

Degradation of Perfluoroalkyl Ether Carboxylic Acids (PFECAs) with Hydrated Electrons: Structure-Reactivity Relationships and Environmental Implications

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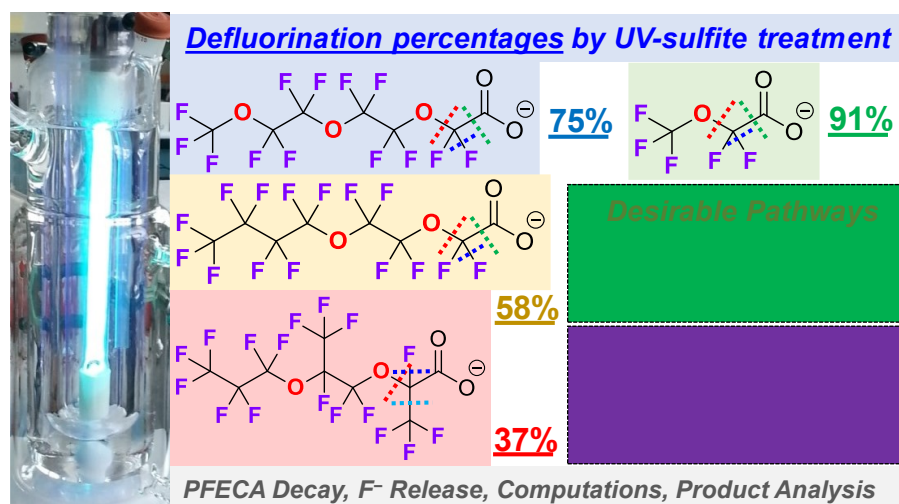
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ABSTRACT

This study explores structure-reactivity relationships for the degradation of emerging perfluoroalkyl ether carboxylic acid (PFECA) pollutants with UV-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 PFECA degradation mechanisms and pathways. In comparison to the traditional full-carbon-chain perfluorocarboxylic acids (PFCAs), the distinct degradation behavior of PFECAs is attributed to their ether structures. The ether oxygen atoms elevate the bond dissociation energy (BDE) of the C–F bonds on the adjacent –CF₂– 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 PFECAs, branched PFECAs has 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 due to 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 bonds make PFAS molecules recalcitrant to natural and engineered degradation,⁶ leading to global PFAS pollution⁷ and worldwide efforts on PFAS regulation.⁸⁻¹¹ Fluorochemical industries have been phasing out the production and use of some legacy PFASs (e.g., PFOA)^{2, 12} due to their heavy pollution to the environment and high toxicities to humans.^{13, 14} Perfluoroalkyl ether carboxylic acids (PFECAs) that contain ether C–O bonds in molecules have been developed as “less bioaccumulative alternatives” to the full-carbon-chain predecessor PFASs.¹⁵ However, as toxicological studies have revealed even higher bioaccumulation potential and toxicity of some PFECAs than PFOA,¹⁶⁻¹⁹ PFECAs 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, PFECAs have been detected in much higher concentrations than legacy PFASs.^{24, 25} Furthermore, due to the facile synthesis of PFECAs from a flexible choice of fluoroalkene oxide building blocks (e.g., **SI 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 the carbon/resin regeneration wastes and membrane rejects still need 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 PFOS. A few studies have investigated the destruction of selected PFECAs, including

sonochemical oxidation with persulfate,³⁶ photocatalytic oxidation with phosphotungstic acid under pressurized O₂,³⁷ and reduction with UV-generated hydrated electrons (e_{aq}^-).^{38, 39} These early studies have revealed a variety of mechanistic insights on PFECA degradation. In particular, reductive degradation of branched PFECAs (e.g., GenX in **Figure 1**) using e_{aq}^- is much more effective than oxidative degradation using sulfate radicals.^{38, 39} 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 e_{aq}^- produced from aqueous sulfite under UV irradiation.⁴⁰ The degradation mechanisms for perfluorocarboxylic acids (PFCAs) and fluorotelomer carboxylic acids (FTCAs) are significantly different. FTCAs ($R_F-CH_2CH_2-COO^-$, R_F representing the fluorocarbon moiety) are much more recalcitrant than PFCAs (R_F-COO^-), especially when the chain length of R_F is short. The incomplete defluorination of PFCAs can also be attributed to the formation of polyfluorinated $R_F-CH_2-COO^-$ products.⁴⁰ These findings indicate the importance of a direct linkage between R_F and $-COO^-$ to allow an effective degradation of full-carbon-chain PFASs using e_{aq}^- . In comparison, the flexible incorporation of ether linkages in PFECAs 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 e_{aq}^- ? (2) Practically, in comparison to full-carbon-chain PFCAs, can PFECAs be treated in higher effectivity by the promising reductive technologies?

To answer these questions, we investigated the reductive defluorination of ten PFECAs 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 and spontaneous bond cleavage upon reaction with e_{aq}^- , and transformation product analyses with high-resolution mass spectrometry. These results collectively reveal and confirm novel mechanistic insights into PFECA degradation. The findings will advance the treatment technologies for existing PFECA pollutants and facilitate the molecular design of fluorochemicals with enhanced degradability.

MATERIAL AND METHODS

This study used ten PFECAs with fine-tuned structural variability in four categories (**A1** through **D2** in **Table 1**) and two special compounds (trifluoropyruvate $CF_3-CO-COO^-$ and polyfluorinated $CF_3-O-CH_2-COO^-$) for mechanistic investigation. Detailed information on these chemicals is included in the Supporting information (**SI**). 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 PFECAs and traditional full-carbon-chain PFCAs. Briefly, photochemical degradation of individual PFECAs 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 of PFECA, 10 mM of Na_2SO_3 , and 5 mM of $NaHCO_3$, and the pH was adjusted to 9.5 with NaOH. Released F^- was measured with an ion-

selective electrode, which has been validated for the quantification accuracy by ion chromatography. All reactions were conducted in triplicates of operations from the preparation of stock solution to the quantification of defluorination percentage (deF%), which is defined as

$$\text{deF}\% = \frac{C_{\text{F}^-}}{C_0 * N_{\text{C-F}}} \times 100\% \quad (1)$$

where C_{F^-} is the molar concentration of F^- ion released in solution, C_0 is the initial molar concentration of the parent PFECAs, and $N_{\text{C-F}}$ 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 transformation products that have pure chemicals available as analytical standards, as well as a liquid chromatography–high resolution mass spectrometer (LC–HRMS) for the screening of transformation products without analytical standards. The quality assurance and quality control of MS analyses have been addressed previously,⁴⁰ with new details provided in the SI for the PFECA degradation samples. Small ionic species including trifluoroacetate, trifluoropyruvate, oxalate, $\text{CF}_3\text{--O--CF}_2\text{--COO}^-$, and $\text{CF}_3\text{--O--CH}_2\text{--COO}^-$ were analyzed by ion chromatography (IC) equipped with a conductivity detector (specific separation conditions are described in the SI).

