Thermolysis of fluoropolymers as a potential source of halogenated organic acids in the environment

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Following the introduction of hydrochlorofluorocarbon (HCFCs) and hydrofluorocarbon (HFCs) gases as replacements for the ozone-destroying chlorofluorocarbons (CFCs), it has been discovered that HCFCs/HFCs can degrade in the atmosphere to produce trifluoroacetic acid[1], a compound with no known loss mechanisms in the environment[2,3], and higher concentrations in natural waters[4] have been shown to be mildly phytotoxic[5]. Present environmental levels of trifluooracetic acid are not accounted by HCFC/HFC degradation alone[8–10]. Here we report that thermolysis of fluorinated polymers, such as the commercial polymers Teflon and Kel-F, can also produce trifluoroacetate and the similar compound chlorodifluoroacetate. This can occur either directly, or indirectly via products that are known to degrade to these haloacetates in the atmosphere[11]. The environmental significance of these findings is confirmed by modelling, which indicates that the thermolysis of fluoropolymers in industrial and consumer high-temperature applications (ovens, non-stick cooking utensils and combustion engines) is likely to be a significant source of trifluoroacetate in urban rain water (~25 ng l^{-1}, as estimated for Toronto). Thermolysis also leads to longer chain polyfluoro- and/or polychlorofluoro- (C3–C14) carboxylic acids which may be equally persistent. Some of these products have recently been linked with possible adverse health[6] and environmental impacts and are being phased out of the US market[7]. Furthermore, we detected CFCs and fluorocarbons—groups that can destroy ozone and act as greenhouse gases, respectively—among the other thermal degradation products, suggesting that continued use of fluoropolymers may also exacerbate stratospheric ozone-depletion and global warming.

The replacement CFC gases HCFC-123 (CF_3CHCl_2), HCFC-124 (CF_3CHClF) and HFC-134a (CF_3CH_2F) are known to degrade in the troposphere, through reaction with hydroxyl radicals, to trifluoroacetate, TFA[1]. TFA is expected to be a long-lived environmental species, and has no known significant loss mechanism[3]. Studies have suggested that at higher concentrations, such as those observed in surface waters with seasonal evaporation–concentration cycles[4], TFA will exhibit mild phytotoxicity[5]. Environmental modelling calculations conducted for TFA predict a concentration of 100–120 ng l^{-1} in rain water between the years 2010 and 2020[3]: these predictions were based on the assumption that TFA originates from the CFC replacement gases. Environmental measurements[8–10] of TFA have shown that current levels cannot be accounted for by these sources alone. In certain regions, concentrations of TFA in rainwater now average 120 ng l^{-1} (ref. 8), and no major alternative source has been identified to explain these observations. Although there is some controversy within the literature, it seems that the TFA observed in precipitation is largely a result of urban activities. For example, TFA concentrations of <2–92 ng l^{-1} have been found at remote sites, compared with 50–1,100 ng l^{-1} for industrialized urban sites[12,13]. The unidentified source of TFA is likely to be anthropogenic in origin, as there are no known naturally occurring trifluoromethylated compounds. A second long-lived fluorinated acetic acid, chlorodifluoroacetic acid (CDFA) has recently been identified in rain water[2]. Direct evidence of a source responsible for its production has yet to be established, although CFC-113 ($CF_2ClCFCl_2$) may contribute.

Agrochemicals, anaesthetics and fluoropolymers are the three main, distinct, categories into which environmental emissions of fluorine-containing anthropogenic organic compounds can be subdivided. Both agrochemicals[14] and anaesthetics[8] have been shown to produce TFA, but they can be eliminated as major contributors due to the quantities that are currently being emitted into the atmosphere[8]. Fluoropolymers, such as polytetrafluoroethylene (PTFE), are potential sources, due to their heavy usage in urban and industrial areas. In 1988 the average annual global consumption of fluorinated polymers was 40,000 tonnes (ref. 15) and by 1997 this figure had risen by almost 220% based upon sales[16], with a projected annual increase of 7%.

