Anal. Chem. **2004,** *76,* 3800−3803

Gas-Phase NMR Technique for Studying the Thermolysis of Materials: Thermal Decomposition of Ammonium Perfluorooctanoate

Paul J. Krusic and D. Christopher Roe*

Central Research and Development, E. I. Du Pont de Nemours & Company, Wilmington, Delaware 19880-0328

The kinetics of the thermal decomposition of ammonium perfluorooctanoate (APFO) has been studied by high-temperature gas-phase nuclear magnetic resonance spectroscopy over the temperature range 196−234 °C. We find that APFO cleanly decomposes by first-order kinetics to give the hydrofluorocarbon 1-H-perfluoroheptane and is completely decomposed (>99%) in a matter of minutes at the upper limit of this temperature range. Based on the temperature dependence of the measured rate constants, we find that the enthalpy and entropy of activation are $\Delta H^{\ddagger} = 150 \pm 11$ kJ mol^{-1} and $\Delta S^{\ddagger} = 3 \pm 23$ J mol^{-1} deg^{-1}. These activation parameters may be used to calculate the rate of APFO decomposition at the elevated temperatures (350−400 °C) at which fluoropolymers are processed; for example, at 350 °C the half-life for APFO is estimated to be less than 0.2 s. Our studies provide the fundamental parameters involved in the decomposition of the ammonium salt of perfluorooctanoic acid and indicate the utility of gas-phase NMR for thermolysis studies of a variety of materials that release compounds that are volatile at the temperature of decomposition and that contain an NMR-active nucleus.

Certain perfluorinated surfactant anions such as perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) have become an environmental concern because they are widely distributed in trace quantities and persist in the environment.[1] Low but measurable amounts of PFOS have been detected in samples obtained from wildlife in remote marine locations such as the Arctic and North Pacific Oceans and at higher levels from more urbanized areas in North America and Europe.[2,3] PFOA and PFOS have been detected and quantified in groundwater contaminated by fire-fighting foams at a number of fire-training areas.[4,5] The occurrence of perfluorinated surfactants in fire-training areas is due to the role of these surfactants in aqueous film forming foams[6] and is environmentally significant because the measurements were conducted after 5 or more years of inactivity at these sites. PFOS and PFOA have also been detected and quantified in surface water collected from the Tennessee River near a fluorochemical manufacturing site,[7] and it was suggested that the effluent from this site was a likely source of organic fluorochemicals in the river.

Ammonium perfluorooctanoate (APFO) is the carboxylate surfactant most commonly used as a processing aid in the production of fluoropolymers and fluoroelastomers.[8] For most commercial products, fluoropolymers are heated in excess of 350 °C, and often above 400 °C, to allow melt processing or sintering of the resin particles.[8] Because of this high-temperature processing of fluoropolymers, it is relevant to understand the rates of thermal decomposition of APFO at these elevated temperatures.[9−11]

APFO is unique among the salts of PFOA in being the most thermally unstable.[12] This result parallels the work of LaZerte et al. on the thermal stability of perfluorobutanoate salts.[13] The latter workers also established that ammonium perfluorobutanoate was unique in providing nearly stoichiometric yields of the hydrofluorocarbon 1-H-perfluoropropane ($CF_3CF_2CF_2H$), whereas the sodium and potassium salts gave high yields of the olefin perfluoropropene ($CF_3CF{=}CF_2$), and other salts gave the olefin along with carbonyl-containing compounds. These studies[12,13] give a sense of the thermal stability of the perfluorocarboxylate salts but say nothing about the kinetics of their thermal decomposition. In view of the high-temperature processing that is used for fluoropolymers that are made using APFO, we have investigated the kinetics of thermal decomposition of this surfactant using high-temperature gas-phase NMR.

Although gas-phase NMR is well established for physical studies,[14] it has been frequently overlooked by chemists as a tool

---

* Corresponding author. Phone: (302)695-3593. Fax: (302)695-9799. E-mail: chris.roe@usa.dupont.com.