RESULTS AND DISCUSSION

Degradation of PFECAs. Different Degradability between PFECAs and Traditional PFCAs. Figure 2 shows the decay and defluorination of four PFASs representing full-carbon-chain PFCAs, linear PFECAs, and branched PFECAs. The parent compound decay is the fastest for the two traditional PFCAs and the slowest for the branched PFECA (Figure 2a). The order of parent compound decay rates for these structures does not match the order of their defluorination percentages. Figure 2b shows distinct defluorination profiles between PFECAs and traditional

PFCAs, as well as between the linear and branched PFECAs. All four PFASs showed an initial period of rapid F^- release, followed by slower F^- release before reaching a plateau. However, the initial rates of defluorination from the two PFECAs are slower than those from the two PFCAs. In particular, the linear PFECA showed a slower initial rate but a significantly deeper defluorination than PFHpA (i.e., 75% vs. 55% of the 13 F atoms in both molecules). In contrast, the branched PFECA showed both a slower rate and a less extent of defluorination than PFNA (i.e., 40% vs. 58% of the 17 F atoms in both molecules). These results suggest new structure-reactivity relationships governing PFECA degradation. To systematically understand the mechanisms, we extended the compound scope to ten individual PFECAs, which exhibited structure-specific profiles of parent compound decay and defluorination (**Table 1** and **Figure 3**).

Different Degradability of the Four PFECA Structure Categories. Category *A* includes structures **A1–A3** with branched $-CF_3$ groups. They are the acid forms of hexafluoropropylene oxide dimer, 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 lower deF% (**Figure 3b**). The defluorination percentages of these branched PFECAs (31–45%) were significantly lower than that of traditional PFCAs (~55%) under the same reaction condition.⁴⁰ Category *B* includes mono-ether structures **B1–B3** with the CF_3O- head group and linear $-(CF_2)_n-$ moieties ($n = 1, 2, \text{ and } 3$, 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 are similar to full-carbon-chain PFCAs (**Figure 2a**).⁴⁰ The final defluorination percentages are also similar (61% and 52% for **B2** and **B3**, respectively vs. 55% for PFCAs). In stark contrast, while the decay of **B1** ($n=1$) was much slower than **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,⁴⁰ 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 hours to complete, but the maximal deF% was around 55% (Table 1, entry E1 vs. E2).

We further tested two linear multi-ether PFECA categories, *C* and *D*. Both categories contain tetrafluoroethylene oxide (TFEO) building blocks, but the head groups are CF_3O- and C_4F_9O- , respectively. With the $-O-CF_2-COOH$ as the ending group, the parent compound decay became slow again (Figures 3e and 3g). Like the decay profile for the long molecule *A3* (Figure 3a), the decay of long molecule *D2* was also incomplete within 48 h. The other three structures *C1*, *C2*, and *D1* showed similar profiles of parent compound decay. The notable difference between these two PFECA categories is that, *C1* and *C2* with the short CF_3O- head group yielded significantly higher deF% (82% and 75%, respectively) than *D1* and *D2* with the long C_4F_9O- head group (58% and 65%, respectively) (Figures 3f versus 3h).

Structural Effects on PFECA Degradation. The kinetic data shown above have indicated the following characteristics of PFECA degradation in comparison to traditional PFCAs: (i) branched PFCAs showed slower decay and lower defluorination; (2) linear PFCAs showed slower decay if the end group is $-O-CF_2-COO^-$, or very similar rate of decay if more than one $-CF_2-$ linkers are present in $-O-(CF_2)_n-COO^-$; (3) linear PFCAs showed at least similar deF%, while those containing shorter oxygen-segregated fluoroalkyl moieties showed even higher deF%. To interpret these interesting results at the molecular level, we conducted theoretical calculations and transformation product analyses.

Theoretical Calculations of C–F and C–O Bond Dissociation Energies (BDEs). The BDEs of C–F and ether C–O bonds in all PFECA structures were calculated with density functional theory (DFT). Representative results are shown in **Figure 4**, and the full data sets are collected in **SI Figures S2–S5**. We identified new trends for C–F BDEs in PFECA structures comparing to full-carbon-chain PFCA structures. First, the ether oxygen elevates the BDE of C–F on the adjacent fluorocarbons. While the terminal $-\text{CF}_3$ in long fluoroalkyl chains has the typical C–F BDE <119 kcal mol $^{-1}$ (**Figures 4d, 4f, 4h and 4i**), the inclusion of ether oxygen atoms increased the C–F BDE to 120–123 kcal mol $^{-1}$ (**Figures 4a–4c and 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 PFCA structures were not found in linear PFECA structures (**Figure 4f** versus **4g and 4h**). In particular, the typical weak C–F bond at the α -position of PFCA structures (i.e., BDE <108 kcal mol $^{-1}$, **Figures 4d and 4f**) does not exist in linear PFECA structures with an ether oxygen at the β -position (i.e., $\text{R}_\text{F}-\text{O}-\text{CF}_2-\text{COO}^-$, BDE >111 kcal mol $^{-1}$, **Figures 4a, 4g, and 4h**). However, when the fluoroalkyl chain adjacent to $-\text{COO}^-$ is longer (i.e., $n = 2$ or 3 in $\text{R}_\text{F}-\text{O}-(\text{CF}_2)_n-\text{COO}^-$), the weak C–F bond at the α -position appears again (**Figures 4b and 4c**). These novel trends on C–F BDEs in linear PFECA structures corroborate the different rates of parent compound decay. The two structures with weak α -position C–F bonds (**B2** and **B3** in **Figure 3c**) showed a similar rate of decay as the full-carbon-chain PFCA structures (**Figure 2a**), while other $\text{R}_\text{F}-\text{O}-\text{CF}_2-\text{COO}^-$ structures showed slower parent compound decay (**B1, C1, and C2** in **Figures 3c and 3e**).

As for the branched PFECA structures, the inclusion of ether oxygen atoms showed a similar effect on elevating the C–F BDEs. In comparison to a full-carbon-chain branched PFCA that contains very weak tertiary C–F bonds,⁴¹ the oxygen atoms in HFPO-TrA significantly strengthen all

secondary and tertiary C–F bonds (**Figure 4i** versus **4j**). Although the HFPO oligomer acids contain distinctly weak tertiary C–F bonds (i.e., BDE <104 kcal mol⁻¹), the rates of parent compound decay were slower than 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,^{38,} 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⁻ (**Figures 4k–4n**). 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⁻ (81–94 kcal mol⁻¹). This phenomenon was observed in all PFECAs regardless of the total number of ether linkages, branched versus linear molecular backbone, or distance between –COO⁻ and the first ether linkage (**Figure 4k** versus **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 **SI Figures S2–S5** for full data sets). However, if the PFECA 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, **Figures 4m** and **4n**). In addition, due to the electron-withdrawing effect by –CF₃ branches, BDEs of these “normal” C–O bonds in branched multi-ether structures (82–84 kcal mol⁻¹) are lower than those in linear multi-ether structures (89–97 kcal mol⁻¹).

