

Atmospheric Lifetime of Fluorotelomer Alcohols

D. A. ELLIS, J. W. MARTIN, AND
S. A. MABURY

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

M. D. HURLEY,
M. P. SULBAEK ANDERSEN, AND
T. J. WALLINGTON*

Ford Motor Company, SRL-3083, P.O. Box 2053,
Dearborn, Michigan 48121-2053

Relative rate techniques were used to study the kinetics of the reactions of Cl atoms and OH radicals with a series of fluorotelomer alcohols, $F(CF_2CF_2)_nCH_2CH_2OH$ ($n = 2, 3, 4$), in 700 Torr of N_2 or air, diluent at 296 ± 2 K. The length of the $F(CF_2CF_2)_n$ group had no discernible impact on the reactivity of the molecule. For $n = 2, 3$, or 4 , $k(Cl + F(CF_2CF_2)_nCH_2CH_2OH) = (1.61 \pm 0.49) \times 10^{-11}$ and $k(OH + F(CF_2CF_2)_nCH_2CH_2OH) = (1.07 \pm 0.22) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Consideration of the likely rates of other possible atmospheric loss mechanisms leads to the conclusion that the atmospheric lifetime of $F(CF_2CF_2)_nCH_2CH_2OH$ ($n \geq 2$) is determined by reaction with OH radicals and is approximately 20 d.

Introduction

Perfluorooctane sulfonate (PFOS) is a globally distributed, persistent, and bioaccumulative (1, 2) contaminant readily found in human blood and the tissues of many different species of marine animals and birds (3–5). Similarly, long-chain perfluoroalkyl carboxylates (PFCAs with notation $(CF_3(CF_2)_xCOOH$ where $x = 6–12$) have recently been observed in fish (6, 7) and mammals (8). Neither PFOS nor the longer chain PFCAs have generally been used directly in consumer or industrial materials other than in aqueous film-forming foams (AFFF) or as polymerization aids in fluoropolymer manufacture (9) and presumably are degradation products of precursor chemicals. The most likely precursors to PFOS are the electrochemically produced polyfluorinated sulfonamidoethanols that were widely used to covalently incorporate the PFOS backbone into polymeric materials (10) and have been identified in recent air sampling campaigns (11, 12). Concern over possible ecological and human health impacts associated with PFOS has led to the phase out of this compound and related chemistries in industrial processes and products. The source for the PFCAs observed is currently not known, although a potential source would include the polyfluorinated alcohols.

The fluorotelomer alcohols (FTOHs) are linear chain polyfluorinated alcohols that are used in analogous applications as the sulfonamidoethanols where the ethanol moiety serves as the means to link the perfluorinated alkyl "tail" to various polymers. Fluorotelomer alcohols are currently used as intermediates in the manufacture of a diverse number of products that have a multitude of uses, including graphic

arts, paints, coatings, polymers, adhesives, waxes, polishes, metals, electronics, and caulks (10). The worldwide production (2000–2002) has been estimated at $5 \times 10^6 \text{ kg yr}^{-1}$, of which 40% is produced in North America. It is estimated that 80% of FTOHs are incorporated into polymeric materials with the remaining 20% used in nonpolymeric applications (13). The generic structure of the FTOHs used in the current study is $F(CF_2CF_2)_nCH_2CH_2OH$ ($n = 2–4$). Fluorotelomer alcohols (FTOHs) are named according to the number of fluorinated carbons within the chain as compared with the number of hydrogenated carbon atoms (e.g., 4:2 FTOH = $F(CF_2CF_2)_2CH_2CH_2OH$). As a result of the telomerization manufacturing process, the fluoroalkyl chains tend to have even-numbered carbon chain lengths (e.g., $C_4, C_6, \dots, C_{16}$). 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH have been measured in the troposphere in two recent studies. Martin et al. reported tropospheric concentrations in the range of $17–87 \text{ pg m}^{-3}$ (11). Stock et al. observed levels up to 135 pg m^{-3} (12). The mechanism by which FTOHs gain entry into the environment is unknown at present. It has been speculated that release into the atmosphere occurs following biotic and/or abiotic degradation of polymer and nonpolymeric materials that incorporate FTOHs. Alternatively, release into the atmosphere may occur due to the presence of residual amounts of the fluorotelomer alcohol that was not covalently linked to the polymer.