In order to produce the CF_3– or CF_2Cl– unit required for the formation of haloacetic acid, the polymer would have to undergo decomposition and subsequent rearrangement. Fluoropolymers are being designed and modified specifically for use in areas of high thermal stress, such as ovens, cookware, industrial and car engines, heat exchangers, high-temperature circuits and a wide variety of other thermal applications. In 1997, 1% of all polymers were used in areas of elevated temperature, a grouping composed primarily of fluoropolymers[17]. The subcategory of plastics known as engineering plastics, in particular fluoropolymers, operate at the extreme of polymers' temperature performance[17]. PTFE, for instance, will endure 260 °C for ~2.3 years (ref. 18) until failure due to degradation[19]. Fluoropolymers are, largely, either recycled or degrade *in situ*[19], resulting in research on the toxicity of the decomposition products[20]. The onset of thermal degradation of fluoropolymers is known to initiate cleavage of the backbone and

Table 1 Positively identified species produced in the thermal decomposition of fluoropolymers

Polymer	Thermal product identified	Per cent produced
PTFE	TFE*†	–
	HFP*†	10.8§
	TFA*†	7.8‡§
	c-OFB†	–
	$CF_3(CF_2)_nCOOH$†	>0.01‡
	$CF_3O(CF_2)_mCOOH$†	–
	DFA†	>0.01‡
	MFA†	>0.01‡
CPTFE	CTFE*†	–
	CPFP*†	13.1§
	CDFA*†	9.5‡§
	TFA*†	>0.1‡§
	DCHB*†	–
	DCHFCB*	–
	TCTFE*	–
	1,3-DCTFP*†	–
	1,1,3-TCTFP*†	–
	$CCl_xF_y(CCl_{x-1}F_z)_xCOOH$†	–
ECTFE	TFA*†	6.3‡§
	CDFA*†	7.2‡§
	HFP*	–
	CPFP*	–
PFEPE	TFA*†	2.5*†
	HFP*	–

A dash indicated that the analyte was positively identified but not quantified. Acronyms used which are not in the body of the text: MFA, monofluoroacetic acid; DFA, difluoroacetic acid; FDCA, fluorodichloroacetic acid; DCFP, dichloroperfluoropentanoic acid; DCFB, dichloroperfluorobutanoic acid; DCHFCB, 1,2-dichlorohexafluorocyclobutane; TCTFE, 1,1,2-trichloro-1,2,2-trifluoroethane; 1,3-DCTFP, 1,3-dichlorotetrafluoropropene; 1,1,3-TCTFP, 1,1,3-trichlorotrifluoropropene; ECTFE, ethylene-chlorotrifluoroethylene; PFEPE, polytetrafluoroethylene-*co*-tetrafluoroethylene perfluoropropylether. For the long-chain acids, n = 1-12, m = 1-7, x = 0-2, y = 1-3, z = 1-2, p = 9-13.
* Identified by NMR.
† Identified by MS.
‡ Quantified by NMR.
§ Quantified by MS.

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subsequent rearrangement to produce significant amounts of trifluoromethylated species[20]. The incineration, or combustion, of fluoropolymers has previously been proposed as a source of TFA[8] and CDFA[2]. These processes differ from thermolysis in that a source of fuel is used in order to purposefully evoke complete decomposition. Furthermore, it is unlikely to yield environmentally significant levels of TFA, or TFA precursors, due to the high temperatures and oxidizing conditions used, which would result in the cleavage of most carbon–fluorine bonds. On the other hand, low-temperature burning of domestic waste, which is an important source of polychlorinated dioxins and furans to the atmosphere[21], may analogously be an important source of fluoroacids.

We aimed to show the possibility of direct and indirect production of haloacetic acids through the thermolysis of fluorinated polymers, and to investigate the production of other perhalogenated compounds that may be of environmental significance. We performed thermolysis of the fluoropolymer by placing the pure polymer in a quartz tube that was connected to a continuous stream of air. The tube was subsequently heated to a temperature of 500 °C. The experiment was also conducted isothermally at 360 °C for PTFE, a temperature that is used routinely in product sintering. The gases were collected as they left the reaction vessel, and immediately analysed. The temperature and conditions are not dissimilar to those that might be found in the burning of domestic wastes[21].

