Degradation of Perfluoroalkyl Ether Carboxylic Acids with Hydrated Electrons: Structure—Reactivity Relationships and Environmental Implications

Michael J. Bentel, Yaochun Yu, Lihua Xu, Hyuna Kwon, Zhong Li, Bryan M. Wong, Yujie Men, and Jinyong Liu*

ABSTRACT: This study explores structure—reactivity relationships for the degradation of emerging perfluoroalkyl ether carboxylic acid (PFECA) pollutants with ultraviolet-generated hydrated electrons (e^-aq). The rate and extent of PFECA degradation depend on both the branching extent and the chain length of oxygen-segregated fluoroalkyl moieties. Kinetic measurements, theoretical calculations, and transformation product analyses provide a comprehensive understanding of the PFECA degradation mechanisms and pathways. In comparison to traditional full-carbon-chain perfluorocarboxylic acids, the distinct degradation behavior of PFECA is attributed to their ether structures. The ether oxygen atoms increase the bond dissociation energy of the C–F bonds on the adjacent C–F,–moieties. This impact reduces the formation of H/F-exchanged polyfluorinated products that are recalcitrant to reductive defluorination. Instead, the cleavage of ether C–O bonds generates unstable perfluoroalcohols and thus promotes deep defluorination of short fluoroalkyl moieties. In comparison to linear PFECA, branched PFECA have a higher tendency of H/F exchange on the tertiary carbon and thus lower percentages of defluorination. These findings provide mechanistic insights for an improved design and efficient degradation of fluorochemicals.

INTRODUCTION

Since the 1940s, per- and polyfluoroalkyl substances (PFASs) have been extensively used in a wide range of applications because of their unique properties (e.g., hydrophobicity, lipophobicity, and thermal stability) as well as their relative ease in chemical design and synthesis.1–5 The highly stable C–F bond makes PFAS molecules recalcitrant to natural and engineered degradation, leading to global PFAS pollution and worldwide efforts on PFAS regulation.6–11 Fluorochemical industries have been phasing out the production and use of some legacy PFASs (e.g., perfluorooctanoic acid (PFOA))12,13 because of their heavy pollution of the environment and high toxicities to humans.14–16 Perfluoroalkyl ether carboxylic acids (PFECA) that contain ether C–O bonds in molecules have been developed as “less bioaccumulative alternatives” to full-carbon-chain predecessor PFASs.17 However, toxicological studies have revealed an even higher bioaccumulation potential and toxicity of some PFECA than PFOA.18–19 and PFECA have been recognized as a new class of contaminants of emerging concern (Figure 1).20–23 At some sites in North America and in Europe, PFECA have been detected in much higher concentrations than legacy PFAS.24–25 Furthermore, because of the facile synthesis of PFECA from flexible choices of fluoroalkene oxide building blocks (e.g., Figure S1)26 and the formation of byproducts,27 the diversity of PFECA contaminants identified in the environment has been rapidly increasing.27–29

While physical separation methods (e.g., carbon adsorption, ion exchange, and membrane filtration) enable rapid PFAS removal from contaminated water,30 concentrated PFASs in carbon/resin regeneration waste and membrane rejects still require degradation treatment. Various novel methods, such as electrochemical,31 sonochemical,32 radiolytic,33 plasmatic,34 and other oxidative and reductive approaches,30,35 have been primarily developed for the degradation of PFOA and perfluorooctane sulfonic acid. A few studies have investigated the destruction of selected PFECA, including sonochemical oxidation with persulfate,30 photocatalytic oxidation with...
phosphotungstic acid under pressurized O₃,⁵⁷ and reduction with ultraviolet (UV)-generated hydrated electrons (eᵦ⁻).⁳⁸,⁳⁹ These early studies have revealed a variety of mechanistic insights on PFECA degradation. In particular, reductive degradation of branched PFCAs (e.g., GenX in Figure 1) using eᵦ⁻ is much more effective than oxidative degradation using sulfate radicals.³⁸,⁳⁹ However, a systematic understanding of reaction pathways and structure-reactivity relationships has not yet been established.

Recently, our research team has systematically studied the reductive defluorination of full-carbon-chain PFASs by eᵦ⁻ produced from aqueous sulfate under UV irradiation.⁴⁰ The degradation mechanisms for perfluorocarboxylic acids (PFCAs) and fluorotelomer carboxylic acids (FTCAs) are significantly different. FTCAs (Rᵦ⁻CH₂CH₂⁻COO⁻, where Rᵦ represents the fluorocarbon moiety) are much more recalcitrant than PFCAs (Rᵦ⁻COO⁻), especially when the chain length of Rᵦ is short. The incomplete defluorination of PFCAs can also be attributed to the formation of polyfluorinated Rᵦ⁻CH₂⁻COO⁻ products.⁴⁰ These findings indicate the importance of a direct linkage between Rᵦ and −COO⁻ to allow an effective degradation of full-carbon-chain PFASs using eᵦ⁻. In comparison, the flexible incorporation of ether linkages in PFCAs generates various oxygen-segregated fluoroalkyl moieties, which can be either branched or linear in variable lengths. This novel structural diversity raises fundamental questions regarding mechanistic understanding and pollution control: (1) Mechanistically, what roles do the ether C–O bond and other structural features play in PFECA degradation using eᵦ⁻? (2) Practically, in comparison to full-carbon-chain PFCAs, can PFECA be treated with a higher efficiency by these promising reductive technologies?

