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Atmospheric Chemistry of 4:2 Fluorotelomer Acrylate [$C_4F_9CH_2CH_2OC(O)CH{=}CH_2$]: Kinetics, Mechanisms, and Products of Chlorine-Atom- and OH-Radical-Initiated Oxidation

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Relative rate techniques were used to measure the rate constants $k[Cl + C_4F_9CH_2CH_2OC(O)CH{=}CH_2] = (2.21 \pm 0.16) \times 10^{-10}$ and $k[OH + C_4F_9CH_2CH_2OC(O)CH{=}CH_2] = (1.13 \pm 0.12) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} in 700 Torr of N_2 or air diluent at 296 K. The atmospheric lifetime of $C_4F_9CH_2CH_2OC(O)CHCH_2$ (4:2 FTAc) is determined by its reaction with OH radicals and is approximately 1 day. The chlorine-atom-initiated oxidation of 4:2 FTAc in 700 Torr of air at 296 K gives $C_4F_9CH_2C(O)H$ in molar yields of 18% and 10% in the absence and presence of NO, respectively. The OH-radical-initiated oxidation of 4:2 FTAc in 700 Torr of air in the presence of NO gives HCHO in a molar yield of (102 ± 7)%, with $C_4F_9CH_2CH_2OC(O)C(O)H$ (4:2 fluorotelomer glyoxylate) as the expected coproduct. The atmospheric fate of the 4:2 fluorotelomer glyoxylate will be photolysis and reaction with OH radicals, which will lead to the formation of $C_4F_9CH_2C(O)H$ and ultimately perfluorinated carboxylic acids. The atmospheric oxidation of fluorotelomer acrylates is a potential source of perfluorinated carboxylic acids in remote locations.

1. Introduction

Perfluorinated carboxylic acids (PFCAs) are global environmental pollutants and are distributed widely in humans,[1,2] wildlife,[3,4] and abiotic media such as seawater.[5] Despite their apparently ubiquitous presence, the sources of PFCA contamination are not well understood, particularly in remote environments. It has been suggested that an indirect mechanism might explain the widespread distribution of PFCAs in the environment. The indirect mechanism involves the release and transport of volatile precursor compounds that degrade by atmospheric oxidation to PFCAs, which subsequently undergo wet and dry deposition. Smog chamber studies in our laboratory and elsewhere have shown that the oxidation of fluorotelomer alcohols (FTOHs),[6,7] fluorosulfonamido alcohols,[8,9] fluorotelomer olefins,[10,11] and fluorotelomer iodides[12] in low-NO_x environments forms PFCAs.

Alternatively, it has been suggested that the observation of PFCAs in marine wildlife in remote locations reflects historical direct emission of PFCAs, mainly perfluorooctanoic acid (PFOA), during fluorochemical manufacturing processes and as residuals in consumer products,[13] followed by global transport in ocean currents.[14,15] Empirical support for the indirect mechanism comes from the fact that deposition fluxes extrapolated from arctic surface snow measurements[16] are consistent with those estimated from atmospheric models.[17] The relative importance of the indirect and direct routes is unclear but is likely to depend on the location, PFCA, and time period under consideration.

Fluorotelomer acrylates [general formula $C_xF_{2x+1}CH_2CH_2OC(O)CH{=}CH_2$, FTAc] are monomers used in the manufacture of fluorotelomer-based polymers. Fluorotelomer-based polymers have wide commercial uses, primarily for their stain repellency. It has been reported that FTAc-based polymers are the largest commercial category of polyfluorinated products.[18] It has been shown that fluorotelomer acrylates are significant residuals in an FTAc-based polymer[18] and can be released to the atmosphere from commercial fluorotelomer-based polymer products in a manner similar to that of FTOHs.[19] The 6:2, 8:2, and 10:2 FTAcs have been detected in the atmosphere at generally low levels (<1−6 pg/m^3, but up to 3000 pg/m^3 near a suspected source in Japan).[20−22]

There are no reported studies of the atmospheric chemistry of FTAcs, and the contribution of these compounds to PFCA burdens observed in remote locations is unclear. Given the commercial importance and presence in the atmosphere of fluorotelomer acrylates, information on their atmospheric chemistry is needed. The goal of the present work was to improve our understanding of the atmospheric chemistry of FTAcs using $C_4F_9CH_2CH_2OC(O)CHCH_2$ (4:2 FTAc) as a representative compound. We report here the results of studies of the kinetics and mechanisms of the chlorine-atom- and OH-radical-initiated oxidations of 4:2 FTAc.

