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Atmospheric Chemistry of *n*-C_xF_{2x+1}CHO ($x = 1, 3, 4$): Mechanism of the $C_xF_{2x+1}C(O)O_2$ + HO_2 Reaction

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Smog chamber/FTIR techniques were used to study the gas-phase reaction of $C_xF_{2x+1}C(O)O_2$ ($x = 1, 3, 4$) with HO_2 radicals in 700 Torr of air, or O_2, diluent at 296 ± 2 K. The reactions proceed by three pathways leading to formation of $C_xF_{2x+1}C(O)OOH$ and O_2, $C_xF_{2x+1}C(O)OH$ and O_3, or $C_xF_{2x+1}C(O)O$ radicals, OH radicals, and O_2. Carboxylic acid yields were 38 ± 4% ($x = 1$), 10 ± 2% ($x = 3$), and 8 ± 2% ($x = 4$). Results are discussed with respect to the potential for the atmospheric degradation of fluorotelomer alcohols, $C_xF_{2x+1}CH_2CH_2OH$, to contribute to the environmental burden of fluorinated carboxylic acids, $C_xF_{2x+1}C(O)OH$. Rate constants for the reactions of Cl atoms with $C_xF_{2x+1}C(O)OH$ and $C_xF_{2x+1}C(O)OOH$ were determined to be $k(Cl+C_xF_{2x+1}C(O)OH) < 2 \times 10^{-17}$ and $k(Cl + C_xF_{2x+1}C(O)OOH) = (2.9 \pm 0.7) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} in 700 Torr of N_2 at 296 ± 2 K.

1. Introduction

Persistent, bioaccumulative,[1,2] and potentially toxic,[3−5] long-chain perfluorinated carboxylic acids (PFCAs, $C_xF_{2x+1}C(O)OH$, where $x = 6-12$) have been observed in remote locations around the world.[6,7] There are no known natural sources of long-chain PFCAs,[8] these compounds are not expected to be mobile in the environment,[9] 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, $C_xF_{2x+1}CH_2CH_2OH$) in the absence of NO_x.[10,11] FTOHs have significant (20 day) atmospheric lifetimes,[12] are present in pg m^{-3} concentrations in ambient air,[13,14] are emitted in substantial amounts (100−1000 tonnes yr^{-1} over North America),[12] 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, $CH_3C(O)O_2$, which can react with HO_2 radicals to give peracetic and acetic acid.[15−21]

$$CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)OOH + O_2 \qquad (1a)$$

$$CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)OH + O_3 \qquad (1b)$$

$$CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)O + O_2 + OH \qquad (1c)$$

Wet and dry deposition of FTOHs is of negligible atmospheric importance.[12] The atmospheric oxidation of FTOHs is initiated by gas-phase reaction with OH radicals giving perfluoroaldehydes[11] which undergo further oxidation to give fluorinated acyl peroxy radicals, $C_xF_{2x+1}C(O)O_2$. 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.[11]

To assess this possibility we have used smog chamber FTIR techniques to determine the products of the reactions of $C_xF_{2x+1}C(O)O_2$ ($x = 1, 3, 4$) radicals with 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*-C_3F_7CHO and *n*-C_4F_9CHO were studied in the present work. For simplicity we will refer to these species as C_3F_7CHO and C_4F_9CHO in the rest of this article.

2. Experimental Section

The apparatus and experimental techniques used in this work are described elsewhere.[22,23] Experiments were performed in a 140-L Pyrex reactor interfaced to a Mattson Sirus 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.

$$Cl_2 + h\nu \rightarrow Cl + Cl \qquad (2)$$

$C_xF_{2x+1}C(O)O_2$ and HO_2 radicals were generated by the UV irradiation of $C_xF_{2x+1}CHO/H_2/Cl_2$ mixtures in 100−700 Torr

