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Environmental significance

Fluorotelomer carboxylic acids (FTCAs) are key intermediates in the environmental transformation of fluorotelomer-based PFAS, yet their abiotic reactivity has remained unclear. This study demonstrates, for the first time, that FTCAs undergo hydroxide-promoted transformation via an E1cb elimination mechanism even at ambient temperature. The results reveal that common mildly alkaline conditions, such as those encountered during laboratory extractions or household cleaning, can drive precursor conversion to new fluorinated products. These findings expand current understanding of PFAS abiotic transformation pathways and highlight the potential for routine environmental and analytical processes to alter PFAS speciation and mass balance assessments.

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Environmental Science: Processes & Impacts Accepted Manuscript

Hydroxide-Promoted Transformation of Fluorotelomer Carboxylic Acids at Ambient Temperature

Liliya Chernysheva,^a Elizabeth G. Curtis,^a and Kyle Doudrick^{a*}

^aDepartment of Civil and Environmental Engineering and Earth Sciences, University of Notre Dame, Notre Dame, Indiana 46556, United States

*Corresponding author's emails and addresses:

Kyle Doudrick

kdoudrick@nd.edu

Department of Civil and Environmental Engineering and Earth Sciences, University of Notre Dame, Notre Dame, Indiana 46556, United States

Revision Date: 03/15/26

Journal: Environmental Science: Processes and Impacts

Abstract

Fluorotelomer carboxylic acids (FTCAs) are key intermediates in the environmental transformation of fluorotelomer-based precursors, yet their abiotic degradation pathways remain poorly understood. This study investigates the hydroxide-promoted transformation of *n*:2 FTCAs at ambient temperature and under controlled laboratory conditions to elucidate reaction mechanisms and kinetics. Equilibrium experiments were performed across sodium hydroxide (NaOH) concentrations ranging from 1×10^{-5} to 1 M, revealing transformation onset between 1×10^{-4} and 2×10^{-4} M. Both 6:2 and 8:2 FTCA were fully converted to the corresponding unsaturated products (FTUCAs) at $\geq 5 \times 10^{-4}$ M NaOH, followed by secondary loss of FTUCA at higher base concentrations ($> 2 \times 10^{-3}$ M) to undetected nontarget products. Minor yields ($< 7\%$) of perfluorocarboxylic acids (PFCAs) were detected at ≥ 0.1 M NaOH. Kinetic experiments at 1

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2 $\times 10^{-2}$ M NaOH showed first-order transformation of 6:2 and 8:2 FTCA, with observed rate
3 constants (k_{obs}) of 0.09 and 0.48 h⁻¹, respectively. When repeated with 0.3% ammonia (NH₃;
4 [OH⁻] $\sim 1.74 \times 10^{-3}$ M) and 6:2 FTCA, the k_{obs} decreased sixfold (0.015 h⁻¹) relative to NaOH,
5 consistent the approximately sixfold lower [OH⁻]. Because 0.3% NH₃ is commonly used in
6 PFAS extraction methods, these results suggest that prolonged extractions may lead to
7 underestimation of FTCAs and potentially other precursors. Experiments with a base-containing
8 consumer cleaning product confirmed that this hydroxide-promoted transformation of 6:2 FTCA
9 to 6:2 FTUCA also occurs in more complex matrices. Mechanistic analysis supports a reversible
10 E1cb pathway in which deprotonation of the α -hydrogen generates a stabilized carbanion
11 intermediate, followed by unimolecular C–F bond cleavage. This study provides the first
12 evidence of abiotic FTCA transformation via an E1cb mechanism and highlights the potential for
13 mild alkaline environments, including those in analytical and household contexts, to promote
14 PFAS precursor transformation.

15 **Keywords**

16 Precursor, Telomer, PFAS, Elimination, Abiotic, Base, Alkaline, Cleaner

17 **Environmental significance**

18 Fluorotelomer carboxylic acids (FTCAs) are key intermediates in the environmental
19 transformation of fluorotelomer-based PFAS, yet their abiotic reactivity has remained unclear.
20 This study demonstrates, for the first time, that FTCAs undergo hydroxide-promoted
21 transformation via an E1cb elimination mechanism even at ambient temperature. The results
22 reveal that common mildly alkaline conditions, such as those encountered in alkaline pH
23 environments, during laboratory extractions, or even household cleaning, can drive precursor
24 conversion to more stable PFAS. These findings expand current understanding of PFAS abiotic
25 transformation pathways and highlight the potential for routine environmental and analytical
26 processes to alter PFAS speciation and mass balance assessments.

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1. Introduction

Fluorotelomer carboxylic acids (FTCAs) are a class of polyfluorinated alkyl acids that are found in the environment and primarily from both biotic and abiotic degradation pathways of precursor compounds.¹⁻⁷ Phillips *et al.* reported that FTCAs exhibit greater toxicity than their perfluorinated analogs.^{6,8} Although abiotic transformation of FTCAs has been studied only sparingly, biotic transformation has been investigated extensively. Hagen *et al.* were among the first to demonstrate that fluorotelomer alcohols (FTOHs) degrade to form FTCAs and ultimately perfluorooctanoic acid (PFOA) in rats.⁹ Subsequent studies have confirmed similar biotic transformation pathways across a range of matrices, including human blood^{10,11}, rats and mice^{12,13}, fish^{5,14,15}, plants⁶, fungi¹⁶, landfills¹⁷, wastewater treatment plants (WWTPs),¹⁸⁻²⁴ and soil.^{25,26} Frequently detected transformation products include even and odd-chain FTCAs, fluorotelomer unsaturated carboxylic acids (FTUCAs), and several perfluorocarboxylic acids (PFCAs).^{13,27} Transformation of *n*:2 FTCA is consistently accompanied by the formation of the corresponding *n*:2 FTUCA as a major product.^{6,28,29}

Abiotic transformation of fluorotelomer precursors has received less attention than biotic pathways, with most studies focused on engineered systems such as ultraviolet photolysis, advanced oxidation processes, or alkaline thermal reactions.³⁰⁻³⁵ For FTCAs in particular, no studies have explicitly examined their abiotic transformation mechanisms. Loewen *et al.*²⁹ observed that *n*:2 FTCA converts to *n*:2 FTUCA in methanol but not in Optima-grade water, with yields increasing at higher temperatures (4 and 20 °C). The reaction was relatively slow, producing only picomole-scale amounts of product over 10 days. The removal of the α -hydrogen and the β -fluorine (i.e., the leaving group) to form the unsaturated product is indicative of an elimination reaction. Because the C–F is a poor leaving group and C–H typically has a high pK_a (>50), we initially hypothesized the reaction proceeds via an E2 mechanism. However, given that the experimental conditions were only mildly basic (i.e., methoxide $\sim 10^{-8.5}$ M) and near ambient temperature, an E2 pathway, while possible, would be kinetically unfavorable.

