J. Phys. Chem. A **2005,** *109,* 1849−1856

Atmospheric Chemistry of 4:2 Fluorotelomer Alcohol (n-$C_4F_9CH_2CH_2OH$): Products and Mechanism of Cl Atom Initiated Oxidation in the Presence of NO_x

M. P. Sulbaek Andersen and O. J. Nielsen

Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

M. D. Hurley, J. C. Ball, and T. J. Wallington*

Ford Motor Company, SRL-3083, PO Box 2053, Dearborn, Michigan 48121-2053

D. A. Ellis, J. W. Martin, and S. A. Mabury

Department of Chemistry, 80 St. George Street, University of Toronto, Toronto, Ontario, Canada M5S 3H6

Received: September 23, 2004; In Final Form: January 3, 2005

Smog chamber/FTIR techniques were used to study the Cl atom initiated oxidation of 4:2 fluorotelomer alcohol ($C_4F_9CH_2CH_2OH$, 4:2 FTOH) in the presence of NO_x in 700 Torr of N_2/O_2 diluent at 296 K. Chemical activation effects play an important role in the atmospheric chemistry of the peroxy, and possibly the alkoxy, radicals derived from 4:2 FTOH. Cl atoms react with $C_4F_9CH_2CH_2OH$ to give $C_4F_9CH_2C^{\bullet}HOH$ radicals which add O_2 to give chemically activated α-hydroxyperoxy radicals, $[C_4F_9CH_2C(OO^{\bullet})HOH]^*$. In 700 Torr of N_2/O_2 at 296 K, approximately 50% of the $[C_4F_9CH_2C(OO^{\bullet})HOH]^*$ radicals decompose "promptly" to give HO_2 radicals and $C_4F_9CH_2CHO$, the remaining $[C_4F_9CH_2C(OO^{\bullet})HOH]^*$ radicals undergo collisional deactivation to give thermalized peroxy radicals, $C_4F_9CH_2C(OO^{\bullet})HOH$. Decomposition to HO_2 and $C_4F_9CH_2CHO$ is the dominant atmospheric fate of the thermalized peroxy radicals. In the presence of excess NO, the thermalized peroxy radicals react to give $C_4F_9CH_2C(O^{\bullet})HOH$ radicals which then decompose at a rate $>2.5 \times 10^6$ s^{-1} to give HC(O)OH and the alkyl radical $C_4F_9CH_2^{\bullet}$. The primary products of 4:2 FTOH oxidation in the presence of excess NO_x are $C_4F_9CH_2CHO$, C_4F_9CHO, and HCOOH. Secondary products include $C_4F_9CH_2C(O)O_2NO_2$, $C_4F_9C(O)O_2NO_2$, and COF_2. In contrast to experiments conducted in the absence of NO_x, there was no evidence ($<2\%$ yield) for the formation of the perfluorinated acid $C_4F_9C(O)OH$. The results are discussed with regard to the atmospheric chemistry of fluorotelomer alcohols.

1. Introduction

Long chain perfluorinated acids (PFCAs, $C_nF_{2n+1}COOH$ where $n \geq 6$) are highly persistent in the environment and have been observed in fauna from the Great Lakes[1] and the Arctic.[2] PFCAs resist degradation via oxidation, hydrolysis, or reduction under biotic and abiotic conditions[3] and are bioaccumulative when the perfluorinated chain is more than 6 carbons in length. Perfluorooctanoic acid (PFOA, $C_7F_{15}COOH$) is potentially toxic,[4−6] and the health effects associated with long-term exposure are the subject of a current EPA risk assessment.[7]

Other than for trifluoroacetic acid (TFA),[8] no natural source of PFCAs has been proposed. PFCAs with a chain length of $n = 1-12$ are minor products emitted to the atmosphere from thermolysis of fluoropolymers;[9] however, thermolysis of fluoropolymers is unlikely to make a significant contribution to the observed global burden of PFCAs. Analysis of rainwater indicates the wide-spread occurrence of short chain PFCAs ($n = 2-7$) at low levels (~1−100 ng/L).[10] Water-soluble PFCA salts are used in the processing of fluoropolymers and may enter local aquatic environments directly; however, it is difficult to explain how involatile PFCA salts would be transported to remote regions since they are removed from the atmosphere via wet and dry deposition on a time scale of a few days.[11] The simplest explanation for the ubiquity of PFCAs in fauna in remote regions is the presence of precursor compounds (presumably of anthropogenic origin) in the atmosphere that are transported over long distances and degrade to give PFCAs.

Fluorotelomer alcohols (FTOHs) have been suggested as plausible sources of perfluorinated carboxylic acids in remote locations.[12,13] FTOHs are linear fluorinated alcohols with the formula $C_nF_{2n+1}CH_2CH_2OH$ ($n = 2, 4, 6, ...$) used in a variety of industrial products, such as paints, coatings, polymers, adhesives, waxes, polishes, electronic materials, and caulks. The telomerization process results in even numbered linear chains and the alcohols are named according to the number of fluorinated and hydrogenated carbons. The fluorotelomer alcohol considered in this study, n-$C_4F_9CH_2CH_2OH$, is referred to as 4:2 fluorotelomer alcohol or 4:2 FTOH. All experiments were performed using the linear isomer n-$C_4F_9CH_2CH_2OH$ and for simplicity we will refer to this compound as $C_4F_9CH_2CH_2OH$. Global production of fluorotelomer alcohols is estimated to be 5×10^6 kg year^{-1} with 40% produced in North America.[14] Fluorotelomer alcohols are volatile, appear to be ubiquitous in the North American atmosphere (17−135 pg m^{-3}),[15,16] have an atmospheric lifetime (approximately 10−20 days) sufficient for widespread hemispheric distribution,[12,17] and undergo atmospheric oxidation in the absence of NO_x to give perfluorocarboxylic acids.[13,18]

While it seems reasonable to conclude that the atmospheric degradation of FTOHs contributes to widespread dissemination

---

* Corresponding author, email: twalling@ford.com.

10.1021/jp045672g CCC: $30.25

of PFCAs, it should be noted that significant gaps in our understanding of the atmospheric chemistry of FTOHs remain. For example, our understanding of the atmospheric chemistry of fluorotelomer alcohols in the presence of NO_x is limited. To remedy this situation, a study of the reaction Cl atoms with $C_4F_9CH_2CH_2OH$ in the presence of NO_x was performed in 700 Torr of N_2/O_2/air diluent at 296 K. Results are discussed with respect to the atmospheric oxidation of fluorotelomer alcohols and the environmental burden of perfluorinated carboxylic acids.

2. Experimental Section

Experiments were carried out in a 140-liter Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer.[19] The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL) which were used to photochemically initiate the experiments. Chlorine atoms were produced by photolysis of molecular chlorine.

$$Cl_2 + h\nu \rightarrow Cl + Cl \qquad (1)$$

Reactant and product concentrations were monitored using in situ Fourier transform infrared spectroscopy. IR spectra were derived from 32 coadded interferograms with a spectral resolution of 0.25 cm^{-1} and an analytical path length of 27 m. Calibrated reference spectra were acquired by expanding known volumes of reference materials into the chamber.

Reactant and reference compounds were monitored using absorption features at the following frequencies (cm^{-1}): $C_4F_9CH_2CH_2OH$, 3672; $C_4F_9CH_2CHO$, 1752; C_4F_9CHO, 1778; $C_4F_9CH_2C(O)O_2NO_2$, 1749 and 1836; $C_4F_9C(O)O_2NO_2$, 1762 and 1848; COF_2, 1944; and HCOOH, 1776. Initial reagent concentrations were: 3.8−4.1 mTorr of $C_4F_9CH_2CH_2OH$, 16−57 mTorr of NO_x (NO or NO_2), and 75−87 mTorr of Cl_2 in 700 Torr of diluent (air, oxygen, or nitrogen). All experiments were performed at 296 K. Reagent and reference compounds were obtained from commercial sources when possible. C_4F_9CHO was synthesized using procedures described in the literature[20] and authenticated using IR spectroscopy.[21] The reference spectrum of $C_4F_9CH_2CHO$ was taken from previous work in our laboratory.[18] All reagents and reference compounds were subjected to repeated freeze−pump−thaw cycling before use.

