵¹
Boiling point (°C)	189–192 ⁵⁰	Not measurable ⁵¹
Water solubility (g L ⁻¹)	3.4 ⁵²	0.519 ⁵¹
Vapor pressure (Pa) at 25 °C	1.33 × 10 ³ Pa	3.31 × 10 ⁴ Pa ⁵¹
Log <i>K</i> _{ow}		Not measurable ⁵¹
<i>K</i> _{aw}	1.02 × 10 ⁻³ ⁵³	<2 × 10 ⁻⁶ ⁵⁴
Henry's law constant	5.0–9.9 mol L ⁻¹ atm ⁻¹ ⁵⁵	3.19 × 10 ⁻⁴ Pa m ³ mol ⁻¹
p <i>K</i> _a	<0.5 ⁵⁶	–3.27 (calculated) ⁵⁷
CMC	~30 mM ²⁹	~2 mM ²⁹

reduction rates of the branched compounds were greater by a factor of 12 compared to the linear analogues. Similar results were observed for the isopropyl radical reduction of PFOS.³⁵

We have previously shown that UV irradiation of aquated iodide solutions can be used as a source of aquated electrons (e_{aq}^- ; $E^\circ_{aq/e} = -2.9$ V) that can be used for reducing perfluoroalkyl sulfonates (PFXS) and perfluoroalkyl carboxylates (PFXA).²¹ Iodide clusters with 4 to 6 water molecules ($I^-(H_2O)_{4-6}$) can eject aquated electrons during UV irradiation *via* charge-transfer-to-solvent (CTTS) states on the femto-second time scale.³⁶ In aquated solution, the hydrated or aquated electron is considered an excess electron surrounded by a small number of water molecules.³⁷ We noted previously that the reduction rates of the perfluoroalkyl sulfonates decrease linearly with decrease in carbon numbers (*i.e.*, reaction rates of C8 > C6 > C4), whereas the carboxylate analogues appear to be independent of carbon number (*i.e.*, C7 $\equiv$ C5 $\equiv$ C3).²¹

We now report results for the indirect photoreduction of six PFCs (PFOA, PFHA, PFBA, PFOS, PFHS, and PFBS) by aquated electrons in water at ambient temperature and under anoxic conditions. The primary objective of this study was to gain further insight into the UV photochemistry of iodide in the absence and presence of PFCs and to access the potential of iodide irradiation as a PFC remediation technology. First, indirect photoreduction *via* iodide photolysis was compared to direct photooxidation by persulfate (*i.e.*, peroxydisulfate, S₂O₈²⁻) photolysis using cyclic voltammetry and batch degradation experiments. Next, indirect PFC photoreduction kinetics, triiodide production kinetics, and time-dependent pH changes were evaluated over a range of initial pH₀, [I]₀, and [PFC]₀. Finally, we semi-quantitatively examined the indirect photoproduction of partially fluorinated gases.

2. Experimental details

2.1. Reagents

Perfluorooctanoate (PFOA: C₇F₁₅CO₂NH₄, 3 M), perfluorohexanoate (PFHA: C₅F₁₁CO₂H, >97%, Fluka), perfluorobutanoate (PFBA: C₃F₇CO₂H, >98%, Aldrich), perfluorooctane sulfonate (PFOS: C₈F₁₇SO₃K, 3 M), perfluorohexane sulfonate (PFHS: C₆F₁₃SO₃K, >98%, Fluka), and perfluorobutane sulfonate (PFBS: C₄F₉SO₃K, 3 M) were used as received. PFC stock solutions were prepared (500 mg L⁻¹) while pH was adjusted to between 6 and 8 with HCl or NH₄OH. 1.0 mol L⁻¹ K₂S₂O₈ (Aldrich) and KI (Fisher) stock solutions were freshly prepared every week and

stored in the dark. Argon (99.96%) used for purging reactions was obtained locally.

2.2. Photolysis experiments

PFCs with K₂S₂O₈ or KI stock solution were diluted with Milli-Q water to the desired concentrations. In most experiments, initial concentrations of PFCs were 10 mg L⁻¹, *i.e.*, [PFOS]₀ = 20 μM; [PFHS]₀ = 25.1 μM; [PFBS]₀ = 33.4 μM; [PFOA]₀ = 24 μM; [PFHA]₀ = 31.9 μM; and [PFBA]₀ = 46 μM. Photolysis was completed in a Pyrex glass reactor with a quartz window and irradiated with 254 nm-light source (UVP, 8 W). For most experiments, argon or air was continuously purged *i.e.*, bubbled, through the aquated solution. For experiments involving gaseous intermediate analysis, argon was continuously flowed through the headspace over the solution. A sample aliquot was taken at different time points during photolysis, and if necessary, diluted prior to analysis. The incident photon flux was determined to be 5.17(±0.06) × 10⁻⁵ mol L⁻¹ min⁻¹ by iodide/iodate actinometry using the intrinsic quantum yield of iodide/iodate as a reference (Fig. S1 in Supplementary Information†).³⁸