Fluorotelomer alcohols have low water solubility and high vapor pressure and are expected to partition into the atmosphere following release to the environment (14). In light of their substantial industrial use, FTOHs would be expected to be observed in the atmospheric gas phase. Environmental monitoring studies (11, 12) indicate that the compounds are indeed widely disseminated in the troposphere with higher concentrations at urban sites relative to rural areas.

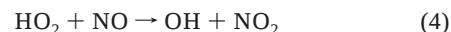
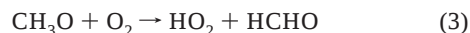
An assessment of the environmental impact of FTOHs requires information concerning their atmospheric persistence and degradation products. Although the atmospheric rate constant for the reaction of OH with primary alcohols is relatively well-established, there does not appear to be any information regarding the effect of a $-(CF_2CF_2)_nF$ group on the reactivity of OH radicals. The goal of the present investigation was to determine the reactivity of OH and Cl toward a series of FTOHs, estimate the atmospheric lifetime of FTOHs, and provide insight into the likely environmental fate of these fluorotelomer alcohols.

Experimental Section

Experiments were performed in a 140-L Pyrex reactor interfaced to a Mattson Sirius 100 FTIR spectrometer (15). 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:



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



Relative rate techniques were used to measure the rate constant of interest relative to a reference reaction whose rate constant has been established previously. To study OH

* Corresponding author phone: (313)390-5574; fax: (313)594-2923; e-mail: twalling@ford.com.

radical kinetics, CH₃ONO/NO/reactant/reference/air mixtures were irradiated using the UV fluorescent blacklamps. The relevant reactions in the system were (eqs 2–6):



In such experiments, the loss of reactant and reference are given by

$$-\frac{d[\text{reactant}]}{dt} = k_5[\text{OH}][\text{reactant}]$$

$$-\frac{d[\text{reference}]}{dt} = k_6[\text{OH}][\text{reference}]$$

Integration gives

$$\ln\left(\frac{[\text{reactant}]_{t_0}}{[\text{reactant}]_t}\right) = k_5[\text{OH}]_t \quad \ln\left(\frac{[\text{reference}]_{t_0}}{[\text{reference}]_t}\right) = k_6[\text{OH}]_t$$

where [reactant]_{t₀}, [reactant]_t, [reference]_{t₀}, and [reference]_t are the concentrations of reactant and reference at times t₀ and t; k₅ and k₆ are the rate constants for reactions 5 and 6; and [OH] is the OH radical concentration. The reactant and reference have equal exposure to OH radicals, hence:

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

Plots of ln([reactant]_{t₀}/[reactant]_t) versus ln([reference]_{t₀}/[reference]_t) should be linear, pass through the origin, and have a slope of k₅/k₆.

The loss of F(CF₂CF₂)_nCH₂CH₂OH (n = 2, 3, or 4) and the reference compounds were monitored by FTIR spectroscopy using an infrared path length of 27 m and a resolution of 0.25 cm⁻¹. Infrared spectra were derived from 32 co-added interferograms. F(CF₂CF₂)₂CH₂CH₂OH and F(CF₂CF₂)₃CH₂CH₂OH are liquids (vapor pressures of 1514 and 802 Pa at 298 K) and were introduced into the chamber by transferring the vapor above the liquid into calibrated volumes. The contents of the calibrated volumes were swept into the chamber using N₂ or diluent air. F(CF₂CF₂)₄CH₂CH₂OH is a solid (vapor pressure of 250 Pa at 298 K) and was introduced into the chamber by passing a fraction of the diluent gas over the solid sample. The concentrations of F(CF₂CF₂)₂CH₂CH₂OH and F(CF₂CF₂)₃CH₂CH₂OH in the chamber were calculated using the measured pressures of their vapor in the calibrated volumes. The concentration of F(CF₂CF₂)₄CH₂CH₂OH in the chamber was estimated by comparison of its integrated absorption feature at 3550–3650 cm⁻¹ (O–H stretch) with those of F(CF₂CF₂)₂CH₂CH₂OH and F(CF₂CF₂)₃CH₂CH₂OH, which have integrated band strengths of (3.5 ± 0.5) × 10⁻¹⁸ cm molecule⁻¹. Reactant and reference compounds were monitored using integrated absorption features over the following wavenumber ranges (cm⁻¹): F(CF₂CF₂)_nCH₂CH₂OH, 3550–3650; C₂H₄, 850–1050; C₂H₅Cl, 640–1350; and C₂H₂, 670–800.

