

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231639747>

# Atmospheric Chemistry of $n\text{-C}_x\text{F}_{2x+1}\text{CHO}$ ( $x = 1, 3, 4$ ): Mechanism of the $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2 + \text{HO}_2$ Reaction

ARTICLE · JUNE 2004

CITATIONS

4

READS

43

3 AUTHORS, INCLUDING:



**M. P. Sulbaek Andersen**

California State University, Northridge

61 PUBLICATIONS 1,806 CITATIONS

SEE PROFILE



**Ole John Nielsen**

University of Copenhagen

263 PUBLICATIONS 4,912 CITATIONS

SEE PROFILE

# Atmospheric Chemistry of $n\text{-C}_x\text{F}_{2x+1}\text{CHO}$ ( $x = 1, 3, 4$ ): Mechanism of the $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2 + \text{HO}_2$ Reaction

M. P. Sulbaek Andersen, C. Stenby, 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, P.O. Box 2053, Dearborn, Michigan 48121-2053

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

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

Received: March 15, 2004; In Final Form: May 11, 2004

Smog chamber/FTIR techniques were used to study the gas-phase reaction of  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$  ( $x = 1, 3, 4$ ) with  $\text{HO}_2$  radicals in 700 Torr of air, or  $\text{O}_2$ , diluent at  $296 \pm 2$  K. The reactions proceed by three pathways leading to formation of  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OOH}$  and  $\text{O}_2$ ,  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OH}$  and  $\text{O}_3$ , or  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}$  radicals, OH radicals, and  $\text{O}_2$ . Carboxylic acid yields were  $38 \pm 4\%$  ( $x = 1$ ),  $10 \pm 2\%$  ( $x = 3$ ), and  $8 \pm 2\%$  ( $x = 4$ ). Results are discussed with respect to the potential for the atmospheric degradation of fluorotelomer alcohols,  $\text{C}_x\text{F}_{2x+1}\text{CH}_2\text{CH}_2\text{OH}$ , to contribute to the environmental burden of fluorinated carboxylic acids,  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OH}$ . Rate constants for the reactions of Cl atoms with  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OH}$  and  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OOH}$  were determined to be  $k(\text{Cl} + \text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OH}) < 2 \times 10^{-17}$  and  $k(\text{Cl} + \text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OOH}) = (2.9 \pm 0.7) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  in 700 Torr of  $\text{N}_2$  at  $296 \pm 2$  K.

## 1. Introduction

Persistent, bioaccumulative,<sup>1,2</sup> and potentially toxic,<sup>3–5</sup> long-chain perfluorinated carboxylic acids (PFCAs,  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OH}$ , where  $x = 6–12$ ) have been observed in remote locations around the world.<sup>6,7</sup> There are no known natural sources of long-chain PFCAs,<sup>8</sup> these compounds are not expected to be mobile in the environment,<sup>9</sup> and it is puzzling that they are observed in remote locations. The most likely explanation for the presence of PFCAs in remote areas is that these compounds are formed as degradation products of one or more precursor chemicals in the atmosphere.

Laboratory studies have shown that perfluorinated carboxylic acids are formed in small yields during the simulated atmospheric oxidation of fluorotelomer alcohols (FTOHs,  $\text{C}_x\text{F}_{2x+1}\text{CH}_2\text{CH}_2\text{OH}$ ) in the absence of  $\text{NO}_x$ .<sup>10,11</sup> FTOHs have significant (20 day) atmospheric lifetimes,<sup>12</sup> are present in  $\text{pg m}^{-3}$  concentrations in ambient air,<sup>13,14</sup> are emitted in substantial amounts ( $100–1000 \text{ tonnes yr}^{-1}$  over North America),<sup>12</sup> and are thus a plausible source for the PFCAs observed in remote locations. It is well-established that the atmospheric oxidation of ethanol gives acetaldehyde and that subsequent oxidation of acetaldehyde gives acetyl peroxy radicals,  $\text{CH}_3\text{C}(\text{O})\text{O}_2$ , which can react with  $\text{HO}_2$  radicals to give peracetic and acetic acid.<sup>15–21</sup>



Wet and dry deposition of FTOHs is of negligible atmospheric importance.<sup>12</sup> The atmospheric oxidation of FTOHs is initiated by gas-phase reaction with OH radicals giving perfluoroaldehydes<sup>11</sup> which undergo further oxidation to give fluorinated acyl peroxy radicals,  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$ . It has been proposed that reaction channels analogous to (1b) are responsible for PFCA formation in laboratory studies of FTOH oxidation and are probably important in the atmospheric chemistry of FTOHs.<sup>11</sup>

To assess this possibility we have used smog chamber FTIR techniques to determine the products of the reactions of  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$  ( $x = 1, 3, 4$ ) radicals with  $\text{HO}_2$  radicals. Results are discussed with respect to the atmospheric chemistry and environmental impact of fluorotelomer alcohols. Peroxy radicals from straight chain isomers  $n\text{-C}_3\text{F}_7\text{CHO}$  and  $n\text{-C}_4\text{F}_9\text{CHO}$  were studied in the present work. For simplicity we will refer to these species as  $\text{C}_3\text{F}_7\text{CHO}$  and  $\text{C}_4\text{F}_9\text{CHO}$  in the rest of this article.

## 2. Experimental Section

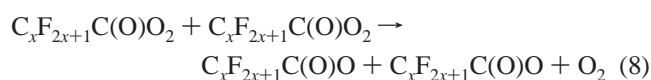
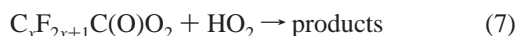
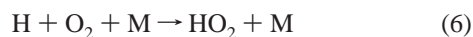
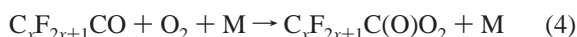
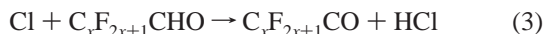
The apparatus and experimental techniques used in this work are described elsewhere.<sup>22,23</sup> Experiments were performed in a 140-L Pyrex reactor interfaced to a Mattson Sirius 100 FTIR spectrometer. The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL) which were used to photochemically initiate the experiments. Chlorine atoms were produced by photolysis of molecular chlorine.



