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Thermal decomposition of low-molecular weight perfluoroalkylethers

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Abstract

Seven low-molecular weight perfluoroalkylethers have been subjected to thermal degradation using a flow pyrolyzer attached to a gas chromatograph, and the results are compared with thermal decomposition of two perfluoroalkanes. Both linear and branched ethers were studied. The major degradation products from the ethers were identified by GC/MS. Products due to specific C–O bond fission were detected from only two of the ethers. Hexafluoropropylene was the most prominent product from all the ethers studied. While the perfluoroalkylethers in general were more stable than perfluoroalkanes, linear ethers were more stable than branched ethers. The stability of the ethers also decreased with increasing number of adjacent C–C bonds.

Keywords: Thermal decomposition; Pefluoroalkylethers; Perfluoroalkanes; Pyrolysis; Model compounds

1. Introduction

There has been considerable interest in recent years in perfluoroethers due to their excellent thermo-oxidative stability and chemical inertness. A few polymeric materials of this class, perfluoropolyalkylethers (PFPAEs), are commercially available and are providing major contributions to technology [1]. During the past three decades, the stability of PFPAEs and their mode of degradation under a variety of conditions have been the subject of extensive investigations [2–15]. A review on the topic has recently been published [16]. However, there is still disagreement as to the actual mechanism of degradation. Most of these studies were made on four different commercial PFPAE fluids [16]. These commercial fluids are all polymeric materials and as such are mixtures of different molecular-weight species. Single compounds are much more satisfactory models for studying properties. However, synthesizing a unimolecular species having very high molecular weight is a difficult task. Therefore it was felt that structure–stability correlations are better made with pure, low-molecular weight, unimolecular material rather than high-molecular weight mixtures; although the high volatility of the former impose practical difficulties.

The original study on the degradation of perfluoroethers by Tiers [17] utilized simple low-molecular weight linear and cyclic ethers and anhydrous $AlCl_3$ as the catalyst. Since then most of the degradation studies reported were conducted with polymeric materials. The thermal stability of several commercial and custom-synthesized PFPAE fluids was recently determined by Helmick and Jones [15] using a tensimeter. Correlating decomposition temperatures with the molecular structures of the primary components of the fluids, they concluded that the stability of the fluids is not substantially affected by intrinsic factors such as carbon chain length, branching or cumulated difluoroformal groups. It was also found that the stability may be limited by the presence of small quantities of thermally unstable materials.

Thermal decomposition studies have been reported on low-molecular weight branched perfluoroalkanes [18–20]. It was established that the bonds that break most easily are those between carbon atoms having maximum substitution by other carbons. A very recent study reports the thermal decomposition of 2H-heptafluoropropane and a series of highly volatile perfluoroamines by passing the samples, diluted with air, through a quartz tube at the temperature range of 300–900 °C [21]. Details of this work are not available to us, but the decomposition is reported to occur between 600 and 900 °C under the experimental conditions used. Similar studies with low-molecular weight perfluoroalkylethers do not appear to have been made. Our interest in structure–property correlation of perfluoroalkylethers led to the present study of a series of pure model compounds of this class. The objective of this study was twofold: (i) to identify any specificity in the site of bond fission from the nature of the primary degradation products formed, and (ii) to evaluate the relative stability of a series of perfluoralkylethers. Both thermal and catalytic

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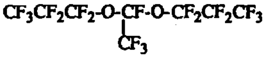
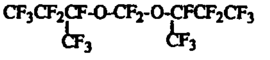
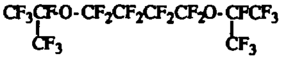
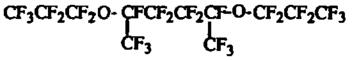
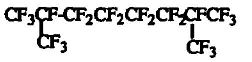
decomposition of these compounds have been studied. This paper describes the thermal decomposition.

2. Experimental details

Thermal decomposition was conducted using a flow pyrolyzer attached to the injection port of a gas chromatograph. For this purpose, a Pyrojector II from SGE International PTY Ltd. was connected to a HP 5890 series II gas chromatograph. The pyrolyzer consisted of a thick-walled 13.5 cm × 2.0 mm (i.d.) quartz tube heated by a furnace capable of temperatures up to 1000 °C. An approximately 7 cm length of the quartz tube was heated by the furnace. The temperature of the furnace, as well as the pressure in the furnace, could be accurately controlled. The decomposition temperature was varied from 600 °C to as high as 950 °C, depending on the compound studied. The pressure of helium passing through the pyrolyzer, as well as the GC column head pressure, could be independently controlled. The pressure differential between these two points was kept constant to assure identical residence times for all the compounds studied, as well as at all the temperatures, so that a comparison of their relative thermal stability could be made. In practice, the helium pressure in the pyrolyzer was kept at 14.9 psi and the injection head pressure was maintained at 10.0 psi. Compounds **1–6** (see Table 1) and their degradation products were separated on the gas chromatograph using a 60 m × 0.25 mm HP 624 fused silica capillary column, and characterized by a HP 5972 mass selective detector in chemical ionization mode using methane, at a scan range of 60–700 amu. The degradation products from compounds **7–9** were not characterized. GC/MS analyses of the pure model compounds **7** and **9** were obtained from a Finnigan 4021 instrument and provided by Chemsys Inc.