(1) Schultz, M. M.; Barofsky, D. F.; Field, J. A. *Environ. Eng. Sci.* **2003**, *20*, 487−501.

(2) Giesy, J. P.; Kannan, K. *Environ. Sci. Technol.* **2001**, *35*, 1339−1342.

(3) Kannan, K.; Koistinen, J.; Beckmen, K.; Evans, T.; Gorzelany, J. F.; Hansen, K. J.; Jones, P. D.; Helle, E.; Nyman, M.: Giesy, J. P. *Environ. Sci. Technol.* **2001**, *35*, 1593−1598.

(4) Moody, C. A.; Field, J. A. *Environ. Sci. Technol.* **1999**, *33*, 2800−2806.

(5) Moody, C. A.; Hebert, G. N.; Strauss, S. H.; Field, J. A. *J. Environ. Monit.* **2003**, *5*, 341−345.

(6) Moody, C. A.; Field, J. A. *Environ. Sci. Technol.* **2000**, *34*, 3864−3870.

(7) Hansen, K. J.; Johnson, H. O.; Eldridge, J. S.; Butenhoff, J. L.; Dick, L. A. *Environ. Sci. Technol.* **2002**, *36*, 1681−1685.

(8) Kissa, E. *Fluorinated Surfactants and Repellents*, 2nd ed.; Marcel Dekker: New York, 2001.

(9) Scheirs, J. *Modern Fluoropolymers: High Performance Polymers for Diverse Applications*; Wiley: New York, 1997.

(10) Ebnesajjad, S. *Non-Melt Processible Fluoroplastics: The Definitive User's Guide and Databook*; PDL: New York, 2000.

(11) Ebnesajjad, S. *Melt Processible Fluoroplastics: The Definitive User's Guide and Databook*; PDL: New York, 2003.

(12) Lines, D.; Sutcliffe, H. *J. Fluorine Chem.* **1984**, *25*, 505−512.

(13) LaZerte, J. D.; Hals, L. J.; Reid, T. S.; Smith, G. H. *J. Am. Chem. Soc.* **1953**, *75*, 4525−4528.

(14) LeMaster, C. B. *Prog. Nucl. Magn. Reson. Spectrosc.* **1997**, *31*, 119−154.

10.1021/ac049667k CCC: $27.50

to study gas-phase reactions. Recent studies have shown that it is a powerful tool for quantitative kinetic studies of homogeneous[15,16] and heterogeneously catalyzed chemical processes[17,18] in the vapor phase at temperatures up to 400 °C. We have previously demonstrated that this technique can be applied to a variety of organofluorine reactions[15,16] and have shown that when compared with other techniques, such as gas chromatography, NMR has advantages for such studies in that the observed peaks provide structural information in addition to molar concentrations, all the volatile organofluorine species may be observed, and the data are acquired in situ. Furthermore, the automation of modern NMR spectrometers makes acquisition and processing of kinetic data very efficient and cost-effective.

EXPERIMENTAL SECTION

Standards and Reagents. Commercial grade APFO (Fluorad FC-143, >90% purity) containing small amounts of branched isomers was obtained from 3M Company. Linear APFO was prepared by treating linear PFOA (Lancaster Synthesis Inc.) with ammonium hydroxide in diethyl ether, and the APFO product was further recrystallized to yield the final sample. APFO was dried in a vacuum oven and kept in a nitrogen glovebox. 1-H-Perfluoroheptane (1-H-pentadecafluoroheptane) was purchased from Lancaster Synthesis Inc., and tetrafluoromethane was prepared in our laboratories.

