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Atmospheric Chemistry of Fluorinated Alcohols: Reaction with Cl Atoms and OH Radicals and Atmospheric Lifetimes

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Relative rate techniques were used to study the kinetics of the reactions of Cl atoms and OH radicals with a series of fluorinated alcohols, $F(CF_2)_nCH_2OH$ ($n = 1-4$), in 700 Torr of N_2 or air diluent at 296 ± 2 K. The length of the $F(CF_2)_n$ group had no discernible impact on the reactivity of the molecule. For $n = 1-4$, $k(Cl + F(CF_2)_nCH_2OH) = (6.48 \pm 0.53) \times 10^{-13}$ and $k(OH + F(CF_2)_nCH_2OH) = (1.02 \pm 0.10) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Product studies of the chlorine initiated oxidation of $F(CF_2)_nCH_2OH$ ($n = 1-4$) in the absence of NO show the sole primary product to be the corresponding aldehyde, $F(CF_2)_nC(O)H$. Consideration of the likely rates of other possible atmospheric loss mechanisms leads to the conclusion that the atmospheric lifetime of $F(CF_2)_nCH_2OH$ ($n \geq 1$) is determined by reaction with OH radicals and is approximately 164 days.

1. Introduction

The detrimental effects of chlorine chemistry on stratospheric ozone levels are well established.[1,2] As a result, there has been a concerted effort to find replacements for chlorofluorocarbons (CFCs) used previously as electronic equipment cleaners, heat transfer agents, refrigerants, and carrier fluids for lubricant deposition. The replacements for CFCs, hydrofluorocarbons (HFCs) and hydrofluorochlorocarbons (HCFCs), have found widespread industrial use over the past decade. Fluorinated ethers and fluorinated alcohols are new classes of compounds currently under consideration for use as CFC replacements.

In light of the potential widespread use of fluorinated alcohols, detailed information on the environmental impact of this class of compounds is needed. In particular, there is a need to quantify the potential for atmospheric oxidation of fluorinated alcohols to act as a source of perfluorinated carboxylic acids.[3] To improve our knowledge of the atmospheric chemistry of fluorinated alcohols in general and $F(CF_2)_nCH_2OH$ ($n = 1-4$) in particular, these compounds were studied using the smog chamber at the Ford Motor Company. The kinetics and mechanism of their simulated atmospheric oxidation was monitored using Fourier transform infrared (FTIR) spectroscopy. Results are reported herein.

2. Experimental Section

Experiments were performed in a 140-liter Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer.[4] 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

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

OH radicals were produced by the photolysis of CH_3ONO in air

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

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

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

Relative rate techniques were used to measure the rate constant of interest relative to a reference reaction whose rate constant has been established previously. Chlorine atom kinetics were studied by irradiating Cl_2/reactant/reference mixtures in air or N_2 diluent using UV fluorescent blacklamps. The relevant reactions in the system were (1, 5, 6):

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

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

In such experiments Cl atoms are in steady state and the loss of reactant and reference are given by

$$Ln\left(\frac{[\text{reactant}]_{t_0}}{[\text{reactant}]_t}\right) = \frac{k_5}{k_6} Ln\left(\frac{[\text{reference}]_{t_0}}{[\text{reference}]_t}\right) \tag{I}$$

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”, k_5 and k_6 are the rate constants for reactions 5 and 6. Plots

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of $Ln([\text{reactant}]_{t0}/[\text{reactant}]_t)$ versus $Ln([\text{reference}]_{t0}/[\text{reference}]_t)$ should be linear, pass through the origin, and have a slope of k_5/k_6.

The loss of $F(CF_2)_nCH_2OH$ ($n = 1-4$) and the reference compounds were monitored by FTIR spectroscopy using an analyzing path length of 27 m and a resolution of 0.25 cm^{-1}. Infrared spectra were derived from 32 co-added interferograms. The reactants are liquids and were introduced into the chamber by transferring the vapor above the liquid via calibrated volumes. The contents of the calibrated volumes were swept into the chamber with the diluent gas (either air or nitrogen). The concentration of reactants in the chamber was calculated using the vapor pressure measured in the calibrated volumes. Reactant and reference compounds were monitored using absorption features over the following wavenumber ranges (cm^{-1}): $F(CF_2)_nCH_2OH$, 3600−3700; CH_3Cl, 1400−1550; $CH_3OC(O)H$, 1700−1800; and C_2H_2, 650−800. Initial reagent concentrations for the Cl atom relative rate experiments were 9−13 mTorr of $F(CF_2)_nCH_2OH$, 15−30 mTorr of the reference compound CH_3Cl, 8−12 mTorr of the reference compound $CH_3OC(O)H$, and 100−120 mTorr of Cl_2 in 700 Torr of either N_2 or air diluent. In the OH radical experiments, the initial reagent concentrations were 14−53 mTorr of $F(CF_2)_nCH_2OH$, 2−10 mTorr of the reference compound C_2H_2, and 50−100 mTorr of CH_3ONO in 700 Torr of air diluent. All experiments were performed at 296 K. Reagents were obtained from commercial sources at purities of >99% and were subjected to repeated freeze−pump−thaw cycling before use. The fluorinated aldehydes used for references in the product studies were synthesized as described elsewhere[5] and purified by vacuum distillation. In smog chamber experiments, it is important to check for unwanted loss of reactants and products via photolysis, dark chemistry, and heterogeneous reactions. Control experiments were performed in which mixtures of reactants (except Cl_2 or CH_3ONO) in N_2 were subjected to UV irradiation for 15−30 min and product mixtures obtained after the UV irradiation of reactant mixtures were allowed to stand in the dark in the chamber for 15 min. There was no observable loss of reactants or reference compounds suggesting that photolysis, dark chemistry, and heterogeneous reactions are not a significant complication in the present work. Quoted uncertainties are two standard deviations from least squares regressions.

