# Formation of perfluorocarboxylic acids (PFCAs) from thermolysis of Teflon model compound

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## Abstract

It has been widely postulated that thermal degradation of polytetrafluoroethylene (PTFE; commercially known as Teflon) under the presence of moisture presents a likely source for the formation of the notorious perfluorocarboxylic acids ($CF_3(CF_2)_nCO(OH)$ PFCAs) and perfluorinated aldehydes ($CF_3(CF_2)_nCO(F/H)$). Thus, deployment of objects laden with Teflon at the peak of their thermal stability may contribute to the atmospheric budget of PFCAs. However, the underlying mechanism remains largely speculative. This study reports potential energy surfaces for reactions that govern oxidative transformation of $n$-$C_8F_{18}$ (as a model compound of PTFE) into tridecafluoroheptanoyl fluoride and perfluoroheptanoic acid. Central to computed pathways are dissociative addition reactions of water over the carbonyl group and elimination of hydroperoxyl radicals. Facile activation enthalpies are encountered in the involved steps. Our analysis discloses that formation of the building monomer $C_2F_4$ should be suppressed under thermolysis oxidation conditions at which synthesis of trifluoroacetic acids is preferred. Constructed kinetic model illustrates a near-complete conversion of the PTFE model compound into perfluorocarboxylic acids ($CF_3(CF_2)_nCO(OH)$ and perfluorinated aldehydes. Outcomes from this study should be instrumental in providing a better understanding of the likely contribution of fluoropolymers in the observed environmental loads of perfluorocarboxylic acids.

**Keywords** Teflon · Thermolysis · Water addition · Mechanisms · Perfluorocarboxylic acids

## Introduction

Fluoropolymers are inherently flame-retardant, but when thermally decomposed, they release toxic gases, such as carbonyl fluoride, hydrogen fluoride, and perfluoroisobutylene (Purser 2014, 1992). These "engineering plastics" are generally deployed at the extreme temperature window of polymer's thermal stability. At sufficiently high doses, their fragments can cause fatal lung edema and inflammation. Products from thermal decomposition and combustion of fluoropolymer generally incur a significantly higher toxic profiles than their parent fluoropolymers (Arito and Soda 1977). Under a specific set of conditions and decomposition

temperatures (450–650 °C with recirculation through the hot zone), perfluorinated polymers produce considerable concentration of nano-sized particles (10–150 nm diameter), which are highly toxic and cause lung inflammation. This is about 1000 times more poisonous than combustion products from wood and similar materials (Purser and Purser 2004). The production of fluoropolymers has peaked at 223,000 tons in 2022 (Ameduri 2020) with polytetrafluoroethylene (PTFE) being the most widely produced polymer in this category and accounts for about 60% of the total international fluoropolymer market in Puts et al. (2019).

Polytetrafluoroethylene (FTFE) which is a semi-crystalline thermoplastic polymer constitutes an important fluoropolymer that was initially manufactured by Plunkett of DuPont Company (Conesa and Font 2001; Simon and Kaminsky 1998). In 1950s, PTFE was commercialized as Teflon®. Other fluorine-containing polymers have been developed. In addition to the neat PTFE, some of fluoropolymer contain other elements such as chlorine, silicon, or nitrogen. These fluorine-bearing chemicals enjoy a wide range of applications, most notably as coating materials.

PTFE consists of recurring tetrafluoroethylene (TFE) monomer units -[$CF_2$-$CF_2$]$_n$-. In addition to granular powder and fine powder, PTFE comes as an aqueous dispersion form. Moreover, it can be diluted with water or other solvents and sprayed on metals or fabrics. End products made from melted polymer include pipelining, wire insulation, and fuel hose tubing, whereas cookware or roofing material is example of dispersed products (Schmidbauer et al. 2009). PTFE is chemically inert and hydrophobic and exhibits superb thermal stability with operating temperature up to 260 °C (Feng et al. 2018; Henri et al. 2020). Such characteristics are attributed to its chemical structure and the C–F chemical bond strength (500 kJ mol$^{-1}$) (Henri et al. 2020). The poor processability is the main drawback of PTFE as it is a non-polar polymer, i.e., non-dissolvable by the common solvents (Ju et al. 2020).