2. Experimental Section

2.1. Kinetic Experiments. Experiments were performed in a 140 L Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer.[23] The reactor was surrounded by 22 fluorescent blacklight lamps (GE F15T8-BL), which were used to photochemically initiate the experiments. Chlorine atoms were produced by photolysis of molecular chlorine

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$$Cl_2 + h\nu \rightarrow Cl + Cl \tag{1}$$

OH radicals were produced by the photolysis of CH_3ONO in air

$$CH_3ONO + h\nu \rightarrow CH_3O + NO \tag{2}$$

$$CH_3O + O_2 \rightarrow HO_2 + HCHO \tag{3}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{4}$$

In the relative rate experiments, the following reactions take place

$$Cl + \text{reactant} \rightarrow \text{products} \tag{5}$$

$$Cl + \text{reference} \rightarrow \text{products} \tag{6}$$

$$OH + \text{reactant} \rightarrow \text{products} \tag{7}$$

$$OH + \text{reference} \rightarrow \text{products} \tag{8}$$

Assuming that the reactant and reference compounds are lost solely through reaction with Cl atoms or OH radicals and that neither the reactant nor the reference is formed in any process, then the decays of the reactant and reference can be plotted using the expression

$$\ln\left(\frac{[\text{reactant}]_{t_0}}{[\text{reactant}]_t}\right) = \frac{k_\text{reactant}}{k_\text{reference}} \ln\left(\frac{[\text{reference}]_{t_0}}{[\text{reference}]_t}\right) \tag{9}$$

where $[\text{reactant}]_{t_0}$, $[\text{reactant}]_t$, $[\text{reference}]_{t_0}$, and $[\text{reference}]_t$ are the concentrations of reactant and reference at times t_0 and t, as indicated, and k_reactant and $k_\text{reference}$ are the rate constants for the reaction of Cl atoms or OH radicals with the reactant and reference, respectively. Plots of $\ln([\text{reactant}]_{t_0}/[\text{reactant}]_t)$ versus $\ln([\text{reference}]_{t_0}/[\text{reference}]_t)$ should be linear, pass through the origin, and have a slope of $k_\text{reactant}/k_\text{reference}$. Unless stated otherwise, quoted uncertainties represent the precision of the measurements and include two standard deviations from regression analyses and uncertainties in the IR analysis (typically ±1% of the initial reactant concentrations).

CH_3ONO was synthesized by the dropwise addition of concentrated sulfuric acid to a saturated solution of $NaNO_2$ in methanol. The reagent, 4:2 FTAc, was obtained from a commercial source (Oakwood Products Inc., 97%, West Columbia, SC) and subjected to repeated freeze/pump/thaw cycling to remove volatile impurities before use. Experiments were conducted at 700 Torr total pressure of N_2 or air diluent at 296 K. Ultra-high-purity synthetic air and nitrogen from Michigan Airgas were used as diluent gases. Concentrations of reactants and products were monitored by FTIR spectroscopy. IR spectra were derived from 32 co-added interferograms with a spectral resolution of 0.25 cm^{-1} and an analytical path length of 27.1 m.

2.2. Product and Mechanistic Experiments. Products of the atmospheric oxidation of 4:2 FTAc with Cl atoms and OH radicals were monitored using FTIR spectroscopy in 700 Torr of air diluent. Mixtures used to study the Cl atom-initiated oxidation consisted of either 7.1 mTorr of 4:2 FTAc and 105 mTorr of Cl_2 or 7.4 mTorr of 4:2 FTAc, 101 mTorr of Cl_2, and 57 mTorr of NO. Mixtures used to study the OH radical-initiated oxidation consisted of 3.8−10.6 mTorr of 4:2 FTAc, 27−100 mTorr of CH_3ONO, and 8.4−15 mTorr of NO. An additional experiment was conducted using deuterated methyl nitrite to investigate the mechanism of OH oxidation. In these experiments, we used mixtures consisting of 7.7 mTorr of 4:2 FTAc, 27 mTorr of CH_2DONO, and 28 mTorr of NO.

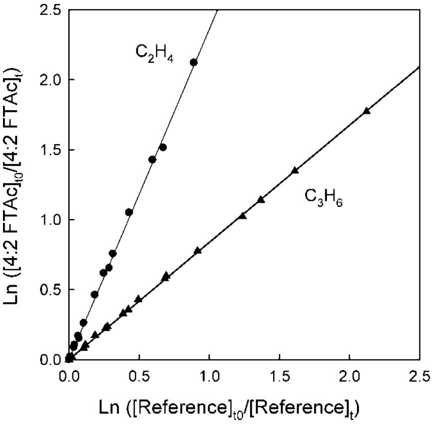

Figure 1. Loss of 4:2 FTAc versus C_2H_4 (●) and C_3H_6 (▲) following UV irradiation of 4:2 FTAc/reference/Cl_2 mixtures in 700 Torr of N_2.