Spontaneous Bond Cleavage in Electron-Added PFECA Radical Anion Structures. The distinctly weak C–O in all PFECAs and 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 $[R_F\text{-COO}]\bullet^{2-}$ upon adding an extra electron (simulating the e_{aq}^-) to the original PFECA anion ($R_F\text{-COO}^-$).⁴⁰ As expected, spontaneous stretching of α -position C–F bonds (**Figures 5a** and **5b**) and ether C–O bonds (**Figures 5c** and **5d**) were observed. The distance between the two atoms went considerably longer than the normal length of C–O and C–F bonds (i.e., bond cleavage). The results for all PFECA structures are collected in **SI Figures S6** and **S7**.

Interestingly, although the calculated C–O bond cleavage in $[R_F\text{-COO}]\bullet^{2-}$ structures indeed occurred at the first ether linkage counted from -COO^- , the cleaved C–O bond was not the “significantly weaker one” as calculated in the original $R_F\text{-COO}^-$ (e.g., **Figure 5c** versus **4n**). This discrepancy could be due to the addition of the extra electron, which altered the bonding structure of PFECA anions. More importantly, the calculation shows that C–O bond cleavage can be a major pathway for PFECA degradation by e_{aq}^- . The previously elucidated cleavage of weak C–F bonds⁴⁰ was also observed both from branched PFECAs (with very weak tertiary C–F bonds) and from the linear structure **B1** $\text{CF}_3\text{-O-CF}_2\text{-COO}^-$ 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 makes many C–F bonds 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. Based on 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^- .⁴⁰ Hence, we hypothesized that the degradation of PFECAs 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) the characteristic

cleavage of ether C–O bonds. To detect the transformation products (TPs) and confirm the degradation pathways, we used both targeted analysis with triple quadrupole mass spectrometry and suspect screening with high-resolution mass spectrometry data (all results collected in **SI Tables S1–S9**). A series of TPs was detected, well supporting all three proposed degradation pathways. The overall TP detection and 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 PFECAs are provided in **SI 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 concentration of **A2** (7.9 μM) and **A1** (3.7 μM) were detected at 8 h and 12 h, respectively. We attribute this transformation to the cleavage of the first C–O bond counted from the terminal $-\text{COO}^-$. The two fragments reacted with H_2O to form two perfluorinated alcohols, which were not stable and subject to HF elimination to acyl fluoride.⁴² ⁴³ The subsequent hydrolysis generated the carboxylic acid, resulting in the net conversion from $\text{R}_\text{F}-\text{CF}_2\text{OH}$ into $\text{R}_\text{F}-\text{COO}^-$ and two F^- ions. The C–O cleavage on the first ether linkage counted from $-\text{COO}^-$ shortens HFPO-TeA into HFPO-TrA, then into HFPO-DA, which can be further degraded into $\text{CF}_3\text{CF}_2-\text{COO}^-$ via another C–O cleavage (**Scheme 1**). Each round of C–O cleavage also generated the same product $\text{CF}_3\text{CF}(\text{OH})-\text{COO}^-$, which underwent further HF elimination into $\text{CF}_3-\text{CO}-\text{COO}^-$ (trifluoropyruvate, TFPy), as structures with F and OH on the same carbon (e.g., FCH_2OH) are generally unstable.⁴⁴ We confirmed the formation of TFPy during the degradation of HFPO-DA with IC detection (**SI Figure S8**). Like CF_3-COO^- (trifluoroacetic acid, TFA), the pure TFPy also showed near-complete defluorination (**SI Figure S9**), and TFA is a possible degradation intermediate (**SI 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 high-resolution MS data identified a series of H/F exchange products from the HFPO oligomer acids. Based on the calculation results, we assign the C–H bonds to the branched carbons (particularly the α -position branched carbon) where weak tertiary C–F bonds are located (**Figure 6b** and **Scheme 1a**). We also observed products missing one or more $-\text{CF}_3$ groups (i.e., H/ CF_3 exchange). By comparing the results with those for linear PFECAs, such TP structures missing $-\text{CF}_3$ groups are specific for branched PFECAs. Therefore, we interpret the transformation pathway to be the cleavage of the branching $-\text{CF}_3$ rather than the terminal $-\text{CF}_3$. In addition, the degradation products and reaction schemes from pure HFPO-TrA and HFPO-DA (**SI Tables S1–S2** and **Schemes S1–S2**) further corroborate the mechanistic insights obtained from HFPO-TeA degradation.

For the degradation of **B3** ($\text{CF}_3\text{O}-\text{CF}_2\text{CF}_2\text{CF}_2\text{COO}^-$), the C–O bond cleavage mechanism was confirmed by the detection of $^-\text{OOC}-\text{CF}_2\text{CF}_2\text{COO}^-$ (**Figure 6c** and **Scheme 2a**). The head CF_3- group was thus believed to be fully defluorinated via the formation of unstable CF_3OH . The *DHEH* mechanism was also confirmed by the generation of **B2** $\text{CF}_3\text{O}-\text{CF}_2\text{CF}_2\text{COO}^-$. 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 multi-ether linear PFECAs **C2** and **D2** also followed the three reaction pathways, which are supported by the TPs identified (**Figures 6e–6h**). Although the C–F BDEs of the α -position $-\text{CF}_2-$ in these structures are higher than in full-carbon-chain PFCAs

(**Figure 4g** versus **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 $-\text{O}-\text{CF}_2-\text{COO}^-$) was supposed to generate $\text{HO}-\text{CF}_2-\text{COO}^-$, which should further decompose into oxalate ($^-\text{OOC}-\text{COO}^-$). IC detection confirmed the formation of oxalate (**SI Figure S11**), thus further consolidating this C–O bond cleavage mechanism.

Overall Mechanistic Insights into Reductive PFECA Degradation. Based on the degradation kinetics, theoretical calculation, and TP analysis, we have confirmed that the PFECAs have three pathways for the reductive degradation by e_{aq}^- : (1) ether C–O bond cleavage, (2) C–C bond cleavage, including the decarboxylation step of *DHEH* and the cleavage of $-\text{CF}_3$ 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 the PFECAs interacting with e_{aq}^- . First, control experiments with UV irradiation without adding sulfite showed very slow and limited degradation (**SI Figure S12**). Second, spontaneous C–O bond cleavage was observed after the PFECA anion received an extra electron (**Figure 5**). Third, the generation of e_{aq}^- from sulfite has been confirmed by spectroscopic observations,^{45, 46} and other chemicals such as iodide⁴⁷ and indole⁴⁸ have also been used as the source of e_{aq}^- and achieved similar results for PFOA defluorination.