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of air, or O_2, diluent at 296 ± 2 K (M represents a third body, N_2 or O_2):

$$Cl + C_xF_{2x+1}CHO \rightarrow C_xF_{2x+1}CO + HCl \quad (3)$$

$$C_xF_{2x+1}CO + O_2 + M \rightarrow C_xF_{2x+1}C(O)O_2 + M \quad (4)$$

$$Cl + H_2 \rightarrow H + HCl \quad (5)$$

$$H + O_2 + M \rightarrow HO_2 + M \quad (6)$$

$$C_xF_{2x+1}C(O)O_2 + HO_2 \rightarrow \text{products} \quad (7)$$

$$C_xF_{2x+1}C(O)O_2 + C_xF_{2x+1}C(O)O_2 \rightarrow C_xF_{2x+1}C(O)O + C_xF_{2x+1}C(O)O + O_2 \quad (8)$$

Initial concentrations of the gas mixtures used were 5.1−22.1 mTorr of $C_xF_{2x+1}CHO$, 204−613 mTorr of Cl_2, and 0.33−11.4 Torr of H_2 in 700 or 100 Torr of air diluent (ultrahigh purity). Reactions 7 and 8 compete as loss mechanisms for $C_xF_{2x+1}C(O)O_2$ in the system. To study the mechanism of reaction 7 a series of experiments were performed in which the initial concentration ratio $[H_2]_o/[C_xF_{2x+1}CHO]_o$ was varied from 0 to 1753. The rate constant ratio k_3/k_5 is $2.1 \times 10^{-12}/1.6 \times 10^{-14} = 131$.[24,25] Thus, the initial rate of production of HO_2 radicals was 0−13.4 times that of $C_xF_{2x+1}C(O)O_2$ radicals. As the $[H_2]_o/[C_xF_{2x+1}CHO]_o$ ratio increases, more HO_2 radicals are generated in the system for a given level of $C_xF_{2x+1}C(O)O_2$ and the relative importance of reaction 7 as a loss mechanism for $C_xF_{2x+1}C(O)O_2$ 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 $[H_2]_o/[C_xF_{2x+1}CHO]_o$ essentially all of the $C_xF_{2x+1}C(O)O_2$ radicals should be lost via reaction 7. At this point, further increases in $[H_2]_o/[C_xF_{2x+1}CHO]_o$ 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_2 radicals with CH_2FO_2,[26] $CH_3C(O)O_2$,[19] and $C_2F_5C(O)O_2$.[27]

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^{-1} 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 $CF_3C(O)OH$, $C_3F_7C(O)OH$, and $C_4F_9C(O)OH$ contains monomer and dimer. Values of $K_{eq}(CF_3C(O)OH) = [\text{dimer}]/[\text{monomer}]^2 = 0.32 \pm 0.03\ Torr^{-1}$, $K_{eq}(C_3F_7C(O)OH) = 0.41 \pm 0.04\ Torr^{-1}$, and $K_{eq}(C_4F_9C(O)OH) = 0.46 \pm 0.05\ Torr^{-1}$[9] 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 $C_xF_{2x+1}CHO$ ($x = 1, 3, 4$) were synthesized as described elsewhere[24] and purified by vacuum distillation. $CF_3C(O)OOH$ was synthesized by reacting trifluoroacetic anhydride with concentrated H_2O_2. 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 trifluoroactyl peroxide.[28] All other reactants were obtained from commercial sources at purities >99%. Ultrahigh purity air (THC < 0.1 ppm) and O_2 (>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_3OH, there was no observable (<2%) loss of reactants or products. Samples of $C_xF_{2x+1}CHO$, $C_xF_{2x+1}C(O)OH$ ($x = 1, 3, 4$), and $CF_3C(O)OOH$ were subjected to UV irradiation in 700 Torr of air diluent for 15 min without any observable loss (<1%) suggesting that photolysis of $C_xF_{2x+1}CHO$, $C_xF_{2x+1}C(O)OH$, and $CF_3C(O)OOH$ is not a significant complication in the present work.

