Atmospheric Chemistry of 4:2 Fluorotelomer Iodide (n-$C_4F_9CH_2CH_2I$): Kinetics and Products of Photolysis and Reaction with OH Radicals and Cl Atoms

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Relative rate techniques were used to study the title reactions and determine rate constants of $k(Cl + C_4F_9CH_2CH_2I) = (1.25 \pm 0.15) \times 10^{-12}$ and $k(OH + C_4F_9CH_2CH_2I) = (1.2 \pm 0.6) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} in 700 Torr total pressure at 295 K. The fluorotelomer aldehyde ($C_4F_9CH_2CHO$), perfluorinated aldehyde (C_4F_9CHO), fluorotelomer acid ($C_4F_9CH_2C(O)OH$), fluorotelomer peracid ($C_4F_9CH_2C(O)OOH$), and several perfluorocarboxylic acids were detected by in situ FTIR spectroscopy and offline analysis as products of the chlorine atom initiated oxidation of $C_4F_9CH_2CH_2I$ in air. The UV−visible spectra of $C_4F_9CH_2CH_2I$ and C_2H_5Cl were recorded over the range of 200−400 nm. Photolysis of $C_4F_9CH_2CH_2I$ gives $C_4F_9CH_2CHO$ as the major observed product. By assumption of a photolysis quantum yield of unity, it was calculated that the atmospheric lifetime of $C_4F_9CH_2CH_2I$ is determined by photolysis and is a few days. A mechanism for the atmospheric oxidation of fluorotelomer iodides, ($C_xF_{2x+1}CH_2CH_2I$, where $x = 2, 4, 6,...$) is proposed. Atmospheric oxidation of fluorotelomer iodides is a potential source of perfluorocarboxylic acids.

1. Introduction

Perfluorocarboxylic acids (PFCAs) are found ubiquitously in water and biota in urban and remote locations such as the Arctic.[1,2] Given their use in products associated with industrial society it is not surprising that PFCAs are found in urban areas. However, as these compounds exist mainly as anions in environmental media and are not subject to long-range atmospheric transport, their presence in remote locations is somewhat surprising. Two hypotheses have been put forward to account for the presence of PFCAs in remote regions: (i) oceanic transport of PFCAs followed by transfer to land by marine aerosols[3−5] and (ii) atmospheric oxidation of volatile precursors to PFCAs followed by deposition in precipitation.[6−8] Evidence supporting the oceanic hypothesis comes from computer modeling studies.[5] Evidence supporting the atmospheric hypothesis comes from field measurements,[9,10] laboratory experiments,[6,7] and computer models.[8] The relative importance of the atmospheric and oceanic pathways is a matter of current debate.

Smog chamber experiments have shown that the atmospheric oxidation of fluorotelomer alcohols (FTOHs),[6,7] fluorosulfamido alcohols,[11,12] and fluorinated olefins[13] are likely sources of PFCAs in remote locations. It is possible that other classes of volatile compounds are additional sources of PFCAs. One such class of compounds is fluorotelomer iodides (FTI), which are used in the synthesis of FTOHs, fluorotelomer olefins, and other products. Production of the FTIs and the telomer products is in the range of millions of kilograms,[14,15] but the level of emission of FTIs is unknown. By consideration of their high use and volatility, it seems reasonable to expect that FTIs will be emitted into the atmosphere; however, no measurements have yet been made to quantify such emissions. To our knowledge, FTIs have not been the subject of any environmental studies.

Assessments of whether FTIs can survive long-range transport and degrade to form PFCAs in the environment require data for the atmospheric chemistry of FTIs. There are no reported studies of the atmospheric chemistry of FTIs. The objective of the present study was to improve our understanding of the atmospheric chemistry of FTIs by examining a representative compound, $CF_3(CF_2)_3CH_2CH_2I$ (4:2 FTI). Smog chamber techniques were used to study (i) the kinetics of reaction of Cl atoms and OH radicals with 4:2 FTI, (ii) the products of the Cl atom initiated oxidation of 4:2 FTI, (iii) the rate of photolysis, and (iv) the products of 4:2 FTI photolysis.

2. Experimental Section

2.1. Smog Chamber Methods. Experiments were performed in a 140-L Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer.[16] The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL), which have maximum emission at approximately 360 nm and were used to photochemically initiate the experiments. Chlorine atoms were produced by photolysis of molecular chlorine

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

OH radicals were produced by photolysis of CH_3ONO in the presence of NO 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

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

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

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

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

Assuming that the reactant and reference compounds are lost solely via reaction with Cl atoms (or OH radicals) and that neither the reactant, nor reference, are reformed in any processes, then it can be shown that

$$\mathrm{Ln}\left(\frac{[\mathrm{X}]_t}{[\mathrm{X}]_{t_0}}\right) = \left(\frac{\mathrm{k}_x}{\mathrm{k}_{\mathrm{ref}}}\right)\mathrm{Ln}\left(\frac{[\mathrm{ref}]_t}{[\mathrm{ref}]t_0}\right) \tag{9}$$

where $[X]_{t0}$, $[X]_t$, $[ref]_{t0}$, and $[ref]_t$ are the concentrations of the compound of interest and reference at times t_0 and t, and k_X and k_{ref} are the rate constants for the reactant and the reference. Plots of $Ln([X]_{t0}/[X]_t)$ vs $Ln([ref]_{t0}/[ref]_t)$ should be linear, pass through the origin, and have a slope of k_X/k_{ref}.