2.3. HPLC-MS PFC analysis

Initial PFC and possible aquated-phase intermediate analysis was completed by HPLC-MS (Agilent 1100 LC and Agilent 2440 MSD Ion Trap) with a Betasil C18 column (Thermo-Electron) (2.1 mm ID × 100 mm length, 5 μm-particle size). A 2 mM aquated ammonium acetate : methanol gradient mobile phase at a flow rate of 0.3 mL min⁻¹ was used for separation. The mass spectrometer was operated in negative ion mode, monitoring molecular ions of PFOS (499 *m/z*), PFHS (399 *m/z*), and PFBS (299 *m/z*), and the decarboxylated ions of PFOA (369 *m/z*), PFHA (269 *m/z*), and PFBA (169 *m/z*). The nebulizer gas pressure was 40 PSI, drying gas flow rate and temperature were 9 L min⁻¹ and 325 °C, the capillary voltage was set at +3500 V and the skimmer voltage was –15 V. HPLC analytical procedures are detailed elsewhere.^{28–30} An 8-point calibration curve containing all PFCs in question (1 to 250 ppb) was used to quantify the aquated PFC concentration. Methanol and water blanks were completed after every five samples and two quality controls (repeats of a calibration curve point) were completed after every ten samples.

2.4. Gaseous fluorinated intermediate GC-MS analysis

Fluorinated intermediates (perfluorooctyl iodide, C₈H₁₇I) produced during the reaction were analyzed by thermal desorption

gas chromatography mass spectrometry (TD-GC-MS). Argon purge gas from studied reactions was directed through a thermal desorption sample collection tube (Carbotrap, Supelco) as it exited the reactor. At the end of the reaction time the purge gas was turned off and the tubes were sealed to atmosphere. Collection tubes were desorbed on an Eclipse 4660 (OI Analytical), transferred to an Agilent 6890 GC, and detected with an Agilent 5973 MSD operated in electron impact (70 eV) ionization mode. Fluorochemical intermediates were identified by searching for characteristic ions, such as the trifluoromethyl cation, 69 m/z , as well as library searches. Adequate retention of the observed analytes on the collection tubes was tested by operating with two collection tubes in series. Products were either not detected or observed at negligible concentrations from the second collection tube, indicating that intermediates are not significantly lost from the first tube. $C_8H_{17}I$ response was calibrated by direct addition of $C_8H_{17}I$ (Aldrich) to collection tubes that were then analyzed identically to the samples.

2.5. PFC cyclic voltammetry

In order to study the redox behavior of the PFCs, cyclic voltammograms were measured using a Potentiostat/Galvanostat 273A (Princeton Applied Research). The cyclic voltammograms of each PFC (5 mM) were obtained with a scan rate of 0.1 V s^{-1} in acetonitrile with 0.1 M $LiClO_4$ as a supporting electrolyte. A Pt wire, a Pt mesh, and an Ag wire were used as working, counter, and (pseudo) reference electrode, respectively. The Ag wire was calibrated to be +0.2 V vs. NHE. Triiodide (I_3^-) was quantified by measuring its absorbance at 352 nm ($\epsilon = 26,400 \text{ M}^{-1} \text{ cm}^{-1}$) with a UV-spectrophotometer (Agilent 8453).

3. Results and discussion

3.1. Comparison of PFC oxidation vs. reduction

3.1.1. PFC oxidation vs. reduction: cyclic voltammetry. Fig. 1 and Figs. S2–S5† show the cyclic voltammograms (CVs) of the perfluoroalkyl carboxylates (PFXA) and perfluoroalkyl sulfonates (PFXS), where X = (O)ctane, (H)exane, and (B)utane. The PFXA family shows a similar tendency towards oxidation (Fig. 1a) with current flow starting above +2.0 V (vs. NHE). Only PFOA exhibits a minor peak at +2.2 V. This suggests that the corresponding oxidation rates are not strongly influenced by the perfluoroalkyl tail number. On the other hand, PFXA reduction behavior is noticeably different, especially when PFOA and PFHA/PFBA are compared. PFOA reduction begins at $E < -0.8$ V with a minor peak appearing at -1.1 V. PFHA and PFBA have two apparent reduction/oxidation peaks at $E = -0.7/-0.5$ V ($E_{1/2}^1 = -0.6$ V), and at $E = -1.1/-1.0$ V ($E_{1/2}^2 = -1.05$ V). This is consistent with stepwise defluorination *via* two sequential one-electron transfers.