While PTFE does not cause skin irritation in rabbits or humans, nor does it causes skin sensitization in humans, the major safety concern with PTFE stems from its pyrolysis products that are reported to irritate mucous membranes, skin, and eyes (Radulovic and Wojcinski 2014). In addition, polymer-fume fever (influenza-like symptoms) can also be triggered by PTFE pyrolysis products (Radulovic and Wojcinski 2014). In nonclinical studies, 25% PTFE was administered to rats for 90 days without causing toxicologically significant effects. For up to 1 year after the injection of PTFE particulate in a glycerin carrier, mice, rabbits, and dogs all developed an inflammatory reaction with progressive tissue growth at the injection site (Radulovic and Wojcinski 2014). It was revealed that in the incineration of PTFE, carbonyl fluoride ($COF_2$) (which is a highly toxic gas with a half-life of approximately 2 weeks in the atmosphere), trifluoroacetic acid (TFA), tetrafluoroethene (TFE), and hydrogen fluoride (HF) are produced. The later compound is a strong inorganic corrosive material that exhibits a high level of reactivity with other molecules in the atmosphere as well as a tendency toward wet deposition and particle attachment (Schmidbauer et al. 2009). Furthermore, it is reported that the thermal degradation of PTFE in air produces several gaseous species such as CO, $CO_2$, and carbonyl fluoride ($COF_2$). The latter signifies a toxic gas that requires a safety precaution (Odochian et al. 2014, 2011). Moreover, the PTFE degraded thermally during vacuum to give mainly CF, $CF_2$, $C_2F_3$, $COF_2$, and $C_2OF_5$ compounds (Luff and White 1968). Along the same line of enquiry, the seminal work by Ellis et al. (2001) has established the potential formation of the notorious long-chain perfluorocarboxylic acid (PFCAs, $CF_3(CF_2)_nCO(OH)$) from thermolysis of PTFE and other fluoropolymers. The proposed mechanisms involve initial fission of the carbon backbone, followed by a series of bimolecular reactions with ambient oxygen and water.

Nonetheless, reaction pathways that dictate oxidative transformation of PTFE into PFCAs and their further decomposition into perfluorinated small fragments remains largely speculative without a verification based on quantum chemical calculations. To this end, this study reports mechanistic pathways and derive kinetic parameters that control the gas phase decomposition of $n$-$C_8F_{18}$ as a model compound of PTFE in air with the presence of moisture ($H_2O$). The main objective is to demonstrate — via means of density functional theory calculations, DFT — the pyrolysis chemistry of PTFE with a prime focus on reaction routes that produce PFCA compounds. The underlying aim of the study is to kinetically assess the likely contribution of teflonized objects (such as frying pans and surgical syringes) in the observed environmental inventory of PFCAs.

## Computational detail

The meta-hybrid M06–2X DFT functional along with the extended basis set 6–311 + G(d,p) (Montgomery Jr et al. 2000) has been utilized to execute structural optimizations and energy calculations as implemented in the Gaussian16 suite of programs (Frisch et al. 2016). It is well-established that the M062X method exhibits an accurate performance in deriving thermokinetic parameters for applications pertinent to organic reactions. A detailed benchmarking disclosed that M062X-calculated bond dissociation enthalpies incur a mean absolute deviation at 1–2 kcal/mol in reference to analogous values computed at CBS-QB3, CBS-APNO, and W1U methods (Purnell Jr and Bozzelli 2018). Along the same line of enquiry, our recent investigations (Adi and Altarawneh 2022; Altarawneh 2021a, 2021b; Altarawneh et al. 2022) on the decomposition of several perfluorinated compounds have thoroughly contrasted M062X-computed reaction rate constants and dissociation enthalpies with analogous experimental values. In general, the M062X method retains its status as the most widely utilized cost-effective approach to address combustion systems (Mardirossian and Head-Gordon 2016).

Reaction rate constants were attained based on the transition state theory (TST) with the aid of the KiSThelP code (Canneaux et al. 2014) where Arrhenius parameters were fitted across the broad temperature range of 200–1500 K. A plausible contribution from tunneling effects was incorporated via the inclusion of a one-dimensional Eckart barrier. The ChemRate software (Mokrushin et al. 2002) derives temperature-dependent thermochemical properties (enthalpies of formations, heat capacities, and standard entropies) (i.e., NASA polynomials required in the modeling).