CH_3ONO was synthesized by the dropwise addition of concentrated sulfuric acid to a saturated solution of $NaNO_2$ in methanol. The $C_4F_9CH_2CHO$ reference spectrum was obtained using a synthesized standard.[7] The $C_4F_9CH_2C(O)OOH$ reference spectrum was derived from the analysis described by Hurley et al.[7] Other reagents were obtained from commercial sources. Experiments were conducted in 700 Torr total pressure of N_2 or N_2/O_2 diluent at 296 K. Compounds were monitored using absorption features at the following wavenumbers (cm^{-1}): $C_4F_9CH_2CH_2I$ (740), $C_4F_9CH_2CHO$ (1752), C_4F_9CHO (1778), $C_4F_9C(O)OOH$ (1450), COF_2 (1944), and CO (2150). To remove volatile impurities, $C_4F_9CH_2CH_2I$ was subjected to repeated freeze/pump/thaw cycling before use. 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. To check for unwanted loss of reactants and reference compounds via heterogeneous reactions, initial reaction mixtures were left to stand in the chamber in the dark for 60 min; there was no observable (<2%) loss of reactants. To check for loss via photolysis a mixture of 8.8 mTorr 4:2 FTI in 700 Torr of air was subjected to 5 min of UV irradiation using the output from 22 blacklamps. There was no discernible loss (<2%) of 4:2 FTI. Photolysis is not a significant loss of 4:2 FTI in experiments using blacklamps (i.e., those described in sections 3.1 and 3.2). Photolysis product studies were carried out in the same setup, except that the 12 blacklamps were replaced with phosphor coated sunlamps (GE-FS40), with maximum emission at approximately 310 nm (see Figure 4 in Taniguichi et al.[17]). Product studies were performed using 17.6−26.4 mTorr of 4:2 FTI in 50 Torr oxygen diluent. Unless stated otherwise, quoted uncertainties are 2 standard deviations from least-squares regressions.

2.2. Offline Sample Collection and Analysis. Offline samples were collected by bubbling approximately 5 L of chamber air through pH 11 aqueous Na_2CO_3 solution. Sodium carbonate solutions were acidified to pH 4 using HCl and analyzed using a Waters Acquity Ultra Performance LC with detection by a Micromass Quattro Micro MS/MS detector. Analytes were separated on a Luna C18 column (2.0 mm × 50 mm × 2.5 μm) maintained at 30 °C. The mobile phase consisted of methanol and water, both containing 10 mM ammonium acetate, with a flow rate 0.2 mL min^{-1}. Separation was achieved using a 7-min gradient starting at 10% methanol and 90% water, holding for 0.5 min, increasing the methanol component over the next 2.5 min to 60%, with that composition held for 1.5 min before returning to initial conditions over 0.5 min, and holding for 2.0 min equilibration period. Analysis was performed in triplicate with 7.5-μL injections using isotopically labeled perfluorobutanoic acid ($^{13}C_4$−PFBA, Wellington Laboratories) as an internal standard. PFCAs were analyzed with a cone voltage of 17 V and collision energy of 9 eV, and the following transitions were monitored: perfluoropentanoic acid (PFPeA) 263 > 219, perfluorobutanoic acid (PFBA) 213 > 169, $^{13}C_4$−PFBA 217 > 172, perfluoropropionic acid (PFPrA) 163 > 119 and trifluoroacetic acid (TFA) 113 > 69.

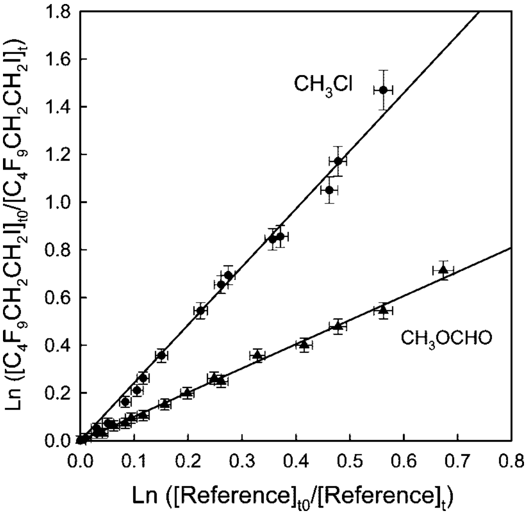

Figure 1. Decay of 4:2 FTI vs CH_3Cl and CH_3OCHO in the presence of Cl atoms in 700 Torr of N_2 at 295 ± 2 K.

