New Insights into the Degradation Mechanism of Perfluorooctanoic Acid by Persulfate from Density Functional Theory and Experimental Data

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ABSTRACT: Thermally activated persulfate is a promising oxidant for in situ remediation of perfluorooctanoic acid (PFOA), yet a comprehensive understanding of the degradation mechanism is still lacking. In this study, we used density functional theory (DFT) calculations and experimental data to map entire reaction pathways for the degradation of PFOA by persulfate, with specific considerations on the influence of pH. The DFT results showed that the rate-limiting step was the first electron abstraction from PFOA, yet the generation of SO\(_4^{2-}\) from the decomposition of persulfate contributed a large part of the free energy of activation (\(\Delta G^\ddagger\)) for the overall reaction. The subsequent steps did not contribute to the \(\Delta G^\ddagger\). For the electron abstraction from PFOA, we investigated reactions using protonated and deprotonated species of PFOA and SO\(_4^{2-}\) and showed that the reaction of anionic PFOA with HSO\(_4^-\) was most favorable with a \(\Delta G^\ddagger\) of 7.2 kJ/mol. This explains why low pH (<3.5) is a sine qua non condition for the degradation of PFOA by persulfate. The overall \(\Delta G^\ddagger\) derived theoretically based on the pathway involved HSO\(_4^-\) was consistent with the \(\Delta G^\ddagger\) determined experimentally. This study provides valuable insight into remediation strategies that include persulfate as an oxidizing agent for perfluoroalkyl carboxylic acids.

INTRODUCTION

Perfluorooctanoic acid (PFOA) belongs to the family of per- and polyfluoroalkyl substances (PFASs) and has been detected in a variety of environmental matrices. Milligrams per liter levels of PFOA were found in the groundwater of military sites where aqueous film-forming foams containing PFASs as key fire extinguishing agents were frequently used for firefighting training. PFOA is bioaccumulative, and chronic exposure to PFOA is closely linked to developmental toxicity, immunotoxicity, and hepatotoxicity. The current U.S. EPA drinking water health advisory level for the total of PFOA and PFOS-contaminated groundwater. This reaction proceeds by the sequential loss of \([\text{CF}_2]\) in the form of CO\(_2\) and F\(^-\), as established experimentally, yet the exact reaction pathway remains mainly speculative because of the difficulty in detecting reaction intermediates. It is well recognized that low pH favors the reaction, and Bruton et al. further suggested that a pH less than 3 is essential. However, the reaction mechanisms behind this low pH requirement are yet to be elucidated.

Determining the role of pH through experiments is very challenging because of the complex interplay of acid–base active molecules in the system. Furthermore, the values of the experimentally derived activation energy for the degradation of PFOA (e.g., 114.3–124.5 kJ/mol at initial pH of ~3.5), are close to that of the persulfate decomposition (125.5 kJ/mol), suggesting a significant role of the production of SO\(_4^{2-}\) to the degradation kinetics of PFOA. However, the dependence on the persulfate decomposition disappears at circumneutral and alkaline pH where no degradation of PFOA is observed. A comprehensive understanding of the degradation...
mechanism and reaction pathways is thus required to identify the steps that control the degradation kinetics of PFOA and to determine the role of pH. Experimental investigations alone based on the thermodynamics and kinetics of overall reactions cannot provide adequate descriptions of individual reaction steps, a shortcoming that can be addressed using density functional theory (DFT) calculation.

DFT is a powerful predictive approach for determining the thermodynamics and kinetics of chemical reactions. DFT has been successfully applied to explain the transformation mechanisms and calculate the transformation rates of organic contaminants such as chlorinated solvents,20,21 chlorinated paraffins,22 and flame retardants.23,24 Niu et al.25 used DFT calculations to propose an optimal reaction route for the mineralization of PFOA in the electrolysis system, and there is no shorter-chain PFCAs involved, which is distinct from the degradation mechanisms by persulfate. Thus, it is necessary to map the entire reaction route of PFOA in persulfate system.

In this study, we used DFT simulations and experimental kinetics data in synergy and investigated the degradation mechanism for the linear isomer of PFOA in a thermally activated persulfate system. The most favorable reaction route was proposed based on the free energy of activation of each step, and the rate-limiting step was identified. We demonstrated the significant role of the decomposition of persulfate to the degradation kinetics of PFOA. Furthermore, we studied the effect of pH by comparing the reaction feasibility for protonated vs deprotonated species of PFOA and SO4**. We show that PFOA can only be oxidized with an acceptable energy barrier by HSO4 and thus explained why low pH is required for the degradation of PFOA by persulfate. To our knowledge, this is the first complete study on the degradation mechanism of PFOA in persulfate system by DFT calculations including both thermodynamics and kinetics considerations.

# METHODOLOGY

## Experimental Details.

PFOA (96%) was purchased from Sigma-Aldrich and has a linear isomer composition of ~99%. Standards of PFCAs (C1−C8), including PFOA, perfluoroheptanoic acid (PFHpA), perfluorohexanoic acid (PFHxA), perfluoropentanoic acid (PFPeA), and perfluorobutanoic acid (PFBA), and the corresponding isotope-labeled PFCAs used for quantification were purchased from Wellington Laboratories. Pentaxfluoropropionic acid (PFPrA, 97%) and trifluoroacetic acid (TFA, ≥99%) were purchased from Sigma-Aldrich. Formula and molecular weight of the investigated PFCAs are provided in Table S1 of the Supporting Information (SI). Sodium persulfate (Na2S2O8, ≥99.0%) was purchased from Sigma-Aldrich.

