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Atmospheric chemistry of C₈F₁₇CH₂CHO: Yield from C₈F₁₇CH₂CH₂OH (8:2 FTOH) oxidation, kinetics and mechanisms of reactions with Cl atoms and OH radicals

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ABSTRACT

Smog chamber/FTIR techniques were used to measure a $92 \pm 7\%$ yield of C₈F₁₇CH₂CHO in the chlorine atom initiated oxidation of C₈F₁₇CH₂CH₂OH (8:2 FTOH) in 700 Torr of air. Relative rate techniques were used to measure $k(\text{Cl} + \text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}) = (1.9 \pm 0.4) \times 10^{-11}$ and $k(\text{OH} + \text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}) = (2.0 \pm 0.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in 700 Torr of N₂ or air diluent at 296 K. The results are discussed with respect to the atmospheric chemistry of fluorotelomer alcohols.

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1. Introduction

Fluorinated alcohols are used in a variety of industrial applications (e.g. paints, coatings, polymers, adhesives, waxes, polishes, electronic materials, caulks). C₈F₁₇CH₂CH₂OH (8:2FTOH) is the principal material used in the manufacture of fluorotelomer based-products. In light of the widespread use of fluorinated alcohols, detailed information on their environmental impact is needed. There is a concern, for example, that atmospheric oxidation processes convert fluorinated alcohols to perfluorinated carboxylic acids (PFCAs) of the form C_nF_{2n+1}C(O)OH. PFCAs are persistent in the environment, resisting degradation via oxidation, hydrolysis, or reduction under biotic and abiotic conditions [1]. Analysis of rainwater indicates the widespread distribution of short-chain PFCAs ($n = 2-7$) at low levels ($\sim 1-100 \text{ ng/L}$) [2]. Long-chain PFCAs are bioaccumulative [3] and have been observed in fish from the Great Lakes [4] and in Arctic fish and mammals [5].

Fluorotelomer alcohols (FTOHs) are a class of fluorinated alcohols that have been suggested as plausible sources of PFCAs in remote locations [6,7]. FTOHs are linear fluorinated alcohols with the formula C_nF_{2n+1}CH₂CH₂OH ($n = 2, 4, 6, \dots$). Fluorotelomer alcohols are volatile, have been detected in the air over North America, Arctic, Europe, and Japan [8–10], have an atmospheric lifetime (approximately 10–20 days) sufficient for widespread hemispheric distribution [6,11] and undergo atmospheric oxidation in the absence of NO_x to give perfluorocarboxylic acids [7,12].

Most studies of fluorinated alcohols have concentrated on smaller members of the class (e.g., CF₃CH₂CH₂OH) because they are easy to handle and appropriate reference standards (e.g., CF₃CH₂CHO and CF₃CHO) are commercially available. It has been assumed that

the chemistry of the larger, more commercially relevant alcohols (e.g., C₈F₁₇CH₂CH₂OH) is the same as the smaller members of the series. To test this assumption we studied the yield of C₈F₁₇CH₂CHO from C₈F₁₇CH₂CH₂OH oxidation and the kinetics and mechanisms of reactions of C₈F₁₇CH₂CHO with Cl atoms and OH radicals. The results are reported here indicate that the atmospheric chemistry of the larger members of the C_nF_{2n+1}CH₂CH₂OH and C_nF_{2n+1}CH₂CHO series are indistinguishable from that of the smaller members.

2. Experimental

Experiments were performed in a 140-liter Pyrex reactor interfaced to a Mattson Sirius 100 FTIR spectrometer [13]. The reactor was surrounded by 22 fluorescent black lamps (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 CH₃ONO 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. The relative rate method is a well established technique for measuring the reactivity of Cl atoms and OH radicals with organic compounds [14]. Kinetic data were derived by monitoring the loss of a reactant compound relative to one or more reference compounds. The decays of the reactant and reference are then plotted using the expression:

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$$\text{Ln}\left(\frac{[\text{reactant}]_{\text{to}}}{[\text{reactant}]_{\text{t}}}\right) = \frac{k_{\text{reactant}}}{k_{\text{reference}}} \text{Ln}\left(\frac{[\text{reference}]_{\text{to}}}{[\text{reference}]_{\text{t}}}\right) \quad (1)$$

where $[\text{reactant}]_{\text{to}}$, $[\text{reactant}]_{\text{t}}$, $[\text{reference}]_{\text{to}}$ and $[\text{reference}]_{\text{t}}$ are the concentrations of reactant and reference at times 'to' and 't', k_{reactant} and $k_{\text{reference}}$ are the rate constants for reactions of Cl atoms or OH radicals with the reactant and reference. Plots of $\text{Ln}([\text{reactant}]_{\text{to}}/[\text{reactant}]_{\text{t}})$ versus $\text{Ln}([\text{reference}]_{\text{to}}/[\text{reference}]_{\text{t}})$ should be linear, pass through the origin, and have a slope of $k_{\text{reactant}}/k_{\text{reference}}$.

$\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$ and $\text{C}_8\text{F}_{17}\text{CH}_2\text{CH}_2\text{OH}$ were monitored by FTIR spectroscopy using an infrared path length of 27 m, a resolution of 0.25 cm^{-1} , and 32 co-added interferograms. All experiments were performed at 700 Torr and $296 \pm 2\text{ K}$. $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$ and $\text{C}_8\text{F}_{17}\text{CH}_2\text{CH}_2\text{OH}$ were introduced into the chamber by flowing the diluent gas slowly over solid samples of these compounds and into the chamber. Liquid reagents were introduced into the chamber by transferring their vapor above the liquid into a calibrated volume. Gaseous reagents were also introduced into the calibrated volume. The contents of the calibrated volume were swept into the chamber with diluent gas (air or nitrogen). With the exception of $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$, all reagents were obtained from commercial sources (with purities > 99%). $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$ was obtained from P&M-Invest with a stated purity of >97%. All reagents were subjected to repeated freeze/pump/thaw cycling before use. Ultra-high-purity synthetic air and nitrogen from Michigan Airgas were used as diluent gases.

Initial reagent concentrations for Cl atom relative rate experiments were 0.7–13.8 mTorr of $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$, 3–5 mTorr of the reference compound ($\text{C}_2\text{H}_5\text{Cl}$ or CH_3OH), and 100–110 mTorr of Cl_2 in 700 Torr of N_2 as diluent. Initial reagent concentrations for OH radical relative rate experiments were 6.2 mTorr of $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$, 2.3 mTorr of C_2H_4 , and 100 mTorr of CH_3ONO in 700 Torr of air as diluent. Reactant and reference compounds were monitored using absorption features over the following wavenumber ranges (cm^{-1}): $\text{C}_8\text{F}_{17}\text{CH}_2\text{CH}_2\text{OH}$, 700–1200; $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$, 1000–1800; C_2H_4 , 900–1000, $\text{C}_2\text{H}_5\text{Cl}$, 920–1320, and CH_3OH , 1000–1100.

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) were subjected to UV irradiation for 5 min and product mixtures obtained after the UV irradiation of reactant mixtures were allowed to stand in the dark in the chamber for 5 min. With one notable exception ($\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$) there was no observable loss of reactants or products, suggesting that photolysis, dark chemistry and heterogeneous reactions are not a significant complication in the present work. Interestingly, irradiation of a mixture of 5.61 mTorr of $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$ in 700 Torr N_2 diluent for 5 min led to a small, but discernable, loss (approximately 1%) of $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$.

Further irradiation of the mixture over a period of 70 min led to further $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$ loss (14% loss after 70 min). The rate of $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$ photolysis in the chamber is sufficiently slow that it will not be a complication in the experiments reported here where the total irradiation times were <5 min. However, it appears that photolysis might be an important atmospheric loss mechanism for this compound. Further work is needed to clarify the role of photolysis but is beyond the scope of the present work. Unless stated otherwise, quoted uncertainties are two standard deviations from least squares regressions.

3. Results

3.1. Relative rate study of $k(\text{Cl} + \text{C}_8\text{F}_{17}\text{CH}_2\text{CHO})$

The kinetics of reaction (5) were measured relative to reactions (6) and (7):



Fig. 1 shows the loss of $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$ versus the reference compounds following the UV irradiation of $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$ /reference/ Cl_2 mixtures in 700 Torr N_2 diluent. The lines through the data in Fig. 1 are linear least squares fits which give $k_5/k_6 = 2.2 \pm 0.2$ and $k_5/k_7 = 0.37 \pm 0.04$. Using $k_6 = 8.0 \times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ [15] and $k_7 = 5.5 \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ [16] we derive $k_5 = (1.8 \pm 0.2) \times 10^{-11}$ and $(2.0 \pm 0.2) \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$.