2.3. UV Spectral Measurements and Photolysis Rate Calculations. The gas-phase UV−visible spectra of ethyl iodide and 4:2 FTI were recorded over the wavelength range 200−400 nm in a 6-cm cell using a commercial dual beam (Lambda 18 Perkin-Elmer) spectrometer with a resolution of 1 nm. Spectra were recorded in 700 Torr of air or nitrogen. Photolysis rates were calculated using the Tropospheric Ultraviolet−Visible (TUV 4.2) package[18] assuming a photolysis quantum yield of unity consistent with other alkyl iodides.[19]

3. Results and Discussion

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

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

$$\mathrm{Cl} + \mathrm{CH_3Cl} \rightarrow \text{products} \tag{11}$$

$$\mathrm{Cl} + \mathrm{CH_3OCHO} \rightarrow \text{products} \tag{12}$$

Reaction mixtures consisted of 1.8−4.9 mTorr of 4:2 FTI, 100−110 mTorr of Cl_2, and either 15−20 mTorr of CH_3Cl or 2.8−5.9 mTorr of CH_3OCHO in 700 Torr of N_2 diluent. The observed loss of 4:2 FTI vs those of the reference compounds is plotted in Figure 1. Linear least-squares analysis of the data in Figure 1 gives $k_{10}/k_{11} = 2.43 \pm 0.21$ and $k_{10}/k_{12} = 1.01 \pm 0.09$. Quoted errors include two standard deviations from the regression analysis and uncertainty in the analysis of the IR spectra.

Using $k_{11} = 4.8 \times 10^{-13}$[20] and $k_{12} = 1.3 \times 10^{-12}$[21] gives $k_{10} = (1.17 \pm 0.11) \times 10^{-12}$ and $(1.31 \pm 0.12) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. We choose to cite a final value which is the average of the individual determinations together with error limits which encompass the extremes of the determinations, hence $k_{10} = (1.24 \pm 0.19) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. While there have been no previous studies of k_{10}, we can compare our result with $k(Cl + 4{:}2\ FTOH) = (1.61 \pm 0.49) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} [6]. Replacement of the alcohol functionality by an iodine atom reduces the reactivity of the molecule toward chlorine atoms by a factor of approximately 13. The presence

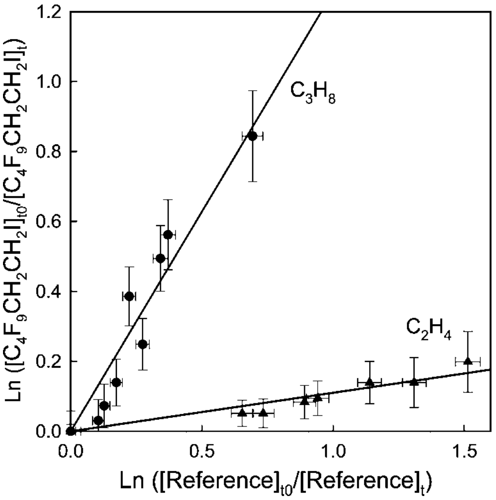

Figure 2. Decay of 4:2 FTI vs C_2H_4 and C_3H_8 in the presence of OH radicals in 700 Torr of air diluent at 295 ± 2 K.

of an alcohol group generally increases the reactivity of neighboring C−H bonds; hence the observed qualitative difference between 4:2 FTI and 4:2 FTOH is consistent with expectations.

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

$$OH + 4{:}2\ FTI \rightarrow products \quad (13)$$

$$OH + C_2H_4 \rightarrow products \quad (14)$$

$$OH + C_3H_8 \rightarrow products \quad (15)$$

Initial reaction mixtures consisted of 7.4−20.6 mTorr of 4:2 FTI 102 mTorr of CH_3ONO, and either 3.2−4.4 mTorr of C_2H_4 or 50−68 mTorr of C_3H_8 in 700 Torr total pressure of air diluent. Figure 2 shows the loss of 4:2 FTI plotted vs loss of the reference compounds. The uncertainty bars indicate uncertainties in the IR analysis. As a result of interfering absorptions from CH_3ONO and its products, the IR analysis of 4:2 FTI has greater uncertainty in the OH than in the Cl rate experiments (compare *y* axis error bars in Figures 1 and 2). The lines through the data in Figure 2 are linear least-squares fits which give $k_{13}/k_{14} = 0.11 \pm 0.04$ and $k_{13}/k_{15} = 1.26 \pm 0.28$, uncertainties include two standard deviations from the regressions and uncertainties associated with the IR analysis. Using $k_{14} = 8.52 \times 10^{-12}$ [22] and $k_{15} = 1.1 \times 10^{-12}$ [20] gives $k_{13} = (9.4 \pm 3.4) \times 10^{-13}$ and $k_{13} = (1.39 \pm 0.31) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Within the admittedly substantial uncertainties, the two determinations are in agreement. We choose to report an average with uncertainties which encompass the extremes of the individual determinations, hence, $k_{13} = (1.2 \pm 0.6) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