3. Results

3.1. Measurement of $k(Cl + C_xF_{2x+1}C(O)OH, x = 3, 4)$ and $k(Cl + CF_3C(O)OOH)$. Prior to the study of the mechanism of reaction 7 experiments were performed to investigate the rate of reaction of Cl atoms with $C_xF_{2x+1}C(O)OH$ ($x = 3, 4$) using the relative rate technique. Mixtures containing 4.4−6.8 mTorr of $C_xF_{2x+1}C(O)OH$, 6.2−11.6 mTorr of CF_2ClH, and 0.85−1.03 Torr of Cl_2 in 700 Torr of N_2 were introduced into the chamber. Irradiation of the gas mixtures for 7.5−10.5 min led to >83% consumption of CF_2ClH but no discernible loss (<2%) of $C_xF_{2x+1}C(O)OH$. Using $k(Cl + CF_2ClH) = 1.7 \times 10^{-15}$ from ref 25 we derive an upper limit of $k(Cl + C_xF_{2x+1}C(O)OH, x = 3, 4) < 2 \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1}. This finding is consistent with previous determinations of $k(Cl + CF_3C(O)OH) < 1 \times 10^{-17}$ from ref 29 and $k(Cl + C_2F_5C(O)OH) < 1.7 \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1} from ref 27.

The rate of reaction of Cl atoms with $CF_3C(O)OOH$ was measured relative to the rates of reaction of Cl atoms with CF_2ClCH_3 and CF_2ClH. Reaction mixtures consisted of either 3.0 mTorr of $CF_3C(O)OOH$, 4.5 mTorr of CF_2ClH, and 99 mTorr of Cl_2 or 1.9 mTorr of $CF_3C(O)OOH$, 19.8 mTorr of CF_2ClH, and 400 mTorr of Cl_2. Experiments were performed in 700 Torr of N_2 at 296 K. Irradiation of the gas mixtures led to discernible losses of $CF_3C(O)OOH$, CF_2ClCH_3, and CF_2ClH from which rate constant ratios of $k(Cl + CF_3C(O)OOH)/k(Cl + CF_2ClCH_3) = 0.80 \pm 0.10$ and $k(Cl + CF_3C(O)OOH)/k(Cl + CF_2ClH) = 0.15 \pm 0.02$ were determined. Using $k(Cl + CF_2ClCH_3) = 3.9 \times 10^{-16}$ and $k(Cl + CF_2ClH) = 1.7 \times 10^{-15}$ gives $k(Cl + CF_3C(O)OOH) = (3.1 \pm 0.4) \times 10^{-16}$ and $(2.6 \pm 0.4) \times 10^{-16}$ cm^3 $molecule^{-1}$ 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, $k(Cl + CF_3C(O)OOH) = (2.9 \pm 0.7) \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}. $CF_3C(O)OOH$ is at least an order of magnitude more reactive than $CF_3C(O)OH$ toward Cl atoms, presumably reflecting a weaker O−H bond in the peracid.

3.2. Products of the $CF_3C(O)O_2 + HO_2$ 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_3CHO, 9.04 Torr of H_2, and 251 mTorr of Cl_2 in 700 Torr of air diluent. The loss of CF_3CHO was 8.3 mTorr. Comparison with reference spectra of $CF_3C(O)OH$ and COF_2 shown in panels C