3. Results and Discussion

3.1. Kinetics of the Cl + 4:2 FTAc Reaction. The rate of reaction 10 was measured relative to the rates of reactions 11 and 12

$$Cl + 4{:}2\ \text{FTAc} \rightarrow \text{products} \tag{10}$$

$$Cl + C_2H_4 \rightarrow \text{products} \tag{11}$$

$$Cl + C_3H_6 \rightarrow \text{products} \tag{12}$$

Reaction mixtures consisted of 7.29−7.48 mTorr of 4:2 FTAc, 98.4−101.5 mTorr of Cl_2, and either 7.35−7.39 mTorr of C_2H_4 or 5.67−7.18 mTorr of C_3H_6, in 700 Torr of N_2 diluent. The observed loss of 4:2 FTAc versus those of the reference compounds is plotted in Figure 1. Linear least-squares analysis of the data in Figure 1 gives $k_{10}/k_{11} = 2.36 \pm 0.15$ ($n = 16$) and $k_{10}/k_{12} = 0.84 \pm 0.05$ ($n = 18$). Using $k_{11} = 9.29 \times 10^{-11}$[24] and $k_{12} = 2.64 \times 10^{-10}$,[25] we derive $k_{10} = (2.19 \pm 0.14) \times 10^{-10}$ and $(2.22 \pm 0.13) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. We choose to cite a final value that is the average of the individual determinations together with error limits that encompass the extremes of the determinations; hence, $k_{10} = (2.21 \pm 0.16) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. We estimate that uncertainties in the reference rate constants contribute approximately an additional 10% uncertainty to k_{10}.

Although there have been no previous studies of k_{10}, we can compare our result with the reactions of the corresponding fluorotelomer alcohol, iodide, and olefin: $k(Cl + C_4F_9CH_2CH_2OH) = (1.61 \pm 0.49) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1},[26] $k(Cl + C_4F_9CH_2CH_2I) = (1.25 \pm 0.15) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1},[12] and $k(Cl + C_4F_9CH{=}CH_2) = (8.9 \pm 1.0) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.[10] The acrylate is more reactive than the alcohol and iodide by factors of 14 and 180, respectively. By analogy to unsaturated hydrocarbons,[27] we expect that the reaction of Cl atoms with the acrylate will proceed predomi-

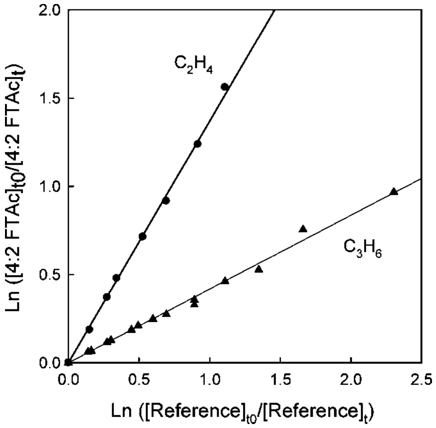

Figure 2. Loss of 4:2 FTAc versus C_2H_4 (●) and C_3H_6 (▲) following UV irradiation of 4:2 FTAc/reference/CH_3ONO mixtures in 700 Torr of air.

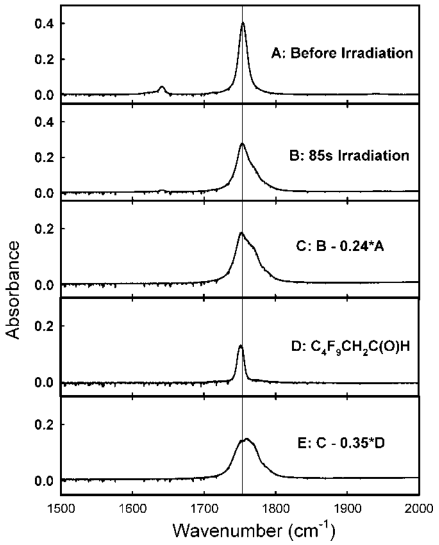

Figure 3. FTIR spectra obtained (A) before and (B) after 85 s of UV irradiation of a mixture of 7.1 mTorr of 4:2 FTAc and 105 mTorr of Cl_2 in 700 Torr of air diluent. (C) Product spectrum obtained by subtracting the IR features of the reactant from the spectrum in B. (D) Reference spectrum of $C_4F_9CH_2C(O)H$. (E) Product spectrum obtained by subtracting IR features of $C_4F_9CH_2C(O)H$ from the spectrum in C.

nately through addition to the >C=C< double bond and will be more rapid than H-abstraction from the $-CH_2-$ groups in the alcohol and iodide. The fluorotelomer acrylate is approximately 2.5 times more reactive than the fluorotelomer olefin. The reactions of chlorine atoms with the acrylate and olefin proceed through electrophilic addition to the >C=C< double bond. The electron-withdrawing effect of the C_4F_9- group is deactivating and will reduce the reactivity of both molecules toward Cl atoms. The ester functional group of 4:2 FTAc increases the distance between the fluorinated tail and the double bond, mitigating the influence of the fluorinated tail.

