

Thermal degradation of perfluorooctanoic acid (PFOA)

Stockenhuber S.^{1*}, Weber N.¹, Dixon L.¹, Lucas J.^{1, 2}, Grimison C.², Bennett M.², Stockenhuber M.¹, Mackie J.¹, Kennedy E.¹

¹Department of Chemical Engineering, The University of Newcastle, Callaghan, NSW, 2308, AUSTRALIA.

²Ventia, Rhodes Corporate Park, 1 Homebush Bay Drive, Rhodes NSW 2138, AUSTRALIA.

*corresponding author: e-mail: Sebastian.stockenhuber@uon.edu.au

Abstract

Per- and polyfluoroalkyl substances (PFAS) are a group of environmental contaminants, that are dispersed throughout the world. A number of areas have been affected by their persistence and biomagnification. PFAS remediation of contaminated material requires extensive knowledge of the species involved. A method to simplify the study of the thermal degradation of PFAS is presented in this paper, providing a solution to experimental and analytical challenges. A three-zone furnace allowed manipulation of both reaction temperature and gas flowrate (and consequently residence time). The PFAS compound could be charged and vaporised in a separate zone. Adopting this experimental methodology, a kinetic model describing the decomposition of the PFAS can be devised. When reacting under an inert nitrogen atmosphere, perfluorooctanoic acid (PFOA) degraded at temperatures above 450 °C. The products observed were found to be hydrofluoric acid (HF) and carbon dioxide (CO₂), along with a perfluoro-1-heptene species. Additional products of 1H-perfluorohexane or 1H-perfluoroheptane were also observed when residence times were increased. The effect of water vapour was also investigated, with similar behaviour to pyrolysis being observed, where a significantly higher concentration of HF was detected under otherwise similar reaction conditions. These preliminary results suggest water vapour accelerates the rate of PFAS decomposition. **Keywords:** Perfluorooctanoic acid, Kinetics, Thermal Decomposition, Pyrolysis, Water vapour

1. Introduction

PFAS compounds were, and still are, used extensively for coatings in textiles and in some firefighting foam products. The two primary PFAS compounds used are perfluorooctanoic acid and perfluorooctanesulfonic acid (PFOS). A study concluded that production of these products should be discontinued amid concerns about the toxicity of the perfluorinated acids (Haukas, Berger, Hop, Gulliksen and Gabrielsen, 2007). However, these continue to exist within the biosphere and even bioaccumulate (Giesy and Kannan, 2001). The persistence of PFOA and PFOS can be attributed to their exceptionally stable C-F bonds, rendering them non-biodegradable (Key, Howell and Criddle, 1997).

Recently, there has been considerable interest in how to treat these recalcitrant compounds, in an effort to remediate areas that were previously affected by their use, such as firefighting test facilities. As of now, the thermal degradation mechanism for PFOA & PFOS is essentially unknown, with basic kinetic parameters such as reaction rates and activation energies not being known. Theoretical studies on similar compounds provide a basis for comparisons between these similar compounds such as perfluorobutanoic acid. It has been asserted that when PFOA and PFOS thermally degrade, they will produce the by-product hydrogen fluoride, due to the dissociation of the hydrogen atom attached to each head group.

Figure 1 displays the structure of the two compounds.

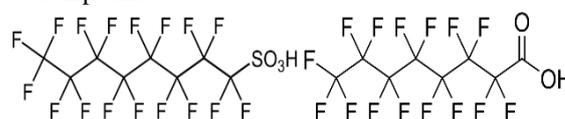


Figure 1. Molecular structure of PFOS (Left) and PFOA (Right)

2. Methodology

A three-zone reactor was used to vaporise and subsequently react the perfluorinated compound under carefully controlled reaction conditions. A bath gas flow was connected to PFA tubing via PFA fittings, which was then connected to an alumina tube (6 mm od) placed inside the a three-zone furnace and reactor. The temperature in each of the three zones was controlled independently, ranging from 40 °C (for the vaporiser zone) to between 300 and 750 °C for the reaction zone. A flow of 90 cm³/min of N₂ was used throughout the experimental trials. A PFA boat was charged with approximately 100 mg of PFOA and manipulated using a metallic wire connected to the PFA boat, prior to being placed within the tubular reactor vaporiser zone. The wire allowed for an accurate and reproducible location of the boat within the reactor, which allowed the prevention of complete vaporisation of the PFOA over the duration of the experiment (typically 40 minutes). The methodology adopted allowed for a plug-in and plug-out system, which was applied to other perfluorinated compounds. Finally, the product gases

were analysed in a real time by FT-IR (Perkin Elmer Spectrum 100 (25 x 5 mm potassium bromide (KBr) 4 mm thick windows). A Shimadzu GC/MS-QP5000 (Plot-Q column 30 m x 0.32 mm) and Agilent GC 6890 MS 5973N (P-5MS column 30 m x 0.25 mm) was used to analyse gaseous products.