$\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$  and  $\text{HO}_2$  radicals were generated by the UV irradiation of  $\text{C}_x\text{F}_{2x+1}\text{CHO}/\text{H}_2/\text{Cl}_2$  mixtures in 100–700 Torr

\* Address correspondence to this author. E-mail: twalling@ford.com.

of air, or O<sub>2</sub>, diluent at 296 ± 2 K (M represents a third body, N<sub>2</sub> or O<sub>2</sub>):



Initial concentrations of the gas mixtures used were 5.1–22.1 mTorr of C<sub>x</sub>F<sub>2x+1</sub>CHO, 204–613 mTorr of Cl<sub>2</sub>, and 0.33–11.4 Torr of H<sub>2</sub> in 700 or 100 Torr of air diluent (ultrahigh purity). Reactions 7 and 8 compete as loss mechanisms for C<sub>x</sub>F<sub>2x+1</sub>C(O)O<sub>2</sub> in the system. To study the mechanism of reaction 7 a series of experiments were performed in which the initial concentration ratio [H<sub>2</sub>]<sub>0</sub>/[C<sub>x</sub>F<sub>2x+1</sub>CHO]<sub>0</sub> was varied from 0 to 1753. The rate constant ratio  $k_3/k_5$  is  $2.1 \times 10^{-12}/1.6 \times 10^{-14} = 131$ .<sup>24,25</sup> Thus, the initial rate of production of HO<sub>2</sub> radicals was 0–13.4 times that of C<sub>x</sub>F<sub>2x+1</sub>C(O)O<sub>2</sub> radicals. As the [H<sub>2</sub>]<sub>0</sub>/[C<sub>x</sub>F<sub>2x+1</sub>CHO]<sub>0</sub> ratio increases, more HO<sub>2</sub> radicals are generated in the system for a given level of C<sub>x</sub>F<sub>2x+1</sub>C(O)O<sub>2</sub> and the relative importance of reaction 7 as a loss mechanism for C<sub>x</sub>F<sub>2x+1</sub>C(O)O<sub>2</sub> increases. The increased importance of reaction 7 should be manifested by a change in the products observed in the chamber. For sufficiently high values of [H<sub>2</sub>]<sub>0</sub>/[C<sub>x</sub>F<sub>2x+1</sub>CHO]<sub>0</sub> essentially all of the C<sub>x</sub>F<sub>2x+1</sub>C(O)O<sub>2</sub> radicals should be lost via reaction 7. At this point, further increases in [H<sub>2</sub>]<sub>0</sub>/[C<sub>x</sub>F<sub>2x+1</sub>CHO]<sub>0</sub> will have no discernible effect on the observed products which can then be ascribed to reaction 7. This approach has been used in previous studies of the reactions of HO<sub>2</sub> radicals with CH<sub>2</sub>FO<sub>2</sub>,<sup>26</sup> CH<sub>3</sub>C(O)O<sub>2</sub>,<sup>19</sup> and C<sub>2</sub>F<sub>5</sub>C(O)O<sub>2</sub>.<sup>27</sup>

Reactant and product concentrations were monitored with in situ Fourier transform infrared spectroscopy. IR spectra were derived from 32 coadded interferograms with a spectral resolution of 0.25 cm<sup>-1</sup> and an analytical path length of 27.1 m. Calibrated reference spectra were acquired by expanding known volumes of reference materials into the chamber. The vapor above liquid CF<sub>3</sub>C(O)OH, C<sub>3</sub>F<sub>7</sub>C(O)OH, and C<sub>4</sub>F<sub>9</sub>C(O)OH contains monomer and dimer. Values of  $K_{\text{eq}}(\text{CF}_3\text{C(O)OH}) = [\text{dimer}]/[\text{monomer}]^2 = 0.32 \pm 0.03 \text{ Torr}^{-1}$ ,  $K_{\text{eq}}(\text{C}_3\text{F}_7\text{C(O)OH}) = 0.41 \pm 0.04 \text{ Torr}^{-1}$ , and  $K_{\text{eq}}(\text{C}_4\text{F}_9\text{C(O)OH}) = 0.46 \pm 0.05 \text{ Torr}^{-1}$  were used to correct for the presence of dimer (5–26% partial pressure) in the calibrated volumes. Analysis of the IR spectra was achieved through a process of spectral stripping in which small fractions of the reference spectrum were subtracted incrementally from the sample spectrum. Unless stated otherwise, all quoted errors are 2 standard deviations from linear least-squares regressions.

Samples of C<sub>x</sub>F<sub>2x+1</sub>CHO ( $x = 1, 3, 4$ ) were synthesized as described elsewhere<sup>24</sup> and purified by vacuum distillation. CF<sub>3</sub>C(O)OOH was synthesized by reacting trifluoroacetic anhydride with concentrated H<sub>2</sub>O<sub>2</sub>. Concentrated hydrogen peroxide was prepared from 50% commercial grade hydrogen peroxide by removing water-enriched vapor under vacuum. An equal volume of dichloromethane was added to the concentrated hydrogen peroxide (approximately 90%) followed by a stoichiometric amount of trifluoroacetic anhydride (assuming a molar ratio of 1:1 for the reaction of hydrogen peroxide and the trifluoroacetic

anhydride). Dichloromethane and any unreacted trifluoroacetic anhydride were removed under a stream of dry nitrogen gas. We caution against using an excess of the trifluoroacetic anhydride due to the possible formation of the potentially explosive trifluoroacetyl peroxide.<sup>28</sup> All other reactants were obtained from commercial sources at purities >99%. Ultrahigh purity air (THC < 0.1 ppm) and O<sub>2</sub> (>99.994%) diluent gases were used as received.

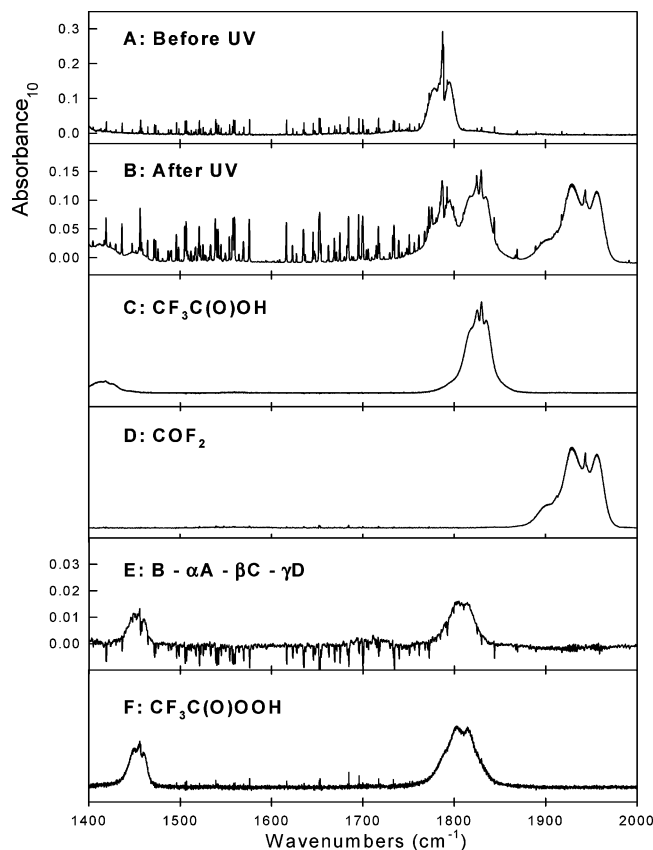
In smog chamber experiments unwanted loss of reactants and products via photolysis and heterogeneous reactions has to be considered. Control experiments were performed in which product mixtures obtained after UV irradiation were allowed to stand in the dark in the chamber for 30 min. With the exception of CF<sub>3</sub>OH, there was no observable (<2%) loss of reactants or products. Samples of C<sub>x</sub>F<sub>2x+1</sub>CHO, C<sub>x</sub>F<sub>2x+1</sub>C(O)OH ( $x = 1, 3, 4$ ), and CF<sub>3</sub>C(O)OOH were subjected to UV irradiation in 700 Torr of air diluent for 15 min without any observable loss (<1%) suggesting that photolysis of C<sub>x</sub>F<sub>2x+1</sub>CHO, C<sub>x</sub>F<sub>2x+1</sub>C(O)OH, and CF<sub>3</sub>C(O)OOH is not a significant complication in the present work.