Data on the relative thermal stability of the model compounds, **1–9**, were obtained using the pyrolyzer in tandem with the GC. The pyrolyzer conditions were the same as above. The analyses were accomplished using a 30 m × 0.25 mm DB-1 fused silica capillary column and a flame ionization detector. The initial helium flow rate was about 1.0 ml min^{-1}. The GC oven temperature was maintained at 35 °C for 5 min at the beginning of the run before raising the temperature to 275 °C at the rate of 15 °C min^{-1}. The injector temperature was maintained at 285 °C and the detector temperature at 300 °C. The percentage of the starting model compound degraded at different pyrolyzer temperatures was determined by external standardization, and the

Table 1
Model compounds, their boiling points, and $T_{1/2}$ (°C) [a]

Compound	Structure	B.p. (°C)	$T_{1/2}$ [a] (°C)
1	$\mathrm{CF_3CF_2CF_2{-}O{-}CF_2{-}O{-}CF_2CF_2CF_3}$	90–91	875
2	 $\mathrm{CF_3CF_2CF_2{-}O{-}\underset{CF_3}{C}F{-}O{-}CF_2CF_2CF_3}$	112–114	855
3	 $\mathrm{CF_3CF_2\underset{CF_3}{C}F{-}O{-}CF_2{-}O{-}\underset{CF_3}{C}FCF_2CF_3}$	106–115	770
4	$\mathrm{CF_3CF_2CF_2{-}O{-}CF_2CF_2CF_2CF_2{-}O{-}CF_2CF_2CF_3}$	122–123	832
5	 $\mathrm{CF_3\underset{CF_3}{C}F{-}O{-}CF_2CF_2CF_2CF_2O{-}\underset{CF_3}{C}FCF_3}$	121–122 (lit. [22] 136)	827
6	 $\mathrm{CF_3CF_2CF_2O{-}\underset{CF_3}{C}FCF_2CF_2\underset{CF_3}{C}F{-}O{-}CF_2CF_2CF_3}$	147	710
7	 $\mathrm{CF_3\underset{CF_3}{C}F{-}O{-}CF_2CF_2CF_2CF_2CF_2CF_2CF_2CF_2{-}O{-}\underset{CF_3}{C}FCF_3}$	77–78 at 6 mmHg	765
8	$\mathrm{CF_3CF_2CF_2CF_2CF_2CF_2CF_2CF_2CF_3}$	125–126	756
9	 $\mathrm{CF_3\underset{CF_3}{C}F{-}CF_2CF_2CF_2CF_2\underset{CF_3}{C}FCF_3}$	62–63 at 40 mmHg	693

[a] Temperature at which 50% of the compound degrades.

temperature at which 50% of the compound degraded ($T_{1/2}$ °C) was taken as a measure of its thermal stability. It is noted that the more accurate internal standard method cannot be used in these studies at high temperatures, as the standard would decompose and interfere. Consequently, these estimations should not be considered any better than semiquantitative. However it provides a fast way of assessing the relative stability of a series of compounds using milligram amounts of materials.

2.1. Model compounds

All the model compounds studied (**1–9**), their boiling points, and their $T_{1/2}$ determined are listed in Table 1. These consist of seven perfluoroethers and two fluorocarbons that are included for comparison. Most of the model compounds were purified by distillation on a spinning band column or by preparative gas chromatography to obtain them in a purity of 99% or higher as determined by GC analysis. Compounds **1–4** were provided by Exfluor Research Corporation, Austin, Texas. Compound **8** was purchased from PCR Inc. Others were synthesized from fluorinated iodides or through their hydrocarbon analogs followed by direct fluorination by Exfluor Research Corporation. All synthesis reactions were conducted in oven-dried glassware or in a high-pressure stainless steel reactor under an atmosphere of dry nitrogen. The fluorinated iodides used were from Allied Chemical Company. All the other chemicals used were commercial samples. NMR spectra were recorded on an NF300 spectrometer at ambient temperature. Elemental analyses were obtained from Chemsys Inc. All temperatures are uncorrected.

Model compounds **5**, **7** and **9** were prepared by coupling of appropriate iodides. The preparation of **5** was reported earlier from this laboratory [22] and involved coupling of the iodide with cadmium metal in acetonitrile. Similar coupling with copper powder in the absence of any solvent also gave the expected products in high yields, and this method was preferred in view of environmental concerns.

2.1.1. Synthesis of perfluoro-1,8-bis(isopropoxy)octane (7)

A mixture of $(CF_3)_2CFO(CF_2)_4I$ (10.0 g; 19.5 mmol) and copper bronze (1.24 g; 19.5 mmol) was placed in a stainless-steel high-pressure reactor under a dry nitrogen atmosphere. The reactor was heated to 150 °C (±5 °C). A pressure of about 100 psi was observed. After one day, the reactor was cooled to ambient temperature. The reactor was opened and the contents filtered to remove the remaining copper bronze and copper(I) iodide, and was washed with Freon 113 (3 × 10 ml). The filtrate was distilled to recover the solvent, and the crude product was distilled on a spinning band column to obtain 6.7 g (yield 89%) of pure **7**. Anal. Calcd. for $C_{14}F_{30}O_2$: C, 21.38; F, 74.01%. Found: C, 21.76; F, 74.07%.

2.1.2. Synthesis of perfluoro-1,4-bis(isopropoxy)butane (5) [22]

Compound **5** was also prepared by copper coupling of $(CF_3)_2CFO(CF_2)_2I$, as described above. It was obtained in 74% yield. Anal. Calcd. for $C_{10}F_{22}O_2$: C, 21.07; F, 73.32%. Found: C, 20.79; F, 72.87%. ^{19}F NMR chemical shifts (ppm), reference, Freon-113: −81.3 (broad multiplet, 2 CF_2O), −81.5 (distorted triplet, 4 CF_3), −126.0 (triplet, 2 CF_2), −145.8 (triplet, 2CFO).