Initial concentrations of the gas mixtures for Cl atom relative rate experiments were 5–10 mTorr of F(CF₂CF₂)_nCH₂CH₂OH, 5–15 mTorr of the reference compounds (C₂H₅Cl or C₂H₄), and 50–100 mTorr of Cl₂ in 700 Torr of either N₂ or diluent air. In the OH radical experiments, the initial reagent concentrations were 5–10 mTorr of F(CF₂CF₂)_nCH₂CH₂OH, 5–8 mTorr of the reference compounds (C₂H₂ or C₂H₄), 100–300 mTorr of CH₃ONO, and 0–28 mTorr NO in 700 Torr of diluent air. All experiments were performed at 296 K.

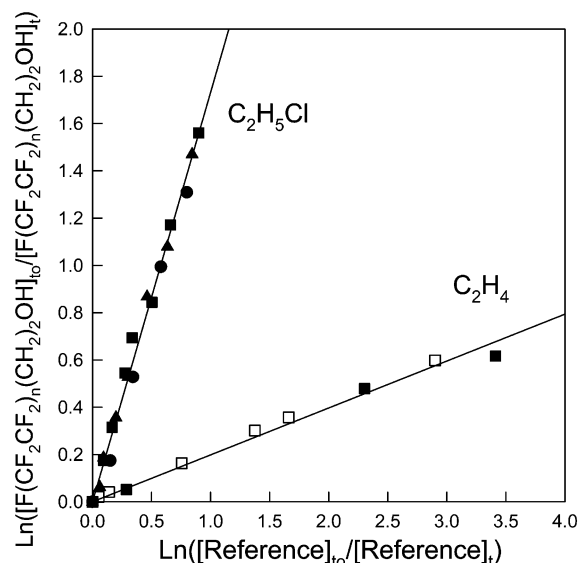


FIGURE 1. Loss of F(CF₂CF₂)_nCH₂CH₂OH (squares, n = 2; circles, n = 3; triangles, n = 4) vs C₂H₄ and C₂H₅Cl following exposure to Cl atoms in 700 Torr of either N₂ (open symbols) or air (filled symbols) diluent at 296 K.

Reagents were obtained from commercial sources at purities >99% and were subjected to repeated freeze–pump–thaw cycling before use. 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 Cl₂ or CH₃ONO) in N₂ were subjected to UV irradiation for 15–30 min (durations exceeding those used in the experiments described below) and product mixtures obtained after the UV irradiation of reactant mixtures were allowed to stand in the dark for 15 min. There was no observable loss of reactants or reference compounds, suggesting that photolysis and heterogeneous reactions are not a significant complication in the present work. Quoted uncertainties are two standard deviations from least squares regressions.

Results

Relative Rate Study of the Reaction of Cl Atoms with F(CF₂CF₂)_nCH₂CH₂OH. The kinetics of reaction 7 were measured relative to reactions 8 and 9:

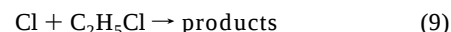
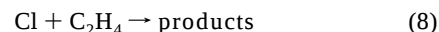


Figure 1 shows the loss of F(CF₂CF₂)_nCH₂CH₂OH versus loss of the reference compounds following the UV irradiation of F(CF₂CF₂)_nCH₂CH₂OH/Cl₂/reference mixtures in air or N₂, diluent. Experiments were performed in which the reactivity of Cl atoms with F(CF₂CF₂)₂CH₂CH₂OH, F(CF₂CF₂)₃CH₂CH₂OH, and F(CF₂CF₂)₄CH₂CH₂OH were measured relative to the reactivity of C₂H₅Cl. As seen in Figure 1, there was no discernible difference in the reactivity of the three different fluoro alcohols. The reactivity of F(CF₂CF₂)₂CH₂CH₂OH was measured relative to that of C₂H₄ in 700 Torr of either N₂ or air, diluent. As seen in Figure 1, there was no discernible effect of diluent gas on the kinetic data. The lines through the data in Figure 1 are linear least-squares fits to the combined data sets, which give values of k₇/k₈ = 0.193 ± 0.033 and k₇/k₉ = 1.78 ± 0.21. Using k₈ = 9.29 × 10⁻¹¹ (16) and k₉ = 8.04 × 10⁻¹² (17), we derive k₇ = (1.80 ± 0.31) × 10⁻¹¹ and (1.43 ± 0.17) × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹. The kinetics

of reaction 8 are dependent on total pressure, the value of k_8 used is appropriate for 700 Torr (16). 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 that is the average of the two determinations together with error limits that encompass the extremes of the individual determinations. Hence, $k_7 = (1.61 \pm 0.49) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. We estimate that systematic uncertainties associated with the reference rate constants contribute an additional 10% uncertainty to k_7 .