The objective of this study was to investigate the hydroxide-promoted elimination of *n*:2 FTCA under controlled alkaline conditions. Equilibrium experiments were conducted across a range of sodium hydroxide (NaOH) concentrations to quantify the formation of the unsaturated product, *n*:2 FTUCA, and its disappearance. Reaction kinetics were then evaluated using both NaOH and ammonia (NH₃) to assess the influence of base strength and identity. Finally, transformation was demonstrated by spiking *n*:2 FTCA into a commercially available base-

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1 containing cleaning agent, and the combined results were used to propose a mechanistic
2 framework for FTCA elimination.
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5 6 7 **2. Methods**

8 9 **2.1. Transformation Reaction Experiments**

10 Single-compound stock solutions of 6:2 FTCA (97%, SynQuest), 6:2 FTUCA (95%,
11 SynQuest), 7:3 FTCA (97%, SynQuest), and 8:2 FTCA (97%, SynQuest) were prepared in 18.2
12 MΩ-cm ultrapure water (UPW) from pure compound. All sample containers were first cleaned
13 with Optima methanol (MeOH; ≥99.8% LC-MS grade; VWR). Each stock was serially diluted
14 in UPW within 15 mL polypropylene centrifuge vials (VWR) to yield working solutions at a
15 target substrate concentration of 0.2 mg/L. An aqueous sodium hydroxide (NaOH; 98 % pellets;
16 Acros) solution was then added to reach a final volume of 10 mL, leaving sufficient headspace
17 for mixing. Sodium hydroxide solutions were prepared in UPW from anhydrous solid

18 Final concentrations in the equilibrium experiments ranged from 1×10^{-5} to 1 M.
19 Equilibrium samples were capped, sealed with Parafilm, and placed on a rotator for passive
20 mixing over 30 days. Samples were taken at 14 days and 30 days to confirm equilibrium was
21 reached (<5% change in measured concentration). Initial concentration (C_0) samples of *n*:2
22 FTCA with no added NaOH were prepared concurrently with NaOH-containing samples and
23 aged under identical conditions. Prior to liquid chromatography–tandem mass spectrometry (LC–
24 MS/MS) analysis, samples were diluted ten-fold to an 80:20 (v/v) methanol:water solvent ratio
25 without neutralization. All equilibrium experiments were conducted in triplicate. Samples were
26 stored at 4 °C until further analysis.

27 Kinetics experiments followed a similar protocol but were designed to minimize external
28 mixing. Samples were not vortexed or rotated to avoid enhancing reaction rates via mechanical
29 agitation. Sodium hydroxide kinetics experiments were performed at a fixed base concentration
30 of 1×10^{-2} M NaOH in each sample. For ammonium hydroxide (NH₄OH; 28–30% as NH₃; VWR)
31 experiments, a 30% stock solution (~15.88 M NH₃) was diluted in UPW to achieve a final
32 concentration of 0.30%, matching that of the US EPA Method 1633.³⁶ Kinetic experiments were
33 conducted at discrete time points (i.e., one sample per time point). At the predefined time points
34 (5 s, 15 s, 30 s, 45 s, 1 min, 5 min, 15 min, 30 min, 1 h, 2 h, 4 h, 8 h, 18 h, and 24 h), samples
35 were neutralized with 0.10 mL of 20% (v/v) acetic acid (HAc; glacial; Fisher) to stop the
36 reaction. The resulting pH was verified using a pH probe (Orion 9103BNWP Semi-Micro

Combination pH), and it consistently reached pH ~4.75 regardless of the substrate or base concentration. For kinetics studies, two C_0 samples were obtained: one matching the equilibrium C_0 samples (substrate in UPW) and another containing substrate and HAc with no additional hydroxide (i.e., experimental control). No substantial (>10%) change in FTCA concentration was observed in the control. All NaOH kinetics experiments were conducted in triplicate, and NH_3 experiments once.

Equilibrium transformation of 6:2 FTCA with a consumer-grade cleaning agent (unnamed) followed a similar setup to equilibrium tests with NaOH. Product selection was driven by analytical feasibility: many commercial formulations contain complex mixtures that interfere with LC-MS/MS analysis and required extensive cleanup beyond simple dilution. The selected product was a multi-purpose concentrate marketed for use on countertops, wood, tile, linoleum, and bathroom surfaces, and intended to be diluted prior to use. Varying water diluted concentrations of the cleaning agent, ranging from 0.1–50% v/v, were spiked with 0.2 mg/L of 6:2 FTCA. Concentrations between 0.1–5% reflected typical consumer use, while 10–50% served as an additional comparison. Experiments were conducted in 20-mL glass vials at a volume of 10 mL for 7 days. Samples were processed through a weak anion exchange (WAX) solid-phase extraction (SPE) column prior to LC-MS/MS analysis, following EPA Method 1633. An extraction internal standard (EIS, $^{13}\text{C}_5$ -PFHxA, Wellington) was added before the SPE step to track losses from sample processing. SPE was followed by elution with 5 mL MeOH and acidification with 25 μL of 20% HAc. Final extracts were diluted 10-fold to an 80:20 MeOH:H₂O matrix, and a non-extraction internal standard (NIS; MPFAC-HIF-IS, Wellington) was added directly to the LC-MS/MS sample vial to monitor instrument performance. A C_0 sample containing 6:2 FTCA, EIS, and NIS without the cleaning agent served as a baseline for evaluating transformation and recovery. The selection of $^{13}\text{C}_5$ -PFHxA as EIS was based on the US EPA Method 1633, which designates $^{13}\text{C}_5$ -PFHxA as the EIS for 5:3 FTCA³⁷ – the most structurally similar target analyte to 6:2 FTCA. EIS recoveries were 99%, 90%, and 89% for samples containing 0% (i.e., C_0), 0.1%, and 2% cleaning agent. At 5% the recovery was only 22% and it got progressively worse with increasing concentration of cleaning agent.

