

Mechanistic Investigations of Thermal Decomposition of Perfluoroalkyl Ether Carboxylic Acids and Short-Chain Perfluoroalkyl Carboxylic Acids

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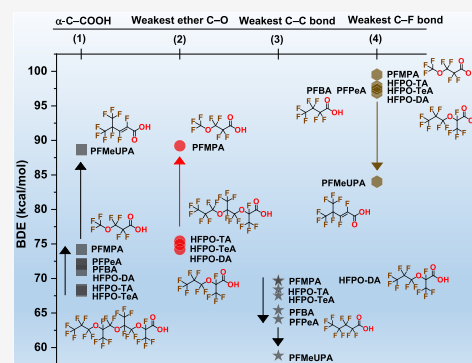
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ABSTRACT: In this study, we investigated the thermal decomposition mechanisms of perfluoroalkyl ether carboxylic acids (PFECAs) and short-chain perfluoroalkyl carboxylic acids (PFCAs) that have been manufactured as replacements for phased-out per- and polyfluoroalkyl substances (PFAS). C–C, C–F, C–O, O–H, and C=C bond dissociation energies were calculated at the M06-2X/Def2-TZVP level of theory. The α -C and carboxyl-C bond dissociation energy of PFECAs declines with increasing chain length and the attachment of an electron-withdrawing trifluoromethyl ($-\text{CF}_3$) group to the α -C. Experimental and computational results show that the thermal transformation of hexafluoropropylene oxide dimer acid to trifluoroacetic acid (TFA) occurs due to the preferential cleavage of the C–O ether bond close to the carboxyl group. This pathway produces precursors of perfluoropropionic acid (PFPeA) and TFA and is supplemented by a minor pathway ($\text{CF}_3\text{CF}_2\text{CF}_2\text{OCFCF}_3\text{COOH} \rightarrow \text{CF}_3\text{CF}_2\text{CF}_2\cdot + \cdot\text{OCFCF}_3\text{COOH}$) through which perfluorobutanoic acid (PFBA) is formed. The weakest C–C bond in PFPeA and PFBA is the one connecting the α -C and the β -C. The results support (1) the C–C scission in the perfluorinated backbone as an effective PFCA thermal decomposition mechanism and (2) the thermal recombination of radicals through which intermediates are formed. Additionally, we detected a few novel thermal decomposition products of studied PFAS.

KEYWORDS: PFAS, thermal transformation, high-resolution mass spectrometry, $\bullet$ C–MS, density functional theory, spent media



INTRODUCTION

Major manufacturers of per- and polyfluoroalkyl substances (PFAS) have phased out the production of perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), and related substances^{1,2} due to public concern about their persistence,^{3–5} toxicity,^{6,7} and ubiquitous presence in the environment.^{8–10} Perfluoroalkyl ether carboxylic acids (PFECAs) and short-chain perfluoroalkyl carboxylic acids (PFCAs) have been introduced into the market to replace PFOA and PFOS.^{11–14} However, these replacement substances are also recalcitrant to degradation^{15,16} and environmentally mobile.^{17,18} PFECAs and short-chain PFCAs, including hexafluoropropylene oxide dimer acid (HFPO-DA), perfluorobutanoic acid (PFBA, C₄), and perfluoropentanoic acid (PFPeA, C₅), have been frequently detected in surface and groundwater worldwide.^{11,16,19–22} Hexafluoropropylene oxide trimer acid (HFPO-TA), a novel alternative to PFOA, has recently been observed in surface water.^{17,23} Acute and long-term toxicological studies have revealed the hazardous properties of HFPO-DA, HFPO-TA, and short-chain PFCAs.^{24–28} The U.S. Environmental Protection Agency (EPA) has recently issued the final health advisory for HFPO-DA and its ammonium salt (“GenX” chemicals) in

drinking water at 10 ng/L.²⁹ In the European Union, the recently updated Drinking Water Directive recommends limits of 100 ng/L for 20 PFAS, including PFBA and PFPeA.³⁰ An impact of these actions will be to make the removal of PFAS from drinking water^{31–34} a global priority.

Currently, sorption methods using granular activated carbon (GAC) or anion exchange (AIX) resins are frequently employed to remove PFAS from water in large-scale operations.^{34–37} More recently, single-use AIX resins have been investigated for removing PFECAs and short-chain PFAS from water in laboratory- and pilot-scale experiments.^{38,39} The predominant residual from GAC and AIX resin systems is the spent adsorbents containing PFAS. It has been observed that regenerating PFAS-laden spent adsorbents can be challenging using organic solvents or brine.^{40–42} For example, methanol

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alone could only extract less than 50% of PFOA and PFOS from GAC.⁴² Liu and Sun demonstrated that brine was ineffective in regenerating PFAS-laden single-use AIX resins.⁴⁰

Thermal-based approaches have emerged as an attractive means^{42–48} to decontaminate PFAS-laden GAC,^{42,46,49–51} resins,⁵² and other solid materials (e.g., soil,^{43,51} biosolids,⁵³ and biomass⁵⁴). Recent studies have demonstrated PFAS decomposition even at relatively low temperatures of 200–500 °C.^{42–46} These temperatures are achievable using the current in situ and ex situ heating technologies.^{50,55,56}

Over the past five years, research on PFAS thermal treatment has quickly evolved^{42–44,46–48,52,57–59} regarding the thermal stability of PFOA and PFOS,^{42,43} the threshold temperatures that thermal degradation may occur,^{42,43,46} the yield of inorganic F from PFOA and PFOS during thermal degradation,^{42,43,46} and the thermal degradation of PFAS (also known as precursor compounds).⁴⁴ As part of this evolution, there has been a strong focus on polar^{44,46} and nonpolar^{45,60} thermal degradation products of PFAS that are produced when subjected to thermal treatments, such as thermal regeneration of spent GAC at temperatures of <400 °C.^{43,44,46} Moreover, increasing attention has been paid to the effects of porous adsorbents, such as GAC,⁴⁶ resin,⁴⁶ and biochar,⁴⁶ and approaches to accelerate PFAS thermal degradation at low temperatures.^{46,60–65}

HFPO-DA is resistant to degradation by ozone¹⁶ and hydroxyl radicals.⁶⁶ The cleavage of C–O ether bonds in HFPO-DA is rarely observed without potent radicals, acids, and bases.^{67,68} Yet, the thermal decomposition of HFPO-DA has been observed at temperatures as low as 150 °C.^{42,43,46} Compared to legacy PFAS (e.g., PFOA), the conceptual and quantitative thermal degradation models for PFECAs, including HFPO-DA, are far from being clear. Such compounds may undergo the same thermal degradation pathways as PFOA, but because they bear an ether group, they can participate in pathways that PFOA cannot. Using density functional theory (DFT), Adi and Altarawneh investigated various possible HFPO-DA thermal decomposition pathways.⁶⁹ While the present study was prepared, Blotevogel et al. reported DFT calculation results on pathways, mechanisms, and kinetics of the thermal decomposition of PFOA and HFPO-DA.⁷⁰ The authors suggest that the initial defluorination of HFPO-DA proceeds through HF elimination at the α -C.⁷⁰ We are only aware of these two studies in the scholarly literature that have investigated the thermal degradation mechanisms of HFPO-DA. It is worth mentioning that PFBA, perfluoropropionic acid (PFPrA), and trifluoroacetic acid (TFA) were not considered thermal decomposition products of HFPO-DA in these two previous studies.^{69,70} Likewise, experimental data of short-chain PFCAs under thermal conditions are practically nonexistent in the literature. For mechanistic considerations, there is a need for a better understanding of thermal decomposition mechanisms and pathways of PFECAs and short-chain PFCAs, including the structures and reactivities of transient intermediates.

To this end, the authors employ a combined experimental and computational approach to understand the thermal degradation mechanisms of HFPO-DA and short-chain PFCAs. Thermal degradation experiments of relevant PFAS were conducted to guide the model development in computational studies. The computational data, in turn, explain the experimental results and illustrate the underlying thermal decomposition mechanisms. An in-depth analysis of the thermal decomposition pathways of HFPO-DA, HFPO-TA, PFBA, and PFPeA was performed. Qualitative and quantitative information on transient inter-

mediates was obtained. High-throughput DFT calculations were carried out to compute C–C, C–F, C–O, O–H, and C=C bond dissociation energies (BDEs) of studied PFAS and to further elucidate their thermal degradation pathways. Through this combined experimental and computational approach, we attempt to answer the following questions: (1) Does the side –CF₃ on the α -C prevent HFPO-DA and other PFECAs (e.g., HFPO-TA) from being degraded during thermal treatment? In UV/persulfate oxidation processes, the –CF₃ group on the α -C has been shown to inhibit the degradation of GenX by sulfate and hydroxyl radicals.⁶⁸ (2) What transient organic intermediates are produced when HFPO-DA, HFPO-TA, and short-chain PFCAs are heated and through which mechanisms? (3) Is this process radical mediated? (4) Will HFPO-DA and HFPO-TA transform to perfluorinated compounds during thermal treatment? (5) Given that they are unsymmetrical ethers, which C–O ether bond in HFPO-DA and HFPO-TA is most likely to break upon heating? Answers to these questions have theoretical and practical implications for modeling PFECA degradation pathways and predicting transient and final degradation products.

MATERIALS AND METHODS

Thermal Treatment of PFAS-Laden Spent Media. In preliminary adsorption and thermal experiments, we included the following perfluorinated compounds in determining the effect of treatment temperature (Table S1): HFPO-DA, HFPO-TA, perfluoro-2,5,8-trimethyl-3,6,9-trioxadecanoic acid (HFPO-TeA), perfluoro-3,6-dioxahexanoic acid (PFO2HpA), perfluoro(3-methoxypropanoic) acid (PFMPA), PFBA (C4), PFPeA (C5), PFOA (C8), perfluorononanoic acid (PFNA, C9), perfluorodecanoic acid (PFDA, C10), perfluoroundecanoic acid (PFUnDA, C11), 4-(trifluoromethyl)hexafluoropent-2-enoic acid (PFMeUPA), and potassium salts of perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS), and PFOS. PFMeUPA is an unsaturated PFCA; unsaturated PFCAs have been detected in sludge-applied soil and grass samples.⁷¹ All of these PFAS were purchased from Sigma-Aldrich (Table S1).