The PFXS analogues have CV curves that are very different from each other (Fig. 1b). Below +2.0 V, PFHS and PFBS yield greater oxidation currents than PFOS, but above +2.2 V the PFOS oxidation current is much greater than those observed for PFHS and PFBS. In a similar fashion, PFHS and PFBS are reduced at $E = -1.2$ and -1.15 V, respectively, while PFOS reduction is initiated at a potential of -1.3 V with a higher current at the onset of reduction (Fig. 1b inset). In summary, the CVs of the six PFCs

Fig. 1 Cyclic voltammograms of (a) perfluorobutanoate (PFBA), perfluorohexanoate (PFHA), perfluorooctanoate (PFOA), and (b) perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHS), perfluorooctane sulfonate (PFOS). Scan rate 0.1 V s^{-1} in acetonitrile (0.1 M $LiClO_4$).

are not reversible, the PFCs are oxidized non-specifically, and PFOA and PFOS are different from their respective short-chain analogues. In all cases, a minimum potential of +2 V is required to initiate oxidation while PFC reduction begins at $E < -1.1$ V. The oxidation and reduction peaks in the blank samples appeared at around -0.8 V and $+1.8$ V, respectively (Fig. 1a and 1b), likely due to impurities of solvent (acetonitrile) and/or electrolyte ($LiClO_4$).

The CV patterns observed here are in qualitative agreement with previous reports. For example, Guan *et al.* oxidized PFOA at a boron-doped diamond (BDD) electrode at +2.54 V.³⁹ Carter and Farrell oxidized PFOS using a rotating disk BDD electrode at an applied potential of +3.2 V.⁴⁰ In the case of PFC reduction, polytetrafluoroethylene (PTFE) was reported to be reduced at < -1.5 V,⁴¹ while linear PFCs, $n-C_6F_{14}$ and $n-C_8F_{18}$, were reduced at -2.4 V and -2.36 V, respectively.⁴² The unsaturated and/or branched PFCs are more readily reduced than their saturated, linear counterparts. This is consistent with the observed lower reduction potentials (*i.e.*, values range from -0.16 to -1.36 V) for perfluoroolefins.⁴² Combellas *et al.*⁴³ investigated the effects of the carbon tail on the electrochemical reduction potentials of C4, C6, and C8 perfluoroalkylphenylcyanides, which clustered around $E = -1.3$ V, indicating no significant tail-length effects. Thus, the higher current yields observed during the electrochemical reduction of PFOS are likely due to further reduction of defluorinated intermediates.

Table 2 Elementary reaction steps and rate constants for iodide and related species generated during photolysis

Elementary Reaction	Rate Constant and pK_a	Ref
(R0) $I^- + h\nu \leftrightarrow I^\bullet + e_{aq}^-$	$QY = 0.28-0.36$	44
(R1) $I^\bullet + I^- \leftrightarrow I_2^-$	$K_1 = k_1/k_{-1} > 1.2 \times 10^4$	58
(R2) $I^\bullet + I^\bullet \rightarrow I_2$	$k_2 = 1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	58
(R3) $I^\bullet + I_2^- \rightarrow I_3^-$	$k_3 \geq 6.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	48
(R4) $I_2^- + I_2^- \rightarrow I_3^- + I^-$	$k_4 = 3.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	48
(R5) $I_2 + I^- \leftrightarrow I_3^-$	$K_5 = k_5/k_{-5} = 7.2 \times 10^2$	48
(R6) $e_{aq}^- + e_{aq}^- \rightarrow H_2 + 2OH^-$	$k_6 = 5.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	47
(R7) $e_{aq}^- + H_2O \rightarrow H^\bullet + OH^-$	$k_7 = 1.9 \times 10^1 \text{ M}^{-1}\text{s}^{-1}$	47
(R8) $e_{aq}^- + H^+ \rightarrow H^\bullet$	$k_8 = 2.3 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$; $pK_a = 9.6$	47
(R9) $e_{aq}^- + O_2 \rightarrow O_2^{\bullet-}$	$k_9 = 1.9 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	47
(R10) $e_{aq}^- + I_2 \rightarrow I_2^-$	$k_{10} = 5.3 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	49
(R11) $e_{aq}^- + I_3^- \rightarrow I^- + I_2^-$	$k_{11} = 3.5 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	49
(R12) $e_{aq}^- + PF_n \rightarrow PF_{n-1}^\bullet + F^-$	See Table 3	
(R13) $H^\bullet + I^- \rightarrow HI^\bullet$	$k_{13} = 3.4 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	59
(R14) $H^\bullet + I^- \rightarrow H^\bullet + I^-$	k_{14}	
(R15) $H^\bullet + H^\bullet \rightarrow H_2$	$k_{15} = 7.7 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	47
(R16) $H^\bullet + I_2 \rightarrow H^\bullet + I_2^-$	$k_{16} = 3.5 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	49
(R17) $H^\bullet + I_2^- \rightarrow H^\bullet + 2I^-$	$k_{17} = 1.8 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	49
(R18) $H^\bullet + I_3^- \rightarrow H^\bullet + I^- + 2I^-$	$k_{18} = 2.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	49
(R19) $H^\bullet + OH^- \rightarrow e_{aq}^-$	$k_{19} = 2.2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	47
(R20) $H^\bullet + O_2 \rightarrow HO_2^\bullet$	$k_{20} = 2.1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	47
(R21) $H^\bullet + HO_2^\bullet \rightarrow H_2O_2$	$k_{21} = \sim 10^{10} \text{ M}^{-1}\text{s}^{-1}$	47
(R22) $H^\bullet + H^+ \leftrightarrow H_2^+$	K_{22} ; $pK_a(H_2^+) = 2.3$	47
(R23) $H_2^+ + I^- \rightarrow I^\bullet + H_2$	k_{23}	
(R24) $H^\bullet + PF_n \rightarrow PF_{n-1}^\bullet + F^- + H^+$	k_{24}	
(R25) $e_{aq}^- + K^+ \rightarrow K^\bullet$	$k_{25} < 5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$	47
(R26) $e_{aq}^- + Na^+ \rightarrow Na^\bullet$	$k_{26} = 2 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$	47
(R27) $e_{aq}^- + NH_4^+ \rightarrow NH_4^\bullet$	$k_{27} = 1 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$	47
(R28) $H^\bullet + NH_4^+ \rightarrow NH_3 + H_2^+$	$k_{28} < 4 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$	47
(R29) $H^\bullet + NH_3 \rightarrow NH_3^\bullet$	$k_{29} = 7.2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	47