Standard enthalpy of formation for the PTFE model compound ($n$-$C_8F_{18}$) was estimated based on an isodesmic reaction. Calculated thermochemical and kinetic parameters constitute a semi-detail kinetic model. The model was executed using the Chemkin-Pro package considering a continuous

stirred tank reactor (CSTR) at 1 atm between 1000 and 2300 K. Supplementary Materials (SMs) enlists Cartesian coordinates for all species and the thermokinetic parameters of the model.

## Results and discussions

Several studies have investigated degradation of PTFE under different operational conditions, namely, temperature, availability of oxygen, the physical form of the particles, and the residence time. These distinct conditions render it a challenge to comprehend a unified underlying degradation mechanism. (Huber et al. 2009). Moreover, the aforementioned parameters in addition to moisture also affect the nature of the formed products (Huber et al. 2009). For instance, it is well known that the thermal degradation of PTFE under inert atmosphere ($N_2$) suppresses the production of toxic compounds such as $CF_2O$ and $CF_5O$, while it is not the case under the air atmosphere (Luff and White 1968) at which a greater amount of hydrolyzed fluorine compounds are generated (Knight and Wright 1972). In this regard, Odochian et al. (2011) and Odochian et al. (2013) concluded that in the thermal degradation of PTFE under nitrogen atmosphere, the monomer TFE can be recovered as a main product. On the contrary in an air atmosphere, the yield of the building monomer is significantly smaller, and more toxic gasses can be formed in higher amounts such as $CF_2O$ and $CO_2$. On the other hand, perfluorocarboxylic acids were observed upon the thermolysis of PTFE in the presence of water (Ellis et al. 2001). The degradation channels suggested in this study consist of several steps including unimolecular decomposition, oxidation (adding $O_2$), hydration ($H_2O$ addition), and the addition of hydrogen atoms.

### Decomposition pathways of PTFE (Teflon-C₈) for the fate of perfluorinated carboxylic acids

A series of chemical reactions triggered by chain scission control the thermal degradation of polymers yielding a variety of free-radical molecules of different molecular weights (Kasaai 2018; Ray and Cooney 2018). Figure 1 depicts pathways that ensue in the oxidative degradation of the PTFE model compound. The fission of a secondary C–F bond requires a very sizable bond dissociation enthalpy of 110.5 kcal/mol. The latter value departs by only 3.5 kcal/mol from a corresponding experimental value in the 2-fluoropropane molecule at 114.0 kcal/mol (Luo 2003). Abstraction of the fluorine atoms by the expected abundant H/F/O radical pool is most likely to be the chief initial decomposition channel at elevated temperature. While these reactions with the PTFE model compounds have not been considered herein, literature provides a detailed kinetic account for

analogous reactions with a wide array of fluorine-bearing alkanes (Babushok et al. 2012). Rapture of C–C bond may assume an importance, especially at high temperature (Patel et al. 2010).

The next suggested step constitutes the addition of an oxygen molecule to form a peroxy adduct through a highly exothermic step of 64.4 kcal/mol. The later value coincides very well with analogous values for the formation of perfluorinated peroxy adducts. For instance, we have found that oxygen addition to the α-hydroxy alkyl radical of $CF_3CF_2CH_2CHOH$ generates 61.2 kcal/mol (Altarawneh and Dlugogorski 2012). The initial production of the peroxy moiety by the addition of $O_2$ was also part of the proposed pathways in the thermolysis of fluoropolymers as a potential source of halogenated organic acids in the environment (Ellis et al. 2001). As described in our recent studies (Altarawneh 2021b; Altarawneh et al. 2022), initially formed peroxy adducts in case of perfluorinated carboxylic and sulfonic acids lead to the generation of perfluorinated aldehyde $CF_3(CF_2)_3C(O)H$.

Phenomenologically, oxygen molecules at ambient conditions can also react with the polymer, resulting in weight loss and a different emission profile from that caused by pyrolysis (Conesa and Font 2001). Fission of the peroxy's O–O bond necessitates 47.0 kcal/mol and results in the formation of an oxygen-centered radical ($CF_3CF(O)(CF_2)_5CF_3$. In the ensuing step, departure of the trifluoride methyl group takes place through a trivial enthalpic barrier of 9.6 kcal/mol via the transition structure TS1. This reaction generates a tridecafluoroheptanoyl fluoride ($C_7F_{14}O$), a product that was detected in Ellis et al. (2001)'s study.