The cleavage of the C–O or C–C bond in PFECAs will generate perfluoroalcohols, which will undergo HF elimination and the following hydrolysis to yield two F^- and the corresponding carboxylic acids. This mechanism has been collectively supported by (1) the decay of HFPO and

TFEO oligomer acids into shorter analogs (**Figures 6a, 6e, and 6g**, supporting C–O cleavage) and the decay of **B3** into **B2** (**Figure 6c**, supporting C–C cleavage), (2) the generation of $^-OOC-CF_2CF_2-COO^-$ from **B3** ($CF_3-O-CF_2CF_2CF_2-COO^-$) and the generation of $^-OOC-COO^-$ from $R_F-O-CF_2-COO^-$ structures, and most importantly (3) the high deF% of linear PFECAs with short oxygen-segregated fluorocarbon moieties. Results in **Figures 3d, 3f, and 3h** show the clear trend that PFECAs containing longer fluorocarbon moieties (rather than the longer molecule) yielded lower deF%. Since the perfluoroalcohol decomposition can only ensure the liberation of two F^- ions, if this step yields a full-carbon-chain PFCA containing two or more fluorocarbons, relatively easy H/F exchange on the α -position will occur, yielding $R_F-CH_2-COO^-$. As previously elucidated, the reductive defluorination of this product is very sluggish, especially when the R_F moiety is short (i.e., lack of weak C–F bonds).⁴⁰

Among all PFECAs, **B1** ($CF_3-O-CF_2-COO^-$) allowed an outstanding deF% at 91% because either C–O cleavage or decarboxylation will trigger the perfluoroalcohol decomposition mechanism to liberate all five F^- 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 $CF_3-O-CH_2-COO^-$ under the same reaction condition (**Figure 7**). As expected, the $-CH_2-$ group at the α -position leads to a high recalcitrance in comparison with **B1** (**Figure 3c and 3d**). However, to our surprise, the degradation at 24 h (30%) was much higher than the full-carbon-chain counterpart $CF_3CH_2-COO^-$ (< 2%).⁴⁰ The overall deF% of 28% indicates a near-complete defluorination of the decayed 30% fraction of the parent compound, and the time profiles of 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 *poly*fluorinated ether structure with a hydrocarbon moiety segregating the –COO^- group from the fluorinated moiety. The rate is faster than in a *poly*fluorinated full-carbon-chain structure but slower than in a *per*fluorinated ether structure.

For comparison, under the same reaction condition, the deF% for the full-carbon $\text{CF}_3\text{CF}_2\text{–COO}^-$ was 53%.⁴⁰ In our previous study, by assuming that $\text{CF}_3\text{CF}_2\text{–COO}^-$ will take either H/F exchange (forming the highly recalcitrant $\text{CF}_3\text{CH}_2\text{–COO}^-$ with negligible further degradation, thus the overall deF% is 40%) or *DHEH* (leading to 100% defluorination via forming $\text{CF}_3\text{–COO}^-$), we estimated that the chance for $\text{CF}_3\text{CF}_2\text{–COO}^-$ taking H/F exchange versus *DHEH* is 75% versus 25%.⁴⁰ Similarly, if all **B1** $\text{CF}_3\text{–O–CF}_2\text{–COO}^-$ first undergoes C–O or C–C bond cleavage, 100% defluorination would be achieved. If all **B1** first undergoes H/F exchange to yield $\text{CF}_3\text{–O–CH}_2\text{–COO}^-$ (deF% = 40% at this step), which then undergoes slow degradation for up to 30%, this would result in $40\% + 60\% \times 30\% = 58\%$ defluorination. Hence, to yield an overall defluorination of 91% through the two competing pathways, the probability for **B1** to take H/F exchange is only 21%. This significantly lowered probability of H/F exchange from 75% to 21% should be attributed to the elevated α -position C–F BDE in the $\text{R}_\text{F}\text{–O–CF}_2\text{–COO}^-$ structures (**Figures 4a, 4g, and 4h**). This mechanistic insight also explains the low deF% for **B2** $\text{CF}_3\text{–O–CF}_2\text{CF}_2\text{–COO}^-$ and **B3** $\text{CF}_3\text{–O–CF}_2\text{CF}_2\text{CF}_2\text{–COO}^-$ as the lower α -position C–F BDEs (**Figures 4b and 4c**) enabled easier H/F exchange. In **Figure 3**, the parent compound decay of **B2** and **B3** were faster than all $\text{R}_\text{F}\text{–O–CF}_2\text{–COO}^-$ compounds. The formation of $\text{–CH}_2\text{–}$ at the α -position significantly slowed down the further degradation. In contrast, all PFECAs that allowed higher deF% than PFCAs ($\sim 55\%$)⁴⁰ contain only short (C1 or C2) fluorocarbon moieties, which suppress the *direct* defluorination via H/F exchange (unfavorable pathway, typically breaking weak C–F bonds) and enhance the *indirect* defluorination via C–O or C–C bond cleavage

(favorable pathway, breaking all C–F bonds on the carbon bearing the –OH, regardless of the BDEs).

The above mechanistic insights also explain the degradation pattern of branched PFECAs. The branching –CF₃ generates distinctly weak tertiary C–F bonds, especially at the α -position (**Figure 4i** and **SI Figure 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 –CF₃ leads to the formation of –CH₂– 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 chance for the unfavorable H/F exchange. Therefore, **A3** showed the lowest deF% among the three branched PFECAs. From the HRMS data for all PFECAs (**SI Tables S1–S9**), in general, the TPs with one H/F exchange increased at the beginning of the reaction, then slowly decreased. In contrast, the two H/F exchange TPs slowly accumulated throughout the reaction, indicating high recalcitrance. In comparison to linear PFECAs and full-carbon-chain PFCAs, the slower parent compound decay of branched PFECAs is probably attributed to the kinetic hindrance by the branching –CF₃.