2.2. Analytics

All PFAS analysis was conducted on an ultra-performance liquid chromatography (UPLC) system (Agilent, 1290 Infinity II LC) coupled to a triple quadrupole mass spectrometer

(MS/MS) (Agilent, MS/MS G6470B) operated in the negative ion mode (Agilent, electrospray ion source G1958-65638). PFAS were separated on a ZORBAX RRHD Eclipse Plus column (Agilent, 959758-902; C18, 95 Å, 2.1×100 mm, 1.8 μm, 1200 bar). The column was kept at 40 °C with the gradient elution flow rate of 0.4 mL min⁻¹ for 17 min. A PFAS Delay Column (Agilent, 5062-8100; 4.6×30 mm, 1200 bar) that sits between the solvent mixer and the injector was used to remove impurities coming from solvents. A PFAS-free LC Conversion Kit was used to replace the original PTFE-containing fittings on the UPLC (Agilent, 5004-0006). Samples were prepared in 80:20 MeOH/H₂O in 300 μL polypropylene vials (9532S-MS-K; Microsolv) with polypropylene screw-top caps (9502S-09-PE; Microsolv). The sample injection volume was 10 μL. The gradient elution started with a solvent mixture of 90% UPW and 10% MeOH for 1 min. After 1 min, the MeOH concentration was increased to 40% and reached 90% linearly for 25 min. After 25 min, the MeOH concentration was decreased to 10%.

Targeted analysis identified 44 potential compounds, including 40 from the US EPA Method 1633 analyte list (including, 3:3 FTCA, 5:3 FTCA, 7:3 FTCA and 8:2 FTS) and four additional compounds: 6:2 FTCA, 6:2 FTUCA, 8:2 FTCA, and 8:2 FTUCA. US EPA Method 1633 analytical standards were used because they were available from concurrent experiments rather than specifically purchased for this study. These standards were analyzed as a single mix of 40 PFAS, prepared from five separate native standard mixes (PFAC-FMXF, PFAC-FMXG, PFAC-FMCH, PFAC-FMXI, PFAC-FMXJ, FHEA, FHUEA, FOEA, and FOUEA; Wellington). The four additional precursors were split into two separate mixes: one containing 6:2 and 8:2 FTCA, and the other containing 6:2 and 8:2 FTUCA.

The freshness of the *n*:2 FTCA analytical standards was critical, as *n*:2 FTCA gradually transformed into *n*:2 FTUCA when stored in 80:20 MeOH/H₂O at 4 °C. Notably, *n*:2 FTUCA was already present in the *n*:2 FTCA standards, and its relative abundance increased over the analysis period, consistent with prior observations by Loewen *et al.* (2005) in 100% MeOH at 4 °C and 20 °C. To distinguish between transformation-derived and native *n*:2 FTUCA, the *n*:2 FTCA and *n*:2 FTUCA compounds were prepared in separate standard mixes. Analytical standards were refrigerated for ~1 month prior to use, though exact synthesis and packaging dates were unknown, potentially contributing to untracked degradation. LC-MS/MS data were corrected using daily quality control responses, and replicate samples were analyzed on the same day to minimize intraday variability.

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Potential analytical interference on LC–MS/MS from the Na⁺ ion in NaOH and HAc introduced during the neutralization of kinetics experiments was assessed. 1×10⁻¹ M sodium chloride (NaCl; VWR) was used to simulate Na⁺ ion levels, reflecting the ten-fold dilution of the highest NaOH concentration (1 M). Similarly, HAc interference was evaluated at 0.1% (v/v), corresponding to 1.7×10⁻² M. Across all tests, recoveries for 6:2 and 8:2 FTCA and FTUCA ranged from 92-104% for NaCl and 94-106% for HAc, indicating minimal analytical interference. As a result, interference from Na⁺ and HAc was considered negligible, and no adjustments were made to the data to account for these effects.

Combustion ion chromatography (CIC) was conducted to assess total F concentrations (Metrohm Profiler F). Samples were combusted at 1050 °C. Oxygen was injected at a flow rate of 300 mL/min and argon was used as a carrier gas at a 100 mL/min rate to direct the off gas into the absorption liquid.

3. RESULTS AND DISCUSSION

3.1. Transformation of *n*:2 FTCA at equilibrium

The concentration of *n*:2 FTCA and its unsaturated transformation product, *n*:2 FTUCA, were measured as a function of the NaOH concentration (1×10⁻⁵ to 1 M) at equilibrium (**Figure 1**). For both 6:2 FTCA and 8:2 FTCA, the transformation is initiated between an NaOH concentration of 1×10⁻⁴ and 2×10⁻⁴ M. At 5×10⁻⁴ M, all *n*:2 FTCA had been transformed, at least partially, into *n*:2 FTUCA. With further increases in base concentration (> 2 × 10⁻³ M NaOH), *n*:2 FTUCA concentrations declined until the compound was no longer detectable, suggesting secondary transformation to one or more non-target products not captured by the analytical method used. Total F analysis for the 6:2 FTCA experiment revealed that the F mass balance was well maintained up to 1×10⁻¹ M (**Figure S1**), at which point FTCA and FTUCA was not detectable despite approximately 80% of the total F still being accounted for. This suggests that the final transformation products of 6:2 FTUCA are a mixture of soluble and (semi-)volatile compounds.