The adsorbents used were single-use AIX resin (Amber-Chrom 1 × 8 or formerly known as Dowex 1 × 8) and GAC (Filtrisorb 200; N₂ BET surface area, 691.4 m²/g; microporosity, 0.3 cm³/g; mesoporosity, 0.07 cm³/g). Standard batch sorption experiments were carried out to assess the adsorption of a single PFAS or a mixture of PFAS to the resin and GAC, following previously established procedures.⁷² The test solution was prepared with distilled water containing 1.0 × 10^{−3} mol/L NaHCO₃ as a buffer and 1.0 × 10^{−3} mol/L NaCl for the ionic strength. After adsorption, the supernatant fluid was decanted. PFAS-laden adsorbent particles were freeze-dried and stored in a desiccator to reach room temperature. Then, these particles were split into two portions.⁴² One portion of the particles was extracted using methanol amended with 100 mol/L ammonium acetate.⁴² The PFAS mass before thermal treatment ($M_{\text{PFAS,solid,initial}}$) was computed using eq 1

$$M_{\text{PFAS,solid,initial}} = (C_{\text{extr}} \times V_{\text{extr}})/E \quad (1)$$

where E (%) is the extraction efficiency, C_{extr} (μmol/L) is the concentration of PFAS in the extract, and V_{extr} (L) is the volume of methanol. The analysis of PFAS and degradation products in the extract was performed using a Waters Acuity ultra-high-pressure liquid chromatograph coupled with a high-resolution

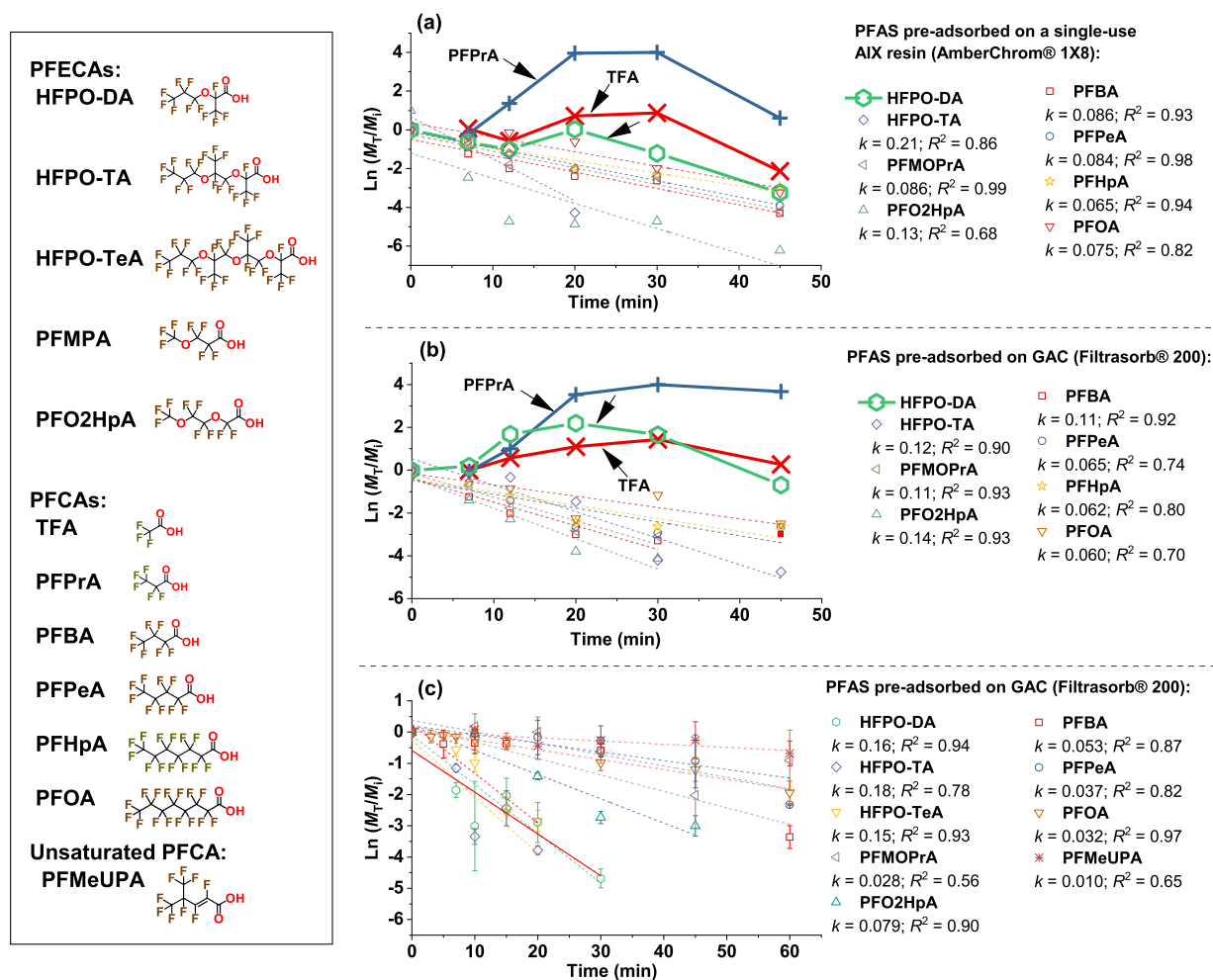


Figure 1. Thermal degradation of PFECAs and PFCAs on adsorbents at 200 °C for up to 60 min in N₂. In panels a and b, the adsorbent was laden with a mixture of the PFAS, whereas the adsorbent was laden with one PFAS chemical in panel c. Initial PFAS loading on GAC ($\mu\text{mol/g}$): HFPO-DA, 5.9–7.6; HFPO-TA, 21.2–42.6; HFPO-TeA, 18.0; PFMPA, 1.2–2.5; PFO2HpA, 1.7–2.6; PFBA, 1.5–2.1; PFPeA, 1.9–3.5; PFHpA, 3.1–4.9; and PFOA, 7.2–12.5. The generation and subsequent degradation of TFA, PFPrA, and HFPO-DA during the treatment are illustrated by arrows. M_i and M_t refer to the mass of PFAS ($\mu\text{mol/g}$) before and after the thermal treatment, respectively (eq 1); for TFA and PFPrA, M_i was the mass after 7 min of heating. The dashed lines represent the best linear fits, assuming a pseudo-first-order degradation. The degradation rate constants (k , min^{-1}) are given. The residual PFECAs after heating for more than 30 min were generally lower than the method detection limits.

mass spectrometer (Synapt G2-S quadrupole time-of-flight mass spectrometer, QToF-MS/MS, Waters Corporation, Milford, MA, USA).^{73,74} Analytical details can be found in the [Supporting Information](#).

In the commercial GAC regeneration process, spent carbon is heated for approximately 30 min with inert gases such as N₂ and CO₂ at relatively low temperatures (≤ 300 °C).⁷⁵ To simulate this process, the other portion of the PFAS-laden adsorbent particles was placed in a pre-cleaned, stainless-steel reactor (7 mL; 45 mm in height and 19 mm in outside diameter) (QAQC Lab Inc., White Stone, VA, USA). The reactor was sealed with a rubber septum and purged with nitrogen for 30 min. The septum was then replaced with a stainless-steel screw cap (QAQC Lab Inc., White Stone, VA, USA). Heating was carried out in a muffle furnace (Neytech, Vulcan 3-550, USA) at a preset temperature (up to 500 °C) for 30 min. To understand the effect of treatment time, we also heated PFAS-laden adsorbent particles at a given temperature for different durations (0–60 min). After thermal treatment and cooling, the reactor was rinsed with methanol containing 100 mol/L ammonium acetate to extract residual PFAS.⁴² PFAS thermal decomposition was assessed by

comparing the residual mass in heated samples to nonheated controls.^{43,46}

Analysis of Decomposition Products. To capture transient intermediates of PFECAs and PFCAs upon heating, we performed additional thermal degradation experiments of individual PFAS in N₂ in a borosilicate reactor following a procedure developed previously.⁴³ After heat treatment and cooling, the reactor was rinsed with distilled water to extract F or methanol containing 100 mol/L ammonium acetate to extract residual PFAS and polar decomposition products.^{43,46} Inorganic F in the water extract was measured using an F-ion selective electrode, as described previously.⁴³

The yield of F from a PFAS with n F atoms was calculated with the following equation

$$\text{Yield(F)} = \frac{M_{\text{F}}}{n[M_{\text{PFAS,i}} - M_{\text{PFAS,T}}]} \times 100\% \quad (2)$$

where M is the mass of PFAS calculated by eq 1. The yield of a transient product from a parent PFAS compound was calculated by