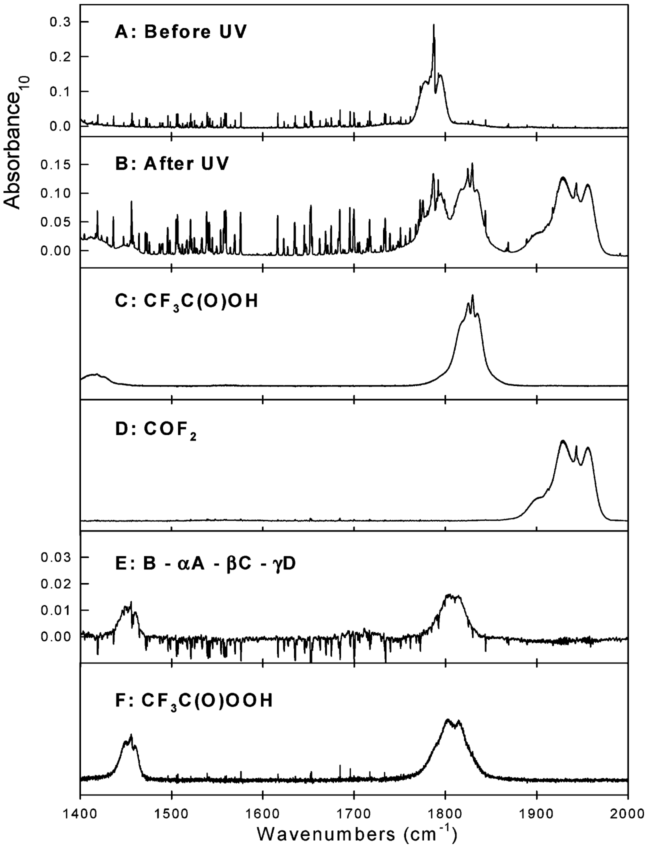

Figure 1. IR spectra obtained before (A) and after (B) a 100-s irradiation of a mixture of 14.8 mTorr of CF_3CHO, 9.04 Torr of H_2, and 251 mTorr of Cl_2 in 700 Torr of air diluent. The consumption of CF_3CHO was 56%. Panels C, D, and F are reference spectra of CF_3COOH, COF_2, and $CF_3C(O)OOH$, respectively. Panel E shows the residual spectrum obtained by subtracting features attributable to CF_3CHO, CF_3COOH, $CF_3C(O)OOH$, and COF_2 from panel B.

and D indicates the formation of these species. The peaks of $CF_3C(O)OH$ and COF_2 are located at 1829 and 1944 cm^{-1}, respectively. Subtraction of IR features attributable to CF_3CHO, $CF_3C(O)OH$, and COF_2 from panel B gives the residual spectrum shown in panel E. The formation of the peracid, $CF_3C(O)OOH$, 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_2 and CF_3OH (circles), $CF_3C(O)OH$ (squares), $CF_3C(O)OOH$ (diamonds), $CF_3O_3CF_3$ (triangles), and O_3 (gray squares) versus loss of CF_3CHO following Cl initiated oxidation in the presence of H_2 (e.g. HO_2) for an experiment employing a $[H_2]_o/[CF_3CHO]_o$ 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_3OH undergoes heterogeneous decomposition in the chamber[30] to give COF_2 and hence it is convenient to combine CF_3OH and COF_2 in the plot. The linearity of the formation of $CF_3C(O)OH$ and $CF_3C(O)OOH$ 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 $CF_3C(O)OH$ or $CF_3C(O)OOH$ and their low reactivity toward Cl atoms. Similarly, the linearity of the plot of the combined yield of CF_3OH and COF_2 suggests that, with the exception of the conversion of CF_3OH into COF_2 noted above, there are no losses of these species in the system.

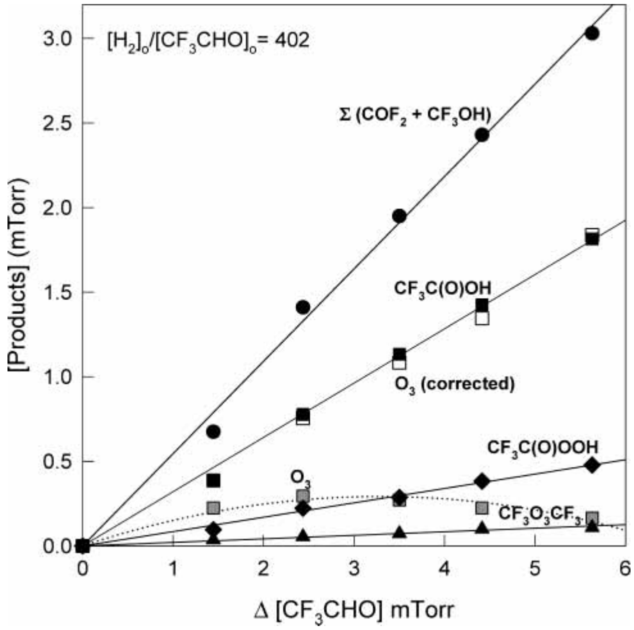

Figure 2. Yields of $\Sigma(COF_2 + CF_3OH)$ (circles), $CF_3C(O)OH$ (squares), $CF_3C(O)OOH$ (diamonds), $CF_3O_3CF_3$ (triangles), and O_3 (gray squares) versus loss of CF_3CHO following Cl initiated oxidation in the presence of H_2 for an experiment employing a $[H_2]_o/[CF_3CHO]_o$ ratio of 402 at 700 Torr of air diluent. The open squares are the result of correcting for loss of O_3 via reaction with Cl atoms (see text for details).