High-Temperature Gas-Phase Nuclear Magnetic Resonance (NMR) Spectroscopy. The detailed features of the experimental approach have been presented previously[15−18] and are summarized here. The reaction vessel consists of a 10 mm o.d. glass ampule of about 4 mL internal volume (after sealing) with a 5 mm o.d. extension to facilitate attachment to a vacuum system. The length of the ampule was chosen so as to restrict the sample to the thermostated region of the NMR probe and to minimize temperature gradients. Micromolar quantities of solids or liquids to be studied are weighed into the ampule, and any gases involved, such as CF_4 which serves as a chemical shift and mass reference, are transferred via quantitative vacuum line techniques prior to sealing the ampule with a torch. Kinetic runs are performed by equilibrating the NMR probe at the desired temperature, and upon sample insertion, automated data acquisition is begun according to a schedule compatible with the kinetic time scale involved. The fastest kinetics which may be observed (i.e., the highest temperatures employed) is limited by the time required for the sample to reach thermal equilibrium, which is less than two minutes. First-order reactions with half-life times approaching 1 min are the fastest that can be studied kinetically by this technique.

The ^{19}F NMR spectra were obtained using a 300 MHz widebore Oxford magnet (^{19}F at 282.538 MHz) and a GE NMR Instruments Omega console. The high-temperature 10 mm probe and variable temperature (VT) controller have an upper temperature rating of 400 °C and were purchased from Nalorac Corporation. A small flip-angle pulse was used (≈15°) in order to achieve relatively uniform excitation over the wide ^{19}F NMR spectral range. Since ^{19}F spin-rotation relaxation is very efficient in the gas phase, 50 ms recycle delays were appropriate and permitted rapid signal averaging (e.g., 512 scans in less than 1 min). For the same reason, the NMR lines are broader in the gas phase than in solution and magnetic field homogeneity is less critical than for solution NMR; consequently no field lock was used and the ampule was not spun. ^{19}F chemical shifts were measured relative to CF_4 at −63.5 ppm on the $CFCl_3$ (F11) scale.

Thermal losses in the probe necessarily lead to sample temperatures that are lower than the variable temperature (VT) controller set point. Temperature calibration was performed with a thin thermocouple positioned in the center of a dummy ampule identical to those used for the actual kinetic runs except for a small hole at the end of the 5 mm stub. The internal temperature in the ampule depends on the flow rates of the nitrogen gas whose temperature is being regulated by the VT controller and on that used for cooling of the peripheral space around the probe dewar. For the flow rates used in this work, T_{delta} (°C) $= 8.39 - 0.0609 \times T_{\mathrm{set}}$ (°C) where T_{delta} is the difference between the VT controller set point T_{set} and the temperature measured with the thermocouple in the center of the dummy ampule. Corrected temperatures are used in this work and were also used in the calculation of the kinetic activation parameters for APFO.

The gas-phase NMR ampules (sodium borosilicate glass), made from sections of standard thin wall 10 mm o.d. NMR tubing, were kept in a vacuum oven before use. In a nitrogen glovebox the desired milligram quantity of dry solids was introduced into the ampule through its 5 mm o.d. neck. An O-ring vacuum adapter was attached to the neck, and the ampule was transferred to a vacuum line equipped with a precision pressure transducer. After evacuation, micromolar amounts of CF_4 internal standard were condensed from a bulb of known volume into the ampule by keeping the latter immersed in liquid nitrogen. After sealing the neck with a propane torch, the ampule was attached to a sample holder by means of a short piece of plastic sleeve (Figure S-1). With the NMR probe at the desired temperature, the tube assembly was lowered into the probe and the automatic acquisition of spectra started. Because of the low heat capacity of the loaded ampule, temperature equilibration took place in about two minutes, representing a kinetic dead time.