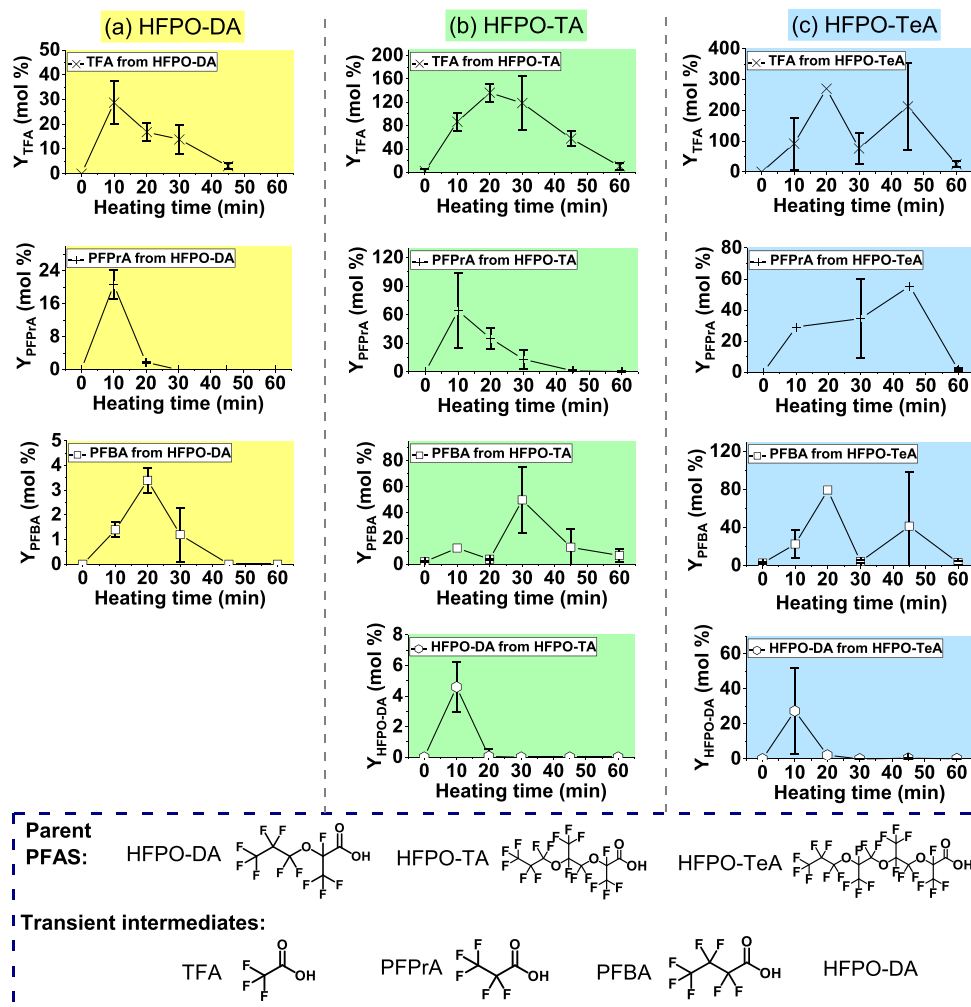


Figure 2. Yields of intermediates from a single PFECA preadsorbed on GAC after heating at 200 °C for different durations.

$$\text{Yield}(\text{product}) = \frac{M_{\text{product,formed}}}{[M_{\text{PFAS,i}} - M_{\text{PFAS,T}}]} \times 100\% \quad (3)$$

Thermal decomposition products of PFAS in the methanol extract were analyzed by ultrahigh-pressure liquid chromatography–quadrupole time-of-flight tandem mass spectrometry (UPLC–QToF-MS/MS), following previously described procedures (or see the [Supporting Information](#) for details).^{43–45} Chromatography was performed using a Waters Acquity UPLC BEH Shield RP18 column (100 × 2.1 mm; 130 Å; 1.7 μm) with a Waters Acquity UPLC BEH Shield RP18 VanGuard pre-column (5 × 2.1 mm; 130 Å; 1.7 μm). MS analysis was performed using the Synapt G2-S quadrupole time-of-flight mass spectrometer with an ESI source operated in a negative ion mode. MassLynx V4.1 software (Waters) was used for instrument control, acquisition, and mass analysis. Standards of two ultra-short chain-PFCAs, TFA (C2) and PFPrA (C3), were purchased to confirm the thermal decomposition products of studied PFAS. A high-resolution precursor ion scan (HRPIS) method⁷⁴ was also employed for nontarget screening of possible thermal degradation products (see the [Supporting Information](#)).

Thermal Desorption–Pyrolysis–Gas Chromatography–MS Experiments. To date, no accurate and sensitive method has been established for capturing gaseous thermal degradation products of PFAS. This is due to the lack of effective adsorbents that can adsorb all gaseous organofluorine species in

the off-gas, as well as the lack of an efficient extraction method for extracting all adsorbed organofluorine species from the adsorbents. Rather than using the traditional adsorption–extraction–cleanup–concentration–GC–MS method, we analyzed gaseous thermal decomposition products of PFAS using thermal desorption–pyrolysis (TD–Pyr) (Frontier 3030D, Frontier Labs Inc., Japan) connected to a GC–MS system (Agilent GC 7890 and 5975C MS; Santa Clara, CA). This system has previously been utilized to analyze gaseous products emitted during the thermal treatment of long-chain PFAS⁴³ and aqueous film-forming foams.^{43,45} A Frontier 30 m Ultra ALLOY capillary column (30 m; Frontier Labs Inc., Japan) was used with an inner diameter of 0.25 mm and a 5% diphenyldimethyl polysiloxane stationary phase with 0.25 μm film thickness. MS analysis was performed with electron ionization in the mass range of 35–850 *m/z*. Ultra-pure helium (99.999%) was used as the carrier gas with a constant flow rate of 1.1 mL/min (more details can be found in the [Supporting Information](#)). Data processing included the MS fragmentation pattern evaluation of a potential pyrolyzate based on the highly curated 2005 National Institute of Standards and Technology library that contains 190,825 spectra. Compounds were considered tentatively identified with a library match quality of >70%.⁴⁵

Computational Studies. A supercomputer (Intel Platinum 48 Core, Beijing Super Cloud Computing Center) was used to perform high-throughput DFT calculations of BDEs of all

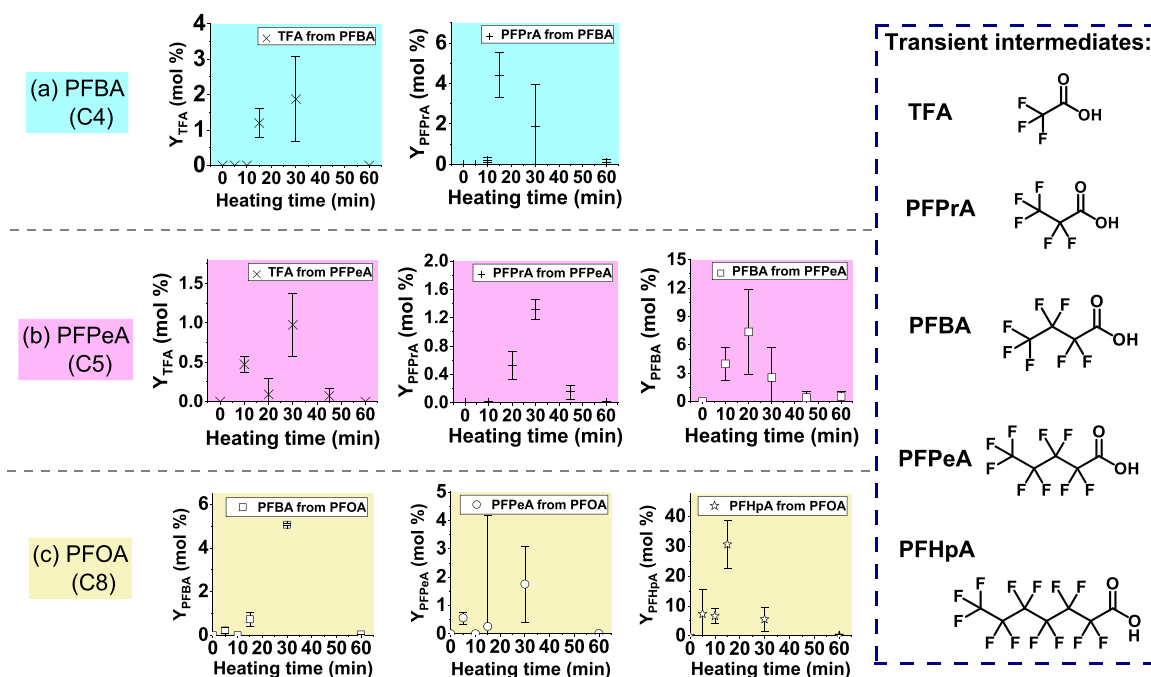


Figure 3. Yields of intermediates from a single PFCA preadsorbed on GAC after heating at 200 °C for different durations.

covalent bonds (C–C, C–F, C–O, O–H, and C=C) in PFECAs, short-chain PFCA, and the unsaturated PFCA (i.e., PFMeUPA). A state-of-the-art M06-2X method⁷⁶ at a 3-zeta basis set of Def2-TZVP was implemented using the state-of-the-art Gaussian 16 program.⁷⁷

RESULTS AND DISCUSSION

Degradation of PFECAs and Short-Chain PFCA on Spent GAC and Resin. Figures S1 and 1 illustrate the thermal degradation of PFECAs and short-chain PFCA preadsorbed on adsorbents. Detailed adsorption isotherms and mechanisms are outside the scope of this paper and will be the subject of another paper in the future. In selected experiments, a high initial mass (up to 75.9 $\mu\text{mol/g}$) of PFECAs was directly added to AmberChrom 1 $\times$ 8 to estimate the maximum percentage removal (Figure S1). Regardless of concentrations of PFAS in the resin, all these PFAS compounds exhibited near-complete degradation (>98.59%) in as little as 30 min at 500 °C. Deformation of the resin beads was seen at 300 °C and above. No attempt was made to reuse the decontaminated resin beads as they are intended for single use only.

Upon heating PFECAs and PFCA at 500 °C, no new noteworthy peaks emerged in UPLC–HRMS chromatograms of full scans and HRPIS, signifying rapid degradation of both parent compounds and transient intermediates at this temperature.^{42,45} For example, Yao et al. demonstrated that perfluoroheptene, a notable thermal decomposition product of PFOA, starts to degrade at a temperature as low as 200 °C.⁴⁵

PFECAs are more prone to degradation than PFCA counterparts, as evidenced by Figure S1 and the apparent yield of inorganic F species (Figure S2). HFPO-DA has a half-life of 4.3 min at 200 °C compared to 13 min for PFBA (Figure 1a). The half-lives of both chemicals decreased as the heating temperature increased (e.g., 5.0 min for PFBA at 400 °C).⁴³ The relatively long half-lives of parent PFAS at low temperatures allow us to compare the thermal stability and capture transient thermal decomposition products. The thermal degradation rate

constants decline in the following order: PFECAs > PFCA > unsaturated PFCA (i.e., PFMeUPA). The most notable features of Figure 1—as well as a side-by-side comparison of Figure 1a,b—are the significant yields of TFA, PFPrA, and HFPO-DA when a mixture of studied PFECAs and PFCA was heated at low temperature (Figure 1b,c). These results indicate the formation of TFA, PFPrA, and HFPO-DA during thermal treatments.

