Downloaded 160 times

Editor's Choice Collection

Special Collection on Fate and Removal of Poly-and Perfluoralkyl Substances (PFAS) in Natural and Engineered Systems

Effectiveness of Photocatalysis, Radiolysis, and Ultrasonic Irradiation in the Remediation of GenX: Computational Study of the Ultrasonically Induced Mineralization

Danni Cui; A. M. Abdullah; Julie R. Peller; Stephen P. Mezyk Show all authors

Authors:

Danni Cui
Research Scientist, Institute of Environment (INWE), Florida International Univ., 11200 SW 8th St., Miami, FL 33199. Email: dcui002@fiu.edu

A. M. Abdullah
Doctoral Student, Dept. of Chemistry and Biochemistry, Florida International Univ., 11200 SW 8th St., Miami, FL 33199. ORCID: https://orcid.org/0000-0003-4666-2432. Email: aabdu040@fiu.edu

Julie R. Peller
Professor, Dept. of Chemistry, Valparaiso Univ., 1116 Kretzmann Hall, Valparaiso, IN 46383. Email: julie.peller@valpo.edu

Stephen P. Mezyk
Professor, Dept. of Chemistry and Biochemistry, California State Univ., 1250 Bellflower Blvd., Long Beach, CA 90840. ORCID: https://orcid.org/0000-0001-7838-1999. Email: stephen.mezyk@csulb.edu

Alexander Mebel
Professor, Dept. of Chemistry and Biochemistry, Florida International Univ., 11200 SW 8th St., Miami, FL 33199. Email: mebela@fiu.edu

Kevin O'Shea
Professor, Dept. of Chemistry and Biochemistry, Florida International Univ., 11200 SW 8th St., Miami, FL 33199 (corresponding author). Email: osheak@fiu.edu

https://doi.org/10.1061/(ASCE)EE.1943-7870.0002066
Received: January 17, 2022
Accepted: June 22, 2022
Published online: September 13, 2022

Journal of Environmental Engineering
Vol. 148, Issue 11 (November 2022)

© 2022 American Society of Civil Engineers

Check for updates

PDF Download

Abstract

Perfluoro-2-propoxypropanoic acid (PFPrOPrA), a free acid form of GenX, is a problematic perfluorinated alkyl substance (PFAS). Standard and advanced wastewater treatment methods are unable to effectively degrade PFAS due to its strong and unreactive C-F bonds. TiO_2 photocatalytic, radiolytic, and ultrasonic irradiation (USI) methods were applied in an attempt to degrade PFPrOPrA. A bimolecular rate constant for the reaction of e_{aq}^- and GenX of $(3.09 \pm 0.03) \times 10^7\ M^{-1} \cdot s^{-1}$ was measured in a buffered aqueous solution by monitoring the transient signal of the hydrated electron as a function of GenX concentration. Corroborating this relatively slow rate constant, less than 2% GenX degradation was observed after 8 h of continuous ^{60}Co gamma radiolysis under a variety of conditions. TiO_2 photocatalysis at 350 nm under alkali conditions showed minimal destruction of GenX without detectable levels of defluorination as measured by the production of fluoride ions. However, upon ultrasonic irradiation at 640 kHz and 396 W in an argon-saturated aqueous solution, greater than 80% of GenX was degraded within 60 min, yielding fluoride ions as the major product. We propose that the ultrasonic-induced degradation of GenX occurs primarily by pyrolysis. Computational methods were used to probe the energetics of the completing degradation pathways and possible pyrolytic products. The results demonstrate ultrasonic-induced pyrolysis is a promising process to mineralize GenX. The process can be accurately monitored and likely extended to mineralize a variety of perfluorinated and polyfluorinated substances.

Practical Applications

This study probed the application of radiolysis, TiO_2 photocatalysis, and USI to degrade an emerging problematic perfluorinated compound, GenX. Under the experimental conditions employed, the degradation of GenX was slow by TiO_2 photocatalysis, and radiolysis. Although reductive transformation of PFAS by hydrated electrons generated during radiolysis has been demonstrated, the reaction did not lead to rapid mineralization and is highly dependent upon reaction conditions. USI, however, resulted in the rapid degradation of GenX and significant mineralization as measured by the formation of fluoride ions. Complementary computational studies of the pyrolytic pathways provide insight about mineralization, which may be extrapolated to different classes of PFAS and thermal-induced degradation. The results of this research illustrate that USI is a powerful method to mineralize GenX and suggest it may be applicable for treatment of an array of PFAS-contaminated waters and wastewaters. Although the energy demand for USI-based water treatments can be high and thus costly, USI is a promising alternative for mineralization of PFAS in preconcentrated or concentrated waste streams.

Introduction

Perfluorinated and polyfluoroalkyl substances (PFAS) are a class of chemicals in which alkyl hydrogen atoms are replaced by fluorine atoms. PFAS have been extensively used in consumer products because of their unique physical, chemical, and biological properties (Prevedouros et al. 2006). Legacy PFAS typically refers to long-straight chain aliphatic compounds, which were widely used in an array of commercial products, including food containers, as coating materials, and firefighting foams. The extensive and decades-long uses of PFAS resulted in the widespread transfer of these chemicals throughout the environment and in multiple biological systems (Lindstrom et al. 2011). These extremely persistent PFAS contaminants have been detected in drinking water sources in proximity to industrial sites, military fire training areas, civilian airports, and wastewater treatment plants (Baran 2001; Buck et al. 2011; D'Hollander et al. 2010; Frömel and Knepper 2010; Hu et al. 2016).