The tridecafluoroheptanoyl fluoride molecule can be consumed by two proposed hydration reaction ($H_2O$ addition) channels characterized by TS5 and TS2. The former transition structure leads to the formation of the perfluoroheptanoic acid (PFHpA) ($CF_3(CF_2)_5C(O)OH$). As Fig. 2 depicts, the transition state TS5 marks the synthesis of the PFHpA in one step that forms an HF molecule via fluorine's atom abstraction and the simultaneous addition of a hydroxyl group at the outer C(O) site. A similar pathway was illustrated by Ellis et al. (2001) in their description for the governing formation routes of perfluorocarboxylic acids (PFCA; $CF_3(CF_2)_nC(O)OH$). The five-centered TS5 incurs a modest activation enthalpy of 35.7 kcal/mol. In a competing pathway via TS2 (34.9 kcal/mol), dissociative addition of a water molecule produces the $(OH)_2C(F)(CF2)_5CF_3$ intermediate in an exothermic reaction of 5.5 kcal/mol. As shown in the lowermost part of Fig. 1, formation of the PFHpA molecule could take place through a three-step pathway that entails fluorine abstraction by the abundant H atoms (TS3), oxygen addition at the apparent radical site in the formed $(OH)_2C(F)(CF2)_5CF_3$ radical, and unimolecular elimination of hydroperoxyl
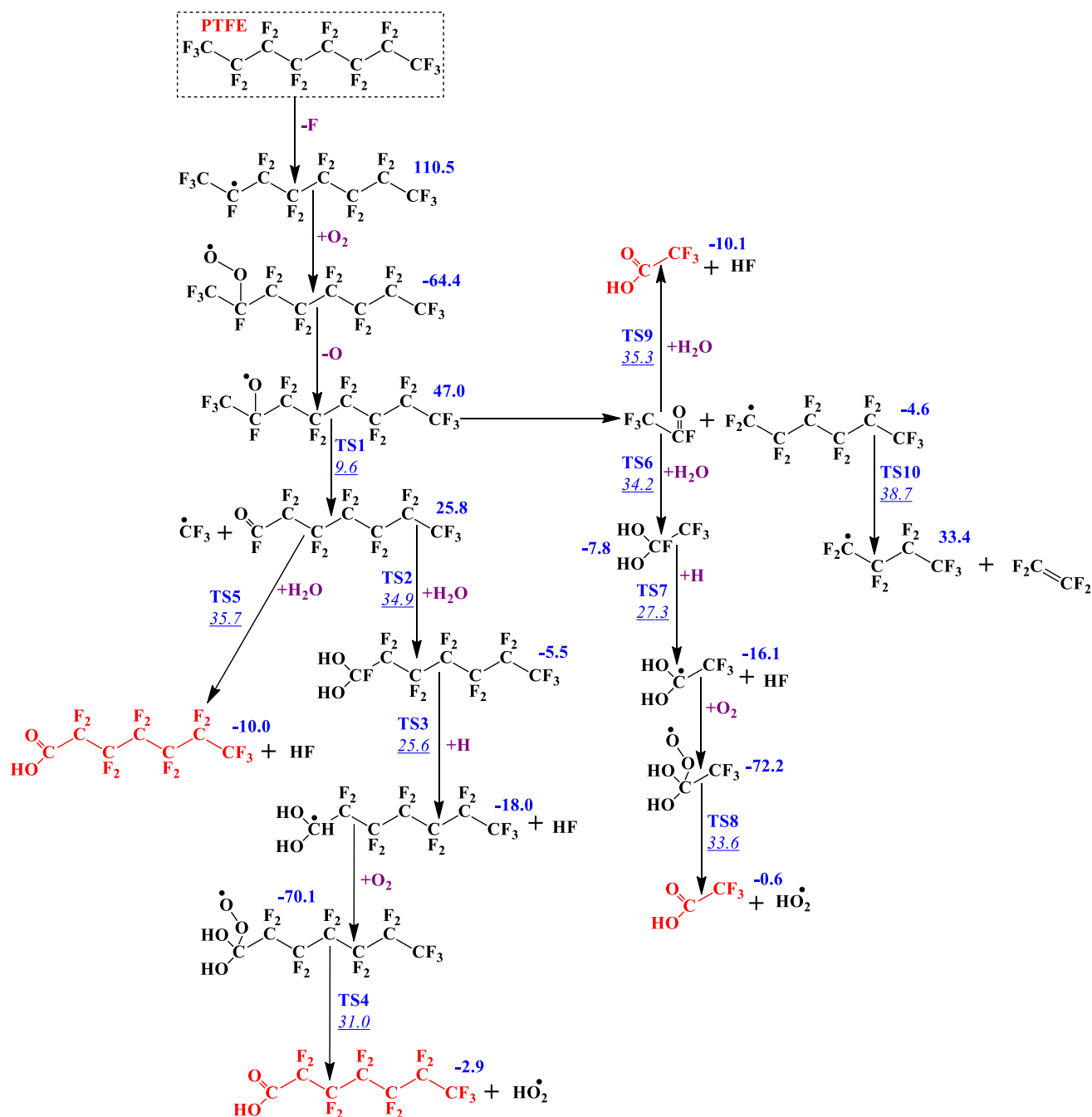
**Fig. 1** Decomposition pathways for the PTFE model compounds. Values are in kcal/mol at 298.15 K. Values in bold and italic (underlined), represent reaction enthalpies and activation enthalpies; respectively