3. Results

3.1. Relative Rate Study of the Reaction of Cl Atoms with $F(CF_2)_nCH_2OH$.

The kinetics of reactions 7 were measured relative to reaction 8 and 9

$$Cl + F(CF_2)_nCH_2OH \rightarrow \text{products} \qquad (7)$$

$$Cl + CH_3Cl \rightarrow \text{products} \qquad (8)$$

$$Cl + CH_3OC(O)H \rightarrow \text{products} \qquad (9)$$

Experiments were performed in which the reactivity of Cl atoms with $F(CF_2)_nCH_2OH$ ($n = 1-4$) was measured relative to the reactivity of CH_3Cl and $CH_3OC(O)H$. Figure 1 shows the loss of $F(CF_2)_nCH_2OH$ versus the reference compounds following UV irradiation of $F(CF_2)_nCH_2OH/Cl_2$/reference mixtures in air (for $n = 2$) or N_2 (for $n = 1$, 3, and 4) diluent. As seen in Figure 1, there was no discernible effect of fluorinated chain length or diluent gas on the kinetic data.

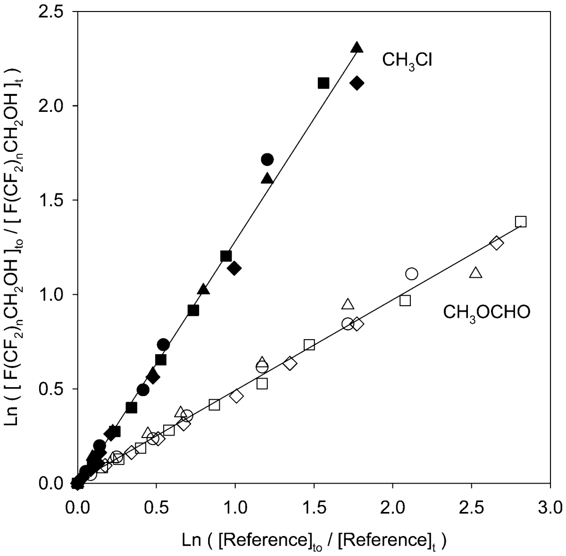

Figure 1. Loss of $F(CF_2)_nCH_2OH$ ($n = 1$, circles; $n = 2$, triangles; $n = 3$, squares; $n = 4$, diamonds) versus CH_3Cl (closed symbols) and CH_3OCHO (open symbols) following UV irradiation of $F(CF_2)_nCH_2OH$/reference/Cl_2 mixtures in 700 Torr of N_2 ($n = 1$, 3, 4) or air ($n = 2$), diluent at 296 K.

The lines through the data in Figure 1 are linear least-squares fits to the combined data sets which give values of $k_7/k_8 = 1.30 \pm 0.05$ and $k_7/k_9 = 0.481 \pm 0.020$. Using $k_8 = 4.8 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} [6] and $k_9 = 1.4 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1},[7] we derive $k_7 = (6.24 \pm 0.24) \times 10^{-13}$ and $(6.73 \pm 0.28) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. Results obtained using the two different reference compounds were, within the experimental uncertainties, indistinguishable. The fact that consistent values of k_7 were derived from experiments using different reference compounds and diluent gas suggests the absence of significant systematic errors in the present work. We choose to cite a final value for k_7 which is the average of the two determinations together with error limits which encompass the extremes of the individual determinations. Hence, $k_7 = (6.48 \pm 0.53) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}.

Papadimitriou et al.[8] used a discharge-flow mass spectrometric technique to determine the $k(Cl + CF_3CH_2OH) = (6.3 \pm 0.9) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 303 K. Kelly and Sidebottom[9] used a relative rate method to measure $k(Cl + CF_3CH_2OH) = (7 \pm 1) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. The result obtained in the present work is indistinguishable, within experimental uncertainties, from those obtained in previous studies.

It is instructive to compare our Cl atom reactivity results with those for ethane, ethanol, and a series of fluorinated ethanols, which is done in Table 1. At ambient temperature the reaction of Cl atoms with CH_3CH_3 proceeds with a rate of $(5.75 \pm 0.46) \times 10^{-11}$ [10] and with CH_3CH_2OH with a rate of $(9.5 \pm 1.9) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.[11] Reaction with CH_3CH_2OH occurs 93% via H-atom abstraction from the CH_2 group[11] demonstrating the activating influence of the OH group. As fluorine is substituted for hydrogen on the methyl group, there is a dramatic decrease in the reactivity of the molecule toward Cl atoms which presumably reflects an increase in strength of the C−H bonds in the CH_2 group. Once the methyl group is fully fluorinated, the addition of CF_2 groups (i.e., C_2F_5 compared to CF_3) has no further effect on reactivity.

The insensitivity of the kinetics of reaction of Cl atoms with $F(CF_2)_nCH_2OH$ to the length of the "fluorinated tail" is consistent with a recent study by Ellis et al.[3] of the reactivity of a series of fluorotelomer alcohols, $F(CF_2CF_2)_nCH_2CH_2OH$ ($n = 2-4$) in which the reactivity of Cl atoms to the

TABLE 1: Rate Constants for the Reaction of Cl Radicals with Ethane, Ethanol and a Series of Fluorinated Ethanols at Ambient Temperature. (rate constants are in units of 10^{-13} cm^3 Molecule^{-1} s^{-1})