Overall, 6:2 FTCA and 8:2 FTCA exhibited nearly identical behavior. As NaOH concentration increased, the extent of *n*:2 FTCA loss and *n*:2 FTUCA formation increased proportionally. Between 1×10⁻⁵ M and 2×10⁻⁴ M NaOH, *n*:2 FTCA was still the dominant species in solution based on the molar mass balance. Around 2 × 10⁻⁴ M NaOH, the two species were approximately equivalent in abundance, beyond which *n*:2 FTUCA predominated while *n*:2

FTCA continued to decline. At 5×10^{-4} M NaOH, $n:2$ FTCA was below the detection limit and $n:2$ FTUCA was the only species identified in solution. At 5×10^{-4} M NaOH, $n:2$ FTCA fell below the detection limit and $n:2$ FTUCA was the sole observable product. Between 5×10^{-4} M and 5×10^{-3} M NaOH, $n:2$ FTUCA concentrations plateaued, with the highest yields observed at 1×10^{-3} M and 2×10^{-3} M NaOH. At 1×10^{-2} M NaOH, $n:2$ FTUCA began to decline and was undetectable at 1×10^{-1} M and 1 M NaOH. No detectable levels of 3:3, 5:3, or 7:3 FTCA were observed in any samples. The potential presence of the corresponding unsaturated homologues (3:3, 5:3, or 7:3 FTUCA) cannot be ruled out because these were not included in the analytical method.¹²

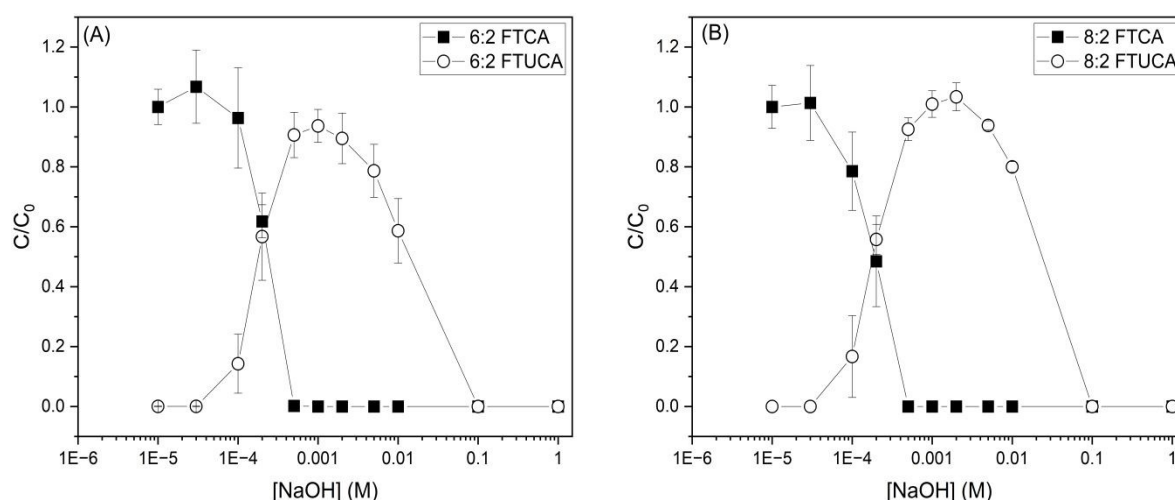


Figure 1. Normalized concentration of 0.2 mg/L $n:2$ FTCA transforming to $n:2$ FTUCA as a function of the NaOH concentration at equilibrium after 14 days in solution for (A) 6:2 and (B) 8:2. Analysis after 30 days showed the no substantial change (>5%) change in concentration, confirming equilibrium was reached. Error bars represent ± 1 standard deviation of four replicates for 6:2, and three replicates for 8:2.

Possible PFCA products were also examined, given that prior studies have reported PFCAs as end-products in $n:2$ FTCA degradation pathways.^{3,38,39} Analyses focused on the samples where $n:2$ FTCA and $n:2$ FTUCA were largely degraded, specifically those treated with 1×10^{-1} M and 1 M NaOH. For 6:2 FTCA, perfluorohexanoic acid (PFHxA) was undetectable in the C_0 sample, detected at approximately 0.9% of the starting molar mass (< LOQ) at 1×10^{-1} M NaOH, and quantified at $\sim 6.6\%$ at 1 M NaOH. A similar pattern was observed for 6:2 FTUCA,

where PFHxA accounted for $\sim 0.6\%$ ($< \text{LOQ}$) at 1×10^{-1} M NaOH and $\sim 4.1\%$ at 1 M NaOH. Perfluoroheptanoic acid (PFHpA) was present in the C_0 samples of both 6:2 FTCA and 6:2 FTUCA and remained unchanged with NaOH treatment, indicating a contaminant source rather than a transformation product. For 8:2 FTCA, perfluorooctanoic acid (PFOA) was absent in the C_0 sample, detected at $\sim 0.2\%$ of the initial molar mass ($< \text{LOQ}$) at 1×10^{-1} M NaOH, and reached $\sim 1.6\%$ at 1 M NaOH. No other PFCA were detected in any sample. These results indicate that PFCA formation occurs only to a minor extent under the tested conditions.

Although $n:3$ FTCAs (e.g., 3:3, 5:3, and 7:3) have been reported as byproducts in microbial biotransformation of fluorotelomer acids and related precursors,³⁹ none of these odd-chain FTCAs that we targeted (3:3, 5:3, and 7:3 FTCA) were detected in our experiments at 0.1 and 1 M NaOH where transformation of FTUCA was most pronounced. Formation of $n:3$ FTCAs in biological systems is generally attributed to enzyme-mediated pathways capable of C–C bond cleavage, oxidation, and backbone rearrangement, such as β -oxidation like processes and other catalytic transformations. These mechanisms differ fundamentally from hydroxide-promoted reactions, which are limited to acid-base and elimination chemistry under the conditions investigated here. In the absence of enzymatic catalysis, strong oxidants, photochemical activation, or elevated temperatures, C–C bond scission within the fluorotelomer backbone is not expected to occur readily under ambient alkaline conditions. Consequently, while odd-chain FTCAs are plausible products in biotic systems, their formation is not expected under the conditions tested herein.