radical (TS4). While the two hydration pathways do not constitute a viable atmospheric synthesis pathway for PFCA (Altarawneh 2021b), they clearly represent a major formation corridor for PFCA under combustion conditions. Through a relatively accessible activation energy of 31.0 kcal/mol via TS4, hydroxyl's H transfer from one of the two OH groups to the outer peroxy's O atom affords the PFHpA molecule and $HO_2$ with an exothermic reaction

enthalpy of 2.9 kcal/mol. Formation of HF through this pathway coincides with the appearance of HF in appreciable concentrations from the degradation of Teflon (Huber et al. 2009). Along the same line of enquiry, thermal degradation of PTFE with 50% relative humidity air, it was proposed that HF originates from hydrolyzed $CF_2O$ due to the effect of water presence (Baker Jr and Kasprzak 1993). In addition to PFHpA, formation of other longer
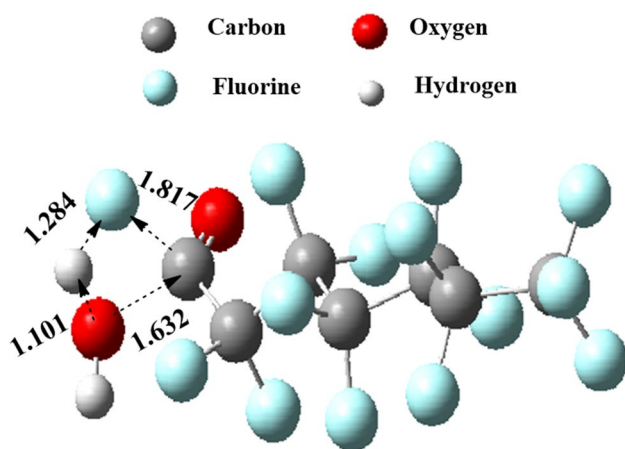
**Fig. 2** Geometrical structure of the transition state (TS5). The distances here are in A°



**Fig. 3** Variation of the activation enthalpy for the dissociation of a water molecule on the carbonyl bond in perfluorinated aldehydes

chain PFCAs ($C_3$-$C_{14}$) was also reported from thermolysis of fluoropolymers that were phased out (Ellis et al. 2001; Huber et al. 2009).

As shown in Fig. 1, fission of a C–C bond leading to trifluoroacetic ($CF_3C(O)CF$) acid and the alkyl chain $CF_2(CF_2)_4CF_3$ represents another potential exit pathway for the initially formed adduct in a slightly exothermic process of only 4.6 kcal/mol. In an analogy to the reaction network that tridecafluoroheptanoyl fluoride endures, trifluoroacetyl fluoride is converted into trifluoroacetate (TFA) via two distinct hydration-assisted channels. Energy profile for the transformation trifluoro acetyl fluoride → trifluoroacetate route is very similar to corresponding values that prevail in the tridecafluoroheptanoyl fluoride → perfluoroheptanoic acid pathway. TFA was also reported among the products from thermolysis of PTFE (Ellis et al. 2001). Thus, it can be concluded that $C_2$-$C_7$ PFCAs share similar formation mechanisms and that the length of the alkyl chain exerts a rather minor influence on the energetics of the generation process. The abundant TFA concentration in the atmosphere (David et al. 2021) could be partly linked with the decomposition of perfluorinated polymers.