	Tyndall et al.[10]	Taatjes et al.[11]	Papadimitriou et al.[8]	Kelly and Sidebottom[9]	this work
CH_3CH_3	575 ± 46				
CH_3CH_2OH		950 ± 190			
CH_2FCH_2OH			196 ± 29	244 ± 25	
CHF_2CH_2OH			29.5 ± 3.9		
CF_3CH_2OH			6.3 ± 0.9	7 ± 1	6.5 ± 0.5
$CF_3CF_2CH_2OH$					6.5 ± 0.5
$CF_3(CF_2)_2CH_2OH$					6.5 ± 0.5
$CF_3(CF_2)_3CH_2OH$					6.5 ± 0.5

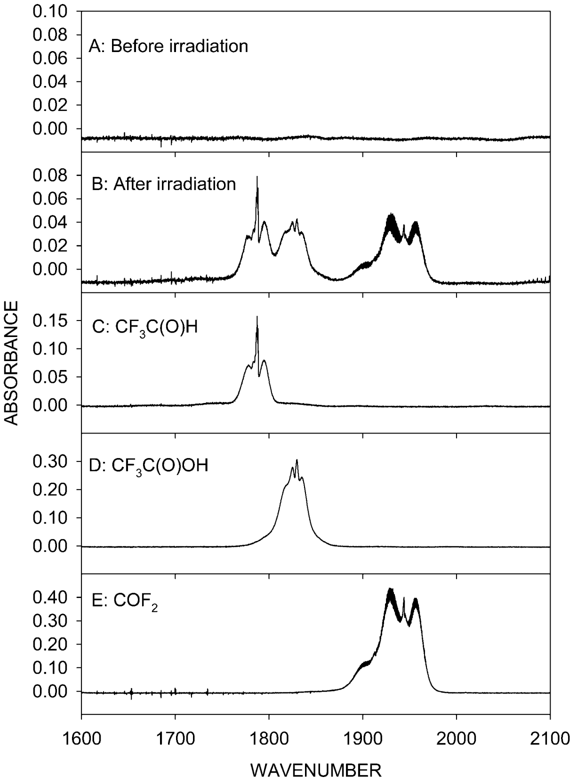

Figure 2. IR spectra obtained before (A) and after (B) 60 s of irradiation of a mixture of 20 mTorr CF_3CH_2OH and 100 mTorr Cl_2 in 700 Torr air. The consumption of CF_3CH_2OH was 41%. Panels C, D, and E are reference spectra of $CF_3C(O)H$, $CF_3C(O)OH$, and COF_2, respectively.

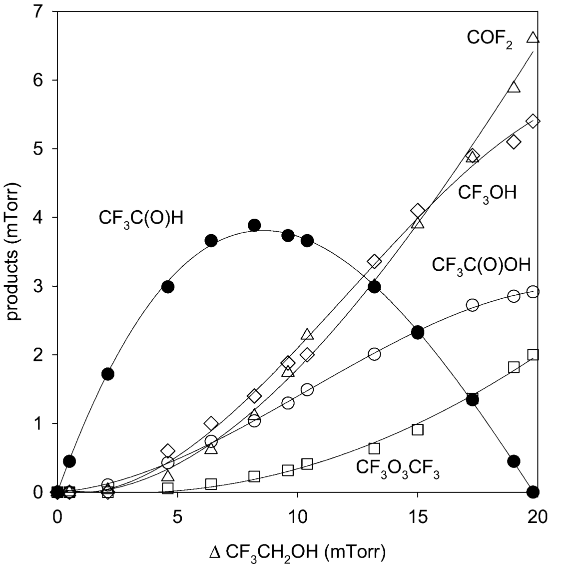

Figure 3. Products versus loss of CF_3CH_2OH for successive irradiations of a mixture of 20 mTorr CF_3CH_2OH and 100 mTorr Cl_2 in air. The products observed are $CF_3C(O)H$ (closed circles), $CF_3C(O)OH$ (open circles), COF_2 (open triangles), CF_3OH (open diamonds), and $CF_3O_3CF_3$ (open squares). Lines are included as a guide to the eye.

fluorotelomer alcohols was found to be $k(Cl + F(CF_2CF_2)_n CH_2CH_2OH) = (1.61 \pm 0.49) \times 10^{-11}$ cm^3 molec^{-1} s^{-1} for $n = 2, 3, 4$.

3.2. Product Study of the Cl + $F(CF_2)_nCH_2OH$ Reaction in 700 Torr of Air.

The Cl atom initiated oxidation of $F(CF_2)_nCH_2OH$ ($n = 1-4$) was investigated by irradiating mixtures containing 10−20 mTorr $F(CF_2)_nCH_2OH$ and 100 mTorr Cl_2 in 700 Torr of air diluent. Figure 2 shows spectra acquired before (A) and after (B) 60 s of irradiation of 20 mTorr CF_3CH_2OH and 100 mTorr Cl_2 in 700 Torr of air. Consumption of CF_3CH_2OH was 41% during irradiation. The IR features in panel B can be compared with the IR spectra of $CF_3C(O)H$, CF_3COOH, and COF_2 shown in panels C, D, and E, respectively. Product features due to CF_3OH and $CF_3O_3CF_3$ were also observed. For the irradiation of mixtures containing $F(CF_2)_nCH_2OH$ ($n = 2-4$), in addition to the trioxide $CF_3O_3CF_3$, there are residual features which are similar to those of $CF_3O_3CF_3$ and consistent with the mixed trioxides $F(CF_2)_xO_3(CF_2)_yF$ ($x = 1-4$, $y = 1-4$).