Thermal Decomposition Products. HFPO-DA. We conducted additional thermal treatment experiments on individual PFECAs (Figure 1c) to capture short-lived transient intermediates of PFECAs and short-chain PFCA. Figure 2 displays the evolution of detected transient intermediates from PFECAs, which can be grouped into two categories: small intermediates and relatively large ones with a UPLC retention time close to that of the parent compound. These transient intermediates were assigned by comparing their UPLC retention time and MS fragmentation patterns with authentic standards.

Three transient organic intermediates (I, II, III) of HFPO-DA were detected by UPLC–HRMS. Compound I with m/z 212.9792 and MS fragments characteristic of PFCA (C_3F_7 , m/z 168.9894; C_2F_5 , m/z 118.9926) were assigned to be PFBA. This is further substantiated by an authentic standard. Compounds II and III were identified as PFPrA and TFA, respectively, confirmed with corresponding authentic standards. Figures 1 and 2 show that they built up rapidly but decomposed within 60 min. To our knowledge, these PFCA were identified for the first time as thermal decomposition products of HFPO-DA.

A novel volatile intermediate (IV) with a molecular weight (m/z 265.9) greater than that of PFBA was also detected (Figures S3–S6). The fragments at m/z 69.0 (CF_3^+), 119.0 (C_2F_5^+), and 169.0 (C_3F_7^+) are characteristic of fluorinated fragments.^{44,74} The fragments at m/z 146.9 and 196.9 represent the successive loss of the fluorinated fragment CF_2 from IV. We assigned the ion at m/z 146.9 to be an unsaturated fluorinated fragment with one C replaced by O (SMILES: $\text{FC(F)} = [\text{O} +]\text{C(F)} = \text{C(F)F}$). The ion at m/z 81.0 represents an

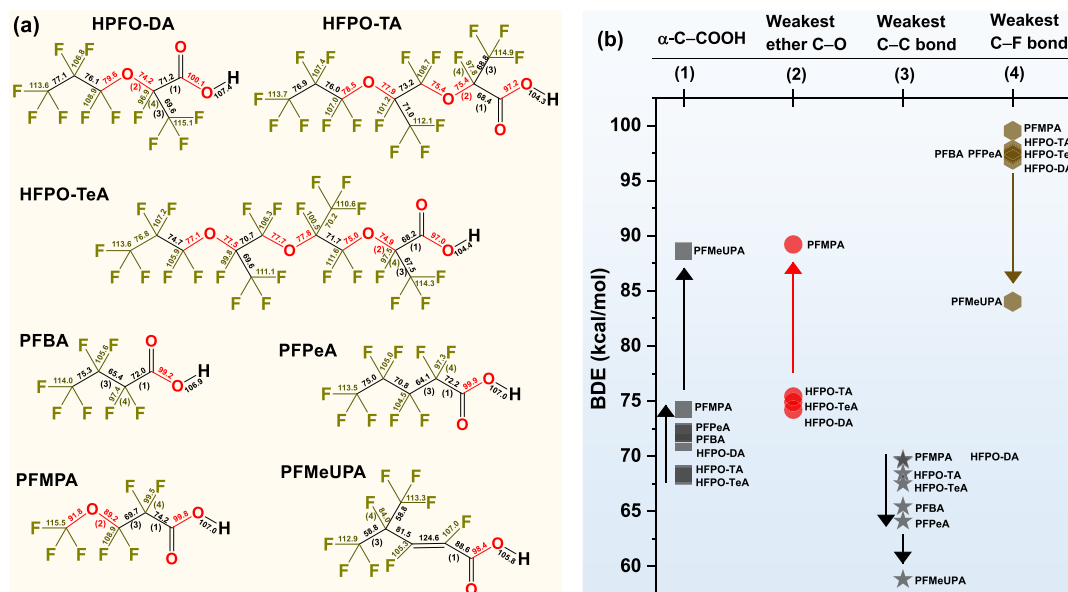


Figure 4. BDEs of PFAS calculated at the M06-2X/Def2-TZVP level of theory using high-performance computing resources.

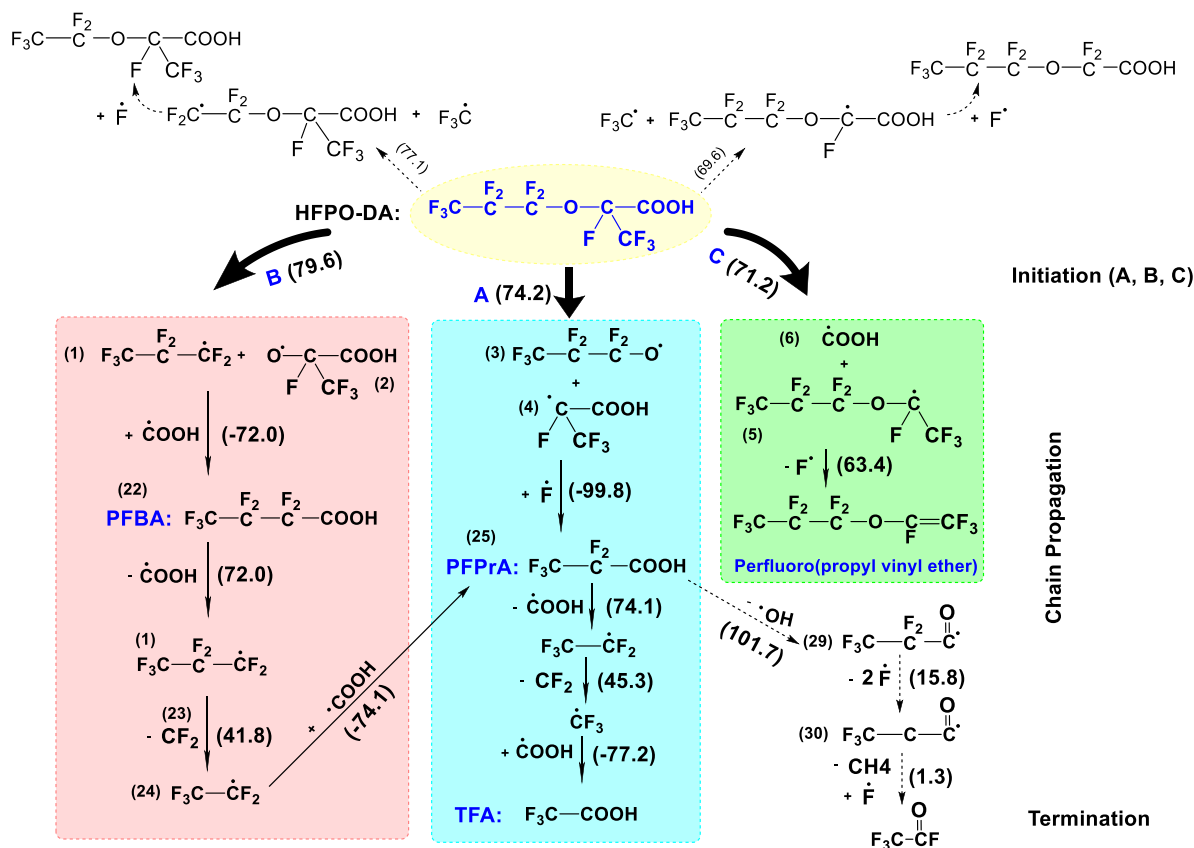


Figure 5. Proposed thermal decomposition pathways of HFPO-DA. Dashed arrows: DFT predicted pathways that are not supported by experimental data. Solid arrows: pathways supported by experimental results. PFBA, PFPrA, TFA, and perfluoro(propyl vinyl ether) are detected as thermal decomposition products of HFPO-DA (Figures 2, S3–S6). The three-digit numbers (e.g., 79.6) indicate the DFT-calculated enthalpy change (kcal/mol). HFPO-DA decomposes primarily through Pathway A, whereas Pathway B serves as a secondary, less predominant route.

unsaturated fluorinated fragment (SMILES: F[C+] = C(F)F). Taken these results together, we assigned IV to be perfluoro(propyl vinyl ether) (SMILES: FC(F) = C(F)OC(F)(F)C(F)(F)C(F)(F)F) (library match quality, 74–80%).

The yields of transient intermediates from HFPO-DA are shown in Figure 2, except for perfluoro(propyl vinyl ether),

which was not quantified due to the lack of an authentic standard. TFA, PFPrA, and PFBA were generated quantitatively from HFPO-DA (Figure 2). TFA was formed in 30% maximum yield but disappeared on the same timescale as HFPO-DA. PFBA was a minor product of HFPO-DA, which disappeared after a slight lag compared to PFPrA.