### 3. Results

**3.1. Measurement of  $k(\text{Cl} + \text{C}_x\text{F}_{2x+1}\text{C(O)OH})$ ,  $x = 3, 4$  and  $k(\text{Cl} + \text{CF}_3\text{C(O)OOH})$ .** Prior to the study of the mechanism of reaction 7 experiments were performed to investigate the rate of reaction of Cl atoms with C<sub>x</sub>F<sub>2x+1</sub>C(O)OH ( $x = 3, 4$ ) using the relative rate technique. Mixtures containing 4.4–6.8 mTorr of C<sub>x</sub>F<sub>2x+1</sub>C(O)OH, 6.2–11.6 mTorr of CF<sub>2</sub>ClH, and 0.85–1.03 Torr of Cl<sub>2</sub> in 700 Torr of N<sub>2</sub> were introduced into the chamber. Irradiation of the gas mixtures for 7.5–10.5 min led to >83% consumption of CF<sub>2</sub>ClH but no discernible loss (<2%) of C<sub>x</sub>F<sub>2x+1</sub>C(O)OH. Using  $k(\text{Cl} + \text{CF}_2\text{ClH}) = 1.7 \times 10^{-15}$  from ref 25 we derive an upper limit of  $k(\text{Cl} + \text{C}_x\text{F}_{2x+1}\text{C(O)OH}, x = 3, 4) < 2 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This finding is consistent with previous determinations of  $k(\text{Cl} + \text{CF}_3\text{C(O)OH}) < 1 \times 10^{-17}$  from ref 29 and  $k(\text{Cl} + \text{C}_2\text{F}_5\text{C(O)OH}) < 1.7 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  from ref 27.

The rate of reaction of Cl atoms with CF<sub>3</sub>C(O)OOH was measured relative to the rates of reaction of Cl atoms with CF<sub>2</sub>ClCH<sub>3</sub> and CF<sub>2</sub>ClH. Reaction mixtures consisted of either 3.0 mTorr of CF<sub>3</sub>C(O)OOH, 4.5 mTorr of CF<sub>2</sub>ClH, and 99 mTorr of Cl<sub>2</sub> or 1.9 mTorr of CF<sub>3</sub>C(O)OOH, 19.8 mTorr of CF<sub>2</sub>ClH, and 400 mTorr of Cl<sub>2</sub>. Experiments were performed in 700 Torr of N<sub>2</sub> at 296 K. Irradiation of the gas mixtures led to discernible losses of CF<sub>3</sub>C(O)OOH, CF<sub>2</sub>ClCH<sub>3</sub>, and CF<sub>2</sub>ClH from which rate constant ratios of  $k(\text{Cl} + \text{CF}_3\text{C(O)OOH})/k(\text{Cl} + \text{CF}_2\text{ClCH}_3) = 0.80 \pm 0.10$  and  $k(\text{Cl} + \text{CF}_3\text{C(O)OOH})/k(\text{Cl} + \text{CF}_2\text{ClH}) = 0.15 \pm 0.02$  were determined. Using  $k(\text{Cl} + \text{CF}_2\text{ClCH}_3) = 3.9 \times 10^{-16}$  and  $k(\text{Cl} + \text{CF}_2\text{ClH}) = 1.7 \times 10^{-15}$  gives  $k(\text{Cl} + \text{CF}_3\text{C(O)OOH}) = (3.1 \pm 0.4) \times 10^{-16}$  and  $(2.6 \pm 0.4) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. The results obtained with two different references are indistinguishable within the experimental uncertainties. We choose to quote a final value that is the average with uncertainties encompassing the extremes of the two determinations. Hence,  $k(\text{Cl} + \text{CF}_3\text{C(O)OOH}) = (2.9 \pm 0.7) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . CF<sub>3</sub>C(O)OOH is at least an order of magnitude more reactive than CF<sub>3</sub>C(O)OH toward Cl atoms, presumably reflecting a weaker O–H bond in the peracid.

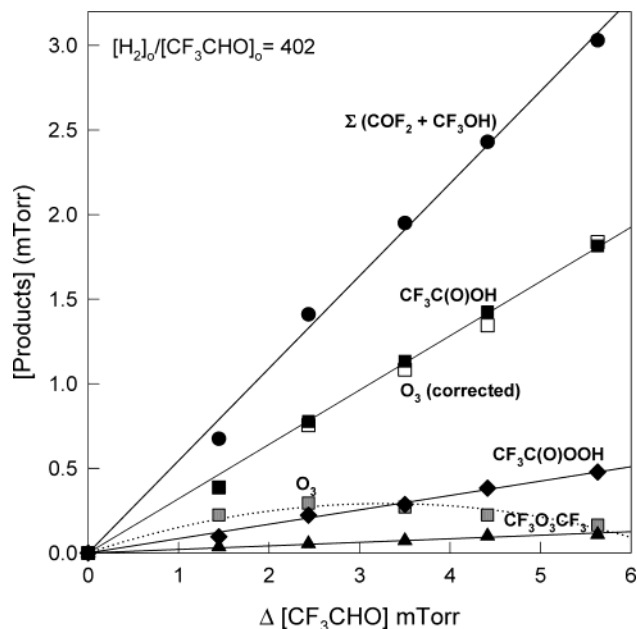
**3.2. Products of the CF<sub>3</sub>C(O)O<sub>2</sub> + HO<sub>2</sub> Reaction.** Figure 1 shows typical spectra acquired before (panel A) and after (panel B) a 100-s irradiation of a mixture of 14.8 mTorr of CF<sub>3</sub>CHO, 9.04 Torr of H<sub>2</sub>, and 251 mTorr of Cl<sub>2</sub> in 700 Torr of air diluent. The loss of CF<sub>3</sub>CHO was 8.3 mTorr. Comparison with reference spectra of CF<sub>3</sub>C(O)OH and COF<sub>2</sub> shown in panels C