RESULTS AND DISCUSSION

As anticipated from the work of Lines and Sutcliffe (see Figure 1 in ref 12), we find that the kinetics of decomposition of APFO can be followed at temperatures near 200 °C. In our preliminary kinetic studies, we used the commercial grade APFO (FC-143) that was widely used industrially for decades. Because of the electrochemical process used for its manufacture, FC-143 necessarily contains small amounts of branched isomers. Typical samples consisted of 67 mg of FC-143 (156 μmol) along with 79 μmol of the CF_4 internal reference. At temperatures below 190 °C, the only gas-phase NMR signal observed is that of the CF_4 internal reference since the ammonium salt has insufficient vapor pressure for NMR detection at this temperature. However, at 196 °C new NMR lines grow in (Figure 1A), where the major product (approximately 90−95%) is linear 1-H-perfluoroheptane, as anticipated by analogy with the product of ammonium perfluorobutanoate decomposition.[13] The identity of this product may be

---

(15) Krusic, P. J.; Roe, D. C.; Smart, B. E. *Isr. J. Chem.* **1999**, *39*, 117−123.

(16) Shtarov, A. B.; Krusic, P. J.; Smart, B. E.; Dolbier, W. R., Jr. *J. Am. Chem. Soc.* **2001**, *123*, 9956−9962.

(17) Kating, P. M.; Krusic, P. J.; Roe, D. C.; Smart, B. E. *J. Am. Chem. Soc.* **1996**, *118*, 10000−10001.

(18) Roe, D. C.; Kating, P. M.; Krusic, P. J.; Smart, B. E. *Top. Catal.* **1998**, *5*, 133−147.

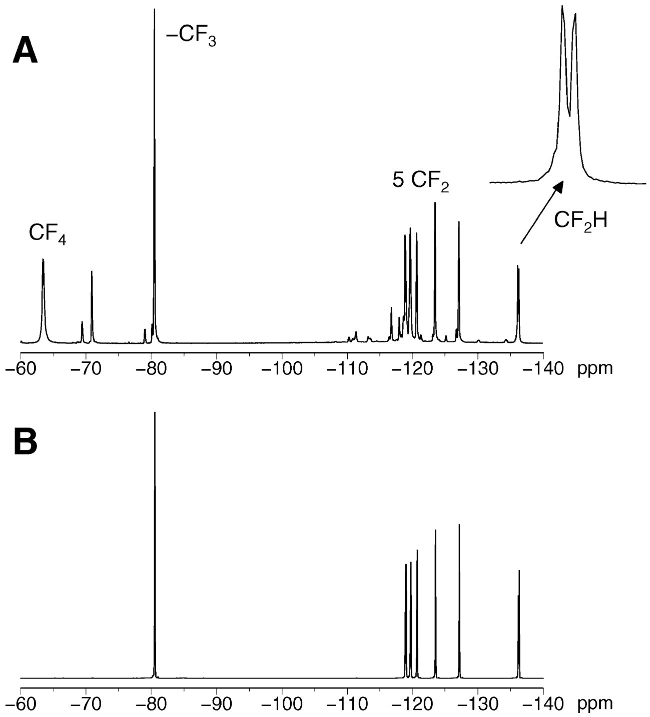

Figure 1. (A) Gas-phase ^{19}F NMR spectrum of 1-H-perfluoroheptane (and CF_4 reference) evolved in the thermolysis of commercial APFO (FC-143) at 196 °C. The more intense CF_3 and CF_2 resonances are from the linear 1-H-perfluoroheptane, and the characteristic $-CF_2H$ resonance is displayed in the right expansion. Minor NMR lines belong to the branched isomers of 1-H-perfluoroheptane. (B) Gas-phase ^{19}F NMR spectrum of authentic linear 1-H-perfluoroheptane at 196 °C.