In smog chamber studies, it is important to control for unwanted loss of reactants and products via dark chemistry, photolysis and heterogeneous reactions. Control experiments were performed in which reaction mixtures (except Cl_2) were subject to UV irradiation for >15 min and where the product mixtures obtained after the UV irradiation were allowed to stand in the dark in the chamber for 15 min. There was no observable loss of reactants or products, suggesting that photolysis, dark chemistry, and heterogeneous reactions are not significant complications in the present work. Unless stated otherwise, quoted uncertainties are two standard deviations from least squares regressions.

3. Results

3.1. Formation of HCOOH, $C_4F_9CH_2CHO$, and C_4F_9CHO as Primary Products. The mechanism of Cl atom initiated oxidation of $C_4F_9CH_2CH_2OH$ in the presence of NO_x was investigated by irradiating mixtures of $C_4F_9CH_2CH_2OH$, NO, and Cl_2 in 700 Torr of N_2/O_2 diluent. Figure 1 shows spectra acquired before (A) and after (B) a 20 s irradiation of a mixture consisting of 3.8 mTorr of $C_4F_9CH_2CH_2OH$, 87 mTorr of Cl_2, and 28 mTorr of NO in 700 Torr of air diluent. The consumption of $C_4F_9CH_2CH_2OH$ was 24%. Comparison of IR features in panel B with the reference spectrum shown in panel D reveals the formation of HCOOH in the system. Panel C shows the result of removing IR features attributable to $C_4F_9CH_2CH_2OH$ and HCOOH from panel B. Comparison of the product spectrum in panel C with reference spectra of $C_4F_9CH_2CHO$ (E) and C_4F_9CHO (F) indicates the formation of these species. After subtraction of features attributable to HCOOH, $C_4F_9CH_2CHO$, and C_4F_9CHO residual IR features remained at 1696, 1729, 1749, and 1837 cm^{-1}. As will be discussed in sections 3.3 and 3.4, these features are typical for fluorinated organic nitrates and/or nitrites.

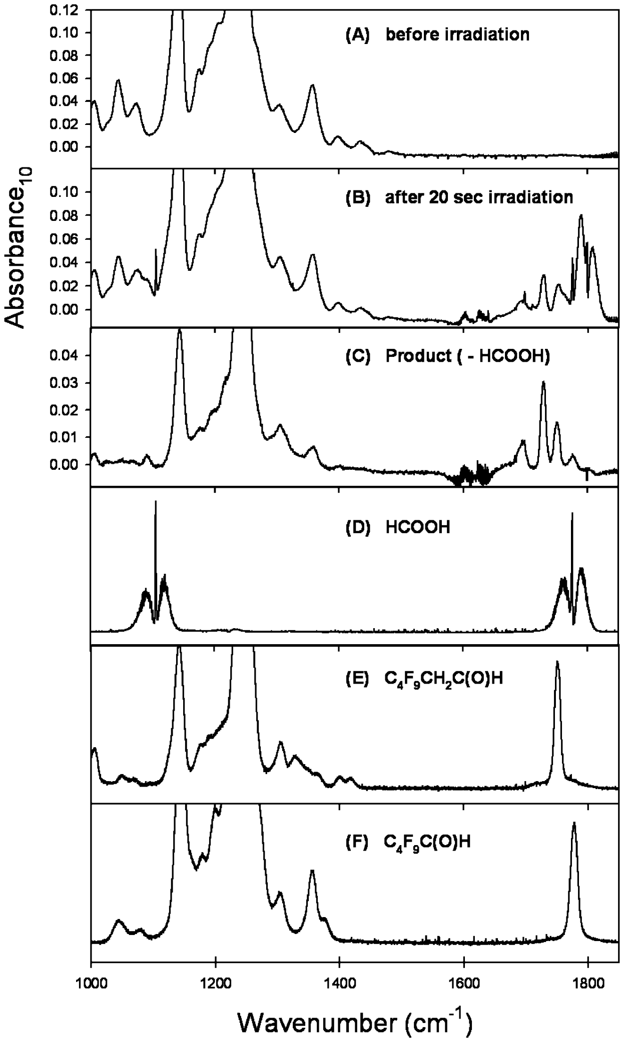

Figure 1. IR spectra obtained before (A) and after (B) a 20 s irradiation of a mixture of 3.8 mTorr of $C_4F_9CH_2CH_2OH$, 87 mTorr of Cl_2, and 28 mTorr of NO in 700 Torr of air diluent. Panel C shows the result of subtracting IR features attributable to $C_4F_9CH_2CH_2OH$ and HCOOH from panel B. Reference spectra of HCOOH, $C_4F_9CH_2CHO$, and C_4F_9CHO are given in panels D−F. Features attributable to NO, NO_2, HNO_3, ClNO, $ClNO_2$, ClONO, and HONO have been removed from the spectra in panels A−C for clarity.

Figure 2A shows a plot of the observed formation of HCOOH, $C_4F_9CH_2CHO$, and C_4F_9CHO vs loss of $C_4F_9CH_2CH_2OH$ for successive irradiations of the mixture used to obtain the spectra given in Figure 1. As seen from Figure 2A, the concentration of HCOOH and C_4F_9CHO increased linearly with $C_4F_9CH_2CH_2OH$ loss. Such behavior indicates that HCOOH and C_4F_9CHO are primary products in the system. The concentration of $C_4F_9CH_2CHO$ increases for small consumptions of $C_4F_9CH_2CH_2OH$ and then decreases at larger consumptions. This behavior suggests that $C_4F_9CH_2CHO$ is a primary product in

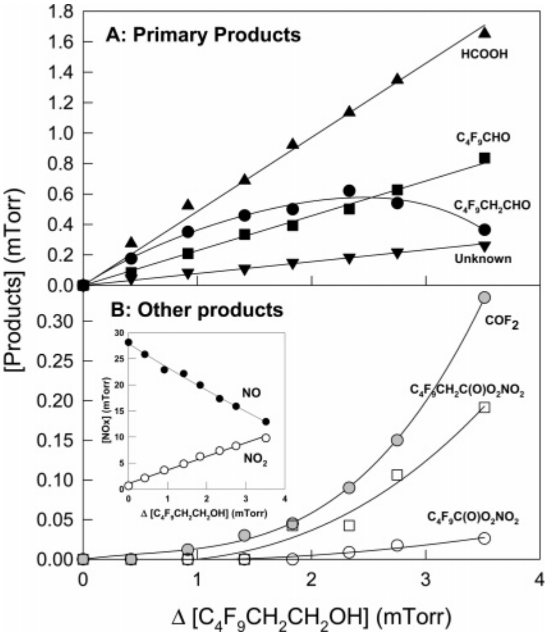

Figure 2. Product formation vs $C_4F_9CH_2CH_2OH$ loss for successive radiations of a mixture of 3.82 mTorr of $C_4F_9CH_2CH_2OH$, 87 mTorr of Cl_2, and 28 mTorr of NO in 700 Torr of air diluent. The primary products observed are shown in black in panel A: $C_4F_9CH_2CHO$ (filled circles), C_4F_9CHO (filled squares), HCOOH (filled triangles up) and unknown product observed at 1729 cm^{-1} (filled triangles down). The concentration of the unknown is in arbitrary units. Panel B shows products observed as secondary or tertiary: $C_4F_9CH_2C(O)O_2NO_2$ (open squares), $C_4F_9C(O)O_2NO_2$ (open circles), and COF_2 (gray circles). The insert shows the NO_x concentration profile during the experiment.

the Cl atom initiated oxidation of 4:2 FTOH, but is lost via secondary reaction with Cl atoms at higher conversions of 4:2 FTOH.