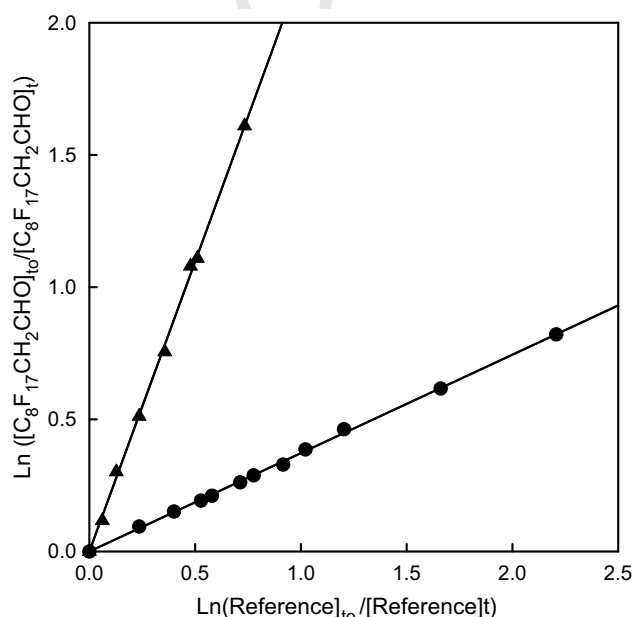


Fig. 1. Loss of $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$ versus $\text{C}_2\text{H}_5\text{Cl}$ (triangles) and CH_3OH (circles) following exposure to Cl atoms in 700 Torr of N_2 diluent at 296 K.

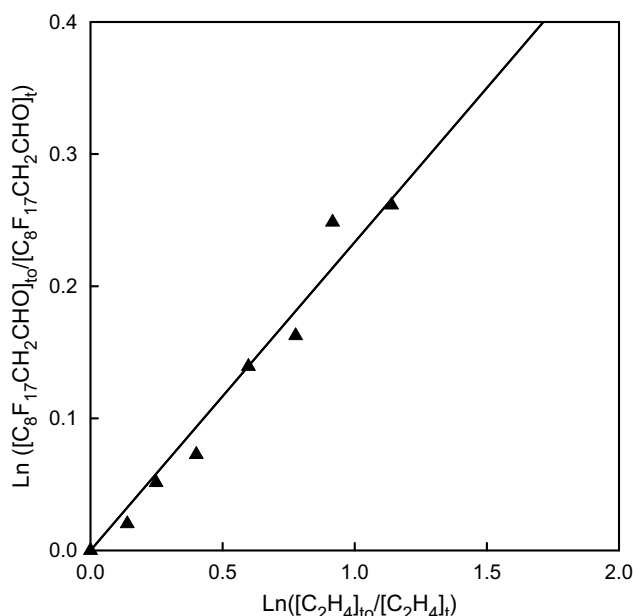


Fig. 2. Loss of $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$ versus C_2H_4 following exposure to OH radicals in 700 Torr of air diluent at 296 K.

respectively. Results obtained using the two different reference compounds were, within the experimental uncertainties, indistinguishable. We cite a final value for k_5 which is the average of the two determinations together with error limits which encompass the extremes of the individual determinations, $k_5 = (1.9 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Kelly et al. [11] measured the reactivity of Cl towards $\text{CF}_3\text{CH}_2\text{CHO}$ relative to $\text{HC}(\text{O})\text{OC}_2\text{H}_5$. Using a value of $k(\text{Cl} + \text{HC}(\text{O})\text{OC}_2\text{H}_5) = 1.0 \times 10^{-11}$ [17,18] gives $k(\text{Cl} + \text{CF}_3\text{CH}_2\text{CHO}) = (1.92 \pm 0.03) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Hurley et al. [12,19] have reported $k(\text{Cl} + \text{CF}_3\text{CH}_2\text{CHO}) = (1.8 \pm 0.3) \times 10^{-11}$ and $k(\text{Cl} + \text{C}_4\text{F}_9\text{CH}_2\text{CHO}) = (1.8 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The reactivities of $\text{CF}_3\text{CH}_2\text{CHO}$, $\text{C}_4\text{F}_9\text{CH}_2\text{CHO}$, and $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$ towards Cl atoms are indistinguishable within the experimental uncertainties. The observation that there is no discernable effect on the size of the C_nF_{n+1} group on the reactivity of the $\text{C}_n\text{F}_{n+1}\text{CH}_2\text{CHO}$ molecule towards Cl atoms is consistent with the expectation that the majority of the reaction occurs via abstraction of the aldehydic hydrogen atom. Changes in the length of the C_nF_{n+1} group are not expected to influence the reactivity at the aldehydic site.