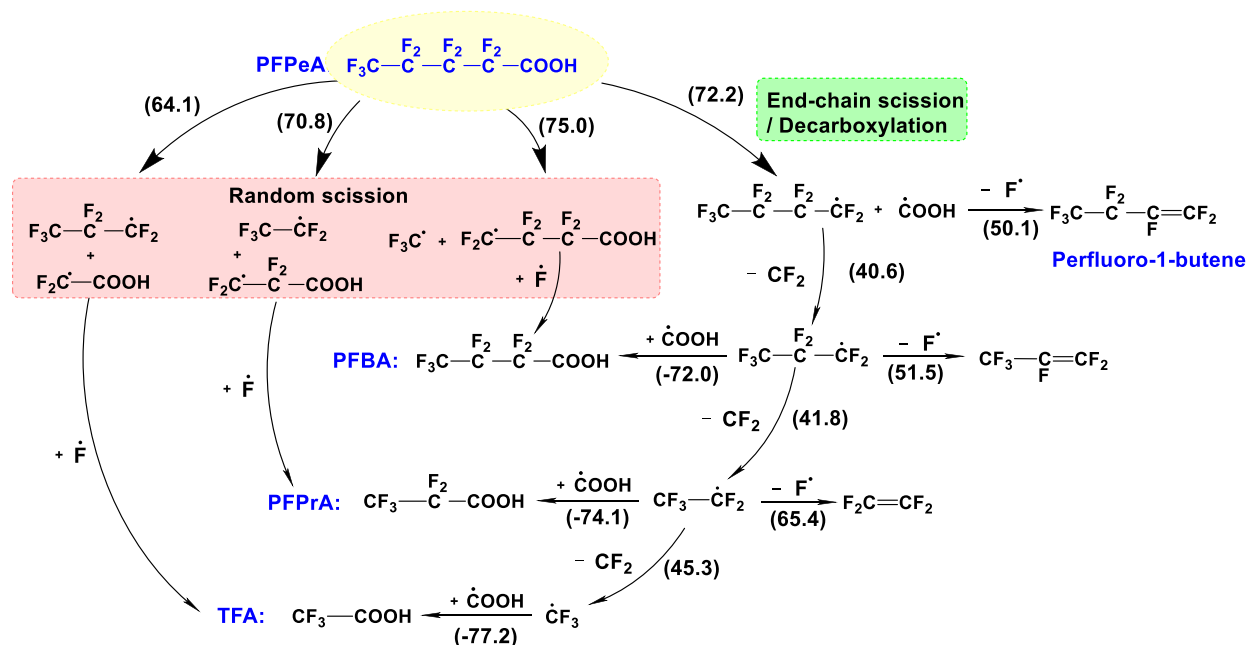


Figure 6. Proposed thermal decomposition pathways (i.e., random-chain scission and end-chain scission) of PFPeA. PFBA, PFPrA, TFA, and perfluoro-1-butene are detected as thermal decomposition products of PFPeA (Figures 3, S9, and S10). The three-digit numbers (e.g., 70.8) indicate the DFT-calculated enthalpy change (kcal/mol).

HFPO-TA and HFPO-TeA. HFPO-TA and HFPO-TeA may be thermally decomposed by a similar pathway judging by the significant quantities of PFPrA and TFA produced during their degradation (Figure 2). The yields of TFA and PFBA from HFPO-TA and HFPO-TeA were much higher than those from HFPO-DA because multiple C–O bonds can break off in HFPO-TA and HFPO-TeA (Figure 2). Interestingly, HFPO-DA was a minor thermal decomposition product of its long-chain homologues (i.e., HFPO-TA and HFPO-TeA).

PFBA. TFA and PFPrA evolved quantitatively from PFBA after 10 min in 4.6% maximum yield but disappeared on the same timescale as PFBA (Figure 3). A novel gaseous thermal decomposition product (V) of PFBA was detected with an empirical formula of C_3F_6 . It has two fewer F atoms than perfluoropropane, with a fragmentation pattern identical to perfluoropropene (CAS no.: 116-15-4).⁷⁸ Therefore, a reasonable but tentative assignment of compound V is perfluoropropene (library match quality, 74–81%) (Figures S7 and S8).

PFPeA. The transformation of PFPeA was similar to that of PFBA. Within minutes of thermal treatment at ≥ 200 °C, almost 100% of PFPeA was removed from spent GAC and resins (Figures S1 and 1). TFA, PFPrA, and PFBA—whose identities were confirmed with authentic standards—were formed from PFPeA but rapidly degraded with a longer treatment time (Figure 1). A novel gaseous product (VI) of PFPeA, perfluoro-1-butene (C_4F_8), was detected (library match quality, 84–94%) (Figures S9 and S10).

Where comparisons can be made, the yield of shorter-chain homologues from a PFCA declines with the chain length of this PFCA. Perfluoroheptanoic acid (C7) forms in ~ 30 mol % yield from PFOA (C8) under the experimental conditions, whereas the yields of PFBA (C4) from PFPeA (C5) and PFPrA (C3) from PFBA are both less than 10 mol % (Figure 3).

Computational Results. BDE, also known as the bond enthalpy, provides critical information on which bonds in PFAS are likely to break off upon thermal, chemical, and physical

treatments. Degradation of a PFECA or PFCA molecule may occur as soon as the temperature is high enough to initiate bond breaking. The bond that is more easily broken is favored. Tables S2–S8 give the DFT calculation details of C–C, C–F, C–O, O–H, and C=C BDEs. These computational results, in combination with the experimental data, yield several interesting and novel observations. (i) The C–C bonds in the perfluorinated backbone of PFPeA and PFBA are generally weaker than the bond (α -C–COOH) connecting the α -C and the carboxyl-C (Figure 4). Therefore, in addition to decarboxylation, the random C–C scission in the perfluorinated chain is a very likely mechanism that dissociates PFPeA and PFBA. (ii) BDE data on PFPeA, PFMPA, and HFPO-DA indicate that the α -C–COOH BDE increases with an electron-donating ether O in the perfluorinated chain but declines with the electron-withdrawing $-CF_3$ moiety attached to the α -C (Figure 4). The result suggests that the side trifluoromethyl group may aid in the decarboxylation of HFPO-DA. (iii) The C=C double bond strengthens the adjacent C–C bonds, including the α -C–COOH bond (Figure 4). (iv) In HFPO-DA, the C–O ether bond ($C-O_{away}$) away from the electron-withdrawing carboxyl group is stronger than the C–O ether bond ($C-O_{nr}$) closer to the carboxyl group (Figure 4). The result indicates the preferential thermal cleavage of the $C-O_{nr}$ bond, supported by experimental data; the minor yield of PFBA (Figure 2) rules out the cleavage of the $C-O_{away}$ bond (pathway B in Figure 5) as a primary thermal degradation pathway for HFPO-DA. The results differ from a previous study by Bentel et al. which found that the $C-O_{nr}$ bond had a considerably higher BDE than the $C-O_{away}$ bond in HFPO-DA.⁶⁷ The discrepancy could be caused by the different DFT methods (e.g., M06-2X/Def2-TZVP in this study). (v) The difference in C–O BDEs in PFECAs decreases with increasing chain length (Figure 4).

Thermal Decomposition Pathways of PFECAs. With these experimental and computational results, it is possible to develop explicit thermal degradation pathways for HFPO-DA.

PFBA, PFPrA, and TFA were not considered thermal decomposition products of HFPO-DA in previous computational studies.^{69,70} Therefore, the detection of these short-chain PFCAs from HFPO-DA upon heating indicates a novel thermal degradation pathway that was not considered previously.

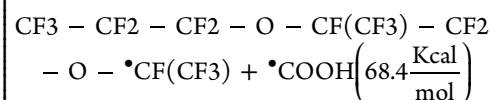
A pathway for the thermal decomposition of HFPO-DA must take into account: (i) the practically instantaneous formation of TFA, PFPrA, and PFBA upon heating of the parent compound; (ii) the relatively large transient yields of TFA and PFPrA; and (iii) the trace yield of PFBA that rules it out as an intermediate along a primary path.

A pathway consistent with these results is the thermal cleavage of the C–O_{nr} bond, leading to the formation of a perfluoropropyl-oxidanyl radical and a precursor of PFPrA ($\cdot$ PFPrA-H) (pathway A in Figure 5). This result is accomplished by the recombination of the $\cdot$ PFPrA-H and $\cdot$ F to form PFPrA (Figure 5), followed by the thermal decomposition of the resulting PFPrA radical to give TFA (Figure 5). The thermal cleavage of the other stronger C–O ether bond is evidenced by the formation of PFBA from HFPO-DA. HFPO-DA decarboxylation (pathway C) generates perfluoro(propyl vinyl ether). The DFT simulations predict a few other pathways involving the cleavage of the trifluoromethyl ($-\text{CF}_3$) group, which are not supported by MS spectral evidence; however, this does not preclude the formation of transient intermediates in small amounts in these DFT-predicted pathways (dashed arrows in Figure 5).

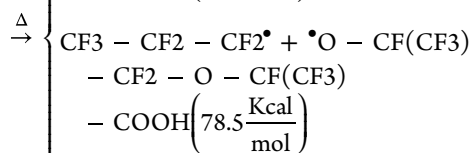
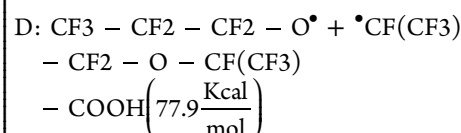
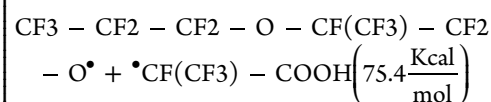
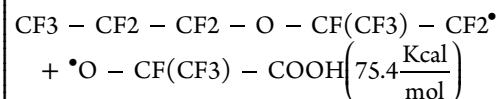
There are five C–C and four C–O ether bonds in an HFPO-TA molecule. We have suggested multiple concurrent HFPO-TA degradation pathways (eq 4) with enthalpy changes in the range of 65–80 kcal/mol (Table S3). The thermal decomposition mechanisms developed here for HFPO-DA and HFPO-TA (Figure 5 and eq 4) involve recombining radicals (e.g., $\cdot$ F) and perfluorinated radicals to yield TFA, PFPrA, and PFBA. For example, HFPO-DA is likely formed from HFPO-TA through the recombination of $\cdot$ F and $\cdot\text{CF}_2\text{CF}_2\text{CF}_2\text{O}-\text{CF}(\text{CF}_3)-\text{COOH}$ in pathway D (eq 4). The partially negatively charged F and O atoms form an electron shell around the partially positively charged perfluorinated carbon chain,⁷⁹ which may inhibit the physical adsorption of PFAS molecules on soil/clay particles.⁷⁹ However, this theoretical shell seems not to prevent the thermal recombination of $\cdot$ F with a perfluoroalkyl radical. The thermal generation of PFOS from 8:2 fluorotelomer sulfonate also likely involves the recombination of perfluoroalkyl radicals with the sulfonate group.⁴⁴

HFPO – TA

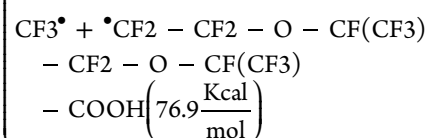
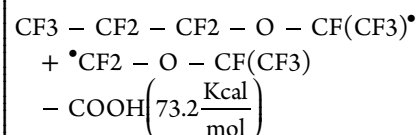
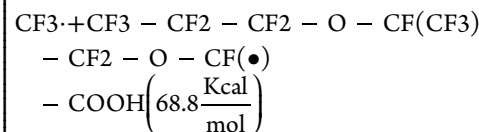
decarboxylation



ether bond cleavage



C – C scission



(4)