It is of interest to compare the primary products ($C_4F_9CH_2CHO$, C_4F_9CHO, and HCOOH) of 4:2 FTOH oxidation observed in the presence of NO_x with those observed in its absence. In experiments conducted in the absence of NO_x there was just one primary product; $C_4F_9CH_2CHO$ in a yield which was indistinguishable from 100%.[18] In the present experiments (in the presence of NO_x) $C_4F_9CH_2CHO$ is a major, *but not the sole*, primary product. Formation of HCOOH as a primary product in a molar yield of approximately 50% in the presence of NO_x is particularly striking given the absence of this species as either a primary, or secondary, product in experiments conducted in the absence of NO_x. The presence of NO_x has a substantial impact on the first step of the oxidation mechanism of 4:2 FTOH.

The reaction of Cl atoms with fluorotelomer alcohols is believed to proceed largely (>90%) via attack at the CH_2 group α to the alcohol functionality to give an α-hydroxy alkyl radical.[12,18] The selectivity of Cl atom attack has been ascribed to a combination of the deactivating effect of fluorine substituents and the activating effect of the OH substituent on the CH_2 groups in the molecule.[12,18] The atmospheric fate of α-hydroxy alkyl radicals, $RC^{\bullet}HOH$, is reaction with O_2 to give excited peroxyradicals, $[RC(OO^{\bullet})HOH]^*$, which have two possible atmospheric fates; elimination of HO_2 to give the corresponding aldehyde, or collisional relaxation to give the thermalized peroxy radical $RC(OO^{\bullet})HOH$. Smaller radicals have lower density of states and decompose more rapidly than larger radicals. The smallest member of the series, $[HOCH_2O_2^{\bullet}]^*$, has a lifetime of approximately 50 ps with respect to decomposition.[22] Under ambient atmospheric conditions collisions between molecules occur on a time scale of approximately 100 ps. $[HOCH_2O_2^{\bullet}]^*$ decomposes before collisional stabilization can occur. Larger $[RC(OO^{\bullet})HOH]^*$ radicals such as those produced in the atmospheric degradation of terpenes have lifetimes with respect to decomposition which are sufficiently long that collisional deactivation can occur and resulting peroxy radicals can react with NO leading to significant quantities of formic acid:[23]

$$RCH(OH)OO^{\bullet} + NO \rightarrow RCH(OH)O^{\bullet} + NO_2 \tag{2}$$

$$RCH(OH)O^{\bullet} \rightarrow R^{\bullet} + HCOOH \tag{3}$$

It seems reasonable to assume that a similar mechanism explains the formation of HCOOH, and C_4F_9CHO, as primary products in the chlorine initiated oxidation of $C_4F_9CH_2CH_2OH$ in the presence of NO_x:

$$C_4F_9CH_2CH_2OH + Cl \rightarrow C_4F_9CH_2C^{\bullet}HOH + HCl \tag{4}$$

$$C_4F_9CH_2C^{\bullet}HOH + O_2 \rightarrow [C_4F_9CH_2C(OO^{\bullet})HOH]^* \tag{5}$$

$$[C_4F_9CH_2C(OO^{\bullet})HOH]^* \rightarrow C_4F_9CH_2CHO + HO_2 \tag{6}$$

$$[C_4F_9CH_2C(OO^{\bullet})HOH]^* + M \rightarrow C_4F_9CH_2C(OO^{\bullet})HOH + M \tag{7}$$

$$C_4F_9CH_2C(OO^{\bullet})HOH \rightarrow C_4F_9CH_2CHO + HO_2 \tag{8}$$

$$C_4F_9CH_2C(OO^{\bullet})HOH + NO \rightarrow C_4F_9CH_2C(O^{\bullet})HOH + NO_2 \tag{9a}$$

$$C_4F_9CH_2C(OO^{\bullet})HOH + NO \rightarrow C_4F_9CH_2C(ONO_2)HOH \tag{9b}$$

$$C_4F_9CH_2C(O^{\bullet})HOH \rightarrow C_4F_9CH_2^{\bullet} + HCOOH \tag{10}$$

$$C_4F_9CH_2^{\bullet} + O_2 \rightarrow C_4F_9CH_2OO^{\bullet} \tag{11}$$

$$C_4F_9CH_2OO^{\bullet} + NO \rightarrow C_4F_9CH_2O^{\bullet} + NO_2 \tag{12a}$$

$$C_4F_9CH_2OO^{\bullet} + NO \rightarrow C_4F_9CH_2ONO_2 \tag{12b}$$

$$C_4F_9CH_2O^{\bullet} + O_2 \rightarrow C_4F_9CHO + HO_2 \tag{13}$$

$$C_4F_9CH_2CHO + Cl \rightarrow \text{Products} \tag{14}$$

The reactivities of Cl atoms toward C_4F_9CHO, $k_{Cl} = (2.1 \pm 0.5) \times 10^{-12}$,[24] and HCOOH, $k_{Cl} = (2.00 \pm 0.25) \times 10^{-13}$,[25] are significantly lower than toward the parent 4:2 FTOH, $k_{Cl} = 1.61 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.[12] Hence, loss of C_4F_9CHO and HCOOH via reaction with Cl atoms will not be a significant complication in the present work. The linearity of plots of the formation of these compounds vs loss of $C_4F_9CH_2CH_2OH$ shown in Figure 2A is consistent with the relative unreactivity of C_4F_9CHO and HCOOH. The linearity of the C_4F_9CHO plot is discussed further in section 3.3.

In contrast to the behavior of C_4F_9CHO and HCOOH, the product yield plot for $C_4F_9CH_2CHO$ in Figure 2A is distinctly curved. Such curvature can be ascribed to secondary loss of $C_4F_9CH_2CHO$ via reaction with Cl atoms. The concentration profile of the reactive primary product, $C_4F_9CH_2CHO$, can be described[26] by the expression

$$\frac{[C_4F_9CH_2CHO]}{[C_4F_9CH_2CH_2OH]_o} = \frac{\alpha(1-x)\{(1-x)^{(k_{14}/k_4)-1} - 1\}}{\{1-(k_{14}/k_4)\}} \tag{I}$$

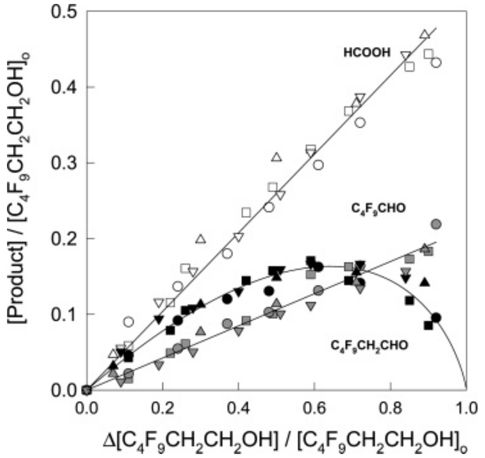

Figure 3. Formation of primary products, HCOOH, $C_4F_9CH_2CHO$, and C_4F_9CHO vs loss of $C_4F_9CH_2CH_2OH$, normalized to the initial alcohol concentration. Experiments were performed in 700 Torr of N_2/O_2 diluent. Initial partial pressures of O_2 and NO were: circles, 140 Torr of O_2 and 28 mTorr of NO; triangles up, 140 Torr of O_2 and 57 mTorr of NO; squares, 400 Torr of O_2 and 29 mTorr of NO; and triangles down, 6 Torr of O_2 and 28 mTorr of NO The line through the $C_4F_9CH_2CHO$ data is a fit of eq I to the data.