3.2. Kinetics of the OH + 4:2 FTAc Reaction. The rate of reaction 13 was measured relative to the rates of reactions 14 and 15

$$\mathrm{OH} + 4{:}2\ \mathrm{FTAc} \rightarrow \text{products} \tag{13}$$

$$\mathrm{OH} + C_2H_4 \rightarrow \text{products} \tag{14}$$

$$\mathrm{OH} + C_3H_6 \rightarrow \text{products} \tag{15}$$

Initial reaction mixtures consisted of 6.46−7.52 mTorr of 4:2 FTAc, 98.1−106.7 mTorr of CH_3ONO, and either 4.31 mTorr of C_2H_4 or 0.31−0.47 mTorr of C_3H_6, in 700 Torr total pressure of air diluent. Figure 2 shows the loss of 4:2 FTAc plotted versus the losses of the reference compounds. The lines through the data in Figure 2 are linear least-squares fits, which give $k_{13}/k_{14} = 1.37 \pm 0.10$ ($n = 8$) and $k_{13}/k_{15} = 0.42 \pm 0.03$ ($n = 16$). Using recommended values of $k_{14} = 8.52 \times 10^{-12}$ [28] and $k_{15} = 2.63 \times 10^{-11}$,[28] we derive $k_{13} = (1.17 \pm 0.08) \times 10^{-11}$ and $(1.10 \pm 0.09) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. We choose to report an average with uncertainties that encompass the extremes of the individual determinations; hence, $k_{13} = (1.13 \pm 0.12) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. We estimate that uncertainties in the reference rate constants contribute approximately an additional 10% uncertainty to k_{13}.

Although there have been no previous studies of k_{13}, we can compare our result with the reactions of the corresponding fluorotelomer alcohol, iodide, and olefin: $k(\mathrm{OH} + C_4F_9CH_2CH_2OH) = (1.2 \pm 0.6) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1},[26] $k(\mathrm{OH} + C_4F_9CH_2CH_2I) = (1.17 \pm 0.57) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1},[12] and $k(\mathrm{OH} + C_4F_9CH{=}CH_2) = (1.3 \pm 0.2) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[10] For reaction with OH radicals, the acrylate is approximately an order of magnitude more reactive than the alcohol, iodide, and olefin. As was the case for chlorine atoms, the reaction of OH radicals with the acrylate is expected to proceed predominately through electrophilic addition to the >C=C< double bond. Addition to >C=C< double bonds proceeds faster than H-abstraction from $-CH_2-$ groups.[28] The ester functional group shields the double bond from the deactivating effect of the C_4F_9- group. The observation that the fluorotelomer acrylate is more reactive than the alcohol, iodide, and olefin is consistent with expectations.

We can also compare our measured value of $k[\mathrm{OH} + C_4F_9CH_2CH_2OC(O)CH{=}CH_2] = (1.13 \pm 0.12) \times 10^{-11}$ to kinetic data for analogous nonhalogenated unsaturated esters: $k[\mathrm{OH} + CH_3OC(O)CH{=}CH_2] = (1.3 \pm 0.1) \times 10^{-11}$,[29] $k[\mathrm{OH} + CH_3CH_2OC(O)CH{=}CH_2] = (1.6 \pm 0.2) \times 10^{-11}$,[29] and $k[\mathrm{OH} + CH_3CH_2CH_2OC(O)CH{=}CH_2] = (1.8 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.[30] The reactivity of $C_4F_9CH_2CH_2OC(O)CH{=}CH_2$ is indistinguishable, within the experimental uncertainties, from that of $CH_3OC(O)CH{=}CH_2$, suggesting that the electron-withdrawing effect of the C_4F_9- group on the reactivity of OH radicals toward the double bond is small.

3.3. Products and Mechanism of the Cl + 4:2 FTAc Reaction in the Presence and Absence of NO$_x$. Figure 3 shows IR spectra acquired (A) before and (B) after 85 s of UV irradiation of a mixture of 7.1 mTorr of 4:2 FTAc and 105 mTorr of Cl_2 in 700 Torr of air diluent. Subtraction of IR features attributable to 4:2 FTAc from the spectrum in panel B gives the residual spectrum in panel C. A reference spectrum of $C_4F_9CH_2C(O)H$ (4:2 fluorotelomer aldehyde, 4:2 FTAL) is shown in panel D. Comparing panel D with panel C shows that $C_4F_9CH_2C(O)H$ is formed as a product in the system. The formation of $C_4F_9CH_2C(O)H$ is plotted versus the loss of 4:2 FTAc as the circles in Figure 4. As seen from Figure 4, the amount of $C_4F_9CH_2C(O)H$ in the chamber increased linearly with 4:2 FTAc loss, consistent with its formation as a primary product. The $C_4F_9CH_2C(O)H$ formation yield was $(18 \pm 0.6)\%$ ($n = 6$) and $(10 \pm 0.9)\%$ ($n = 7$) in the absence and presence of NO, respectively. Subtraction of IR features attributable to $C_4F_9CH_2C(O)H$ from the product spectrum (panel C) gives the

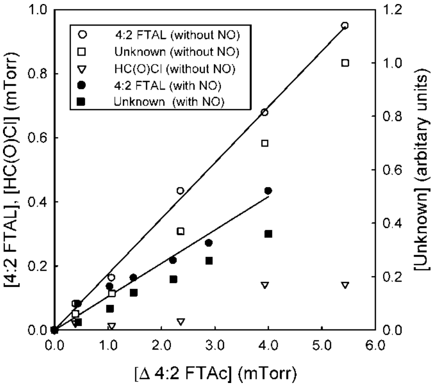

Figure 4. Yields of $C_4F_9CH_2C(O)H$ (4:2 FTAL), unknown residual product (panel E in Figure 3), and HC(O)Cl versus depletion of 4:2 FTAc after irradiation of a mixture of 7.1 mTorr of 4:2 FTAc and 105 mTorr of Cl_2 in 700 Torr of air diluent (identified as "without NO") and 7.4 mTorr of 4:2 FTAc, 101 mTorr of Cl_2, and 57 mTorr of NO in 700 Torr of air diluent (identified as "with NO"). Lines are linear regressions to the 4:2 FTAL data.