2.1.3. Preparation of perfluoro-2,7-dimethyl octane (9)

This compound was prepared by the coupling of $(CF_3)_2CF(CF_2)_2I$ in presence of copper bronze as described above. Yield, 76%. Anal. Calcd. for $C_{10}F_{22}$; C, 22.32; F, 77.68%. Found: C, 22.48; F, 78.85%. ^{19}F NMR chemical shifts (ppm), reference, Freon-113: −72.0 (multiplet, 4 CF_3), −115.0 (multiplet, 2CF_2), −121.0 (multiplet, 2 CF_2), −186 (multiplet, 2CF).

2.1.4. Preparation of perfluoro-5,8-dimethyl-4,9-dioxadodecane (6)

The hydrocarbon analog of compound **6**, $[CH_3CH_2CH_2OCH(CH_3)CH_2]_2$, was prepared as follows: a 3 l four-necked round bottom flask was charged with NaH (19.0 g, 0.792 mol) in 700 ml of anhydrous diethyl ether. The flask was fitted with a thermometer, a stirrer, an addition funnel and a water condenser with a nitrogen gas inlet. The contents of the flask were mildly refluxed (≈35 °C) and 2,5-hexanediol (25.6 g, 0.217 mol) was slowly added during 2 h. The contents were stirred at about 35 °C for another 2 h and *n*-propyl chloride (35.5 g, 0.452 mol) and DMSO (165 g) were added separately from the addition funnel. The reaction mixture was refluxed for 4 d. During the course of the reaction, additional amounts of *n*-propyl chloride (5–8 g) and NaH (1–2 g) each were added periodically (ten times). The reaction mixture was cooled to ambient temperature and added carefully to moist ether (125 ml); and when all the residual NaH had completely reacted, treated carefully with water (350 ml). The organic layer was separated and the aqueous layer was extracted with diethyl ether (2 × 200 ml). The combined organic layer was washed with water (6 × 30 ml) and dried over anhydrous $MgSO_4$. Distillation yielded $[CH_3CH_2CH_2OCH(CH_3)CH_2]_2$, (38.5 g, b.p. 72 °C/2.0 mmHg). Yield 88% (based on the diol). MS (EI) m/z: 203 $(M+1)^+$. Anal. Calcd. for $C_{12}H_{26}O_2$: C, 71.23; H, 12.95%. Found: C, 71.70; H, 13.46%.

This precursor was subjected to direct fluorination by Exfluor Research Corporation. The product received was purified by distillation on a spinning band column to obtain pure **6**. Anal. Calcd. for $C_{12}F_{26}O_2$: C, 21.51; F, 72.72%. Found: C, 20.95; F, 70.25%. ^{19}F NMR, chemical shifts (ppm), reference, Freon-113: −78.81 and −79.14 (multiplet, 2CF_3 next to CF), −81.3 to −82.5 (2 overlapping AB patterns, 2 CF_2 between CF_2 and O), −82.08 (multiplet, 2 CF_3 next to CF_2), −119.0 to −123.0 (2 overlapping AB patterns, 2 CF_2 next to CF), −130.07 and −130.11 (doublet and unresolved doublet, 2 CF_2 between CF_3 and CF_2), −140.4 and −141.7 (quartet, doublet, 2 CF).

2.2. Mass spectra

The mass spectral data of all the model compounds studied as well as the degradation products observed are included below. Spectra were obtained in the chemical ionization mode with methane as the reagent gas unless otherwise indicated.

2.2.1. Model compounds

Compound 1, *m/z*: 401 $(M-F)^+$, 235 $(C_3F_7OCF_2)^+$ (100% RA), 185 $(C_3F_7O)^+$, 169 $(C_3F_7)^+$, 147 $(C_2F_5CO)^+$, 119 $(C_2F_5)^+$, 97 $(CF_3CO)^+$, 69 $(CF_3)^+$.

Compound 2, *m/z*: 451 $(M-F)^+$, 285 $(C_3F_7OC_2F_4)^+$, 185 $(C_3F_7O)^+$, 169 $(C_3F_7)^+$, 147 $(C_2F_5CO)^+$, 119 $(C_2F_5)^+$, 97 $(CF_3CO)^+$ (100% RA), 69 $(CF_3)^+$.

Compound 3, *m/z*: 501 $(M-F)^+$, 285 $(C_4F_9OCF_2)^+$ (100% RA), 219 $(C_4F_9)^+$, 181 $(C_4F_7)^+$, 169 $(C_3F_7)^+$, 131 $(C_3F_5)^+$, 100 $(C_2F_4)^+$, 69 $(CF_3)^+$.

Compound 4, *m/z*: 551 $(M-F)^+$, 385 $(C_3F_7OC_4F_8)^+$, 335 $(C_3F_7OC_3F_6)^+$, 235 $(C_3F_7OCF_2)^+$, 197 $(C_3F_7CO)^+$, 169 $(C_3F_7)^+$ (100% RA), 147 $(C_2F_5CO)^+$, 119 $(C_2F_5)^+$, 97 $(CF_3CO)^+$, 69 $(CF_3)^+$.