where $x = 1 - ([C_4F_9CH_2CH_2OH]/[C_4F_9CH_2CH_2OH]_0)$ is the fractional consumption of $C_4F_9CH_2CH_2OH$ and α is the yield of $C_4F_9CH_2CHO$ from reaction of Cl atoms with $C_4F_9CH_2CH_2OH$ in the presence of oxygen and NO. Figure 3 shows a plot of [primary products]/$[C_4F_9CH_2CH_2OH]_0$ vs $\Delta[C_4F_9CH_2CH_2OH]/[C_4F_9CH_2CH_2OH]_0$ for experiments in which the oxygen concentration was varied from 6 Torr to 140 Torr and $[NO]_o$ was varied from 28 to 57 mTorr. As seen from Figure 3, the formation of $C_4F_9CH_2CHO$, C_4F_9CHO, and HCOOH were independent of O_2 and NO concentration over the range studied. A fit of eq I to the data in Figure 3 gives $\alpha = 0.44 \pm 0.03$ and $k_{14}/k_4 = 0.96 \pm 0.11$. The lines through the HCOOH and C_4F_9CHO data in Figure 3 are linear least-squares fits (forced through zero) giving molar yields of 52 ± 4% HCOOH and 21 ± 3% C_4F_9CHO. Quoted uncertainties are two standard deviations from the linear regressions together with our estimation of the uncertainties associated with the calibration of our reference spectra. Hurley et al.[18] reported $k_{14}/k_4 = 1.14 \pm 0.05$ ($\alpha = 1.00 \pm 0.03$) for experiments conducted in the absence of NO_x. The value of k_{14}/k_4 measured in this work is consistent with our previous measurement.[18] The presence of NO_x affects the mechanism, diminishing the yield of $C_4F_9CH_2CHO$ by approximately a factor of 2.5, but does not affect the kinetics of the system.

$C_4F_9CH_2C(O^\bullet)HOH$ radicals formed in reaction 9a can either undergo decomposition to give $C_4F_9CH_2$ radicals and HCOOH, or react with O_2 to give $C_4F_9CH_2C(O)OH$. Evidence for the formation of $C_4F_9CH_2C(O)OH$ was sought but not found, and an upper limit of 5% was established for this species. By analogy to the existing database for other alkoxy radicals[27] it seems reasonable to assume a rate constant of the order of 10^{-14} cm^3 molecule^{-1} s^{-1} for reaction with O_2. Hence, the upper limit of 5% for the yield of $C_4F_9CH_2C(O)OH$ in the presence of 400 Torr of O_2 provides a lower limit for the rate of decomposition of $C_4F_9CH_2CO^\bullet HOH$ radicals of $k_{10} > 2.5 \times 10^6$ s^{-1}. As with other reactions of peroxy radicals with NO,[28] it is possible that the $C_4F_9CH_2CO^\bullet HOH$ radicals formed in reaction 9a have sufficient chemical activation to decompose promptly. The lower limit of $k_{10} > 2.5 \times 10^6$ s^{-1} is appropriate for $C_4F_9CH_2CO^\bullet HOH$ radicals formed in reaction 9a which may, or may not, be chemically activated. On the basis of the formation of $C_4F_9CH_2CHO$ and HCOOH, we can account for 96 ± 7% of the loss of $C_4F_9CH_2CH_2OH$ in the initial phase of the degradation.

3.2. Fate of $[C_4F_9CH_2COO^\bullet HOH]^*$ and $C_4F_9CH_2COO^\bullet HOH$ Radicals. As discussed in the previous section, $C_4F_9CH_2C^\bullet HOH$ radicals react with O_2 to give chemically excited peroxy radicals $[C_4F_9CH_2COO^\bullet HOH]^*$. There are two possible fates of $[C_4F_9CH_2COO^\bullet HOH]^*$: (i) collisional deactivation to give thermalized $C_4F_9CH_2COO^\bullet HOH$ radicals (reaction 7) and (ii) “prompt” (i.e., rapid compared to collisional deactivation) decomposition to give HO_2 radicals and $C_4F_9CH_2CHO$ via reaction 6. There are two possible fates of thermalized $C_4F_9CH_2COO^\bullet HOH$ radicals: (i) decomposition via reaction 8 to give HO_2 radicals and $C_4F_9CH_2CHO$ and (ii) reaction with NO leading to the formation of HCOOH via reactions 9a and 10.

From the yields of $C_4F_9CH_2CHO$ and HCOOH reported in section 3.1, we conclude that under ambient conditions (atmospheric pressure, 296 K) approximately 50% of $[C_4F_9CH_2COO^\bullet HOH]^*$ radicals decompose promptly via (6) to give $C_4F_9CH_2CHO$. From the invariance of the $C_4F_9CH_2CHO$ and HCOOH yields with $[NO]_0$ (see Figure 3), we conclude that under the present experimental conditions (i.e., [NO] > 28 mTorr) reaction with NO dominates the loss of thermalized $C_4F_9CH_2COO^\bullet HOH$ radicals. Adopting a value of $k_9 = 1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, typical for a reaction of a peroxy radical with NO, and assuming $k_9[NO]/k_8 > 5$, gives an upper limit of $k_8 < 2 \times 10^3$ s^{-1}. The Cl initiated oxidation of $C_4F_9CH_2CH_2OH$ in the absence of NO (but with all other conditions essentially identical to those reported herein) gives $C_4F_9CH_2CHO$ in essentially 100% yield.[11] The simplest explanation for this observation is that in the absence of NO, decomposition via reaction 8 is the dominant fate of $C_4F_9CH_2COO^\bullet HOH$ radicals. Self-reaction is a potential competing loss mechanism for $C_4F_9CH_2COO^\bullet HOH$ radicals. Peroxy radical self-reactions have rate constants typically of the order of 10^{-12} cm^3 molecule^{-1} s^{-1} (e.g., k($HOCH_2O_2 + HOCH_2O_2$) = 7×10^{-13} cm^3 molecule^{-1} s^{-1} [29]) and such a reaction would preclude the formation of $C_4F_9CH_2CHO$.[30] A simple modeling exercise for the experiment shown in Figure 2 of Hurley et al.,[11] assuming that (i) self-reaction and decomposition via reaction 8 are competing losses for $C_4F_9CH_2COO^\bullet HOH$, (ii) the self-reaction rate constant for $C_4F_9CH_2COO^\bullet HOH$ radicals is 10^{-12} cm^3 molecule^{-1} s^{-1}, and (iii) self-reaction accounts for <10% of the loss of $C_4F_9CH_2COO^\bullet HOH$ radicals, gives a lower limit of $k_8 > 10$ s^{-1}. Hence, from the present work and that of Hurley et al.,[11] we estimate that under ambient conditions the rate of thermal decomposition of $C_4F_9CH_2COO^\bullet HOH$ radicals lies in the range $k_8 = 10-2000$ s^{-1}.

In the present smog chamber experiments, reaction with NO dominates the loss of $C_4F_9CH_2COO^\bullet HOH$ radicals. However, in the atmosphere the concentration of NO is several orders of magnitude lower than in the present experiments and reaction with NO may not be an important fate for $C_4F_9CH_2COO^\bullet HOH$ radicals. To establish the relative importance of reactions 8 and 9 in the atmosphere we need to consider the ratio $k_8/(k_9[NO])$. Adopting a value of $k_9 = 1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} it follows that reaction 8 will be the dominant fate of $C_4F_9CH_2COO^\bullet HOH$ radicals in environments with [NO] < 40 ppb. Since this requirement is met for all but highly polluted urban areas we conclude that decomposition via reaction 8 is the dominant atmospheric fate of $C_4F_9CH_2COO^\bullet HOH$ radicals. The above analysis ignores the effect of altitude and hence temperature. At higher altitudes the temperature decreases and the unimolecular decomposition reaction 8 will slow substantially (by a factor of 3×10^3 from 296 to 220 K assuming $E_a = 13.6$ kcal mol^{-1} [22]). In contrast, the kinetics of reaction 9 are expected to be relatively insensitive to changes in temperature. However, at high altitudes the concentration of [NO] is sufficiently low that loss of $C_4F_9CH_2COO^{\bullet}HOH$ radicals via unimolecular decomposition will still dominate. The considerations above indicate that while reaction with NO is an important loss mechanism for $C_4F_9CH_2COO^{\bullet}HOH$ in the present smog chamber studies, this reaction is not likely to be of importance in the real atmosphere where the concentration of NO is much lower. This conclusion is similar to that reached by Peeters et al.[31] in a study of the fate of α-hydroxy peroxy radicals formed during the OH initiated oxidation of α-pinene.