3. Results and Discussion

3.1. Pyrolysis of PFOA

Perfluorooctanoic acid decomposition was examined at various temperatures and residence times. GC/MS analysis identified one of the reaction products as 1H-perfluorohexane. An increase in reaction temperature coupled with a reduction in bath gas flow rate resulted in a relative decrease in the concentration of 1H-perfluorohexane and an increase in CO concentration. During these experiments, there was a notable absence in peaks within the 3500-4500 cm^{-1} range, which confirms the consumption of HF. Only at low residence times HF was observed, and when the residence time was decreased to approximately 6 s. **Figure 2** presents a typical FT-IR spectrum obtained under these conditions.

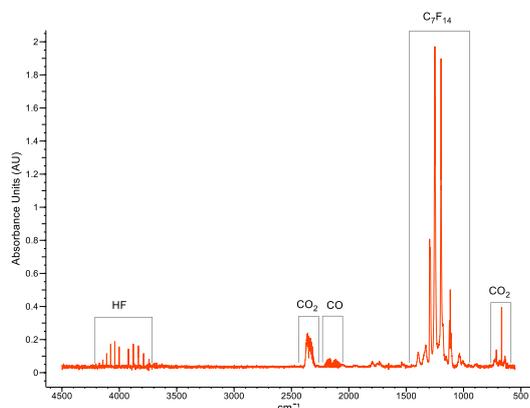


Figure 2. FT-IR spectrum of gas phase pyrolysis products of PFOA at 550 °C and a 5.5 s residence time, highlighting HF, CO and CO₂ production. Various C_nF_m products are visible in the 1000-1500 cm^{-1} region.

Mechanistic analysis suggests the concentration of HF and CO₂ will depend on reaction temperature and residence time; see Figure 3. Two parallel reactions, following the initial elimination of HF, may compete, and at temperatures lower than 400-500 °C under these conditions, HF should be observed as a reaction product.

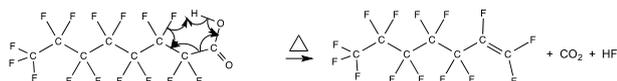


Figure 3. Proposed mechanism for thermal decomposition of PFOA, highlighting the initial formation of the products 1-perfluorooheptene, HF and CO₂

The HF can, in turn, react with the 1-perfluorinated alkene product. In this case, temperature has less influence than residence time on the reaction, where if given enough time to react, HF would be consumed via this secondary reaction, and the concentration of HF would be reduced. A similar observation has been made

for thermal decomposition of PFOS, where pyrolysis appears to have a similar reaction mechanism to PFOA. That is, at lower residence times (2-4 seconds) HF is observed.

3.2. Kinetic analysis

A temperature-programmed method was adopted to obtain the kinetic data of PFOA undergoing pyrolysis. In these experiments, the third reaction zone in the reactor was not at a constant temperature but was programmed to increase from 300–600 °C at a rate of 6 °C/min during the reaction (approximately 40 minutes). There were two flowrates studied, 20 and 40 cm^3/min , which produced residence times ranging from 46-28 s and 23-11 s respectively. These produced rate constants of the values in Table 1 below, not accounting for the conversion of the system.

Table 1. Reaction Constants for pertinent temperatures at 20 (46-28 s residence time) & 40 (23-11 s residence time) cm^3/min for Novel Temperature-Programmed Kinetic analysis.

Temperature (°C)	Reaction Constant at 46-28 s residence time (s^{-1})	Reaction Constant at 23-11 s residence time (s^{-1})
400	3.20×10^{-6}	2.50×10^{-6}
450	3.57×10^{-5}	1.50×10^{-5}
500	4.71×10^{-5}	4.22×10^{-5}
550	7.75×10^{-5}	5.76×10^{-5}
600	9.90×10^{-5}	5.83×10^{-5}

These rate constants are similar to the data reported by Krusic (Krusic, Marchione and Roe, 2005). An Arrhenius activation energy was found to be 113 $\text{kJ/mol} \pm 2 \text{ kJ/mol}$. Using Gaussian09 software, Altarawneh computed the possible decomposition products and mechanisms of perfluorobutanoic acid (Altarawneh, 2012). A similar mechanism was observed in our calculations using Gaussian09, resulting in formation of HF and a perfluorinated backbone. This is the initial stage of the mechanism predicted by the Gaussian09 program, and the activation energies observed confirm this, as the computational energy was determined to be 109.6 kJ/mol , in good agreement with the experimental value (113 $\text{kJ/mol} \pm 2 \text{ kJ/mol}$).

References

- M.Altarawneh, *A theoretical study on the pyrolysis of perfluorobutanoic acid as a model compound for perfluoroalkyl acids*. Tetrahedron Letters, 2012. **53**(32): p. 4070-4073.
- J.P. Giesy and K. Kannan, *Global Distribution of Perfluorooctane Sulfonate in Wildlife*. Environmental Science & Technology, 2001. **35**(7): p. 1339-1342.
- M.Haukas, et al., *Bioaccumulation of per- and polyfluorinated alkyl substances (PFAS) in selected species from the Barents Sea food web*. Environ Pollut, 2007. **148**(1): p. 360-71.
- B.D. Key, et al., *Fluorinated Organics in the Biosphere*. Environmental Science & Technology, 1997. **31**(9): p. 2445-2454.
- P.J. Krusic, et al., *Gas-phase NMR studies of the thermolysis of perfluorooctanoic acid*. Journal of Fluorine Chemistry, 2005. **126**(11): p. 1510-1516.