With recent reports and increased incidents of negative human health effects from exposure to PFAS, the USEPA announced a lifetime advisory level of $70\ ng/L$ for combined concentration of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) in drinking water (USEPA 2016). Due to their potent toxicity, restrictions on and/or voluntary withdrawal of the use of legacy PFAS began approximately 20 years ago in the US, Europe, and other countries. Alternative perfluorinated substances including short-chain and ether-functionalized compounds, commonly referred to as emerging PFAS, were produced to replace the legacy PFAS.

Among the most problematic emerging PFAS is perfluoro(2-methyl-3-oxahexanoic) acid (PFProPrA), also called hexafluoropropylene oxide dimer acid (HFPO-DA). PFPrOPrA is predominantly produced as an ammonium-carboxylate salt and marketed under the trade name GenX, which readily dissociates in aqueous media. GenX was initially employed as a replacement for PFOA in the manufacturing of fluoropolymer resins and Teflon polytetrafluorethylene (DuPont Marketing 2010). Although the manufacturing uses of emerging PFAS are well-documented, the presence of GenX in aquatic systems was first reported in the Cape Fear River in 2012 (Sun et al. 2016). GenX has since been detected around the world including in Germany, the Netherlands, and China (Gebbink and van Leeuwen 2020; Heydebreck et al. 2015).

GenX is a member of a subclass of PFAS, perfluoroether carboxylic acids (PFECAs) where the carbon backbone contains ether functionality. In comparison with legacy PFAS, GenX possesses a relatively short carbon-ether backbone chain and thus is expected to have higher mobility and be less fat soluble (USEPA 2021). A toxicokinetic model for male rats showed that GenX has higher toxic potency than PFOA (Gomis et al. 2018), and additional studies indicated GenX could lead to liver damage (Chappell et al. 2020).

The use of the names GenX and PFPrOPrA have been used interchangeability in the literature when describing their presence in aqueous media. Due to its low pKa, GenX (PFPrOPrA) is negatively charged and highly soluble at the natural pH of water (Beekman et al. 2016). Although GenX is marketed as an ammonium salt upon dissolution in aqueous media, it dissociates into PFPrOPrA or the carboxylate form depending on the solution pH. This study will use the trade name GenX to describe PFPrOPrA.

Conventional water treatment methods have been applied to successfully remove PFOA from contaminated water. Although activated carbon (AC) can achieve an efficiency of 99% or higher to remove long-chain PFAS, the adsorption capacity for GenX decreases significantly (Du et al. 2014; Olsen et al. 2017). Cyclodextrins have been used to encapsulate emerging PFAS (Weiss-Errico and O'Shea 2017), and it was found that the branched backbone in GenX weakens its binding, which may contribute to the lower removal of GenX by adsorption as compared with other PFAS. Removal of GenX by employing anion exchange resins was relatively poor compared with removal of legacy PFAS (Dixit et al. 2020). Although adsorption is attractive for removal of legacy PFAS (Wang et al. 2019), further treatment is still required to destroy the PFOA and PFOS concentrated through the adsorption.

Advanced oxidation (AOP) and advanced reduction processes (ARP) have proven to be powerful options for the remediation of a wide variety of water pollutants (Deng and Zhao 2015; Hu et al. 2016; Vellanki et al. 2013). Although oxidative treatment methods using ozone, hydrogen peroxide, and Fenton reagent exhibited poor or slow degradation of PFAS and showed a strong dependence on the functionality of the head group (Trojanowicz et al. 2018), ARP have shown promise for the remediation of PFAS in water (Cui et al. 2020). The degradation of a series of PFAS using hydrated electrons generated under short-wavelength ultraviolet (UV) irradiation combined with sulfite has been reported (Bental et al. 2019). The reductive degradation was also shown to be dependent on the chain length and PFAS head group (Ross et al. 2018). Hydrated electrons generated by UV/sulfite can successfully degrade GenX to greater than 97%, with 50% defluorination of GenX after 48 h of treatment. Two degradation pathways, H/F exchange and chain-length shortening, were proposed for carboxylic acid–functionalized PFAS (Bental et al. 2019). However, sulfur-containing intermediates produced by UV/sulfite processes can result in secondary contamination in the environment.