There are no previous data for reactions of Cl atoms with $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$ with which we can compare our results. We find that $\text{F}(\text{CF}_2\text{CF}_2)_2\text{CH}_2\text{CH}_2\text{OH}$, $\text{F}(\text{CF}_2\text{CF}_2)_3\text{CH}_2\text{CH}_2\text{OH}$, and $\text{F}(\text{CF}_2\text{CF}_2)_4\text{CH}_2\text{CH}_2\text{OH}$ have indistinguishable reactivities toward Cl atoms. This seems reasonable based upon expectations that the $\text{F}(\text{CF}_2\text{CF}_2)_n$ - group will not react with Cl atoms and that its influence on the reactivity of the two $-\text{CH}_2-$ groups will not change markedly upon increasing “ n ” from 2 to 4. Hence, the results presented herein can be generalized to $k(\text{Cl} + \text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}) = (1.61 \pm 0.49) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $n \geq 2$.

Kinetic data are available for reactions of Cl atoms with several nonfluorinated alcohols. At ambient temperature, the reaction of Cl atoms with $\text{C}_2\text{H}_5\text{OH}$ proceeds with a rate constant of $(9.5 \pm 1.9) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with $93 \pm 2\%$ of reaction occurring via attack on the $-\text{CH}_2-$ group (18). Reaction of Cl atoms with n - $\text{C}_3\text{H}_7\text{OH}$ occurs with a rate constant of $1.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (19). It is clear that the “fluorinated tail” of the $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$ molecule causes a substantial deactivation of the reactivity of the $-\text{CH}_2-$ groups toward Cl atoms. This effect presumably reflects an increase in C–H bond strength caused by fluorination of the molecule. This observation is consistent with the body of literature data showing that Cl atoms react with hydrofluorocarbons at rates that are generally much lower than the rates of reaction with corresponding alkanes (19).

Kelly and Sidebottom (20) have reported values of $k(\text{Cl} + \text{CF}_3\text{CH}_2\text{OH}) = (7 \pm 1) \times 10^{-13}$ and $k(\text{Cl} + \text{CF}_3\text{CH}_2\text{CH}_2\text{OH}) = (2.22 \pm 0.08) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. Papadimitriou et al. (21) have reported $k(\text{Cl} + \text{CF}_3\text{CH}_2\text{OH}) = (6.3 \pm 0.9) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 303 K. Comparison with the results of the present work suggest that the deactivating effect of the CF_3 - and $\text{F}(\text{CF}_2\text{CF}_2)_n$ - groups are very similar and that the majority of the reaction of Cl atoms with $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$ proceeds via attack on the $-\text{CH}_2-$ group α to the alcohol function.

Relative Rate Study of the Reaction of OH Radicals with $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$. The reactivity of OH radicals toward $\text{F}(\text{CF}_2\text{CF}_2)_2\text{CH}_2\text{CH}_2\text{OH}$ was studied relative to reactions 11 and 12. The reactivity of $\text{F}(\text{CF}_2\text{CF}_2)_3\text{CH}_2\text{CH}_2\text{OH}$ and $\text{F}(\text{CF}_2\text{CF}_2)_4\text{CH}_2\text{CH}_2\text{OH}$ were studied relative to reaction 11:

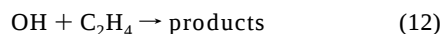
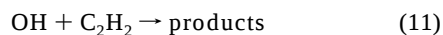
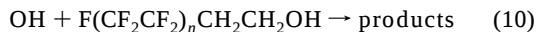


Figure 2 shows the loss of $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$ versus loss of the reference compounds on exposure to OH radicals. It can be seen from Figure 2 that there is no discernible difference in the reactivity of $\text{F}(\text{CF}_2\text{CF}_2)_2\text{CH}_2\text{CH}_2\text{OH}$, $\text{F}(\text{CF}_2\text{CF}_2)_3\text{CH}_2\text{CH}_2\text{OH}$, and $\text{F}(\text{CF}_2\text{CF}_2)_4\text{CH}_2\text{CH}_2\text{OH}$ relative to C_2H_2 reference. The lines through the data in Figure 2 are linear least-squares fits to the combined data sets, which give values of $k_{10}/k_{11} = 1.18 \pm 0.15$ and $k_{10}/k_{12} = 0.131 \pm 0.018$. Using