Figure 3 shows the observed formation of $CF_3C(O)H$, CF_3COOH, COF_2, CF_3OH, and $CF_3O_3CF_3$ versus the loss of CF_3CH_2OH following successive irradiations of the mixture described above. The product profiles shown in Figure 3 are consistent with $CF_3C(O)H$ being the main primary product and CF_3COOH, COF_2, CF_3OH, and $CF_3O_3CF_3$ being secondary products formed from the reaction of $CF_3C(O)H$ with Cl in air

$$Cl + CF_3CH_2OH \rightarrow CF_3CHOH + HCl \tag{10}$$

$$CF_3CHOH + O_2 \rightarrow \alpha\, CF_3C(O)H + HO_2 \tag{11}$$

$$Cl + CF_3C(O)H \rightarrow \text{products} \tag{12}$$

The concentration profile of a reactive primary product can be described[12] by the expression

$$\frac{[CF_3C(O)H]_t}{[CF_3CH_2OH]_{t_0}} = \left\{\frac{\alpha}{(1-(k_{12}/k_{10}))}\right\}(1-x)\{(1-x)^{(k_{12}/k_{10})-1}-1\} \tag{II}$$

where $x = 1 - ([CF_3CH_2OH]_t/[CF_3CH_2OH]_{t_0})$ (the fractional consumption of CF_3CH_2OH at time t) and α is the yield of $CF_3C(O)H$ from the reaction of Cl with CF_3CH_2OH in the presence of oxygen. Figure 4 shows a plot of $[CF_3C(O)H]_t/[CF_3CH_2OH]_{t_0}$ versus $\Delta[CF_3CH_2OH]_t/[CF_3CH_2OH]_{t_0}$ for two experiments. A fit of eq II to the data in Figure 4 gives $\alpha = 0.97 \pm 0.03$ and $k_{12}/k_{10} = 2.92 \pm 0.15$. Using the value for k_{10} determined in this study, $(6.48 \pm 0.53) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, gives $k_{12} = (1.90 \pm 0.25) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

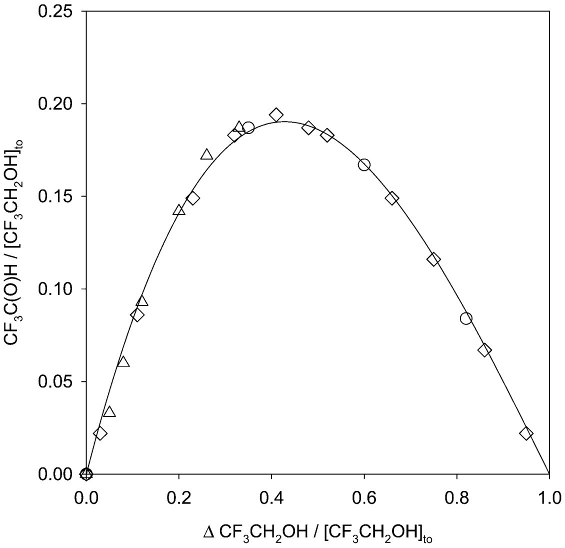

Figure 4. Plot of the observed concentration of $CF_3C(O)H$ normalized to the initial CF_3CH_2OH concentration versus the fractional loss of CF_3CH_2OH following the irradiation of either 10 (triangles), 11.6 (circles), or 20 mTorr (diamonds) CF_3CH_2OH and 100 mTorr Cl_2 in 700 Torr air. The line is a fit of equation II to the data. See text for details.

TABLE 2: Results of Fitting Equation II to the $F(CF_2)_nCH_2OH$ Primary Product Data

	$F(CF_2)_nC(O)H$ yield	k_{12}/k_{10}	$k(Cl + F(CF_2)_nC(O)H)$ cm^3 $molecule^{-1}$ s^{-1}
CF_3CH_2OH	0.97 ± 0.03	2.92 ± 0.15	$1.90 \pm 0.25 \times 10^{-12}$
$CF_3CF_2CH_2OH$	1.01 ± 0.08	3.60 ± 0.36	$2.35 \pm 0.42 \times 10^{-12}$
$CF_3(CF_2)_2CH_2OH$	1.01 ± 0.05	3.94 ± 0.22	$2.56 \pm 0.35 \times 10^{-12}$
$CF_3(CF_2)_3CH_2OH$	1.02 ± 0.04	3.82 ± 0.17	$2.48 \pm 0.31 \times 10^{-12}$

Experiments with $F(CF_2)_nCH_2OH$ ($n = 2-4$) gave similar results, which are summarized in Table 2. Again, within experimental error, the reactivity of Cl toward the fluorinated aldehydes are indistinguishable, and we chose to cite a final value which is the average of individual values with error limits which encompass the extremes of the individual measurements, $k(Cl + F(CF_2)_nC(O)H) = (2.3 \pm 0.7) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}.

There are three previous measurements of the reactivity of Cl toward perfluorinated aldehydes. Wallington et al.[13] used a relative rate technique to determine $k(Cl + CF_3C(O)H) = (1.79 \pm 0.4) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, whereas Scollard et al.,[14] also using relative rate techniques, determined $k(Cl + CF_3C(O)H) = (2.71 \pm 0.11) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. In a recent paper, Andersen et al.[5] used relative rate techniques to determine $k(Cl + CF_3CF_2C(O)H) = (1.97 \pm 0.28) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. The studies of Wallington et al.[13] and Andersen et al.[5] were conducted in the absence of O_2, whereas as discussed elsewhere,[13] that of Scollard et al.[14] *may* have been conducted in the presence of O_2. The presence of O_2 is an important consideration as it will lead to the formation of CF_3O radicals which are likely to react with the fluorinated aldehyde. Hence, to the extent that CF_3O radical chemistry contributes to the loss of $F(CF_2)_nC(O)H$, relative rate experiments conducted in the presence of O_2 will probably overestimate $k(Cl + F(CF_2)_nC(O)H)$. Accordingly, the values given in Table 2 should be considered upper limits for $k(Cl + F(CF_2)_nC(O)H)$. Finally, in light of the fact that the values of $k(Cl + F(CF_2)_nC(O)H)$ for $n = 1$ and 2 in Table 2 are indistinguishable from those of Wallington et al.[13] and Andersen et al.[5] obtained in N_2 diluent, it seems likely that the magnitude of the any unwanted CF_3O chemistry is modest.