The data presented here and by Hurley et al.[11] allow us to reach two conclusions regarding the atmospheric fate of $[C_4F_9CH_2COO^{\bullet}HOH]^*$ and $C_4F_9CH_2COO^{\bullet}HOH$ radicals. First, under ambient conditions, approximately 50% of $[C_4F_9CH_2COO^{\bullet}HOH]^*$ radicals decompose promptly to give HO_2 radicals and $C_4F_9CH_2CHO$ while the remaining 50% are collisionally stabilized to give $C_4F_9CH_2COO^{\bullet}HOH$ radicals. Second, the atmospheric fate of thermalized $C_4F_9CH_2COO^{\bullet}HOH$ radicals is decomposition to give HO_2 radicals and $C_4F_9CH_2CHO$. For the sake of simplicity the atmospheric fate of $C_4F_9CH_2C^{\bullet}HOH$ radicals can be written as

$$C_4F_9CH_2C^{\bullet}HOH + O_2 \rightarrow C_4F_9CH_2CHO + HO_2$$

3.3. Formation of $C_4F_9CH_2ONO$ and $C_4F_9CH_2ONO_2$ as Primary Products. Given our conclusion in section 3.1 that decomposition via reaction 10 is the sole fate of $C_4F_9CH_2C(O^{\bullet})HOH$ and the expectation that $C_4F_9CH_2^{\bullet}$ radicals are converted into C_4F_9CHO via reactions 11, 12a, and 13, the yields of HCOOH and C_4F_9CHO would be expected to be comparable. However, as seen from Figure 3, the yield of C_4F_9CHO is approximately half that of HCOOH. In addition, given the substantial loss of $C_4F_9CH_2CHO$ via secondary reaction with Cl atoms and the expectation that at least some of this would be converted into C_4F_9CHO, it is surprising that the yield plot of CF_3CHO in Figure 3 does not exhibit upward curvature at large $C_4F_9CH_2CH_2OH$ consumptions. It appears that there are other processes in the system which compete with one or all of reactions 11, 12a, and 13. Alkyl radicals such as $C_4F_9CH_2^{\bullet}$ add O_2 rapidly (with rate constants of the order of 10^{-12} cm^3 molecule^{-1} s^{-1}). It is difficult to imagine a process that could compete with reaction 11. In their reactions with NO, fluorinated peroxy radicals give low yields (few % or less) of organic nitrates and it seems unlikely that reaction 12b can explain the discrepancy between HCOOH and C_4F_9CHO.

The limited existing kinetic database for reactions of fluorinated alkoxy radicals with O_2 suggests that reaction 13 proceeds slowly with a rate constant of the order of 10^{-16} cm^3 molecule^{-1} s^{-1} at ambient temperature.[27,32] In addition to reaction with O_2 to give C_4F_9CHO, the $C_4F_9CH_2O^{\bullet}$ radicals formed in reaction 9a can also react with NO and NO_2 to form $C_4F_9CH_2ONO$ and $C_4F_9CH_2ONO_2$ or C_4F_9CHO and HNO_x:

$$C_4F_9CH_2O^{\bullet} + NO \rightarrow C_4F_9CH_2ONO \tag{15a}$$

$$C_4F_9CH_2O^{\bullet} + NO \rightarrow C_4F_9CHO + HNO \tag{15b}$$

$$C_4F_9CH_2O^{\bullet} + NO_2 \rightarrow C_4F_9CH_2ONO_2 \tag{16a}$$

$$C_4F_9CH_2O^{\bullet} + NO_2 \rightarrow C_4F_9CHO + HNO_2 \tag{16b}$$

By analogy with the existing database for alkoxy radicals,[27] the rate constants for reactions 15 and 16 will be of the order of 10^{-11} cm^3 molecule^{-1} s^{-1}. The $[O_2]/[NO_x]$ ratio used in the present work was 200−10000 and is significantly lower than the rate constant ratio $k_{15}/k_{13} \approx 10^5$. We conclude that reaction with NO_x is likely to be an important, perhaps dominant, fate of $C_4F_9CH_2O^{\bullet}$ radicals and that reaction 15b and possibly reaction 16b make an important contribution to the observed C_4F_9CHO product.

As shown in Figure 1C, IR features of an unknown product were observed at 1696 and 1729 cm^{-1}. There are three pieces of information that lead us to believe that these features are attributable to $C_4F_9CH_2ONO$. First, the IR features, 1729, 1696, 1092, and 962 cm^{-1} scale linearly in all experiments, suggesting (but not proving) they are associated with one compound. Second, the pattern of formation follows the linear yield of a primary product (see symbols labeled “unknown” in Figure 2A). Third, the position and the relative intensity of the intense doublet with IR features at 1729 (N═O stretching, trans isomer) and 1696 cm^{-1} (N═O stretching, cis isomer) are consistent with the absorption frequencies expected from a fluorine substituted organic nitrite (e.g., CF_3CH_2ONO absorbs at 1695 and 1736 cm^{-1}).[33,34]

In the later stages of the experiments, a less intense IR feature at 1695 cm^{-1} was observed. During the course of the experiments NO is converted into NO_2. As NO_2 accumulates in the system, the importance of reaction 16 increases. The feature at 1695 cm^{-1} is consistent with the asymmetric N−O stretching in a NO_2 group of an organic nitrate and would be consistent with the formation of $C_4F_9CH_2ONO_2$ during the later stages of the experiment. Likely contributions by reactions 15b and 16b to the formation of C_4F_9CHO complicate the interpretation of the yield of this species. In the absence of kinetic and mechanistic data for reactions 15 and 16, we are unable to offer a detailed interpretation of the linearity of the C_4F_9CHO yield plot at high $C_4F_9CH_2CH_2OH$ consumptions shown in Figure 3.

3.4. IR Spectrum of $C_4F_9CH_2C(O)O_2NO_2$. Experiments were performed to record the IR spectrum of $C_4F_9CH_2C(O)O_2NO_2$.

A mixture of 3.92 mTorr of $C_4F_9CH_2CH_2OH$, 75 mTorr of Cl_2, and 15.8 mTorr of NO_2 in 700 Torr of air diluent were subjected to UV irradiation. As outlined in section 3.2, the reaction of Cl atoms with $C_4F_9CH_2CH_2OH$ in the presence of O_2 (and absence of NO) leads to formation of $C_4F_9CH_2CHO$ in essentially 100% yield. Subsequently $C_4F_9CH_2C(O)O_2$ radicals will be formed by reaction of the primary product, $C_4F_9CH_2CHO$, with Cl atoms. By analogy to the behavior of other acyl peroxy radicals, it is expected that $C_4F_9CH_2C(O)O_2$ radicals will react rapidly with NO_2 to give the acyl peroxynitrate, $C_4F_9CH_2C(O)O_2NO_2$:

$$C_4F_9CH_2CHO + Cl \rightarrow C_4F_9CH_2C(O)^{\bullet} + HCl \tag{14}$$

$$C_4F_9CH_2C(O)^{\bullet} + O_2 \rightarrow C_4F_9CH_2C(O)O_2^{\bullet} \tag{17}$$

$$C_4F_9CH_2C(O)O_2^{\bullet} + NO_2 + M \rightarrow C_4F_9CH_2C(O)O_2NO_2 \tag{18}$$