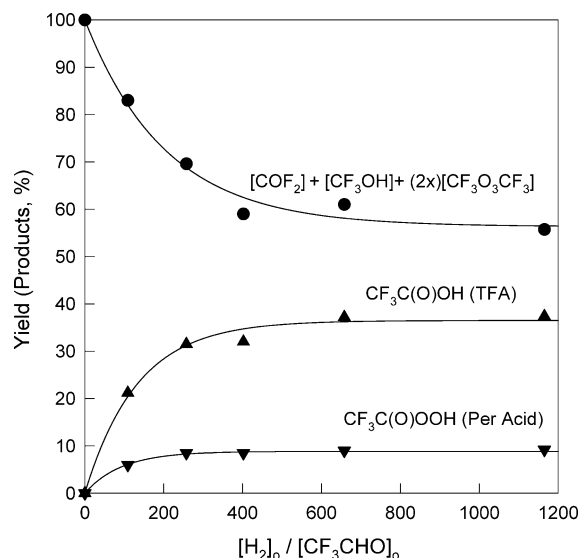
**Figure 1.** IR spectra obtained before (A) and after (B) a 100-s irradiation of a mixture of 14.8 mTorr of CF<sub>3</sub>CHO, 9.04 Torr of H<sub>2</sub>, and 251 mTorr of Cl<sub>2</sub> in 700 Torr of air diluent. The consumption of CF<sub>3</sub>CHO was 56%. Panels C, D, and F are reference spectra of CF<sub>3</sub>COOH, COF<sub>2</sub>, and CF<sub>3</sub>C(O)OOH, respectively. Panel E shows the residual spectrum obtained by subtracting features attributable to CF<sub>3</sub>CHO, CF<sub>3</sub>COOH, CF<sub>3</sub>C(O)OOH, and COF<sub>2</sub> from panel B.

and D indicates the formation of these species. The peaks of CF<sub>3</sub>C(O)OH and COF<sub>2</sub> are located at 1829 and 1944 cm<sup>-1</sup>, respectively. Subtraction of IR features attributable to CF<sub>3</sub>CHO, CF<sub>3</sub>C(O)OH, and COF<sub>2</sub> from panel B gives the residual spectrum shown in panel E. The formation of the peracid, CF<sub>3</sub>C(O)OOH, is evident by comparison of panel E with the reference spectrum in panel F.

Figure 2 shows a plot of the yields of the sum of COF<sub>2</sub> and CF<sub>3</sub>OH (circles), CF<sub>3</sub>C(O)OH (squares), CF<sub>3</sub>C(O)OOH (diamonds), CF<sub>3</sub>O<sub>3</sub>CF<sub>3</sub> (triangles), and O<sub>3</sub> (gray squares) versus loss of CF<sub>3</sub>CHO following Cl initiated oxidation in the presence of H<sub>2</sub> (e.g. HO<sub>2</sub>) for an experiment employing a [H<sub>2</sub>]<sub>0</sub>/[CF<sub>3</sub>CHO]<sub>0</sub> ratio of 402 at 700 Torr of air diluent. The straight lines through the data in Figure 2 are linear fits (unweighted, forced through origin), and the curved dotted line is a second-order fit to aid visual inspection of the data trend. CF<sub>3</sub>OH undergoes heterogeneous decomposition in the chamber<sup>30</sup> to give COF<sub>2</sub> and hence it is convenient to combine CF<sub>3</sub>OH and COF<sub>2</sub> in the plot. The linearity of the formation of CF<sub>3</sub>C(O)OH and CF<sub>3</sub>C(O)OOH shown in Figure 2 suggest that losses of these species are not significant during these experiments. This is consistent with expectations given the absence of photolytic or heterogeneous losses of CF<sub>3</sub>C(O)OH or CF<sub>3</sub>C(O)OOH and their low reactivity toward Cl atoms. Similarly, the linearity of the plot of the combined yield of CF<sub>3</sub>OH and COF<sub>2</sub> suggests that, with the exception of the conversion of CF<sub>3</sub>OH into COF<sub>2</sub> noted above, there are no losses of these species in the system.



**Figure 2.** Yields of Σ(COF<sub>2</sub> + CF<sub>3</sub>OH) (circles), CF<sub>3</sub>C(O)OH (squares), CF<sub>3</sub>C(O)OOH (diamonds), CF<sub>3</sub>O<sub>3</sub>CF<sub>3</sub> (triangles), and O<sub>3</sub> (gray squares) versus loss of CF<sub>3</sub>CHO following Cl initiated oxidation in the presence of H<sub>2</sub> for an experiment employing a [H<sub>2</sub>]<sub>0</sub>/[CF<sub>3</sub>CHO]<sub>0</sub> ratio of 402 at 700 Torr of air diluent. The open squares are the result of correcting for loss of O<sub>3</sub> via reaction with Cl atoms (see text for details).



**Figure 3.** Product yields following Cl initiated oxidation of CF<sub>3</sub>CHO in the presence of HO<sub>2</sub> radicals versus [H<sub>2</sub>]<sub>0</sub>/[CF<sub>3</sub>CHO]<sub>0</sub> in 700 Torr of air diluent, at 296 ± 2 K.

The observed yields of CF<sub>3</sub>C(O)OH, CF<sub>3</sub>C(O)OOH, and Σ(COF<sub>2</sub> + CF<sub>3</sub>OH + 2CF<sub>3</sub>O<sub>3</sub>CF<sub>3</sub>) from the various experiments are plotted versus [H<sub>2</sub>]<sub>0</sub>/[CF<sub>3</sub>CHO]<sub>0</sub> in Figure 3. As seen from Figure 3, the yield of CF<sub>3</sub>C(O)OH and CF<sub>3</sub>C(O)OOH increases as the concentration ratio [H<sub>2</sub>]<sub>0</sub>/[CF<sub>3</sub>CHO]<sub>0</sub> is increased from 0 to 600, presumably reflecting the increased importance of reaction 1 as a loss of CF<sub>3</sub>C(O)O<sub>2</sub> radicals. Concurrently, the combined yield of COF<sub>2</sub>, CF<sub>3</sub>OH, and CF<sub>3</sub>O<sub>3</sub>CF<sub>3</sub> decreases. For concentration ratios greater than 600, there is no observable dependence of product yields on [H<sub>2</sub>]<sub>0</sub>/[CF<sub>3</sub>CHO]<sub>0</sub> suggesting that, under these conditions, essentially all the CF<sub>3</sub>C(O)O<sub>2</sub> radicals are consumed by reaction with HO<sub>2</sub> radicals. Averaging the product data obtained in experiments with [H<sub>2</sub>]<sub>0</sub>/[CF<sub>3</sub>CHO]<sub>0</sub> of 600 or more gives the following product yields: CF<sub>3</sub>C(O)-