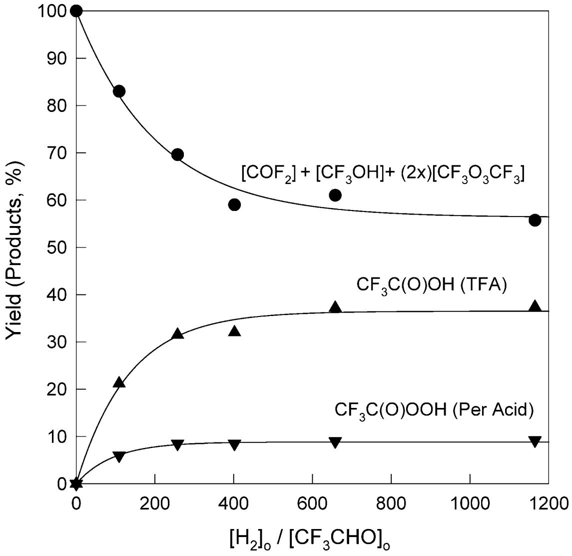

Figure 3. Product yields following Cl initiated oxidation of CF_3CHO in the presence of HO_2 radicals versus $[H_2]_o/[CF_3CHO]_o$ in 700 Torr of air diluent, at 296 ± 2 K.

The observed yields of $CF_3C(O)OH$, $CF_3C(O)OOH$, and $\Sigma(COF_2 + CF_3OH + 2CF_3O_3CF_3)$ from the various experiments are plotted versus $[H_2]_o/[CF_3CHO]_o$ in Figure 3. As seen from Figure 3, the yield of $CF_3C(O)OH$ and $CF_3C(O)OOH$ increases as the concentration ratio $[H_2]_o/[CF_3CHO]_o$ is increased from 0 to 600, presumably reflecting the increased importance of reaction 1 as a loss of $CF_3C(O)O_2$ radicals. Concurrently, the combined yield of COF_2, CF_3OH, and $CF_3O_3CF_3$ decreases. For concentration ratios greater than 600, there is no observable dependence of product yields on $[H_2]_o/[CF_3CHO]_o$ suggesting that, under these conditions, essentially all the $CF_3C(O)O_2$ radicals are consumed by reaction with HO_2 radicals. Averaging the product data obtained in experiments with $[H_2]_o/[CF_3CHO]_o$ of 600 or more gives the following product yields: $CF_3C(O)$-

OH, 38 ± 4%; $CF_3C(O)OOH$, 9 ± 4%; and $\sum(COF_2 + CF_3OH + 2xCF_3O_3CF_3)$, 56 ± 5%;. Quoted errors are 2 standard deviations from the linear least-squares regressions. Together, $CF_3C(O)OH$, $CF_3C(O)OOH$, COF_2, CF_3OH, and $CF_3O_3CF_3$ account for 103 ± 12% of the loss of CF_3CHO.

O_3 is an expected coproduct of $CF_3C(O)OH$ and was observed by virtue of its characteristic IR features at 1000−1100 cm^{-1}. The pronounced curvature of the O_3 yield plot in Figure 2 can be rationalized by the fact that Cl atoms react with O_3 at a rate that is 1.2×10^{-11} (ref 25)/2.1×10^{-12} (ref 24) = 6 times faster than the reaction with CF_3CHO. Hence, loss of O_3 via secondary reaction with Cl atoms is substantial for the fractional consumptions of CF_3CHO employed in the present work. The importance of O_3 loss via secondary reaction with Cl atoms is dependent upon the fractional consumption of CF_3CHO. The open squares in Figure 2 show the result of correcting the observed O_3 concentrations for loss via reaction with Cl atoms.[31] As seen from Figure 2, when corrected for loss via reaction with Cl atoms, the O_3 yield is indistinguishable from that of $CF_3C(O)OH$. This observation is consistent with the formation of O_3 and $CF_3C(O)OH$ 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 $CF_3C(O)O_2$ with 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 $k_{9c}/(k_{9a} + k_{9b} + k_{9c}) = 0.56 \pm 0.05$.