To answer these questions, we investigated the reductive defluorination of 10 PFCAs with (i) varying numbers of ether C–O bonds, (ii) varying chain lengths of oxygen-segregated fluoroalkyl moieties, and (iii) branched versus linear fluoroalkyl structures. To achieve a comprehensive understanding, we conducted kinetic measurements on parent compound decay and fluoride ion (F⁻) release, theoretical calculations on C–F/C–O bond dissociation energies, spontaneous bond cleavage upon reaction with eᵦ⁻, and transformation product (TP) analyses with high-resolution mass spectrometry. These results collectively reveal and confirm novel mechanistic insights into PFECA degradation. These findings will advance treatment technologies for existing PFECA pollutants and facilitate the molecular design of fluorochemicals with enhanced degradability.

## MATERIALS AND METHODS

This study utilized 10 PFCAs with fine-tuned structural variability in 4 categories (A1 through D2 in Table 1) and 2 special compounds [trifluoropyruvate (TFPy) CF₃⁻CO⁻COO⁻ and trifluoromethoxyacetate (TFMOA) CF₃⁻O⁻CH₂⁻COO⁻] for mechanistic investigations. Detailed information on these chemicals is included in the Supporting Information. Preparation of PFECA stock solutions, photochemical reaction settings, sample analysis, and theoretical calculations have been fully described in our previous work (Open Access).⁴⁰ We used consistent reaction conditions to compare the degradation behavior between PFECA and traditional full-carbon-chain PFCAs. Briefly, the photochemical degradation of individual PFECA was carried out in 600 mL closed-system batch reactors equipped with a low-pressure mercury lamp (254 nm, 18 W, enclosed in a quartz immersion well). Both the reactor and immersion well were connected to circulating cooling water at 20 °C. The reaction mixture contained 25 μM PFECA, 10 mM Na₂SO₃, and 5 mM NaHCO₃, and the pH was adjusted to 9.5 with NaOH. The released F⁻ was measured with an ion-selective electrode, which has been validated for quantification accuracy by ion chromatography (IC). All reactions were conducted in

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![Table 1. Overall DeFluorination Percentages of PFCAs after 48 Hours of Reaction](#)

<table>
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<th>Entry</th>
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<td>61.2 ± 7.5</td>
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<td>3</td>
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<td>2-10</td>
<td>54.5 ± 3.5</td>
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³⁷Reaction conditions: PFAS (0.025 mM), Na₂SO₃ (10 mM), carbonate buffer (5 mM), 254 nm irradiation (a 18 W low-pressure Hg lamp for 600 mL solution) at pH 9.5 and 20 °C.⁴⁰Data from ref 40 for comparison. The average and standard deviation of the del% value for n = 2~10 is based on 27 data points (nine PFCA structures with triplicates).
triplicates of operations from the preparation of stock solution to the quantification of the defluorination percentage (deF %), which is defined as

$$\text{deF} \% = \frac{C_F}{C_0 \times N_{C-F}} \times 100\%$$ (1)

where $C_F$ is the molar concentration of F$^-$ released in solution, $C_0$ is the initial molar concentration of parent PFECA, and $N_{C-F}$ is the number of C–F bonds in the parent PFECA molecule. Reaction samples were analyzed with a liquid chromatography–triple quadrupole mass spectrometer (LC–MS/MS) for the quantification of parent compounds and TPs that have pure chemicals available as analytical standards. A liquid chromatography–high-resolution mass spectrometer (LC-HRMS) was also used for the screening of TPs without analytical standards. The quality assurance and quality control of our MS analyses have been addressed previously, with new details provided in the Supporting Information for the PFECA degradation samples. Small ionic species including trifluoroacetate, TFPyO, oxalate, perfluoroxyacetate (PERAO, CF$_3$O–CF$_2$–COO$^-$), and TFMOA (CF$_3$O–CH$_2$–COO$^-$) were analyzed by an ion chromatograph equipped with a conductivity detector (specific separation conditions are described in the Supporting Information).

**RESULTS AND DISCUSSION**

**Degradation of PFECA. Different Degradability between PFECA and Traditional PFCAs.** Figure 2 shows the decay and defluorination of four PFASs representing full-carbon-chain PFCAs, linear PFECA, and branched PFECA.