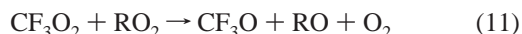
OH,  $38 \pm 4\%$ ;  $\text{CF}_3\text{C}(\text{O})\text{OOH}$ ,  $9 \pm 4\%$ ; and  $\Sigma(\text{COF}_2 + \text{CF}_3\text{-OH} + 2x\text{CF}_3\text{O}_3\text{CF}_3)$ ,  $56 \pm 5\%$ . Quoted errors are 2 standard deviations from the linear least-squares regressions. Together,  $\text{CF}_3\text{C}(\text{O})\text{OH}$ ,  $\text{CF}_3\text{C}(\text{O})\text{OOH}$ ,  $\text{COF}_2$ ,  $\text{CF}_3\text{OH}$ , and  $\text{CF}_3\text{O}_3\text{CF}_3$  account for  $103 \pm 12\%$  of the loss of  $\text{CF}_3\text{CHO}$ .

$\text{O}_3$  is an expected coproduct of  $\text{CF}_3\text{C}(\text{O})\text{OH}$  and was observed by virtue of its characteristic IR features at  $1000\text{--}1100\text{ cm}^{-1}$ . The pronounced curvature of the  $\text{O}_3$  yield plot in Figure 2 can be rationalized by the fact that Cl atoms react with  $\text{O}_3$  at a rate that is  $1.2 \times 10^{-11}$  (ref 25)/ $2.1 \times 10^{-12}$  (ref 24) = 6 times faster than the reaction with  $\text{CF}_3\text{CHO}$ . Hence, loss of  $\text{O}_3$  via secondary reaction with Cl atoms is substantial for the fractional consumptions of  $\text{CF}_3\text{CHO}$  employed in the present work. The importance of  $\text{O}_3$  loss via secondary reaction with Cl atoms is dependent upon the fractional consumption of  $\text{CF}_3\text{CHO}$ . The open squares in Figure 2 show the result of correcting the observed  $\text{O}_3$  concentrations for loss via reaction with Cl atoms.<sup>31</sup> As seen from Figure 2, when corrected for loss via reaction with Cl atoms, the  $\text{O}_3$  yield is indistinguishable from that of  $\text{CF}_3\text{C}(\text{O})\text{OH}$ . This observation is consistent with the formation of  $\text{O}_3$  and  $\text{CF}_3\text{C}(\text{O})\text{OH}$  in reaction channel 9b.

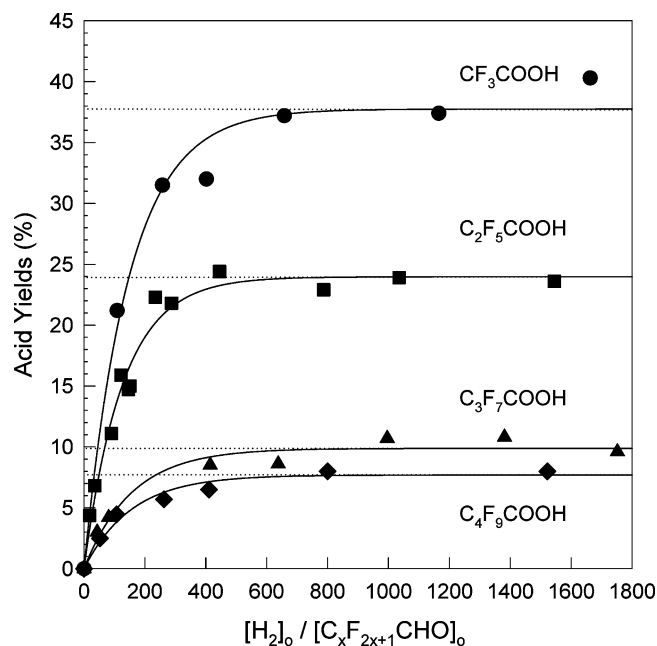
The simplest explanation for the observed products is that under the present experimental conditions (296 K, 700 Torr) the reaction of  $\text{CF}_3\text{C}(\text{O})\text{O}_2$  with  $\text{HO}_2$  proceeds via three channels with  $k_{9a}/(k_{9a} + k_{9b} + k_{9c}) = 0.09 \pm 0.04$ ,  $k_{9b}/(k_{9a} + k_{9b} + k_{9c}) = 0.38 \pm 0.04$ , and  $k_{9c}/(k_{9a} + k_{9b} + k_{9c}) = 0.56 \pm 0.05$ .



$\text{CF}_3\text{C}(\text{O})\text{O}$  radicals formed in reaction 9c will eliminate  $\text{CO}_2$  to give  $\text{CF}_3$  radicals which will react to give  $\text{CF}_3\text{OH}$  (which decomposes to give  $\text{COF}_2$ ) and  $\text{CF}_3\text{O}_3\text{CF}_3$



**3.3. Products of the  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$  ( $x = 3, 4$ ) +  $\text{HO}_2$  Reactions.** The products of the reaction of  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$  ( $x = 3, 4$ ) and  $\text{HO}_2$  radicals were investigated in experiments similar to those described in the previous section with  $\text{C}_3\text{F}_7\text{-CHO}$  or  $\text{C}_4\text{F}_9\text{CHO}$  used in place of  $\text{CF}_3\text{CHO}$ . Studies of the reaction products of longer chain acyl peroxy radicals,  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$  ( $x = 3, 4$ ), are more challenging than those described above for the shortest member of the series because it is more difficult to obtain samples of the likely products and hence more difficult to calibrate the FTIR system. For example, in experiments with  $\text{C}_3\text{F}_7\text{CHO}$  and  $\text{C}_4\text{F}_9\text{CHO}$  one or more unknown products with large and broad absorption features at  $1000\text{--}1400\text{ cm}^{-1}$  are formed. By comparison with the available spectra for  $\text{CF}_3\text{O}_3\text{CF}_3$  and  $\text{C}_2\text{F}_5\text{O}_3\text{CF}_3$ ,<sup>32</sup> the unknown products are probably mixed trioxides (e.g., for  $x = 4$ :  $\text{C}_4\text{F}_9\text{O}_3\text{CF}_3$ ,  $\text{C}_3\text{F}_7\text{O}_3\text{-CF}_3$ , and  $\text{C}_2\text{F}_5\text{O}_3\text{CF}_3$ ) formed by addition of  $\text{CF}_3\text{O}$  to  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$  radicals. However, calibrated spectra for the mixed trioxides are not available and it was not possible to quantify the yields



