

The pyrolysis of perfluorocarboxylic acids - effect of chain length

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Abstract

Per- and polyfluoroalkyl substance (PFAS) are increasingly becoming the contamination issue of our time, due to their environmental persistence, bioaccumulation and mounting evidence of their toxicity. Herein we examined the pyrolytic decomposition of a series of perfluorocarboxylic acids via the production of CO and CO₂, utilizing FTIR and GC/MS analysis.

We observed the presence of a parallel surface-mediated reaction in conjunction with the gas-phase pyrolysis.

Keywords: perfluorocarboxylic acids, pyrolysis

1. Introduction

The perfluorocarboxylic acids (PFCAs) are a subgroup of per- and polyfluoroalkyl substances (PFASs) conforming to the general structure of C_{n-1}F_{2n-1}COOH. PFAS have risen to notoriety in recent years as contaminants of concern, after having been identified as environmentally persistent, bioaccumulative and toxic.

With the advent of increased monitoring, improved analytical techniques and global inventories it is apparent that there is an ever-growing list of PFAS compounds being identified in the environment and biota.

We have sought to contribute to addressing this backlog of PFCAs, in the thermal remediation space, by examining the pyrolysis of a homologous series of PFCAs, namely: trifluoroacetic acid (TFA), perfluorobutyric acid (PFBA), perfluorooctanoic acid (PFOA) and perfluorododecanoic acid (PFDDA).

2. Materials & Methodology

2.1. Experimental Apparatus

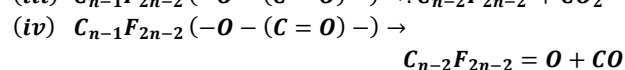
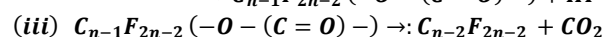
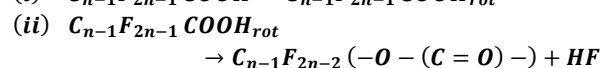
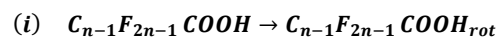
An alumina furnace tube was inserted into a three-zone furnace (3216 Eurotherm PID controllers) to form a plug flow-style reactor. Solid PFCA samples (100 mg) were loaded onto sample boats and maneuvered into the vaporization zone of the furnace (zone 1). Similarly, the liquid PFCA samples were injected into the vaporization zone using a gas tight syringe (SGE 1700) fitted with a reducing union interfaced with a length of gas chromatography column; the sample feed was controlled

by syringe pump (TJ-2A/L0107). A controlled flow of N₂ was used to transport the vaporized PFCA samples from zone 1 to the high temperature reaction area (300-700 °C) in zone 3. The product gases were then analysed by an inline FTIR (Perkin Elmer Spectrum 100, 11 cm path length) fitted with a Teflon gas cell (25x5 mm KBr windows). Offline gas and rinsate samples were analysed by a Shimadzu GCMS-QP5000 (Plot-Q column) and Agilent GC 6890 MS 5973N (HP-5MS column), respectively. Gas-products identified in FTIR spectra were quantified using the regional integration and substitution capabilities of the QASoft program (Infrared Analysis Inc). Preliminary quantum chemical calculations were performed to inform our experimental work at the B3LYP/6-31G(2df,p) and G4MP2 levels of theory.

3. Results and Discussion

3.1 Pyrolysis of PFCAs

Quantum chemical calculations of the pyrolytic decomposition of the PFCAs identified two potential reaction pathways; both proceeding initially by the rotation of the carboxylic H (i), eliminating HF and resulting in a lactone intermediate (ii). The lactone can decompose via two routes: the elimination of CO₂ and formation of a perfluorocarbene (iii) or the elimination of CO and formation of a carbonyl difluoride (iv). At both levels of theory, the CO pathway is predicted to be dominant:



Experimentally, the PFCAs were pyrolyzed non-isothermally between 300-500 °C (5 °C/min) and 500-700 °C (5 °C/min), with a residence time between 2-4 s. The progress of the decomposition of the PFCAs was

monitored indirectly via the production of the major products of the reaction CO and CO₂.