We note that earlier studies by Bao *et al.*^{38, 39} on the degradation of HFPO oligomer acids (**A1**, **A2**, and **A3**) observed 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 (sixteen similar UV lamps for a 45-mL solution), tripled basicity (pH 10), and doubled sulfite concentration (20 mM). Because the duplication of 20 mM sulfite at pH 10 in our photoreactors (one UV lamp for a 600-mL solution) achieved limited improvements on deF% (**SI 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 (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),⁴⁶⁻⁴⁹ plasma treatment,³⁴ and high-energy irradiation³³ all involve e_{aq}^- as a primary reactive species. In general, the switch from full-carbon-chain PFCA 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 $-\text{CH}_2-$ separating the fluoroalkyl moiety and the $-\text{COO}^-$), a desirable structural feature is $\text{R}_F\text{O}-\text{CF}_2-\text{COO}^-$. In other words, the last building block of the PFECA molecule can be a tetrafluoroethylene oxide; after the epoxide ring opens, the alcohol product $\text{R}_F\text{O}-\text{CF}_2\text{CF}_2\text{OH}$ will transform to $\text{R}_F\text{O}-\text{CF}_2-\text{COO}^-$. 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 atoms. If the chain length is C1 (either $\text{CF}_3\text{-O-}$ or $\text{-O-CF}_2\text{-O-}$), the C-O cleavage is expected to provide complete defluorination of that fluorocarbon moiety. This prediction, which is based on model PFECAs studied in this work, can be further examined when chemicals containing $\text{-O-CF}_2\text{-O-}$ moieties (e.g., $\text{CF}_3\text{-(O-CF}_2\text{)}_n\text{-O-CF}_2\text{-COO}^-$, $n = 1$ to 3)^{24, 27} become available for experimental tests. Because the oxygen atoms substantially elevate 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., $\text{-O-CF}_2\text{CF}_2\text{-O-}$), the formation of $\text{-O-CF}_2\text{-COO}^-$ 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 the *direct* defluorination cannot be fully avoided, effective degradation of the recalcitrant *poly*fluorinated products will be necessary to ensure a deep or complete defluorination. While we observed poor defluorination from the branched PFECAs 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 high UV intensity. Therefore, coordinated efforts from both fluorochemical design (e.g., developing PFECAs 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 to the environment.

404 **ASSOCIATED CONTENT**

405 **Supporting Information**

406 The Supporting Information is available free of charge on the ACS Publications website at DOI:
407 10.1021/acs.est.xxxxxxx.

408 Additional tables, figures, discussions, and detailed experimental procedures.

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412 **Notes**

413 The authors declare no competing financial interest.

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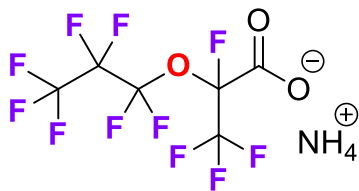
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Table 1. Overall Defluorination Percentages of PFECAs after 48 Hours of Reaction.^a

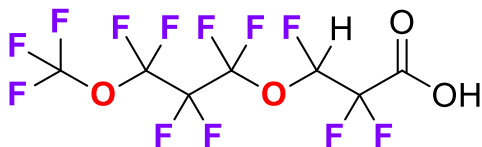
Entry	Structure	<i>n</i>	deF%
<i>A. Branched (HFPO oligomers)</i>			
<i>A1</i>		1	44.9 ± 5.3
<i>A2</i>		2	36.5 ± 2.9
<i>A3</i>		3	30.8 ± 4.2
<i>B. Mono-ether with head CF₃O-</i>			
<i>B1</i>		1	90.5 ± 2.1
<i>B2</i>		2	61.2 ± 7.5
<i>B3</i>		3	52.3 ± 3.1
<i>C. TFEO oligomers with head CF₃O-</i>			
<i>C1</i>		1	82.3 ± 4.4
<i>C2</i>		2	75.0 ± 3.8
<i>D. TFEO oligomers with head C₄F₉O-</i>			
<i>D1</i>		1	58.0 ± 4.0
<i>D2</i>		2	65.4 ± 6.3
<i>E. Full-carbon-chain PFCAs^b</i>			
<i>E1</i>		1	98.2 ± 5.0
<i>E2</i>		2-10	54.5 ± 3.5

^aReaction condition: 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.

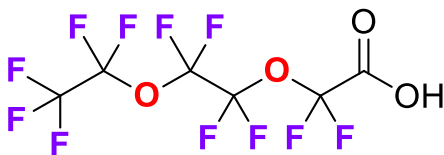
^bData from Ref. 40 for comparison. The average and standard deviation of the deF% value for n=2–10 is based on 27 data points (nine PFCA structures with triplicates).



Perfluoro(2-methyl-3-oxahexanoate)
(GenX, CAS No. 62037-80-3)



3H-perfluoro-3-[(3-methoxy-propoxy)
propionic acid]
(ADONA, CAS No. 958445-44-8)



Perfluoro[(2-ethyloxy-ethoxy)acetic acid]
(EEA, CAS No. 908020-52-0)

430
431 **Figure 1.** Examples of commercial perfluorinated (GenX and EEA) and polyfluorinated
432 (ADONA) ether carboxylic acids detected in the environment.

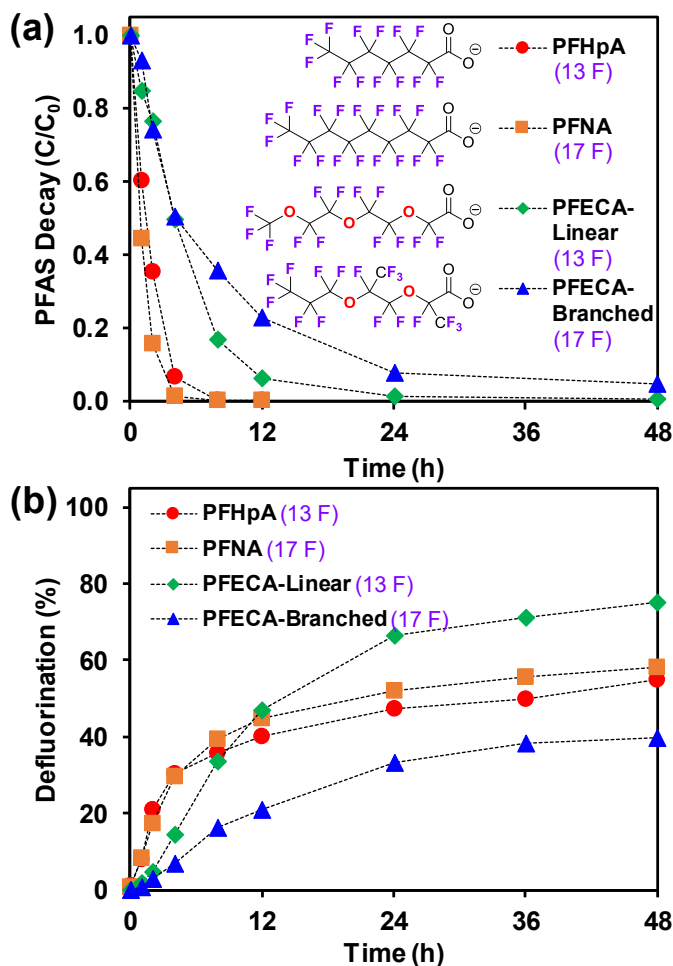


Figure 2. Time profiles for (a) parent compound decay and (b) defluorination percentages for two full-carbon-chain PFCAs with 13 and 17 F atoms, a linear PFECA with 13 F atoms, and a branched PFECA with 17 F atoms. Reaction conditions: PFAS (0.025 mM), Na_2SO_3 (10 mM), carbonate buffer (5 mM), 254 nm irradiation (a 18 W low-pressure Hg lamp for 600 mL solution) at pH 9.5 and 20°C.