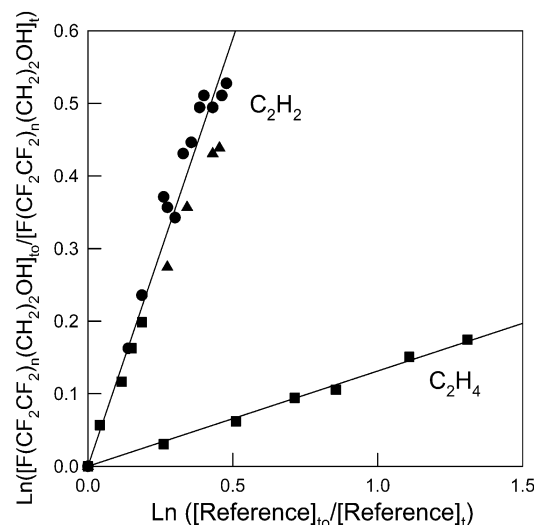


FIGURE 2. Loss of $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$ (squares, $n = 2$; circles, $n = 3$; triangles, $n = 4$) vs C_2H_2 and C_2H_4 following exposure to OH radicals in 700 Torr of air diluent at 296 K.

$k_{11} = 8.5 \times 10^{-13}$ (22) and $k_{12} = 8.66 \times 10^{-12}$ (23), we derive $k_{10} = (1.00 \pm 0.13) \times 10^{-12}$ and $(1.13 \pm 0.16) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Within the experimental uncertainties, consistent results were obtained in experiments conducted using the two different reference compounds. We choose to cite a final value for k_{10} that is the average of the two determinations together with error limits that encompass the extremes of the individual determinations. Hence, $k_{10} = (1.07 \pm 0.22) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. We estimate that systematic uncertainties associated with the reference rate constants contribute an additional 10% uncertainty to k_{10} .

As was the case for the Cl atom kinetics, $\text{F}(\text{CF}_2\text{CF}_2)_2\text{CH}_2\text{CH}_2\text{OH}$, $\text{F}(\text{CF}_2\text{CF}_2)_3\text{CH}_2\text{CH}_2\text{OH}$, and $\text{F}(\text{CF}_2\text{CF}_2)_4\text{CH}_2\text{CH}_2\text{OH}$ have indistinguishable reactivities toward OH radicals. Using the logic presented in the previous section, it seems reasonable to generalize our result; for $n \geq 2$, $k(\text{OH} + \text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}) = (1.07 \pm 0.22) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. There have been no previous studies of the reactions of OH atoms with $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$. However, our result can be compared with $k(\text{OH} + \text{CF}_3\text{CH}_2\text{OH}) = 1.0 \times 10^{-13}$ (20, 24), $k(\text{OH} + \text{CF}_3\text{CH}_2\text{CH}_2\text{OH}) = 1.1 \times 10^{-12}$ (20), $k(\text{OH} + \text{CF}_3\text{CF}_2\text{CH}_2\text{OH}) = 1.0 \times 10^{-13}$ (25, 26), $k(\text{OH} + \text{CH}_3\text{CH}_2\text{OH}) = 3.2 \times 10^{-12}$ (19), and $k(\text{OH} + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}) = 5.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (19). The presence of fluorinated substituents deactivate $-\text{CH}_2-$ groups toward reaction with OH radicals. In contrast, the $-\text{OH}$ functionality provides an activating influence (27). Hence, the values of $k(\text{OH} + \text{CF}_3\text{CH}_2\text{OH}) = 1.0 \times 10^{-13}$ and $k(\text{OH} + \text{CF}_3\text{CF}_2\text{CH}_2\text{OH}) = 1.0 \times 10^{-13}$ provide an estimate for the upper limit of the reactivity of the $-\text{CH}_2-$ group β to the alcohol function in $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$. Combining this with our measured value of the overall reactivity of the molecule, $k(\text{OH} + \text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}) = (1.07 \pm 0.22) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, it can be concluded that the bulk (>90%) of reaction with OH is likely to occur at the α - CH_2- group.

Finally, it is of interest to compare the reactivity of OH radicals toward $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$ measured herein with that predicted using the widely used structure–activity relationship (SAR) proposed by Kwok and Atkinson (27). The SAR method predicts $k_{10} = 4.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is a factor of approximately 4 higher than the measured value. As noted previously (25, 27), the SAR method has difficulty in predicting the reactivity of OH radicals with highly fluorinated compounds.