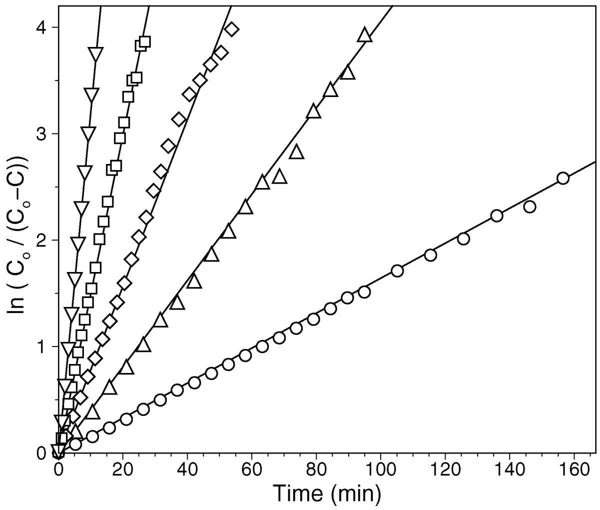

Figure 2. First-order kinetic plot for the production of 1-H-perfluoroheptane corresponding to the loss of APFO at 196 °C (circle), 206 °C (triangle up), 215 °C (diamond), 224 °C (square), and 234 °C (triangle down).

judged by the characteristic doublet of the terminal $-CF_2H$ fluorine resonance at −135.8 ppm due to the 2-bond $^1H-^{19}F$ coupling constant of 52.3 Hz (Figure 1A, right inset) and by comparison with the gas-phase NMR spectrum for authentic linear 1-H-perfluoroheptane obtained under similar conditions (Figure 1B).

Also visible in the spectrum of Figure 1A are some small peaks that are attributed to the branched isomers of 1-H-perfluoroheptane. No peaks other than those attributed to the linear and branched isomers of 1-H-perfluoroheptane (and the CF_4 internal standard) are observed. The most significant of these minor peaks is the CF_3 resonance at −71.1 ppm which may reasonably be assigned to the terminal (magnetically equivalent) CF_3's of 1-H-5-trifluoromethylperfluorohexane ($(CF_3)_2CFCF_2CF_2CF_2CF_2H$) by comparison with the CF_3 chemical shift reported for this compound in deuterioacetone solvent[19] using trifluoroacetic acid (TFA) as an external chemical shift reference. If the chemical shift of TFA relative to F11 is taken to be −78.5 ppm,[20] the CF_3 chemical shift for 1-H-5-trifluoromethylperfluorohexane in deuterioacetone solvent may be estimated as −74.5 ppm, in fair agreement with our measurements relative to F11. Exact agreement cannot be expected considering the changes in NMR chemical shifts in going from liquid phase to vapor phase. Four methine CF resonances are observed in the region −182 to −188 ppm (data not shown), and of these four, the most intense signal at −182.9 ppm is assigned to 1-H-5-trifluoromethylperfluorohexane. The occurrence of other methine CF resonances (−182.0, −183.7, and −186.8 ppm, data not shown) and CF_3 resonances (−69.5, −79.1, and −80.2 ppm, Figure 1A) is consistent with the presence of additional branched isomers, as is the observation that the methine and branched CF_3 peaks are completely absent in the sample of linear APFO derived from linear PFOA.

The rate of appearance of the distinct CF_3 signals belonging to the branched isomers of 1-H-perfluoroheptane occurs by first-order kinetics and is in each case within ≈10% of the rate of appearance of the fluorine resonances belonging to linear 1-H-perfluoroheptane (Figure S-2). Integration over all the 1-H-perfluoroheptane fluorine resonances after 168 min at 196 °C, and comparison with the integral for the CF_4 mass standard, indicates that 88% conversion of the starting APFO has taken place. Since the formation of linear and branched 1-H-perfluoroheptane is not yet complete at this point in the kinetics (Figure S-2), we conclude (i) that the thermal decomposition of FC-143 goes to completion with the formation of linear 1-H-perfluoroheptane, CO_2 and NH_3 (eq 1) together with minor amounts of branched isomers and (ii) that its rate of decomposition can be determined by following the rate of formation of 1-H-perfluoroheptane.

$$CF_3(CF_2)_5CF_2CO_2NH_4 \xrightarrow{k_1} CF_3(CF_2)_5CF_2H + CO_2 + NH_3 \tag{1}$$