The degradation and mineralization of GenX using radiolysis, TiO_2 photocatalysis, and ultrasonic irradiation are investigated in this article. These methods have been demonstrated for the destruction of an extensive number of pollutants and toxins and can facilitate oxidation, reduction, and/or thermal degradation processes. Radiolysis employs ionizing radiation of aqueous media to generate several reactive species (Buxton et al. 1988), including hydrated electrons and hydroxyl radicals, as described in Eq. (1) (Mezyk et al. 2007). The numbers in parenthesis are the radiation chemical yields of individual species (G-values) ($\mu mol\ Gy^{-1}$) of absorbed energy (Buxton et al. 1988). The bimolecular rate constants of PFOA and PFOS with e_{aq}^- are on the order of $10^7\ M^{-1}\ s^{-1}$, as estimated by the radiolytic degradation of PFOA and PFOS (Szajdzinska-Pietek and Gebicki 2000). A recent report on electron beam treatment resulted in greater than 85% degradation of PFOA and approximately 26% degradation of PFOS in lab spiked water and sand samples (Kowald et al. 2021)

$$H_2O \wedge\wedge \rightarrow e_{aq}^-(0.27) + \cdot H(0.06) + \cdot OH(0.28) + H_2(0.05) + H_2O_2(0.07) + H_{aq}^+(0.27) \quad (1)$$

TiO_2 photocatalysis generates an electron/hole pair with the electron generated in the conduction band, e_{CB}^-, acting as a potential reducing agent and the valence band hole, h_{VB}^+, as an oxidizing agent. TiO_2 photocatalysis has been extensively studied for the oxidative degradation of an extensive number of organic compounds (Lin et al. 2011; Zheng et al. 2010). To promote oxidation, the solution is saturated with air or oxygen because molecular oxygen serves as an e_{CB}^- scavenger to inhibit e_{CB}^-/h_{VB}^+ recombination and extend the lifetime of the h_{VB}^+. The h_{VB}^+ can oxidize target compounds directly or from hydroxyl radicals produced via the oxidation of water, which can subsequently react with the target compound. To promote reduction during TiO_2 photocatalysis, molecular oxygen can be eliminated from solution (argon purged) and electron donors can be added to react with h_{VB}^+ to extend the lifetime and availability of the e_{CB}^-. The degradation of PFOA by UV TiO_2 with oxalic acid as the hole scavenger under nitrogen atmosphere has been reported to be effective (Wang and Zhang 2011).

Ultrasonic irradiation (USI) has been classified as an AOP due to the generation of hydroxyl radicals, HO·, as one of the primary reactive species leading to the degradation of organic pollutants in aqueous media. Although recent studies demonstrated that the power and frequency of irradiation can have a pronounced impact on the nature of ultrasonically induced processes (Pflieger et al. 2021), high-frequency ultrasonic irradiation can lead to cavitation, historically characterized as the process of formation, growth, and collapse of gas bubbles (Colussi et al. 1998; Mason and Tiehm 2001; Suslick et al. 1999). The cavitation process has been defined into three zones: (1) a hot-spot, located at the interior of the cavitation bubble, which possesses extremely high temperature (greater than 5,000 K) and high pressure (up to 5.07×10^7 Pa) (Colussi et al. 1998; Suslick et al. 1999), (2) a gas–liquid interface, the boundary layer between the solution and hot-spot, which also posses temperatures up to 2,000 K and pressures above 3.04×10^7 Pa (Colussi et al. 1998), and (3) a bulk solution, which remains near ambient temperature and pressure. Hydroxyl radicals are produced by the pyrolysis of water molecules in the hot-spot and at the gas–liquid interface. Target pollutants can partition to the interface and hot-spot regions to be degraded by the thermal processes (Cui et al. 2017; Hudder et al. 2007; Kim et al. 2016; Song et al. 2005; Song and O'Shea 2007).

Ultrasonic irradiation has shown to be effective for the degradation of several PFAS compounds (Cao et al. 2020; Sidnell et al. 2022; Singh Kalra et al. 2021). The degradation efficiency can be affected by operational parameters, temperature, saturation gas, and the structure of PFAS (Campbell et al. 2009). Greater than 90% mineralization of PFOA and PFOS was achieved after 2 h of ultrasonic irradiation (Vecitis et al. 2008). The ultrasonic and reductive transformation of a limited number of PFAS have been reported (Ma et al. 2017; Park et al. 2011; Singh Kalra et al. 2021; Vecitis et al. 2008); however, there are not sufficient reports on the ultrasonic or reductive transformation of emerging PFAS. Herein, we report on the radiolysis, TiO_2 photocatalysis and USI, and the computational predictions for the reaction pathways of the pyrolytic mineralization of GenX.

Experiment Materials and Methods

Materials

PFPrOPrA (free acid form of GenX) was purchased from Thermo Fisher Scientific (Waltham, Massachusetts). All solutions were prepared with Millipore filtered water (18 MΩ·cm). All solvents used for liquid chromatograph-mass spectrometry (LC-MS) analysis were high-performance liquid chromatography (HPLC) grade from Fisher Chemical (Waltham, Massachusetts). Degussa P25 TiO_2 was employed for photocatalysis with a Rayonet reactor (The Southern New England Ultraviolet Co., Branford, Connecticut) equipped with 350-nm emitting bulbs. All other chemicals were purchased from Fisher Scientific and used without further purification. Gases were from Airgas (Radnor, Pennsylvania).