3.2. Transformation kinetics of $n:2$ FTCA with NaOH

After confirming $n:2$ FTCA transformation under equilibrium conditions, reaction kinetics were examined to determine transformation rates and apparent reaction order. Results for 0.2 mg L^{-1} $n:2$ FTCA reacted with 1×10^{-2} M NaOH are shown in **Figure 2**. Both 6:2 FTCA and 8:2 FTCA displayed similar temporal trends and followed apparent first-order kinetics with respect to FTCA loss. The observed rate constants (k_{obs}) were 0.09 h^{-1} for 6:2 FTCA and 0.48 h^{-1} for 8:2 FTCA, indicating that 8:2 FTCA degraded approximately five times faster than 6:2 FTCA.

The faster transformation kinetics observed for 8:2 FTCA relative to 6:2 FTCA indicate that chain length exerts a strong control on the likelihood and rate of HF elimination under alkaline conditions. This trend is consistent with recent observations from microbial

transformation studies,³⁹ which also report enhanced reactivity for longer-chain fluorotelomer acids. Collectively, these results suggest that chain length governs both abiotic and biotic transformation propensity, with longer-chain fluorotelomer acids being more susceptible to HF elimination than their shorter-chain analogues.

Concentrations of the corresponding unsaturated products (*n*:2 FTUCA) exhibited transient rise profiles that did not fit simple first- or second-order models, consistent with their simultaneous formation and subsequent transformation observed under equilibrium conditions (**Figure 1**). The initial rate of 8:2 FTUCA formation ($\sim 48 \text{ nM h}^{-1}$) was slower than that of 6:2 FTUCA ($\sim 86 \text{ nM h}^{-1}$), suggesting that 8:2 FTUCA undergoes faster secondary reactions to nontarget by-products, resulting in lower steady-state accumulation.

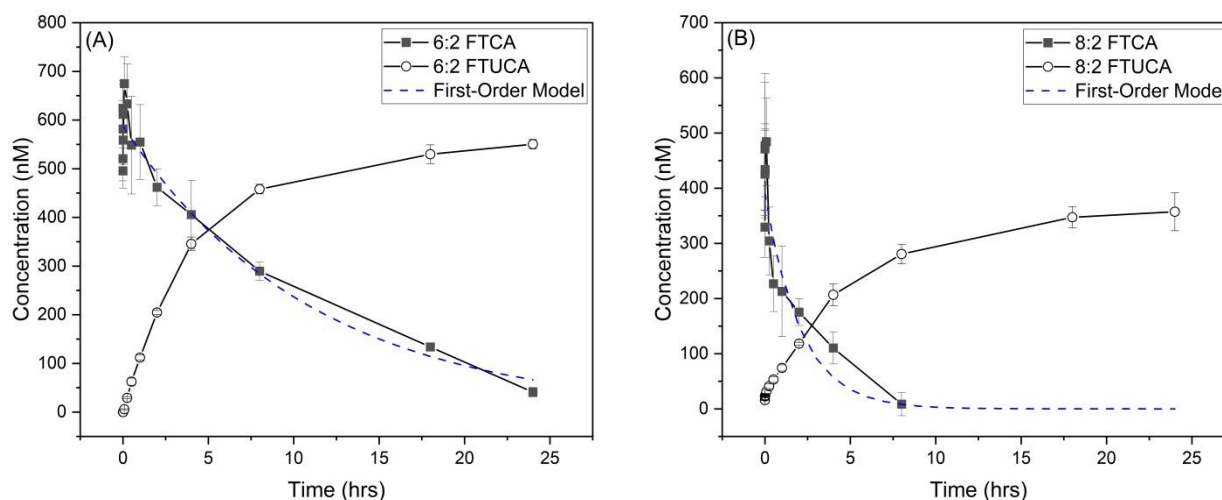


Figure 2. Transformation kinetics of 0.2 mg/L *n*:2 FTCA to *n*:2 FTUCA in the presence of $1 \times 10^{-2} \text{ M NaOH}$ during the first 24 hours for (A) 6:2 FTCA and (B) 8:2 FTCA.

3.3. Transformation kinetics of 6:2 FTCA with NH_3

Kinetic experiments were also performed with 0.3% NH_3 (corresponding to approximately $1.74 \times 10^{-3} \text{ M OH}^-$, $1.74 \times 10^{-3} \text{ M NH}_4^+$, $1.56 \times 10^{-1} \text{ M NH}_3$, and $6.34 \times 10^{-12} \text{ M H}^+$) (**Figure 3**). The observed first-order rate constant for NH_3 ($k_{obs} = 0.015 \text{ h}^{-1}$) was sixfold lower than that measured for NaOH at $1 \times 10^{-2} \text{ M}$ ($k_{obs} = 0.09 \text{ h}^{-1}$). This difference corresponds directly to the approximately sixfold lower $[\text{OH}^-]$, indicating that the transformation rate scales linearly with $[\text{OH}^-]$. The conjugate-acid pK_a of NH_3 (9.25) is nearly identical to the apparent $\alpha\text{-C-H}$ pK_a of FTCA determined from equilibrium experiments ($\sim 9\text{--}10$). This parity implies that NH_3 is only marginally strong enough to deprotonate the α -carbon, so deprotonation proceeds

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almost entirely via the small amount of hydroxide present at equilibrium, resulting in a rate directly proportional to $[\text{OH}^-]$. Such proportional behavior indicates that hydroxide concentration, rather than base identity, governs the reaction rate under these conditions.