A $\beta$ C–C bond fission in the $CF_2(CF_2)_4CF_3$ radical liberates the PTFE monomer $C_2F_4$ monomer (tetrafluoroethylene; TFE) via an activation enthalpy of 38.7 kcal/mol. The formation of TFE from the thermal degradation of PTFE was reported in several studies. It was inferred that the yield of TFE under thermolysis and atmospheric conditions is lower than that obtained under purely pyrolytic conditions (i.e., under inert atmosphere ($N_2$)) (Baker Jr and Kasprzak 1993; Luff and White 1968; Odochian et al. 2013, 2011). This may entail that the presence of the oxygen and water molecules alters the decomposition mechanism. Indeed, we have demonstrated herein that reactions leading to PCFA and perfluorinated aldehydes are principal sink pathways
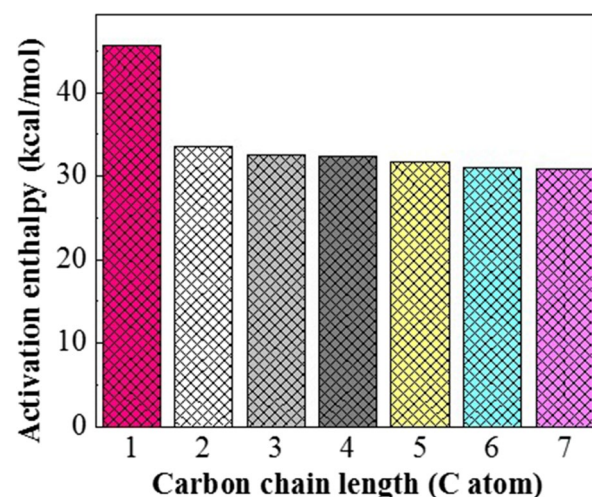
for the perfluorinated alkyl chain. The latter decomposes predominantly to TFA in the absence of oxygen and water molecules.

As water addition to the perfluorinated aldehydes assumes a central significance in the proposed formation mechanism of PFCAs, it is of an interest to assess the effect of perfluoroalkyl chain on the activation enthalpy of this reaction. Figure 3 demonstrates that beyond the first carbon atom, activation enthalpy for the dissociative addition of a water molecule to perfluorinated aldehyde remains insensitive to the length of the perfluoroalkyl chain. A high-activation barrier in case of water addition to trifluoroacetyl fluoride might stem from a strong hybridization in its trifluoromethyl group (Mullinax et al. 2014).

## Kinetic model

Kinetic simulations were performed using a CSTR model (with a volume of 1 $cm^3$ and residence time of 1 s). The inlet feed consists of 0.5% $C_4F_{10}$ in air along with a 1% concentration of $H_2O$ and H atoms. The latter serves to represent the hydrogen reservoirs developed from the degradation of polymeric constituents often deployed with PTFE. Table 1 enlists computed reaction rate constants for the reactions that are included in the model. Activation enthalpies for barrierless reactions were set at their reaction enthalpies for endothermic reactions and at 0.0 kcal/mol for exothermic reactions. The intent from the reduced model is not to provide a detailed kinetic account for all plausible products but rather to illustrate the potential formation of PFCAs from thermolysis of PTFE.

As demonstrated in Fig. 4, decomposition the PTFE model compound commences at about 1600 K and exhibited

**Table 1** Arrhenius parameters ($k(T) = AT^n \, e^{-(Eal(RT))}$) for reactions that participate in the thermal decomposition of PTFE (Teflon®, $C_8$), fitted in the temperature range of 200 and 1500 K