Experimental Methods

A pulsed mode ultrasonic transducer UES 15-660 Pulsar (Ultrasonic Energy Systems, Panama City, Florida) equipped with a disk-shaped horn attached to a glass reactor (500 mL) was employed for all experiments. A detailed description and diagram of the reactor have been previously reported (Cui et al. 2018). Operating conditions were set at a pulse duration of 0.62 s, pulse repetition of 2.5 s, and frequency of 650 kHz under operational power of 396 W. The power density of the sonication was $0.79\ W/mL$ with an ultrasonic horn diameter of 9 cm. Ultrasound traveled through 5 cm of water and 38 μm of the polyethylene film to reach the 500-mL solution inside the 9-cm-diameter reaction vessel. The reactor was submerged in an ice bath, and the temperature range inside the reaction vessel maintained at 10°C ± 2°C throughout the reaction. The aqueous solution containing the target compound was added into the reaction vessel, gently bubbled with Ar for 15 min prior to irradiation, and kept under a positive pressure of argon throughout. Samples were taken at specific treatment intervals and analyzed immediately or stored in the refrigerator.

Fluoride ion analyses were conducted using a Thermo Scientific Orion Fluoride Ion Selective Electrode (Thermo Scientific, Waltham, Massachusetts) connected to a Mettler Toledo ion-selective electrode (ISE) meter (Mettler-Toledo, LLC, Columbus, Ohio). A total ionic strength adjustment buffer (TISAB) solution was premade to provide a constant background ionic strength, and a low-level TISAB (TISAB II) solution was used for lower concentrations of F^-.

The pulse radiolysis experiments were performed at US Department of Energy Notre Dame Radiation Laboratory in Indiana. An 8-MeV model TBS-8/16-1S linear accelerator from Titan Beta was employed to conduct the electron pulse radiolysis. All experiments were performed in static cells (approximately 3 mL solution) with an average of eight replicate pulses. All solutions were presaturated with N_2 at neutral pH for 5 min for e_{aq}^- measurement. To determine the rate constant for the reaction of GenX with e_{aq}^-, the direct absorption and lifetime of e_{aq}^- was monitored at 720 nm as a function of the initial concentration of GenX (Buxton et al. 1988).

Steady-state gamma radiolysis studies were carried out using a Shepherd & Associates (San Fernando, California) Model 109-68R Irradiation ^{60}Co source with a dose rate of $97.0\ Gy/min$, as calculated by Fricke dosimetry. These GenX solutions were saturated with N_2, N_2O, and/or O_2 gas.

For photochemical reactions, 60-mL aliquots of $3.03\ \mu M$ GenX and 2.5-mM TiO_2 with excess ethanol (EtOH) or oxalate (0.2 mM) dispersion were prepared in Milli-Q water in a 100-mL aluminum-foil-wrapped glass tube. The tube was sealed with a rubber stopper and gently bubbled with N_2 for 15 min. Then, the tube was placed in a Rayonet photochemical reactor, followed by a 3 h irradiation using low-pressure mercury lamps at 350 nm. Similar experiments were also conducted under alkaline conditions ($pH = 10$). The concentrations of GenX (PFPrOPrA) and F^- by ultra-high performance liquid chromatography (UPLC-MS) and a fluoride selective electrode, respectively. The concentration of GenX was determined by an UPLC-MS instrument at Valparaiso University. The UPLC-MS (Waters Corporation, Milford, Massachusetts) consisted of a Waters Acquity UPLC H-class system equipped BEH C18 column ($1.7\ \mu m$ and $2.1 \times 50\ mm$), a QDa detector, and a sample manager. The adopted mobile phase was 15% of $5\ mM/L$ ammonium acetate in water and 85% of $5\ mM/L$ ammonium acetate in methanol and water ($80 : 20\ v/v$) using an isocratic mode at a flow rate of $0.3\ mL/min$. The detection of GenX was achieved using negative mode with a cone voltage of 15 V and a capillary voltage of 0.8 kV. A calibration curve was predetermined for the range 0.5 to $10\ \mu mol/L$.

The geometry optimization, frequency, and the pyrolytic mechanistic calculations for GenX were carried out employing the Density Functional Theory wB97XD method with 6-311G** in Gaussian 09. All transition structures were identified by frequency calculations, and all energies were corrected by zero-point energy.

Results and Discussion

Radiolysis of GenX

Kinetic Studies of Reaction of GenX with Aqueous Electrons

Pulse radiolysis was employed to directly generate hydrated electrons in GenX-containing aqueous solutions (Buxton et al. 1988). The decay of hydrated electron was monitored at 720 nm (Hug 1981). The increasing rates of e_{aq}^- decay in the presence of 100 to $500\ \mu mol/L$ of GenX in buffered solution are shown in Fig. 1(a). The pseudo-first-order rate constants for e_{aq}^- and GenX reaction were obtained by fitting a single exponential decay function to these data (Mezyk et al. 2006). The second-order reaction rate constant was obtained by plotting the pseudo-first-order rate constants as a function of the GenX concentration, as shown in Fig. 1(b), giving a value of $k = (3.09 \pm 0.03) \times 10^7\ M^{-1}\ s^{-1}$. Although initial experiments were conducted by simple addition of GenX to N_2-saturated water, the resulting low solution pH due to the ammonium ion dissociation gave an artificially high reactivity for the hydrated electron (second-order rate constants of greater than $10^{10}\ M^{-1}s^{-1}$). This reactivity was significantly reduced when GenX reactions with the hydrated electron were conducted in aqueous solutions buffered at pH 7.0. The measured value under these real-world conditions is now consistent with that previously measured for other PFAS systems (Fennell et al. 2022; Szajdzinska-Pietek and Gebicki 2000). Notable is the dramatic influence solution pH can have of the reduction of GenX.