The 0.3 % NH_3 concentration is commonly employed in extraction procedures, such as those described in U.S. EPA Method 1633.³⁷ In this method, environmental matrices such as soils and biosolids are extracted three times with 0.3 % NH_3 in methanol, each extraction lasting 20–40 min, resulting in approximately 2 h of direct contact between PFAS and NH_3 . Subsequent purification, acidification, and solvent evaporation under heated nitrogen can extend this exposure by an additional 1–3 h. Thus, the conditions used in Method 1633 can promote limited abiotic transformation of certain PFAS precursors. While the conversion of $n:2$ FTCA to $n:2$ FTUCA under these conditions appears to remain below 20%, well within analytical uncertainty for typical extraction durations, the possibility of transformation of more reactive precursors such as $n:2$ fluorotelomer alcohols (FTOHs) remains uncertain. Because FTOHs are known to be more susceptible to base-promoted reactions than FTCA or FTUCA intermediates, unrecognized conversions during alkaline extraction or evaporation steps could contribute to variability in reported PFAS concentrations.⁴⁰

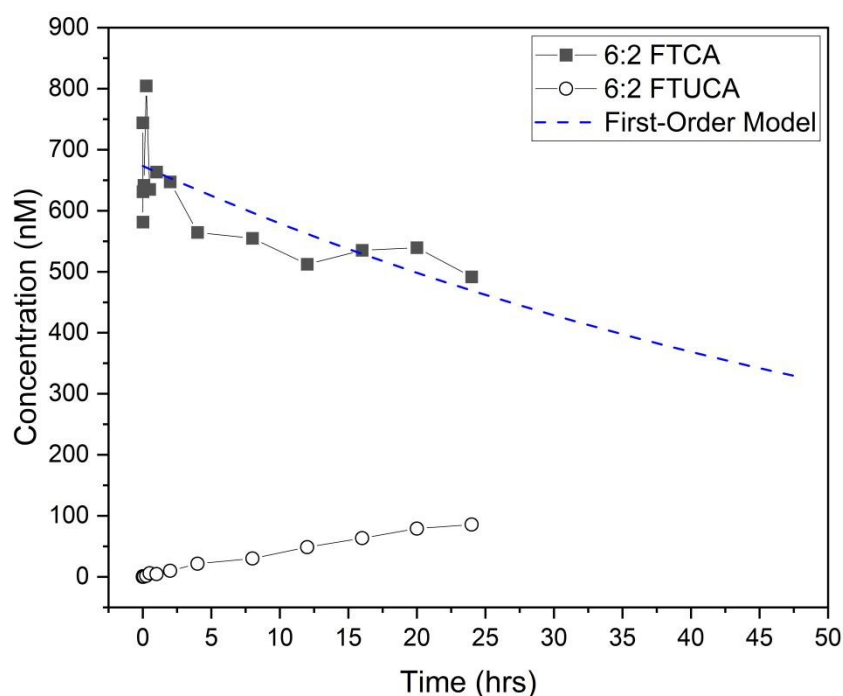


Figure 3. Transformation kinetics of 0.2 mg/L 6:2 FTCA to 6:2 FTUCA in the presence of 0.3% NH_3 .

3.4. Transformation of 6:2 FTCA with a cleaning agent

To evaluate the potential for n :2 FTCA transformation under realistic indoor conditions, reactions were conducted using a consumer-grade cleaning product that lists a strong base as one of its primary active ingredients (**Figure 4**). The C_0 had a 6:2 FTCA concentration of 145 nM and it also contained 4.6 nM of background 6:2 FTUCA. In the presence of 0.1%, 2%, and 5% cleaner, the 6:2 FTCA concentration decreased to 101 nM ($C/C_0 = 70\%$), 53 nM ($C/C_0 = 37\%$), and 31 nM ($C/C_0 = 22\%$), respectively, while 6:2 FTUCA increased to 34 nM, 66 nM, and decreased to 40 nM. Increasing the concentration of the cleaning agent up to 50% decreased both 6:2 FTCA and 6:2 FTUCA, but these values are not reported quantitatively due to poor EIS recoveries. The decrease in 6:2 FTCA concentration was not equimolar to the increase in 6:2 FTUCA, suggesting either incomplete extraction, matrix suppression, or transformation of the FTUCA to additional products not captured by the analytical method. The latter explanation agrees with the equilibrium outcomes in water (**Figure 1**). Overall, these findings demonstrate that 6:2 FTCA, and by extension, n :2 FTCA, can undergo transformation in alkaline consumer cleaning formulations under conditions relevant to indoor use.

Although cleaner concentrations were chosen to reflect consumer use, the 7-day exposure time does not represent typical contact durations, which are much shorter in real-world cleaning. As a result, the experiment should be interpreted as a proof-of-concept demonstration rather than a kinetic study. The findings nonetheless indicate that under sufficiently basic and prolonged conditions, indoor-use products containing bases could promote abiotic transformation of fluorotelomer-based compounds.

Cleaning products are not the only potential indoor matrices capable of inducing n :2 FTCA transformation. Zhou *et al.* (2022) reported substantial PFAS emissions and potential transformation during floor waxing, noting that many acrylic floor polishes contain fluorosurfactants (0.01–0.05% by mass).⁴¹ In that study, high airborne PFAS levels were observed during wax stripping, a process that typically employs alkaline wash solutions containing bases such as NaOH, potassium hydroxide (KOH), or ammonium hydroxide (NH₄OH). Such conditions may promote hydrolysis or elimination reactions, yielding additional fluorinated transformation products. Future research could examine n :2 FTCA and other PFAS interactions with wax strippers under controlled laboratory conditions, using air capture or real-time gas-phase analysis to identify volatile intermediates and end-products. However, due to the

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high complexity and surfactant content of such matrices, extensive purification and cleanup would be necessary for quantitative analysis.