3.1.2. PFC oxidation vs. reduction: batch degradation – persulfate and iodide UV photolysis. Based on the above results, we have chosen to examine in greater detail the UV/iodide system for the reduction of PFCs, and to compare the reductive pathways and kinetics induced by aquated electrons with an oxidative pathway initiated by sulfate radical anions ($E^\circ(SO_4^{\bullet-}/SO_4^{2-}) = +2.4 \text{ V}$) generated *via* the photolytic cleavage of the peroxy bond of persulfate ($-O_3SO-O_3SO^-$; O1–O3) (Table 2 and Table 3).^{12,16–18}

In both systems, PFOA and PFOS degradation follows second-order kinetics (E1–3).

$$d[PFOX]/dt = -k \cdot [R] \cdot [PFOX] \quad (E1)$$

where, R refers to e_{aq}^- and $SO_4^{\bullet-}$ in iodide and persulfate solutions, respectively. If we assume that [R] is at a steady-state (*i.e.*, constant concentration), which is much lower than [PFOX]; then E1 collapses to a simple pseudo first-order kinetic equation, E2, where, $k_{app} = k \cdot [R]$.

$$d[PFOX]/dt = -k_{app}[PFOX] \quad (E2)$$

$$[PFOX]_t = [PFOX]_0 \cdot \exp(-k_{app} \cdot t) \quad (E3)$$

Table 3 Reaction rate constants of aquated electron and hydroxyl radical with fluorocarbons and hydrocarbons

Reaction	Rate constant ($\text{M}^{-1} \text{s}^{-1}$)	Ref.
$e_{aq}^- + C_7F_{15}COO^-NH_4^+$	$5.1 \times 10^7 (<CMC)$	60
$e_{aq}^- + C_7F_{15}COO^-NH_4^+$	$1.3 \times 10^7 (>CMC)$	60
$e_{aq}^- + C_7F_{15}COO^-$	$1.7 \times 10^7 (\mu = 0.01 \text{ M})$	61
$e_{aq}^- + C_3F_7COO^-$	$7.1(\pm 0.3) \times 10^6$	61
$e_{aq}^- + CF_3COO^-$	$1.9(\pm 0.2) \times 10^6$	61
$e_{aq}^- + C_7H_{15}COO^-Na^+$	3.3×10^6	60
$e_{aq}^- + CF_3(OCF_2)_nCOO^-NH_4^+$	$4(\pm 2) \times 10^6$	60
$e_{aq}^- + C_8F_{17}SO_3^-N(C_2H_5)_4^+$	7.3×10^7	60
$e_{aq}^- + CH_3SO_3^-$	$< 1 \times 10^6$	47
$e_{aq}^- + CH_3CH_2SO_3^-$	3.5×10^7	47
$^\bullet OH + C_7H_{15}COO^-Na^+$	$5.6(\pm 0.3) \times 10^9$	47
$^\bullet OH + C_7F_{15}COO^-NH_4^+$	$\leq 3 \times 10^7$	60
$^\bullet OH + C_8F_{17}SO_3^-N(C_2H_5)_4^+$	no reaction	60

The data presented in Fig. 2 shows that the UV/persulfate system degrades PFOS and PFOA more rapidly than the UV/iodide system. This result is at variance with the results of Qu *et al.*²² who reported iodide photolysis to be significantly more effective than persulfate photolysis. The difference is likely due to different reaction conditions, for example, we utilized persulfate and iodide concentrations of 10 mM whereas Qu *et al.* utilized concentrations