$$CF_3C(O)O_2 + HO_2 \rightarrow CF_3C(O)OOH + O_2 \tag{9a}$$

$$CF_3C(O)O_2 + HO_2 \rightarrow CF_3C(O)OH + O_3 \tag{9b}$$

$$CF_3C(O)O_2 + HO_2 \rightarrow CF_3C(O)O + O_2 + OH \tag{9c}$$

$CF_3C(O)O$ radicals formed in reaction 9c will eliminate CO_2 to give CF_3 radicals which will react to give CF_3OH (which decomposes to give COF_2) and $CF_3O_3CF_3$

$$CF_3 + O_2 + M \rightarrow CF_3O_2 + M \tag{10}$$

$$CF_3O_2 + RO_2 \rightarrow CF_3O + RO + O_2 \tag{11}$$

$$CF_3O + H_2 \rightarrow CF_3OH + H \tag{12}$$

$$CF_3OH \rightarrow COF_2 + HF \tag{13}$$

$$CF_3O + CF_3O_2 + M \rightarrow CF_3O_3CF_3 + M \tag{14}$$

3.3. Products of the $C_xF_{2x+1}C(O)O_2$ (x = 3, 4) + HO_2 Reactions. The products of the reaction of $C_xF_{2x+1}C(O)O_2$ (x = 3, 4) and HO_2 radicals were investigated in experiments similar to those described in the previous section with C_3F_7CHO or C_4F_9CHO used in place of CF_3CHO. Studies of the reaction products of longer chain acyl peroxy radicals, $C_xF_{2x+1}C(O)O_2$ (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 C_3F_7CHO and C_4F_9CHO one or more unknown products with large and broad absorption features at 1000−1400 cm^{-1} are formed. By comparison with the available spectra for $CF_3O_3CF_3$ and $C_2F_5O_3CF_3$.[32] the unknown products are probably mixed trioxides (e.g., for x = 4: $C_4F_9O_3CF_3$, $C_3F_7O_3CF_3$, and $C_2F_5O_3CF_3$) formed by addition of CF_3O to $C_xF_{2x+1}O_2$ radicals. However, calibrated spectra for the mixed trioxides are not available and it was not possible to quantify the yields of these species. In contrast, the formation of COF_2, CF_3OH, and $C_xF_{2x+1}C(O)OH$ (x = 3, 4) was easily quantifiable with use of calibrated IR spectra.[9] After subtraction of features attributable to $C_xF_{2x+1}CHO$, $C_xF_{2x+1}C(O)OH$, COF_2, and CF_3OH there were no residual features that could be ascribed to the peracids $C_xF_{2x+1}C(O)OOH$ (x = 3, 4). On the basis of our experience with $CF_3C(O)OOH$, we would expect that if significant amounts of $C_xF_{2x+1}C(O)OOH$ (x = 3, 4) were formed in the chamber we would observe these compounds. Using the observed absorption strength of $CF_3C(O)OOH$ as a guide, we estimate upper limits of 3% for the yield of $C_xF_{2x+1}C(O)OOH$ (x = 3, 4).