Degradation of PFOA was conducted in triplicate in 15 mL polycarbonate centrifuge tubes containing 10 mL of solution. ASTM Type I water was used in all experiments. The initial concentrations of PFOA and persulfate were 80 μM and 100 mM, respectively. The tubes were shaken at 175 rpm at 25–40 °C in the dark. At the prescribed reaction time, an aliquot of 50 μL of the aqueous solution was sampled and diluted in 0.45 mL of methanol to terminate the reactions. The samples were stored at −20 °C before analysis. When necessary, H2SO4 and phosphate buffer were added to obtain an initial pH in the acidic and circumneutral range, respectively. The decomposition of persulfate was conducted in exactly the same manner without addition of PFOA in a water bath at 40–70 °C. An aliquot of 50 μL of the aqueous solution was sampled after a prescribed reaction time and diluted in 0.95 mL ice water to scavenge the reaction. The samples were stored at 4 °C before analysis. Quantitative analysis of PFCAs (C1−C8) was performed with a Shimadzu UHPLC system coupled to an AB Sciex 5500 QTRAP mass spectrometer (Table S2). Persulfate was analyzed by the spectrophotometric method.26 Details are provided in the SI (SI-2).

## Computational Details.

The Gaussian16 program suite was used to conduct all the calculations27 using the M06-2X functional in combination with the 6-311++G(2d,2p) basis set and SMD model28 to account for solvation energies in water at 298.15 K and 1 atm. The M06-2X functional was chosen because of its excellent performance regarding main-group thermochemistry involving radical species.29,30 Frequency analysis was conducted to verify that the optimized geometries were the true minima for reactant and product molecules.

Conformational search of C9F18COOH was performed by the GMMX add-on model in Gaussian09 using both the Cartesian and Bonds search methods (details provided in SI-3). The conformation with the lowest Gibbs free energy of formation (Gg, kJ/mol) was identified as the global minimum and used in further calculations (Figure S1, Table S3).

For each reaction step, distinct reaction pathways were investigated. The Gibbs free energy (ΔG, kJ/mol) gives a measure of the thermodynamic feasibility of the proposed reactions. The kinetic feasibility was compared by calculating the free energy of activation (ΔG‡, kJ/mol) and the one with the lowest ΔG‡ was considered as the most favorable pathway. ΔG‡ for reactions with electron transfer was calculated following the Marcus theory31 according to eq 1:

\[
ΔG^\ddagger = \frac{(ΔG + λ)^2}{4λ}
\]

where λ (kJ/mol) is the reorganization energy, which is defined as the energy to move the structure of the system, including solvent molecules, from initial to final coordinates without transferring the electron. λ contains inner sphere (λin) and outer sphere (λout) parts with λ = λin + λout. The detailed methods to calculate λin and λout are provided in SI-4.

ΔG‡ for reactions with bond breakage and formation was calculated based on the transition state (TS) theory. To obtain a TS, a potential energy surface (PES) scan was performed, in which the forming bond distance was constrained by increasing or reducing it stepwise; then the structure at the highest energy point was selected as the input for TS search. A TS was confirmed to be the first-order saddle-point by verifying the presence of a single imaginary frequency. Intrinsic reaction coordinate (IRC) analysis was also performed to verify that the obtained TS connects the designated reactants and products. ΔG‡ was taken as the difference between the G‡ of the TS and the total G‡ of the individual reactants. The ΔG and ΔG‡ values were reported at the standard state of 1 M solution at 298.15 K, which was corrected from that of 1 atm gas by reducing 7.92 J/mol for each of the molecules and TS.

### Experimentally Derived Activation Energy.

The experimentally derived ΔG‡ was obtained by first plotting the rate constants measured at different temperatures to the linear form of Eyring equation and then calculated through the fitted enthalpy (ΔH‡, kJ/mol) and entropy (ΔS‡, kJ/mol) of activation (eqs 2–4):

\[
k = \frac{k_B T}{h} e^{-\frac{(ΔH^\ddagger)}{RT}}
\]
\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \]  

\[ \ln \frac{k}{T} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} + \ln \frac{k_b}{h} \]  

where \( k (\text{h}^{-1}) \) is the pseudo-first order rate constant; \( T \) (K) is the absolute temperature; \( R \) (=8.31 J/(mol·K)) is the gas constant; \( k_b (=1.38 \times 10^{-23} \text{J/K}) \) is the Boltzmann constant; \( h (=6.626 \times 10^{-34} \text{J} \cdot \text{s}) \) is Planck's constant.

**RESULTS AND DISCUSSION**

**Effect of pH on the Degradation of PFOA.** Degradation of PFOA by thermally activated persulfate was first studied in an unbuffered system at 40 °C. The persulfate ion (S\(_{2}\)O\(_{8}\)\(^{2-}\)) readily undergoes scavenging reactions with H\(_2\)O to produce H\(^+\), which lowered the initial pH (pH\(_0\)) to 3.5 in our experiments and caused the pH to decrease continuously during the reaction (eq 5).

\[ \text{S}_2\text{O}_8^{2-} + \text{H}_2\text{O} \rightarrow 2\text{SO}_4^{2-} + 2\text{H}^+ + \frac{1}{2}\text{O}_2 \]  

Figure 1A shows that 98.9% of the added PFOA was degraded by persulfate after 144 h, while the control containing only PFOA without persulfate showed a negligible loss. The degradation intermediates consisted of shorter-chain (C\(_2\)–C\(_7\)) PFCAs, with PFHpA (C\(_7\)) reaching its peak concentration first, followed by PFHxA (C\(_6\)), PFPa (C\(_5\)), PFBA (C\(_4\)), PFPa (C\(_4\)), and TFA (C\(_2\)) (Figure 1B), which is consistent with the mechanism of the sequential loss of [CF\(_2\)] units reported previously.\(^{14,18}\) The molar percentage of total shorter-chain PFCAs (\(\sum\text{PFCAs}\)) relative to the initial added PFOA reached the maximum of 86.9% at 72 h, and only 7.5% remained at 288 h. We were unable to detect any organic intermediates other than shorter-chain PFCAs. The PFOA and the shorter-chain PFCAs are eventually mineralized to HF and CO\(_2\) as reported elsewhere.\(^{14}\)