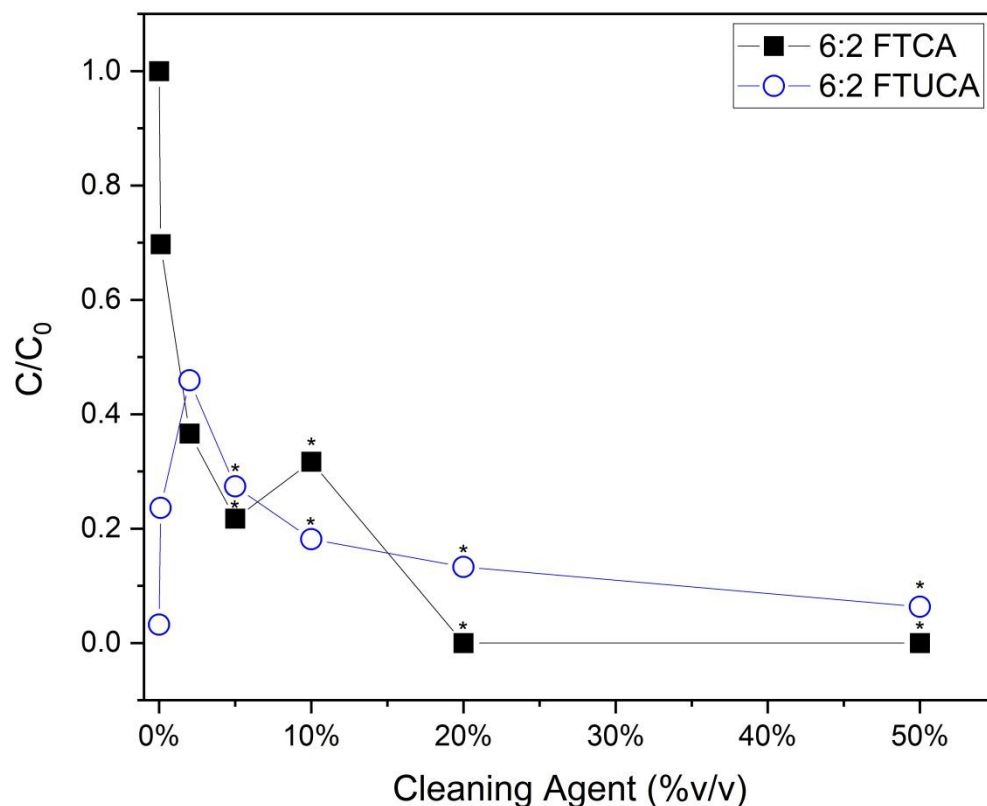


Figure 4. Transformation of 0.2 mg/L 6:2 FTCA and formation of 6:2 FTUCA in a consumer-grade cleaning agent (0–50% v/v) after 7 days reaction. Sample points represent discrete experimental results, and the lines serve only as a visual guide. The asterisk (*) indicates an EIS recovery <50%. The EIS recovery at 5% was 22% and it got progressively worse with increasing concentration of the cleaning agent.

3.5. Proposed Reaction Mechanism

The formation of an unsaturated byproduct indicates that the transformation proceeds via an elimination pathway. Three classical mechanisms are possible: E1, E2, and E1cb. An E1 reaction involves initial cleavage of the C–F bond to form a carbocation intermediate; however, this step has a prohibitively high energy barrier because fluorine is a poor leaving group. Thus, an E1 mechanism can be excluded.

An E1cb or E2 mechanism remains plausible. In the E1cb pathway, deprotonation of the α -hydrogen occurs first, forming a carbanion intermediate, whereas in an E2 process, C–H and

C–F bond breaking occurs concertedly. For ordinary alkanes, α -hydrogen deprotonation is highly unfavorable ($\text{pK}_a > 50$), so the unimolecular E2 mechanism tends to dominate. PFAS, however, differ substantially from typical alkanes because the perfluoroalkyl chain exerts a strong electron-withdrawing effect that markedly acidifies the α -hydrogen.

Equilibrium data (**Figure 1**) support the substantial acidification of the α -hydrogen, with an onset of transformation between 10^{-5} and 10^{-4} M NaOH, corresponding to an apparent pK_a of ~ 9 – 10 . Under these conditions, several observations collectively support an E1cb mechanism rather than an E2 pathway: (1) E2 eliminations are disfavored when the leaving group is poor, as fluorine is; (2) the reaction proceeds in anhydrous methanol, a solvent that is only weakly basic ($\sim 10^{-8.5}$ M methoxide), implying that the elimination is driven by intrinsic thermodynamics rather than by a strong external base; and (3) the experimentally observed first-order kinetics are inconsistent with a bimolecular E2 process, except under very high base concentrations.

The first step of an E1cb reaction is deprotonation of the α -hydrogen, so its pK_a becomes the key thermodynamic parameter governing whether a given telomer can undergo transformation under mildly basic conditions. To evaluate this dependence, we conducted an equilibrium experiment with 8:2 FTS, which is expected to possess a significantly less acidified α -hydrogen ($\text{pK}_a > 14$). At 1×10^{-4} M $[\text{OH}^-]$, no detectable transformation of 8:2 FTS was observed. This result supports the requirement for sufficient α -hydrogen acidity to enable the initial deprotonation step, thus the transformation is controlled by acid-base thermodynamics rather than simply by hydroxide presence.

Additional kinetic evidence further supports this interpretation. The reaction rate of 8:2 FTCA was greater than 6:2 FTCA. Increasing chain length amplifies the cumulative inductive electron-withdrawing effect of $-\text{CF}_2-$ units, which further acidifies the α -hydrogen adjacent to the carboxylate group and stabilizes the resulting carbanion intermediate. Both effects favor the pre-equilibrium deprotonation step required for an E1cb elimination mechanism and lower the energetic barrier for the subsequent C–F bond cleavage. The larger reaction rate constant of 8:2 FTCA demonstrates that these inductive effects are kinetically relevant even under mild alkaline conditions. When NaOH was replaced with NH_3 (a system in which the majority of base exists as NH_3 with only small amounts of OH^- at equilibrium), the observed rate constant decreased sixfold (from 0.09 to 0.015 h^{-1}), matching the sixfold reduction in $[\text{OH}^-]$ between the two experiments. This 1:1 proportionality between k_{obs} and $[\text{OH}^-]$ confirms that hydroxide concentration directly controls the transformation rate. Such linear dependence on $[\text{OH}^-]$ is

characteristic of specific-base behavior, consistent with a mechanism in which hydroxide participates only in the deprotonation pre-equilibrium.

Together, these findings indicate that $n:2$ FTCA transforms via a reversible E1cb mechanism. The two main challenges to this mechanism are the low intrinsic acidity of the α -hydrogen and the potential instability of the resulting carbanion. The first issue is mitigated by the strong electron-withdrawing effect of the fluorinated carbon chain, which substantially lowers the α -hydrogen pK_a and allows deprotonation under the mildly basic conditions tested. The second issue concerns the stability of the carbanion intermediate, which might be compromised by the proximity of the negatively charged carboxylate head group. Although the pK_a $n:2$ FTCA is not known experimentally or theoretically, the basic conditions used in this study ensure that the head group is likely ionized. Despite this, two effects can stabilize the carbanion: (1) inductive charge delocalization along the fluorinated chain, and (2) resonance and hydrogen-bonding interactions associated with the carboxylate group. Additionally, methanol is a weaker acid than water and has a lower dielectric constant, both of which can further stabilize the carbanion. This solvent effect may explain why the reaction proceeds in pure methanol but not in water at $[OH^-] < 10^{-5}$ M. Altogether, these considerations suggest that the carbanion intermediate is sufficiently stabilized for the reaction to proceed via an E1cb mechanism.