The parent compound decay is the fastest for the two traditional PFCAs and the slowest for the branched PFACA (Figure 2a). The order of parent compound decay rates for these structures does not match the order of their defluorination percentages. Figure 2b shows the distinct defluorination profiles between PFECA and traditional PFCAs as well as between linear and branched PFCAs. All four PFASs showed an initial period of rapid F$^-$ release, followed by a slower F$^-$ release before reaching a plateau. However, the initial rates of defluorination from the two PFECA are slower than those from the two PFCAs. In particular, the linear PFECA showed a slower initial rate but a significantly deeper defluorination than perfluorohexanoic acid (i.e., 75 vs 55% of the 13 F atoms in each molecule). In contrast, the branched PFECA showed both a slower rate and a lower extent of defluorination than perfluorononanoic acid (i.e., 40 vs 58% of the 17 F atoms in each molecule). These results suggest new structure–reactivity relationships governing PFECA degradation. To systematically understand these mechanisms, we extended our study to 10 individual PFCAs, which exhibited structure-specific profiles of parent compound decay and defluorination (Table 1 and Figure 3).

**Different Degradability of Four PFECA Structure Categories.** Category A includes structures A1–A3 with branched −CF$_3$ groups, which are the acid forms of hexafluoroxyacetate, trimer, and tetramer (HFPO–DA, HFPO–TrA, and HFPO–TeA), respectively. The initial rates of parent compound decay were similar (Figure 3a), but longer structures showed a lower deF % (Figure 3b). The defluorination percentages of these branched PFCAs (31–45%) were significantly lower than those of traditional PFCAs (~55%) under the same reaction conditions. Category B includes monoether structures B1–B3 with the CF$_3$O– head group and linear −(CF$_2$)$_n$– moieties ($n$ = 1, 2, and 3, respectively) before the terminal −COO$^-$ group. The decay of B2 and B3 finished within 12 h (Figure 3c), and the time profiles for their parent compound decay were similar to full-carbon-chain PFCAs (Figure 2a). The final defluorination percentages are also similar (61 and 52% for B2 and B3, respectively, vs 55% for PFCAs). In stark contrast, whereas the decay of B1 ($n$ = 1) was much slower than those of B2 and B3, the deF % was substantially higher (91%). From the kinetic data, it seems that these CF$_3$O–(CF$_2$)$_n$–COO$^-$ structures behave similarly to F(CF$_2$)$_n$–COO$^-$ under reductive treatment. In our previous study, the decay of CF$_3$–COO$^-$ took 24 h to complete while the deF % was almost 100%, whereas the decay of all longer PFCAs took 8–12 h to complete, but the maximal deF % was ~55% (Table 1, entry E1 vs E2).

We further tested two linear multiether PFECA categories, C and D. Both categories contain tetrafluoroethylene oxide (TFEO) building blocks, but the head groups are CF$_2$O– and C$_4$F$_5$O–, respectively. With −O–CF$_2$–COO$^-$ as the end group, the parent compound decay became slow again (cf. Figure 3e,g). Like the decay profile for the long-molecule A3 (Figure 3a), the decay of the long-molecule D2 was also incomplete within 48 h. The other three structures C1, C2, and D1 showed profiles similar to the decay of B1. The notable difference between these two PFECA categories is that C1 and C2 with their short CF$_2$O– head groups yielded a significantly higher deF % (82 and 75%, respectively) than D1 and D2 with their long C$_4$F$_5$O– head groups (58 and 65%, respectively) (cf. Figure 3f vs 3h).
Structural Effects on PFECA Degradation. The kinetic data shown above indicates the following characteristics of PFECA degradation in comparison to traditional PFCAs: (1) branched PFECAs show slower decay and lower defluorination; (2) linear PFECAs exhibit slower decay if they contain \(-\text{O}–\text{CF}_2–\text{COO}^–\) end groups or a very similar rate of decay if more than one \(-\text{CF}_2–\) linker is present in the \(-\text{O}–(\text{CF}_2)_n–\text{COO}^–\) functional group; (3) linear PFECAs containing shorter oxygen-segregated fluoroalkyl moieties showed a higher deF %. To interpret these interesting results on the molecular level, we conducted theoretical calculations and TP analyses.

Theoretical Calculations of C–F and C–O BDEs. The bond dissociation energies (BDEs) of C–F and ether C–O bonds in all PFECA structures were calculated with density functional theory. Representative results are shown in Figure 4, and the full data sets are collected in Figures S2–S5. We identified new trends for C–F BDEs in PFECAs compared to full-carbon-chain PFCAs. First, the ether oxygen increases the BDE of C–F on the adjacent fluorocarbons. While the terminal \(-\text{CF}_3\) in long fluoroalkyl chains has a typical C–F BDE < 119 kcal mol\(^{-1}\) (Figure 4d,f,h,i), the inclusion of ether oxygen atoms increased the C–F BDE to 120–123 kcal mol\(^{-1}\) (Figure 4a–c,g). In fluorinated molecules, the ether oxygen acts as an electron-donating group like the \(-\text{CH}_2–\) group in FTCAs (Figure 4e). With multiple oxygen atoms in the chain, the relatively weak C–F bonds in long-chain PFCAs were not
found in linear PFECAs (cf. Figure 4f vs 4g,h). In particular, the typically weak C–F bond at the α-position of PFCAs (i.e., BDE < 108 kcal mol\(^{-1}\), Figure 4d,f) does not exist in linear PFECAs with an ether oxygen at the β-position (i.e., \(R_p=O\cdots CF_2\cdots COO\), BDE > 111 kcal mol\(^{-1}\), Figure 4a,g,h). However, when the fluororalkyl chain adjacent to –COO\(^-\) is longer (i.e., \(n = 2\) or \(3\) in \(R_p=O\cdots(CF_2)_n\cdots COO\(^-\)), the weak C–F bond at the α-position appears again (Figure 4b,c). These novel trends on C–F BDEs in linear PFECAs corroborate the different rates of parent compound decay. The two structures with the weak α-position C–F bonds (B2 and B3 in Figure 3c) showed a rate of decay similar to the full-carbon-chain PFCA (Figure 2a), whereas the other \(R_p=O\cdots CF_2\cdots COO\) structures showed slower parent compound decay (B1, C1, and C2 in Figure 3c,e).