Atmospheric Implications

The value of k_{10} measured here can be used to provide an estimate of the atmospheric lifetime of $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$ with respect to reaction with OH radicals. Assuming an atmospheric lifetime for CH_3CCl_3 with respect to reaction with OH radicals of 5.7 yr (28) and a rate constant for the $\text{CH}_3\text{CCl}_3 + \text{OH}$ reaction of $1.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (29) leads to an estimate of the atmospheric lifetime of $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$ of $(1.0 \times 10^{-14})/(1.1 \times 10^{-12}) \times 5.7 \times 365 \approx 20 \text{ d}$. The optimal temperature for such a scaling analysis is 272 K (30) (rather than 296 K used here), but we do not have any data for k_{10} at 272 K. By analogy to other fluorinated organics (28), the temperature dependence of reaction 1 is expected to be similar to that for reaction of OH radicals with CH_3CCl_3 . Hence, the use of 296 K rather than 272 K is not expected to have any material impact on the estimated atmospheric lifetime. 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 (31). The atmospheric lifetime of $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$ with respect to reaction with OH radicals will be substantially longer at high latitudes in winter than at low latitudes in summer. The lifetime derived herein is an estimate of the global average lifetime with respect to reaction with OH radicals.

In addition to reaction with OH radicals, organic compounds are removed from the atmosphere via photolysis, wet deposition, dry deposition, and reaction with NO_3 radicals, Cl atoms, and O_3 . For saturated compounds such as $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$, reaction with NO_3 radicals and O_3 are typically too slow to be of importance. The average concentration of Cl atoms in the troposphere is several orders of magnitude less than that of OH radicals (32). In the present study, we observe that Cl atoms are 15 times more reactive than OH radicals toward $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$. Loss via reaction with Cl atoms will not be a significant atmospheric loss mechanism for $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$. Alcohols do not absorb at UV wavelengths $>200 \text{ nm}$ (33), and fluorination causes a blue shift in their UV spectra (34). Hence, photolysis of $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$ will not be important in the troposphere.

The rate of wet deposition can be calculated for the 8:2 FTOH using the method first described by Brimblecombe and Dawson (35) and further refined by Shepson et al. (36). The method involves the assumption that wet deposition for the water-soluble species is a simple first-order loss process. We assume that the telomer is removed by wet deposition resulting from equilibration with water in precipitating stratus for mid-latitudes. The calculated air/water dimensionless Henry's law constant (H^*), using a measured water solubility (C_w) of $148 \mu\text{g/L}$ and a vapor pressure (V_p) of 250 Pa at 298 K, was found to be 316 (37). The first-order removal constant (k_{WD}) was calculated using expression II:

$$k_{\text{WD}} = (R_i E e^{(-z/Zx)}) / (Zx(H^* + \phi)) \quad (\text{II})$$

where R_i is the annual rainfall rate, taken to be $3.2 \times 10^{-8} \text{ m/s}$; E is the enhancement factor due to evaporation of falling rain droplets, taken to be 1.33; z is the characteristic height of stratus clouds (3.5 km); Zx is the scale height for the 8:2 FTOH (2.3 km), and ϕ is the fraction of air volume occupied by liquid water content (1×10^{-6}).

Using this method, the rainout constant was calculated to be $1.28 \times 10^{-14} \text{ s}^{-1}$. Thus, the expected lifetime ($\tau_{\text{WD}} = 1/k_{\text{WD}}$) of 8:2 FTOH with respect to wet deposition is estimated to be $2.5 \times 10^6 \text{ yr}$. Relative to OH as a tropospheric sink, wet deposition is therefore expected to be an insignificant loss mechanism. Moving from 8:2 to the 6:2 and 4:2 FTOHs, the

length of the hydrophobic fluoro tail in the molecule decreases, which results in an increase in both water solubility and vapor pressure. In terms of Henry's law constant, the changes in water solubility and vapor pressure will approximately offset each other. Therefore, the Henry's law constants for the 4:2 and 6:2 FTOHs are expected to be comparable to that for 8:2 FTOH. In light of the very long ($2.5 \times 10^6 \text{ yr}$) estimated lifetime of 8:2 FTOH with respect to wet deposition, it seems reasonable to conclude that wet deposition is a negligible loss mechanism for $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$.