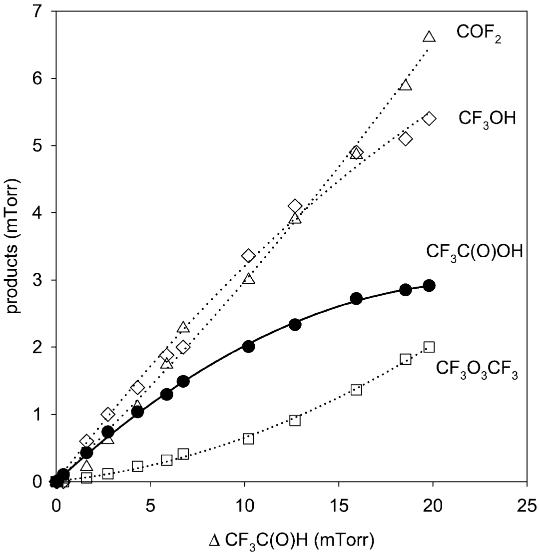

Figure 5. Product formation versus $CF_3C(O)H$ loss during successive irradiations of a mixture of 20 mTorr CF_3CH_2OH and 100 mTorr Cl_2 in air. The products observed are $CF_3C(O)OH$ (closed circles), COF_2 (open triangles), CF_3OH (open diamonds), and $CF_3O_3CF_3$ (open squares). The solid line is a second-order polynomial fit to the $CF_3C(O)OH$ profile. The initial $CF_3C(O)OH$ yield is 0.26 ± 0.01. The broken lines are included as a guide to the eye.

In all cases, the aldehyde, $F(CF_2)_nC(O)H$, was the sole primary product of the reaction of $F(CF_2)CH_2OH$ with Cl in air. $F(CF_2)_nCOOH$, COF_2, CF_3OH, and $CF_3O_3CF_3$ were observed as secondary products. Since the aldehyde is formed in 100% yield, the amount of aldehyde that has reacted in the system can be equated to the difference between the observed loss of alcohol and the observed formation of aldehyde

$$\Delta F(CF_2)_nC(O)H = \Delta F(CF_2)_nCH_2OH - F(CF_2)_nC(O)H \qquad \text{(III)}$$

Hence, the formation of the secondary products can be plotted versus the loss of the aldehyde. This plot is shown in Figure 5 for $CF_3C(O)H$. The product profile of CF_3COOH is curved with an initial yield of 0.25 ± 0.02. The other observed products, COF_2, CF_3OH, and $CF_3O_3CF_3$, are those expected from decomposition. Plots of $F(CF_2)_nCOOH$ versus $\Delta F(CF_2)_nC(O)H$ ($n = 2-4$) give $F(CF_2)_nCOOH$ yields of 0.18 ± 0.01, 0.07 ± 0.01, and 0.06 ± 0.01 for $n = 2-4$, respectively. Andersen et al.[15] have studied the reaction of $CF_3CF_2C(O)O_2$ with HO_2 and report formation of $CF_3CF_2C(O)OH$ in a yield of 24 ± 2%. The slightly lower $CF_3CF_2C(O)OH$ yield is probably attributable to lower HO_2 concentrations in the present study and the fact that reaction with HO_2 is not likely to be the sole fate of $CF_3CF_2C(O)O_2$ radicals. The reason for the curved $F(CF_2)_nCOOH$ profiles is unclear. It is unlikely that the curvature is due to reaction of the acids with Cl, considering that Andersen et al.[15] established an upper limit for the rate constant of Cl atoms with $CF_3CF_2C(O)OH$, $k(Cl + CF_3CF_2C(O)OH) < 1 \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1}. Curvature is more likely to be caused by a decrease of the HO_2 radical concentration during the period of the experiment.

The observed products from the Cl initiated oxidation of CF_3CH_2OH are consistent with the following reactions. Reaction of $F(CF_2)_nCH_2OH$ ($n = 1-4$) is initiated by the abstraction of hydrogen, followed by reaction with oxygen, leading to formation of the aldehyde, $F(CF_2)_nC(O)H$

$$F(CF_2)_nCH_2OH + Cl \rightarrow F(CF_2)_nCHOH + HCl \quad (13)$$

$$F(CF_2)_nCHOH + O_2 \rightarrow F(CF_2)_nC(O)H + HO_2 \quad (14)$$

Cl then abstracts the aldehydic hydrogen from $F(CF_2)_nC(O)H$, which reacts with oxygen to form the peroxy radical, $F(CF_2)_n$-$C(O)O_2$

$$F(CF_2)_nC(O)H + Cl \rightarrow F(CF_2)_nC(O) + HCl \quad (15)$$

$$F(CF_2)_nC(O) + O_2 \rightarrow F(CF_2)_nC(O)O_2 \quad (16)$$

The peroxy radical reacts with HO_2 to form the perfluorinated carboxylic acid and ozone. HO_2 radicals can react with other HO_2 radicals, whereas the alkyl peroxy radical can react with other peroxy radicals to form the alkoxy radical

$$F(CF_2)_nC(O)O_2 + HO_2 \rightarrow F(CF_2)_nC(O)OH + O_3 \quad (17)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \quad (18)$$

$$F(CF_2)_nC(O)O_2 + RO_2 \rightarrow F(CF_2)_nC(O)O + RO + O_2 \quad (19)$$

Reaction 19 leads to decomposition of $F(CF_2)_nC(O)O$, first through the elimination of CO_2 followed by reaction with oxygen to form the peroxy radical, $F(CF_2)_nO_2$