3.2. Relative rate study of the reaction of OH radicals with $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$

The rate of reaction (8) was measured relative to reaction (9):

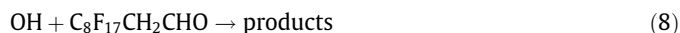


Fig. 2 shows the loss of $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$ versus the loss of C_2H_4 following the UV irradiation of a mixture of 6.2 mTorr $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$, 2.4 mTorr C_2H_4 , and 100 mTorr CH_3ONO mixtures in 700 Torr air diluent. The line through the data is a linear least squares fit which gives $k_8/k_9 = 0.23 \pm 0.04$ and using $k_9 = 8.66 \times 10^{-12}$ [20] we derive $k_8 = (2.0 \pm 0.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Sellevåg et al. [21], Kelly et al. [11], and Hurley et al. [19] have reported $k(\text{OH} + \text{CF}_3\text{CH}_2\text{CHO}) = (3.6 \pm 0.3) \times 10^{-12}$, $(2.96 \pm 0.04) \times 10^{-12}$, and $(2.6 \pm 0.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. Hurley et al. [19] measured a rate constant ratio $k(\text{OH} + \text{CF}_3\text{CH}_2\text{CHO})/k_9 = 0.336 \pm 0.045$ which can be compared to the ratio $k_8/k_9 = 0.23 \pm 0.04$ measured here. With respect to reaction with OH