residual spectrum (panel E). The spectra of residual products did not change shape significantly throughout the time course of the experiment, suggesting the formation of one or more stable product(s). The magnitude of the residual absorption increased linearly with the consumption of 4:2 FTAc, suggesting that the compound(s) responsible for the absorption feature in the panel E spectrum is (are) a primary product(s).

As discussed in section 3.1, the bulk of the reaction of chlorine atoms with $C_4F_9CH_2CH_2OC(O)CH{=}CH_2$ is expected to proceed through addition to the >C=C< double bond (Figure 5). Addition of chlorine to the terminal carbon leads to a more stable radical and is thermodynamically favored. Reaction of the carbon radical with oxygen yields the chloroperoxy radical, followed by reaction with NO or RO_2 to yield the chloroalkoxy radical shown in Figure 5.

There are three potential fates of the chloroalkoxy radical intermediate. In pathway A (see Figure 5), the chloromethyl radical, CH_2Cl, is eliminated, giving $C_4F_9CH_2CH_2OC(O)C(O)H$ (4:2 fluorotelomer glyoxylate, 4:2 FTGly). In 700 Torr of air, chloromethyl radicals react to give HC(O)Cl, which has a characteristic absorption feature at 1783 cm^{-1}. Examination of the product spectra revealed that only trace quantities (approximately 3% yield) of HC(O)Cl were formed. We conclude that pathway A is not of major importance.

Decomposition by pathway C (see Figure 5) gives chloroacetaldehyde, $CH_2ClC(O)H$. Features attributable to this product were sought but not found in the product spectra, and we conclude that pathway C is not of major importance. Having excluded pathways A and C as playing major roles, we conclude that reaction with oxygen (pathway B) is the main fate of the chloroalkoxy radical intermediate formed by addition of Cl to 4:2 FTAc. This behavior is similar to that of α-chloro alkoxy radicals formed following reaction of chlorine atoms with other alkenes (e.g., ethene[31]). We conclude that the residual product spectrum in panel E of Figure 3 reflects the formation of $C_4F_9CH_2CH_2OC(O)C(O)CH_2Cl$ in the system.

The reaction of chlorine atoms with 4:2 FTAc can also occur by H-abstraction from the $C_4F_9CH_2CH_2OC(O)-$ portion of the compound (pathway D). Abstraction most likely occurs from the carbon adjacent to the ester function. Reaction of this radical intermediate with oxygen followed by NO or RO_2 will give the alkoxy radical, $C_4F_9CH_2C(O\bullet)HOC(O)CH{=}CH_2$. The likely fate of this alkoxy radical would be decomposition to yield $C_4F_9CH_2C(O)H$ and α-ester rearrangement to give $C_4F_9CH_2C(O)$ radicals and the acid $HOC(O)CH{=}CH_2$. A reference spectrum for $HOC(O)CH{=}CH_2$ was not available and thus it was not possible to determine whether this compound was formed in our experiments. The observed formation of $C_4F_9CH_2C(O)H$ in yields of 18% and 10% in the absence and presence of NO, respectively, might reflect the contribution of pathway D.

Finally, we note that the above is a simplified discussion of the mechanism of the chlorine-atom-initiated oxidation of 4:2 FTAc. In the absence of NO the self- and cross-reactions of peroxy radicals will be important. In addition to the radical channel of these reactions leading to alkoxy radicals, there will be molecular channels that give a variety of alcohol and carbonyl compounds.[32] Furthermore, HO_2 radicals formed in the system (e.g., in pathway B; see Figure 5) will react with peroxy radicals to give hydroperoxides.[32] In the presence of NO, the HO_2 radicals will be converted into OH radicals, and the oxidation of 4:2 FTAc will be initiated by a mixture of Cl-atom and OH-radical attack. The decreased yield of $C_4F_9CH_2C(O)H$ in the presence of NO probably reflects the contribution of OH-radical-initiated oxidation. The goal of the present study was to elucidate the atmospheric oxidation mechanism of fluorotelomer acrylates. In light of the complexity and minor atmospheric importance of chlorine-atom-initiated oxidation, further experiments and analysis were not pursued.