$$F(CF_2)_nC(O)O \rightarrow F(CF_2)_n + CO_2 \quad (20)$$

$$F(CF_2)_n + O_2 \rightarrow F(CF_2)_nO_2 \quad (21)$$

Reaction of $F(CF_2)_nO_2$ with other peroxy radicals leads to the formation of alkoxy radicals, $F(CF_2)_nO$, which are known to eliminate COF_2

$$F(CF_2)_nO_2 + RO_2 \rightarrow F(CF_2)_nO + RO + O_2 \quad (22)$$

$$F(CF_2)_nO \rightarrow F(CF_2)_{n-1} + COF_2 \ (n > 1) \quad (23)$$

Repetition of reactions 21, 22, and 23 results in the unzipping of the radical and the formation of $n - 1$ molecules of COF_2 for $F(CF_2)_nCH_2OH$ ($n = 1-4$). The last radical formed, CF_3O, reacts with CF_3O_2 to form the trioxide, $CF_3O_3CF_3$, or abstracts a H-atom from a hydrogen containing molecule (e.g., $F(CF_2)_n$-$C(O)H$, H_2O_2, HCl) or radical (e.g., HO_2) in the system

$$CF_3O + HO_2 \rightarrow CF_3OH + O_2 \quad (24)$$

Another fate of alkoxy and peroxy radicals formed in reactions 18−20 is reaction to form trioxides

$$F(CF_2)_nOO + F(CF_2)_nO \rightarrow F(CF_2)_nO_3(CF_2)_nF \quad (25)$$

$CF_3O_3CF_3$ was an observed product. Small unidentified residual IR features were present in the product spectra. The residual spectra were similar to $CF_3O_3CF_3$ and indicate the presence of higher trioxides.

3.3. Relative Rate Study of the Reaction of OH Radicals with $F(CF_2)_nCH_2OH$. The reactivity of OH radicals toward $F(CF_2)_nCH_2OH$ ($n = 1,2,3,4$) was studied relative to reaction 24

$$OH + F(CF_2)_nCH_2OH \rightarrow \text{products} \quad (26)$$

$$OH + C_2H_2 \rightarrow \text{products} \quad (27)$$

Figure 6 shows the loss of $F(CF_2)_nCH_2OH$ versus the loss of the reference compound, C_2H_2, on exposure to OH radicals. It can be seen from Figure 6 that there is no discernible difference in the reactivity of $F(CF_2)_nCH_2OH$ ($n = 1-4$) relative to the reference. The line through the data in Figure 6 is a linear least-squares fit to the combined data sets which gives $k_{26}/k_{27} = 0.12 \pm 0.01$. Using $k_{27} = 8.5 \times 10^{-13}$,[16] we derive $k_{26} = (1.02 \pm 0.10) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

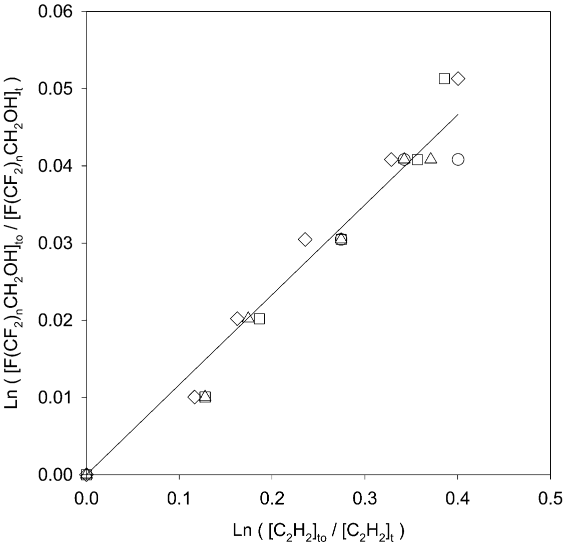

Figure 6. Loss of $F(CF_2)_nCH_2OH$ ($n = 1$, circles; $n = 2$, triangles; $n = 3$, squares; $n = 4$, diamonds) versus the reference compound, C_2H_2, following UV irradiation of $F(CF_2)_nCH_2OH$/reference/CH_3ONO mixtures in 700 Torr air diluent at 296 K.

The reactivity of OH toward CF_3CH_2OH has been measured previously. Wallington et al.[17] used a flash photolysis technique to measure the absolute rate constant and reported $k(OH + CF_3CH_2OH) = (9.55 \pm 0.66) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. Tokuhashi et al.[18] used absolute rate techniques and reported $k(OH + CF_3CH_2OH) = (1.00 \pm 0.04) \times 10^{-13}$ and $k(OH + CF_3CF_2CH_2OH) = (1.02 \pm 0.04) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Chen et al.[19] used the relative rate technique and derived $k(OH + CF_3CF_2CH_2OH) = (1.15 \pm 0.08) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. There is excellent consistency in the kinetic database for reaction of OH radicals with alcohols of the general formula $F(CF_2)_nCH_2OH$. It is clear that there is no effect of fluorinated chain length on the reactivity of these molecules and that $k(OH + F(CF_2)_nCH_2OH) \approx 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