Compound 5, *m/z*: 551 $(M-F)^+$ (100% RA), 529, 385 $(C_3F_7OC_4F_8)^+$, 335 $(C_3F_7OC_3F_6)^+$, 235 $(C_3F_7OCF_2)^+$, 169 $(C_3F_7)^+$, 131 $(C_3F_5)^+$, 97 $(CF_3CO)^+$, 69 $(CF_3)^+$.

Compound 6, *m/z*: 651 $(M-F)^+$, 485 $(C_3F_7OC_6F_{12})^+$, 447 $(C_3F_7OC_6F_{10})^+$, 335 $(C_3F_7OC_3F_6)^+$, 319 $(C_6F_{13})^+$, 297 $(C_5F_{11}CO)^+$, 231 $(C_5F_9)^+$, 169 $(C_3F_7)^+$ (100% RA), 147 $(C_2F_5CO)^+$, 119 $(C_2F_5)^+$, 97 $(CF_3CO)^+$, 69 $(CF_3)^+$.

Compound 7, *m/z*: 751 $(M-F)^+$, 585 $(M-OC_3F_7)^+$, 419 $(C_8F_{17})^+$, 235 $(C_3F_7OCF_2)^+$ (100% RA), 169 $(C_3F_7)^+$.

Compound 9, (EI) *m/z* 519 $(M-F)^+$, 369 $(C_7F_{15})^+$, 269 $(C_5F_{11})^+$, 219 $(C_4F_9)^+$, 181 $(C_4F_7)^+$, 131 $(C_3F_5)^+$, 69 $(CF_3)^+$ (100% RA).

2.2.2. Degradation products

$CF_3CF_2CF_2OCF_3$, *m/z*: 235 $(M-F)^+$ (100% RA), 169 $(C_3F_7)^+$, 167 $(C_3F_6O+1)^+$, 147 $(C_3F_5O)^+$, 119 $(C_2F_5)^+$, 69 $(CF_3)^+$. [This compound had the same retention time as C_4F_{10} under the conditions of GC analysis.]

$CF_3CF_2CF_2OCF_2CF_3$, *m/z*: 285 $(M-F)^+$ (100% RA), 169 $(C_3F_7)^+$, 147 $(C_3F_5O)^+$, 119 $(C_2F_5)^+$, 117 $(C_2F_4O+H)^+$, 97 $(CF_3CO)^+$, 69 $(CF_3)^+$. [This compound had the same retention time as C_3F_6 under the conditions of GC analysis.]

Two isomers of C_6F_{14}, *(a)* *m/z*: 319 $(M-F)^+$, 181 $(C_4F_7)^+$ (100% RA), 69 $(CF_3)^+$. *(b)* *m/z*: 319 $(M-F)^+$ (100% RA), 181 $(C_4F_7)^+$, 69 $(CF_3)^+$. [Three additional ions seen in this spectrum of C_6F_{14} are attributed to $C_6F_{12}O$: 317 $(M+1)^+$, 297 $(M-F)^+$ and 231 $(297-COF_2)^+$.]

Two isomers of C_5F_{12}. The isomers were not well-separated. Both gave the following ions: *m/z*: 269 $(M-F)^+$ (100% RA), 181 $(C_4F_7)^+$, 131 $(C_3F_5)^+$, 119 $(C_2F_5)^+$, 69 $(CF_3)^+$. [Two additional ions seen in the spectra are attributed to $C_5F_{10}O$: 267 $(M+1)^+$, 247 $(M-F)^+$.]

C_4F_{10}, *m/z*: 219 $(M-F)^+$, 69 $(CF_3)^+$. [Also had additional ions attributed to C_4F_8O: 197 $(M-F)^+$ and 97 $(CF_3CO)^+$.]

C_4F_8. Two of four isomers were seen depending on the starting material and the temperature of degradation. The most prominent isomer in all degradations had *m/z*: 181 $(M-F)^+$ (100% RA) and 69 $(CF_3)^+$.

$CF_3CF_2CF_3$, *m/z*: 169 $(M-F)^+$ (100% RA), 119 $(C_2F_5)^+$, 100 $(C_2F_4)^+$ and 69 $(CF_3)^+$. [Showed additional ions at higher temperatures attributed to C_3F_6O: 147 $(M-F)^+$ and 97 $(CF_3CO)^+$.]

$CF_3CF{=}CF_2$. This was the most prominent degradation product in most degradations studied. *m/z*: 150 (M^+), 149 $(M-1)^+$ and 131 $(M-F)^+$ (100% RA).

CF_3CF_3, *m/z*: 119 $(C_2F_5)^+$, and 69 $(CF_3)^+$. [Showed a fragment at higher temperatures of degradation attributed to C_2F_4O: 97 $(CF_3CO)^+$ $(M-F)^+$.]

$CF_2{=}CF_2$, *m/z*: 101 $(M+1)^+$, 100 (M^+) (100% RA) and 69 $(CF_3)^+$.

In addition, a number of spectra showed the following ions: 85 $(M-F)^+$ attributed to SiF_4 and 71 $(CF_3H+1)^+$ probably formed by interaction of radicals formed, with the surface hydroxyl groups of quartz.

Initially, some degradation products were studied in the electron impact (EI) mode. All of these showed ions at 28 and 44 amu as background attributed to CO and CO_2.