The degradation of PFOA by persulfate at pH\(_0\) 3.5 under 40 °C followed pseudo-first order kinetics with respect to PFOA concentration, and a rate constant (\(k(\text{PFOA})\)) of 0.0322 h\(^{-1}\) was obtained over the period of 0–96 h (Table S5). The reaction was slower in the first 24 h (0–24 h, \(k(\text{PFOA}) = 0.0190 \text{h}^{-1}\)) than in the rest of the reaction period (24–96 h, \(k(\text{PFOA}) = 0.0370 \text{h}^{-1}\)) (Figure 1C), and the solution pH gradually decreased to 2.3 at 24 h and then to 1.7 at 96 h (Table S5). The results are consistent with those reported elsewhere that low pH favors the degradation of PFOA by persulfate.\(^{16}\)

To further ascertain the role of pH, we adjusted the pH\(_0\) of the solution to either 1.6 by adding H\(_2\)SO\(_4\), or 6.7 by adding 10 mM of phosphate buffer. At pH\(_0\) 1.6, the overall rate constant (\(k(\text{PFOA})\)) was 0.0322 h\(^{-1}\) was obtained over the period of 0–96 h (Table S5). The reaction was slower in the first 24 h (0–24 h, \(k(\text{PFOA}) = 0.0190 \text{h}^{-1}\)) than in the rest of the reaction period (24–96 h, \(k(\text{PFOA}) = 0.0370 \text{h}^{-1}\)) (Figure 1C), and the solution pH gradually decreased to 2.3 at 24 h and then to 1.7 at 96 h (Table S5). The results are consistent with those reported elsewhere that low pH favors the degradation of PFOA by persulfate.\(^{16}\)

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Figure 2. Hypothesized reaction route proposed in the literature (Route 1) and the optimal reaction route proposed in the current study based on DFT calculations (Route 2) for the degradation of PFOA by thermally activated persulfate. The difference of Route 2 from Route 1 is shown in red.

One common hypothesis for the changes in PFOA degradation rates with pH is the dependence of SO4\(^{2-}\) generation on pH. Indeed, the thermal decomposition rate of persulfate is known to accelerate at acidic pH.32 Using eq 6,

\[ k_1(S_2O_8^{2-}) = k_{s_2o_8^{2-},neutral} + k_{s_2o_8^{2-},acidic}[H^+] + k_{s_2o_8^{2-},basic}[OH^-] \]  

and the neutral (\(k_{s_2o_8^{2-},neutral}\), neutral, 0.0013 h\(^{-1}\)), acidic (\(k_{s_2o_8^{2-},acidic}\), acidic, 0.0998 M\(^{-1}\) h\(^{-1}\)), and basic (\(k_{s_2o_8^{2-},basic}\), basic, 0.0046 M\(^{-1}\) h\(^{-1}\)) rate constants at 40 °C estimated therein, the decomposition rate of persulfate \((k(S_2O_8^{2-}), h^{-1})\) at different pH was calculated. It is clear from Figure 1D that at low pH (<3.5), the change in the rate constants of PFOA degradation is qualitatively similar to those of persulfate decomposition. At higher pH, however, the persulfate decomposition remained unchanged with pH, whereas the degradation of PFOA ceased.

Another hypothesis is the increased scavenging of SO4\(^{2-}\) occurs at higher pH by OH\(^-\) and HPO4\(^{2-}\). However, as also stated by Bruton et al.,4 the percentage of SO4\(^{2-}\) reacting with OH\(^-\) or HPO4\(^{2-}\), calculated based on the second order rate constants of SO4\(^{2-}\) with S2O8\(^{2-}\), H2O, OH\(^-\), and HPO4\(^{2-}\) (eqs 7–10), is too small (0–3.7%, pH 1–7, 10 mM phosphate buffer) to affect the degradation of PFOA (Table S6).

\[ \text{SO}_4^{2-} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{SO}_4^{2-} + \text{S}_2\text{O}_8^{2-} \quad k = 1.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1} \]  

\[ \text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{OH}^- + \text{H}^+ \text{[H}_2\text{O]} = 660 \text{s}^{-1} \]  

\[ \text{SO}_4^{2-} + \text{OH}^- \rightarrow \text{SO}_4^{2-} + \text{OH}^- \quad k = 6.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1} \]  

\[ \text{SO}_4^{2-} + \text{HPO}_4^{2-} \rightarrow \text{SO}_4^{2-} + \text{HPO}_4^{2-} \quad k = 1.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1} \]  

These results clearly indicate that the pH dependence of PFOA degradation cannot be explained by the production dynamics or scavenging of SO4\(^{2-}\). Another step along the PFOA degradation route may also depend on pH, which can only be known by investigating the detailed reaction path.

**Computation of PFOA Degradation.** The degradation of PFOA by persulfate is a complex process involving several reaction steps. It has been hypothesized that the reaction starts with SO4\(^{2-}\) attacking the ionic PFOA (C7F15COO\(^-\)) to generate a perfluorooctanoic carboxyl radical (step I, C7F15(COO\(^-\))), which undergoes decarboxylation to produce a perfluoroheptyl radical (step II, C7F15\(^-\)). C7F15\(^-\) is then hydrated to form a perfluorinated alcohol (step III, C7F15(OH)) before HF elimination to generate its acid fluoride (step IV, C7F15(COF)). Hydrolysis of the acid fluoride results in a PFCA with one less CF2 unit (step V, PFHpA) (Figure 2–Route 1).14,35 The subsequent reaction of the resulting PFHpA with SO4\(^{2-}\) follows a similar route as for PFOA, and the reaction repeats itself until all the PFCAs are completely mineralized. Potential participation of oxygen was not considered because its presence had no significant influence on the degradation kinetics and products of PFOA by persulfate.35 These pathways, however, have not been verified because the proposed intermediates cannot be easily detected and have not been reported. Moreover, some of the proposed reactions cannot occur easily from a thermodynamics standpoint. DFT calculation offers the opportunity to test the reliability of these pathways systematically and identify the rate-limiting step.