Gamma Radiolysis

Steady-state gamma radiolysis experiments were performed for $15.2\ \mu M$ of PFPrOPrA in various aqueous solutions. Under N_2-saturated conditions, e_{aq}^- and HO· are the two dominant reactive species produced during the irradiation process. Samples were taken after 0, 1, 2, 4, and 8 h of radiation at a dose rate of $97.0\ Gy/min$. The concentration of GenX (PFPrOPrA) in each sample was measured by UPLC-MS. To measure the mineralization of GenX, the concentration of F^- was determined employing a fluoride selective electrode. The degradation of GenX and F^- production were plotted as a function of irradiation dose, as shown in Fig. S1. After 8 h of radiolysis, minimal degradation of GenX was observed, and less than 2% F^- was produced based on total fluoride production from GenX. This is consistent with the reaction of aqueous electrons with GenX being a very slow process. This indicates that e_{aq}^-, HO·, and O_2^- reactions all lead to relatively slow degradation of GenX. We propose that the hydrated electron initially adds to GenX, likely to the antibonding sigma orbital or the carboxylate group, to produce radical anionic species, which can subsequently lose an electron to revert to the original species without any degradation or bond fragmentation occurring, as illustrated in Eq. (2). Under our conditions, it appears that electron-induced reduced reductive GenX degradation is only a minor pathway; however, the partitioning of these pathways can be significantly impacted by the reaction conditions and thus influence the effectiveness of radiolytic treatment

$$C_3F_7OCF(CF_3)CO_2^- + e_{aq}^- \Leftrightarrow [C_3F_7OCF(CF_3)CO_2]^{2-\cdot} \rightarrow \text{products} \quad (2)$$

To further probe the role of HO·, a 15.2-μM PFPrOPrA solution was presaturated with N_2O to convert e_{aq}^- to HO· and eliminate the production of O_2^-. After 8 h of irradiation under these conditions, the measured degradation of GenX (PFPrOPrA) was again insignificant (below 1%), as was the production of F^- ($1.76\ \mu M$, approximately 1%). Concentrations of F^- after 0, 1, 2, and 4 h were below our instrument detection limit, and no intermediates were observed in LC-MS analysis of the treated solution. The dose rate of $97.0\ Gy/min$ corresponded to 3.42 mM HO· produced each hour for a pure aqueous system. However, under N_2O-saturated conditions, the production of HO· was effectively doubled to $0.59\ \mu mol/Gy$ due to the production of HO· from the reaction of e_{aq}^- with N_2O (Buxton et al. 1988). The results demonstrated that HO· leads to minimal degradation of PFAS, consistent with literature reports (Bao et al. 2018).

Under oxygen-saturated conditions, radiolysis of an aqueous solution leads to the diffusion-controlled reaction of O_2 with e_{aq}^- producing superoxide, $O_2^{\cdot -}$, which can act as an oxidant or a reductant. To probe the role of $O_2^{\cdot -}$, the radiolysis of GenX (prepared from PFPrOPrA) in an oxygen-saturated solution was carried out, and the results were plotted in Fig. S1. Under these conditions, minimal degradation (close to 1%) of GenX was observed after 8 h of irradiation (dose of 46 kGy) with the production of approximately 1% F^-. The reaction of superoxide radical anion with GenX via a reductive defluorination mechanism cannot be completely ruled out based on the minimal production of F^-, but such a transformation under our conditions was again exceedingly slow. The results obtained under N_2O- and O_2-saturated conditions lead to minimal or insignificant degradation of GenX (approximately 1%), suggesting that neither HO· and O_2^- effectively degrade GenX.

pH Effect on the Radiolysis Degradation of GenX

GenX consists of a hydrophobic carbon backbone and a hydrophilic carboxylate group. The radiolytic treatments of GenX were carried out under acidic ($pH = 5$), neutral ($pH = 7$), and alkali conditions ($pH = 10$). The reported pK_a value of GenX is 3.8 (Gomis et al. 2015), which means under the solution pH used for our experiments, GenX was mostly ionized to the carboxylate. Parallel gamma radiolysis experiments were conducted under N_2-, N_2O-, and O_2-saturated conditions. The concentration of GenX after 8 h of radiation was compared with the starting concentration, and these results are plotted in Fig. S2. The results showed that less than 2% degradation of GenX was achieved regardless of pH among the different saturation gases.

In summary, it was found that radiolysis gave slow GenX degradation, and mineralization to fluoride was insignificant under natural, acidic, neutral, and alkali conditions. Effective degradation of PFOA and PFOS has been reported to occur under an extreme alkali conditions ($pH = 13$) (Ma et al. 2017; Trojanowicz et al. 2019). Zhang et al. (2014) reported that similar radiolysis dose rates ($96\ Gy/min$) yielded 99% degradation of PFOA under N_2-saturated alkaline conditions after 6 h of irradiation (Zhang et al. 2014). The dramatically enhanced degradation under strong alkaline conditions may be the result of direct hydroxyl anion–mediated conversion of PFAS and/or production of oxide anion radicals at pH above 12, which may offer an additional degradation pathway. Zhang et al. (2014) reported the degradation of PFOA was induced by a synergetic effect of e_{aq}^- and O^- reaction, where O^- was converted from HO· under alkaline conditions (Zhang et al. 2014). Despite promotion of specific reactive species by solution saturation with different gases, oxidation reaction by HO·, O^-, reactions with O_2^- or reduction by e_{aq}^- under our specific experimental conditions did not lead to significant degradation of GenX.