Fig. 2 (a) Time-profiled decay curves of PFOA and PFOS in UV 254 nm-irradiated aquated persulfate and iodide solutions. (b) Effects of carbon tail number on the degradation rates of various PFCs in UV-irradiated aquated persulfate and iodide solutions. All PFCs are identically 10 mg L⁻¹ (see experimental section). $[K_2S_2O_8]_0 = [KI]_0 = 10 \text{ mM}$. Air-equilibrated in persulfate solution and argon purged in iodide solution. k_{app} values of iodide/PFCs in (b) were taken from ref. 21 for comparison.

of 0.9 and 0.3 mM, respectively. Also, our experiments were completed in an open system that allows radical consuming intermediates to transfer to the gas-phase, whereas Qu *et al.* completed their experiments in a closed system. The observations under conditions utilized in this report indicate that even though UV/iodide is the favored system in terms of electrochemical potential, UV/persulfate has a faster reaction for PFOX. Reduction of PFCs by aquated electrons is also kinetically faster than oxidation by persulfate radicals. For example, the bimolecular reaction rate constants of e_{aq}^- reacting with C_6F_5OH and $C_6F_5NH_2$ are greater than those of corresponding reactions with $SO_4^{\cdot-}$ by factors of 6 and 3.5, respectively.^{31,32} This result is in agreement with a study on PFOA that reported bimolecular reaction rates to be at least two orders of magnitude faster with aquated electrons as compared to sulfate radicals.⁵⁹ The faster rates obtained in the UV/persulfate irradiation, therefore, may be due to a higher photolytic production rate of sulfate radicals (*i.e.*, $[SO_4^{\cdot-}] > [e_{aq}^-]$). The quantum yield for e_{aq}^- production at $\lambda = 254$ nm in aquated KI solution was determined to be 29%⁴⁴ and the corresponding value for $SO_4^{\cdot-}$ at $\lambda = 248$ nm has been reported to be 100%.⁴⁵ Alternatively, the faster UV/persulfate oxidation rates may be due to a competitive quenching of aquated electrons by other species, whereas there will be no competition for $SO_4^{\cdot-}$ besides a self-reaction in the persulfate system. Our observed degradation rates obtained with the UV/persulfate system are somewhat lower than those reported by Hori *et al.*,¹⁷ who used elevated O_2 pressures (>10 bar) to achieve higher reaction rates. Our results also show that in both the UV/persulfate and UV/iodide systems PFOS is degraded faster than PFOA.

Apparent rate constants of photolytic persulfate oxidation and photolytic iodide reduction as a function of PFC tail number are shown in Fig. 2b. These data show 1) the PFXS photolytic degradation rates are dependent on the tail carbon number, while the corresponding PFXA photolytic degradation rates are almost invariant with carbon number, 2) the PFOS degradation rates are greater than the degradation rates of PFHS/PFBS, which are similar to PFXA rates, and 3) persulfate photolysis is slightly more effective than iodide photolysis towards aquated PFC degradation. In addition, we tested two other photolytic oxidation systems, the photolysis of periodate, IO_4^- , and H_2O_2 (*i.e.*, indirect photooxidation *via* hydroxyl radical) for PFOS and PFOA. No measurable loss of the PFCs was observed under irradiation at $\lambda = 254$ nm during 2.5 h of illumination with either system, indicating that either the sulfate radical is a more effective PFC oxidant than the hydroxyl radical or that steady-state sulfate radical concentration is significantly greater than the steady-state hydroxyl radical concentration (due to lack of a sulfate radical sink; $H_2O_2 + HO^\cdot \rightarrow HO_2^\cdot + H_2O$).

3.2. UV-Iodide photolysis PFC concentration-dependent reduction kinetics

In Fig. 3, we illustrate the effects of initial $[I^-]_0$ and $[PFOX]_0$ concentrations on the observed degradation rates. At $[I^-]_0 < 10$ mM, the PFOS degradation rate ($k_{app,PFOS}$) increases with increasing $[I^-]$ and levels off at $[I^-] \geq 10$ mM (Fig. 3a). $k_{app,PFOA}$ has a similar but less pronounced concentration dependence. The leveling-off of k_{app} at $[I^-] \geq 10$ mM may be attributed to complete absorption of incoming 254 nm irradiation by iodide (Fig. 3a). However,

Fig. 3 Effects of (a) initial iodide concentrations and (b) initial PFOX concentrations on degradation rates of PFOX. UV-vis absorption spectrum of iodide (1, 5, 10, 25, and 50 mM from left) were overlapped in (a); the amounts of PFOX degraded ($\Delta[PFOX]_{deg}$) were shown in (b). $[PFOS]_0 = 20$ μM; $[PFOA]_0 = 24$ μM; $[KI]_0 = 10$ mM; argon was continuously purged through the solution.

the numbers of photons absorbed by iodide were estimated to be almost invariant with $\sim 1\%$ difference in the iodide concentration range of this study (1–50 mM). This implies the existence of other interfering chemical reactions for PFOX (see below).