The kinetics of the thermal decomposition of pure linear APFO (68 mg) was subsequently studied in the temperature range from 196 °C to 234 °C by following the formation of linear 1-H-perfluoroheptane as described above. The formation of the latter, and consequently the disappearance of APFO, follows rigorously first-order kinetics as indicated by the linearity of the curves in the logarithmic plot shown in Figure 2. The rate constants k_1 at each temperature were obtained by directly fitting the single-exponential growth of 1-H-perfluoroheptane and are presented in Table 1 together with the calculated half-lives ($t_{1/2} = \ln(2)/k_1 =$

---

(19) Yu Huai-Gen *Youji Huaxue (Organic Chemistry)* **1990**, *10*, 517−520.

(20) Berger, S.; Braun, S.; Kalinowski, H.-O. *NMR Spectroscopy of the Non-Metallic Elements*; John Wiley & Sons: New York, 1997.

Table 1. Rate Constants for Decay (and Half-Lives) of Linear APFO as a Function of Temperature as Measured by the Formation of 1-H-Perfluoroheptane

temp (°C)	k_1 (min^{-1})^a	$t_{1/2}$ (min)^a
196	0.0158 (0.0002)	43.8 (0.66)
206	0.0388 (0.0007)	17.8 (0.32)
215	0.0787 (0.0020)	8.8 (0.22)
224	0.152 (0.0028)	4.6 (0.08)
234	0.312 (0.0101)	2.2 (0.07)

[a] Numbers in parentheses refer to ±95% confidence limits.

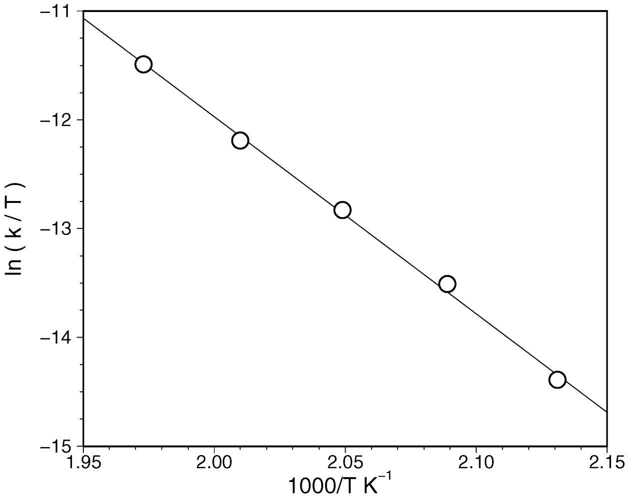

Figure 3. Eyring plot for the temperature dependence of the first-order rate constants for the decomposition of APFO.

$0.693/k_1$). The value for k_1 obtained at 196 °C from the linear APFO component in the commercial FC-143 sample described above was within 11% of that reported in Table 1 for the linear APFO derived from linear PFOA.

The data in Table 1 are well described by the transition state (Eyring) treatment of the temperature dependence of reaction rate constants[21] as judged by the linearity of the corresponding Eyring plot in Figure 3. The activation enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) were determined by direct nonlinear least-squares fitting[22] of these parameters to the Eyring equation ($k_1 = (k_BT/h)\ \exp(\Delta S^{\ddagger}/R)\ \exp(-\Delta H^{\ddagger}/RT)$) using the temperature and rate constant data in Table 1 (k_1 converted to units of s^{-1} and T to absolute temperature (K); k_B is Boltzmann's constant, h is Planck's constant, and R is the universal gas constant). This fitting procedure gave the parameter estimates $\Delta H^{\ddagger} = 150 \pm 11$ kJ mol^{-1} and $\Delta S^{\ddagger} = 3 \pm 23$ J mol^{-1} deg^{-1} (the corresponding Arrhenius parameters are $E_a = 154 \pm 11$ kJ mol^{-1} and $\log(A/s^{-1}) = 13.6 \pm 1.2$). The stated uncertainties represent 95% confidence limits and were obtained using an estimated error in the rate constants of 10% and an estimated error in temperature of 2 °C. The major sources of error in these parameter estimates are the uncertainty in the temperature and the relatively narrow temperature range in which the rate constants can be measured; the latter limitation in particular contributes to the relatively large error in the entropy of activation. In accord with the first-order nature of the decomposition, similar results were obtained with 32 mg of APFO, and the activation parameters obtained from the latter experiments are essentially identical to those just presented.