An estimation of the dry deposition velocity of the 8:2 alcohol to a body of water was conducted in a fashion similar to that outlined by van Pul et al. (38) using expression III:

$$v_d = 1 / ((r_a + r_b + r_s)) \quad (\text{III})$$

where r_a and r_b are the resistances to transport for the layer, taken to be 192 and 67 s m^{-1} , respectively. The r_s constant for the surface resistance of a gaseous substance can be further defined as H^*r_w , in which r_w is 105 s m^{-1} . The dry deposition velocity of a compound to water is typically greater than that to land. As such, this can be taken as an upper limit to the significance of dry deposition occurring. Using this method, the dry deposition velocity (v_d) was calculated to be $8.69 \times 10^{-6} \text{ m s}^{-1}$, and thus the dry deposition rate ($k_{\text{DD}} = v_d/Zx$) can be estimated to be $3.78 \times 10^{-9} \text{ s}^{-1}$ and the expected lifetime due to this process to be in the order of $\approx 8.4 \text{ yr}$. As was the case for wet deposition, dry deposition is not expected to be a significant atmospheric loss mechanism for $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$.

The atmospheric lifetime of $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$ is determined by its reaction with OH radicals and is approximately 20 d. Several important conclusions can be drawn from this lifetime estimate. First, the combination of this lifetime with the observed atmospheric concentrations can be used to estimate the flux of $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$ into the atmosphere. Hence, assuming that these compounds are restricted to the Northern Hemisphere and are well-mixed in the troposphere (0–10 km), it can be calculated that a flux on the order of $100\text{--}1000 \text{ t yr}^{-1}$ is needed to maintain the observed atmospheric concentrations (11). It should be stressed that this is a crude calculation and that more extensive spatial sampling of the FTOHs is required to refine this estimate. Second, given its relatively short atmospheric lifetime, $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$ will have a negligible global warming potential. Third, consistent with the observational record (11, 12), the spatial distribution of $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$ will be inhomogeneous. Fourth, $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$ will be transported downwind long distances from its point of emission (the global average wind speed is 4 m s^{-1} , which corresponds to 13.8 km h^{-1} ; an air mass traveling at this speed covers 7000 km in 20 d). The degradation mechanism and ultimate atmospheric oxidation products of $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$ deserve study. In particular the contribution or lack thereof of $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$ oxidation to the burden of perfluorocarboxylic acids observed in humans and wildlife in remote locations (8) needs clarification.

Acknowledgments

This research was funded, in part, by an NSERC Strategic Grant.

Literature Cited

- (1) Martin, J. W.; Mabury, S. A.; Solomon, K. R.; Muir, D. C. G. *Environ. Toxicol. Chem.* **2003**, 22, 189.
- (2) Martin, J. W.; Mabury, S. A.; Solomon, K. R.; Muir, D. C. G. *Environ. Toxicol. Chem.* **2003**, 22, 196.