UV TiO_2 Photocatalysis of GenX

TiO_2 photocatalysis involves generation of an electron/hole pair, giving the potential for reductive or oxidative initiated degradation. The predominant TiO_2 photocatalytic–induced degradation of organic compounds typically occurs via hydroxyl radical–mediated processes. The hydroxyl radical can be formed by the hole oxidation of a water molecule. The addition of a hole scavenger to the solution can inhibit electron/hole pair recombination and promote the electron-based reduction processes.

As shown in Fig. S3, under natural pH, the concentration of GenX after 6 h of treatment in the presence of oxalate was effectively unchanged; however, approximately 6% GenX disappearance was observed when EtOH was added as the hole scavenger. Under the alkali condition, approximately 9% degradation of GenX was observed in the presence of oxalic acid or EtOH. No fluoride was detected in any samples subjected to UV TiO_2 photocatalysis. Although TiO_2 photocatalysis can lead to some degradation of GenX in the presence of hole scavengers, the process is very slow with the potential formation of fluorinated organic by-products and without measurable mineralization even for extended treatment.

Sonolytic Degradation of GenX

Kinetic Studies of the Degradation of GenX

High-frequency ultrasonic irradiations of GenX (PFPrOPrA) in aqueous media were conducted at different concentrations, 0.6, 1.5, 3.0, and 6.1 μM. Samples were taken at specific time intervals, and the concentration of GenX as a function of treatment time is shown in Fig. 2. The half-lives for the ultrasonically induced degradation of GenX in our studied concentration range were less than 30 min. GenX consists of a hydrophobic head and a hydrophilic tail, and thus this molecule may partition to the gas–liquid interface, with the tail residing near the interface (hydrophobic) and its charged carboxylate group associated more with the hydrophilic bulk solution. Although the initial concentrations of GenX were varied 10-fold, the observed degradations as a function of treatment time were similar. For ultrasound-induced degradation, the gas–liquid interface can be viewed as an interface or reactive surface (Hua and Hoffmann 1997).

Solution saturation with different gases can have a pronounced influence on the temperature of cavitation, influencing pyrolytic processes and the production of the reactive species. Argon has a high heat capacity and low thermal conductivity (Budavari et al. 1996); thus, the cavitation under argon saturation produces a higher temperature and pressure in the gas bubbles, leading to a greater pyrolytic degradation. Faster ultrasonic-induced degradations of PFOS and PFOA were reported under argon compared with air saturation (Moriwaki et al. 2005).

The ultrasonic transformation of GenX under argon saturation was studied over a concentration range from 0.3 to $3.0\ \mu M$, and the production of fluoride is plotted as a function of treatment time in Fig. 3(a). There are 11 fluorine atoms in each GenX molecule; therefore, the theoretical fluoride concentration is 11 times higher than the concentration of GenX. To determine the defluorination percentage, the concentration of produced fluoride ions at time *t* normalized for initial GenX concentration is shown in Fig. 3(b). Within 30 min, approximately 50% mineralization was observed, and greater than 85% was achieved after 120 min for an initial GenX concentration of $0.3\ \mu M$. Mineralization to fluoride ions greater than 60% was achieved at higher GenX concentrations with extended treatment.

Computational Studies

The ultrasonically induced degradation of GenX results in considerable mineralization by pyrolytic processes. The effective and rapid conversion of GenX to fluoride ions suggest the degradation likely involves unstable radical products that spontaneously degrade, as proposed for other PFAS compounds (Bental et al. 2019). We were unable to identify or detect any fluoro-organic by-products through LC-MS analyses of the solution during treatment. Although product studies are critical to the fundamental understanding of the degradation pathways, the absence of detectable products makes it implausible to elucidate the reaction mechanisms under our experimental conditions, and thus computational methods were pursued to help understand the pyrolytic degradation processes and reaction pathways.