The reactivity of 4:2 FTI toward OH radicals can be estimated using the SAR method. Using the approach described by Kwok and Atkinson,[23] the reactivity of 4:2 FTI is given as $k_{total} = k(-CH_2-)*F(-CF_2-)*F(-CH_2I) + k(-CH_2-)*F(-CH_2-)*F(-I)$. The database concerning reactions of OH radicals with iodoalkanes was very limited at the time that Kwok and Atkinson developed their SAR factors and consequently the factor $F(-CH_2I)$ was not included in their analysis. Recently, Carl and Crowley[24] have reported $k(OH+CH_3CH_2CH_2I) = 1.47 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. In SAR terms the rate constant $k(OH + CH_3CH_2CH_2I)$ can be expressed as $k(-CH_3)*F(-CH_2-) + k(-CH_2-)*F(-CH_3)*F(-CH_2I) + k(-CH_2-)*F(-CH_2-)*F(-I)$. Taking values of $k(-CH_3) = 1.36 \times 10^{-14}$, $k(-CH_2-) = 9.34 \times 10^{-13}$, $F(-CH_2-) = 1.23$, $F(-CH_3) = 1.0$, and $F(-I) = 0.53$, we derive $F(-CH_2I) = 0.90$. Using this factor we can estimate $k(OH + 4{:}2\ FTI) = 9.34 \times 10^{-13} \times 0.018 \times 0.90 + 9.34 \times 10^{-13} \times 1.23 \times 0.53 = 0.15 \times 10^{-13} + 6.09 \times 10^{-13} = 6.24 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} with the majority (98%) of the reactivity occurring at the $-CH_2I$ group. Kwok and Atkinson[23] noted that for the case of haloalkanes there were often significant disagreements (>factor of 2) between rate constants estimated using the SAR method and those measured experimentally. The measured value of $k(OH + 4{:}2\ FTI) = (1.2 \pm 0.6) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} is reasonably consistent with expectations based upon SAR calculations.

The value of $k(OH + 4{:}2\ FTI)$ measured in the present work can be used to provide an estimate of the atmospheric lifetime of 4:2 FTI. Using a global weighted-average OH concentration[25] of 1.0×10^6 cm^{-3} leads to an estimated lifetime of 4:2 FTI with respect to reaction with OH radicals of approximately 10 days. The approximate nature of this lifetime estimate should be stressed; the average daily concentration of OH radicals and temperature vary significantly with both location and season. The quoted lifetime is a global average, but local lifetimes could be significantly shorter or longer. On the basis of production of FTOHs and related products,[15] it seems reasonable to expect environmental release of 6:2, 8:2, and 10:2 FTIs to be the most significant. Studies have shown there is no effect of fluorinated chain length on OH reaction rates for telomer compounds, indicating that lifetimes with respect to OH reaction of higher fluorinated FTIs will be similar to those measured in this study.

3.3. Products of Cl + 4:2 FTI Reaction. The mechanism of Cl atom initiated oxidation of 4:2 FTI was investigated using mixtures of 4:2 FTI and Cl_2 in air. Figure 3 shows IR spectra acquired before (A) and after (B) 10 min of UV irradiation (blacklamps) of a mixture of 12.2 mTorr of 4:2 FTI and 100 mTorr Cl_2 in 700 Torr of air. The UV irradiation led to 32% (3.9 mTorr) consumption of 4:2 FTI. Subtracting IR features attributable to 4:2 FTI from Figure 3B gives the product spectrum shown in Figure 3C. Comparison with reference spectra of the fluorotelomer peracid, $C_4F_9CH_2C(O)OOH$, and fluorotelomer aldehyde, $C_4F_9CH_2CHO$, in panels D and E shows the formation of these compounds. The small IR feature at 1673 cm^{-1} in panel C does not match any features in our reference library and is attributed to an unknown product. The product feature centered at 1944 cm^{-1} in panel Figure 3C reflects the formation of COF_2. For the experiment shown in Figure 3, the yields of $C_4F_9CH_2C(O)OOH$, $C_4F_9CH_2CHO$, and COF_2 were 1.32 mTorr, 0.44 mTorr, and 0.33 mTorr, respectively. In addition, 0.16 mTorr of $C_4F_9CH_2C(O)OH$, 0.17 mTorr of C_4F_9CHO, and 1.51 mTorr of CO were observed by FTIR spectroscopy. The products observed by FTIR spectroscopy account for 59% of the 4:2 FTI loss (evaluated on basis of carbon). By analogy to CH_3I,[26] it is possible that the chloride $C_4F_9CH_2CH_2Cl$ is formed and accounts for some of the 4:2FTI loss. We do not have a reference spectrum for the chloride and are not able to analyze for its formation. Offline analysis by LC-MS-MS revealed the presence of small amounts (of the order of 1% of 4:2 FTI loss) of the perfluorinated carboxylic acids PFPeA (perfluoropentanoic acid), PFBA (perfluorobutanoic acid), PFPrA (perfluoropropanoic acid), and TFA (trifluoroacetic acid) in samples taken after 28 min of irradiation.

3.4. UV Spectra and Photolysis Kinetics. Mixtures for UV spectral measurements consisted of 3.0−6.0 Torr of ethyl iodide or 2.0−5.0 Torr of 4:2 FTI in 700 Torr of air or nitrogen. The UV absorption spectra of 4:2 FTI and ethyl iodide recorded in the present work are shown in Figure 4 and given in tabular