3.4. Products and Mechanism of the OH + 4:2 FTAc Reaction in the Presence of NO_x. To investigate the products and mechanism of OH-radical-initiated oxidation, a series of experiments were conducted using 4:2 $FTAc/CH_3ONO/NO$/air mixtures. The UV irradiation of these mixtures led to the formation of one or more carbonyl-containing product(s) with a broad absorption feature centered at approximately 1750 cm^{-1}. The absorption feature did not match those for any compounds in our reference library. However, it is possible to formulate a reaction mechanism based our findings and those from other laboratories.[30,33]

As discussed in section 3.2, the reaction of OH radicals with 4:2 FTAc proceeds mainly through addition to the >C=C< double bond. Addition to the terminal carbon leads to a more stable radical and is thermodynamically favored. Addition of oxygen to the carbon radical gives a hydroxy peroxy radical, which then reacts with NO to give the hydroxy alkoxy radical shown in Figure 6.

As with the chloro alkoxy radical discussed in the previous section, there are three potential fates of the hydroxy alkoxy radical intermediate. Elimination of a CH_2OH radical in pathway A (see Figure 6) gives the 4:2 fluorotelomer glyoxylate. The CH_2OH radical will then react with O_2 to give HCHO. Reaction with oxygen in pathway B gives the hydroxyl dicarbonyl compound shown in Figure 6. Finally, decomposition by the C−C bond scission shown in pathway C gives glycolaldehyde ($HOCH_2CHO$) and the $C_4F_9CH_2CH_2OC(O)$ radical. Using our calibrated reference spectrum of $HOCH_2CHO$, we searched for IR product features that could be attributed to glycolaldehyde but found none. Similarly, we looked for characteristic −OH stretch features in the 3500−3230 cm^{-1} region in the product spectra that could be attributed to hydroxyl dicarbonyl compound but found none. We conclude that pathways B and C (see Figure 6) are not significant.

The formation of HCHO is a marker for the importance of pathway A. The chemical system used to generate OH radicals (photolysis of CH_3ONO) generates substantial amounts of HCHO (through reactions 2 and 3; see section 2.1) and complicates quantification of HCHO formation during 4:2 FTAc oxidation. To investigate the formation of HCHO during the

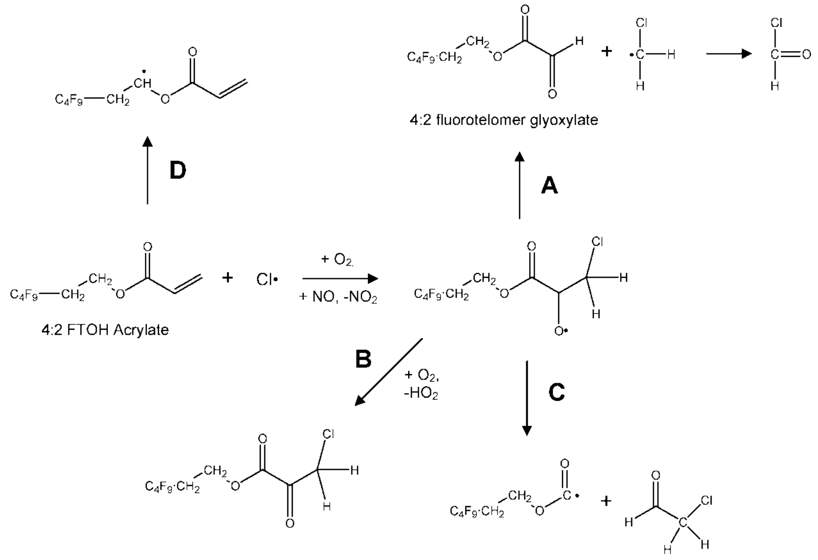

Figure 5. Simplified mechanism of Cl-atom oxidation of 4:2 FTAc.

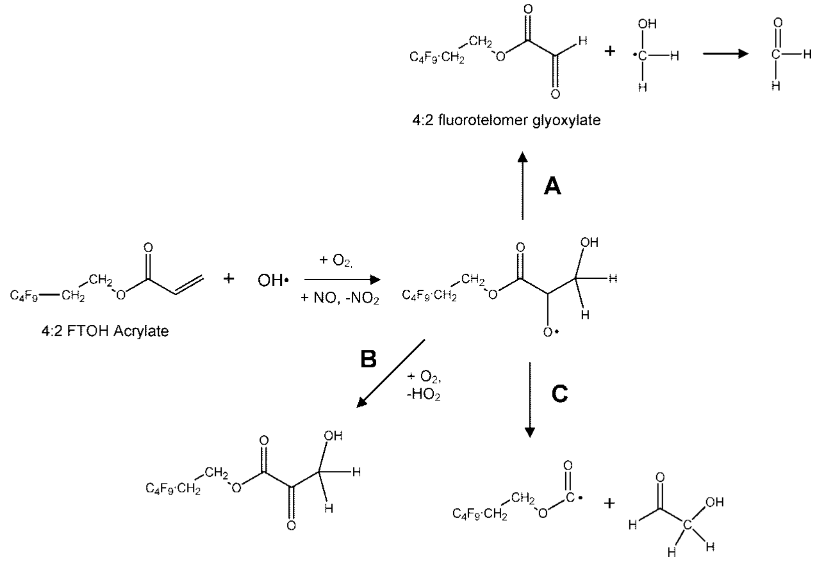

Figure 6. Simplified mechanism of OH-radical oxidation of 4:2 FTAc.