The activation parameters obtained above may be used in the Eyring equation to calculate the rate of APFO decomposition at temperatures where the rate would be too fast to measure by gas-phase NMR. For example, at the elevated temperatures specified to process fluoropolymers, the half-lives for APFO are extrapolated to be 0.14 (+0.11, −0.06) s at 350 °C and 0.015 (+0.017, −0.008) s at 400 °C. At a given temperature, the extrapolated half-life is associated with uneven 95% confidence limits (given in parentheses) because of the exponential temperature dependence of the rate constant.

In an attempt to simulate the effect of steam on the thermolysis of APFO, we also studied the kinetics of thermal decomposition of linear APFO (32 mg) in the presence of a 10-fold molar excess of water (13 μL), after ensuring that the glass ampules withstood the increased internal pressure at the temperatures needed for decomposition. No hydrolysis of APFO to perfluorooctanoic acid was observed in the vapor phase, and the observed rates were not affected strongly by the excess of water. The kinetic data are well represented by the Eyring parameters $\Delta H^{\ddagger} = 167 \pm 6$ kJ mol^{-1} and $\Delta S^{\ddagger} = 38 \pm 12$ J mol^{-1} deg^{-1} ($E_a = 172 \pm 6$ kJ mol^{-1} and $\log(A/s^{-1}) = 15.4 \pm 0.6$). The net effect of these changes is to make the rates of decomposition of APFO in the presence of steam slightly higher above 200 °C and slightly lower below 200 °C compared to APFO in the absence of steam. Under these conditions, the half-lives and 95% confidence limits for APFO are extrapolated to be 0.060 (+0.020, −0.015) s at 350 °C and 0.005 (+0.002, −0.001) s at 400 °C.

CONCLUSIONS

The experiments described above demonstrate that ammonium perfluorooctanoate decomposes rapidly at the elevated temperatures which are most often used to melt process or sinter fluoropolymers. Our studies provide the fundamental parameters involved in the decomposition of APFO and illustrate the utility of gas-phase NMR for studying the thermal behavior of fluorochemicals.[23]

ACKNOWLEDGMENT

We are grateful to Dr. Ming H. Hung for supplying a sample of linear ammonium perfluorooctanoate and for useful advice, to Dr. Bruce E. Smart for insightful discussions, to Alexander A. Marchione and Rita S. McMinn for valuable technical assistance, and to Steve A. Hill for skillful and dedicated experimental work.

SUPPORTING INFORMATION AVAILABLE

Diagram of the gas-phase NMR ampule attached to a vacuum system before being sealed off with a propane torch (Figure S-1) and kinetics of formation of both linear and branched 1-H-perfluoroheptane from the thermolysis of commercial APFO (Figure S-2). This material is available free of charge via the Internet at http://pubs.acs.org.

Received for review March 2, 2004. Accepted April 1, 2004.

AC049667K

---

(21) Marshall, A. G. *Biophysical Chemistry*; John Wiley & Sons: New York, 1978.

(22) Conway, G. R.; Glass, N. R.; Wilcox, J. C. *Ecology* **1970**, *51*, 503−507.

(23) Ellis, D. A.; Martin, J. W.; Muir, D. C. G.; Mabury, S. A. *The Analyst* **2003**, *128*, 756−764.