4. Atmospheric Implications

The value of $k(OH + F(CF_2)_nCH_2OH)$ ($n = 1-4$) measured here can be used to provide an estimate of the atmospheric lifetime of $F(CF_2)_nCH_2OH$ with respect to reaction with OH radicals by scaling to CH_3CCl_3. The optimal temperature for such a scaling analysis is 272 K[20] rather than 296 K used here. The Arrhenius rate constant of CH_3CCl_3 has been determined to be $k(OH + CH_3CCl_3) = 1.6 \times 10^{-12} \exp(-1520/T)$.[6] Although we do not have kinetic data for k_{26} at 272 K, it is reasonable to assume a temperature dependence similar to CF_3-CF_2CH_2OH. Tokuhashi et al.[18] determined the Arrhenius rate constant of $CF_3CF_2CH_2OH$ to be $k(OH + CF_3CF_2CH_2OH) = (1.40 \pm 0.27) \times 10^{-12} \exp[-(780 \pm 60)/T]$. Using these two Arrhenius expressions, the rate constants at 272 K are calculated to be $k(OH + CH_3CCl_3) = 6.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} and $k(OH + F(CF_2)_nCH_2OH) = 8.0 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. Assuming an atmospheric lifetime for CH_3CCl_3 with respect to reaction with OH radicals of 5.99 years[21] leads to an estimate of the atmospheric lifetime of $F(CF_2)_nCH_2OH$ ($n = 1-4$) of

TABLE 3: Physicochemical Properties of $F(CF_2)_2CH_2OH$ Used in EQC Level III Calculations

molar mass (g/mol)	Henry's law constant, K_h (Pa m^3/mol)	water solubility[a] (g/m^3)	vapor pressure (Pa)	log K_{OW}[b]	melting point (°C)	half-life τ_{OH} (h)
150	7.2	98 000	4700	2.6	−56	1900

[a] Calculated water solubility from K_H and V_p. [b] K_{ow} for $F(CF_2)_2CH_2OH$ assumed to be similar order of magnitude as $F(CF_2)_3CH_2OH$.

TABLE 4: Half-Times for Partition between Environmental Phases

partition	half-time (days)
air to water	73.9
air to soil	556
water to air	51.3
water to sediments	4640
soil to air	359
soil to water	486

$(6.0 \times 10^{-15})/(8.0 \times 10^{-14}) \times 5.99 \times 365 = 164$ days. The approximate nature of the atmospheric lifetime estimate provided here should be stressed. The average daily concentration of OH radicals in the atmosphere varies significantly with both location and season.[22] The estimates presented here are for the global average lifetime with respect to reaction with OH radicals.

The calculated behavior of a chemical in a model environment provides a basis for evaluating its environmental fate. The equilibrium criterion or EQC model[23] is a widely used evaluative model that treats an area of 10^5 km^2 with 10% of the area being covered by water. This model has been used for the evaluation of the environmental dissemination of fluorinated aromatics.[24] The temperature in the EQC environment is set at 25 °C, which is a common temperature at which physicochemical properties are measured. An evaluation of the atmospheric fate of $F(CF_2)_2CH_2OH$ was conducted using this model. The EQC level III model allows nonequilibrium conditions to exist between connected media at steady state. The output data is useful in determining how the media of release affects environmental fate and can also identify important transformation and interphase partition processes.[25] The model requires the input of key physicochemical data for the fluorinated alcohol, which are given in Table 3. For $F(CF_2)_2CH_2OH$, the required physicochemical data appears in the literature,[26−28] limiting the necessity for assumptions concerning these to be made. The atmospheric fate of the alcohol has been assessed solely through direct input into that compartment.

The half-life ($t_{1/2}$) of a chemical, which is defined as the time required for the concentration of a reactant to fall to one-half of its initial concentration, is a required parameter of this model. The half-life of the fluorinated alcohols is given by the following equation:

$$t_{1/2} = \frac{0.693}{k(\mathrm{OH} + \mathrm{F(CF_2)_2CH_2OH})[\mathrm{OH}]} = 1887\ \mathrm{h}$$

where $k(\mathrm{OH} + \mathrm{F(CF_2)_2CH_2OH}) = 1.02 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} and $[\mathrm{OH}] = 1 \times 10^6$ cm^{-3}. Due to the relatively long half-life of this alcohol from reaction with OH ($t_{1/2} = 1887$ h) and taken in conjunction with the K_H of the alcohol (7.24 Pa m^3/mol), interphase partition phenomena, particularly air−water partitioning ($t_{1/2} = 1773$ h), is comparable in importance with OH kinetics. The model indicates that the overall distribution of $F(CF_2)_2CH_2OH$ due to this process would be 74.6%:25.4% (air:water ratio). The model indicates that partitioning from water to sediment is expected to be an insignificant process.

The calculated half-times for partitioning between environmental compartments are given in Table 4. Within the atmosphere, loss processes such as partition to aerosols (1.55×10^{-6} %), dry deposition (10 m/h), and rainout (1×10^{-4} m/h) are insignificant processes compared with OH reaction and direct air−water partition.

It is worth noting that as the fluorocarbon chain length increases for the alcohols the air−water partition is expected to decrease, and hence, OH kinetics will start to govern, as was found to be the case for fluorotelomer alcohols.[3] Furthermore, in geographic locations with little or no bodies of water, OH reactions will completely predominate.

Loss of $F(CF_2)_nCH_2OH$ $n > 4$ via wet deposition, dry deposition, photolysis, or reaction with atmospheric constituents other than OH is expected to be of minor importance. The atmospheric lifetime of $F(CF_2)_nCH_2OH$ is determined by reaction with OH radicals and is approximately 164 days. As discussed above, the atmospheric oxidation of $F(CF_2)_nCH_2OH$ gives small, but significant yields of perfluorocarboxylic acids, $F(CF_2)_nC(O)OH$. In light of the toxic[29] and bioacculumative[30−32] nature of long ($>C_6$) chain perfluorocarboxylic acids, further studies of the atmospheric chemistry and environmental impact of long ($>C_6$) chain $F(CF_2)_nCH_2OH$ are needed prior to any large scale industrial use.

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References and Notes

(1) Molina, M. J.; Rowland, F. S. *Nature* **1974**, *249*, 810.

(2) Farman, J. D.; Gardiner, B. G.; Shanklin, J. D. *Nature* **1985**, *315*, 207.