Thermal Decomposition Pathways of Short-Chain PFCAs. Because of the strong C–F bond, the thermal decomposition of short-chain PFCAs should be initiated by the cleavage of the relatively weak C–X bond in which X stands for elements such as C other than F. For PFCAs, only two types of C–X bonds can break: (1) the α -C–COOH bond connecting the perfluorinated chain and the carboxyl group and (2) the C–C covalent bond on the perfluorinated backbone. The bonds that tend to break first are the weakest in the structure. Xiao et al. previously interpreted HRMS data of PFOA and PFOS thermal degradation products in an “unzip” mechanism involving the end-chain scission and random C–C scission at seemingly random points in the perfluorinated chain.^{44,46} The experimental and computational data obtained in this study support this mechanism. Equation S3 in Supporting Information and Figure 6 illustrate the degradation pathways of two short-chain PFCAs (i.e., PFBA and PFPeA) through both pathways. End-chain scission occurs through decarboxylation that breaks

PFCAs' α -C-COOH bond (Figures 5 and 6). The weakest C-C bond in both PFPeA and PFBA, however, is the one connecting the α -C and the β -C. The β -C- γ -C bond is also weaker than the α -C-COOH bond in PFPeA. Therefore, both computational and experimental results suggest random scission in the perfluorinated chain as a degradation mechanism for these short-chain PFCAs (eq S3 in Supporting Information and Figure 6).

Little research has been geared toward developing a mechanistic picture of the thermal decomposition mechanisms of PFCAs and short-chain PFCAs that is evidence-based. Therefore, the present study makes several contributions to the field. This study provides the first evidence for a C-C scission mechanism on the perfluorinated backbone through which short-chain PFCAs decompose thermally. It gives C-C, C-F, C-O, O-H, and C=C BDEs of PFAS of interest and illustrates the effect of functionality and chain length. We find several interesting bond dissociation trends. Some BDE data are reported for the first time, adding to the current knowledge base or challenging existing knowledge. For example, we found that the C-O_{nr} bond in HFPO-DA is weaker than the C-O_{away} bond and that the side -CF₃ group on the α -C may aid in HFPO-DA decarboxylation. This study is also among the first to investigate the thermal degradation of PFAS on spent resin.

Furthermore, as our understanding of the thermal stability and decomposition of PFAS has evolved, it has become clear that thermal processes are nonselective and effective for degrading PFAS. However, acquiring critical information on the formation and speciation of PFAS incomplete thermal degradation products (PIDs) is necessary. This information is vital for designing and operating thermal technologies and ensuring treatment targets are achieved while minimizing undesired product formation. This study reports the formation of PIDs from three primary PFAS—HFPO-DA, PFBA, and PFPeA, which is potentially useful for many technological applications involving their removals, such as thermal regeneration of spent GAC^{42,46,50} and low-temperature thermal desorption (<300 °C).⁵⁶

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.3c00294>.

UPLC-QToF-MS/MS method, HRPIS experiments, TD-Pyr-GC-MS method, DFT calculations, PFAS chemicals used in this study, BDEs of HFPO-DA, BDEs of HFPO-TA, BDEs of HFPO-TeA, BDEs of PFMeUPA, BDEs of PFMPA, BDEs of PFBA, BDEs of PFPeA, thermal decomposition of various PFAS preadsorbed on a single-use resin and GAC, apparent yield of F from PFCAs and PFCAs during thermal treatment, TD-Pyr-GC-MS chromatograms of HFPO-DA at 200–500 °C, TD-Pyr-GC-MS chromatogram and spectrum of HFPO-DA at 200 °C, TD-Pyr-GC-MS chromatogram and spectrum of HFPO-DA at 300 °C, TD-Pyr-GC-MS chromatogram and spectrum of HFPO-DA at 500 °C, TD-Pyr-GC-MS chromatogram and spectrum of PFBA heated at 200 °C, TD-Pyr-GC-MS chromatogram of PFBA heated at 300 °C, TD-Pyr-GC-MS chromatogram of PFPeA heated at 200 °C, and TD-Pyr-GC-MS chromatogram of PFPeA heated at 300 °C (PDF)

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Author Contributions

A.A. and H.S. contributed equally to this work and share first authorship. A.A. was responsible for experimental execution and data analysis, while H.S. calculated BDEs using DFT and generate plots. K.L. analyzed the gaseous products of PFAS, and R.S. assisted with experimental execution. A.K. also analyzed the gaseous products of PFAS and contributed to manuscript review and editing. W.Z. participated in manuscript evaluation, while Y.L. offered insightful feedback during the review and editing process. Finally, F.X. was responsible for the overall conception and design of the study, including experimental design, data visualization, thermal decomposition pathways of HFPO-DA, HFPO-TA, PFPeA, and PFBA, and manuscript and Supporting Information preparation.