3. Results and discussion

Thermal decomposition of the model compounds was studied at different temperatures, generally in 25–50 °C increments. The trend in decomposition at different temperatures is illustrated by taking compound **4** as an example. Fig. 1 shows the GC/MS total ion chromatogram (TIC) of **4** at (a) 750 °C, (b) 775 °C and (c) 875 °C. Under the experimental conditions used, the earliest sign of decomposition was observed at 750 °C for compound **4**. Three small peaks appeared in the TIC (a), with retention times between 4.4 and 5.0 min. These were identified by MS as $CF_2{=}CF_2$, 101 $(M+1)^+$, C_4F_{10}, 219 $(M-F)^+$ and $CF_3CF{=}CF_2$, 131 $(M-F)^+$. TIC (b) shows these three peaks in slightly higher intensities. The middle peak among the products due to C_4F_{10} (retention time ≈ 4.6 min) now also shows a fragment at 197 $(M-F)^+$ attributed to C_4F_8O. The peak with retention time of 4.77 min, due to $CF_3CF{=}CF_2$, now shows additional ions, 150 $(M)^+$ and 149 $(M-1)^+$. Further, in trace (b) another peak appears before $CF_2{=}CF_2$, which is attributed to $CF_3CF_2CF_3$, 169 $(M-F)^+$. At 875 °C (see TIC, c) the starting ether, **4**, has almost completely degraded. The most prominent product is $CF_3CF{=}CF_2$, while more products, as listed in Table 2, are formed. It is interesting to note that the concentration of all the decomposition products other than $CF_3CF{=}CF_2$ remains relatively low. One has to conclude that

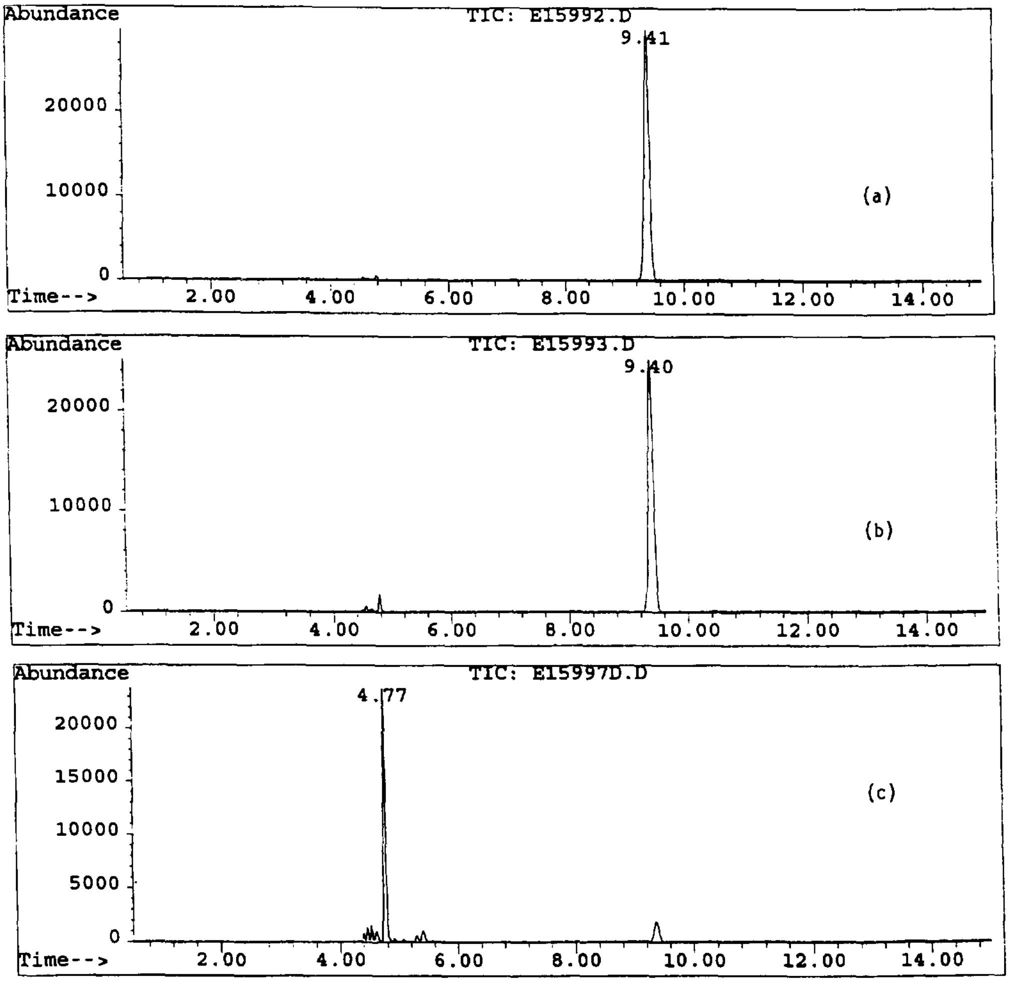


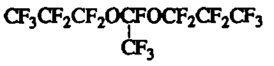
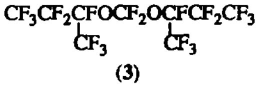
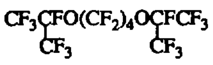
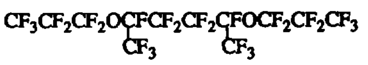
Fig. 1. GC/MS trace of the pyrolysis of compound **4** at (a) 725 °C, (b) 750 °C, and (c) 875 °C.

$CF_3CF{=}CF_2$ has the highest thermodynamic stability of all the products formed in these decompositions. Similar products were formed in the degradation of all the perfluoroethers studied. However, compounds **1** and **2** gave, in addition, $CF_3CF_2CF_2OCF_3$ and $CF_3CF_2CF_2OCF_2CF_3$, respectively. These lower-molecular weight ethers are obviously formed due to the fission of one of the C–O bonds in **1** and **2**. The radical formed can then abstract a fluorine atom giving rise to the products.