We thus explored alternative pathways beyond those shown in Route 1 and calculated their \(\Delta G\) and \(\Delta G^2\) (Table 1). The good agreement between the theoretical and experimental geometry parameters for several molecules and radicals involved in the reactions indicates the reliability of the M06-2X functional, basis sets, and solvation model adopted in the

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DOI: 10.1021/acs.est.9b00797

Table 1. Possible Reaction Pathways for the Degradation of PFOA by Persulfate for Each Proposed Step in Figure 2 with Their Respective Free Energy (\(\Delta G\)) and Free Energy of Activation (\(\Delta G^\ddagger\)) at the M06-2X/6-311++G(2d,2p) Level of Theory Using SMD as the Solvation Modela,b.

<table>
<thead>
<tr>
<th>Step 0</th>
<th>(\Delta G) (kJ/mol)</th>
<th>(\Delta G^\ddagger) (kJ/mol)</th>
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<tbody>
<tr>
<td>(\Delta )</td>
<td>(S_2O_4^{2-} \rightarrow SO_4^{2-} + SO_4^{2-}) (R0)</td>
<td>95.7</td>
</tr>
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</table>

| Step I | \(\Delta \) | \(C_2F_5COO^- + SO_4^{2-} \rightarrow C_2F_5COO^- + SO_4^{2-}\) (RI-a) | 90.9 | 91.2 |
|--------|----------------------|-----------------------------|
| | \(C_2F_5COOH + SO_4^{2-} \rightarrow C_2F_5COOH^{2+} + SO_4^{2-}\) (RI-b) | 245.5 | |

| Step II | \(\Delta \) | \(C_2F_5COOH + H_2O \rightarrow C_2F_5COO^- + HSO_4^-\) (RII) | \(-128.3\) | 3.7 |

| Step III | \(\Delta \) | \(C_2F_5COO^- + \cdot OH \rightarrow C_2F_5\cdot OSO_3^- + CO_2\) (RIII-a) | \(66.6\) | 120.4 |
| | \(C_2F_5\cdot OSO_3^- + H_2O \rightarrow C_2F_5\cdot OSO_3^- + H^+\) (RIII-b) | \(62.0\) | 234.7 |

| Step IV | \(\Delta \) | \(C_2F_5\cdot OSO_3^- + H_2O + \cdot OH \rightarrow C_2F_5\cdot OSO_3^- + H^+\) (RIII-c) | \(-382.6\) | 236.9 |

| Step V | \(\Delta \) | \(C_2F_5\cdot OSO_3^- + \cdot OH \rightarrow C_2F_5\cdot OSO_3^- + CO_2 + 2HF\) (RIII-d) | \(-421.7\) | no barrier |

| - | \(\Delta \) | \(C_2F_5\cdot OSO_3^- + \cdot OH \rightarrow C_2F_5\cdot OSO_3^- + CO_2 + 2HF\) (RIII-e) | \(-57.5\) | 19.4 |

| - | \(\Delta \) | \(C_2F_5\cdot OSO_3^- + \cdot OH \rightarrow C_2F_5\cdot OSO_3^- + CO_2 + 2HF\) (RIII-f) | \(-69.8\) | 7.7 |

| - | \(\Delta \) | \(C_2F_5\cdot OSO_3^- + \cdot OH \rightarrow C_2F_5\cdot OSO_3^- + CO_2 + 2HF\) (RIII-g) | \(-75.7\) | 15.6 |

| - | \(\Delta \) | \(C_2F_5\cdot OSO_3^- + \cdot OH \rightarrow C_2F_5\cdot OSO_3^- + CO_2 + 2HF\) (RIII-h) | \(-86.6\) | 13.1 |

| - | \(\Delta \) | \(C_2F_5\cdot OSO_3^- + \cdot OH \rightarrow C_2F_5\cdot OSO_3^- + CO_2 + 2HF\) (RIII-i) | \(-95.7\) | 95.7 |

| - | \(\Delta \) | \(C_2F_5\cdot OSO_3^- + \cdot OH \rightarrow C_2F_5\cdot OSO_3^- + CO_2 + 2HF\) (RIII-j) | \(-103.6\) | 156.1 |

| - | \(\Delta \) | \(C_2F_5\cdot OSO_3^- + \cdot OH \rightarrow C_2F_5\cdot OSO_3^- + CO_2 + 2HF\) (RIII-k) | \(-128.3\) | 236.9 |

| - | \(\Delta \) | \(C_2F_5\cdot OSO_3^- + \cdot OH \rightarrow C_2F_5\cdot OSO_3^- + CO_2 + 2HF\) (RIII-l) | \(-148.6\) | (165.1) |

| - | \(\Delta \) | \(C_2F_5\cdot OSO_3^- + \cdot OH \rightarrow C_2F_5\cdot OSO_3^- + CO_2 + 2HF\) (RIII-m) | \(-199.8\) | (110.2) |

| - | \(\Delta \) | \(C_2F_5\cdot OSO_3^- + \cdot OH \rightarrow C_2F_5\cdot OSO_3^- + CO_2 + 2HF\) (RIII-n) | \(-260.0\) | (91.2) |

| - | \(\Delta \) | \(C_2F_5\cdot OSO_3^- + \cdot OH \rightarrow C_2F_5\cdot OSO_3^- + CO_2 + 2HF\) (RIII-o) | \(-382.6\) | (68.4) |

| - | \(\Delta \) | \(C_2F_5\cdot OSO_3^- + \cdot OH \rightarrow C_2F_5\cdot OSO_3^- + CO_2 + 2HF\) (RIII-p) | \(-421.7\) | no barrier |