As for the branched PFECAs, the inclusion of ether oxygen atoms showed a similar effect on increasing the C–F BDEs. In comparison to a full-carbon-chain branched PFCA that contains very weak tertiary C–F bonds,\(^{27}\) the oxygen atoms in HFPO–TrA significantly strengthen all secondary and tertiary C–F bonds (cf. Figure 4i vs 4j). Although the HFPO oligomer acids contain distinctly weak tertiary C–F bonds (i.e., BDE < 104 kcal mol\(^{-1}\)), the rates of the parent compound decay were slower than those of most of the linear PFECAs (Figure 3). Thus, other mechanisms and considerations beyond the cleavage of weak C–F bonds are likely responsible for the degradation of branched PFECAs.

As the cleavage of ether C–O bonds has been proposed for the degradation of HFPO–DA,\(^{35,39}\) we further examined the BDEs of C–O bonds in all PFECAs. A very interesting phenomenon is the “asymmetric” strength of the two C–O bonds on the first ether linkage counted from the terminal –COO\(^-\) (Figure 4k–n). On this ether oxygen atom, the C–O bond away from –COO\(^-\) has a considerably lower BDE (63–73 kcal mol\(^{-1}\)) than the other one closer to –COO\(^-\) (78–94 kcal mol\(^{-1}\)). This phenomenon was observed in all PFECAs regardless of the total number of ether linkages, branched versus linear molecular backbone, or the distance between –COO\(^-\) and the first ether linkage (cf. Figure 4k vs 4l). The BDE difference between those two C–O bonds in the three branched PFECAs ranges from 14.7 to 18.3 kcal mol\(^{-1}\), and the difference in linear PFECAs is even greater, from 19.8 to 23.3 kcal mol\(^{-1}\) (see Figures S2–S5 for full data sets). However, if the PFECAs molecule contains multiple ether oxygens, the pairs of C–O bonds in the remaining ether linkages have similar BDEs (i.e., only with small differences ranging from 0.1 to 3.4 kcal mol\(^{-1}\), Figure 4m,n). In addition, because of the electron-withdrawing effect by the –CF\(_3\) branches, the BDEs of these “normal” C–O bonds in branched multiterier structures (82–84 kcal mol\(^{-1}\)) are lower than those in linear multiterier structures (89–97 kcal mol\(^{-1}\)).

**Spontaneous Bond Cleavage in Electron-Added PFCA Radical Anion Structures.** The distinctly weak C–O bond in all PFECAs and the relatively weak tertiary C–F bonds in branched PFECAs imply the potential cleavage of these bonds during the reaction. To verify this hypothesis, we further conducted geometry optimization of the radical anion \([R_p=COO]^\ddagger\) upon adding an extra electron (which simulates an \(e_{aq}^\ddagger\)) to the original PFCA anion (\(R_p=COO^\ddagger\)). As expected, the spontaneous stretching of the α-position C–F bonds (Figure 5a,b) and ether C–O bonds (Figure 5c,d) was observed. The distance between the two atoms stretched considerably longer than the normal length for C–O and C–F bonds (i.e., bond cleavage). The results for all PFCEA structures are collected in Figures S6 and S7.

![Figure 4](image1.png)

**Figure 4.** Calculated C–F BDEs (a−j) and C–O BDEs (k−n) (in kcal mol\(^{-1}\)) of selected PFECAs at the B3LYP-D3(BJ)/6-311+G(2d,2p) level of theory. Results for all PFCA structures are collected in Figures S2–S5. Data for (d−j) are from refs 40 and 41.