It is interesting to speculate why compounds **1** and **2** alone give identifiable low-molecular weight ethers. The most obvious reason is perhaps the higher stability of these two product ethers compared to the stability of similar ethers that would be formed from compounds **3–6**. It is known that a C–O bond is often more stable than a C–C bond in fluorinated compounds. The C–O bond dissociation energy in CF_3OCF_3 is reported to be 105.2 kcal mol^{-1} compared to 98.7 kcal mol^{-1} for the C–C bond in CF_3CF_3. Further, poly(CF_2CF_2O) decomposes at about a tenth the rate of poly(CF_2CF_2) at 585 °C [23]. Thus, under the conditions studied, at least some of the C–C bonds may undergo fission before, or together with, C–O bond fission. The resulting products could undergo further degradation depending on their stability. Regarding the stability of perfluorocarbons, which is limited only by the strengths of their C–C bonds, it has been suggested that the stability decreases with increasing chain branching as well as chain length [18–20,23]. The two low-molecular weight ethers $CF_3CF_2CF_2OCF_3$ and $CF_3CF_2CF_2OCF_2CF_3$, detected in the decomposition of compounds **1** and **2**, have a maximum of three adjacent carbon atoms. Similar ethers produced by the scission of a single C–O bond in metal compounds **3–6** would all contain more than three adjacent carbon atoms. The resulting lower stability due to increased chain length in the ether formed from compound **4**, and due to chain branching in ethers from compounds **3**, **5** and **6**, might explain why no such ethers could be detected in the degradation of model compounds **3–6**.

Thermal decomposition is a free-radical process, and a linear fluorocarbon free radical can undergo recombination, elimination of F· or $CF_3\cdot$ leading to olefins, and rearrangements. It has been suggested that it can also decompose by elimination of CF_2 units [24]. Two such units can combine to give $CF_2{=}CF_2$ which can combine with another CF_2 to form $CF_3CF{=}CF_2$ [25]. In the presence of radical trap like toluene or H, the corresponding hydrides are formed. In order to understand the nature of free radicals formed during pyrol-

Table 2
Thermal degradation products of PFPAE model compounds (identified by GC/MS in chemical ionization mode using methane as the reagent gas)

Perfluoro compound	Degradation products	
	Initial products	Additional products detected at higher temperatures
$CF_3CF_2CF_2OCF_2OCF_2CF_2CF_3$ (1)	$CF_3CF{=}CF_2$ [a] $CF_3CF_2CF_2OCF_3$ [c] $CF_2{=}CF_2$	C_2F_6, C_3F_8, C_4F_{10}, $CF_3C(O)F$ C_4F_8O Isomers of C_4F_8 [b,d]
 $CF_3CF_2CF_2O\underset{CF_3}{CF}OCF_2CF_2CF_3$ (2)	{$CF_3CF_2CF_2OCF_2CF_3$ + probably $CF_3CF{=}CF_2$} [a,e]	$CF_2{=}CF_2$, C_4F_{10}, C_3F_8, C_4F_8O C_2F_6, $CF_3C(O)F$, isomers of C_4F_8 [b,d]
 $CF_3CF_2\underset{CF_3}{CF}OCF_2O\underset{CF_3}{CF}CF_2CF_3$ (3)	$CF_3CF{=}CF_2$ [a]	C_3F_8, C_4F_{10} C_2F_6, $CF_2{=}CF_2$, Isomers of C_5F_{12} and C_4F_8 [b,d] C_4F_8O [f], $CF_3C(O)F$ [f]
$CF_3CF_2CF_2O(CF_2)_4OCF_2CF_2CF_3$ (4)	$CF_3CF{=}CF_2$ [a] $CF_2{=}CF_2$ C_4F_{10}	C_2F_6, C_3F_8, $CF_3C(O)F$ C_3F_6O, C_4F_8O Isomers of C_4F_8
 $CF_3\underset{CF_3}{CF}O(CF_2)_4O\underset{CF_3}{CF}CF_3$ (5)	$CF_3CF{=}CF_2$ [a] $CF_2{=}CF_2$ C_4F_{10}, C_4F_8O	C_2F_6, C_3F_8, $CF_3C(O)F$ C_3F_6O, Isomers of C_4F_8 [b,d] C_5F_{12}, $C_5F_{10}O$
 $CF_3CF_2CF_2O\underset{CF_3}{CF}CF_2CF_2\underset{CF_3}{CF}OCF_2CF_2CF_3$ (6)	$CF_3CF{=}CF_2$ [a] $CF_2{=}CF_2$ [b]	C_4F_{10} [c], C_4F_{10}, C_4F_8O C_5F_{12}, C_6F_{14}, C_3F_8 $C_5F_{10}O$ [f], $C_6F_{12}O$ [f]

[a,b,c] The major products in decreasing order of their prominence.
[d] One of the isomers with a retention time of 5.4 min was the most prominent among all C_4F_8.
[e] These two compounds have identical retention time under the conditions of separation.
[f] These oxygenated products are seen only towards the end of degradation.

ysis, a mixture of toluene and model compounds **4**, **5**, and **6** were individually pyrolyzed at 825 °C, 775 °C, and 725 °C, respectively. The concentration of the most prominent product $CF_3CF{=}CF_2$ had substantially decreased in all these pyrolyses conducted in the presence of toluene. All three compounds gave products corresponding to $CF_3\cdot$, $CF_3CF_2\cdot$ and $C_3F_7\cdot$ radicals. Compound **5** also gave $(CF_3)_2CFOCF_2CF_2H$ [m/z: 267 $(M-F)^+$ (100%), 167 $(M-C_2F_5)^+$, and 101 $(C_2F_4+1)^+$] as well as $(CF_3)_2CFOCF_2CF_2CF_2H$ [m/z: 317 $(M-F)^+$ and 71 $(CF_3H+1)^+$]. Formation of these two hydrogen-containing fluoroethers might suggest elimination of CF_2 units from the initial radical formed, but we were unable to detect CF_2H_2 as one of the products in these degradations.