**Figure 4.** Product yields following Cl initiated oxidation of  $\text{C}_x\text{F}_{2x+1}\text{-CHO}$  ( $x = 1\text{--}4$ ) in the presence of  $\text{HO}_2$  radicals versus  $[\text{H}_2]_0/[\text{C}_x\text{F}_{2x+1}\text{-CHO}]_0$  in 700 Torr of air diluent,  $296 \pm 2\text{ K}$ .

of these species. In contrast, the formation of  $\text{COF}_2$ ,  $\text{CF}_3\text{OH}$ , and  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OH}$  ( $x = 3, 4$ ) was easily quantifiable with use of calibrated IR spectra.<sup>9</sup> After subtraction of features attributable to  $\text{C}_x\text{F}_{2x+1}\text{CHO}$ ,  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OH}$ ,  $\text{COF}_2$ , and  $\text{CF}_3\text{-OH}$  there were no residual features that could be ascribed to the peracids  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OOH}$  ( $x = 3, 4$ ). On the basis of our experience with  $\text{CF}_3\text{C}(\text{O})\text{OOH}$ , we would expect that if significant amounts of  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OOH}$  ( $x = 3, 4$ ) were formed in the chamber we would observe these compounds. Using the observed absorption strength of  $\text{CF}_3\text{C}(\text{O})\text{OOH}$  as a guide, we estimate upper limits of 3% for the yield of  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OOH}$  ( $x = 3, 4$ ).

The observed yields of  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OH}$  ( $x = 3, 4$ ) together with results for  $x = 1$  discussed in the previous section and  $x = 2$  reported elsewhere<sup>27</sup> are plotted versus  $[\text{H}_2]_0/[\text{C}_x\text{F}_{2x+1}\text{-CHO}]_0$  in Figure 4. As seen from Figure 4, the variation of acid yield with  $[\text{H}_2]_0/[\text{C}_x\text{F}_{2x+1}\text{-CHO}]_0$  was the same shape for  $x = 1, 2, 3$ , and 4. This observation is reasonable since we would expect a similar competition between reactions 7 and 8 for the available  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$  radicals in the four systems. For concentration ratios greater than 600, there are no observable dependence of acid yields on  $[\text{H}_2]_0/[\text{C}_x\text{F}_{2x+1}\text{-CHO}]_0$  suggesting that, under these conditions, essentially all the  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$  radicals are consumed by reaction with  $\text{HO}_2$  radicals. Averaging the product data obtained with  $[\text{H}_2]_0/[\text{C}_x\text{F}_{2x+1}\text{-CHO}]_0$  of 600 or more gives the following acid yields:  $\text{C}_3\text{F}_7\text{C}(\text{O})\text{OH}$ ,  $10 \pm 2\%$ , and  $\text{C}_4\text{F}_9\text{C}(\text{O})\text{OH}$ ,  $8 \pm 2\%$ .

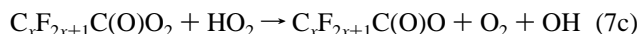
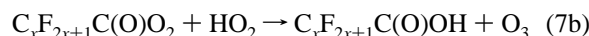
As discussed in section 3.2, it is expected that  $\text{O}_3$  will be formed in amounts comparable to those of  $\text{C}_3\text{F}_7\text{C}(\text{O})\text{OH}$  and  $\text{C}_4\text{F}_9\text{C}(\text{O})\text{OH}$ . Evidence for the formation of  $\text{O}_3$  in the product spectra was sought, but not found. As discussed previously for experiments with  $\text{C}_2\text{F}_5\text{CHO}$ ,<sup>27</sup> the fact that  $\text{O}_3$  was below the detection limit is explained by its low yield and high reactivity toward Cl atoms.

The simplest explanation for the observed products is that under the present experimental conditions (296 K, 700 Torr), very little, if any, of reaction 7 for  $n = 3$  and 4 proceeds via channel 7a, a small but significant fraction proceeds via channel

**TABLE 1: Branching Ratios in Reactions of  $\text{RC}(\text{O})\text{O}_2$  with  $\text{HO}_2$  Radicals under Ambient Conditions (700–760 Torr,  $296 \pm 2$  K)**

$\text{RC}(\text{O})\text{O}_2$	products			ref
	$\text{RC}(\text{O})\text{OOH} + \text{O}_2$	$\text{RC}(\text{O})\text{OH} + \text{O}_3$	$\text{RC}(\text{O})\text{O} + \text{O}_2 + \text{OH}$	
$\text{CH}_3\text{C}(\text{O})\text{O}_2$	$0.40 \pm 0.16$	$0.20 \pm 0.08$	$0.40 \pm 0.16$	21
$\text{CF}_3\text{C}(\text{O})\text{O}_2$	$0.09 \pm 0.04$	$0.38 \pm 0.04$	$0.56 \pm 0.05$	this work
$\text{C}_2\text{F}_5\text{C}(\text{O})\text{O}_2$	$<0.06$	$0.24 \pm 0.04$	$0.76 \pm 0.04$	27
$\text{C}_3\text{F}_7\text{C}(\text{O})\text{O}_2$	$<0.03$	$0.10 \pm 0.02$	$\approx 0.90$	this work
$\text{C}_4\text{F}_9\text{C}(\text{O})\text{O}_2$	$<0.03$	$0.08 \pm 0.02$	$\approx 0.90$	this work

7b to give the acid, and the bulk of the reaction proceeds via channel 7c.



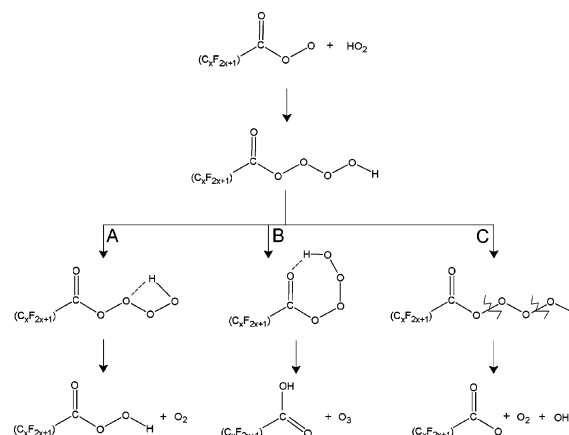
We conclude that for  $x = 3$  and 4,  $k_{7a}/(k_{7a} + k_{7b} + k_{7c}) < 0.03$  and  $k_{7c}/(k_{7a} + k_{7b} + k_{7c}) \approx 0.90$ . For  $x = 3$ ,  $k_{7b}/(k_{7a} + k_{7b} + k_{7c}) = 0.10 \pm 0.02$ . For  $x = 4$ ,  $k_{7b}/(k_{7a} + k_{7b} + k_{7c}) = 0.08 \pm 0.02$ .