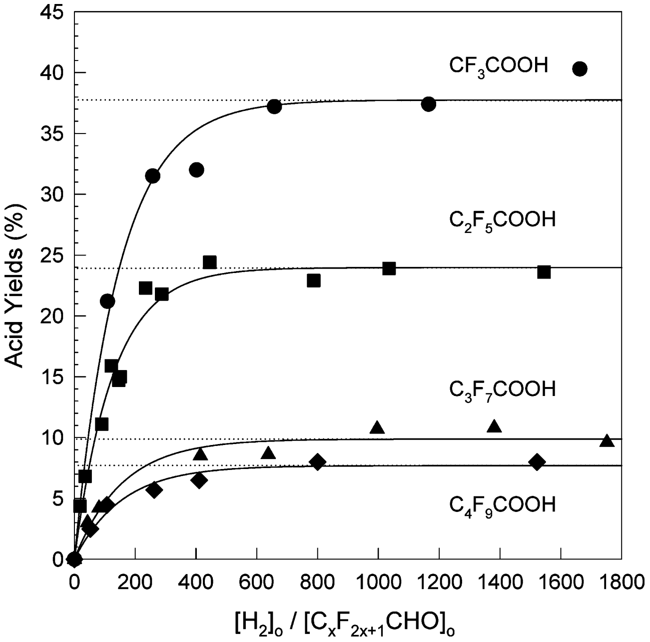

Figure 4. Product yields following Cl initiated oxidation of $C_xF_{2x+1}CHO$ (x = 1−4) in the presence of HO_2 radicals versus $[H_2]_o/[C_xF_{2x+1}CHO]_o$ in 700 Torr of air diluent, 296 ± 2 K.

The observed yields of $C_xF_{2x+1}C(O)OH$ (x = 3, 4) together with results for x = 1 discussed in the previous section and x = 2 reported elsewhere[27] are plotted versus $[H_2]_o/[C_xF_{2x+1}CHO]_o$ in Figure 4. As seen from Figure 4, the variation of acid yield with $[H_2]_o/[C_xF_{2x+1}CHO]_o$ 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 $C_xF_{2x+1}C(O)O_2$ radicals in the four systems. For concentration ratios greater than 600, there are no observable dependence of acid yields on $[H_2]_o/[C_xF_{2x+1}CHO]_o$ suggesting that, under these conditions, essentially all the $C_xF_{2x+1}C(O)O_2$ radicals are consumed by reaction with HO_2 radicals. Averaging the product data obtained with $[H_2]_o/[C_xF_{2x+1}CHO]_o$ of 600 or more gives the following acid yields: $C_3F_7C(O)OH$, 10 ± 2%, and $C_4F_9C(O)OH$, 8 ± 2%.

As discussed in section 3.2, it is expected that O_3 will be formed in amounts comparable to those of $C_3F_7C(O)OH$ and $C_4F_9C(O)OH$. Evidence for the formation of O_3 in the product spectra was sought, but not found. As discussed previously for experiments with C_2F_5CHO,[27] the fact that 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 $RC(O)O_2$ with HO_2 Radicals under Ambient Conditions (700−760 Torr, 296 ± 2 K)

	products			
$RC(O)O_2$	$RC(O)OOH + O_2$	$RC(O)OH + O_3$	$RC(O)O + O_2 + OH$	ref
$CH_3C(O)O_2$	0.40 ± 0.16	0.20 ± 0.08	0.40 ± 0.16	21
$CF_3C(O)O_2$	0.09 ± 0.04	0.38 ± 0.04	0.56 ± 0.05	this work
$C_2F_5C(O)O_2$	<0.06	0.24 ± 0.04	0.76 ± 0.04	27
$C_3F_7C(O)O_2$	<0.03	0.10 ± 0.02	≈0.90	this work
$C_4F_9C(O)O_2$	<0.03	0.08 ± 0.02	≈0.90	this work

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

$$C_xF_{2x+1}C(O)O_2 + HO_2 \rightarrow C_xF_{2x+1}C(O)OOH + O_2 \quad (7a)$$

$$C_xF_{2x+1}C(O)O_2 + HO_2 \rightarrow C_xF_{2x+1}C(O)OH + O_3 \quad (7b)$$

$$C_xF_{2x+1}C(O)O_2 + HO_2 \rightarrow C_xF_{2x+1}C(O)O + O_2 + OH \quad (7c)$$

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 HO_2 radicals are listed in Table 1. Comparing the data for $C_xF_{2x+1}C(O)O_2$ 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 $C_3F_7C(O)O_2$ and $C_4F_9C(O)O_2$. On the other hand, the substantial decrease in $C_xF_{2x+1}C(O)OH$ 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 $C_xF_{2x+1}C(O)O_2$ 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 $C_xF_{2x+1}C(O)OH$ 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.,[21] it was believed that under ambient conditions the reaction of $CH_3C(O)O_2$ with HO_2 radicals proceeded via two channels with $k_{1a}/(k_{1a} + k_{1b}) = 0.80$ and $k_{1b}/(k_{1a} + k_{1b}) = 0.20$.[20] It is now clear that the reaction of $CH_3C(O)O_2$ with 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[27] that the radical-forming channel is the dominant reaction pathway for reactions of $C_xF_{2x+1}C(O)O_2$ (x =1−4) with 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 HO_2 radicals.