Acyl peroxy nitrates are thermally unstable and decompose to re-form acetyl peroxy radicals and NO_2 on a time scale of hours at 296 K.[35] In the presence of excess NO_2 thermal decomposition of $C_4F_9CH_2C(O)O_2NO_2$ will be masked by its re-formation via reaction 18. Following UV irradiation of the $C_4F_9CH_2CH_2OH/NO_2/Cl_2$/air mixture described above four carbon containing products were observed; $C_4F_9CH_2CHO$, C_4F_9CHO, HCOOH, and a product with the IR features shown

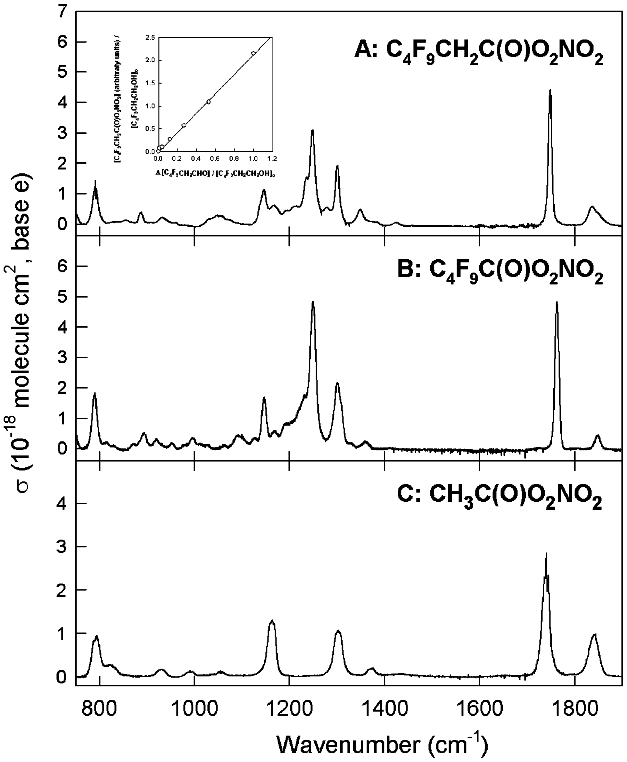

Figure 4. Infrared spectra of $C_4F_9CH_2C(O)O_2NO_2$ (Panel A), $C_4F_9C(O)O_2NO_2$ (Panel B) and $CH_3C(O)O_2NO_2$ (PAN) (Panel C). The insert in panel A shows the calibration curve for $C_4F_9CH_2C(O)O_2NO_2$ (see text for details).

in Figure 4A. The product features at 791, 1301, 1749, and 1837 cm^{-1} are characteristic of the NO_2 deformation, NO_2 symmetric stretch, NO_2 asymmetric stretch, and CO stretching modes in acetyl peroxy nitrates. We assign the spectrum shown in Figure 4A to $C_4F_9CH_2C(O)O_2NO_2$. For comparison spectra of $C_4F_9C(O)O_2NO_2$[24] and $CH_3C(O)O_2NO_2$[36] are shown in Figure 4, parts B and C.

As mentioned above, in addition to $C_4F_9CH_2C(O)O_2NO_2$, small amounts of C_4F_9CHO and HCOOH were observed (yields of 5.9 ± 0.7% and 5.0 ± 0.5%, respectively). Formation of these products can be ascribed to conversion of $C_4F_9CH_2C(OO^\bullet)HOH$ into $C_4F_9CH_2C(O^\bullet)HOH$ radicals by reaction with traces of NO (formed unavoidably by photolysis of NO_2) in the system followed by reactions (10−13). It is interesting that unlike in experiments performed with excess NO (see section 3.2) the yields of C_4F_9CHO and HCOOH were comparable. This probably reflects the importance of reaction 16b in the system.

Assuming that reaction 18 is the sole fate of $C_4F_9CH_2C(O)O_2^\bullet$, then the yield of $C_4F_9CH_2C(O)O_2NO_2$ can be equated to the consumption of $C_4F_9CH_2CHO$ in the system. In turn, the consumption of $C_4F_9CH_2CHO$ can be equated to the difference between the loss of $C_4F_9CH_2CH_2OH$ and the sum of the observed formation of $C_4F_9CH_2CHO$ and C_4F_9CHO. The inset in Figure 4A shows a plot of the increase in IR absorption attributable to $C_4F_9CH_2C(O)O_2NO_2$ vs the consumption of $C_4F_9CH_2CH_2OH$ normalized to the initial concentration of 4:2FTOH. The linearity of the plot suggests that assumptions given above are reasonable. The slope of the plot provides a means to calibrate the $C_4F_9CH_2C(O)O_2NO_2$ spectrum. The integrated band strength (1700−1800 cm^{-1}) of the NO_2 asymmetric stretching feature centered on 1749 cm^{-1} is $(6.27 \pm 1.25) \times 10^{-17}$ and is similar to those of $(5.14 \pm 0.10) \times 10^{-17}$ and $(5.53 \pm 1.11) \times 10^{-17}$ cm molecule^{-1} for the corresponding features in $CH_3C(O)O_2NO_2$[37] and $C_4F_9C(O)OONO_2$.[24]

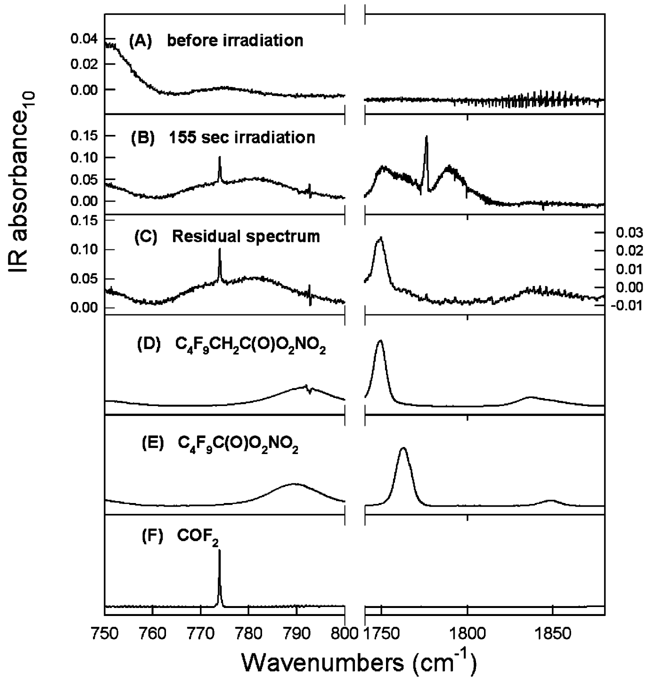

Figure 5. IR spectra obtained before (A) and after (B) 155 s of irradiation of a mixture consisting of 3.8 mTorr of $C_4F_9CH_2CH_2OH$, 87 mTorr of Cl_2 and 28 mTorr of NO in 700 Torr of air diluent. Panel C shows the residual product spectrum obtained after subtraction of the IR features of the reactant shown in Panel A and of the IR features from all primary products. Panels D, E, and F are reference spectra of $C_4F_9CH_2C(O)O_2NO_2$, $C_4F_9C(O)O_2NO_2$, and COF_2. All spectra have been stripped of IR features attributable to NO, NO_2, and H_2O (see text for details).

3.5. Formation of $C_4F_9CH_2C(O)O_2NO_2$, $C_4F_9C(O)O_2NO_2$, and COF_2 as Secondary Products. Figure 5 shows spectra from an experiment similar to that illustrated in Figure 1 after a longer irradiation time (and higher conversion of 4:2 FTOH). The spectra were acquired before (A) and after (B) a 155 s irradiation of a gas mixture consisting of 3.8 mTorr of $C_4F_9CH_2CH_2OH$, 87 mTorr of Cl_2 and 28 mTorr of NO in 700 Torr of air diluent. During the irradiation, 90% of the $C_4F_9CH_2CH_2OH$ was consumed and the residual product spectrum (C) was obtained by subtracting IR features of $C_4F_9CH_2CH_2OH$ and the primary products $C_4F_9CH_2CHO$, HCOOH, and C_4F_9CHO. Comparison of the IR features in C, with reference spectra for $C_4F_9CH_2C(O)O_2NO_2$ (D), $C_4F_9C(O)O_2NO_2$ (E), and COF_2 (F) shows the formation of these compounds.