| - | \(\Delta \) | \(C_2F_5\cdot OSO_3^- + \cdot OH \rightarrow C_2F_5\cdot OSO_3^- + CO_2 + 2HF\) (RIII-q) | \(-421.7\) | no barrier |

| - | \(\Delta \) | \(C_2F_5\cdot OSO_3^- + \cdot OH \rightarrow C_2F_5\cdot OSO_3^- + CO_2 + 2HF\) (RIII-r) | \(-421.7\) | no barrier |

| - | \(\Delta \) | \(C_2F_5\cdot OSO_3^- + \cdot OH \rightarrow C_2F_5\cdot OSO_3^- + CO_2 + 2HF\) (RIII-s) | \(-421.7\) | no barrier |

| - | \(\Delta \) | \(C_2F_5\cdot OSO_3^- + \cdot OH \rightarrow C_2F_5\cdot OSO_3^- + CO_2 + 2HF\) (RIII-t) | \(-421.7\) | no barrier |

| - | \(\Delta \) | \(C_2F_5\cdot OSO_3^- + \cdot OH \rightarrow C_2F_5\cdot OSO_3^- + CO_2 + 2HF\) (RIII-u) | \(-421.7\) | no barrier |

| - | \(\Delta \) | \(C_2F_5\cdot OSO_3^- + \cdot OH \rightarrow C_2F_5\cdot OSO_3^- + CO_2 + 2HF\) (RIII-v) | \(-421.7\) | no barrier |

| - | \(\Delta \) | \(C_2F_5\cdot OSO_3^- + \cdot OH \rightarrow C_2F_5\cdot OSO_3^- + CO_2 + 2HF\) (RIII-w) | \(-421.7\) | no barrier |

| - | \(\Delta \) | \(C_2F_5\cdot OSO_3^- + \cdot OH \rightarrow C_2F_5\cdot OSO_3^- + CO_2 + 2HF\) (RIII-x) | \(-421.7\) | no barrier |

| - | \(\Delta \) | \(C_2F_5\cdot OSO_3^- + \cdot OH \rightarrow C_2F_5\cdot OSO_3^- + CO_2 + 2HF\) (RIII-y) | \(-421.7\) | no barrier |

| - | \(\Delta \) | \(C_2F_5\cdot OSO_3^- + \cdot OH \rightarrow C_2F_5\cdot OSO_3^- + CO_2 + 2HF\) (RIII-z) | \(-421.7\) | no barrier |

“The \(\Delta G\) and \(\Delta G^\ddagger\) values at the same level of theory but with IEPFCM as the solvation model for some reactions are shown in parentheses. a indicates the optimal reaction pathway. The values of \(\Delta G^\ddagger\) from the solvation model of IEPFCM for RIV-g and RV-a from IEPFCM and SMD models, the \(\Delta G^\ddagger\) of RIV-b, RIV-i, and RV-b by SMD model should be very close to that of IEPFCM.”

DFT calculations (Figure S2). Other studies have used spot-checks with higher-level wave function-based methods such as CCSD(T)36 to refine calculation accuracy. Unfortunately, the size and linear structure of the molecules explored in this study imply prohibitively long computational time with this functional choice. The results of the PES scan are provided in Figure S3, and the IRC plots connecting the TS to the corresponding reactants and products are shown in Figures 3 and S4. Cartesian coordinates of the optimized geometries for the reactants, products, and TS are provided in Table S7. Profiles of the potential energy surface for all the steps are shown in Figure 4 with optimal pathways represented by black lines and alternative pathways by colored lines.

Step 0. This step is the decomposition of persulfate to produce SO_4^{2-} (R0), and it is the reverse of the barrierless radical recombination reaction (SI-9, Figure S5). Thus, R0 has no TS, and the \(\Delta G\) (95.7 kJ/mol) was regarded as the \(\Delta G^\ddagger\). \(\Delta G^\ddagger\) of R0 obtained from plotting the rate constants for the decomposition of persulfate at different temperatures to the Eyring eq (eq 4) was 114.0 ± 3.4 kJ/mol at 40 °C (Figure S6). The deviation of the theoretical calculation from experimental data for R0 probably originated from the imperfections in the
Figure 3. Relative electronic energy ($\Delta$EE, kJ/mol) to the reactants versus intrinsic reaction coordinate (IRC) plot for (A) the decarboxylation of C$_7$F$_{15}$COO$^-$ (RII); (B) the defluorination of C$_7$F$_{15}$OH in the absence (RIV-g) and presence of one (RIV-h) and two water (RIV-i) molecules as reactants; (C) the defluorination of C$_7$F$_{15}$O$^-$ (RIV-j); and (D) the hydrolysis of C$_6$F$_{13}$COF in the presence of one (RV-a) and two (RV-b) water molecules as reactants. The IRC analysis was performed at the M06-2X/6-311++G(2d,2p) level of theory using SMD for RII, RIV-g, RIV-j, and RV-a, and IEFPCM for RIV-h, RIV-i, and RV-b as the solvation models. The geometries for the optimized structures of reactants, products, and transition state (TS) with bond lengths (Å) for each reaction are shown.

Figure 4. Scheme of the potential energy surface for the degradation of PFOA by thermally activated persulfate at the M06-2X/6-311++G(2d,2p) level of theory using SMD as the solvation model. The optimal reaction route is shown in black, while alternative, unfavorable pathways proposed for each step are represented by different colors.
description of the aqueous solvation effect for $\text{SO}_4^{2-}$ and $\text{SO}_4^{2-}^{\text{de}}$.37