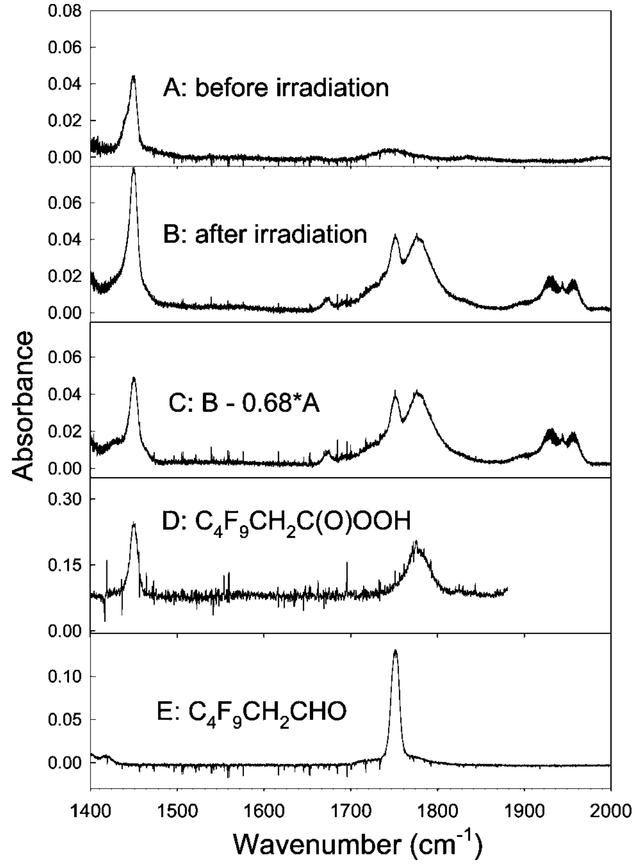

Figure 3. FTIR spectra of a mixture of 12.2 mTorr 4:2 FTI and 100 mTorr Cl_2 in 700 Torr of air before (A) and after (B) 10 min UV (blacklamps) irradiation. Panel C is the product spectrum. Reference spectra of the peracid $C_4F_9CH_2C(O)OOH$ and the aldehyde $C_4F_9CH_2CHO$ are given in panels D and E.

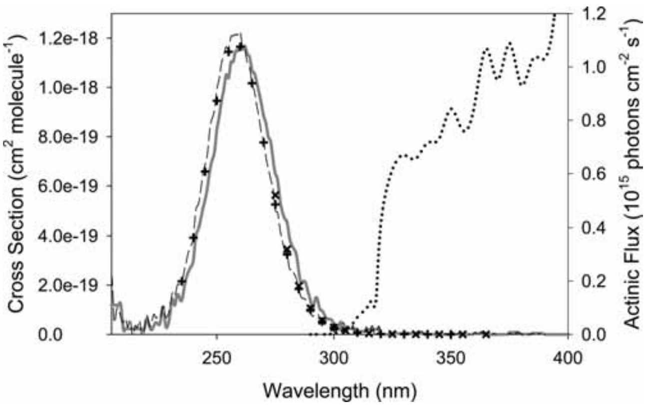

Figure 4. UV−visible absorption cross sections for 4:2 FTI (gray) and ethyl iodide (dashed) compared to actinic flux at the surface (dotted). Symbols represent literature data from Roehl et al. (×)[27] and Rattigan et al. (+).[28]

TABLE 1: 24-Hour Averaged Photolysis Rate Constants and Lifetimes for Ethyl Iodide and 4:2 FTIs in Toronto, ON, Canada

	rate constant (10^{-6} s^{-1})		lifetime (days)	
	ethyl iodide	4:2 FTI	ethyl iodide	4:2 FTI
winter solstice	1.1	4.5	11	2.6
spring equinox	3.6	13	3.2	0.9
summer solstice	5.9	21	2.0	0.6
autumn equinox	3.5	13	3.3	0.9
yearly average	3.5	12.8	3.3	0.9

format (each 1 nm) in the Supporting Information. As shown in Figure 4, our absorption cross sections for ethyl iodide are in good agreement with the previous measurements by Roehl et al.[27] and Rattigan et al.[28] A slight red shift is observed for 4:2 FTI compared to the hydrocarbon analogues. The maximum for 4:2 FTI is 260 nm, while that of ethyl iodide is 257 nm. Red shifts are common in fluorinated compounds and have been demonstrated up to 26 nm in fluorinated propanones,[29] but the separation from the absorptive group and the fluorinated tail in these species presumably decreases the effect. The similarity of the spectra of 4:2 FTI and ethyl iodide is not unreasonable, given the fact that in both molecules the iodine chromophore is attached to a $-CH_2CH_2X$ group, where X is H or C_4F_9. The UV absorption by alkyl iodides involves an n to σ^* transition with the promotion of a non bonding electron on the halogen to an antibonding σ orbital of the C−I bond.[30] In a saturated molecule such as XCH_2CH_2I, the nature of X is not expected to have major impact on the n to σ^* transition. The quantum yields for photolysis were assumed to be unity, in accordance with short-chain alkyl iodides.[30] The effect of fluorination on the quantum yield is unknown. There is a possibility that it could decrease the quantum yield, in which case the photolysis rates presented are upper limits. Photolysis rate constants and lifetimes for 4:2 FTI and ethyl iodide were calculated for the atmosphere over the city of Toronto, ON, Canada (43.72° N, 79.33° W) using the TUV program package and are shown in Table 1. Calculated lifetimes of a few days for ethyl iodide are in agreement with previous studies.[27,28,30] As indicated in Table 1, we calculate a lifetime for 4:2 FTI with respect to photolysis in Toronto of a few days. Photolysis rate constants for 4:2 FTI as a function of latitude are shown in Figure S1 of Supporting Information. As seen from Figure 5, the absorption by 4:2 FTI