| No | Reaction | $A$ ($s^{-1}$ or $cm^3$ $molecule^{-1}$ $s^{-1}$) | $n$ | $\Delta H_{Rxn.}$ (cal mole$^{-1}$) | $E_a$ (cal mole$^{-1}$) |
|---|---|---|---|---|---|
| 1 | $C_8F_{18} \rightarrow F + C_8F_{17}$ | $1.00 \times 10^{13}$ | 0 | 110 500 | 110,466 |
| 2 | $C_8F_{17} + O_2 \rightarrow C_8F_{17}O_2$ | $1.00 \times 10^{13}$ | 0 | $-64\ 400$ | 0 |
| 3 | $C_8F_{17}O_2 \rightarrow O + C_8F_{17}O$ | $1.00 \times 10^{13}$ | 0 | 47 000 | 47,041 |
| 4 | $C_8F_{17}O \rightarrow CF_3 + C_7F_{14}O$ | $1.17 \times 10^{13}$ | 0.38 | 25 800 | 9952 |
| 5 | $C_7F_{14}O + H_2O \rightarrow C_7H_2F_{14}O_2$ | $1.97 \times 10^{02}$ | 2.1 | $-5500$ | 33,654 |
| 6 | $C_7H_2F_{14}O_2 + H \rightarrow C_7H_2F_{13}O_2 + HF$ | $1.50 \times 10^{03}$ | 4.34 | $-18\ 000$ | 23,200 |
| 7 | $C_7H_2F_{13}O_2 + O_2 \rightarrow C_7H_2F_{13}O_4$ | $1.00 \times 10^{13}$ | 0 | $-70\ 100$ | 0 |
| 8 | $C_7H_2F_{13}O_4 \rightarrow HO_2 + CF_3(CF_2)_5C(O)OH$ | $2.58 \times 10^{+07}$ | 3.41 | $-2900$ | 29,101 |
| 9 | $C_7F_{14}O + H_2O \rightarrow HF + CF_3(CF_2)_5C(O)OH$ | $2.32 \times 10^{+01}$ | 2.64 | $-10\ 000$ | 34,508 |
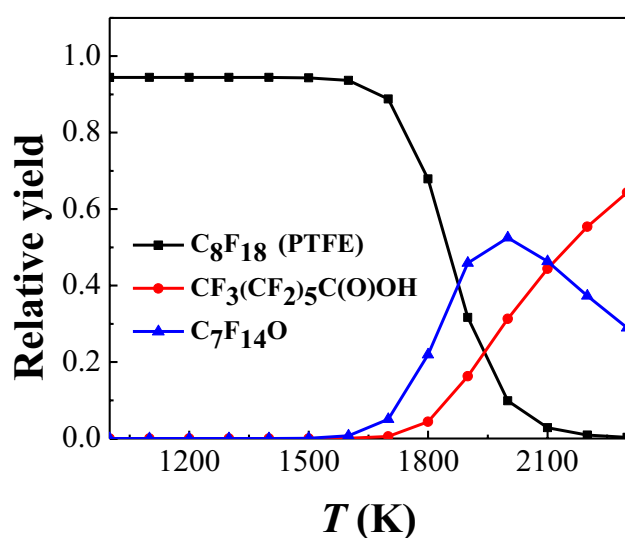


**Fig. 4** Relative yield profiles of PTFEA model compounds, tridecafluoroheptanoyl fluoride, and perfluoroheptanoic computed at CSTR at a residence time of 1 s. Values are normalized in respect to the initial number of PTFE moles

almost complete destruction at a relatively high temperature of 2200 K. It was reported that, at 252 °C (798.15 K), Teflon® with 6 carbon atoms went through gross degradation in air with 50% relative humidity which is slightly below the maximum operating temperature (260 °C (533.15 K)) reported by Henri et al. (2020) for thermal stability of PTFE. In addition, it was found that the maximum recommended processing temperature of Teflon is 425 °C (698.15 K) (Baker Jr and Kasprzak 1993). Using TG–DTA thermal technique, Odochian et al. (2013) found that the final thermal degradation temperature of PTFE under air atmosphere is 602.6 °C (875.75 K). Moreover, according to a study about polytetrafluoroethylene decomposition in air, it was reported that for a noticeable degradation to occur, temperatures above 400 °C (673.15 K) are needed (Conesa and

Font 2001). The noticeable discrepancy in the predicted and experimentally measured onset temperature for the decomposition of PTFE arises from plausible reactions between adjacent perfluoroalkyl chain in the condensed phase of PTFE. Such aspect will be investigated in due course.