The relative thermal stability of perfluoroethers **1–6**, as well as another ether with eight carbon atoms in between oxygen atoms (compound **7**) and two fluorocarbons (**8** and **9**), was also determined. As indicated in the experimental part, the decompositions were studied at identical residence times for comparison. A flame ionization detector was used in the gas chromatograph, and the amounts of the model compounds consumed were determined by external standardization. Fig. 2(a) and (b) shows the standardization plots which show reasonable linearity. The maximum scatter was observed for compound **2**. The amounts of the compound consumed in each degradation was determined from the GC peak area using these plots. Fig. 3(a) and (b) shows the concentration of model compounds at different temperatures. From these plots the temperature at which 50% of the material decomposed ($T_{1/2}$ °C) was determined. These values are included in Table 1. Although these values are higher than the true decomposition temperatures, due to the short residence time of these compounds in the pyrolyzer, they do provide a means for comparing the relative stability of a series of compounds. The first three compounds in Table 1 (**1–3**) contain the –O–C–O– grouping. Compound **1**, which is linear, shows the highest thermal stability among all the compounds studied. However our preliminary studies on the catalytic degradation of these –O–C–O– containing compounds, which will be published later, show that such compounds have much lower stability in the presence of FeF_3. This has also been observed in a study of polymeric materials such as Fomblin Z which contain the –O–C–O– group. Compounds **4–6** have four-carbon chains between the two ether oxygen atoms.

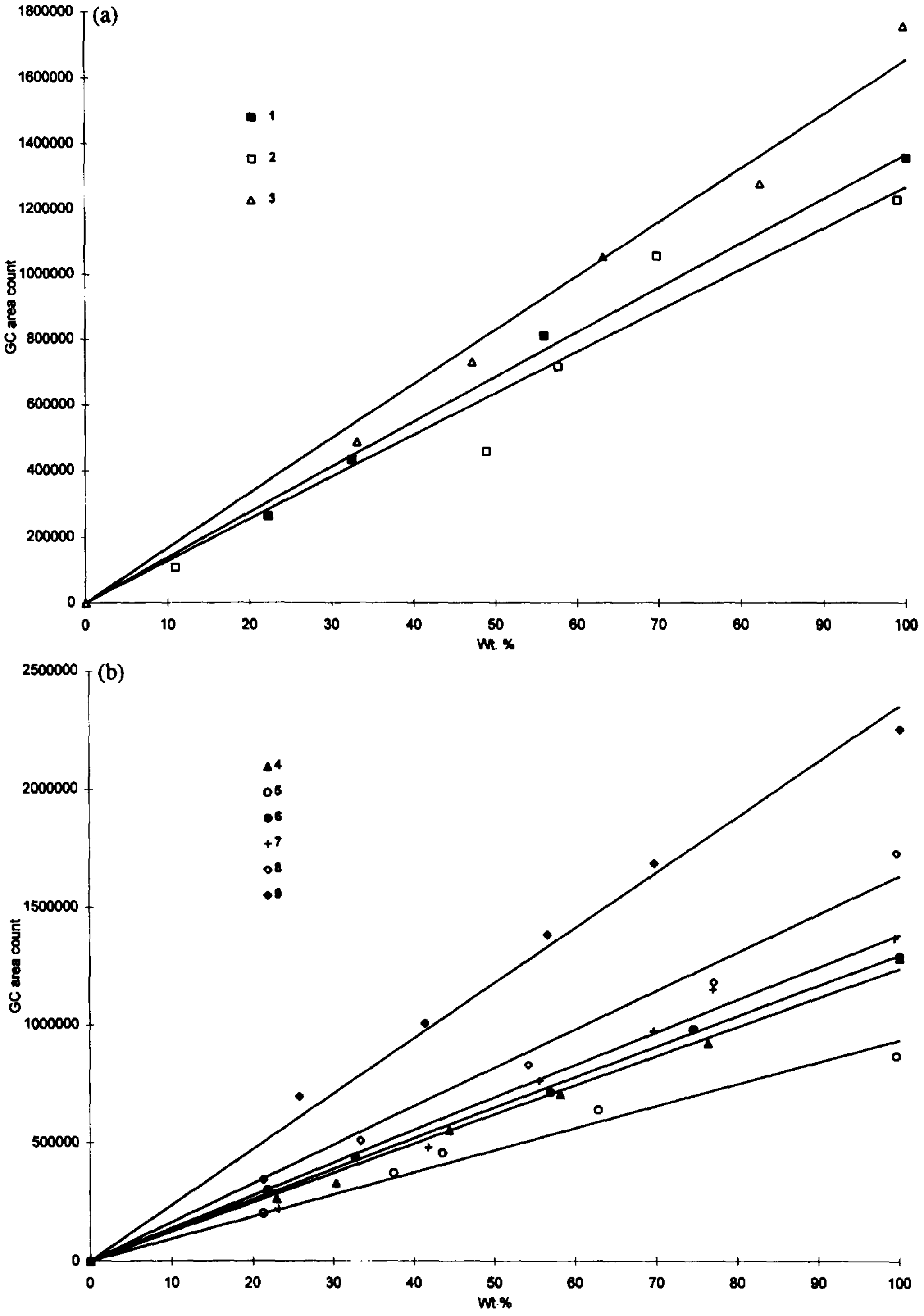


Fig. 2. (a) External standardization plots of compounds **1**–**3**. (b) External standardization plots of compounds **4**–**9**.