The initial PFOX concentration ($[PFOX]_0$) also influenced the observed degradation kinetics and the extent of degradation (Fig. 3b). The values of $k_{app,PFOS}$ are greater at lower initial PFOX concentrations ($[PFOX]_0 < 10^{-6}$ M), and the relative differences between $k_{app,PFOS}$ and $k_{app,PFOA}$ are significant. At higher PFOX concentrations (10^{-6} M $< [PFOX]_0 < 3 \times 10^{-5}$ M) k_{app} (PFOS *vs.* PFOA) is approximately invariant. However, the extent of absolute PFOX degradation ($\Delta[PFOX]_{deg}$) increases with increasing $[PFOX]_0$, when $[PFOX]_0 \geq 1$ μM. For example, when $[PFOS]_0$ is increased by a factor of 10^2 (*e.g.*, 0.1 μM to 10 μM), $k_{app,PFOS}$ decreases by a factor of 13 (0.04 min⁻¹ to 0.0028 min⁻¹), even though $\Delta[PFOS]_{deg}$ increases seven-fold (7×10^{-9} moles to 49×10^{-9} moles). At all initial concentrations, $k_{app,PFOS}$ is greater than or equal to $k_{app,PFOA}$.

Since the PFOX degradation rates are correlated to $[I^-]_0$, we need to consider several kinetic and mechanistic aspects of iodide photochemistry. The UV irradiation of iodide and subsequent electron ejection results in the sequential formation of iodine radical (R0), iodine/iodine radical anion (R1, R2), and triiodide (I_3^-) ion according to reactions R3 to R5 (Scheme 1 and

Scheme 1 A schematic depiction of the aquated iodide photocycle.

Table 2). Fig. 4 shows $[I_3^-]$ increasing rapidly during the initial stages of photolysis and then reaching a photostationary state at $t \geq 60$ min. The apparent steady-state condition is due to I_3^- reduction by aquated electrons (R11) or hydrogen atoms (R18) competing with I_3^- formation. Aquated electron quenching by cations, such as K^+ (R25) and NH_4^+ (R27), is relatively slow ($< 10^6 \text{ M}^{-1} \text{ s}^{-1}$) and thus can be neglected. It is clear that the reduction of I_3^- by aquated electrons competes with the parallel PFOX reduction pathway. Such a competing or interfering reaction should limit the effect of iodide concentration on the PFOX reduction. Interestingly, Rahn reported that the steady-state $[I_3^-]$ rapidly increased with increasing $[I^-]$ up to approximately 10–15 mM and then gradually leveled off from $[I^-] > 25 \text{ mM}$.⁴⁶ Hence the leveling-off of k_{app} at $[I^-] \geq 10 \text{ mM}$ (Fig. 3a) may be ascribed to the saturation of $[I_3^-]_{ss}$ (*i.e.*, maximized interfering effect) at $[I^-] \geq 10 \text{ mM}$. It should be pointed that this relative competition increases with increasing $[PFOX]_0$.

The formation of I_3^- can be expressed as follows:

$$d[I_3^-]/dt = k_3[I^*][I_2^-] + k_4[I_2^-]^2 - k_{11}[I_3^-][e_{aq}^-] - k_{18}[H^*][I_3^-] \quad (E4)$$

and E4 can be reduced to:

$$[I_3^-]_t = (\alpha - e^{-\beta t})/\beta \quad (E5)$$

where $\alpha = k_3[I^*][I_2^-] + k_4[I_2^-]^2$ and $\beta = k_{11}[e_{aq}^-] + k_{18}[H^*]$. At a steady state, $d[I_3^-]/dt = 0$ (at $t \sim 150$ min):

$$[I_3^-]_{ss} = (k_3[I^*][I_2^-] + k_4[I_2^-]^2)/(k_{11}[e_{aq}^-] + k_{18}[H^*]) = \alpha/\beta \quad (E6)$$

$[I_3^-]_{ss}$ approaches α/β as $t \rightarrow \infty$. In reduction from E4 to E5, both α and β are considered constant with time and hence α/β should be independent of reaction time under the steady state constraint. It should be pointed that although each concentration of the reactive species in α and β may vary with time, the overall values of α and β are assumed to be constant with time or the effect of the variation is considered minor. As shown in Fig. 4a, b, and c, $[I_3^-]_{ss}$ and α/β increase and β decreases with increasing $[PFOS]_0$, due to increased competition for aquated electrons. However, the apparent quenching is not linearly correlated with $[PFOS]_0$, (α/β vs. $[PFOS]_0$; Fig. 4b). The increase in α/β at higher $[PFOS]_0$ indicates that total electron quenching occurs more effectively resulting in a larger fraction of PFOS to be degraded despite a decrease in $k_{app,PFOS}$ at higher $[PFOS]_0$ (see Fig. 3b). In addition, β decreases from 0.08 min^{-1} to 0.04 min^{-1} (Fig. 4c), and $([e_{aq}^-] + [H^*])_{ss}$ decreases from $3.0 \times 10^{-13} \text{ M}$ to $0.7 \times 10^{-13} \text{ M}$ as $[PFOS]_0$ is increased from $0.1 \text{ }\mu\text{M}$ to $100 \text{ }\mu\text{M}$. The relatively minor decrease in the steady-state reductant concentration with a large increase