Figure 2B shows the observed formation of $C_4F_9CH_2C(O)O_2NO_2$, $C_4F_9C(O)O_2NO_2$, and COF_2 after successive irradiations of the mixture described above. The product profiles are consistent with $C_4F_9CH_2C(O)O_2NO_2$ and $C_4F_9C(O)O_2NO_2$ being secondary products formed following reaction of Cl atoms with $C_4F_9CH_2CHO$ and C_4F_9CHO. The decreasing NO and increasing NO_2 concentrations (see Figure 2B insert) during the experiment contribute to the curvature of the $C_4F_9CH_2C(O)O_2NO_2$ and $C_4F_9C(O)O_2NO_2$ yield plots.

COF_2 is the product expected from decomposition of the C_4F_9- tail of $C_4F_9CH_2CH_2OH$ which "unzips" through the following reactions:

$$CF_3(CF_2)_xCF_2^\bullet + O_2 \rightarrow CF_3(CF_2)_xCF_2OO^\bullet \quad (19)$$

$$CF_3(CF_2)_xCF_2OO^\bullet + NO \rightarrow CF_3(CF_2)_xCF_2O^\bullet + NO_2 \quad (20)$$

$$CF_3(CF_2)_xCF_2O^\bullet + M \rightarrow CF_3(CF_2)_{x-1}CF_2^\bullet + COF_2 + M \quad (21)$$

Repetition of reactions 19−21 results in the “unzipping” of the fluorinated moiety and the formation of three COF_2 molecules. The last radical formed, CF_3, will be converted into COF_2 via reactions 22−24:

$$CF_3 + O_2 \rightarrow CF_3OO^\bullet \qquad (22)$$

$$CF_3OO^\bullet + NO \rightarrow CF_3O^\bullet + NO_2 \qquad (23)$$

$$CF_3O^\bullet + NO \rightarrow COF_2 + FNO \qquad (24)$$

As seen from Figure 2B, COF_2 is formed as a secondary (and possibly tertiary) product, with a yield which increases with the fractional consumption of $C_4F_9CH_2CH_2OH$. This behavior presumably reflects the loss of the primary product C_4F_9CHO via reaction with Cl atoms followed by reaction of the $C_4F_9C(O)O_2$ radical with NO leading to the formation of C_4F_9 radicals which “unzip” via reactions (19−24). We conclude that $C_4F_9CH_2C(O)O_2NO_2$, $C_4F_9C(O)O_2NO_2$, and COF_2 are secondary products of 4:2 FTOH oxidation.

Evidence for the formation of the acid $C_4F_9C(O)OH$ was sought but not found in these experiments and an upper limit of 2% was established for the molar yield of this compound in the Cl atom initiated oxidation of 4:2 FTOH in the presence of NO_x.

4. Implications for Atmospheric Chemistry

The motivation for the present work was to provide insight into the atmospheric oxidation mechanism of fluorotelomer alcohols. In the present work Cl atoms were used to initiate the oxidation of 4:2 FTOH. OH radicals will be produced in the system (via HO_2 + NO reaction); however, the loss of 4:2 FTOH will be dominated by reaction with Cl atoms. In the atmosphere, the oxidation of 4:2 FTOH is initiated by reaction with OH radicals; FTOHs have an atmospheric lifetime of approximately 10−20 days.[12,17] Cl atoms and OH radicals react with 4:2 FTOH via the same mechanism (abstraction of a hydrogen atom α to the OH group) and give the same radical products.[12] Hence, the study of the Cl atom initiated oxidation described herein provides information concerning the OH radical initiated atmospheric degradation of 4:2 FTOH. The longer chain commercially important fluorotelomer alcohols (6:2 FTOH, 8:2 FTOH, 10:2 FTOH) have molecular structures very similar to 4:2 FTOH and it seems reasonable to generalize our results to all members of the $C_nF_{2n+1}CH_2CH_2OH$ ($n = 2, 4, 6, ...$) series. A simplified atmospheric oxidation mechanism for 4:2 FTOH based upon the results from the present work and literature data is given in Figure 6. The mechanism given in Figure 6 does not include the formation of HCOOH and $C_4F_9CH_2ONO_x$. These compounds were observed in the present smog chamber studies but are not expected to be formed in the real atmosphere (see section 3.3 for details).

We show that $C_4F_9CH_2CHO$, C_4F_9CHO, and HCOOH are primary products of the atmospheric oxidation of 4:2 FTOH in the *presence* of NO_x in the present smog chamber experiments. This result can be contrasted with results from our previous study showing that $C_4F_9CH_2CHO$ is the sole primary product in the Cl initiated oxidation in the *absence* of NO_x.[18] The presence of NO_x alters the atmospheric degradation mechanism. LeBras et al.[17] reported CF_3CH_2CHO yields from oxidation of $CF_3CH_2CH_2OH$ in the presence, and absence, of NO_x in the range 50−100%, which is consistent with the findings of this work.

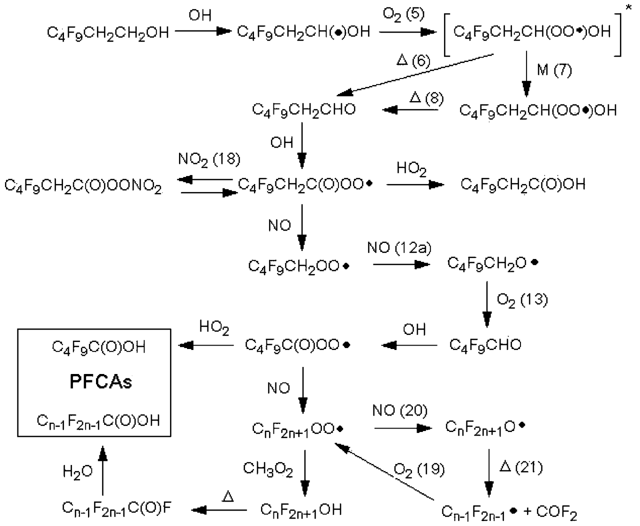

Figure 6. Simplified atmospheric oxidation mechanism for 4:2 FTOH, numbers in parentheses refer to the reaction numbering used herein. CH_3O_2 is the most abundant α-hydrogen containing peroxy radical in the atmosphere and was chosen to represent all such peroxy radicals in the reaction leading to $C_nF_{2n+1}OH$.

The oxidation of the primary product $C_4F_9CH_2CHO$ in the presence of excess NO_x gives C_4F_9CHO, $C_4F_9CH_2C(O)O_2NO_2$, and $C_4F_9CH_2ONO$. The latter product will not be formed in the atmosphere where the NO concentrations are much lower than those employed in the present experiments.

No evidence for the formation of perfluorocarboxylic acids was found in the present experiments. On the basis of the results reported here, we conclude that gas-phase atmospheric oxidation of $C_4F_9CH_2CH_2OH$ *in the presence of excess NO* is not a significant source of perfluorocarboxylic acid, $C_4F_9C(O)OH$. However, it should be noted that in the *absence of* NO_x, perfluorocarboxylic acid formation is observed during the Cl atom initiated oxidation of $C_4F_9CH_2CH_2OH$, as a result of the reaction of $C_4F_9C(O)O_2$ with HO_2 radicals and reactions of $C_nF_{2n+1}O_2$ radicals with peroxy radicals containing an α-hydrogen atom.[11,13,38]

The present work builds upon a large and growing body of laboratory studies aimed to clarify the atmospheric oxidation mechanism of FTOHs.[11,12,13,17,20,25,38] We have established qualitatively that FTOHs are a source of perfluorocarboxylic acids in low NO_x environments.[13] However, the magnitude, and hence significance, of this source is unclear. A modeling study would be helpful in providing a more quantitative assessment of the contribution of FTOH degradation to the environmental perfluorocarboxylic acid burden.