4.2. Mechanism of the $C_xF_{2x+1}C(O)O_2 + HO_2$ Reaction. It is expected that the reaction of HO_2 with $C_xF_{2x+1}C(O)O_2$ (x = 1, 3, 4) radicals proceeds via the formation of a short-lived tetroxide intermediate. As illustrated in Figure 5, the tetraoxide can decompose via cyclic transition states to give either the peracid, $C_xF_{2x+1}C(O)OOH$ and O_2, or the acid, $C_xF_{2x+1}C(O)OH$ and O_3. Decomposition can also occur via $C_xF_{2x+1}C(O)O$−OOOH or $C_xF_{2x+1}C(O)OOO$−OH bond scission to give $C_xF_{2x+1}C(O)O$ radicals, O_2, and OH. While it has been postulated for several decades that a tetroxide intermediate is formed in the reaction of peroxy radicals with 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.

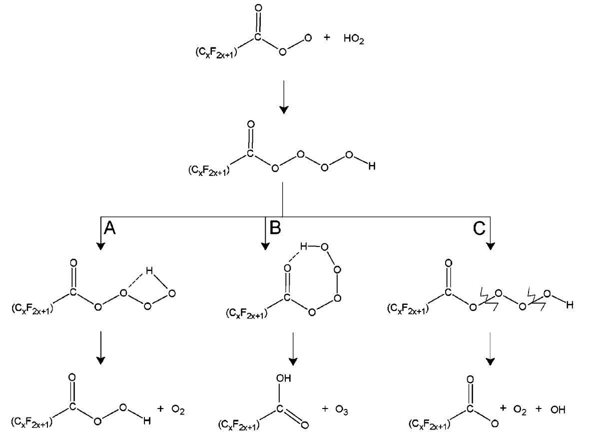

Figure 5. Mechanistic pathways for the $C_xF_{2x+1}C(O)O_2 + HO_2$ reaction.

5. Implications for Atmospheric Chemistry

The goal of the present work was to investigate the possibility that the gas-phase reaction of $C_xF_{2x+1}C(O)O_2$ with 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 $C_xF_{2x+1}C(O)O_2$ (x = 1, 3, 4) with HO_2 radicals gives $C_xF_{2x+1}C(O)OH$ (x = 1, 3, 4) in yields of 38 ± 4% (x = 1), 10 ± 2% (x = 3), and 8 ± 2% (x = 4). As discussed in section 4.1 it seems likely that reactions of $C_xF_{2x+1}C(O)O_2$ ($x > 4$) with HO_2 radicals will give the perfluorocarboxylic acid $C_xF_{2x+1}C(O)OH$ 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 OH radicals are competing atmospheric fates of $C_xF_{2x+1}CHO$. Reaction with OH leads to the formation of $C_xF_{2x+1}C(O)O_2$ radicals in 100% yield. Recent experiments with CF_3CHO indicate that the atmospheric photolysis is slow (lifetime >27 days).[33] However, the rate and products of photolysis of longer chain members of the $C_xF_{2x+1}CHO$ series are unclear and so it is difficult to establish the fraction of $C_xF_{2x+1}CHO$ that is converted into $C_xF_{2x+1}C(O)O_2$. Second, reactions with NO and HO_2 radicals are competing atmospheric fates for $C_xF_{2x+1}C(O)O_2$ radicals. Oxidation of $C_xF_{2x+1}CHO$ in the presence of excess NO does not lead to the formation of $C_xF_{2x+1}C(O)OH$.[24,27] In the absence of kinetic data for reactions with NO and HO_2 it is difficult to estimate the fraction of $C_xF_{2x+1}C(O)O_2$ that reacts with 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 $CH_3C(O)O_2$ radicals the channel giving the acid increases in importance as the temperature is lowered.[20] Decreasing temperature increases the tetraoxide lifetime, which provides greater opportunity for the complex molecular rearrangement of the tetraoxide 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.

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