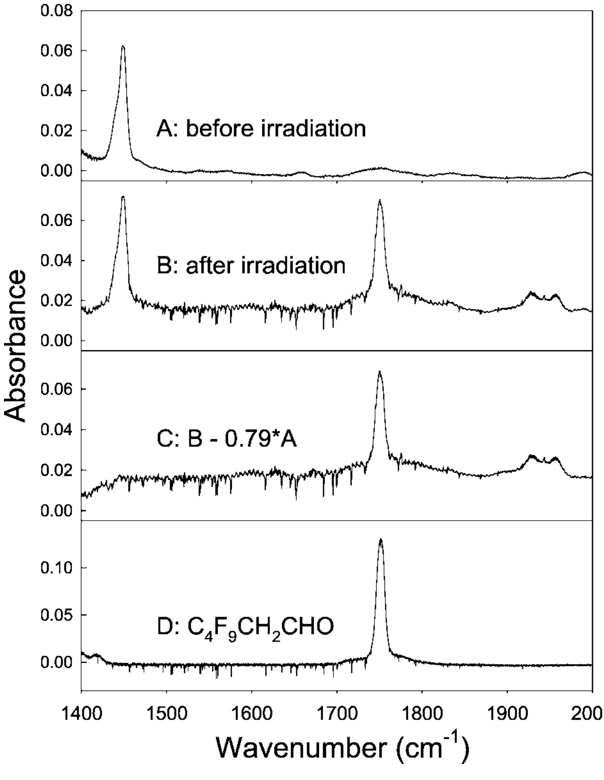

Figure 5. FTIR spectra of a mixture of 18.5 mTorr of 4:2 FTI in 50 Torr of O_2 diluent before (A) and after (B) 137 min of UV (sunlamp) irradiation. Panel C shows the result of subtracting features attributable to 4:2 FTI from panel B. A reference spectrum of $C_4F_9CH_2CHO$ is given in panel D.

at atmospherically relevant wavelengths near 300 nm is weak. Consequently, the relative uncertainties in the absorption cross sections, and hence our estimation of the photolysis lifetimes, are significant. The UV spectra for larger FTIs are expected to be indistinguishable from that for 4:2 FTI and the lifetime estimate for 4:2 FTI photolysis applies to larger FTIs. We conclude from the data in Figure 4 and Table 1 that the atmospheric lifetime of FTIs with respect to photolysis is comparable to that of ethyl iodide and is approximately a few days in the summer and a few weeks in the winter at midlatitudes.

3.5. Photolysis Products. Figure 5 shows IR spectra before (A) and after (B) 137 min of UV irradiation (sunlamps) of a mixture of 18.5 mTorr of 4:2 FTI in 50 Torr of O_2 diluent. The consumption of 4:2 FTI was 17% (3.1 mTorr). Subtracting IR features attributable to 4:2 FTI from Figure 5B gives the product spectrum shown in 6C. Comparison with a reference spectrum of the fluorotelomer aldehyde, $C_4F_9CH_2CHO$, shows the formation of this compound in a yield of 0.89 mTorr. The IR product feature at 1944 cm^{-1} is COF_2, which was formed in a yield of 0.21 mTorr. In addition, CO was observed at a yield of 0.62 mTorr. The observed $C_4F_9CH_2CHO$ accounts for only 29% of the loss of 4:2 FTI. It is expected that photolysis of 4:2 FTI will proceed via elimination of the iodine atom leading to the formation of $C_4F_9CH_2CHO$ as the primary product

$$C_4F_9CH_2CH_2I + h\nu \rightarrow C_4F_9CH_2CH_2 + I \quad (16)$$

$$C_4F_9CH_2CH_2 + O_2 + M \rightarrow C_4F_9CH_2CH_2O_2 + M \quad (17)$$

$$C_4F_9CH_2CH_2O_2 + C_4F_9CH_2CH_2O_2 \rightarrow C_4F_9CH_2CH_2O + C_4F_9CH_2CH_2O + O_2 \quad (18a)$$

$$C_4F_9CH_2CH_2O_2 + C_4F_9CH_2CH_2O_2 \rightarrow C_4F_9CH_2CH_2OH + C_4F_9CH_2CHO + O_2 \quad (18b)$$

$$C_4F_9CH_2CH_2O + O_2 \rightarrow C_4F_9CH_2CHO + HO_2 \quad (19)$$

There are no data concerning the UV spectrum or photolysis quantum yield of $C_4F_9CH_2CHO$. However, by analogy to CF_3CH_2CHO and $C_6F_{13}CH_2CHO$,[31,32] it is expected that (i) $C_4F_9CH_2CHO$ will undergo photolysis in the chamber leading to the formation of C_4F_9CHO as a secondary product and (ii) C_4F_9CHO will undergo photolysis approximately an order of magnitude more rapidly than $C_4F_9CH_2CHO$. The fact that the observed yield of $C_4F_9CH_2CHO$ accounts for only 29% of the loss of 4:2 FTI may reflect loss of $C_4F_9CH_2CHO$ (and C_4F_9CHO) via photolysis. Reaction with iodine containing species formed in the chamber may also contribute to consumption of $C_4F_9CH_2CHO$.