![Figure 5](image2.png)

**Figure 5.** Geometry-optimized structure of the adducts of PFCA anions with an \(e_{aq}^\ddagger\) (PFCA\(^\ddagger\)) at the B3LYP-D3(BJ)/6-311+G(2d,2p) level of theory, showing the stretching of C–F (blue) and C–O (red) bonds. Results for all PFCA structures are collected in Figures S6 and S7.
importantly, the calculation shows that C–O bond cleavage can be a major pathway for PFECA degradation by eq. The previously elucidated cleavage of weak C–F bonds was also observed both from branched PFECA (with very weak tertiary C–F bonds) and from the linear structure B1 CF3–O–CF2–COO where the α-position C–F BDE is relatively high (112 kcal mol\(^{-1}\)). These results suggest that C–F bond cleavage can be another degradation pathway, even if the inclusion of ether oxygen atoms causes many C–F bonds to be more recalcitrant than those in full-carbon-chain PFCAs.

**PFECA Degradation Product Analysis.** The above theoretical calculations have indicated the possibility of C–F and C–O bond cleavage. On the basis of our previous study, the decarboxylation–hydroxylation–HF elimination–hydrolysis (DHEH) is another major degradation pathway for structures with the fluoroalkyl moiety directly linked with −COO\(^{−}\). Hence, we hypothesized that the degradation of PFCAs takes place via at least three pathways: (i) cleavage of weak C–F bonds and the formation of C–H bonds (i.e., H/F exchange), (ii) DHEH, and (iii) characteristic cleavage of ether C–O bonds. To detect the TPs and confirm the degradation pathways, we used both targeted analysis with triple quadruple mass spectrometry and suspect screening with high-resolution mass spectrometry data (all results are collected in Tables S1–S9). A series of TPs was detected, which supports all three proposed degradation pathways. The overall TP detection and the corresponding degradation pathways from the longest PFECA in each of the four structure categories are discussed below (Figure 6, and Schemes 1 and 2). The reaction schemes proposed for individual PFECA are provided in Schemes S1–S10.

As shown in Figure 6a, the degradation of A3 HFPO−TeA generated A2 HFPO−TrA and A1 HFPO−DA daughter products. The maximum concentrations of A2 (7.9 μM) and A1 (3.7 μM) were detected at 8 and 12 h, respectively. We attribute this transformation to the cleavage of the first C–O bond counted from the terminal −COO\(^{−}\) group. The two fragments reacted with H\(_2\)O to form two perfluorinated alcohols, which were not stable and subject to HF elimination to acyl fluoride.\(^{42,43}\) The subsequent hydrolysis generated carboxylic acid, resulting in the net conversion from RF–CF2OH into RF–COO\(^{−}\) and two F\(^{−}\) ions. The C–O cleavage on the first ether linkage counted from −COO\(^{−}\) shortens HFPO−TeA into HFPO−TrA and then into HFPO−DA,
which can be further degraded into \( \text{CF}_3\text{CF}_2\text{−COO}^- \) via another \( \text{C}−\text{O} \) cleavage (Scheme 1). Each round of \( \text{C}−\text{O} \) cleavage also generated the same product \( \text{CF}_3\text{CF(OH)}\text{−COO}^- \), which underwent further HF elimination into \( \text{CF}_3\text{−CO}−\text{COO}^- \) (TFPy), as structures with F and OH on the same carbon (e.g., \( \text{FCH}_2\text{OH} \)) are generally unstable.\(^{44}\) We confirmed the formation of TFPy during the degradation of HFPO−DA with IC detection (Figure S8). Like \( \text{CF}_3\text{−COO}^- \) (trifluoroacetic acid, TFA), pure TFPy also showed near-complete defluorination (Figure S9), and TFA is a possible degradation intermediate (Figure S10). Although TFA was not detected in our samples from HFPO−DA degradation, we have elucidated that TFA can be generated from both \( \text{CF}_3\text{CF}_2\text{−COO}^- \) and TFPy and then completely mineralized via the DHEH pathway (Scheme 1b).\(^{40}\)

Suspect screening using the HRMS data identified a series of H/F exchange products from the HFPO oligomer acids. On the basis of our calculations, we assign the \( \text{C}−\text{H} \) bonds to the branched carbons (particularly the \( \alpha \)-position branched carbon) where weak tertiary \( \text{C}−\text{F} \) bonds are located (Figure

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Scheme 2. Degradation Pathways for the Three PFECA Structure Categories Starting from the Longest Compound (a) B3, (b) C2, and (c) D2; Detected TPs are Highlighted

Scheme 1. Degradation Pathways for (a) HFPO Oligomer Acids Starting from the Longest Compound A3 and (b) the Daughter Product PFPrA; Detected TPs are Highlighted

https://dx.doi.org/10.1021/acs.est.9b05869
6b and Scheme 1a). We also observed products missing one or more −CF<sub>3</sub> groups (i.e., H/CF<sub>3</sub> exchange). By comparing the results with those for linear PFECAs, such TP structures missing −CF<sub>3</sub> groups are specific for branched PFECAs. Therefore, we interpret the transformation pathway to be the cleavage of the branching −CF<sub>3</sub> rather than the terminal −CF<sub>3</sub>. In addition, the degradation products and reaction schemes from pure HFPO–DA and HFPO–TrA (Tables S1 and S2 and Schemes S1 and S2) further corroborate the mechanistic insights obtained from HFPO–TeA degradation.