Tetrafluoroethene (TFE), hexafluoropropene (HFP) and *cyclo*-octafluorobutane (*c*-OFB) were the main gases produced upon thermolysis of the pure fluorinated polymers and of the commercially available products tested (Table 1); CPTFE (chloropolytrifluoroethylene) analogously yielded chlorotrifluoroethene (CTFE), chloropentafluoropropene (CPFP) and 1,2-dichlorohexafluorocyclobutane (DCHB). HFP has the potential to react with OH radicals in the troposphere to produce TFA (100% conversion)[11]. The reaction kinetics of CPFP with OH radicals are expected to be similar to that of HFP, based upon its reaction with other radicals[22] and the behaviour of similar molecules[11] producing CDFA in the troposphere. As well as PTFE and CPTFE, fluoropolymers ECTFE and PFEPE were also tested; see Table 1.

A large, previously unidentified, class of thermolysis compounds, perhalogenated acids, is also shown in Table 1. TFA and CDFA were the main acids to be observed in the thermolysis of the fluoro- and chlorofluoropolymers, while other longer-chain perhalogenated acids were also identified.

We propose a mechanism for the thermal degradation of PTFE, primarily involving the reaction of a CF_2 carbene unit, for the production of the main compounds observed (Fig. 1). This mechanism is supported by key products observed by several other workers (see Fig. 1 legend) and the additional products observed in this investigation. CPTFE and other polyfluorinated polymers have not been studied in nearly the same depth. We suggest that the mechanism for their degradation is similar, based upon the distribution of related products observed in this investigation.

Fluoropolymers are also incorporated into commercial products that may be exposed to high temperatures (such as the teflonized engine additive Slick 50, teflonized frying pans and surgical syringes). By heating these commercial products, we found that the incorporated fluoropolymers decomposed in such a way as to produce the same products as the pure polymers, that is, TFA and/or CDFA along with numerous other perhalogenated acids. Although the significance of any single source may be small, the incorporation of fluorinated polymers into commercial materials continues to increase, and could result in the accumulation of these compounds in the environment.

These results may explain the high TFA concentrations currently observed in precipitation (especially in urban areas), and the presence of other chlorofluoroacids, such as CDFA. They may also help to account for the seemingly contradictory reports that, in some instances, urban areas have higher concentrations of TFA in comparison with remote locations, while others have reported that the