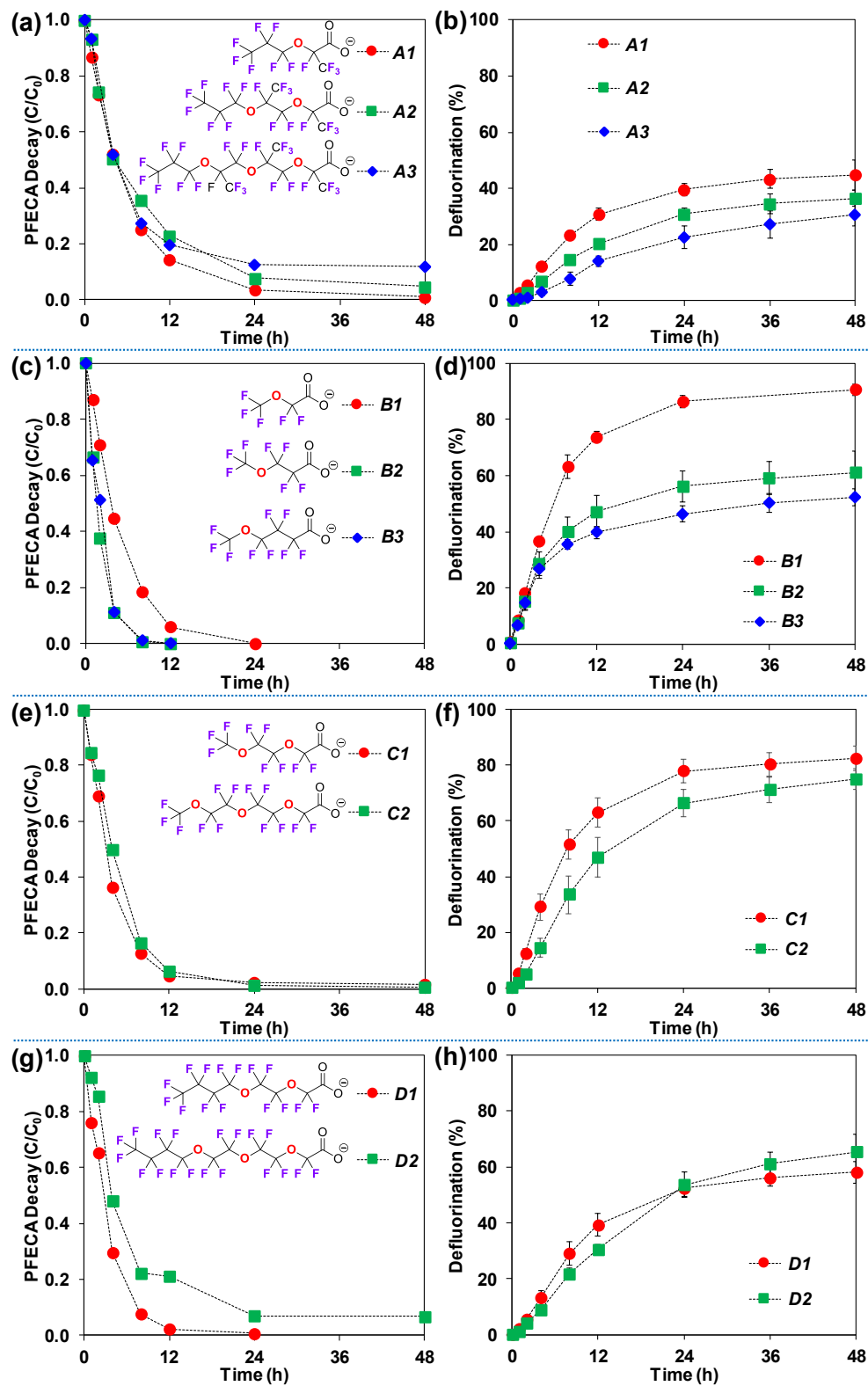


Figure 3. Time profiles of parent compound decay and defluorination for the four PFECA structure categories. Reaction conditions are described in the title of **Figure 2**.

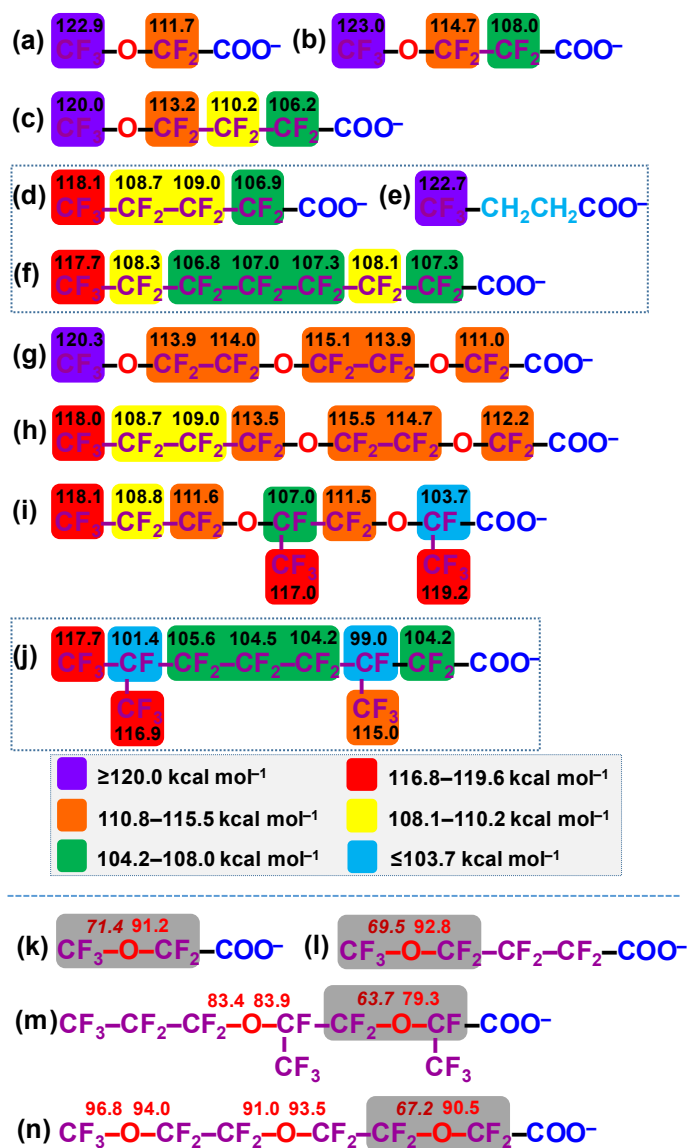


Figure 4. Calculated C–F BDEs (a to j) and C–O BDEs (k to n) (in kcal mol⁻¹) of selected PFASs at the B3LYP-D3(BJ)/6-311+G(2d,2p) level of theory. Results for all PFECA structures are collected in SI Figures S2–S5. Data for (d)–(f) and (j) are from Ref 40 and Ref 41, respectively.