For the degradation of B3 (CF<sub>3</sub>−O−CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>−COO<sup>−</sup>), the C−O bond cleavage mechanism was confirmed by the detection of “OOC−CF<sub>2</sub>CF<sub>2</sub>−COO<sup>−</sup>” (Figure 6c and Scheme 2a). The head CF<sub>3</sub>− group was thus believed to be fully defluorinated via the formation of unstable CF<sub>3</sub>−OH. The DHEH mechanism was also confirmed by the generation of B2 CF<sub>3</sub>−O−CF<sub>2</sub>CF<sub>2</sub>−COO<sup>−</sup>. The HRMS detection of two products with one and two H/F exchanges on the parent compound (most probably at the α-position) is not surprising (Figure 6d).

The degradation of the two multiter linear PFECAs C2 and D2 also followed the three reaction pathways, which are supported by the TPs identified (Figure 6e−h). Although the C−F BDEs of the α-position −CF<sub>3</sub>− in these structures are higher than those in full-carbon-chain PFCAs (Figure 4g vs 4f), the H/F-exchanged TPs were detected, thus corroborating the spontaneous C−F bond stretching by theoretical calculations (Figure 5a).

Additionally, the C−O bond cleavage in B1 (also in category C and D structures that contain −O−CF<sub>3</sub>−COO<sup>−</sup>) was supposed to generate HO−CF<sub>2</sub>−COO<sup>−</sup>′, which should further decompose into oxalate (“OOC−COO<sup>−</sup>′”). IC detection confirmed the formation of oxalate (Figure S11), thus further consolidating this C−O bond cleavage mechanism.

Overall Mechanistic Insights into Reductive PFECA Degradation. On the basis of the degradation kinetics, theoretical calculations, and TP analyses, we have confirmed that the PFECAs have three pathways for the reductive degradation by e<sub>aq</sub>−: (1) ether C−O bond cleavage, (2) C−C bond cleavage, including the decarboxylation step of DHEH and the cleavage of −CF<sub>3</sub> from branched PFECAs, and (3) direct C−F bond cleavage followed by H/F exchange. Here, we categorize the first two as indirect pathways for defluorination and the third one as a direct pathway for defluorination. It is worth noting here that all three independent pathways are enabled upon PFECAs interacting with e<sub>aq</sub>−. First, control experiments with UV irradiation without adding sulfinite showed very slow and limited degradation (Figure S12). Second, spontaneous C−O bond cleavage was observed after the PFPECA anion received an extra electron (Figure S5). Third, the generation of e<sub>aq</sub>− from sulfinite has been confirmed by spectroscopic observations<sup>35,40</sup> and other chemicals such as iodide<sup>47</sup> and indole<sup>48</sup> have also been used as the source of e<sub>aq</sub>−, which have achieved similar results for PFOA defluorination.

The cleavage of the C−O or C−C bond in PFECAs will generate perfluorocarboxyls, which will undergo HF elimination and the following hydrolysis to yield two F<sup>−</sup> and the corresponding carboxylic acids. This mechanism has been collectively supported by (1) the decay of HFPO and TFEO oligomer acids into shorter analogues (Figure 6a,e,g, supporting C−O cleavage) and the decay of B3 into B2 (Figure 6c, supporting C−C cleavage), (2) the generation of “OOC−CF<sub>2</sub>CF<sub>2</sub>−COO<sup>−</sup>′ from B3 (CF<sub>3</sub>−O−CF<sub>2</sub>CF<sub>2</sub>−COO<sup>−</sup>) and the generation of “OOC−COO<sup>−</sup>′ from R<sub>6</sub>−O−CF<sub>2</sub>−COO<sup>−</sup>′ structures, and most importantly (3) the high deF % of linear PFECAs with short oxygen-segregated fluorocarbon moieties. The results in Figure 3df,h show a clear trend that PFECAs containing longer fluorocarbon moieties (rather than a longer length of the molecule) yield a lower deF %. Because the perfluorocarboxyl decomposition can only ensure the liberation of two F<sup>−</sup> ions, if this step yields a full-carbon-chain PFCFA containing two or more fluorocarbons, a relatively easy H/F exchange on the α-position will occur, yielding R<sub>6</sub>−CH<sub>4</sub>−COO<sup>−</sup>′. As previously elucidated, the reductive defluorination of this product is very sluggish, especially when the R<sub>6</sub> moiety is short (i.e., lack of weak C−F bonds).<sup>40</sup>

Among all PFECAs, B1 (CF<sub>3</sub>−O−CF<sub>2</sub>−COO<sup>−</sup>′) allowed an outstanding deF % at 91% because either C−O cleavage or decarboxylation will trigger the perfluorocarboxyl decomposition mechanism to liberate all five F<sup>−</sup> ions from the two oxygen-segregated single fluorocarbons. We hypothesized that the incomplete defluorination was attributed to the minor chance of H/F exchange on the α-position (Figure 5a). To verify this hypothesis, we examined the degradation of polyfluorinated CF<sub>3</sub>−O−CH<sub>3</sub>−COO<sup>−</sup> under the same reaction conditions (Figure 7). As expected, the −CH<sub>3</sub>− group at the α-position leads to a high recalcitrance in comparison with B1 (Figure 3c,d).