**Step I.** Given that the degradation of PFOA by persulfate only takes place at a significant rate at pH values below 3.5, the acid/base speciation of $\text{SO}_4^{2-}$ and PFOA has to be explored. The $pK_v$ value for the $\text{HSO}_4^-/\text{SO}_4^{2-}$ couple is expected to be less than that of the $\text{HSO}_3^-/\text{SO}_4^{2-}$ couple (1.99).38 The $pK_v$ of PFOA is also low with experimentally determined values ranging from 1.01 to 3.8.39,40 Molecular modeling values ranging from ~0.5 to 0.2,41,42 and the calculated value of 0.1 in our study (Table S8; detailed method in SI-11). The larger $pK_v$ values compared to model predictions have been explained by the aggregation of PFOA in an aqueous solvent at mM concentrations.40 $\text{C}_7\text{F}_{15}\text{COO}^-$ and $\text{SO}_4^{2-}$ are thus most likely to be the predominant species at the investigated pH range, and it is reasonable to assume that the reaction is initiated by an electron transfer from $\text{C}_7\text{F}_{15}\text{COO}^-$ to $\text{SO}_4^{2-}$ to form $\text{C}_7\text{F}_{15}\text{COO}^-$ (RI-a, Table 1). Yet reactions involving $\text{HSO}_4^-$ or $\text{C}_7\text{F}_{15}\text{COOH}$ (RI-b, c, d) should impart less electrostatic repulsion, as was also proposed by Bruton et al.18 Moreover, if $\text{HSO}_4^-$ or $\text{C}_7\text{F}_{15}\text{COOH}$ proved to be better suited for this reaction than their deprotonated forms, their low concentrations at a pH of ~3.5, would not limit the reaction because of their constant generation from their deprotonated forms toward maintaining acid/base equilibrium, according to the Le Chatelier principle.

Since RI-a, b, c are electron transfer reactions, the $\Delta G^\circ$ were calculated following Marcus theory (eq 1) using $\Delta G^\circ$ and reorganization energy ($\lambda$). The $\Delta G$ of RI-a was 90.9 kJ/mol, and the magnitude of this positive value indicates RI-a is energetically unfavorable. $\lambda$ for RI-a was 82.6 kJ/mol, with $\alpha_{\text{eq}}$ (68.5 kJ/mol) accounting for most of it (Table S4). Following Marcus theory, the $\Delta G^\circ$ of RI-a was calculated to be 91.2 kJ/mol using eq 1 (dark blue lines in Figure 4). The high $\Delta G^\circ$ of RI-a is expected, since both the reactants are negatively charged and need to overcome electrostatic repulsion to interact. In some studies, electron transfer from $\text{C}_7\text{F}_{15}\text{COOH}$ to $\text{SO}_4^{2-}$ (RI-b) was also proposed as the initial step,14,35 but the much higher $\Delta G$ of RI-b (245.5 kJ/mol) compared to RI-a excludes the possibility of this reaction in practice (brown lines in Figure 4). In comparison, the negative $\Delta G$ (−26.8 kJ/mol) of the electron transfer reaction from $\text{C}_7\text{F}_{15}\text{COO}^-$ to $\text{HSO}_4^-$ (RI-c) shows that this reaction is thermodynamically favorable. $\lambda$ for RI-c was 72.6 kJ/mol, which is similar to RI-a (Table S4). However, because of the much lower $\Delta G$, $\Delta G^\circ$ of RI-c was calculated to be only 7.2 kJ/mol using eq 1 (Figure S7). We also explored RI-d, which involves H-transfer from $\text{C}_7\text{F}_{15}\text{COOH}$ to $\text{SO}_4^{2-}$, as another means to afford $\text{C}_7\text{F}_{15}\text{COO}^-$. The $\Delta G$ of this reaction was 38.7 kJ/mol, a lower value than that of RI-a. No saddle point was found using PES for RI-d and thus no TS was obtained. Since the $\Delta G$ of RI-d is already higher than the $\Delta G^\circ$ of RI-c, RI-d was not further considered (yellow lines in Figure 4). Taken as a whole, the results indicated that the electron transfer from $\text{C}_7\text{F}_{15}\text{COO}^-$ to $\text{HSO}_4^-$ is the most favorable step I to afford $\text{C}_7\text{F}_{15}\text{COO}^-$. **Step II.** The decarboxylation of $\text{C}_7\text{F}_{15}\text{COO}^-$ (RII) to form $\text{C}_7\text{F}_{15}^-^{\text{fl}}$ then ensued. The $\Delta G$ of RII was −128.3 kJ/mol and the calculated $\Delta G^\circ$ through TS search (Figure 3A) was only 3.7 kJ/mol. This low $\Delta G^\circ$ confirms RII is the step II in the degradation process. **Step III.** The directed hydration of $\text{C}_7\text{F}_{15}^-^{\text{fl}}$, with the production of either "OH (RIII-a) or H" (RIII-b), has been proposed in many previous studies.14,25,35 However, RIII-b is an energetically unfavorable reaction to give $\text{C}_7\text{F}_{15}\text{OH}$ with a $\Delta G$ of 62.0 kJ/mol and a calculated $\Delta G^\circ$ through TS search of 234.7 kJ/mol (Figure S4, purple lines in Figure 4). The high $\Delta G^\circ$ is due to the difficulty in homolytic cleavage of the O–H bond in H$_2$O, which is unlikely in the highly polar environment. RIII-a proceeds with a much lower $\Delta G^\circ$ (120.4 kJ/mol) and forms $\text{C}_7\text{F}_{15}\text{H}$, but the subsequent defluorination reactions (RIV-a, b, c, d, and RIV, Table S9) to give $\text{C}_7\text{F}_{15}\text{COOH}$ are highly energetically unfavorable (orange lines in Figure 4). Thus, the direct reaction of $\text{C}_7\text{F}_{15}^-^{\text{fl}}$ with H$_2$O is unlikely in practice. Niu et al.25 proposed the barrierless radical recombination reaction between $\text{C}_7\text{F}_{15}$ and $\text{OH}$ to form $\text{C}_7\text{F}_{15}\text{OH}$ (RIII-d), with highly negative $\Delta G$, in the electrochemical mineralization system enriched in OH. In the persulfate system, $\text{SO}_4^{2-}$ is the predominant radical. Thus, we proposed the reaction of $\text{C}_7\text{F}_{15}^-$ with $\text{SO}_4^{2-}$ and H$_2$O (RIII-c) to form $\text{C}_7\text{F}_{15}\text{OH}$. Despite the highly negative $\Delta G$ of RIII-c (−382.6 kJ/mol), the large $\Delta G^\circ$ of 236.9 kJ/mol excludes its participation in the reaction path (pink lines in Figure 4). By reacting with H$_2$O (eq 8), 0.5% of $\text{SO}_4^{2-}$ would become $\text{OH}$ under the investigated conditions (Table S6). Given that $\text{C}_7\text{F}_{15}^-^{\text{fl}}$ reacts with $\text{OH}$ barrierlessly (Figure S5) and the highly negative $\Delta G$ (−421.7 kJ/mol), RIII-d would be the most likely pathway to form $\text{C}_7\text{F}_{15}\text{OH}$. **Step IV.** For the defluorination of $\text{C}_7\text{F}_{15}\text{OH}$, we initially explored reactions with oxidizing radicals such as $\text{HSO}_4^-$ and $\text{OH}$ to give $\text{C}_7\text{F}_{15}\text{O}^-^{\text{de}}$ through H-abstraction (RIV-a, b, RIV-b). Both RIV-a and RIV-b were uphill reactions and their $\Delta G^\circ$ through TS search were 95.0 and 71.2 kJ/mol, respectively (Figure S4). Defluorination of $\text{C}_7\text{F}_{15}\text{O}^-^{\text{de}}$ would give $\text{C}_7\text{F}_{15}\text{O}^-$ and H* with a $\Delta G^\circ$ of 136.0 kJ/mol (RIV-c, Figure S4) through TS search. H* would react with H$_2$O and form $\text{OH}$ and HF (RIV-d) (RII-d would be the most likely pathway to form $\text{C}_7\text{F}_{15}\text{OH}$ as well). The pathway through RIV-e is much more energetically favorable than RIV-c (red and light blue lines in Figure 4). RIV-e cannot lead to the formation of $\text{C}_7\text{F}_{15}\text{COOH}$, which is an observed intermediate in our experiments. This thus suggests that $\text{C}_7\text{F}_{15}\text{OH}$ cannot participate in the reaction path and another route needs to be explored.