Photolysis of C_4F_9CHO will give C_4F_9 radicals which will add O_2 to give $C_4F_9O_2$ radicals and undergo a series of reactions in which the molecule "unzips" by shedding COF_2 units and is degraded to give a CF_3O radical. CF_3O radicals will combine with CF_3O_2, $C_2F_5O_2$, $C_3F_7O_2$, and $C_4F_9O_2$ radicals to give trioxides ($CF_3O_3C_xF_{2x+1}$).[33] Modest residual product IR features were observed in the region 1050−1300 cm^{-1}, which would be consistent with the formation of such trioxides. It should be noted that trioxides are not formed in the atmosphere because of the extremely low concentration of $C_xF_{2x+1}O_2$ radicals and the availability of other reaction partners (NO and CH_4) for CF_3O radicals. Finally, we note that the fate of the iodine atoms in the chamber system is unclear.

4. Atmospheric Implications

4.1. FTI Lifetime. The calculated lifetime of 4:2 FTI with respect to photolysis is substantially shorter than that with respect to reaction with OH. We conclude that the atmospheric fate of 4:2 FTI, and by analogy other fluorotelomer iodides, is likely dominated by photolysis. At midlatitudes the atmospheric lifetime of fluorotelomer iodides is approximately a few days in the summer and a few weeks in the winter.

4.2. Oxidation and Photolysis Products. It is of interest to compare the observed products of the photolysis and the Cl atom initiated oxidation of 4:2 FTI (compare Figures 5C and 3C). The fluorotelomer aldehyde $C_4F_9CH_2CHO$ and small amounts of COF_2 and CO were the only observable products of the photolysis of 4:2 FTI. In contrast, $C_4F_9CH_2C(O)OOH$, $C_4F_9CH_2CHO$, $C_4F_9CH_2C(O)OH$, C_4F_9CHO, COF_2, and CO were observed following Cl atom initiated oxidation of 4:2 FTI. As discussed in section 3.5, the fluorotelomer aldehyde $C_4F_9CH_2CHO$ is the expected primary product of the photolysis of 4:2 FTI. The formation of $C_4F_9CH_2CHO$ can be explained by a simple mechanism consisting of reactions 16−19). The relatively low amount of $C_4F_9CH_2CHO$ observed can be attributed to loss via photolysis and possibly via reaction with iodine containing species in the chamber.

In the Cl atom initiated oxidation experiments we observed the formation of $C_4F_9CH_2C(O)OOH$, $C_4F_9CH_2CHO$, $C_4F_9CH_2C(O)OH$, C_4F_9CHO, COF_2, and CO. The simplest qualitative explanation of these products is to propose that, as with $C_4F_9CH_2CH_2OH$, reaction with Cl atoms leads to the formation of the fluorotelomer aldehyde $C_4F_9CH_2CHO$ as the sole primary product which is then oxidized further to give secondary products.[7,34] However, a quantitative analysis shows that this simple explanation is not entirely adequate. By combination of $k(Cl + C_4F_9CH_2CHO) = 1.84 \times 10^{-11}$ [7] with $k(Cl + C_4F_9CH_2CH_2I) = 1.25 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} measured in the present work and by assumption that reaction with Cl converts $C_4F_9CH_2CH_2I$ into $C_4F_9CH_2CHO$ in 100% yield, we can calculate that for the conditions relevant to the experiment shown in Figure 3 with a 32% consumption of $C_4F_9CH_2CH_2I$ the yield of $C_4F_9CH_2CHO$ should be 0.60 mTorr. This is somewhat larger than the observed concentration of 0.44 mTorr suggesting the presence of additional $C_4F_9CH_2CHO$ loss processes (perhaps involving iodine containing species). The large yield of the peracid $C_4F_9CH_2C(O)OOH$ and the fact that this species is formed in a yield substantially (factor of approximately 8) greater than that of the acid $C_4F_9CH_2C(O)OH$ is particularly striking. The large yield of the peracid can not be reconciled with the available data concerning the mechanism of chlorine atom oxidation of $C_4F_9CH_2CHO$.[7,34] This may reflect complexities associated with the presence of reactive iodine atoms or IO radicals in the chlorine atom initiated oxidation of $C_4F_9CH_2CH_2I$ in the smog chamber. The goal of the present work was to improve our understanding of the atmospheric chemistry of $C_4F_9CH_2CH_2I$. Given that we show photolysis dominates the atmosphere fate of $C_4F_9CH_2CH_2I$, experiments to understand the mechanism of Cl atom initiated oxidation were not pursued further.