GenX and the Parent Compound

As a baseline for the influence of fluorination on bond strengths, calculations were conducted on GenX and its analogous nonfluorinated compound. Bond energies were calculated by measuring the energy differences between the original structure and the radicals formed during bond cleavage. In general, C-F bonds are the strongest single bonds in organic chemistry with bond dissociation energies (BDE) values on the order of $100\ \mathrm{kcal/mol}$. The calculated BDE, represented as homolytic cleavage energies for the weaker C-C and C-O bonds that comprise the backbone of GenX, are summarized in Fig. 4. The BDEs of bonds $\mathrm{C\text{-}C_a}$, $\mathrm{C\text{-}C_b}$, $\mathrm{C\text{-}O_c}$, and $\mathrm{C\text{-}O_d}$ labeled in Fig. 5 for GenX, illustrate fluorination strengthens the C-C and C-O bonds by ~ 1 to $9\ \mathrm{kcal/mol}$, with the exception of the $\mathrm{C\text{-}C_e}$ bond. Deprotonation of GenX increases the C-C and C-O bonds strengths with the exception of $\mathrm{C\text{-}O_c}$, which exhibits a decrease of $\sim 20\ \mathrm{kcal/mol}$. The BDE of the $\mathrm{C\text{-}C_f}$ bond in GenX is the weakest among all the bonds, at $77.3\ \mathrm{kcal/mol}$. The BDEs of the $\mathrm{C\text{-}C_d}$ and $\mathrm{C\text{-}C_e}$ are also relatively weak with values of 80.0 and $79.3\ \mathrm{kcal/mol}$, respectively. Among the BDEs for the backbone bonds in GenX, the $\mathrm{C\text{-}C_f}$ is the weakest and most likely to undergo homolytic cleavage, and $\mathrm{C\text{-}O_d}$ and $\mathrm{C\text{-}C_e}$ are next most likely to fragment. It has been reported that the carboxylic group $\mathrm{C\text{-}C_e}$ is the most likely to dissociate in perfluoroether carboxylic acid [P. D. Brothers et al., "Abatement of fluoroether carboxylic acids or salts employed in fluoropolymer resin manufacture," US Patent No. 12/436,273 (2015)]. We found the BDE of $\mathrm{C\text{-}C_e}$ was within $2\ \mathrm{kcal/mol}$ of $\mathrm{C\text{-}C_f}$, which is within the calculation accuracy limits, typically considered to be approximately $3\ \mathrm{kcal/mol}$.

A comparison of the DBEs for GenX and its carboxylate form is included in the Fig. 4. The dissociation energy of $\mathrm{C\text{-}O_c}$ for the GenX carboxylate was $65.3\ \mathrm{kcal/mol}$, 20% lower than the rest of the backbone bonds and nearly $20\ \mathrm{kcal/mol}$ lower than the corresponding bond in the parent GenX. The deprotonation of GenX has a significant effect on the bond dissociation energies of the entire structure. The $\mathrm{C\text{-}O_c}$ has the lowest dissociation energy and thus is the most favored to undergo homolytic dissociation for the carboxylate. The results also suggest the pyrolysis-induced degradation of GenX and the corresponding carboxylate will undergo cleavage of different bonds.

Partitioning of Reaction Pathways of the Homolytic Dissociation Products of GenX

Homolytic bond cleavage is a common pathway during pyrolysis (Cui et al. 2017) and can lead to carbon-centered radical intermediates from PFAS. These carbon-centered radicals are susceptible to rapid rearrangements and/or fragmentations (Ratkiewicz and Truong 2012). The possible initial homolytic bond cleavages of the GenX backbone are defined in Fig. 4. More detailed information of the transition states involved in the degradation pathways are listed in Fig. S4. Geometry optimization and transition state (TS) energies for these possible primary, secondary, and tertiary reaction pathways leading to carbon- and/or oxygen-centered radicals as well as subsequent fragmentation and rearrangements were explored computationally.

The cleavage of $\mathrm{C\text{-}C_a}$ yields the trifluoromethyl radical a1, and product a2. The carbon centered radical a2 can undergo β-scission to form tetrafluoroethylene, a2-p1, and the radical a2-p2 with a TS energy of $36\ \mathrm{kcal/mol}$. For the secondary product, a2-p2, three β-scission reaction pathways are possible shown in Fig. S4(a), among which the lowest energy barrier, $6\ \mathrm{kcal/mol}$, was calculated for the pathway leading to trifluoroacetyl fluoride and the carboxylic acid radical. In the second pathway, a2-p2, a $10\text{-}\ \mathrm{kcal/mol}$ TS energy barrier exists for the formation of trifluoromethyl radical and 2-fluoro-2-oxoacetic acid. The highest transition-state energy barrier, $40.2\ \mathrm{kcal/mol}$, was calculated for the β-scission pathway leading to the formation of a fluorine atom and trifluoropyruvic acid. Based on the relative TS energies for the reaction pathways of the carbon-centered radicals resulting from cleavage of $\mathrm{C\text{-}C_a}$, the major products will be tetrafluoroethylene, trifluoroacetyl fluoride, carboxylic acid radical, trifluoromethyl radical, and 2-fluoro-2-oxoacetic acid.

The cleavage of $\mathrm{C\text{-}C_b}$ yields the pentafluoroethyl radical, b1, and second carbon-centered radical, b2, in Fig. 5. Subsequent collapse of b2 can form carbonyl fluoride and the secondary product b2-p2 with a transition state energy barrier of $12.5\ \mathrm{kcal/mol}$, indicated as ts4 in Fig. S4. Despite repeated attempts and geometry optimization, we could not find a well-defined transition state for subsequent β-scission bond cleavages of radical b2-p2 with relatively high calculated energy barriers of 69.0 and $69.1\ \mathrm{kcal/mol}$ for products 2,3,3-trifluoroacrylic acid, 2,3,3,3-tetrafluoroprop-1-en-1-one, fluorine radical, and hydroxyl radical, shown in Fig. 5.