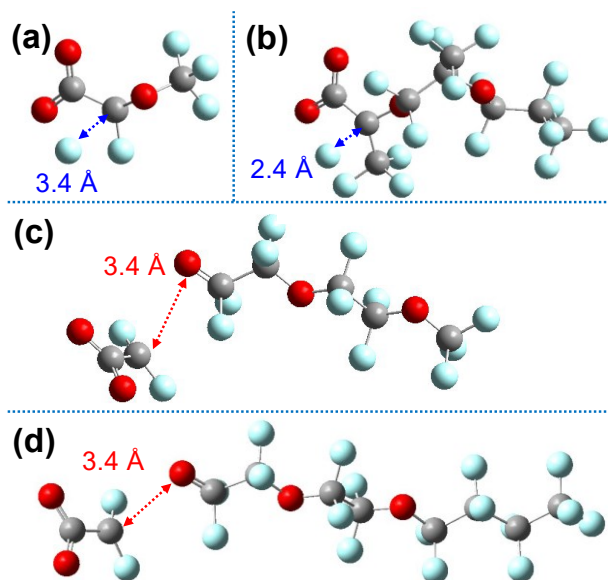


Figure 5. Geometry-optimized structure of the adducts of PFECA anions with an e_{aq}^- (PFECA $\bullet^{2-}$) at the B3LYP-D3(BJ)/6-311+G(2d,2p) level of theory, showing the stretching of C-F (blue) and C-O (red) bonds. Results for all PFECA structures are collected in **SI Figures S6–S7**.

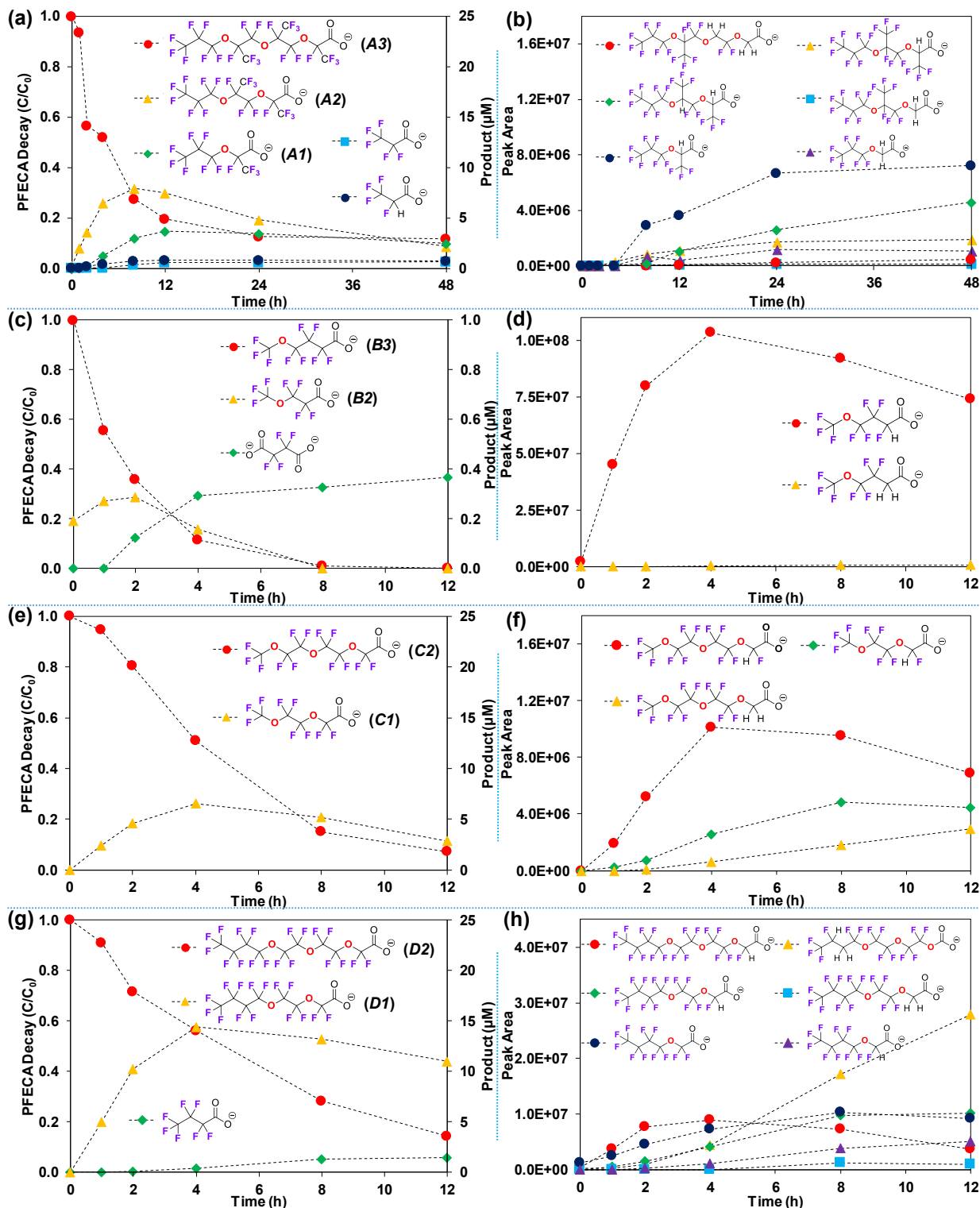


Figure 6. Representative degradation products of the longest compound in each structure category (*A3*, *B2*, *C2*, and *D2*, $C_0 = 25 \mu\text{M}$). Reaction conditions are described in the title of **Figure 2**. For each structure, quantified products with standard compounds are shown in the left panel, and species without standard compounds are presented in peak areas in the right panel. All detected species are listed in SI Tables S1–S9.