#### 4. Discussion

**4.1. Comparison with Previous Work.** The available data concerning the branching ratios of reactions of acyl peroxy with  $\text{HO}_2$  radicals are listed in Table 1. Comparing the data for  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$  species there is a trend of decreased peracid and acid yields and increased radical yields as  $x$  increases from 1 to 3. On moving from  $x = 3$  to 4 there is no significant change in the branching ratios. This observation is not surprising given the expectation that the chemical environment of the peroxy radical reactive site will be very similar in  $\text{C}_3\text{F}_7\text{C}(\text{O})\text{O}_2$  and  $\text{C}_4\text{F}_9\text{C}(\text{O})\text{O}_2$ . On the other hand, the substantial decrease in  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OH}$  yield in moving from  $x = 2$  to 3 (see Table 1) is surprising. While it can be argued that the chemical environment of the acyl peroxy functionality in  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$  radicals changes significantly from  $x = 1$  to 2, it seems unlikely that increasing  $x$  from 2 to 3 would have a comparable effect. Interestingly, the magnitude of the change in the  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OH}$  yield observed from  $x = 1$  to 2 is comparable to that observed on moving from  $x = 2$  to 3 (see Table 1).

Prior to recent work by Hasson et al.,<sup>21</sup> it was believed that under ambient conditions the reaction of  $\text{CH}_3\text{C}(\text{O})\text{O}_2$  with  $\text{HO}_2$  radicals proceeded via two channels with  $k_{1a}/(k_{1a} + k_{1b}) = 0.80$  and  $k_{1b}/(k_{1a} + k_{1b}) = 0.20$ .<sup>20</sup> It is now clear that the reaction of  $\text{CH}_3\text{C}(\text{O})\text{O}_2$  with  $\text{HO}_2$  radicals actually proceeds via three channels with a sizable fraction of the overall reaction leading to radical products via reaction 1c (see Table 1). We show herein and elsewhere<sup>27</sup> that the radical-forming channel is the dominant reaction pathway for reactions of  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$  ( $x = 1\text{--}4$ ) with  $\text{HO}_2$  radicals. In light of the discussion above it would seem reasonable to revisit the analysis of kinetic and product data obtained in studies of other peroxy radicals to determine whether the radical-forming channel is a general feature of reactions of peroxy radicals with  $\text{HO}_2$  radicals.

**4.2. Mechanism of the  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2 + \text{HO}_2$  Reaction.** It is expected that the reaction of  $\text{HO}_2$  with  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$  ( $x = 1, 3, 4$ ) radicals proceeds via the formation of a short-lived tetroxide intermediate. As illustrated in Figure 5, the tetroxide can decompose via cyclic transition states to give either the peracid,  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OOH}$  and  $\text{O}_2$ , or the acid,  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OH}$  and  $\text{O}_3$ .



**Figure 5.** Mechanistic pathways for the  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2 + \text{HO}_2$  reaction.

$\text{OH}$  and  $\text{O}_3$ . Decomposition can also occur via  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}-\text{OOOH}$  or  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OOO}-\text{OH}$  bond scission to give  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}$  radicals,  $\text{O}_2$ , and  $\text{OH}$ . While it has been postulated for several decades that a tetroxide intermediate is formed in the reaction of peroxy radicals with  $\text{HO}_2$  radicals, this intermediate has never been observed. Computational studies are needed to shed light on the role of the tetroxide intermediate and the factors responsible for the changes in reaction mechanisms of the different peroxy radicals.

#### 5. Implications for Atmospheric Chemistry

The goal of the present work was to investigate the possibility that the gas-phase reaction of  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$  with  $\text{HO}_2$  radicals is an atmospheric source of perfluorocarboxylic acids. We show here that in 700 Torr of air diluent at 296 K the reaction of  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$  ( $x = 1, 3, 4$ ) with  $\text{HO}_2$  radicals gives  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OH}$  ( $x = 1, 3, 4$ ) in yields of  $38 \pm 4\%$  ( $x = 1$ ),  $10 \pm 2\%$  ( $x = 3$ ), and  $8 \pm 2\%$  ( $x = 4$ ). As discussed in section 4.1 it seems likely that reactions of  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$  ( $x > 4$ ) with  $\text{HO}_2$  radicals will give the perfluorocarboxylic acid  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OH}$  in a yield of approximately 10%.

Translation of the results from the present work into an estimation of the fraction of fluorinated aldehydes in the atmosphere which are converted into fluorinated acids is complicated by at least three factors. First, photolysis and reaction with  $\text{OH}$  radicals are competing atmospheric fates of  $\text{C}_x\text{F}_{2x+1}\text{CHO}$ . Reaction with  $\text{OH}$  leads to the formation of  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$  radicals in 100% yield. Recent experiments with  $\text{CF}_3\text{CHO}$  indicate that the atmospheric photolysis is slow (lifetime  $> 27$  days).<sup>33</sup> However, the rate and products of photolysis of longer chain members of the  $\text{C}_x\text{F}_{2x+1}\text{CHO}$  series are unclear and so it is difficult to establish the fraction of  $\text{C}_x\text{F}_{2x+1}\text{CHO}$  that is converted into  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$ . Second, reactions with  $\text{NO}$  and  $\text{HO}_2$  radicals are competing atmospheric fates for  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$  radicals. Oxidation of  $\text{C}_x\text{F}_{2x+1}\text{CHO}$  in the presence of excess  $\text{NO}$  does not lead to the formation of  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OH}$ .<sup>24,27</sup> In the absence of kinetic data for reactions with  $\text{NO}$  and  $\text{HO}_2$  it is difficult to estimate the fraction of  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{O}_2$  that reacts with  $\text{HO}_2$  radicals. Third, mechanistic data for reaction 7 are needed at temperatures in the atmospherically relevant range 220–300 K. In the analogous reaction of  $\text{CH}_3\text{C}(\text{O})\text{O}_2$  radicals the channel giving the acid increases in importance as the temperature is lowered.<sup>20</sup> Decreasing temperature increases the tetroxide lifetime, which provides greater opportunity for the complex molecular rearrangement of the tetroxide intermediate inherent in channel 7b. While it seems

likely that channel 7b will play a greater role in the overall reaction at lower temperatures this needs to be investigated experimentally.

We show herein that the gas-phase reaction of  $C_xF_{2x+1}C(O)O_2$  (formed during the atmospheric degradation of FTOHs) with  $HO_2$  radicals offers a *qualitative* explanation for the presence of fluorinated carboxylic acids,  $C_xF_{2x+1}C(O)OH$ , observed in the environment. However, further laboratory and modeling work is required to provide a *quantitative* assessment of the significance of this gas-phase  $C_xF_{2x+1}C(O)OH$  source.