We therefore propose the following reaction mechanism and kinetic sequence. Hydroxide participates in a pre-equilibrium deprotonation step (**Eq. 1**), which is the defining feature of the E1cb mechanism. In this step, deprotonation of the α -hydrogen forms a carbanion intermediate (FTCA²⁻) stabilized by resonance and inductive effects. Increasing $[OH^-]$ shifts this equilibrium toward the carbanion intermediate, leading to higher FTUCA yields. The carbanion's p-orbital then aligns antiperiplanar to the σ^* orbital of the β -C-F bond, facilitating electron transfer to form the α - β π -bond and releasing fluoride (F⁻). This subsequent fluorine-elimination step is rate-determining (**Eq. 2**). The equilibrium expression (**Eq. 3**) is substituted into the rate law (**Eqs. 4 and 5**) to obtain an observed first-order rate constant (**Eq. 6**) that is proportional to $[OH^-]$. At sufficiently high $[OH^-]$, FTCA becomes fully deprotonated and the rate becomes independent of base concentration (**Eq. 7**). This kinetic transition from base-dependent to base-independent behavior confirms that the rate-determining step is the unimolecular C-F bond cleavage, consistent with a reversible E1cb mechanism (**Figure 5**). The mechanistic sequence is as follows:

Step 1. Pre-equilibrium deprotonation**Step 2: Rate-determining fluoride elimination****Equilibrium relationship**

$$K_{\text{eq}} = \frac{[\text{FTCA}^{2-}]}{[\text{FTCA}^-][\text{OH}^-]} \quad (\text{Eq. 3})$$

Substitution into rate expression

$$[\text{FTCA}^{2-}] = K_{\text{eq}}[\text{FTCA}^-][\text{OH}^-] \quad (\text{Eq. 4})$$

$$r = k_2[\text{FTCA}^{2-}] = k_2K_{\text{eq}}[\text{OH}^-][\text{FTCA}^-] \quad (\text{Eq. 5})$$

Observed first-order rate law

Because $[\text{OH}^-] \gg [\text{FTCA}]$, the observed first-order rate constant can be defined as

$$k_{\text{obs}} = k_2K_{\text{eq}}[\text{OH}^-] \Rightarrow r = k_{\text{obs}}[\text{FTCA}^-] \quad (\text{Eq. 6})$$

High-base limit

At sufficiently high $[\text{OH}^-]$, complete deprotonation of FTCA occurs, and the rate becomes independent of $[\text{OH}^-]$:

$$[\text{FTCA}^{2-}] \approx [\text{FTCA}_0^-] \Rightarrow r \approx k_2[\text{FTCA}_0^-] \quad (\text{Eq. 7})$$

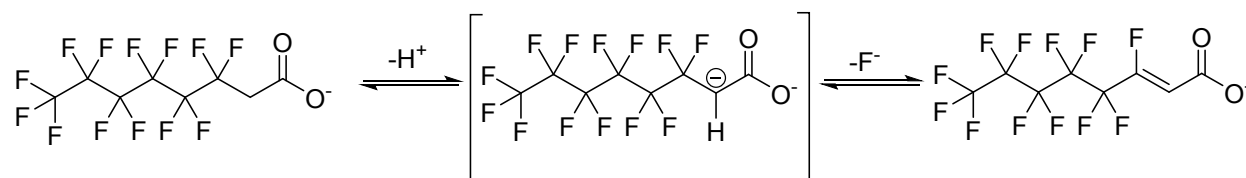


Figure 5. Reaction scheme for the E1cb (reversible) transformation of n:2 FTCA to n:2 FTUCA.

4. Conclusions

This study provides the first experimental evidence of abiotic transformation of FTCAs under basic conditions, establishing a reversible E1cb elimination mechanism. Both 6:2 and 8:2

FTCA underwent hydroxide-promoted conversion to their corresponding unsaturated products (FTUCAs) at ambient temperature, with reaction onset between 1×10^{-4} and 2×10^{-4} M $[\text{OH}^-]$. Kinetic results confirmed first-order transformation with rates proportional to $[\text{OH}^-]$, consistent with specific-base catalysis reaction. Minor yields of perfluorocarboxylic acids were detected only at relatively high base concentrations (≥ 0.1 M).

Experiments using NH_3 and a base-containing consumer cleaning product demonstrated that these transformations can also occur under conditions relevant to laboratory and household environments. Collectively, these findings reveal that mild alkaline conditions are sufficient to initiate FTCA transformation and that such reactions may proceed inadvertently during PFAS extractions or product use. The identification of an E1cb elimination mechanism provides a new foundation for understanding abiotic precursor chemistry and underscores the need to consider hydroxide-promoted reactions when assessing precursors fate, transformation, and analytical recovery.

Conflict of Interest

The authors have no conflicts of interest to declare. This research was conducted independently, with no financial or personal relationships that could have influenced the results or interpretation of the findings.

Acknowledgements

We express our gratitude to the Sloan Foundation for generously funding this project and the Air & Waste Management Association (A&WMA) for their scholarship awards on solid and hazardous waste research. We thank Drs. Paul Westerhoff and Zunhui Lin at Arizona State University (ASU) for use of their CIC and assistance with sample analysis. Special appreciation goes to the University of Notre Dame's Mass Spectrometry and Proteomics Facility (MSPF), with thanks to Bill Boggess, Heather Whitehead, and Alyssa Wicks for their expertise related to LC-MS/MS. We also acknowledge the Center for Environmental Science and Technology (CEST), particularly John Loftus and Mike Brueseke, for their support throughout this study. Lastly, we thank Prof. Dan McCurry (EPFL) for fruitful discussions on elimination reactions.

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