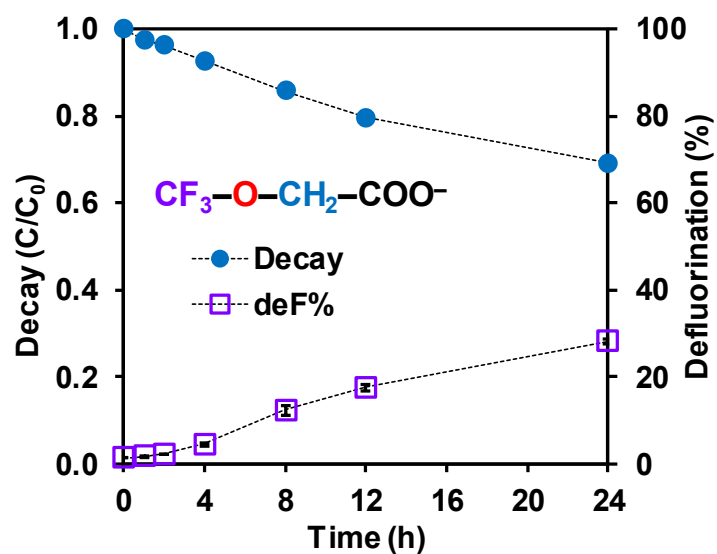
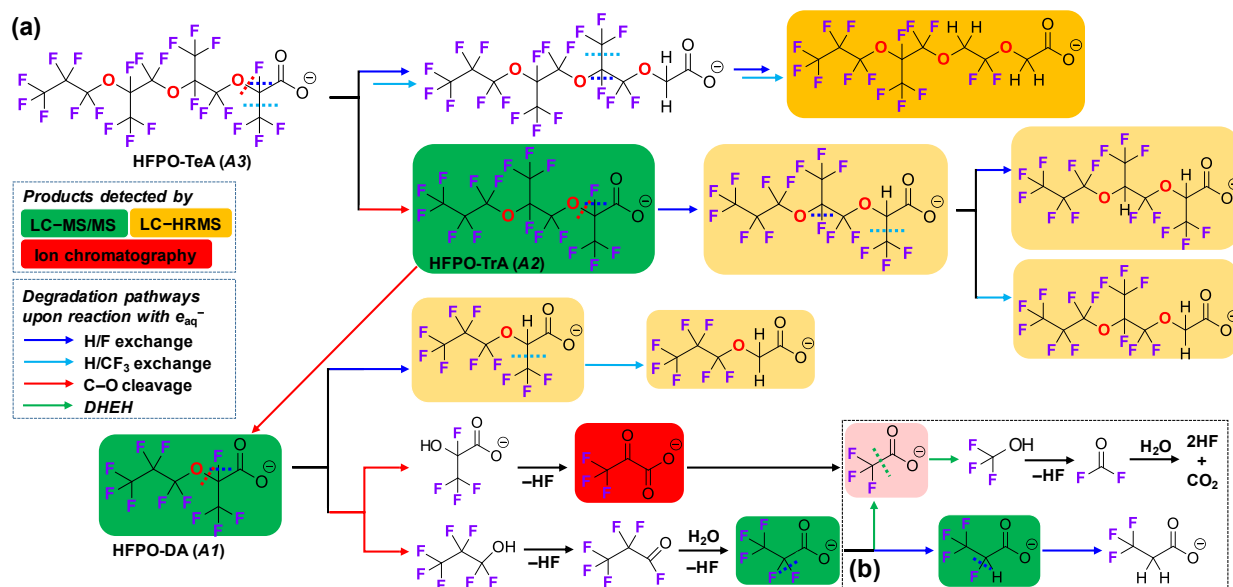
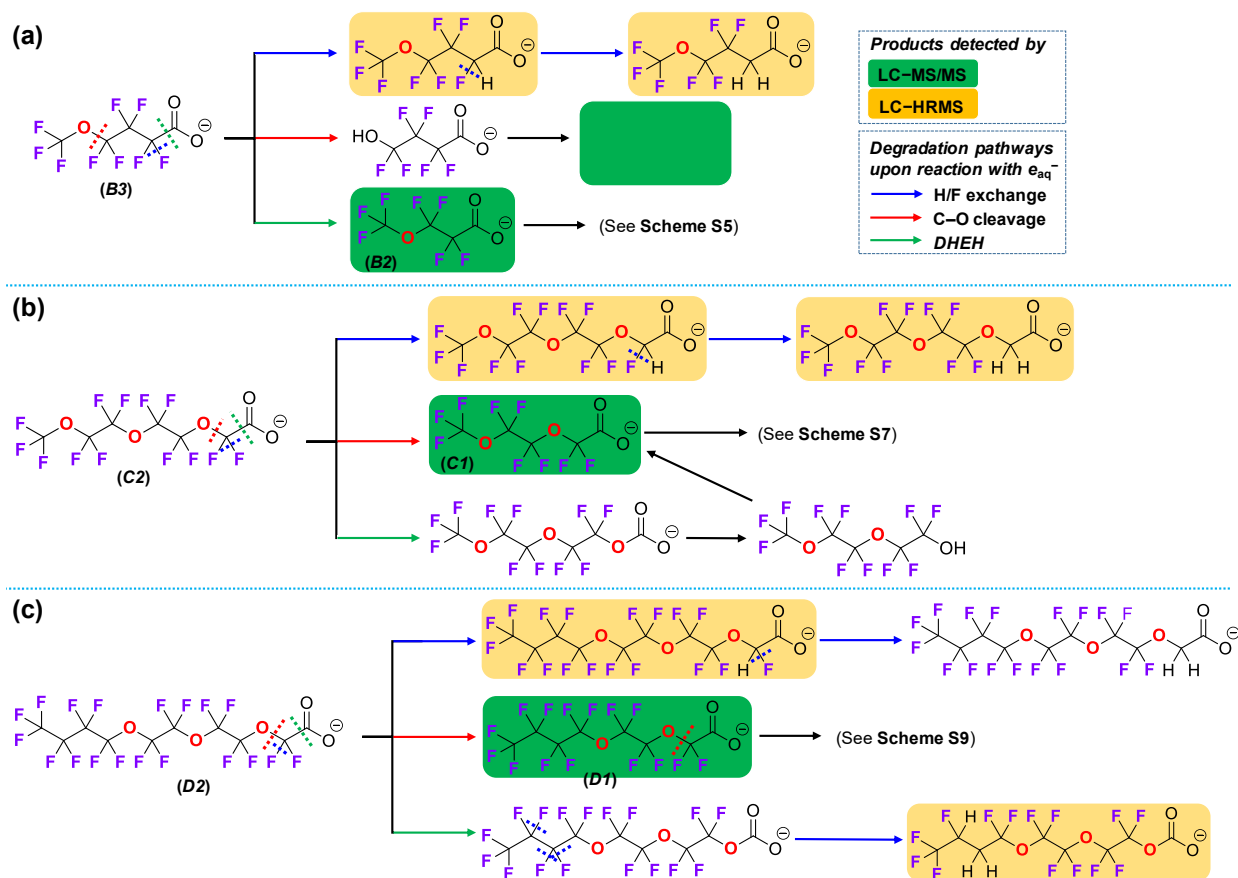


Figure 7. Time profiles of parent compound decay and defluorination for polyfluorinated $\text{CF}_3\text{-O-CH}_2\text{-COO}^-$ under the same reaction condition for all other PFECAs (described in the title of **Figure 2**).



Scheme 1. Degradation pathways for (a) HFPO oligomer acids starting from the longest compound A3 and (b) the daughter product PFPrA. Detected transformation products are highlighted.



Scheme 2. Degradation pathways for the three PFECA structure categories starting from the longest compound (a) **B3**, (b) **C2**, and (c) **D2**. Detected transformation products are highlighted.

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