Some general conclusions can be made from the data in Table 1. For instance, the linear ethers are more stable than comparable branched ethers. This is seen from the $T_{1/2}$ value of **1** when compared to those of **2** and **3** and also from the $T_{1/2}$ value of **4** when compared to those of **5** and **6**. However, it may be noted that the difference between the $T_{1/2}$ values of **4** and **5** is not significant. Ethers in general are more stable than fluorocarbons of comparable structures. For instance, one can compare structures **4** and **8** and also **5** and **9**. As pointed out earlier, reduced thermal stability with increased branching as well as increased chain length has been reported in fluorocarbons. Our studies suggest that the same is true in perfluoroalkylethers. Thermal stability of perfluoroalkylethers decreases with increasing number of adjacent carbon atoms, and branching of the carbon chains contributes to additional instability.

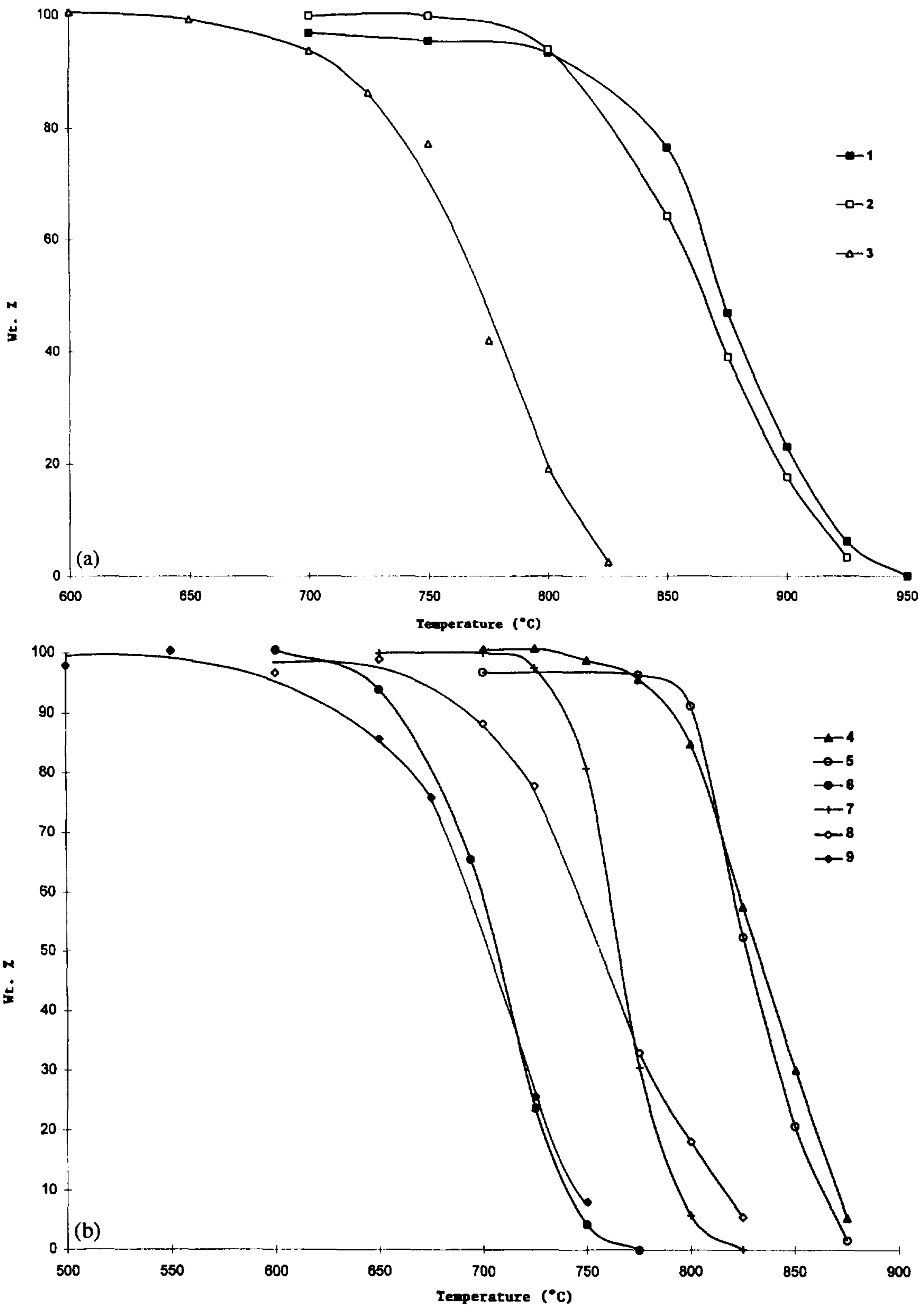


Fig. 3. (a) Percentage of undecomposed model compounds 1-3 at different temperatures. (b) Percentage of undecomposed model compounds 4-9 at different temperatures.

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