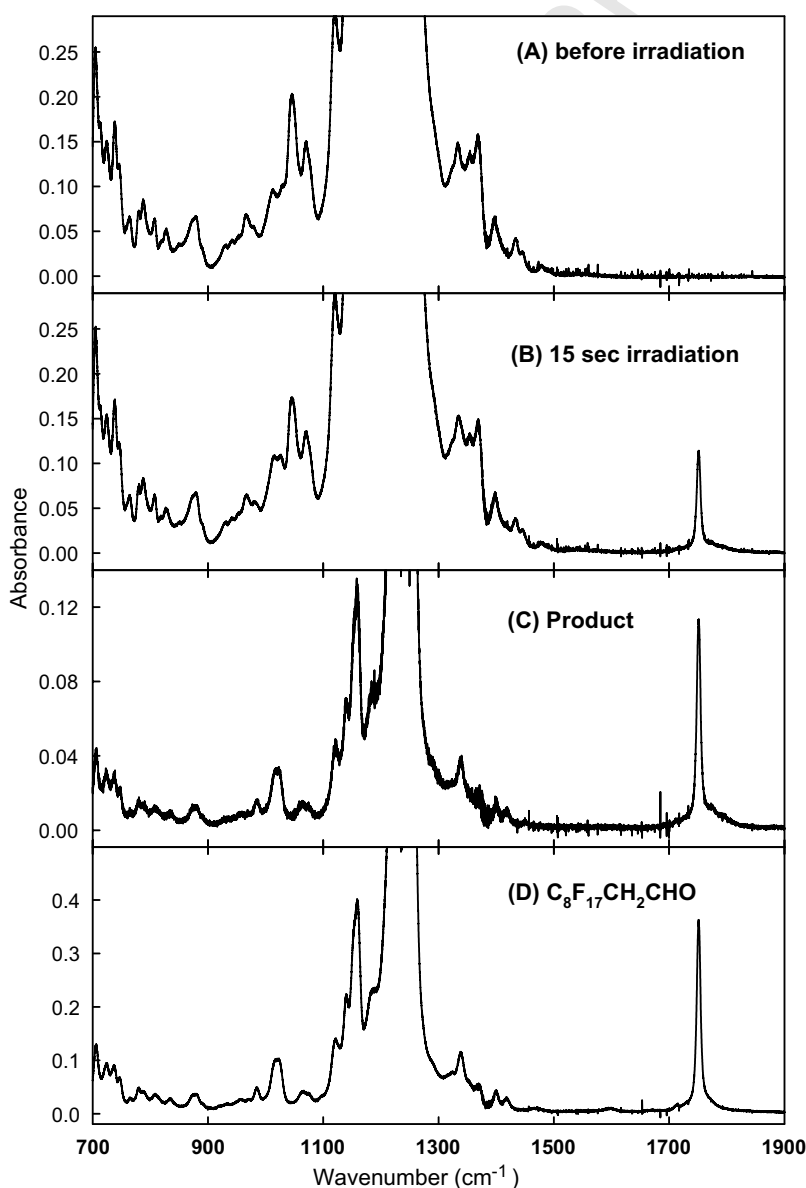


Fig. 3. IR spectra obtained before (A) and after (B) a 15 s irradiation of 11.9 mTorr $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$ and 100 mTorr Cl_2 in 700 Torr air. Panel (C) shows the IR product spectrum. Panel (D) is a reference spectrum of $\text{C}_8\text{F}_{17}\text{CH}_2\text{CHO}$.

radicals, the reactivity of $C_8F_{17}CH_2CH_2CHO$ is similar to, but slightly less than, that of CF_3CH_2CHO .

3.3. Formation of $C_8F_{17}CH_2CH_2CHO$ in the Cl atom initiated oxidation of $C_8F_{17}CH_2CH_2CH_2OH$

Fig. 3 shows IR spectra recorded before (A) and after (B) a 15 s irradiation of a mixture of 11.9 mTorr $C_8F_{17}CH_2CH_2CH_2OH$ and 100 mTorr Cl_2 in 700 Torr of air. Panel C is the product spectrum obtained by subtracting features attributable to $C_8F_{17}CH_2CH_2CH_2OH$ from panel B. The consumption of $C_8F_{17}CH_2CH_2CH_2OH$ was 18%. Panel D is a reference spectrum of the aldehyde $C_8F_{17}CH_2CH_2CHO$. It is clear from comparison of panels C and D that $C_8F_{17}CH_2CH_2CHO$ is a major product in the system. The vapor pressure of $C_8F_{17}CH_2CH_2CHO$ is sufficiently low that it cannot be measured accurately with the equipment available to us. The reference spectrum of $C_8F_{17}CH_2CH_2CHO$ was obtained by flowing diluent gas over the solid $C_8F_{17}CH_2CH_2CHO$ and into the chamber. Calibration of the $C_8F_{17}CH_2CH_2CHO$ reference spectrum was achieved by subjecting a $C_8F_{17}CH_2CH_2CHO/Cl_2/N_2$ mixture to UV irradiation and equating the observed formation of HCl with the $C_8F_{17}CH_2CH_2CHO$ loss. The inset in Fig. 4 shows the $C_8F_{17}CH_2CH_2CHO$ calibration plot.

Fig. 4 shows a plot of the observed $C_8F_{17}CH_2CH_2CHO$ formation versus the $C_8F_{17}CH_2CH_2CH_2OH$ loss. Assuming that $C_8F_{17}CH_2CH_2CHO$ is formed following reaction (10) and is lost solely via reaction (5), then its concentration profile can be described by expression (II) [22]:

$$\frac{[C_8F_{17}CH_2CH_2CHO]}{[C_8F_{17}CH_2CH_2CH_2OH]_0} = \frac{\alpha(1-x)\{(1-x)^{(k_5/k_{10})-1} - 1\}}{\{1 - (k_5/k_{10})\}} \quad (II)$$

where $x = 1 - ([C_8F_{17}CH_2CH_2CH_2OH]/[C_8F_{17}CH_2CH_2CH_2OH]_0)$ is the fractional consumption of $C_8F_{17}CH_2CH_2CH_2OH$, α is the yield of $C_8F_{17}CH_2CH_2CHO$ from the Cl atom initiated oxidation of $C_8F_{17}CH_2CH_2CH_2OH$, and k_5 and k_{10} are the rate constants for reactions (5) and (10):