oxidation of 4:2 FTAc, an additional series of experiments was performed using deuterated methyl nitrite (CH_2DONO) as a source of OH radicals. The formaldehyde originating from the CH_2DONO is mainly HCDO

$$CH_2DONO + h\nu \rightarrow CH_2DO + NO \qquad (16)$$

$$CH_2DO + O_2 \rightarrow HCDO + HO_2 \qquad (17)$$

$$CH_2DO + O_2 \rightarrow HCHO + DO_2 \qquad (18)$$

The branching ratio, k_{17}/k_{18} is 0.88/0.12 (±0.011).[34] The observed formation of HCDO was combined with the rate constant ratio k_{17}/k_{18} to calculate, and correct for, the HCHO resulting from photolysis of CH_2DONO.

HCHO reacts with OH radicals

$$HCHO + OH \rightarrow \text{products} \qquad (19)$$

The rate constant for reaction 19 has been determined: $k_{19} = 8.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[35]

The concentration profile of HCHO can be described[36] by the expression

$$\frac{[\text{HCHO}]}{[\text{4:2 FTAc}]_0} = \frac{\alpha(1 - x)[(1 - x)^{(k_{19}/k_{13})-1} - 1]}{[1 - (k_{19}/k_{13})]} \qquad (\text{I})$$

where $x = 1 - ([\text{4:2 FTAc}]/[\text{4:2 FTAc}]_0)$ is the fractional consumption of 4:2 FTAc and α is the molar yield of HCHO in the OH-radical-initiated oxidation of 4:2 FTAc. Figure 7 shows a plot of [HCHO]/[4:2 FTAc]$_0$ versus Δ[4:2 FTAc]/[4:2 FTAc]$_0$. The best-fit line gives $\alpha = 1.02 \pm 0.07$ and $k_{19}/k_{13} = 0.70 \pm 0.05$. We can combine $k_{19}/k_{13} = 0.70 \pm 0.07$ with $k_{19} = 8.5 \times 10^{-12}$ to obtain a value of $k_{13} = (1.21 \pm 0.12) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, which is indistinguishable from that derived in section 3.2. The fact that the HCHO yield is indistinguishable from 100% indicates that nitrate formation in the RO_2 + NO reactions in the system is not substantial, and we conclude that

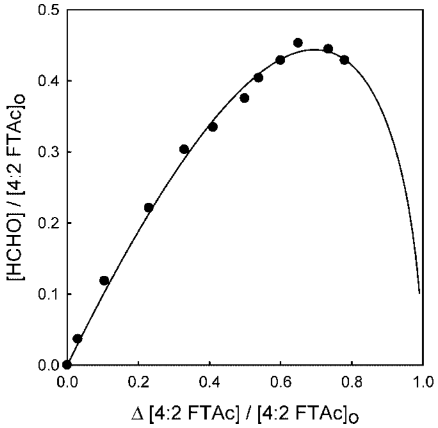

Figure 7. Formation of HCHO versus loss of 4:2 FTAc, normalized to the initial 4:2 FTAc concentration, following the UV irradiation of 4:2 FTAc/CH_2DONO/NO mixtures in 700 Torr of air at 296 K. The curve is a fit of eq I to the data.

the oxidation of 4:2 FTAc can be represented in atmospheric models by the equation

$$OH + C_4F_9CH_2CH_2OC(O)CH{=}CH_2 \rightarrow C_4F_9CH_2CH_2OC(O)CHO + HCHO \quad (20)$$

This conclusion is consistent with the recent finding by Blanco and Teruel[30] that butyl glyoxylate is the main product of the OH-initiated oxidation of butyl acrylate.

4. Implications for Atmospheric Chemistry

4.1. Atmospheric Lifetime. The atmospheric oxidation of 4:2 FTAc is initiated by reaction with OH radicals. Chlorine atoms are present in the atmosphere at levels that are typically several orders of magnitude lower than those for OH, and chlorine-atom-initiated oxidation will not be significant. Loss by photolysis is considered negligible because unsaturated esters do not photolyze in the actinic region.[29] Assuming that 4:2 FTAc and methyl acrylate[37] have similar reactivities toward ozone, we can estimate $k(O_3 + 4{:}2\ FTAc) = 1 \times 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1}. Taking a typical value of the ozone concentration in urban areas as 50 ppb, then the lifetime of 4:2 FTAc with respect to reaction with ozone is approximately 9 days. From $k(OH + 4{:}2\ FTAc) = 1.1 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} (section 3.2) and an OH radical concentration of 1×10^6 molecules cm^{-3},[38] the atmospheric lifetime of 4:2 FTAc with respect to reaction with OH radicals is estimated to be approximately 1 day. We conclude that the atmospheric lifetime of 4:2 FTAc is determined by reaction with OH radicals and is approximately 1 day. It should be noted that the lifetime of 4:2 FTAc will vary seasonally and geographically with local OH radical concentrations.