Acknowledgment. M.P.S.A. and O.J.N. thank the Danish Research council for a research grant. This research was funded, in part, by an NSERC Strategic Grant.

References and Notes

(1) Martin, J. W.; Whittle, D. M.; Muir, D. C. G.; Mabury, S. A. *Environ. Sci. Technol.* **2004**, *38*, 5379.

(2) Martin, J. W.; Smithwick, M. M.; Braune, B. M.; Hekstra, P. F.; Muir, D. C. G.; Mabury, S. A. *Environ. Sci. Technol.* **2004**, *38*, 373.

(3) Ellis, D. A.; Moody, C. A.; Mabury, S. A. Trifluoroacetic Acid and Longer Chain Perfluoro Acids—Sources and Analysis. In *Handbook of Environmental Chemistry*: *Part N, Organofluorines*; Nielson, A.; Ed.; Springer-Verlag: Heidelberg, Germany, 2002, Vol. 3.

(4) Berthiaume, J.; Wallace, K. B. *Toxicol. Lett.* **2002**, *129*, 23.

(5) Upham, B. L.; Deocampo, N. D.; Wurl, B.; Trosko, J. E. *Int. J. Cancer.* **1998**, *78*, 491.

(6) Biegel, L. B.; Hurtt, M. E.; Frame, S. R.; Connor, J. O.; Cook, J. C. *Toxicol. Sci.* **2001**, *60*, 44.

(7) *Preliminary risk assessment of the developmental toxicity associated with exposure to perfluorooctanoic acid and its salts*; OPPT-2003−0012; US Environmental Protection Agency, Office of Pollution Prevention and Toxics, Risk Assessment Division: Washington, DC, 2003.

(8) Frank, H.; Christoph, E. H.; Holm-Hansen, O.; Bullister, J. L. *Environ. Sci. Technol.* **2002**, *36*, 12.

(9) Ellis, D. A.; Mabury, S. A.; Martin, J. W.; Muir, D. C. G. *Nature* **2001**, *412*, 321.

(10) Scott, B. F.; Spencer, C.; Moody, C. A.; Mabury, S. A.; MacTavish, D.; Muir, D. C. G. Poster presented at the 13th Annual SETAC Europe Meeting, Hamburg, Germany, 2003.

(11) Hurley, M. D.; Andersen, S. M. P.; Wallington, T. J.; Ellis, D. A.; Martin, J. W.; Mabury, S. A. *J. Phys. Chem. A* **2004**, *108*, 615.

(12) Ellis, D. A.; Martin, J. W.; Mabury, S. A.; Hurley, M. D.; Andersen, S. M. P.; Wallington, T. J. *Environ. Sci. Technol.* **2003**, *37*, 3816.

(13) Ellis, D. A.; Martin, J. W.; De Silva, A. O.; Mabury, S. A.; Hurley, M. D.; Andersen, S. M. P.; Wallington, T. J. *Environ. Sci. Technol.* **2004**, *38*, 3316.

(14) Telomer Research Program Update. Presentation to USEPA-OPPT, November 25, 2002, US Public Docket AR226−1141.

(15) Martin, J. W.; Muir, D. C. G.; Moody, C. A.; Ellis, D. A.; Kwan, W. C.; Solomon, K. R.; Mabury, S. A. *Anal. Chem.* **2002**, *74*, 584.

(16) Stock, N. L.; Lau, F. K.; Ellis, D. A.; Martin, J. W.; Muir, D. C. G.; Mabury, S. A. *Environ. Sci. Technol.* **2004**, *38*, 991.

(17) Le Bras, G.; Bossoutrot, V.; Magneron, I. *Study of the Atmospheric Fate of Fluorinated Alcohols, Final Report to the Fluorotelomer Research Program*, July 2003.

(18) Hurley, M. D.; Ball, J. C.; Wallington, T. J.; Andersen, S. M. P.; Ellis, D. A.; Martin, J. W.; Mabury, S. A. *J. Phys. Chem. A.* **2004**, *108*, 5635.

(19) Wallington, T. J.; Japar, S. M. *J. Atmos. Chem.* **1989**, *9*, 399.

(20) Andersen, S. M. P.; Hurley, M. D.; Wallington, T. J.; Ball, J. C.; Martin, J. W.; Ellis, D. A.; Mabury, S. A.; Nielsen, O. J. *Chem. Phys. Lett.* **2003**, *379*, 28.

(21) Hashikawa, Y.; Kawasaki, M.; Waterland, R. L.; Hurley, M. D.; Ball, J. C.; Wallington, T. J.; Sulbaek Andersen, M. P.; Nielsen, O. J. *J. Fluorine Chem.* **2004**, *125*, 1925.

(22) Dibble, T. S. *Chem. Phys. Lett.* **2002**, *335*, 193.

(23) Orlando, J. J.; Noziere, B.; Tyndall, G. S.; Orzechowska, G. E.; Paulson, S. E.; Rudich, Y. *J. Geophys. Res.* **2000**, *105*, 11561.

(24) Andersen, S. M. P.; Nielsen, O. J.; Hurley, M. D.; Ball, J. C.; Wallington, T. J.; Stevens, J. E.; Martin, J. W.; Ellis, D. A.; Mabury, S. A. *J. Phys. Chem. A* **2004**, *108*, 5189.

(25) Wallington, T. J.; Andino, J. M.; Ball, J. C.; Japar, S. M. *J. Atmos. Chem.* **1990**, *10*, 301.

(26) Meagher, R. J.; McIntosh, M. E.; Hurley, M. D.; Wallington, T. J. *Int. J. Chem. Kinet.* **1997**, *29*, 619.

(27) Orlando, J. J.; Tyndall, G. S.; Wallington, T. J. *Chem. Rev.* **2003**, *103*, 4657.

(28) Wallington, T. J.; Hurley, M. D.; Fracheboud, J. M.; Orlando, J. J.; Tyndall, G. S.; Sehested, J.; Møgelberg, T. E.; Nielsen, O. J. *J. Phys. Chem.* **1996**, *100*, 18116.

(29) Veyret, B.; Lesclaux, R.; Rayez, M.-T.; Rayez, J.-C.; Cox, R. A.; Moortgat, G. K. *J. Phys. Chem.* **1989**, *93*, 2368.

(30) Burrows, J. P.; Moortgat, G. K.; Tyndall, G. S.; Cox, R. A.; Jenkin, M. E.; Hayman, G. D.; Veyret, B. *J. Phys. Chem.* **1989**, *93*, 2375.

(31) Peeters, J.; Vereecken, L.; Fantechi, G. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5489.

(32) Wu, F.; Carr, R. W. *J. Phys. Chem. A* **1996**, *100*, 9352.

(33) Haszeldine, R. N.; Jander, J. *J. Chem. Soc.* **1954**, 691.

(34) Haszeldine, R. N.; Mattinson, B. J. H. *J. Chem. Soc.* **1955**, 4172.

(35) Wallington, T. J.; Sehested, J.; Nielsen, O. J. *Chem. Phys. Lett.* **1994**, *226*, 563.

(36) Caralp, F.; Foucher, V.; Lesclaux, R.; Wallington, T. J.; Hurley, M. D. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3509.

(37) Tsalkani, N.; Toupance, G. *Atmos. Environ.* **1989**, *23*, 1849.

(38) Andersen, S. M. P.; Stenby, C.; Nielsen, O. J.; Hurley, M. D.; Ball, J. C.; Wallington, T. J.; Martin, J. W.; Ellis, D. A.; Mabury, S. A. *J. Phys. Chem. A* **2004**, *108*, 6325.