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) EPA. Risk Management for Per- and Polyfluoroalkyl Substances (PFASs) under TSCA. 2017, <https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/risk-management-and-polyfluoroalkyl-substances-pfass> (accessed June 2017).
- (2) Wang, T.; Wang, Y. W.; Liao, C. Y.; Cai, Y. Q.; Jiang, G. B. Perspectives on the inclusion of perfluorooctane sulfonate into the Stockholm Convention on persistent organic pollutants. *Environ. Sci. Technol.* **2009**, *43*, 5171–5175.
- (3) Houtz, E. F.; Higgins, C. P.; Field, J. A.; Sedlak, D. L. Persistence of perfluoroalkyl acid precursors in AFFF-impacted groundwater and soil. *Environ. Sci. Technol.* **2013**, *47*, 8187–8195.
- (4) Schröder, H. F.; Meesters, R. J. W. Stability of fluorinated surfactants in advanced oxidation processes – A follow up of degradation products using flow injection-mass spectrometry, liquid chromatography-mass spectrometry and liquid chromatography-multiple stage mass spectrometry. *J. Chromatogr. A* **2005**, *1082*, 110–119.
- (5) Mejia-Avendano, S.; Vo Duy, S.; Sauve, S.; Liu, J. Generation of perfluoroalkyl acids from aerobic biotransformation of quaternary ammonium polyfluoroalkyl surfactants. *Environ. Sci. Technol.* **2016**, *50*, 9923–9932.
- (6) Fenton, S. E.; Ducatman, A.; Boobis, A.; DeWitt, J. C.; Lau, C.; Ng, C.; Smith, J. S.; Roberts, S. M. Per- and Polyfluoroalkyl Substance Toxicity and Human Health Review: Current State of Knowledge and Strategies for Informing Future Research. *Environ. Toxicol. Chem.* **2021**, *40*, 606–630.
- (7) Grandjean, P.; Andersen, E. W.; Budtz-Jorgensen, E.; Nielsen, F.; Molbak, K.; Weihe, P.; Heilmann, C. Serum vaccine antibody concentrations in children exposed to perfluorinated compounds. *JAMA* **2012**, *307*, 391–397.
- (8) Evich, M. G.; Davis, M. J. B.; McCord, J. P.; Acree, B.; Awkerman, J. A.; Knappe, D. R. U.; Lindstrom, A. B.; Speth, T. F.; Tebes-Stevens, C.; Strynar, M. J.; Wang, Z. Y.; Weber, E. J.; Henderson, W. M.; Washington, J. W. Per- and polyfluoroalkyl substances in the environment. *Science* **2022**, *375*, No. eabg9065.
- (9) Chen, H.; Munoz, G.; Duy, S. V.; Zhang, L.; Yao, Y. M.; Zhao, Z.; Yi, L. X.; Liu, M.; Sun, H. W.; Liu, J. X.; Sauve, S. Occurrence and Distribution of Per- and Polyfluoroalkyl Substances in Tianjin, China: The Contribution of Emerging and Unknown Analogues. *Environ. Sci. Technol.* **2020**, *54*, 14254–14264.
- (10) Nickerson, A.; Rodowa, A. E.; Adamson, D. T.; Field, J. A.; Kulkarni, P. R.; Kornuc, J. J.; Higgins, C. P. Spatial trends of anionic, zwitterionic, and cationic PFASs at an AFFF-Impacted site. *Environ. Sci. Technol.* **2021**, *55*, 313–323.
- (11) Ateia, M.; Maroli, A.; Tharayil, N.; Karanfil, T. The overlooked short- and ultrashort-chain poly- and perfluorinated substances: A review. *Chemosphere* **2019**, *220*, 866–882.
- (12) Calafat, A. M.; Kato, K.; Hubbard, K.; Jia, T.; Botelho, J. C.; Wong, L. Y. Legacy and alternative per- and polyfluoroalkyl substances in the US general population: Paired serum-urine data from the 2013–2014 National Health and Nutrition Examination Survey. *Environ. Int.* **2019**, *131*, 105048.
- (13) Lin, Y. F.; Ruan, T.; Liu, A. F.; Jiang, G. B. Identification of Novel Hydrogen-Substituted Polyfluoroalkyl Ether Sulfonates in Environmental Matrices near Metal-Plating Facilities. *Environmental Science & Technology* **2017**, *51*, 11588–11596.
- (14) Evich, M. G.; Davis, M.; Weber, E. J.; Tebes-Stevens, C.; Acree, B.; Henderson, W. M.; Goodrow, S.; Bergman, E.; Washington, J. W. Environmental Fate of Cl-PFECAs: Predicting the Formation of PFAS Transformation Products in New Jersey Soils. *Environ. Sci. Technol.* **2022**, *56*, 7779–7788.
- (15) Dixit, F.; Barbeau, B.; Mostafavi, S. G.; Mohseni, M. Efficient removal of GenX (HFPO-DA) and other perfluorinated ether acids from drinking and recycled waters using anion exchange resins. *J. Hazard. Mater.* **2020**, *384*, 121261.
- (16) Sun, M.; Arevalo, E.; Strynar, M.; Lindstrom, A.; Richardson, M.; Kearns, B.; Pickett, A.; Smith, C.; Knappe, D. R. Legacy and emerging perfluoroalkyl substances are important drinking water contaminants in the Cape Fear River watershed of North Carolina. *Environ. Sci. Technol. Lett.* **2016**, *3*, 415–419.
- (17) Pan, Y.; Zhang, H.; Cui, Q.; Sheng, N.; Yeung, L. W. Y.; Sun, Y.; Guo, Y.; Dai, J. Worldwide Distribution of Novel Perfluoroether Carboxylic and Sulfonic Acids in Surface Water. *Environ. Sci. Technol.* **2018**, *52*, 7621–7629.
- (18) Joerss, H.; Xie, Z.; Wagner, C. C.; von Appen, W. J.; Sunderland, E. M.; Ebinghaus, R. Transport of Legacy Perfluoroalkyl Substances and the Replacement Compound HFPO-DA through the Atlantic Gateway to the Arctic Ocean-Is the Arctic a Sink or a Source? *Environ. Sci. Technol.* **2020**, *54*, 9958–9967.
- (19) Guillet, T. C.; McCord, J.; Guillet, M.; Polera, M. E.; Rachels, K. T.; Morgeson, C.; Kotlarz, N.; Knappe, D. R. U.; Reading, B. J.; Strynar, M.; Belcher, S. M. Elevated levels of per- and polyfluoroalkyl substances in Cape Fear River Striped Bass (*Morone saxatilis*) are associated with biomarkers of altered immune and liver function. *Environ. Int.* **2020**, *136*, 105358.
- (20) Yao, J. Z.; Pan, Y. T.; Sheng, N.; Su, Z. B.; Guo, Y.; Wang, J. S.; Dai, J. Y. Novel Perfluoroalkyl Ether Carboxylic Acids (PFECAs) and Sulfonic Acids (PFESAs): Occurrence and Association with Serum Biochemical Parameters in Residents Living Near a Fluorochemical Plant in China. *Environ. Sci. Technol.* **2020**, *54*, 13389–13398.
- (21) Strynar, M.; Dagnino, S.; McMahan, R.; Liang, S.; Lindstrom, A.; Andersen, E.; McMillan, L.; Thurman, M.; Ferrer, I.; Ball, C. Identification of Novel Perfluoroalkyl Ether Carboxylic Acids (PFECAs) and Sulfonic Acids (PFESAs) in Natural Waters Using Accurate Mass Time-of-Flight Mass Spectrometry (TOFMS). *Environ. Sci. Technol.* **2015**, *49*, 11622–11630.
- (22) Li, F.; Duan, J.; Tian, S.; Ji, H.; Zhu, Y.; Wei, Z.; Zhao, D. Short-chain per- and polyfluoroalkyl substances in aquatic systems: Occurrence, impacts and treatment. *Chem. Eng. J.* **2020**, *380*, 122506.
- (23) Pan, Y.; Zhang, H.; Cui, Q.; Sheng, N.; Yeung, L. W. Y.; Guo, Y.; Sun, Y.; Dai, J. First Report on the Occurrence and Bioaccumulation of Hexafluoropropylene Oxide Trimer Acid: An Emerging Concern. *Environ. Sci. Technol.* **2017**, *51*, 9553–9560.
- (24) Weatherly, L. M.; Shane, H. L.; Lukomska, E.; Baur, R.; Anderson, S. E. Systemic toxicity induced by topical application of heptafluorobutyric acid (PFBA) in a murine model. *Food Chem. Toxicol.* **2021**, *156*, 112528.
- (25) Moro, G.; Liberi, S.; Vascon, F.; Linciano, S.; De Felice, S.; Fasolato, S.; Foresta, C.; De Toni, L.; Di Nisio, A.; Cendron, L.; Angelini, A. Investigation of the Interaction between Human Serum Albumin and Branched Short-Chain Perfluoroalkyl Compounds. *Chem. Res. Toxicol.* **2022**, *35*, 2049–2058.
- (26) Sheng, N.; Pan, Y.; Guo, Y.; Sun, Y.; Dai, J. Hepatotoxic Effects of Hexafluoropropylene Oxide Trimer Acid (HFPO-TA), A Novel Perfluorooctanoic Acid (PFOA) Alternative, on Mice. *Environ. Sci. Technol.* **2018**, *52*, 8005–8015.
- (27) Li, C. H.; Ren, X. M.; Guo, L. H. Adipogenic Activity of Oligomeric Hexafluoropropylene Oxide (Perfluorooctanoic Acid Alternative) through Peroxisome Proliferator-Activated Receptor gamma Pathway. *Environ. Sci. Technol.* **2019**, *53*, 3287–3295.
- (28) Xie, X.; Zhou, J.; Hu, L.; Shu, R.; Zhang, M.; Sun, L.; Wu, F.; Fu, Z.; Li, Z. Oral exposure to a hexafluoropropylene oxide trimer acid (HFPO-TA) disrupts mitochondrial function and biogenesis in mice. *J. Hazard. Mater.* **2022**, *430*, 128376.
- (29) USEPA. Technical Fact Sheet: Drinking Water Health Advisories for Four PFAS (PFOA, PFOS, GenX chemicals, and PFBS). 2022, <https://www.epa.gov/system/files/documents/2022-06/technical-factsheet-four-PFAS.pdf> (accessed June 2022).
- (30) EU. Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption. 2020, <https://eur-lex.europa.eu/eli/dir/2020/2184/oj> (accessed July 2022).