The direct HF elimination from $\text{C}_7\text{F}_{15}\text{OH}$ is the generally accepted pathway to give $\text{C}_7\text{F}_{15}\text{COF}$ (RIV-g),14,35,43 but the calculated $\Delta G^\circ$ through TS search (Figure 3B) was 203.0 kJ/mol. The large $\Delta G^\circ$ of RIV-g is consistent with the high reaction barrier of HF elimination from $\text{C}_7\text{F}_{15}\text{OH}$ and CF$_3$CF$_2$OH in the gas phase as reported elsewhere.44,45 However, it is known that addition of water can considerably lower the reaction barrier of HF elimination reactions from perfluorinated alcohols.44,45 This is attributed to the ability of H-bonding to stabilize the TS, as well as to the formation of cyclic TS structures that facilitate proton transfer. We found that by adding one water molecule (RIV-h), the $\Delta G$ was lowered to 91.2 kJ/mol, and the TS showed a 6-membered cyclic structure; when two water molecules were added (RIV-i), the $\Delta G$ was lowered to 68.4 kJ/mol by forming an 8-membered cyclic TS (Figure 3B, green lines in Figure 4).

Because of the high electronegativity of fluorine, perfluorinated alcohol are electronically analogous to carboxylic acids and can undergo proton loss. The calculated $pK_v$ of the $\text{C}_7\text{F}_{15}\text{OH}/\text{C}_7\text{F}_{15}\text{O}^-^{\text{de}}$ couple was 2.0 (Table S8). Under the pH
conditions of the current study (pH 1.7–3.5), 33.4–96.9% of the C-F_{12}OH would be deprotonated to form C-F_{12}O^{−}, which can easily eliminate F in the presence of H_{3}O^{+} (RIV-j) with a calculated ΔG^‡ of 7.7 kJ/mol through TS search (Figure 3C). Both RIV-i and RIV-j are more favorable pathways than the ones involving C-F_{12}O^{−}, but RIV-j would proceed more easily at the investigated acid conditions.

**Step V.** The hydrolysis of C_{6}F_{13}COF (RV-a) to form C_{6}F_{13}COOH is an S_{N}2 nucleophilic substitution reaction that is typical for hydrolysis of acyl chloride.46 The reaction is overall downhill with a ΔG of −49.7 kJ/mol, but the calculated ΔG^‡ through TS search (Figure 3D) was 148.6 kJ/mol. The ΔG^‡ is almost twice the value for hydrolysis of acetyl chloride,46 likely because fluorine is a poorer leaving group than chlorine. Similar to RIV-g, the ΔG^‡ of RV-a was lowered to 110.2 kJ/mol by adding a second water molecule (RV-b) to mediate the proton transfer.47

On the basis of the DFT calculation results presented above, an optimal reaction route for the degradation of PFOA by persulfate was proposed and shown as Route 2 in Figure 2 and featured in black in Figure 4. First, S_{2}O_{8}^{2−} produces SO_{4}^{−} with a ΔG^‡ of 95.7 kJ/mol and no TS was identified for this reaction. At low pH, SO_{4}^{−} would be partially protonated and another 7.2 kJ/mol is required for HSO_{4}^{−} to abstract one electron from C_{7}F_{15}COO^{−} to form C_{7}F_{15}COO^{−}. From this point onward, the reactions are overall downhill, thus step I is identified as the rate-limiting step but the production of SO_{4}^{−} is a prerequisite. Therefore, the ΔG^‡ calculated from DFT for the degradation of PFOA by persulfate is 95.7 + 7.2 = 102.9 kJ/mol. The formed C_{7}F_{15}COO^{−} undergoes decarboxylation reaction as in Route 1, but C_{7}F_{15}OH is generated from C_{7}F_{15}S^{−} reacting with OH. Instead of direct dehydrofluorination, C_{7}F_{15}OH undergoes deprotonation and the formed C_{7}F_{15}O^{−} eliminates a F in the acid reaction conditions and gives C_{7}F_{15}COO^{−}. Lastly, the hydrolysis of C_{7}F_{15}COF forms C_{7}F_{15}COOH as in Route 1, and this process is facilitated by the involvement of a second water molecule.