4.3. Formation of PFCAs. In section 4.1 we concluded that photolysis is the dominant atmospheric loss pathway of FTIs and that the atmospheric lifetime of FTIs is of the order of a few days. The available data for smaller alkyl iodides such as CH_3I,[35,36] C_2H_5I,[37] and C_3H_7I[35] and the results from the present work (section 3.5) indicate that photolysis of FTIs

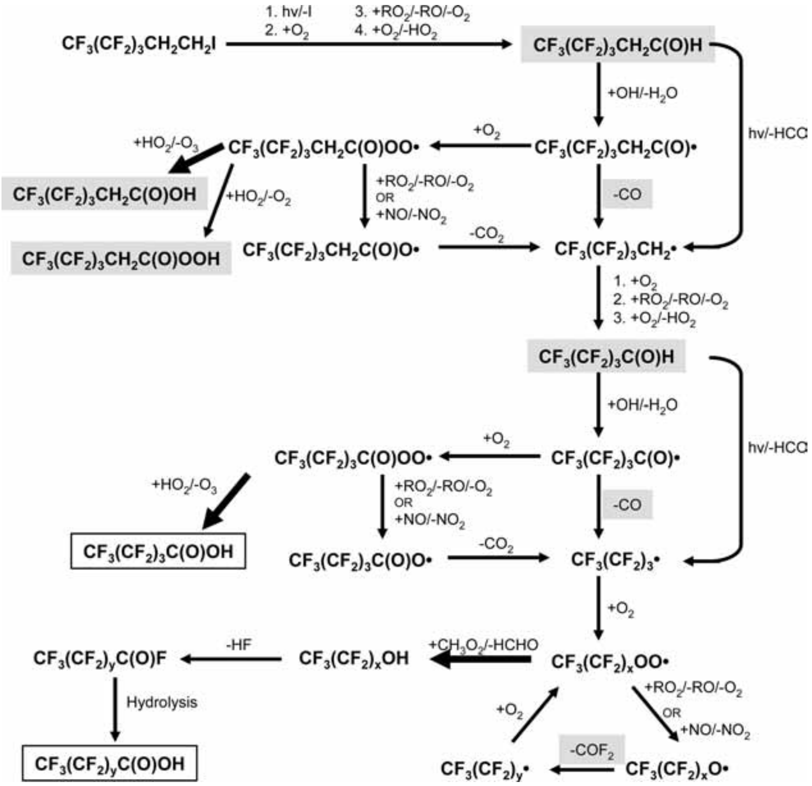

Figure 6. Proposed mechanism for atmospheric oxidation of 4:2 FTI. Shaded compounds were observed in FTIR spectra, compounds in boxes were observed in offline analyses. Subscript "x" represents 0−3, and subscript "y" represents 0−2, where the values will depend on the number of times through the degradation cycle. Thick arrows indicate steps that require a low-NO$_x$ environment (see text for details).

occurs via elimination of the iodine atom leading to the formation of the fluorotelomer aldehyde ($C_xF_{2x+1}CH_2CHO$)

$$C_xF_{2x+1}CH_2CH_2I + h\nu \rightarrow C_xF_{2x+1}CH_2CH_2 + I \quad (20)$$

$$C_xF_{2x+1}CH_2CH_2 + O_2 + M \rightarrow C_xF_{2x+1}CH_2CH_2O_2 + M \quad (21)$$

$$C_xF_{2x+1}CH_2CH_2O_2 + NO \rightarrow C_xF_{2x+1}CH_2CH_2O + NO_2 \quad (22)$$

$$C_xF_{2x+1}CH_2CH_2O + O_2 \rightarrow C_xF_{2x+1}CH_2CHO + HO_2 \quad (23)$$

$C_xF_{2x+1}CH_2CHO$ is removed from the atmosphere via photolysis and reaction with OH. While there are considerable uncertainties (particularly in the value of the photolysis quantum yield) the available data indicate that the lifetime of $C_xF_{2x+1}CH_2CHO$ is approximately 4 days and is determined by its reaction with OH radicals.[31,38] As indicated in the proposed atmospheric degradation mechanism for FTIs in Figure 6, the oxidation of $C_xF_{2x+1}CH_2CHO$ gives the perfluoroaldehyde $C_xF_{2x+1}CHO$. $C_xF_{2x+1}CHO$ has a lifetime of approximately a day with respect to photolysis and approximately 20 days with respect to reaction with OH radicals. As discussed elsewhere[6] and indicated in Figure 6, there are two mechanisms by which the oxidation of $C_xF_{2x+1}CHO$ can lead to the formation of perfluorocarboxylic acids (PFCAs). First, reaction with OH gives $C_xF_{2x+1}CO$ radicals some fraction of which will add O_2 to give $C_xF_{2x+1}C(O)O_2$ radicals which can then react with HO_2 to give PFCAs. Second, photolysis leads directly and reaction with OH leads indirectly to the formation of C_xF_{2x+1} radicals which can add O_2 to give the corresponding peroxy radicals which in low NO$_x$ environments can react with CH_3O_2 radicals to give perfluoroalcohols which via the intermediacy of acyl fluorides are converted into PFCAs.

The approximately 5−10 day time scale over which FTIs are converted into perfluoroaldehydes during the summer months is sufficient to allow transport over long distances (1700−3400 km at the global average wind speed of approximately 4 m s^{-1}). We show here that the atmospheric degradation of FTIs 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 FTIs into the atmosphere are required. Further work is needed to provide such estimates.

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Supporting Information Available: Tabular UV cross-sections and photolysis rate constants by time of year and latitude. This information is available free of charge via the Internet at http://pubs.acs.org.

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