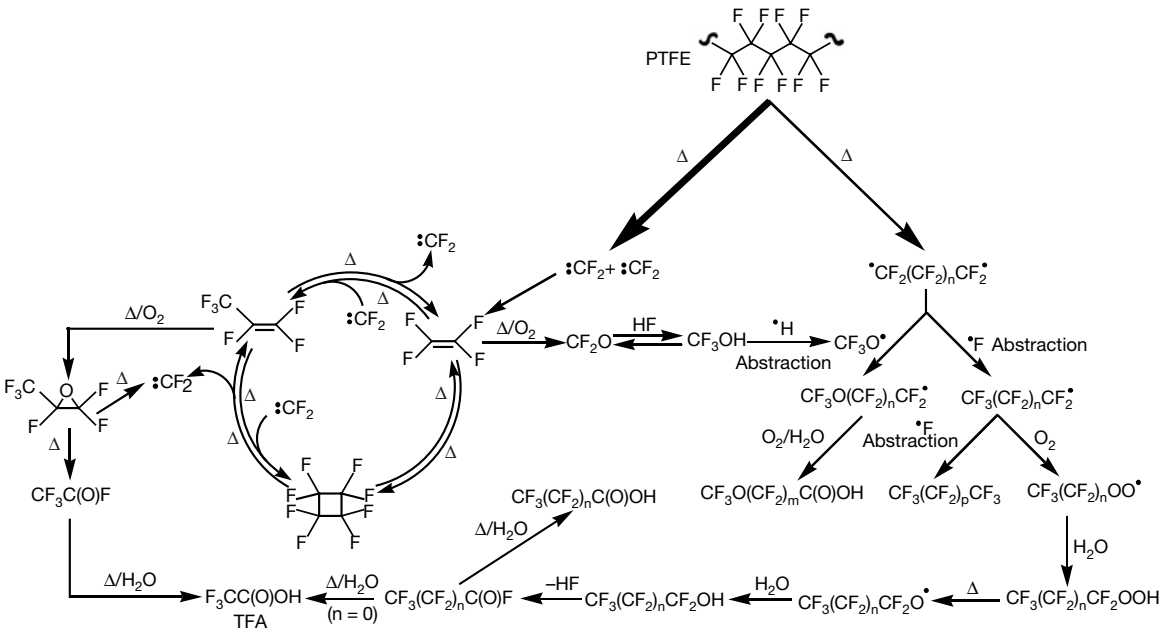

Figure 1 Proposed significant pathways in the thermal decomposition of fluoropolymers. The explicit major pathways for the production of TFA (trifluoroacetate) are shown. Evidence for the mechanism was obtained from this work and from previous observations[19,20,25,28,29]. As indicated by the bold arrow, the most significant step in the thermal decomposition is the formation of carbene radicals. Longer-chain diradicals are also formed, which can undergo fluorine abstraction or reaction with carbonyl fluoride to produce radical fluorinated alkanes ($p = 0–4$) or ethers. These radicals then react with constituents present in the air, oxygen and trace amounts of water, to form perfluorinated acids ($n = 0–12$, $m = 1–7$), the yield being inversely proportional to the number of carbon atoms in the chain. The distribution of product yield depends on temperature and the composition of the atmosphere. PTFE, polytetrafluoroethylene; Δ, heat.

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concentrations are similar in both regions. These observations can be attributed to haloacetic acids being produced in two ways: directly through thermolysis of the polymer, and then undergoing short-range transport; and also indirectly, from the reaction of OH radicals with propenes, which may allow for longer-range transport. (We note that the tropospheric life-time of HFP is 9 days, based on its reaction kinetics with OH radicals; ref. 11). It has also been suggested that if HFP is produced from fluoropolymers, even to a small degree, that this would be a significant environmental burden of TFA[11].

Our hypothesis is that thermal degradation of fluoropolymers can lead to the formation of TFA. We have used environmental modelling to predict the concentration of TFA that is expected in Toronto rain. (Details of the model and the calculation are given in Supplementary Information.) A two-box environmental model was used; the smaller box (representing Toronto and the surrounding atmosphere) was contained within the larger box, representing North America. We first considered the flux of fluoropolymer-derived TFA to the atmosphere; this process was assumed to occur in Toronto and in North America as a whole. We then considered the flux of TFA into and out of the Toronto 'box'. After consideration of all other major fluxes, the average TFA concentrations in Toronto rainfall was estimated. The main uncertainty in these calculations is the percentage of fluoropolymers that ultimately undergo thermolytic degradation. We have used a value of 0.1% per year of the lowest estimated amount of fluoropolymer present in North America. This value is conservative due to the prevalent use of sintering–the pre-application heating of PTFE—involving temperatures (360–382 °C) that our work has shown causes slow thermal breakdown. Further, the reported application of these polymers in areas of high thermal stress exceeds this value[17]. Finally, known indirect production of TFA through atmospheric oxidation of a significant thermal product, HFP, was not included within the model[11].

The model shows that there is the potential for a TFA concentration of $\sim 21\ \mathrm{ng\,l^{-1}}$ in Toronto rainwater as a direct result of fluoropolymer thermolysis. These results are in accordance with those which have been experimentally observed[2]; furthermore, they are close to the level of urban enrichment recently observed in a study in California[23].