The curve through the data in Fig. 4 is a fit of expression (II) to the data which gives $\alpha = 0.92 \pm 0.07$ and $k_5/k_{10} = 1.08 \pm 0.07$. Using a value of $k_{10} = (1.6 \pm 0.5) \times 10^{-11}$ [6] gives $k_5 = (1.7 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; consistent with the value reported in Section 3.1. The observed formation of $C_8F_{17}CH_2CH_2CHO$ in a yield which is close to 100% is consistent with previous findings that CF_3CH_2CHO and $C_4F_9CH_2CHO$ are formed in essentially 100% yields from $CF_3CH_2CH_2CH_2OH$ and $C_4F_9CH_2CH_2CH_2OH$, respectively [12,19]. The observation of $C_8F_{17}CH_2CH_2CHO$ as the dominant product of the Cl atom initiated oxidation of $C_8F_{17}CH_2CH_2CH_2OH$ suggests that reaction (10) proceeds predominantly via hydrogen abstraction from the terminal carbon atom:



4. Implications for atmospheric chemistry

The goal of this work was to test the assumption that the chemistry of large, commercially relevant, fluorinated alcohols such as $C_8F_{17}CH_2CH_2CH_2OH$ can be predicted by studying smaller members of the series such as $CF_3CH_2CH_2CH_2OH$ and $C_4F_9CH_2CH_2CH_2OH$ which are easier to handle in the laboratory. We find that (i) as with the smaller members of the series, the chlorine atom initiated oxidation of $C_8F_{17}CH_2CH_2CH_2OH$ gives the corresponding aldehyde, $C_8F_{17}CH_2CH_2CHO$, in a yield which is close to 100%; (ii) the reactivity of $C_8F_{17}CH_2CH_2CHO$ towards chlorine atoms is indistinguishable from that of the smaller members of the series; (iii) the reactivity of $C_8F_{17}CH_2CH_2CHO$ towards hydroxyl radicals is similar to, but slightly less than, that of CF_3CH_2CHO . The available data suggest that the chemistry of large, commercially relevant, fluorinated alcohols such as $C_8F_{17}CH_2CH_2CH_2OH$ can be predicted by studying smaller members of the series.

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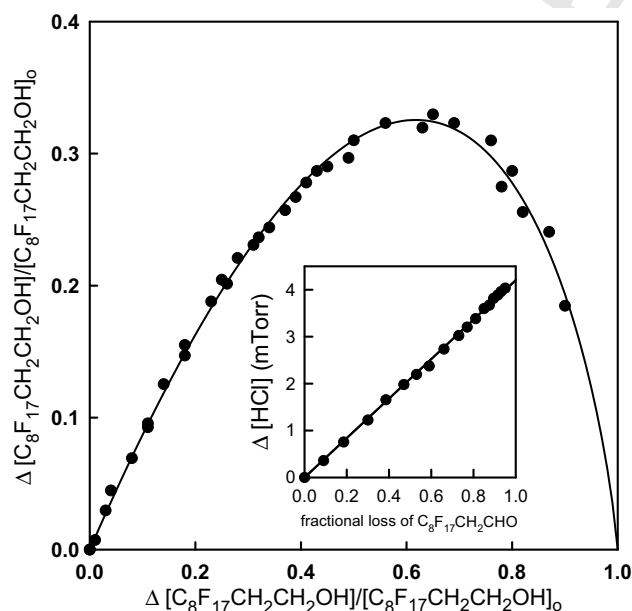


Fig. 4. Concentration of $C_8F_{17}CH_2CH_2CHO$ (normalized to the initial $C_8F_{17}CH_2CH_2CH_2OH$ concentration) versus the fractional consumption of $C_8F_{17}CH_2CH_2CH_2OH$ observed following the UV irradiation of $C_8F_{17}CH_2CH_2CH_2OH/Cl_2$ mixtures in 700 Torr air. The inset shows the formation of HCl (in units of mTorr) versus the loss of $C_8F_{17}CH_2CH_2CHO$ (expressed as a fraction of the reference spectrum) following irradiation of $C_8F_{17}CH_2CH_2CHO/Cl_2/air$ mixtures, the slope provided the absolute calibration of the $C_8F_{17}CH_2CH_2CHO$ reference spectrum.

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