- (31) Appleman, T. D.; Higgins, C. P.; Quiñones, O.; Vanderford, B. J.; Kolstad, C.; Zeigler-Holady, J. C.; Dickenson, E. R. Treatment of poly- and perfluoroalkyl substances in U.S. full-scale water treatment systems. *Water Res.* **2014**, *51*, 246–255.
- (32) Schaefer, C. E.; Andaya, C.; Urtiaga, A.; McKenzie, E. R.; Higgins, C. P. Electrochemical treatment of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) in groundwater impacted by aqueous film forming foams (AFFFs). *J. Hazard. Mater.* **2015**, *295*, 170–175.
- (33) Hopkins, Z. R.; Sun, M.; DeWitt, J. C.; Knappe, D. R. U. Recently Detected Drinking Water Contaminants: GenX and Other Per- and Polyfluoroalkyl Ether Acids. *J. AWWA* **2018**, *110*, 13–28.
- (34) Herkert, N. J.; Merrill, J.; Peters, C.; Bollinger, D.; Zhang, S.; Hoffman, K.; Ferguson, P. L.; Knappe, D. R. U.; Stapleton, H. M. Assessing the Effectiveness of Point-of-Use Residential Drinking Water Filters for Perfluoroalkyl Substances (PFASs). *Environ. Sci. Technol. Lett.* **2020**, *7*, 178–184.
- (35) Rahman, M. F.; Peldszus, S.; Anderson, W. B. Behaviour and fate of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in drinking water treatment: A review. *Water Res.* **2014**, *50*, 318–340.
- (36) Dixit, F.; Munoz, G.; Mirzaei, M.; Barbeau, B.; Liu, J.; Duy, S. V.; Sauve, S.; Kandasubramanian, B.; Mohseni, M. Removal of zwitterionic PFAS by MXenes: Comparisons with anionic, nonionic, and PFAS-specific resins. *Environ. Sci. Technol.* **2022**, *56*, 6212–6222.
- (37) Burkhardt, J. B.; Burns, N.; Mobley, D.; Pressman, J. G.; Magnuson, M. L.; Speth, T. F. Modeling PFAS Removal Using Granular Activated Carbon for Full-Scale System Design. *J. Environ. Eng.* **2022**, *148*, 1.
- (38) Fang, Y.; Ellis, A.; Choi, Y. J.; Boyer, T. H.; Higgins, C. P.; Schaefer, C. E.; Strathmann, T. J. Removal of Per- and Polyfluoroalkyl Substances (PFASs) in Aqueous Film-Forming Foam (AFFF) Using Ion-Exchange and Nonionic Resins. *Environ. Sci. Technol.* **2021**, *55*, 5001–5011.
- (39) Ellis, A. C.; Liu, C. J.; Fang, Y.; Boyer, T. H.; Schaefer, C. E.; Higgins, C. P.; Strathmann, T. J. Pilot study comparison of regenerable and emerging single-use anion exchange resins for treatment of groundwater contaminated by per- and polyfluoroalkyl substances (PFASs). *Water Res.* **2022**, *223*, 119019.
- (40) Liu, Y. L.; Sun, M. Ion exchange removal and resin regeneration to treat per- and polyfluoroalkyl ether acids and other emerging PFAS in drinking water. *Water Res.* **2021**, *207*, 117781.
- (41) Boyer, T. H.; Ellis, A.; Fang, Y. D.; Schaefer, C. E.; Higgins, C. P.; Strathmann, T. J. Life cycle environmental impacts of regeneration options for anion exchange resin remediation of PFAS impacted water. *Water Res.* **2021**, *207*, 117798.
- (42) Xiao, F.; Sasi, P. C.; Yao, B.; Kubatova, A.; Golovko, S. A.; Golovko, M. Y.; Soli, D. Thermal stability and decomposition of perfluoroalkyl substances on spent granular activated carbon. *Environ. Sci. Technol. Lett.* **2020**, *7*, 343–350.
- (43) Alinezhad, A.; Challa Sasi, P.; Zhang, P.; Yao, B.; Kubatova, A.; Golovko, S. A.; Golovko, M. Y.; Xiao, F. An investigation of thermal air degradation and pyrolysis of per- and polyfluoroalkyl substances and aqueous film-forming foams in soil. *ACS EST Engg.* **2022**, *2*, 198–209.
- (44) Xiao, F.; Sasi, P. C.; Alinezhad, A.; Golovko, S. A.; Golovko, M. Y.; Spoto, A. Thermal Decomposition of Anionic, Zwitterionic, and Cationic Polyfluoroalkyl Substances in Aqueous Film-Forming Foams. *Environ. Sci. Technol.* **2021**, *55*, 9885–9894.
- (45) Yao, B.; Sun, R.; Alinezhad, A.; Kubatova, A.; Simcik, M. F.; Guan, X.; Xiao, F. The first quantitative investigation of compounds generated from PFAS, PFAS-containing aqueous film-forming foams and commercial fluorosurfactants in pyrolytic processes. *J. Hazard. Mater.* **2022**, *436*, 129313.
- (46) Sasi, P. C.; Alinezhad, A.; Yao, B.; Kubatova, A.; Golovko, S. A.; Golovko, M. Y.; Xiao, F. Effect of granular activated carbon and other porous materials on thermal decomposition of per- and polyfluoroalkyl substances: Mechanisms and implications for water purification. *Water Res.* **2021**, *200*, 117271.
- (47) Longendyke, G. K.; Katel, S.; Wang, Y. X. PFAS fate and destruction mechanisms during thermal treatment: A comprehensive review. *Environ. Sci.: Processes Impacts* **2022**, *24*, 196–208.
- (48) Wang, J.; Lin, Z.; He, X.; Song, M.; Westerhoff, P.; Doudrick, K.; Hanigan, D. Critical review of thermal decomposition of per- and polyfluoroalkyl substances: Mechanisms and implications for thermal treatment processes. *Environ. Sci. Technol.* **2022**, *56*, 5355–5370.
- (49) Watanabe, N.; Takata, M.; Takemine, S.; Yamamoto, K. Thermal mineralization behavior of PFOA, PFHxA, and PFOS during reactivation of granular activated carbon (GAC) in nitrogen atmosphere. *Environ. Sci. Pollut. Res. Int.* **2018**, *25*, 7200–7205.
- (50) DiStefano, R.; Feliciano, T.; Mimna, R. A.; Redding, A. M.; Matthis, J. Thermal destruction of PFAS during full-scale reactivation of PFAS-laden granular activated carbon. *Remediation* **2022**, *32*, 231–238.
- (51) Duchesne, A. L.; Brown, J. K.; Patch, D. J.; Major, D.; Weber, K. P.; Gerhard, J. I. Remediation of PFAS-contaminated soil and granular activated carbon by smoldering combustion. *Environ. Sci. Technol.* **2020**, *54*, 12631–12640.
- (52) Dastgheib, S. A.; Mock, J.; Ilangovan, T.; Patterson, C. Thermogravimetric studies for the incineration of an anion exchange resin laden with short- or long-chain PFAS compounds containing carboxylic or sulfonic acid functionalities in the presence or absence of calcium oxide. *Ind. Eng. Chem. Res.* **2021**, *60*, 16961–16968.
- (53) Thoma, E. D.; Wright, R. S.; George, L.; Krause, M.; Presezz, D.; Villa, V.; Preston, W.; Deshmukh, P.; Kauppi, P.; Zemek, P. G. Pyrolysis processing of PFAS-impacted biosolids, a pilot study. *J. Air Waste Manag. Assoc.* **2022**, *72*, 309–318.
- (54) Zhang, W. L.; Cao, H. M.; Mahadevan Subramanya, S.; Savage, P.; Liang, Y. N. Destruction of perfluoroalkyl acids accumulated in *Typha latifolia* through hydrothermal liquefaction. *ACS Sustain. Chem. Eng.* **2020**, *8*, 9257–9262.
- (55) Sorengard, M.; Lindh, A. S.; Ahrens, L. Thermal desorption as a high removal remediation technique for soils contaminated with per- and polyfluoroalkyl substances (PFASs). *PLoS One* **2020**, *15*, No. e0234476.
- (56) Crownover, E.; Oberle, D.; Kluger, M.; Heron, G. Perfluoroalkyl and polyfluoroalkyl substances thermal desorption evaluation. *Remed. J.* **2019**, *29*, 77–81.
- (57) Riedel, T. P.; Wallace, M. A. G.; Shields, E. P.; Ryan, J. V.; Lee, C. W.; Linak, W. P. Low temperature thermal treatment of gas-phase fluorotelomer alcohols by calcium oxide. *Chemosphere* **2021**, *272*, 129859.
- (58) Sonmez Baghizade, B.; Zhang, Y.; Reuther, J. F.; Saleh, N. B.; Venkatesan, A. K.; Apul, O. G. Thermal regeneration of spent granular activated carbon presents an opportunity to break the forever PFAS cycle. *Environ. Sci. Technol.* **2021**, *55*, 5608–5619.
- (59) Winchell, L. J.; Ross, J. J.; Wells, M. J. M.; Fonoll, X.; Norton, J. W.; Bell, K. Y. Per- and polyfluoroalkyl substances thermal destruction at water resource recovery facilities: A state of the science review. *Water Environ. Res.* **2021**, *93*, 826–843.
- (60) Wang, J.; Song, M.; Abusallout, I.; Hanigan, D. Thermal Decomposition of Two Gaseous Perfluorocarboxylic Acids: Products and Mechanisms. *Environ. Sci. Technol.* **2023**, *57*, 6179–6187.
- (61) Wu, B. R.; Hao, S. L.; Choi, Y. J.; Higgins, C. P.; Deeb, R.; Strathmann, T. J. Rapid destruction and defluorination of perfluorooctanesulfonate by alkaline hydrothermal reaction. *Environ. Sci. Technol. Lett.* **2019**, *6*, 630–636.
- (62) Hao, S.; Choi, Y. J.; Wu, B.; Higgins, C. P.; Deeb, R.; Strathmann, T. J. Hydrothermal alkaline treatment for destruction of per- and polyfluoroalkyl substances in aqueous film-forming foam. *Environ. Sci. Technol.* **2021**, *55*, 3283–3295.
- (63) Zhang, W. L.; Liang, Y. N. Effects of hydrothermal treatments on destruction of per- and polyfluoroalkyl substances in sewage sludge. *Environ. Pollut.* **2021**, *285*, 117276.
- (64) Trang, B.; Li, Y.; Xue, X. S.; Ateia, M.; Houk, K. N.; Dichtel, W. R. Low-temperature mineralization of perfluorocarboxylic acids. *Science* **2022**, *377*, 839–845.
- (65) Xiao, F.; Challa Sasi, P.; Alinezhad, A.; Sun, R.; Abdulmalik Ali, M.; Sun, R. Thermal Phase Transition and Rapid Degradation of

Forever Chemicals (PFAS) in Spent Media Using Induction Heating. *ACS ES&T Engg.* **2023**, DOI: 10.1021/acsestengg.3c00114.

(66) Pica, N. E.; Funkhouser, J.; Yin, Y.; Zhang, Z.; Ceres, D. M.; Tong, T.; Blotevogel, J. Electrochemical Oxidation of Hexafluoropropylene Oxide Dimer Acid (GenX): Mechanistic Insights and Efficient Treatment Train with Nanofiltration. *Environ. Sci. Technol.* **2019**, *53*, 12602–12609.

(67) Bentel, M. J.; Yu, Y. C.; Xu, L. H.; Kwon, H.; Li, Z.; Wong, B. M.; Men, Y. J.; Liu, J. Y. Degradation of perfluoroalkyl ether carboxylic acids with hydrated electrons: Structure-reactivity relationships and environmental implications. *Environ. Sci. Technol.* **2020**, *54*, 2489–2499.

(68) Bao, Y. X.; Deng, S. S.; Jiang, X. S.; Qu, Y. X.; He, Y.; Liu, L. Q.; Chai, Q. W.; Mumtaz, M.; Huang, J.; Cagnetta, G.; Yu, G. Degradation of PFOA Substitute: GenX (HFPO-DA Ammonium Salt): Oxidation with UV/Persulfate or Reduction with UV/Sulfite? *Environ. Sci. Technol.* **2018**, *52*, 11728–11734.

(69) Adi, M. A.; Altarawneh, M. Thermal decomposition of heptafluoropropylene-oxide-dimer acid (GenX). *Chemosphere* **2022**, *289*, 133118.

(70) Blotevogel, J.; Giraud, R. J.; Rappé, A. K. Incinerability of PFOA and HFPO-DA: Mechanisms, kinetics, and thermal stability ranking. *Chem. Eng. J.* **2023**, *457*, 141235.

(71) Washington, J. W.; Jenkins, T. M.; Weber, E. J. Identification of unsaturated and 2H polyfluorocarboxylate homologous series and their detection in environmental samples and as polymer degradation products. *Environ. Sci. Technol.* **2015**, *49*, 13256–13263.

(72) Xiao, F.; Jin, B.; Golovko, S. A.; Golovko, M. Y.; Xing, B. Sorption and desorption mechanisms of cationic and zwitterionic per- and polyfluoroalkyl substances in natural soils: Thermodynamics and hysteresis. *Environ. Sci. Technol.* **2019**, *53*, 11818–11827.

(73) Xiao, F.; Hanson, R. A.; Golovko, S. A.; Golovko, M. Y.; Arnold, W. A. PFOA and PFOS are generated from zwitterionic and cationic precursor compounds during water disinfection with chlorine or ozone. *Environ. Sci. Technol. Lett.* **2018**, *5*, 382–388.

(74) Xiao, F.; Golovko, S. A.; Golovko, M. Y. Identification of novel non-ionic, cationic, zwitterionic, and anionic polyfluoroalkyl substances using UPLC-TOF-MS(E) high-resolution parent ion search. *Anal. Chim. Acta* **2017**, *988*, 41–49.

(75) Marsh, H.; Rodríguez-Reinoso, F. *Activated Carbon*; Elsevier: Amsterdam; London, 2006; p 536.

(76) Zhao, Y.; Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, *120*, 215–241.

(77) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16*, Rev. A.03; Gaussian: Wallingford, CT, 2016.

(78) Perfluoropropene GC-MS spectrum. 2022, <https://pubchem.ncbi.nlm.nih.gov/compound/8302#section=Mass-Spectrometry> (accessed May 2022).

(79) Xiao, F.; Zhang, X.; Penn, L.; Gulliver, J. S.; Simcik, M. F. Effects of monovalent cations on the competitive adsorption of perfluoroalkyl acids by kaolinite: Experimental studies and modeling. *Environ. Sci. Technol.* **2011**, *45*, 10028–10035.

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