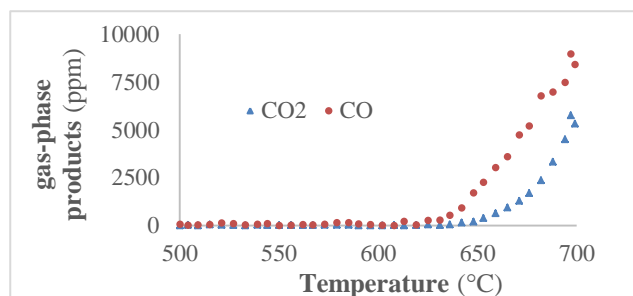


Figure 1. Example of the parallel production of CO and CO₂ over time during the pyrolysis of TFA (500-700 °C).

3.2 Spectroscopic results

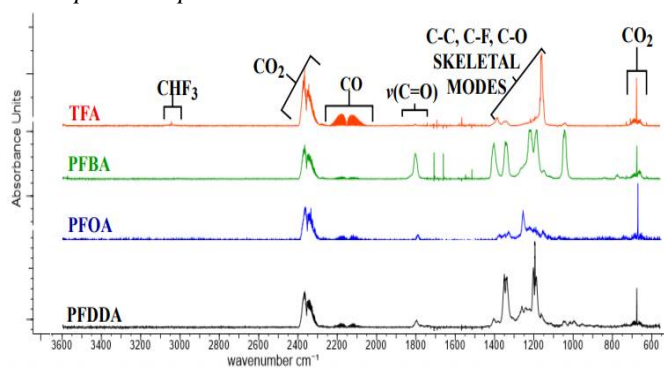


Figure 2. Infrared spectra of the pyrolysis products of the four PFCAs at 700 °C.

As depicted in Figure 2, numerous features of the FTIR spectra for the homologous series are readily identifiable. With the assistance of GC/MS, specific fluorocarbon products were identifiable; for example, the decomposition products of PFBA included: 1-H-perfluoropropane, hexafluoropropene and perfluoropropanone. The fluorocarbon products, across

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the homologous series, tended to appear as 1-H-C_{n-1}perfluoroalkanes, C_{n-1}perfluoroalkenes and a variety of carbonyl-species.

3.3 Influence of surface assisted reactions

The non-isothermal experiments revealed greater concentrations of CO₂ than predicted by our theoretical work, as exemplified in Figure 1. Moreover, we observed the production of gas-phase products after the reactant feed had been removed and HF was conspicuously absent from our gas phase spectra – strongly evincing the presence of a surface reaction.

To investigate surface activity, we pyrolysed PFOA at 700 °C both in the presence and absence of alumina fragments. As illustrated in Figure 3, despite the significantly reduced reactor volume due to the added alumina, a significant concentration of CO₂ was still produced, while the concentration of CO remained approximately constant (not depicted). This experiment provides strong evidence for the presence of wall effects – precluding the determination of intrinsic kinetic data, but nonetheless providing useful insights into the nature of the reaction.

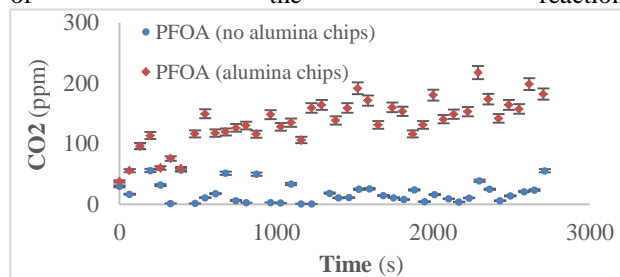


Figure 3. Effect of increased alumina surface area on CO₂ production during isothermal pyrolysis of PFOA at 700 °.

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