From an environmental-fate perspective, thermal degradation of the polymers produces monomeric units that will degrade in the troposphere to CO_2 (ref. 24), or halogenated propenes[25,26] (Fig. 2) that degrade to produce long-lived haloacetic acids[11]. Haloacetic acids and perhalogenated acids produced directly from the polymer are expected to be terrestrially deposited through wet and dry deposition[4]. Several perhalogenated acids, such as perfluorooctanoic acid and perfluorodecanoic acid, have been shown to act as peroxisome proliferators and as inhibitors of gap junctional intercellular communication[6]. (We note that perfluorooctanoic acid uses are being phased out by the manufacturer due to environmental persistence and pervasiveness[7].) CFCs were produced through the decomposition of chlorofluoropolymers and may migrate to the stratosphere causing an effect on the ozone layer. The short-chain perfluorinated alkanes and cycloalkanes produced have an estimated tropospheric half-life of greater than 2,000 years,

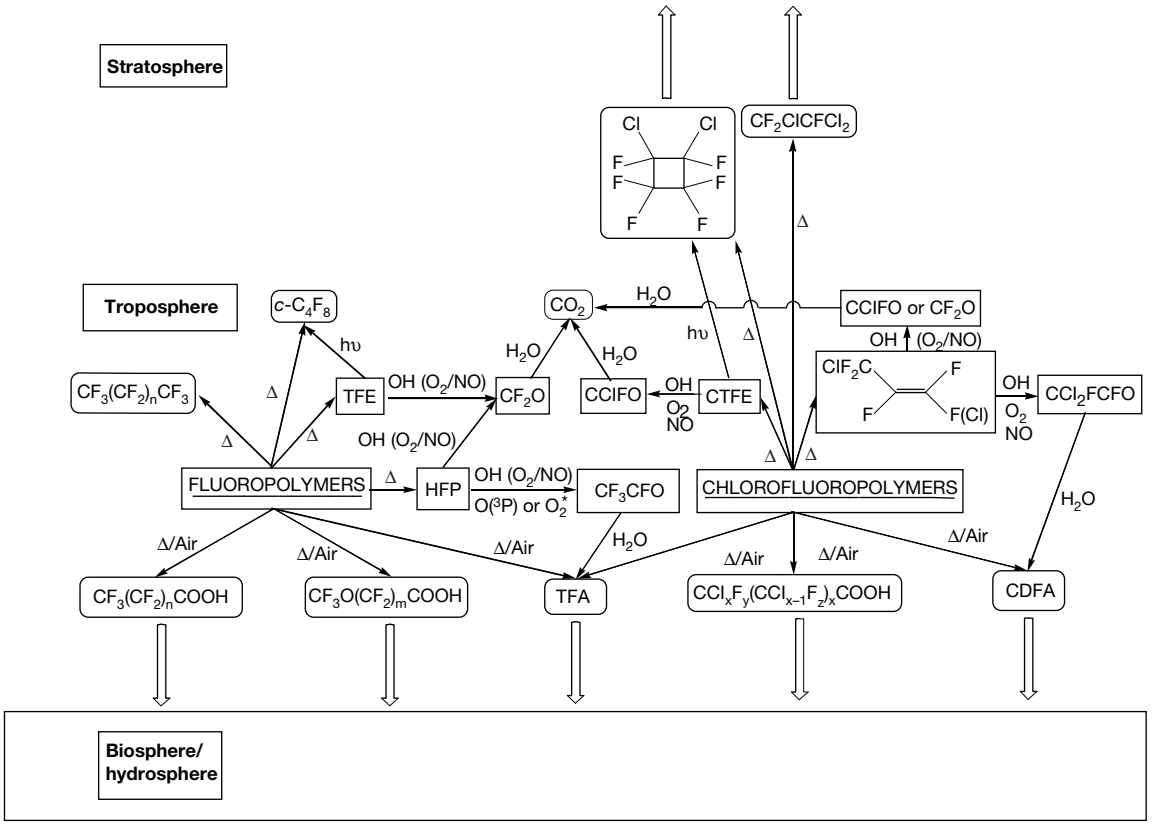

Figure 2 Proposed environmental reaction pathways for the thermal degradation of fluoro- and chlorofluoro- polymers. Rectangular boxes represent environmentally transient species ($t_{1/2} < 10$ years) and important environmental impacts. Reaction processes are either proposed on the basis of this study, or are based on refs 11, 20, 27, 30, 31. A significant concentration of perhaloacids ($x = 0–2$, $y = 1–3$, $z = 1–2$, $n = 1–12$, $m = 1–7$) are produced, primarily TFA (trifluoroacetate) and CDFA (chlorodifluoroacetic acid) (1–10 wt%). Tropospheric oxidation of the perhalopropenes also predominantly leads to, or is expected to lead to, the formation of TFA and CDFA. The thermal decomposition of the chlorofluoropolymers leads to the production of saturated chlorofluorocarbons (CFCs). TFE, tetrafluoroethylene; HFP, hexafluoropropene; CTFE, chlorotrifluoroethylene.

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and have been proposed to effect global climate by acting as greenhouse gases[26].

We have shown that the thermolysis of fluorinated polymers results in the production of a range of compounds, most of which are extremely persistent, and whose environmental impact has yet to be fully assessed. Further studies are needed to quantify the actual emissions of these compounds from various sources. □

Methods

General thermolysis procedure

The polymer of interest (2 g) was placed in a quartz boat that was then inserted into a quartz tube (60 cm), and placed in an oven. Air was continually passed over the sample ($\sim$2 l min^{-1}). The oven temperature was then increased to 500 °C at a rate of 11 °C min^{-1}. The evolved thermolysis materials were collected as described below. Product distribution was also confirmed at the lower isothermal temperature of 360 °C.