Fig. 4 (a) Time-profiled production curves of triiodide as a function of $[PFOS]_0$, and dependences of (b) α/β and (c) β on $[PFOS]_0$. $[KI]_0 = 10 \text{ mM}$; argon was purged through the solution continuously. See text for information on α and β .

in PFOS indicates that iodide is regenerated during a closed photolytic cycle, as illustrated in Scheme 1.

3.3. UV-Iodide photolytic PFC reduction: pH effects and mechanism

The influence of pH on the photoreduction kinetics is illustrated in Fig. 5a and 5b. In the absence of PFOX, pH increases abruptly during irradiation ($\lambda = 254 \text{ nm}$). This rise is due the formation of hydroxide (R7) or the consumption of protons (R8) by aquated electrons coupled with formation of H_2 (R15). We also observed that the pH increase was less pronounced when oxygen was supplied by a continuous air purge (R9).

Fig. 5 Time profiled pH changes during the photolysis of (a) KI-PFBS solutions ($S = B, H, O$) with identical PFXS concentration of 10 ppm (see Fig. 2 caption) and (b) KI-PFOS solutions with varying initial $[PFOS]_0$. $[KI]_0 = 10$ mM; Ar-purged through the solution continuously (in the cases of no description in legend). (c) Effects of initial pH on the degradation rates of PFOX in UV 254 nm-irradiated iodide solutions. $[PFOS]_0 = 20$ μM; $[PFOA]_0 = 24$ μM; $[KI]_0 = 10$ mM; Ar is continuously purged through the solution.

In contrast, the time-dependent pH behavior changes noticeably in the presence of PFOX. For example, the photo-degradation of PFBS (Fig. 5a) leads quickly to a pH increase to ~8.5, and then the pH remains relatively constant during the remainder of the photolytic reaction. In the case of PFHS photolysis, the pH rises to pH ~8.5, but then decreases after 10 min of irradiation. During PFOS photo-degradation, the pH also decreases upon extended irradiation (pH = 5.7 after 2.5 h of illumination; $pH_0 = 6.5$). The initial increase of pH can be attributed to proton consumption

(R7, R8), while the subsequent release of protons can be attributed to defluorination yielding HF (*i.e.*, $pK_a(HF) = 3.45$). These results are consistent with observations of fluoride release from PFBS (5 μmol), PFHS (23 μmol), and PFOS (57 μmol) after 2.5 h of 254 nm irradiation in the presence of iodide.²¹

The $[PFOS]_0$ also impacts the pH values *vs.* time. As shown in Fig. 5b, when $[PFOS]_0 = 0.2$ and 20 μM, the time-dependent ΔpH is similar to I^- irradiation in the absence of PFOS. However, when $[PFOS]_0 = 200$ μM, the pH decreases immediately upon irradiation. This result is consistent with the hypothesis that HF production is responsible for the pH decrease upon extended irradiation at lower $[PFOS]_0$ (Scheme 1).

We also need to consider the possibility that hydrogen atoms may be involved in PFC degradation. H-atoms would be produced *via* a reaction of aquated electrons with water (R7) and/or protons (R8) at diffusion-controlled rates. Even though there is a fast inter-conversion between hydrogen atoms and aquated electrons, their physicochemical properties differ substantially. On one hand, $H^\bullet$ has a larger aquated-phase diffusion coefficient, $D_{H^\bullet} = 8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, than aquated electrons, where $D(e_{aq}^-) = 5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, while, on the other hand, $H^\bullet$ has a less negative reduction potential, *i.e.*, $E(H^+/H^\bullet) = -2.1 \text{ V}$ and $E(e_{aq}^-) = -2.9 \text{ V}$.⁴⁷

Since the pK_a of hydrogen atom is 9.6 (R8),⁴⁷ a fraction of the photo-generated e_{aq}^- is likely to result in $H^\bullet$ production during prolonged irradiation. To investigate this possibility, we examined the iodide photolysis of PFOX as a function of initial pH. As shown in Fig. 5c, as the initial pH is varied from 1.5 to 12, there is little impact on the observed PFOX reduction kinetics. This indicates either that the rate of $H^\bullet$ production is too slow to affect PFOX reduction rates (kinetic aspect), or that $H^\bullet$ cannot reductively degrade PFOX due to its lower reduction potential, *i.e.*, $H^\bullet$ is a weaker nucleophile and weaker reductant than the aquated electron.