**Acknowledgment.** M.P.S.A. thanks the Danish Research Agency for a research grant and Dean Sengupta (College of Engineering and Computer Science, University of Michigan—Dearborn) for helpful comments. This research was funded, in part, by an NSERC Strategic Grant.

## References and Notes

- (1) Martin, J. W.; Mabury, S. A.; Solomon, K. R.; Muir, D. C. G. *Environ. Toxicol. Chem.* **2003**, *22*, 189.
- (2) Martin, J. W.; Mabury, S. A.; Solomon, K. R.; Muir, D. C. G. *Environ. Toxicol. Chem.* **2003**, *22*, 196.
- (3) Berthiaume, J.; Wallace, K. B. *Toxicol. Lett.* **2002**, *129*, 23.
- (4) Upham, B. L.; Deocampo, N. D.; Wurl, B.; Trosko, J. E. *Int. J. Cancer* **1998**, *78*, 491.
- (5) Biegel, L. B.; Hurtt, M. E.; Frame, S. R.; O'Connor, J.; Cook, J. C. *Toxicol. Sci.* **2001**, *60*, 44.
- (6) Moody, C. A.; Martin, J. W.; Kwan, W. C.; Muir, D. C. G.; Mabury, S. A. *Environ. Sci. Technol.* **2002**, *36*, 545.
- (7) Martin, J. W.; Smithwick, M.; Braune, B.; Hoekstra, P. F.; Muir, D. C. G.; Mabury, S. A. *Environ. Sci. Technol.* **2004**, *38*, 373.
- (8) Ellis, D. A.; Moody, C. A.; Mabury, S. A. Trifluoroacetic Acid and Longer Chain Perfluoro Acids—Sources and Analysis. In *Organofluorines*; Neilson, A. H., Ed.; Springer-Verlag: Berlin, Germany, 2002.
- (9) Hurley, M. D.; Wallington, T. J.; Sulbaek Andersen, M. P.; Ellis, D. A.; Martin, J. W.; Mabury, S. A. *J. Phys. Chem. A* **2004**, *108*, 615.
- (10) Hurley, M. D.; Ball, J. C.; Wallington, T. J.; Sulbaek Andersen, M. P.; Ellis, D. A.; Martin, J. W.; Mabury, S. A. *J. Phys. Chem. A* **2004**, *108*, 5635–5642.
- (11) Ellis, D. A.; Martin, J. W.; De Silva, A. O.; Mabury, S. A.; Hurley, M. D.; Sulbaek Andersen, M. P.; Wallington, T. J. *Environ. Sci. Technol.* **2004**, *38*, 3316.
- (12) Ellis, D. A.; Martin, J. W.; Mabury, S. A.; Sulbaek Andersen, M. P.; Hurley, M. D.; Wallington, T. J. *Environ. Sci. Technol.* **2003**, *37*, 3816.
- (13) Martin, J. W.; Muir, D. C. G.; Kwan, W. C.; Moody, C. A.; Solomon, K. R.; Mabury, S. A. *Anal. Chem.* **2002**, *74*, 584.
- (14) Stock, N. L.; Lau, F. K.; Martin, J. W.; Muir, D. C. G.; Mabury, S. A. *Environ. Sci. Technol.* **2004**, *38*, 991.
- (15) Stockwell, W. R.; Milford, J. B.; Dongfen, G.; Yang, Y.-J. *Atmos. Environ.* **1995**, *29*, 1591.
- (16) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. *J. Phys. Chem.* **1985**, *89*, 588.
- (17) Moortgat, G. K.; Veyret, B.; Lesclaux, R. *Chem. Phys. Lett.* **1989**, *160*, 443.
- (18) Horie, O.; Moortgat, G. K. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 3305.
- (19) Crawford, M.; Wallington, T. J.; Szente, J. J.; Maricq, M. M.; Francisco, J. S. *J. Phys. Chem.* **1999**, *103*, 365.
- (20) Tyndall, G. S.; Cox, R. A.; Granier, C.; Lesclaux, R.; Moortgat, G. K.; Pilling, M. J.; Ravishankara, A. R.; Wallington, T. J. *J. Geophys. Res.* **2001**, *106*, 12157.
- (21) Hasson, A. S.; Orlando, J. J.; Tyndall, G. S. *J. Phys. Chem. A*. Submitted for publication.
- (22) Wallington, T. J.; Japar, S. M. *J. Atmos. Chem.* **1989**, *9*, 399.
- (23) Takahashi, K.; Matsumi, Y.; Wallington, T. J.; Hurley, M. D. *J. Geophys. Res.* **2002**, *107*, CH 4–1.
- (24) Sulbaek Andersen, M. P.; Nielsen, O. J.; Hurley, M. D.; Ball, J. C.; Wallington, T. J.; Stevens, J. J. *Phys. Chem. A* **2004**, *108*, 5189.
- (25) Sander, S. P.; Friedl, R. R.; Golden, D. M.; Kurylo, M. J.; Huie, R. E.; Orkin, V. L.; Moortgat, G. K.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J.; Finlayson-Pitts, B. J. *JPL Publication No. 02-25*; NASA Jet Propulsion Lab.: Pasadena, CA, 2003.
- (26) Wallington, T. J.; Hurley, M. D.; Schneider, W. F.; Sehested, J.; Nielsen, O. J. *Chem. Phys. Lett.* **1994**, *218*, 34.
- (27) Sulbaek Andersen, M. P.; Hurley, M. D.; Wallington, T. J.; Ball, J. C.; Martin, J. W.; Ellis, D. A.; Mabury, S. A. *Chem. Phys. Lett.* **2003**, *381*, 14.
- (28) Kopitsky, R.; Willner, H.; Hermann, A.; Oberhammer, H. *Inorg. Chem.* **2001**, *40*, 2693.
- (29) Wallington, T. J.; Hurley, M. D. *Int. J. Chem. Kinet.* **1995**, *27*, 189.
- (30) Sehested, J.; Wallington, T. J. *Environ. Sci. Technol.* **1993**, *27*, 146.
- (31) Meagher, R. J.; McIntosh, M. E.; Hurley, M. D.; Wallington, T. J. *Int. J. Chem. Kinet.* **1997**, *29*, 619.
- (32) Sehested, J.; Ellermann, T.; Nielsen, O. J.; Wallington, T. J.; Hurley, M. D. *Int. J. Chem. Kinet.* **1993**, *25*, 701.
- (33) Sellevåg, S. R.; Kelly, T.; Sidebottom, H.; Nielsen, C. J. *Phys. Chem. Chem. Phys.* **2004**, *6*, 1243.