The pyrolytic cleavage of $\mathrm{C\text{-}O_c}$ yields the formation of perfluoropropyl radical, c1, and radical c2. The perfluoropropyl radical (c1) undergoes β-scission to form tetrafluoroethylene and the trifluoromethyl radical with an energy barrier of $43.1\ \mathrm{kcal/mol}$. Product c2 is identical with the secondary product a2-p2 and subject to the reaction pathways presented previously.

Homolytic fragmentation of $\mathrm{C\text{-}O_d}$ leads to carbonyl fluoride and pentafluoroethyl radicals with a low energy barrier of $2.9\ \mathrm{kcal/mol}$. Radical d2 is the same as the radical b2-p2 discussed previously in the section related to the degradation pathways of $\mathrm{C\text{-}C_b}$.

The cleavage of $\mathrm{C\text{-}C_e}$ leads to products e1-p1 and trifluoroacetyl fluoride (e1-p2) with a transition state of $18.2\ \mathrm{kcal/mol}$. Product e1-p1is the same as product c1 and follows the same reaction pathways. The fluorine atom from e1 can dissociate but with a relatively high energy barrier of $69.7\ \mathrm{kcal/mol}$, producing 1,1,1,2,2,3,3-heptafluoro-3-((1,2,2-trifluorovinyl)oxy)propane as another product (e1-p3).

The fragmentation of $\mathrm{C\text{-}C_f}$ yields the carbon centered radicals f1 and trifluoro radical, f2. The f1 product can undergo two competing β-scission reaction pathways. Radical f2-p1 (same as radical c1) and 2-fluoro-2-oxoacetic acid are generated with an energy barrier of $19.8\ \mathrm{kcal/mol}$. The energy barrier for the competing pathway is much higher, $75.6\ \mathrm{kcal/mol}$, with hydroxyl radical and product f2-p3, which was only $0.4\ \mathrm{kcal/mol}$ lower than the transition state. The intermediate can subsequently collapse to yield product f2-p3 and hydroxyl radical with a $2.6\text{-}\ \mathrm{kcal/mol}$ energy barrier.

These computational results indicate that the fluorine atom is unlikely to form during the pyrolytic pathways. However, many predicted products have acyl fluoride functionality, which can readily hydrolyze to give the fluoride ion.

Based on our results, we predict that the GenX carboxylate degradation is mostly to occur at $\mathrm{C\text{-}O_c}$, and therefore subsequent reaction pathway was considered, as shown in Fig. 6. The cleavage formed the radical ion $\mathrm{OCFCF_3\ COO^{-}\cdot}$ (c2') and a trifluoromethyl radical $\mathrm{CF_3\cdot}$ (c1). The radical ion $\mathrm{OCFCF_3\ COO^{-\cdot}}$ collapses into $\mathrm{CO_2^{-\cdot}}$ and trifluoroacetyl fluoride spontaneously. The acyl fluoride is converted to fluoride upon hydrolysis, consistent with the high yield of fluoride ions observed during the ultrasonic treatment of GenX.

Conclusions

GenX was not readily degraded by $\mathrm{TiO_2}$ photocatalysis or radiolysis under a variety of conditions. Adjustment of conditions to produce specific radical species, $\mathrm{HO\cdot}$, $\mathrm{O_2^{-\cdot}}$, $\mathrm{e_{aq}^{-}}$, and $\mathrm{e_{cb}^{-}}$, leads to no or minimal conversion of GenX to fluoride ions under our conditions. GenX and $\mathrm{e_{aq}^{-}}$ react relatively slowly as measured by pulse radiolysis, and the slow degradation of GenX under gamma radiolysis conditions suggests that the yield or partitioning for $\mathrm{e_{aq}^{-}}$-induced GenX destruction may be a limiting step. The radiolysis and $\mathrm{TiO_2}$ photocatalysis may lead to modest destruction of GenX under different reaction conditions but elimination of fluorinated by-products and/or mineralization to fluoride ions would require exhaustive treatment. Given the limited reactivity of hydroxyl radicals in the degradation of GenX, it appears the effective degradation and mineralization of this PFAS by USI observed in our studies is primarily the result of pyrolysis.

Computational studies established the possible reaction pathways and assessed the likelihood of primary, secondary, and tertiary intermediates. A number of acyl fluorides were predicted as intermediate products, which, in the presence of water, are susceptible to hydrolysis to form fluoride ions. The relative rapid destruction of GenX and high levels of mineralization to fluoride ions illustrate the promise of ultrasonic induced destruction as an effective method for remediation of GenX and likely a variety of PFAS in contaminated aqueous media. Detailed product studies are planned to determine specific reaction pathways and establish the fluorine atom mass balance during the USI treatment process.

Data Availability Statement

All data, models, and codes generated or used during the study appear in the published article.

Acknowledgments

The authors are grateful for the hospitality, experimental assistance, and intellectual discussions with Professor Prashant Kamat during visits to NDRL. This research was partially supported by the National Science Foundation Award No. CBET-1805718.

Supplemental Materials

Figs. S1–S4 are available online in the ASCE Library (www.ascelibrary.org).

Supplemental Materials

supplemental_materials_ee.1943-7870.0002066_cui.pdf (130 KB)

© 1996–2022, American Society of Civil Engineers

This website uses cookies to ensure you get the best experience on our website. Learn more

Got it!