Collection procedures

For ^{19}F NMR analysis of the volatile organics, the products were collected in a round-bottomed flask at −78 °C. The flask was then cooled to −196 °C, transferred to a vacuum line ($\sim$16 torr), and evacuated. An NMR tube containing 700 μl of CD_3CN cooled to −196 °C was connected in series with the flask. The flask was then allowed to warm to room temperature and the products transferred to the NMR tube. After one hour, the NMR tube was sealed, allowed to warm to room temperature, and an NMR spectrum collected immediately. Positive identification of products was done by comparing the spectra with those of authentic samples.

Analyses

For the analysis of perhalo-acids, the polymer decomposition off-gases were bubbled through an aqueous Na_2CO_3 solution (pH 10.2). For determination of quantities by ^{19}F NMR, 500 μl of this solution was added to an NMR tube containing 500 μl of CD_3CN spiked with a known concentration of the internal standard, trifluoromethoxyacetanalide. Quantities were determined by comparison to an external calibration using a method similar to that of ref. 13. For identification and quantification using gas chromatography–mass spectrometry (GC-MS), aqueous samples were added to ethyl acetate containing 2,4-difluoroaniline and dicyclohexylcarbodiimide to produce the acid analide in a method similar to that of ref. 2.

To measure the quantities of volatile gases produced in the polymer decomposition, the off-gases were collected in a glass vessel of known volume at −78 °C. After decomposition was complete, the vessel was sealed and allowed to warm to room temperature. Aliquots were removed using a gas-tight syringe and directly analysed using GC-MS. Quantification was performed by comparison to an external calibration.

Blanks consisting of all reagents were run to ensure that products observed were produced as a direct result of polymer decomposition.

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The role of microbial mats in the production of reduced gases on the early Earth

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The advent of oxygenic photosynthesis on Earth may have increased global biological productivity by a factor of 100–1,000 (ref. 1), profoundly affecting both geochemical and biological evolution. Much of this new productivity probably occurred in microbial mats, which incorporate a range of photosynthetic and anaerobic microorganisms in extremely close physical proximity[2,3]. The potential contribution of these systems to global biogeochemical change would have depended on the nature of the interactions among these mat microorganisms.

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