However, to our surprise, the degradation at 24 h (30%) was much higher than the full-carbon-chain counterpart CF<sub>3</sub>−CH<sub>2</sub>−COO<sup>−</sup>′ (<2%).<sup>40</sup> The overall deF % of 28% indicates near-complete defluorination of the decayed 30% fraction of the parent compound, and the time profiles of the parent compound decay and defluorination are highly symmetric. These results support the degradation mechanism of C−O bond cleavage rather than a stepwise H/F exchange. Therefore, C−O bond cleavage can still occur in a perfluorinated ether structure, with a hydrocarbon moiety segregating the −COO<sup>−</sup>′ group from the fluorinated moiety. The rate is faster than in a polyfluorinated full-carbon-chain structure but slower than in a perfluorinated ether structure.

For comparison, under the same reaction conditions, the deF % for the full-carbon CF<sub>3</sub>−CF<sub>2</sub>−COO<sup>−</sup>′ was 53%.<sup>40</sup> In our previous study, by assuming that CF<sub>3</sub>−CF<sub>2</sub>−COO<sup>−</sup>′ will take either H/F exchange (forming the highly recalcitrant CF<sub>3</sub>−CH<sub>2</sub>−COO<sup>−</sup>′ with negligible further degradation, with an overall deF % of 40%) or DHEH (leading to 100% defluorination via forming CF<sub>3</sub>−COO<sup>−</sup>′), we estimated that the probability of CF<sub>3</sub>−CF<sub>2</sub>−COO<sup>−</sup>′ undergoing the H/F exchange versus DHEH is 75 versus 25%.<sup>40</sup> Similarly, if all
B1 CF$_3$−O−CF$_2$−COO$^-$ first undergoes C−O or C−C bond cleavage, 100% defluorination would be achieved. If all B1 first undergoes H/F exchange to yield CF$_3$−O−CH$_2$−COO$^-$ (deF % = 40% at this step), which then undergoes slow degradation for up to 30%, this would result in 40% + 60% × 30% = 58% defluorination. Hence, to yield an overall defluorination of 91% through the two competing pathways, the probability for B1 to undergo H/F exchange is only 21%. This significantly decreased probability of H/F exchange from 75% to 21% should be attributed to the increased α-position C−F BDE in the R$_8$−O−CF$_3$−COO$^-$ structures (Figure S13g,h). This mechanistic insight also explains the low def% for B2 CF$_3$−O−CF$_2$F$_2$−COO$^-$ and B3 CF$_3$−O−CF$_2$F$_2$−COO$^-$, as the lower α-position C−F BDEs (Figure 4b,c) enabled easier H/F exchange. In Figure 3, the parent compound decays of B2 and B3 were faster than those of all R$_8$−O−CF$_2$−COO$^-$ compounds. The formation of −CH$_2$− at the α-position significantly slowed down further degradation. In contrast, all PFECA structures that allowed higher deF % than PFCAs (~55%)$^{40}$ contain only short (C1 or C2) fluorocarbon moieties, which suppress the direct defluorination via H/F exchange (an unfavorable pathway, typically breaking weak C−F bonds) and enhance the indirect defluorination via C−O or C−C bond cleavage (a favorable pathway, breaking all C−F bonds on the carbon bearing −OH, regardless of the BDEs).

The above mechanistic insights also explain the degradation pattern of branched PFECA compounds. The branching −CF$_3$ generates distinctly weak tertiary C−F bonds, especially at the α-position (Figures 4i and S2). As shown in Figures 5b and 6b, these structures have a high tendency to undergo H/F exchange. The following cleavage of the branching −CF$_3$ leads to the formation of −CH$_2$− at the α-position, thus retarding further degradation. The longest structure A3 has three tertiary C−F bonds; thus, the parent A3 and the C−O cleavage products A2 and A1 all have a high probability of an unfavorable H/F exchange. Therefore, A3 showed the lowest deF % among the three branched PFECA compounds. From the HRMS data for all PFECA structures (Tables S1−S9), in general, the TPs with one H/F exchange increased at the beginning of the reaction and then slowly decreased. In contrast, the two H/F exchange TPs slowly accumulated throughout the reaction, indicating high recalcitrance. In comparison to linear PFECA structures and full-carbon-chain PFCAs, the slower parent compound decay of branched PFECA is probably attributed to the kinetic hindrance by the branching −CF$_3$.