It has been previously reported that the quantum yield for iodine or triiodide production has a linear dependence on the square root of $[H^+]$ at pH < 3 and is invariant at pH > 3.^{48,49} In addition, hydrogen atom production constituted a very minor reaction path at $[I^-] \leq 4 \text{ mM}$.⁴⁹ Shoute *et al.*^{31,32} have compared the relative reaction kinetics of aquated electrons and hydrogen atoms for the reduction of pentafluorophenol and pentafluoroaniline in aquated solution. They reported that the reaction rate constants of aquated electrons (at pH 4.6) were greater than those of hydrogen atoms (at pH 0.6) by a factor of ~20. The much smaller rate constants for hydrogen atom reduction even under highly acidic conditions suggests that the $H^\bullet$ reduction pathway is insignificant relative to direct reduction by e_{aq}^- at pH > 3. Thus, we conclude that the minor effect of pH on PFOX degradation rate is due to e_{aq}^- as the dominant reductant in our system. However, these results do not preclude the role of $H^\bullet$ acting as an e_{aq}^- carrier in solution.

3.4. UV-Iodide photolytic PFC reduction: gaseous products and intermediates

PFOS reduction can produce a number of gaseous reaction intermediates containing fluorine, hydrogen, iodine, and carbon, in particular perfluoroalkyl iodides ($C_xF_{2x+1}I$) were identified during PFXS ($C_xF_{2x+1}SO_3^-$) photoreduction.²¹ However, the quantification of these reaction intermediates is challenging due to the lack of

Fig. 6 (above) Total ion chromatogram (TIC) of gaseous intermediates trapped during the course of 2.5h-photolysis of aquated PFOS with KI of 10 mM. (below) Extracted ion chromatogram (EIC) of 69 m/z (CF_3) for $C_8F_{17}I$ with retention time of *ca.* 5.84 min. A full set of EICs of (a) was shown in Fig. S7 in Supplementary Information.[†]

available authentic standards. Thus, a representative, commercially available fluoro-intermediate, perfluorooctane iodide ($C_8F_{17}I$), was selected and quantified to estimate the overall mass of gaseous fluorinated reaction intermediates that are produced during iodide photolysis (see Fig. S6 for calibration curve and Fig. S7 and S8 for individual GC-MS spectra[†]).

The presence of $C_xF_{2x+1}I$ indicates that the sulfonate group is readily cleaved during irradiation. After 2.5 h of photolysis, $0.422 \pm 0.016 \mu g$ of $C_8F_{17}I$ was produced (Fig. 6). This amount corresponds to 0.14% of $[PFOS]_0$ ($10 \text{ mg L}^{-1} \times 0.03 \text{ L} = 300 \mu g$) and approximately 0.44% of PFOS that was actually degraded over this timeframe ($\Delta[PFOS]_{\text{deg}, 2.5h} = \sim 0.32 \times [PFOS]_0$). If we assume a response factor for the other gaseous fluorinated intermediates, then approximately 8.4% of $[PFOS]_0$ (26% of $\Delta[PFOS]_{\text{deg}, 2.5h}$) was converted to the identifiable gaseous intermediates. This is in agreement with our previous study that observed production of

1 fluoride per carbon atom during UV/iodide PFOS reduction accounting for 50% of the PFC fluorine. Thus, gaseous fluorocarbon and fluoride can account for 76% of the initial PFC fluorine, suggesting the rest may be account for in partially-defluorinated aquated PFC reduction intermediates. However, a close examination of HPLC-ESI-MS chromatograms did not reveal any predominant partially-defluorinated aquated intermediates.

4. Conclusions

In summary, the UV/iodide photolytic production of the aquated electron results in the indirect reductive degradation of a homologous series of perfluoroalkyl compounds or PFCs; perfluoroalkylcarboxylates and perfluoroalkylsulfonates. Cyclic voltammetry indicated that PFC reduction was more thermodynamically favorable than PFC oxidation. However, in practice, UV/iodide

photolytic production of the strongly reducing aquated electron was less effective towards PFC degradation than UV/persulfate photolytic PFC oxidation *via* the strongly oxidizing sulfate radical. The lower activity of the UV/iodide system towards PFC degradation was likely a result of triiodide scavenging of aquated electrons. UV/iodide PFC photoreduction kinetics were observed to be influenced by a variety of factors, such as initial concentrations of iodide and PFC, the nature of the hydrophilic PFC surfactant head-groups, and the PFC fluorocarbon tail length. Initial pH had minimal effects on PFC photoreduction kinetics indicating that the aquated electron was the predominant reductant. A large number of gaseous fluorocarbon photoreduction intermediates were detected and were determined to account for ~25% of the initial PFOS mass.

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