Following the decomposition of the PTFE representative compound, the model predicts formation of tridecafluoroheptanoyl fluoride (between 1600 and 2000 K) and perfluoroheptanoic acid starting from 1650 K. Noticeably and as demonstrated in Fig. 4, the relative yield of tridecafluoroheptanoyl fluoride attains almost 50% yield around 1900 K. As the tridecafluoroheptanoyl fluoride molecule serves as a precursor for perfluoroheptanoic acid, the decline in the yield of the former coincides with the observed increase in the yield of the latter compound. Nonetheless, it should be noted that under real pyrolytic environment and the coexistence of polymeric constituents with the PTFE, radical pool is expected to initiate degradation of PTFE at a significantly lower temperature and that perfluorinated aldehydes and PFCAs may emerge at temperature relevant to the thermal stability boundaries of PFTF as obtained in the TGA experiments.

The absolute rate of production analysis was carried out aiming to comprehend the set of reaction pathways that control the yield of the perfluoroheptanoic acid. Figure 5 illustrates that both reaction channels $C_7F_{14}O + H_2O \rightarrow HF + CF_3(CF_2)_5C(O)OH$ and $C_7H_2F_{13}O_4 \rightarrow HO_2 + CF_3(CF_2)_5C(O)OH$ are the main reactions that lead to the production of the perfluoroheptanoic acid. However, it appears that the bimolecular reaction $C_7F_{14}O + H_2O \rightarrow HF + CF_3(CF_2)_5C(O)OH$ accounts for the major production of the perfluoroheptanoic acid. From Fig. 4 a and b, it can be noticed that the production rate of the latter compound, raised up from $2.83 \times 10^{-18}$ to $1.45 \times 10^{-8}$ mol cm$^{-3}$ s$^{-1}$ as the temperature increases from 1200 to 2200 K. This indicates a consumption of the PTFE model compound toward the perfluoroheptanoic acid.
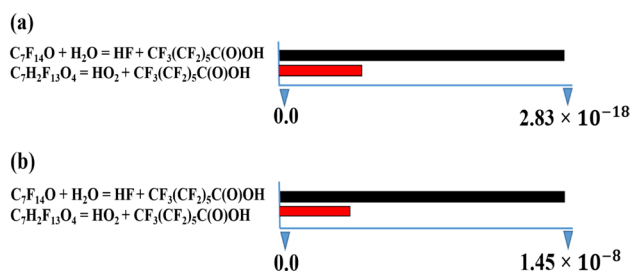
**(a)**

$C_7F_{14}O + H_2O = HF + CF_3(CF_2)_5C(O)OH$
$C_7H_2F_{13}O_4 = HO_2 + CF_3(CF_2)_5C(O)OH$

0.0                    $2.83 \times 10^{-18}$

**(b)**

$C_7F_{14}O + H_2O = HF + CF_3(CF_2)_5C(O)OH$
$C_7H_2F_{13}O_4 = HO_2 + CF_3(CF_2)_5C(O)OH$

0.0                    $1.45 \times 10^{-8}$

**Fig. 5** Absolute rate of production of $CF_3(CF_2)_5C(O)OH$ at CSTR with 1 cm.$^3$ volume at 1800 K (**a**) and at 2200 K (**b**)

## Conclusions

In this study, a kinetic model was developed to describe salient features that underpin thermolysis of $C_4F_{18}$ as a model compound of Teflon (PFTE) with a prime focus on reactions that lead to the formation of PFCAs. It was illustrated that oxygen addition at an apparent radical site in the perfluoroalkyl chain leads first to the formation of perfluoroalkyl aldehydes. Dissociative water addition at the carbonyl group or simultaneous addition of a hydroxyl group and abstraction of a fluorine atom forms PFCA structure. Enthalpic barriers for the former process seem insensitive to the length of perfluoroalkyl chain ($C_2$-$C_7$). Formation of the shortest PFCAs and important atmospheric species, the trifluoroacetic acid, takes place following a facile fission of a FC(O)-F bond. This process also ensues to generate the $C_2F_4$ monomers. Absolut rate of production analysis portrays the important reactions that participate in the production of the PFCA molecule $CF_3(CF_2)_5C(O)OH$. The developed model signifies an important milestone toward understanding the widely postulated contribution of PTFE thermolysis in the environmental burdens of PFCAs.

## Declarations

**Ethics approval and consent to participate** Not applicable.

**Consent for publication** Not applicable.

**Competing interests** The authors declare no competing interests.

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