We note that earlier studies by Bao et al.$^{38,39}$ on the degradation of HFPO oligomer acids (A1, A2, and A3) observed a significantly faster parent compound decay and higher deF % than our observations. In comparison to our reaction settings (one UV lamp for a 600 mL solution, pH 9.5, and 10 mM sulfite), Bao et al. used considerably more favorable conditions, including intense UV irradiation (16 similar UV lamps for a 45 mL solution), tripled basicty (pH 10), and a doubled sulfite concentration (20 mM). Because the duplication of using 20 mM sulfite at pH 10 in our photocatalysts (one UV lamp for a 600 mL solution) achieved limited improvements on deF % (Figure S13), the significantly higher defluorination observed by Bao et al.$^{38,39}$ should be attributed to the higher intensity of the 254 nm UV irradiation. Nonetheless, by comparing all PFECA compounds, we have identified new structural features allowing much deeper defluorination than HFPO oligomers. We expect that further enhanced degradation of PFECA structures can be achieved under energy-efficient reaction conditions, which are under optimization in our lab.

Implications for Fluorochemical Design and Environmental Remediation. As seen from the diverse PFECA structures involved in this study, the design of PFECA is highly flexible as multiple fluorinated building blocks can be integrated into the molecule in various sequences. Although the design rationale of individual PFECA compounds (e.g., branched vs linear and the length of oxygen-segregated fluorocarbon moieties) and their targeted properties for specific industrial applications remain largely unknown to the environmental chemistry community, we are able to identify critical molecular features that can lead to enhanced PFECA degradation using reductive approaches. UV irradiation (on sulfite, iodide, indole, or hydroxyl radical scavengers),$^{36−39}$ plasma treatment,$^{31}$ and high-energy irradiation$^{43}$ all involve eq$_{O_2}$ as a primary reactive species. In general, the switch from full-carbon-chain PFCAs to PFECA has indeed brought in unique advantages that enable deeper defluorination, including (1) spontaneous defluorination from alcohol intermediates upon C−O cleavage and (2) suppressed H/F exchange due to the strong C−F bonds. To minimize the incomplete defluorination caused by the conversion into recalcitrant products (e.g., with −CH$_2$− separating the fluoroalkyl moiety and −COO$^-$), a desirable structural feature is R$_8$−O−CF$_2$−COO$^-$. In other words, the last building block of the PFECA molecule can be a TFEO; after the epoxide ring opens, the alcohol product R$_8$−O−CF$_3$HOH will transform to R$_8$−O−CF$_2$−COO$^-$. As elucidated in earlier sections, the relatively high BDE of the α-position C−F favors indirect defluorination through C−O cleavage and decarboxylation. The other desirable structural feature is to limit the length of other fluorocarbon moieties segregated by ether oxygen atom. If the chain length is C1 (either CF$_3$−O− or −O−CF$_2$−O−), the C−O cleavage is expected to provide complete defluorination of that fluorocarbon moiety. This prediction, which is based on model PFECA structures studied in this work, can be further examined when chemicals containing −O−CF$_2$−O− moieties (e.g., CF$_3$−(O−CF$_2$)$_n$−O−CF$_2$−COO$^-$, n = 1 to 3)$^{24,27}$ become available for experimental tests. Because the oxygen atoms substantially increase C−F BDEs (Figure 4), direct H/F exchange on C1 or C2 fluorocarbon moieties (not linked with −COO$^-$) is less likely. However, for C2 fluorocarbon moieties (e.g., −O−CF$_2$F$_2$O−), the formation of −O−CF$_2$F$_2$COO$^-$ will still induce a low probability of H/F exchange.

On the other hand, the mechanistic insights from this study will guide the development of PFECA degradation technologies. In particular, if direct defluorination cannot be fully avoided, effective degradation of the recalcitrant polyfluorinated products will be necessary to ensure deep or complete defluorination. Although we observed poor defluorination from the branched PFECA structures that contain very weak tertiary C−F bonds and a long C3 fluorocarbon moiety, studies by Bao et al.$^{38,39}$ have achieved deep defluorination of those structures by applying a high UV intensity. Therefore, coordinated efforts from both fluorochemical design (e.g., developing PFECA with high degradability) and environmental remediation (e.g., optimizing the consumption of energy and chemicals) can be expected to transform the development, use, and treatment of fluorinated chemicals, with minimal adverse impact on the environment.
Detailed experimental procedures; LC–MS data; calculation results; ion-chromatography analyses of small ionic TPs; additional kinetics data; and proposed PFCA degradation mechanisms (PDF)

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Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acs.est.9b05869

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

Financial support was provided by the UCR Initial Complement for J.L., the UCR Collaborative Seed Grant for J.L., B.M.W., L.X., and H.K., the National Science Foundation (CHE-1709719 for J.L. and CHE-1709286 for Y.M. and Y.Y.), and the Strategic Environmental Research and Development Program (ER-1289 for J.L., M.J.B., and B.M.W.). M.J.B. also received a scholarship from the UCR Water SENSE Integrative Graduate Education and Research Traineeship (IGERT) supported by the NSF. UCR undergraduate researchers Andrew Dalmacio, Duy Dao, Maggy Harake, Vivian Ngo, and Wenxiaoshan Sui provided technical assistance on photochemical reactions. We also thank Dr. Mark Strynar for kindly providing compound B1.

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