**Comparison of DFT Calculation with Experimental Data.** To demonstrate the validity of our theoretical results, we compared the ΔG^‡ value calculated from DFT simulation to the experimentally derived one, obtained from rate constants for PFOA degradation by persulfate under different temperatures at pH_{0} 3.5 (Figure 5A). The rate constants were plotted against the temperature through the Eyring eq (eq 4) (Figure 5B) and the obtained ΔH^‡ and ΔS^‡ was 115.5 ± 1.7 kJ/mol and 0.0284 ± 0.0055 kJ/mol, respectively. Then the ΔG^‡ was calculated to be 106.6 (±3.4) - 107.0 (±3.3) kJ/mol at 25−40 °C (eq 3). The values are similar to the activation energy reported by others using the empirical Arrhenius equation at similar pH.6,17 The ΔG^‡ derived from DFT calculations is 102.9 kJ/mol at 25 °C and the difference from the experimental ΔG^‡ is only 4.1 kJ/mol. Accordingly, the calculated rate constant (0.021 h^−1, 25 °C, eq 2) is only 5.4 times our experimentally determined rate constant (0.0038 h^−1). A difference of 1−2 orders of magnitude between the rate constants obtained from DFT calculations and experiments is generally considered to be in very good agreement, especially for reactions of relatively large systems in solution such as the ones studied herein.37 Thus, the small difference between the theoretical and experimental results suggests the reliability of the calculated results.

The proposed novel route for the degradation of PFOA by persulfate (Route 2 in Figure 2) explains our experimental observations for this reaction. First, the fact that the rate-limiting step is found to be the reaction of C_{7}F_{15}COO^{−} with HSO_{4}^{−} (step I) is consistent with the overall reaction being pseudo-first order on PFOA. Second, the much smaller ΔG^‡ for the reaction of C_{7}F_{15}COO^{−} with HSO_{4}^{−} (7.2 kJ/mol) compared with SO_{4}^{−} (91.2 kJ/mol) explains why the degradation of PFOA by persulfate only occurs at low pH. SO_{4}^{−} is the dominant species at the commonly investigated pH range because of the low pK_{a} of HSO_{4}^{−}. For example, at pH 7, the molar concentration of [SO_{4}^{−}] would be 10^{9} times of [HSO_{4}^{−}] when the pK_{a} was assumed to be 1.99. Thus, low pH is required to have sufficient concentration of HSO_{4}^{−} (Figure S8) to undertake reaction RI-c in step I, otherwise at higher pH, step I has to react through SO_{4}^{−}− (RI-a) and a much larger ΔG^‡ (95.7 + 91.2 kJ/mol) would have to be overcome. Therefore, the degradation of PFOA never occurs at circumneutral pH. The decrease in pH, however, favors the degradation through increasing the protonation of SO_{4}^{−} to generate HSO_{4}^{−} as well as the decomposition of persulfate to produce SO_{4}^{−}.

Lastly, although step I is identified as the rate-limiting step for the degradation of PFOA by persulfate, the decomposition of persulfate to produce SO_{4}^{−} (step 0) contributes most of...
the $\Delta G^\ddagger$ (95.7 vs. 102.9 kJ/mol). The dominance of the energy required for persulfate decomposition in the overall $\Delta G^\ddagger$ is consistent with the similar $\Delta G^\ddagger$ values derived experimentally for PFOA degradation (106.6 ± 3.4 kJ/mol, 40 °C) and for persulfate decomposition (114.0 ± 3.4 kJ/mol, 40 °C) in the current study. This finding is important for developing drinking water treatment or groundwater remediation strategies that use SO$_4^{2-}$ for PFAS oxidation or mineralization. Other methods aside from heat-activated persulfate that are milder or less energy intensive can also produce SO$_4^{2-}$, such as activated peroxymonosulfate and transient metal catalyzed sulfite auto-oxidation system. It is worthwhile to explore their degradation and transformation potential toward PFCAs in future work.

This study shows the significance of investigations on the entire reaction process for a complete understanding of the degradation and transformation mechanisms of contaminants in the environment. The method established in this study is readily applicable to the degradation or transformation of other fluorochemicals.

**ASSOCIATED CONTENT**

*SUPPORTING INFORMATION*

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b00797.

Formula, molecular weight, and quantitative analytical method of PFCAs; method for persulfate analysis; conformer search method and results for C$_{n}$F$_{2n+2}$COOH; calculation method and results of $\lambda_1$; rate constant of PFOA degradation; the percentage of SO$_4^{2-}$, reacting with major species; geometry parameters from theoretical calculations and experimental data; results of PES scan and $\Delta$EE versus IRC plot; Cartesian coordinates; PES scan for R0 and RIII-d; Eyering plot for persulfate decomposition; calculation method and results of pK$_a$; energy diagram and optimized geometry for RI-a and RI-c; alternative reaction pathways for step IV and V; and change in percentage of HSO$_4^-$ over pH (PDF)

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors acknowledge the funding support by Canada Foundation for Innovation (Grant No. 30291), NSERC Strategic Project Grant (Grant No. STPGP478774–15), NSERC Discovery Grant (RGPIN-2016-05022, RGPAS 492998), and valuable comments provided by Professor Erin Johnson at Dalhousie University.

**REFERENCES**


(20) Patterson, E. V.; Cramer, C. J.; Truhlar, D. G. Reductive dechlorination of hexachloroethane in the environment: Mechanistic