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

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

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

(6) Sander, S. P.; Friedl, R. R.; Golden, D. M.; Kurylo, M. J.; Huie, R. E.; Orkin, V. L.; Moortgat, G. K.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J.; Finlayson-Pitts, B. J. *JPL Publication No. 02−25;* NASA Jet Propulsion Lab.: Pasadena, California, 2003.

(7) Wallington, T. J.; Hurley, M. D.; Ball, J. C.; Jenkin, M. E. *Chem. Phys. Lett.* **1993**, *211*, 41.

(8) Papadimitriou, V. C.; Prosmitis, A. V.; Lararou, Y. G.; Papagiannakopoulos, P. *J. Phys. Chem. A* **2003**, *107*, 3733.

(9) Kelly, T.; Sidebottom, H. A kinetic and mechanistic study of the atmospheric oxidation of 3,3,3-trifluoropropanol. PosterCMD-2; Presented at the Eurotrac 2 Symposium, Garmisch-Partenkirchen, March 2002 (http://imk-aida.fzk.de/CMD/AR2001/GPP18_4.pdf).

(10) Tyndall, G. S.; Orlando, J. J.; Wallington, T. J.; Dill, M.; Kaiser, E. W. *Int. J. Chem. Kinet.* **1997**, *29*, 43.

(11) Taatjes, C. A.; Christensen, L. K.; Hurley, M. D.; Wallington, T. J. *J. Phys. Chem. A* **1999**, *103*, 9805.

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

(13) Wallington, T. J.; Hurley, M. D. *Int. J. Chem. Kinet.* **1993**, *25*, 819.

(14) Scollard, D. J.; Treacy, J. J.; Sidebottom, H. W.; Balestra-Garcia, C.; Laverdet, G.; LeBras, G.; MacLeod, H.; Teton, S. *J. Phys. Chem.* **1993**, *97*, 4683.

(15) Sulbaek Andersen, M. P.; Hurley, M. D.; Wallington, T. J.; Ball, J. C.; Martin, J. W.; Ellis, D. A.; Mabury, S. A. *Chem. Phys. Lett.* **2003**, *381*, 14.

(16) Sorensen, M.; Kaiser, E. W.; Hurley, M. D.; Wallington, T. J.; Nielsen, O. J. *Int. J. Chem Kinet.* **2003**, *35*, 191.

(17) Wallington, T. J.; Dagaut, P.; Kurylo, M. J. *J. Phys. Chem.* **1988**, *92*, 5024.

(18) Tokuhashi, K.; Nagai, H.; Takahashi, A.; Kaise, M.; Kondo, S.; Sekiya, A.; Takahashi, M.; Gotoh, Y.; Suga, A. *J. Phys. Chem. A* **1999**, *103*, 2664.

(19) Chen, L.; Fukuda, K.; Takenaka, N.; Bandow, H.; Maeda, Y. *Int J. Chem. Kinet.* **2000**, *32*, 73.

(20) Spivakovsky, C. M.; Logan, J. A.; Montzka, S. A.; Balkanski, Y. L.; Foreman-Fowler, M.; Jones, D. B. A.; Horowitz, L. W.; Fusco, A. C.; Brenninkmeijer, C. A. M.; Prather, M. J.; Wofsy, S. C.; McElroy, M. B. *J. Geophys. Res.* **2000**, *105*, 8931.

(21) Prinn, R. G.; Huang, J.; Weiss, R. F.; Cunnold, D. M.; Fraser, P. J.; Simmonds, P. G.; McCulloch, A.; Harth, C.; Salameh, P.; O'Doherty, S.; Wang, R. H. J.; Porter, L.; Miller B. R. *Science* **2001**, *292*, 1882.

(22) Klecrnka, G.; Boethling, R.; Franklin, J.; Grady, L.; Howard, P. H.; Kannan, K.; Larson, R. J.; Mackay, D.; Muir, D.; van de Meent, D. *Evaluation of Persistence and Long-Range Transport of Organic Chemicals in the Environment*; SETAC Press: Pensacola, FL, 2000; p 45, ISBN 1-880611-22-8.

(23) Mackay, D.; Di Guardo, A.; Paterson, S.; Cowan, C. *Environ. Toxicol. Chem.* **1996**, *15*, 1627.

(24) Ellis, D. A.; Cahill, T. M.; Mabury S. A.; Cousins, I.; MacKay, D. Partitioning of Organofluorine Compounds in the Environment. In *The Handbook of Environmental Chemistry*; Neilson, A., Ed.; 2002; Vol 3, Part N, pp 63−83.

(25) Mackay, D. *Multimedia Environmental Models: The Fugacity Approach*, 2nd ed.; Lewis Publishers: Boca Raton, FL, 2001.

(26) Chen, L.; Takenaka, N.; Bandow, H.; Maeda, Y. *Atmos. Environ*. **2003**, *37*, 4817.

(27) Oman, C. *Environ. Sci. Technol.* **2001**, *35*, 232.

(28) Meeks, A. C.; Goldfarb, I. J. *J. Chem. Eng. Data* **1967**, *12*, 196.

(29) USEPA. *Preliminary Risk Assessment of the Developmental Toxicity Associated with Exposure to Perfluorooctanoic Acid (PFOA) and its Salts*; OPPT, Risk Assessment Division: Washington, DC, 2003.

(30) Moody, C. A.; Martin, J. W.; Kwan, W. C.; Muir, D. C. G.; Mabury, S. A.; *Environ. Sci. Technol.* **2002**, *36*, 545.

(31) Moody, C. A.; Kwan, W. C.; Martin, J. W.; Muir, D. C. G.; Mabury, S. A. *Anal. Chem.* **2001**, *73*, 2200.

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