The reactivity toward OH radicals, and hence the atmospheric lifetime of FTOHs, is not dependent on chain length.[26] It seems reasonable to assume that the same will be true for fluorotelomer acrylates and that the kinetic data reported here for 4:2 FTAc will be applicable to the more commercially relevant longer-chain fluorotelomer acrylates of the general formula, $C_xF_{2x+1}CH_2CH_2OC(O)CH{=}CH_2$. Our results show that fluorotelomer acrylates will be oxidized into fluorotelomer glyoxalates close to the emission sources on a time scale of approximately 1 day.

A recent analysis of residuals from a commercial fluorotelomer-based polymer showed similar levels of FTACs and FTOHs.[18] Residuals from commercial products can be significant emission sources of FTAcs and FTOHs in urban areas. The limited available data suggest that the concentrations of FTAcs in the atmosphere are substantially lower than those of FTOHs.[20−22] The low levels of FTAcs are consistent with their short atmospheric lifetimes and might also reflect lower rates of emission for these compounds. Further work is needed to better define the emission fluxes of fluorotelomer compounds into the atmosphere.

4.2. Contribution to the PFCA Burden in Remote Locations. The atmospheric oxidation of fluorotelomer acrylates [$C_xF_{2x+1}CH_2CH_2OC(O)CH{=}CH_2$] is initiated by reaction with OH radicals and gives fluorotelomer glyoxylates [$C_xF_{2x+1}CH_2CH_2OC(O)C(O)H$, FTGly] in a molar yield that is indistinguishable from 100%. The atmospheric fate of fluorotelomer glyoxylates will be photolysis and reaction with OH radicals. It is expected that the reaction of OH radicals with fluorotelomer glyoxylates will proceed predominately by hydrogen abstraction from the aldehyde group, and hence the rate constant is probably similar to that for reaction with $CH_3C(O)C(O)H$. Further work is needed to confirm this expectation, especially in light of the approximately linear yield plot of methyl glyoxylate in the chlorine-atom-initiated oxidation of methyl propionate reported by Cavalli et al.,[39] which suggests that glyoxylates might be somewhat less reactive than glyoxals. Proceeding on the assumption that $k(OH + FTGly) = k[OH + CH_3C(O)C(O)H] = 1.5 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} [28] and taking a diurnal average OH concentration of 10^6 molecule cm^{-3} leads to an estimate of 18 h for the lifetime of FTGly with respect to reaction with OH radicals. The dicarbonyl chromophores in FTGly and $CH_3C(O)C(O)H$ are similar. For a solar zenith angle of 45°, the photolysis rate of $CH_3C(O)C(O)H$ is 10^{-4} s^{-1} at 0.5 km altitude for a cloudless sky.[28] This photolysis rate is equivalent to a lifetime of 3 h. It is probable that FTGlys have a similarly short lifetime with respect to photolysis. We conclude that photolysis is probably the major atmospheric fate of FTGlys. By analogy to $CH_3C(O)C(O)H$,[28] photolysis will occur through rupture of the $C_xF_{2x+1}CH_2CH_2OC(O){-}C(O)H$ bond. Photolysis will initiate a sequence of reactions leading to the formation of $C_4F_9CH_2CHO$

$$C_4F_9CH_2CH_2OC(O)C(O)H + h\nu \rightarrow C_4F_9CH_2CH_2OC(O) + HCO \quad (21)$$

$$C_4F_9CH_2CH_2OC(O) + O_2 \rightarrow C_4F_9CH_2CH_2OC(O)OO \quad (22)$$

$$C_4F_9CH_2CH_2OC(O)OO + NO \rightarrow C_4F_9CH_2CH_2O + CO_2 + NO_2 \quad (23)$$

$$C_4F_9CH_2CH_2O + O_2 \rightarrow C_4F_9CH_2CHO + HO_2 \quad (24)$$

Whether initiated by photolysis or by reaction with OH, the oxidation of FTGlys will proceed to give fluorotelomer aldehydes ($C_xF_{2x+1}CH_2CHO$) on a time scale of probably less than 1 day. As discussed in detail previously,[17] the oxidation of $C_xF_{2x+1}CH_2CHO$ proceeds on a time scale of approximately 6 days[40,41] and gives $C_xF_{2x+1}CHO$, which, in turn, is oxidized to COF_2 (on a time scale of approximately 1−2 days [42]) as the major product, with perfluorocarboxylic acids as minor products (in approximately 1−10% molar yield).[17] Hence, the atmospheric oxidation of fluorotelomer acrylates is expected to lead to the formation of perfluorocarboxylic acids in an approximately 1−10% molar yield. The time scale of conversion of FTAcs into PFCAs is sufficiently slow (approximately 10 days) to allow transport of FTAcs and their oxidation products over large distances (3500 km at the global average wind speed of approximately 4 m s^{-1}). We show here that the atmospheric degradation of FTAcs has the *potential* to contribute to the observed burden of PFCA pollution in remote locations. To assess the magnitude of this contribution, estimates for the flux of FTAcs into the atmosphere are required. Further work is needed to provide such estimates.

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