- (3) Hansen, K. J.; Clemen, L. A.; Ellefson, M. E.; Johnson, H. O. *Environ. Sci. Technol.* **2001**, 35, 766.
- (4) Giesy, J. P.; Kannan, K. *Environ. Sci. Technol.* **2001**, 35, 1339.
- (5) Kannan, K.; Franson, J. C.; Bowerman, W. M.; Hansen, K. J.; Jones, P. D.; Giesy, J. P. *Environ. Sci. Technol.* **2001**, 35, 3065.
- (6) Moody, C. A.; Martin, J. W.; Kwan, W. C.; Muir, D. C. G.; Mabury, S. A. *Environ. Sci. Technol.* **2002**, 36, 545.
- (7) Moody, C. A.; Kwan, W. C.; Martin, J. W.; Muir, D. C. G.; Mabury, S. A. *Anal. Chem.* **2001**, 73, 2200.
- (8) Martin, J. W.; Mabury, S. A.; Smithwick, M.; Sonne-Hansen, C. D.; Gamber, M.; Braune, B.; Muir, D. C. G. Presented at the Canadian Arctic Contaminants Assessment Symposium, Northern Contaminants Program, Ottawa, March 4–7, 2003.
- (9) Determination of low levels of fluoropolymer polymerization aids - a guidance document. SPI Literature Catalogue BZ-102; The Society of the Plastics Industry: New York, 2003.
- (10) Kissa, E. In *Fluorinated Surfactants, Synthesis, Properties, and Applications*; Schick, M. J., Fowkes, F. M., Eds.; Marcel Dekker: New York, 1994.
- (11) Martin, J. W.; Muir, D. C. G.; Kwan, W. C.; Moody, C. A.; Solomon, K. R.; Mabury, S. A. *Anal. Chem.* **2002**, 74, 584.
- (12) Stock, N. L.; Lau, F. K.; Martin, J. W.; Muir, D. C. G.; Mabury, S. A. *Environ. Toxicol. Chem.* (manuscript in preparation).
- (13) Telomer Research Program Update. Presentation to USEPA-OPPT, November 25, 2002; U.S. Public Docket AR226-1141.
- (14) Ellis, D. A.; Cahill, T. M.; Mabury, S. A.; Cousins, I.; Mackay, D. Organofluorines. In *Handbook of Environmental Chemistry*; Nielson, A., Ed.; Springer-Verlag: Heidelberg, Germany, 2002; pp 63–83.
- (15) Wallington, T. J.; Japar, S. M. *J. Atmos. Chem.* **1989**, 9, 399.
- (16) Wallington, T. J.; Andino, J. M.; Lorkovic, I. M.; Kaiser, E. W.; Marston, G. *J. Phys. Chem.* **1990**, 94, 3644.
- (17) Wine, P. H.; Semmes, D. H. *J. Phys. Chem.* **1983**, 87, 3572.
- (18) Taatjes, C. A.; Christensen, L. K.; Hurley, M. D.; Wallington, T. J. *J. Phys. Chem. A* **1999**, 103, 9805.
- (19) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F., Jr.; Kerr, J. A.; Rossi, M. J.; Troe, J. *J. Phys. Chem. Ref. Data* **1997**, 26, 521.
- (20) Kelly, T.; Sidebottom, H. A kinetic and mechanistic study of the atmospheric oxidation of 3,3,3-trifluoropropanol. Poster CMD-2; Presented at the Eurotrac 2 Symposium, Garmisch-Partenkirchen, March 2002 (http://imk-aida.fzk.de/CMD/AR2001/GPP18_4.pdf).
- (21) Papadimitriou, V. C.; Prossimitis, A. V.; Lazarou, Y. G.; Paggiannakopoulos, P. *J. Phys. Chem. A* **2003**, 107, 3733.
- (22) Wallington, T. J.; Andino, J. M.; Lorkovic, I. M.; Kaiser, E. W.; Marston, G. *J. Phys. Chem.* **1990**, 94, 3644.
- (23) Calvert, J. G.; Atkinson, R.; Kerr, J. A.; Madronich, S.; Moortgat, G. K.; Wallington, T. J.; Yarwood, G. *The Mechanisms of Atmospheric Oxidation of the Alkenes*; Oxford University Press: Oxford, 2000.
- (24) Wallington, T. J.; Dagaut, P.; Kurylo, M. J. *J. Phys. Chem.* **1988**, 92, 5024.
- (25) 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.
- (26) Chen, L.; Fukuda, K.; Takenaka, N.; Bandow, H.; Maeda, Y. *Int. J. Chem. Kinet.* **2000**, 32, 73.
- (27) Kwok, E. S. C.; Atkinson, R. *Atmos. Environ.* **1995**, 14, 1685.
- (28) Prinn, R. G.; Weiss, R. F.; Miller, B. R.; Huang, J.; Alyea, F. N.; Cunnold, D. M.; Fraser, P. J.; Hartley, D. E.; Simmonds, P. G. *Science* **1995**, 269, 187.
- (29) DeMore, W. B.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J. *JPL Publication No. 97-4*; NASA Jet Propulsion Lab: Pasadena, CA, 1997.
- (30) Spivakovskiy, 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.
- (31) Klečka, 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.
- (32) Finlayson-Pitts, B. J.; Pitts, J. N., Jr. *Atmospheric Chemistry: Fundamentals and Experimental Techniques*; John Wiley and Sons: New York, 1986.
- (33) Calvert, J. G.; Pitts, J. N., Jr. *Photochemistry*; John Wiley: New York, 1966.
- (34) Schneider, W. F.; Wallington, T. J.; Minschwaner, K.; Stalberg, E. A. *Environ. Sci. Technol.* **1995**, 29, 247.
- (35) Brimblecombe, P.; Dawson, G. A. *J. Atmos. Chem.* **1984**, 2, 95.
- (36) Shepson, P. B.; MacKay, E.; Muthuramu, K. *Environ. Sci. Technol.* **1996**, 30, 3618.
- (37) Unpublished data from this research group.
- (38) van Pul, W. A. J.; de Leeuw, F. A. A. M.; van Jaarsveld, J. A.; van der Gaag, M. A.; Sliggers, C. J. *Chemosphere* **1998**, 37, 113.

Received for review February 16, 2003. Revised manuscript received May 21, 2003. Accepted June 2, 2003.

ES034136J